

GROUNDWATER GEOCHEMISTRY, GEOLOGY, AND MICROBIOLOGY OF
ARSENIC-CONTAMINATED HOLOCENE ALLUVIAL AQUIFERS,
MANIKGANJ, BANGLADESH

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THESIS ABSTRACT

GROUNDWATER GEOCHEMISTRY, GEOLOGY, AND MICROBIOLOGY OF ARSENIC-CONTAMINATED HOLOCENE ALLUVIAL AQUIFERS, MANIKGANJ, BANGLADESH

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A multi-disciplinary study, using integrated aspects of geology, groundwater geochemistry including carbon isotope geochemistry, scanning electron microscopy, energy dispersive spectroscopy, and geochemical modeling, reveals linked geochemical and microbial processes that cause natural arsenic-contamination of Holocene alluvial aquifers in Manikganj, Bangladesh. Natural arsenic contamination in south Asia is considered to be the worst environmental crisis in the world. It is estimated that more than 25 million people in Bangladesh and West Bengal, India are consuming drinking water containing dangerous concentrations of arsenic. Existing and new data indicate that groundwaters in Manikganj aquifers contain elevated concentrations of As, Fe, Mn,

Ba, Sr, and HCO_3^- . Elevated dissolved H_2 gas contents (1.3 to 2.4 nM), predominantly reducing ORP values (-125 to +103 mV), carbon isotopic signatures [-3.32‰ to +4.07‰ DIC, -22.8‰ to -25.0‰ DOC (VPDB)], presence of authigenic siderite concretions in aquifer sediments, and high organic carbon contents (up to 4%) of sediments indicate that bacterial Fe(III)-reduction is responsible for elevated As and Fe concentrations. Strong correlations between elevated As and Fe^{2+} concentrations support the hypothesis that bacterial reduction of (insoluble) hydrous-ferric-hydroxide minerals causes release of associated sorbed arsenic back into solution. Sulfate concentrations are very low where As levels are greater than 0.03 mg/L, indicating biogenic sulfate reduction is limited by low levels of dissolved sulfate. This implies that only an insignificant fraction of As were removed by iron-sulfide solids. Geochemical modeling indicates that precipitation and dissolution of Fe- and Mn-minerals controls the mobility of trace metals in groundwater. Geochemical speciation models show that highly toxic As(III) is the dominant As species in Manikganj groundwater geochemical conditions. Moreover, adsorption-desorption geochemical models show that desorption is not the sole mechanism for As release.

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INTRODUCTION

Naturally-occurring arsenic contamination of groundwater is a widespread problem in Holocene aquifers worldwide. This study focuses on Manikganj, Bangladesh, but may have implications for many other south Asian locales, such as West Bengal region of India, Cambodia, Vietnam, Taiwan, and Nepal. Certain geological, microbiological, and geochemical conditions exist in these shallow aquifers which cause unusually high levels of As, Sr, Ba, Mn, and Fe in groundwater (Dowling et al., 2002, Akai et al., 2004).

Arsenic is a highly toxic metalloid. Long-term consumption of water containing arsenic concentrations >0.05 mg leads to severe health problems such as various cancers, skin discoloration and lesions, birth complications, and damage to the kidneys, bladder, and liver (Anawar et Al., 2002). The British Geological Survey estimates that at least 25 million people in the area of Bangladesh and West Bengal are exposed to elevated levels of arsenic in water (>0.05 mg/l), and an estimated 3.58 million people consume groundwater with extremely high arsenic levels (>0.20 mg/l) (British Geological Society, 1999). Groundwater is the only viable source of potable drinking water in Bangladesh and West Bengal, and the Bangladeshi government promotes the use of groundwater to prevent the spread of waterborne diseases associated with surface waters.

Several different mechanisms have been invoked to explain the high As levels in the region. The primary geochemical causes are most likely: (1) microbial reduction of

Fe(III)-oxyhydroxides (HFOs) causing desorption and dissolution of sorbed arsenic (Bhattacharya et al., 1997; Nickson et al., 1998, 2000; McArthur et al., 2001; Zheng et al., 2002), and (2) limited amounts of dissolved SO_4^{2-} (sulfate) which limits the biogenic precipitation of sulfide minerals and coprecipitation of dissolved arsenic from groundwater (Nickson et al., 2000). Other, perhaps secondary, mechanisms attributed to raised As levels are oxidation of As-bearing pyrite in the alluvium (Mallick and Rajagopal, 1996; Mandal et al., 1998), and competitive ion-exchange with phosphates and other ions associated with excessive fertilizer application replacing arsenic sorbed onto aquifer minerals (Acharya et al., 2000).

Although many studies have focused on the major-ion and trace-element geochemistry of inorganic species in Bangladesh and West Bengal groundwater, little attention was given to the mineralogical and microbiological aspects of the problem. Microbial activities could control arsenic mobility in reducing and oxidizing aquifer conditions, and this has been largely overlooked. More recent studies agree that reductive dissolution of Fe(III)-oxyhydroxides (HFOs) is the primary release mechanism that puts arsenic into solution, which is driven by microbial metabolic processes (Bhattacharya et al., 1997; Nickson et al., 1998, 2000; McArthur et al., 2001; Zheng et al., 2004). However, the complex water-sediment-bacteria interactions leading to As mobilization remains poorly understood.

GEOLOGIC AND HYDROGEOLOGIC SETTING

Arsenic-rich groundwaters in Bangladesh and other south Asian countries commonly occur long distances (>100 km) away from their ultimate sources, apparently in associated mountain ranges, where chemical weathering of As-bearing minerals is most likely enhanced by rapid tectonic uplift and Pleistocene to recent glaciation. Upon weathering, As species readily adsorb to Fe-oxyhydroxides, primarily in aerobic fluvial settings. As-enriched sediments are subsequently transported by surface waters, and are deposited in alluvial settings along with elevated levels of organic matter. Subsequently, Fe-reducing bacteria present in alluvial aquifers reductively dissolve Fe-oxyhydroxides, causing the release of sorbed As under moderately reducing conditions. As a result of this As-cycling mechanism, two distinct lithofacies in Bangladesh are associated with high arsenic enrichment: sandy channel-fill deposits and fine-grained over-bank deposits (Ahmed et al., 2004).

Elevated arsenic concentrations occur in alluvial aquifers and glacial deposits worldwide, in locations such as Alaska, Cambodia, China, Chile, Ghana, Hungary, Illinois, Mexico, Nepal, Vietnam, and Taiwan (Fig. 1). Arsenic cycling in alluvial aquifers in central Alabama has also been documented (Saunders et al., 1997). Several million people in Vietnam are consuming As-rich waters drawn from the Red River Basin, an alluvial setting similar to the West Bengal Basin (Berg et al., 2001). However, the single largest contamination in the world is in the lower Ganges/lower

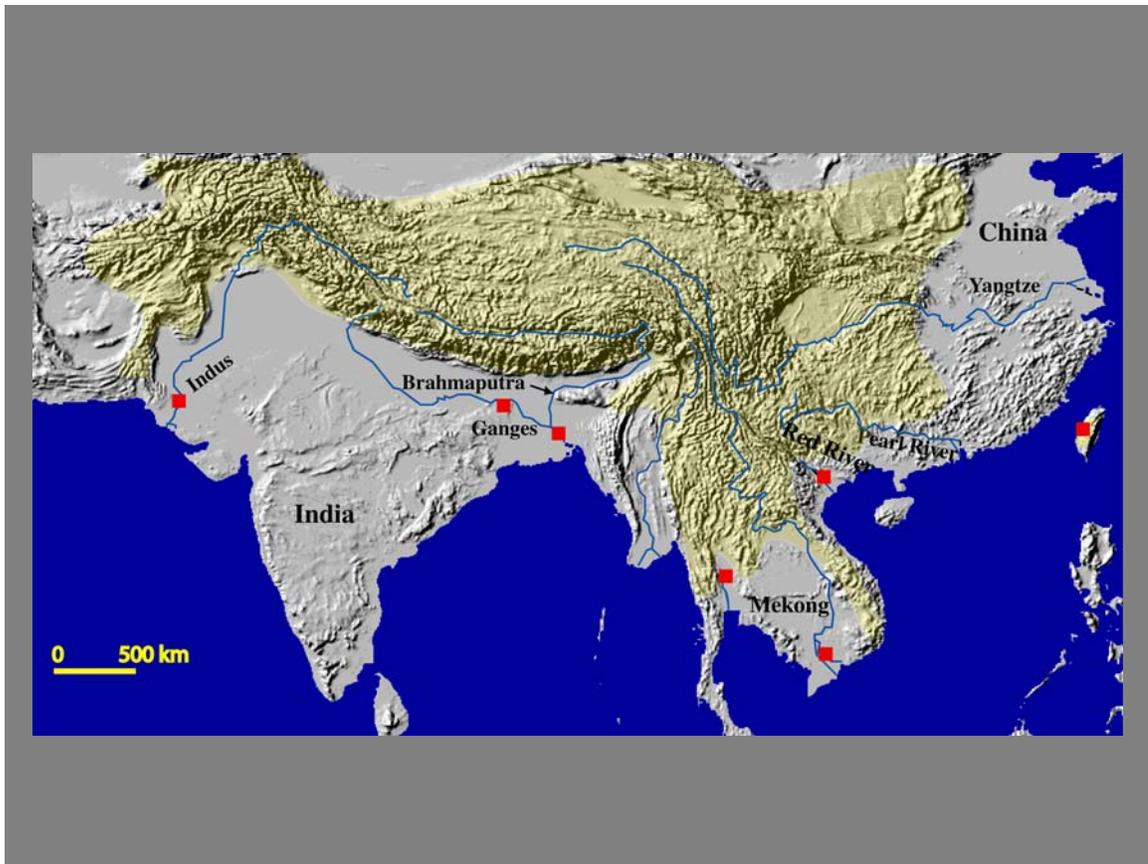


Figure 1. South Asian arsenic hotspots. Red squares depict regions associated with major alluvial deposits with As levels in groundwater exceeding the World Health Organization (WHO) drinking water standard of 10 ppb. Yellow color shows areas covered by Pliocene glacial ice that expedited Holocene weathering of As-bearing minerals, leading to the transport of As through the hydrologic cycle (modified after Saunders et al., 2005).

Meghna region of Bangladesh and West Bengal, India, where an estimated 25 million people are exposed to elevated arsenic levels (Nickson et al., 1998; McArthur et al., 2001).

Regional Geology

The Bengal basin in Bangladesh and part of West Bengal, India is surrounded by the Precambrian Indian Shield to the west, the uplifted block of Precambrian Shillong Plateau to the north, and the Indo-Burman ranges to the east (Fig. 2) (Ahmed et al., 2004). Sediments derived from the Indo-Burman and Himalayan ranges fill the basin and include over 16 km of synorogenic Cenozoic sediments, Tertiary sandstones and shales, and overlying Pliocene clays and Holocene alluvium (Uddin and Lundberg, 1998).

The Ganges, Brahmaputra, and Meghna (GBM) river systems drain the Himalayas and Tibetan Plateau and deposit sediments into the Bengal basin. This alluvial system currently transports the largest sediment flux in the world into this basin (Dowling et al., 2002). The GBM system drains an area of 2×10^6 km², and the floodplain in Bangladesh and India is 2.5×10^5 km² (Dowling et al., 2003). The Ganges river flows through highly weathered sediments and transports a sediment load high in clay. The Brahmaputra River drains young, unweathered rocks which results in a sedimentary load consisting of silts and sands (Dowling et al., 2003). Generally, the GBR subsurface delta mineralogy is dominated by quartz (57-99%), with lesser amounts of plagioclase, potassium feldspar (0-23%), and volcanic, metamorphic, and sedimentary fragments (0-20%) (Uddin and Lundberg, 1998).

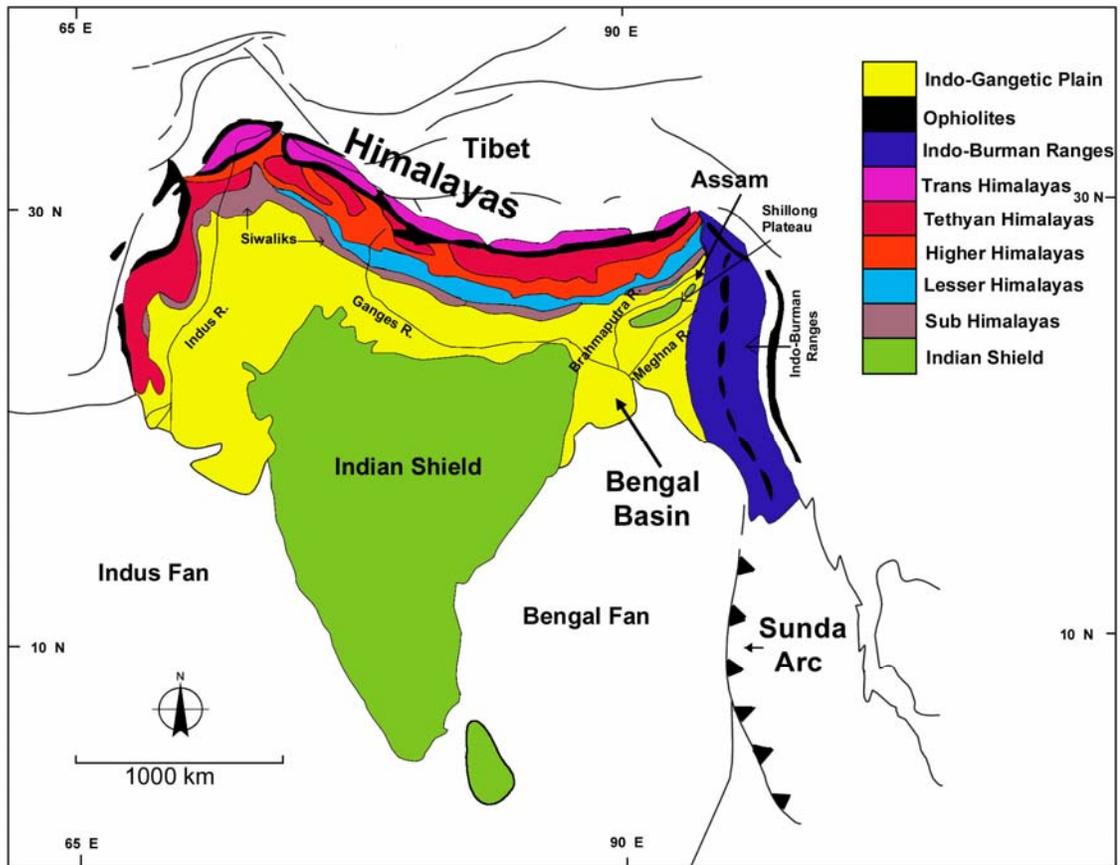


Figure 2. Regional geological framework of south Asia, showing the Bengal Basin and adjacent tectonic elements. Modified after Uddin and Lundberg (1998).

Delta plains and flood plains of the Brahmaputra and Ganges systems are moderately to severely affected by As problems, with greater than 60% of tube wells enriched with arsenic. Severely affected are the extremely enriched shallow alluvial aquifers of the Meghna delta and river basin, with more than 80% of tube wells affected (Ahmed et al., 2004). Conversely, Tertiary and Pleistocene upland aquifers are low in arsenic, due to their evolved and oxidized geochemical nature. The sediments enriched in As source from the collision suture and fold and thrust belt of the recycled orogen provenance (Ahmed et al., 2004). The Himalayan uplift is tectonically active and rapidly weathering, which in turn controls aquifer mineralogy and the groundwater geochemistry of the basin. For example, uplifted Himalayan granites rich in arsenic-bearing mica are a possible point source of arsenic, and weathered carbonates are the probable source for the elevated levels of barium and strontium (Dowling et al., 2002).

Sediment grain size also plays an important role in controlling distribution and mobility of arsenic. There is a strong correlation between arsenic and fine-grained clay minerals, noncrystalline aluminosilicate phases, and amorphous Fe, Mn, and Al hydroxides because of their volumetrically high surface area, which thereby allows adsorption of large amounts of arsenic and associated trace metals (Anawar et al., 2003). Fine-grained sediments contain high levels of organic matter, and a correlation between organic carbon content and arsenic distribution suggests that organic matter plays a significant role in arsenic mobilization and transport (Anawar et al., 2003).

Manikganj Geology

Well core samples were obtained from the Department of Public Health and Engineering (DPHE) in the study area, Manikganj Thana, located about 70 km northwest of the capital city Dhaka. Under the supervision of Bangladesh Water Development Board, an exploratory hole was drilled to a depth of 184 m within the Department of Public Health and Engineering compound in 1999 prior to the installation of 3 public supply wells. A lithologic log of the exploratory hole is shown in Figure 3. The subsurface geology of the study area consists of Quaternary deposits that can be divided into three general units. The lower unit is a grey to yellow fine- to medium-grained sand that occurs from the total drilling depth (184 m) up to 100-110 m. This lower unit is considered to be the lower aquifer. Locally there is a 5-10 m thick clay unit at about 100 m depth that separates the upper and lower aquifer, but is discontinuous in areas and appears to allow hydraulic communication throughout the sedimentary sequence. The middle unit is a grey sandy unit with a thickness of about 80 m. This unit generally fines upwards, has several interbedded clay units, and coarse sands and gravels near the bottom. The upper 10-15 m is an alluvial deposit of grey silty clay and very-fine sand. Sediment analyses of the core samples were conducted by the Geohazard Research Group, Dhaka University and the Hydrogeology Group at University College of London in 2002. Statistical grain size data shows that the samples are composed predominantly of fine to medium sand and are moderately to moderately well sorted. Point count data were used to quantitatively calculate detrital modes using quartz, feldspar, and lithic grain (QFL) ternary diagrams to classify sands, using the technique of McBride (1963).

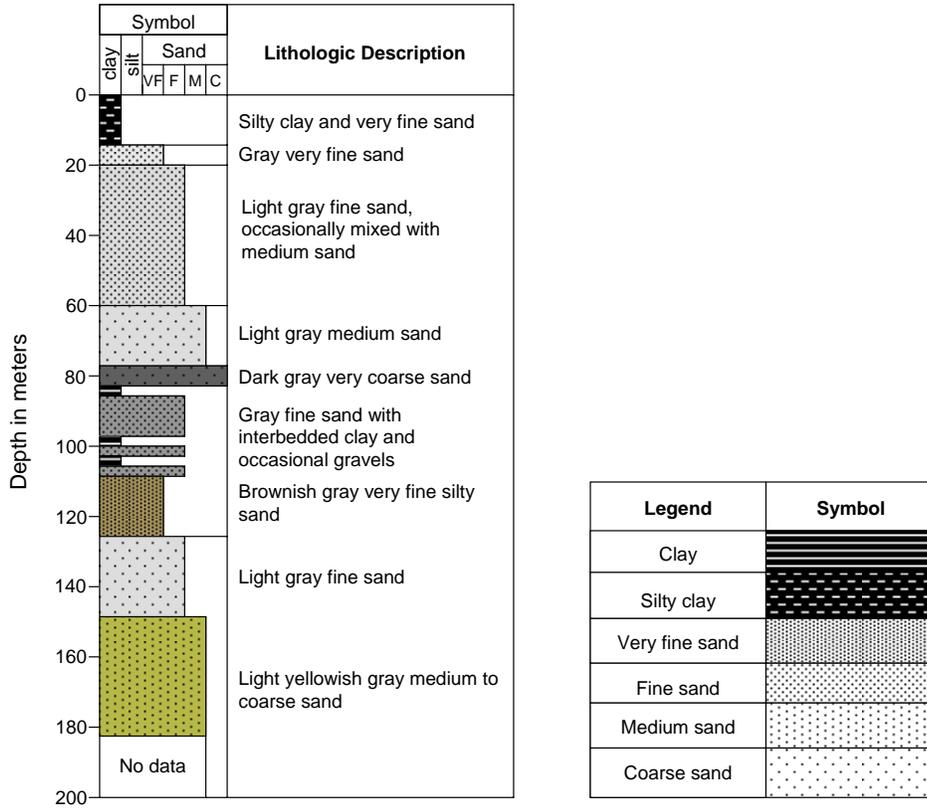


Figure 3. Lithologic log of the exploratory drill hole at the Department of Public Health and Engineering compound, Manikganj. Modified after the Geohazard Research, Dhaka University and the Hydrogeology Group at University College of London (2002).

Results show the sands belong to the sublitharenite petrofacies, which is characterized by >75% quartz, with lithic fragments dominating over feldspars.

The Geohazard Research group and the Hydrogeology Group (2002) also conducted some pumping tests outside of the study area. In conjunction with grain size analyses, their pumping tests indicate that the upper aquifer is hydraulically leaky, with transmissivity of approximately 3500 m²/d. In general, hydraulic conductivity is reported as 1.5 m/d for the fine sands in the shallow aquifer above 50 m depth, and approximately 25 m/d for the coarser sands below 50 m (Geohazard Research group and Hydrogeology Group, 2002). The permeability of the discontinuous clay can be inferred as very low, based only on its lithology.

The groundwater in the shallow Holocene aquifers in Manikganj is characterized by neutral pH, and is moderately reducing in nature. Measured oxidation-reduction potential (ORP) levels are typically around -100 mV. The principle anion is HCO₃⁻, and typical groundwater characteristics are low levels of sulfate and nitrate, and high levels (up to 2%) of dissolved organic carbon (DOC).

METHODOLOGY

Groundwater sampling and geochemical analysis

Geochemical sampling of groundwater was conducted at 15 tubewells (Fig. 4) in the district of Thana Manikganj, Bangladesh. Sadia Arafin (2003) conducted a prior investigation of 51 wells in Manikganj, and geochemical results from her work are used in conjunction with this study. Wells not previously sampled by Arafin were targeted in this investigation. Fieldwork was conducted by a team of five, the author, Ming-Kuo Lee, and Ashraf Uddin from Auburn University, and Tareq Chowdury and Salim Reza from the University of Dhaka.

Wells were purged for an average of 10 minutes prior to sampling to expel water sitting in the well casing and pull samples representative of aquifer formation water into the well. At each well, raw water was pumped into a plastic beaker in which the field parameters temperature, oxidation-reduction potential (ORP), pH, and specific conductance were measured using hand-held instruments. H₂S measurements were taken in the field using HACH colorimetric methods. Raw water samples were collected into two 60 mL plastic bottles for analyses of $\delta^{13}\text{C}$ of DIC and DOC, alkalinity, and anions. A sample was forced through a 0.45 μm filter into a 60 mL bottle and was acidified with ultra-pure HNO₃ for cation and trace metal analyses. ACTLABS conducted analyses of cations and trace metals using inductively coupled plasma mass spectrometry (ICP-MS). ACTLABS measured anion concentrations using ion chromatography (IC). $\delta^{13}\text{C}$

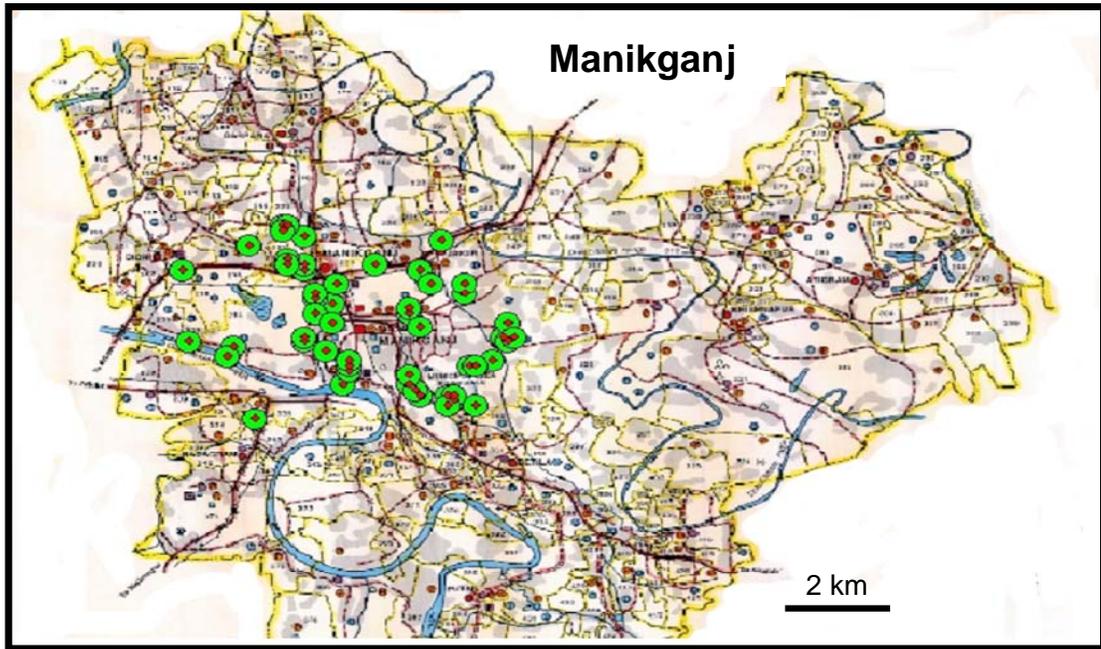


Figure 4. Study area map of Manikganj, Bangladesh. Sampling locations from both this study and Arafin's (2003) study are depicted as green and red circles. Dhaka City is located about 70 km to the southeast. Map modified from the Local Government Engineering Department UNDP/ILO Project BGD/89/041, 1994 document.

analyses of both dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) were conducted by the National High Magnetics Field Laboratory at Florida State University.

H₂ gas measurements: bubble stripping method

Dissolved hydrogen levels in Manikganj groundwater were measured in the field at 6 sampling locations using the bubble-stripping method (McInnes and Kampbell, 2000). The bubble-stripping method is based on the principle that gases such as H₂ will undergo equilibrium partitioning between a vapor phase and a liquid phase (Fig. 5). After purging the well, tubewell hand pumps were disassembled and removed from the wellhead by Abu Kaiser, a DPHE technician. Plastic tubing was inserted to the bottom of the well and run to a peristaltic pump powered by a portable car battery. A Microseeps[©] closed cell was filled up by groundwater withdrawn from the well. After removing bubbles by gentle tilting of the cell, 20 mL of air was injected into the cell to create a headspace. Water was pumped from the well for 15 minutes at a constant rate of 400 mL/minute into the Microseeps[©] closed cell. Due to a gradient between H₂ levels in the headspace and water, dissolved hydrogen in the groundwater partitioned into a gas phase in the headspace. When equilibrium conditions were reached (after 15 minutes of pumping) between the dissolved H₂ in solution and H₂ in the headspace, the pump was turned off and 15 mL of gas sample in the headspace was withdrawn with an airtight syringe and injected into a vacuum vial. Partial pressure of hydrogen gas in the solution's headspace (C_g) was measured by Microseeps with a reduction gas analyzer. The

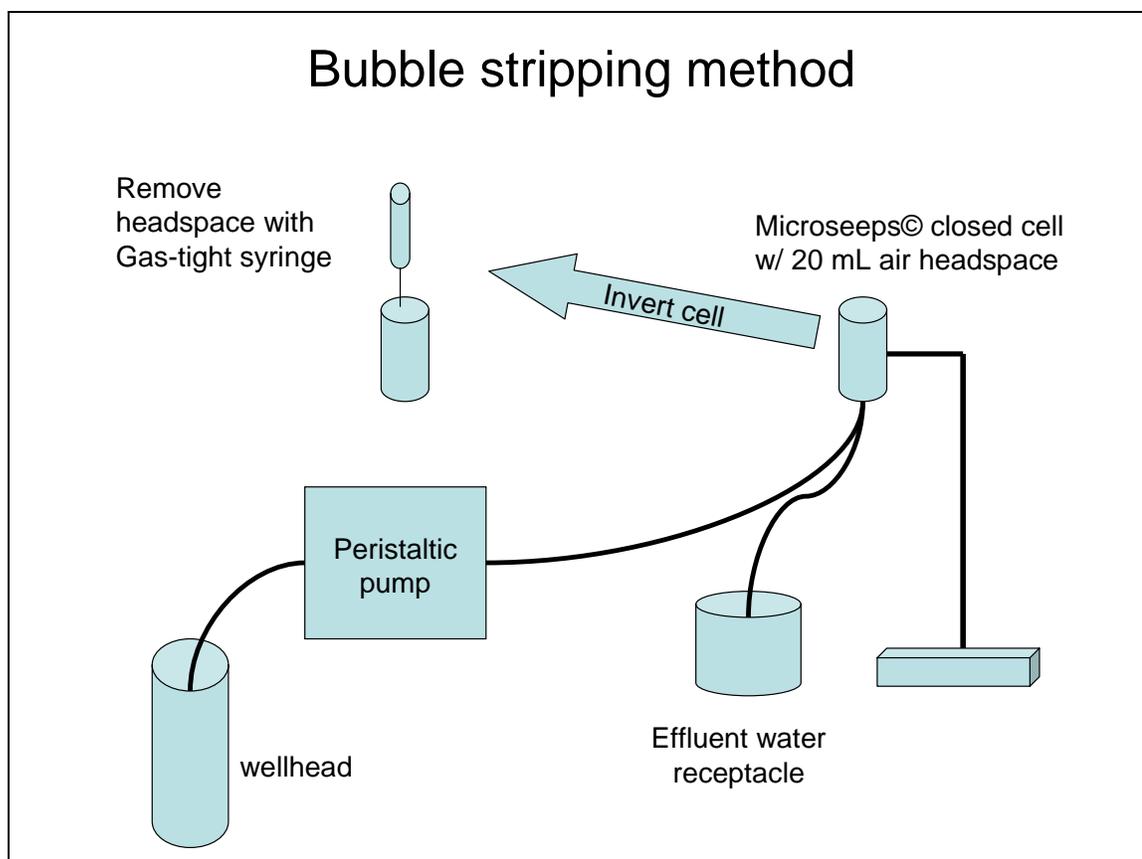


Figure 5. Diagram representing the bubble stripping method for measuring dissolved H_2 gas levels in the field (after McInnes and Kampbell, 2000). Plastic tubing was inserted to the bottom of a purged, disassembled tubewell. A battery-powered peristaltic pump was used to pump aquifer water at a constant rate of 400 mL/m into a Microseeps© closed cell with 20 mL of air headspace for 15 minutes. The pump was then turned off, the closed cell inverted, and the headspace removed with an airtight syringe, and injected into a vacuum vial to be analyzed in the lab with a reduction gas analyzer.

dissolved hydrogen levels in water (C_{ag}) were then calculated using Henry's Law (equation 1)

$$C_g \text{ (nM)} = C_{ag} \text{ (nM)} * 50.7 \text{ at } 21^\circ\text{C}. \quad (1)$$

Pilot field bioremediation experiment

An inexpensive nutrient injection experiment was conducted on tubewell ML-65 in Manikganj, in a cost-effective attempt to stimulate activities of indigenous sulfate reducing bacteria (SRB) and immobilize dissolved As by precipitating biogenic Fe-sulfides. Approximately 80 kg of sulfured molasses, purchased from a local source in Dhaka, was injected to provide soluble sulfate (serves as electron acceptor) and reactive organic carbon sources in attempt to stimulate SRB. In addition to our five man team, two locals and our van driver Babu were hired for the day to assist with the injection. 40 kg of molasses were added at a time into a 250 gallon collapsible rubber tank. The tank was then filled with buckets of water from a nearby well about 200 meters away, agitated to dissolve the molasses, and then poured through a funnel into the well. The silty aquifer we injected into has low hydraulic conductivity, and was initially taking less than 1 gal/min. Babu engineered a plunger out of bamboo, cloth, and tape, and used it to force the injection solution into the well. Subsequently, the aquifer was accepting 5 gal/min. All 80 lbs of molasses and 500 gallons of solution were successfully added to the well. After the injection, Tareq Chowdury monitored the injection well bi-weekly for H_2S content, Eh, pH, temperature, and conductivity.

Well core analysis

Well core samples were obtained from a DPHE public supply well in Manikganj. Core samples were collected in 1999. The Geohazard Research Group at Dhaka University and the Hydrogeology Group at University College of London performed statistical grain size analysis and quantitative point-count analysis to determine detrital modes. The core samples were stored in paraffin wax-capped 2" PVC at Dhaka University, where we collected the samples in January 2005. 2' core intervals were taken every 10 feet from the ground surface to 200 feet below ground surface. 2' core intervals were taken every 100 feet from 200 feet to 600 feet below ground surface. Sediment splits were collected from each interval and gently disaggregated. Grains exhibiting secondary mineral overgrowths or authigenic concretionary textures were separated using a binocular microscope. A Field Emission Scanning Electron Microscope (FESEM) with Energy Dispersive Spectroscopy (EDS) was used to (1) quantitatively analyze chemical composition and elemental weight percent of precipitated solids, and (2) investigate the texture, aggregated nature, and grain size of authigenic overgrowths. Minerals of special interest are primarily siderite (FeCO_3) and rhodocrosite (MnCO_3) that likely formed from Fe- and Mn-rich groundwater with high alkalinity. Precipitation of such minerals can affect the mobility of Fe, Mn, and As in the alluvial aquifer. Sediment splits with FeCO_3 and MnCO_3 concretions were analyzed at Florida State University for bulk ^{13}C isotopic composition.

Organic carbon content analysis of the core sediments was conducted at Auburn University. Bulk sediment samples were extracted from core at 10 foot intervals from 0 to 100 feet, and at 200, 300, 400, and 500 feet. The bulk samples were pulverized using a

mortar and pestal. Bulk samples were dried, split, and weighed. One split was immersed in a 10% HCl solution for carbonate-digestion, dried, and re-weighed to calculate carbonate %. The other split was left raw. Raw and carbonate-digested sediment splits were passed through carbon-free borosilicate glass filters. The sediment splits were analyzed for total organic carbon (TOC) contents using a LECO combustion analyzer.

Scanning Electron Microscopy and Energy Dispersive Spectroscopy

Sediment grains exhibiting secondary mineral overgrowths, extracted from the Department of Public Health and Engineering well core, were imaged using Auburn University's field emission scanning electron microscope (SEM). The SEM is equipped with an energy dispersive x-ray spectroscope (EDS). Energy dispersive spectroscopy is a procedure performed in conjunction with an SEM for identifying and quantifying elemental composition of sample areas as small as a few micrometers. When the sample is bombarded by the electron beam of the SEM, electrons are ejected from the atoms comprising the sample's surface. A resulting electron vacancy is filled by an electron from a higher shell, and an x-ray is emitted to balance the energy difference between the two electrons. The EDS x-ray detector measures the number of emitted x-rays versus their energy. The energy of the x-ray is characteristic of the element from which the x-ray was emitted. A spectrum of the energy versus relative counts of the detected x-rays is obtained and evaluated for qualitative and quantitative determinations of the elements present in the sampled volume.

Geochemical Modeling

Modeling of As speciation, double-layer adsorption-desorption, and reaction-path bacterial Fe(III) and Mn(IV) reduction in Manikganj groundwater was accomplished using *Geochemist's Workbench* (GWB) (Bethke, 1996). Geochemical data from Manikganj wells were used to set up the numerical model in the *React* feature of GWB. Initial conditions represent aerobic depositional conditions with groundwater at 25°C in equilibrium with hematite (Fe₂O₃) and pyrolusite (MnO₂), and Eh set to +600 mV. The model linearly slides Eh down to -200 mV and simultaneously titrates 500 μmol of acetate (as organic matter) into 1 kg of initial fluid in the system, representing post-burial water-sediment-bacteria interactions within the aquifer in which Fe(III)- and Mn(IV)-reduction occur. Model output includes mineral reactions and speciation of aqueous species which provides insight to groundwater geochemical evolution and mineralogic reaction sequence during Fe- and Mn- bacterial reduction.

GENERAL ARSENIC GEOCHEMISTRY

Speciation

Arsenic has two main oxidation states: As(III) which is more toxic, and As(V). Elevated levels of As(III) are present in Bangladesh aquifers under Fe-reducing conditions. An Eh-pH diagram for As speciation in the presence of S was calculated using Geochemists Workbench (GWB) software. Figure 6 shows that under oxidizing conditions H_2AsO_4^- and H_3AsO_4 are dominant species at low pH (<7) while HAsO_4^{2-} and AsO_4^{3-} become dominant at higher pH. Under reducing conditions H_3AsO_3 predominates over a wide range of pH. Under highly reducing conditions, the solid arsenic sulfides orpiment (As_2S_3) and thioarsenite ($\text{HAsS}_2, \text{AsS}_2^-$) aqueous complexes become the dominant phase in the absence of iron.

Adsorption/desorption

Hydrous ferric oxyhydroxides (HFOs) have very large surface area to volume ratios and are ubiquitous in alluvial and coastal plain aquifers under aerobic conditions. HFOs act as electron acceptors and provide surface sites for cations such as As, Ba, Sr, Cd, Co, Ni, and Zn to sorb onto, and they often occur as oxic river sediment coatings. Typically, these ferruginous coatings in Bengal basin aquifers are formed on sand grains and altered biotite micas (Ahmed et al., 2004). Arsenic sorbed onto the HFOs will remain stable under oxidizing conditions, or more specifically positive values of redox potential.

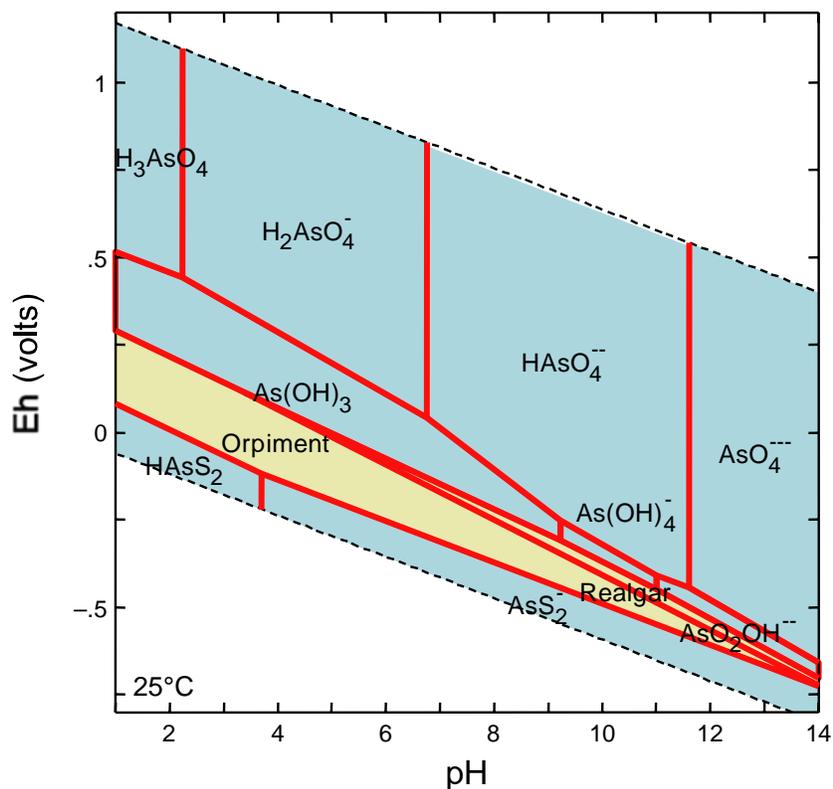


Figure 6. Eh-pH diagram of aqueous species in an As – S – H₂O system. Log As activity = -4, log SO₄²⁻ activity = -1. Aqueous As(V) species (H₃AsO₄, H₂AsO₄⁻, HAsO₄²⁻, AsO₄³⁻) are stable in oxidizing conditions (Eh > 0), whereas more toxic As(III) aqueous species [As(OH)₃, AsO₂OH⁻] are mobilized in moderately reducing conditions (Eh < 0). Realgar (AsS) and orpiment (As₂S₃) are redox-controlled precipitates. Model was created using GWB.

These conditions typically exist in rivers, the shallow subsurface, and the vadose zone of aquifers. Subsequently, oxidized sediments and associated sorbed As are buried together with organic matter to depths below the water table in anaerobic conditions. Bacterial reduction begins to take place, for example, Fe(III) is reduced to aqueous Fe^{2+} , causing As to desorb and remobilize. pH has a significant effect on adsorption of As(III) and As(V) by HFOs. Figure 7 shows that high pH values (>8.5) cause strong desorption of arsenic(V) and minor desorption of As(III). Figure 8 shows that As(III) and As(V) become desorbed under acidic pH conditions (<3.5). Most As-rich groundwaters from alluvial aquifers in Bangladesh have near-neutral pH values (6-8), implying that As contents in the groundwater could not have been derived solely from desorption, and that alternative mechanisms such as bacterial dissolution of HFOs are more important. Moreover, kinetic processes may cause desorption. For example, phosphate has a stronger thermodynamic affinity for HFO surfaces than arsenic, replacing sorbed As on solid phases and re-mobilizing aqueous As species (Bose and Sharma, 2002).

Solubility of Fe- and As-sulfides

Variations in Eh, pH, dissolved oxygen, and H_2S contents in groundwater directly affect solubility of As-bearing mineral orpiment. In S-rich systems, As concentrations may be controlled by solid As sulfide phases such as orpiment and realgar. Lee et al. (2005) show that orpiment solubility reaches a minimum value at $\log \text{H}_2\text{S}_{(\text{aq})}$ activity ≈ -4.5 and becomes relatively soluble with reduction in $\text{H}_2\text{S}_{(\text{aq})}$ activity. At high activity of H_2S , the formation of aqueous thioarsenite complexes would enhance As solubility (Fig. 9).

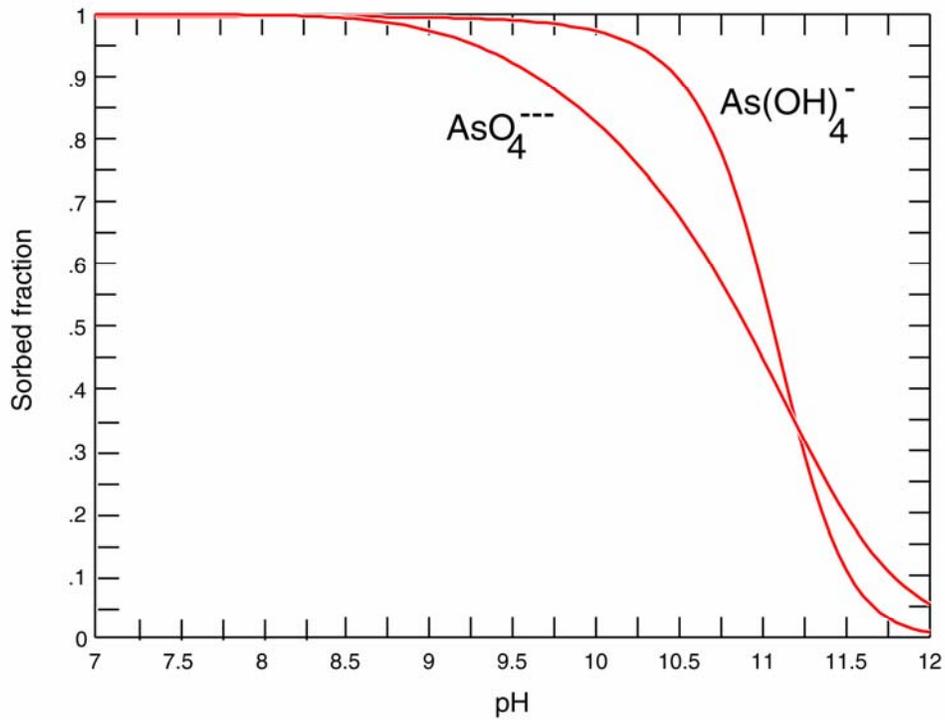


Figure 7. Double-layer adsorption-desorption model showing the desorption of As(OH)_4^- [As(III)] and AsO_4^{3-} [As(V)] at elevated pH. In 1 Kg of water, 0.001 mg of As(OH)_4^- and 0.001 mg of AsO_4^{3-} are almost completely sorbed to 1 gram of Fe(OH)_3 from neutral pH up to pH 8.5. As(V) progressively desorbs as pH increases above 8.5. As(III) begins to significantly desorb at pH exceeding 9.5. At pH > 12 both species completely desorb.

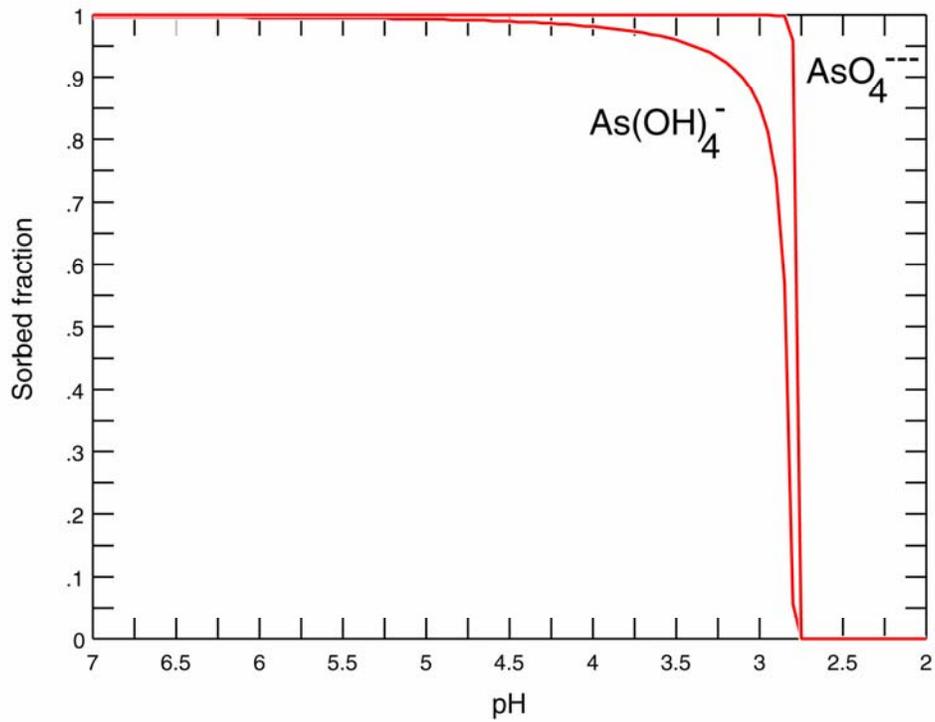


Figure 8. Double-layer adsorption-desorption model showing As(III) and As(V) at low pH. As (III) is strongly sorbed from pH 7 to 5, and partially desorbs from pH 5 to 3. As(V) remains strongly sorbed from pH 7 to 2.75. Below pH 2.75 both species completely desorb.

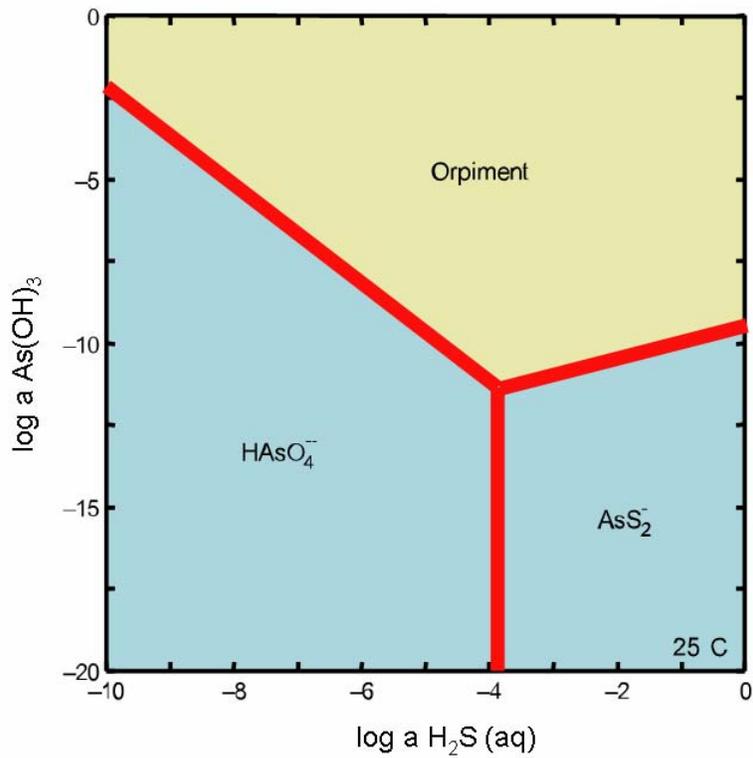
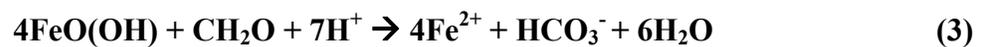


Figure 9. Activity-activity diagram of As(OH)_3 vs $\text{H}_2\text{S(aq)}$ created with Act2 in GWB. Initial conditions represent fluvial settings in presence of $\text{O}_2(\text{aq})$ at $\text{pH}=7$. Red lines represent equilibrium conditions between orpiment and aqueous As species. Increased levels of dissolved As(V) correlate with lower H_2S levels. When \log activity $\text{H}_2\text{S} \approx -4$, As is at a minimum solubility. As H_2S levels increase As(III) solubility increases.

In Fe- and S-rich systems, As concentrations in water are dictated by co-precipitation or sorption with iron sulfide solids, such as pyrite, mackinawite, and pyrrhotite. The solubility of these Fe sulfides generally decreases as pH rises, thus bacterial sulfate reduction (see Bacterial Sulfate Reduction section) could promote the precipitation of Fe sulfides by increasing pH and remove dissolved As from the solution. As(III) is more soluble at low pH, and As(V) is extremely soluble at high pH.

Bacterial Iron and Manganese Reduction

Upon the onset of reducing conditions anaerobes such as Mn(IV)- and Fe(III)-reducing bacteria reduce HFOs in the presence of reactive carbon sources in sediments, releasing reduced Fe, Mn, and sorbed As into solution (Cummings et al., 1999) by the following reactions (equations 2, 3):



There are strong correlations among high levels of dissolved As, Fe, high alkalinity, and elevated pH values in Bengal basin aquifers due to these bacterially-mediated reactions (Dowling et al., 2002). The presence of Fe(III)-reducing bacteria such as *Geobacter* (Saunders et al., 2005) and *Shewanella* (Cummings et al., 1999) in As-rich alluvial aquifers supports the hypothesis that bacterial reduction of HFOs causes As release to groundwater. Also, arsenic is mobilized at negative Eh levels, as well as elevated pH

levels, both conditions consistent with zones of bacterial reduction. Reduced Fe^{2+} and Mn^{2+} may react with HCO_3^- released from organic carbon sources to form minerals such as siderite (FeCO_3) and rhodochrosite (MnCO_3). Such minerals are found in alluvial sediments in Bangladesh (see Scanning Electron Microscopy section) as secondary, authigenic concretions, typically $< .5$ mm in size, with colliform textures.

Bacterial Sulfate Reduction

Relative to most alluvial aquifers worldwide, there are low amounts of dissolved sulfate in Bengal basin aquifers (see Geologic and Hydrogeologic Setting section). Such geochemical conditions play a direct role in the high concentrations of dissolved Fe and As in groundwater. Typically under sulfate reducing conditions, authigenic precipitation of biogenic Fe-sulfides removes As and Fe from solution due to the activities of sulfate reducing bacteria (SRB). SRB convert sulfate to H_2S , which subsequently reacts with Fe to form relatively insoluble iron sulfide. Fe-sulfide minerals containing high levels of arsenic may locally occur in the Bengal basin aquifers where bacterial sulfate reduction is not limited by sulfate. The following is a generic bacterially-mediated sulfate reduction reaction (equation 4):



This bacteria-driven process causes H^+ protons to react with sulfate and organic carbon to form H_2S . Activities of SRB are detectable in the field by very low ORP values and

by a “rotten egg” smell associated with formation of hydrogen sulfide. Next, metals react with the hydrogen sulfide (equation 4) to form insoluble solid sulfides (equation 5):

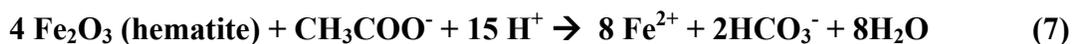
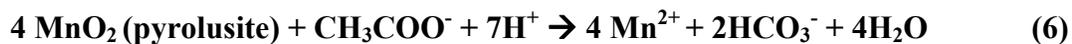


Arsenic has a strong affinity for Fe and usually coprecipitates by substitution for S in the formation of biogenic pyrite (FeS₂) or Fe monosulfide (mackinawite).

Low levels of dissolved sulfate probably limit these reactions from occurring extensively in West Bengal, India and Bangladesh. In other aquifers around the world, Fe and As are often immobilized by natural attenuation due to the activities of naturally occurring SRB (Kirk et al., 2004). However, the presence of some dissolved sulfides in alluvial aquifers in Bangladesh indicates that sulfate reduction does occur locally, especially in finer grained sediments under reducing conditions (Ahmed et al., 2004), but does not represent a significant sink for As in West Bengal, India and Bangladesh groundwater (Zheng et al., 2004). In sulfate-limited geochemical systems, bioremediation or immobilization of As may be achieved by adding sulfate salts and a reactive source of carbon (such as molasses) to stimulate the metabolic activities of SRB in groundwater.

GEOCHEMICAL MODELING OF BACTERIAL REDUCTION OF Fe(III) AND Mn(IV) OXIDES

GWB was used to trace the sequence of biogeochemical reactions that occur during bacterial Fe(III) and Mn(IV) oxide reduction, the major trigger for As release in alluvial aquifer systems. Initial conditions for the geochemical model are based on water chemistry data from Manikganj well ML-68 equilibrated under aerobic conditions at 25°C in equilibrium with hematite (Fe₂O₃) and pyrolusite (MnO₂). The model then simulates the geochemical effects of titration of organic matter (acetate) into the system. The transformation of pyrolusite and hematite are considered by the following redox reactions (equations 6, 7):



In the simulation, fluid reactants containing 500 μmol of acetate (CH₃COO⁻) displace existing fluid from the system and the Eh values slide from +600 mV to -200 mV over the course of the reaction path. The predicted mineral reactions show that pyrolusite in the initial system becomes thermodynamically unstable during bacterial reduction and

transforms over time to a sequence of progressively more stable manganese minerals and species (equation 8) at lower oxidation states:



Once the reduction of Mn minerals has nearly completed, the iron redox reactions begin (Fig. 10) and hematite (Fe_2O_3) begins to dissolve to form more stable siderite (FeCO_3) or pyrite (FeS_2) at very low oxidation states. During bacterial reduction under moderately reducing conditions, reduced metal species also combine with HCO_3^- released from organic sources to form rhodochrosite (MnCO_3) and siderite. The modeling results are supported by SEM and EDS studies of core samples, which show the formation of authigenic carbonates in As-rich sand aquifers. Under strongly reducing conditions, reduced metals species react with H_2S released during sulfate reduction to form Fe-sulfide minerals such as pyrite (FeS_2). Figure 11 shows the calculated Mn and Fe concentrations in fluid over the same reaction path. It clearly demonstrates how the precipitation and dissolution of various Mn- and Fe- minerals control the mobility of metals in groundwater.

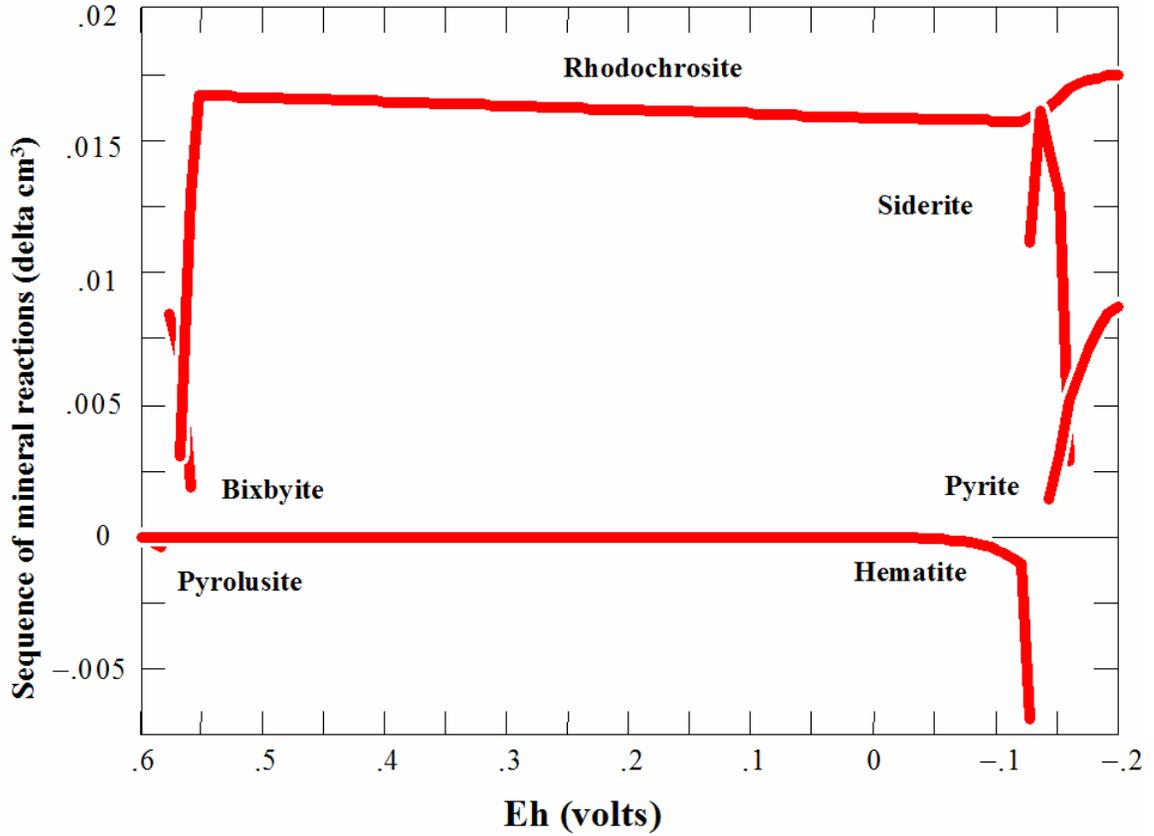


Figure 10. Predicted sequence of mineralogical reactions resulting from bacterial reduction of Fe and Mn oxides in equilibrium with Bangladesh groundwater in a Manikganj well. The plot shows changes in mineral volume as acetate is titrated into the system and Eh decreases with time. Positive changes indicate precipitation, and negative changes show dissolution.

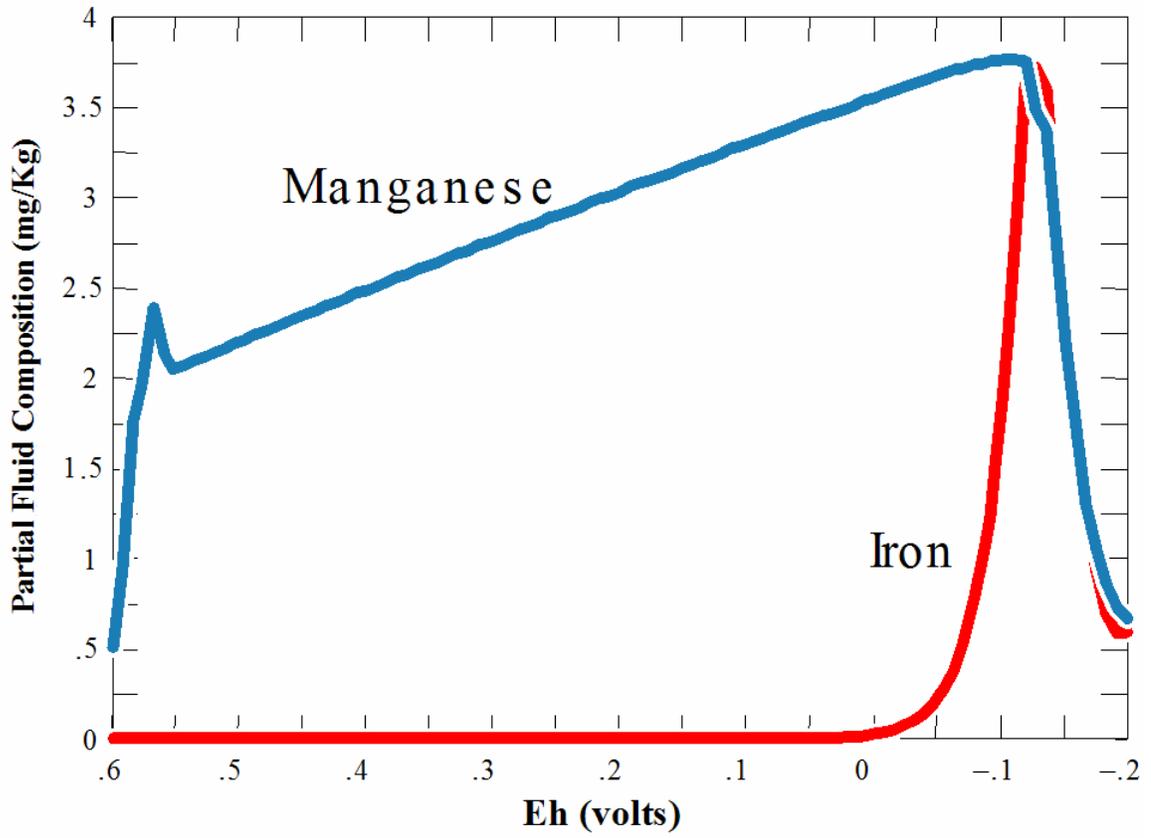


Figure 11. Calculated total Mn and Fe concentrations in fluid predicted by the same reaction path model in Fig. 10.

CORE SAMPLE ANALYSIS

Scanning Electron Microscopy

Authigenic mineral concretions of siderite are present in the Department of Public Health and Engineering well core drilled in the study area. Core sediments were gently disaggregated, and a binocular microscope was used to extract grains with secondary mineral concretions (Fig. 12). Grains exhibiting secondary concretions were very sparse in well core samples at depths between 100 and 300 feet. Grains with secondary mineralization were present predominantly at depths greater than 400 feet. The concretions were only found in porous and permeable sections of the aquifer in fine sands. No siderite concretions were found in silty or muddy sections of the aquifer. Eight selected grains were imaged and analyzed at Auburn University's field emission scanning electron microscope (SEM) (Fig. 13). These concretions typically form on quartz grains, are typically $\leq .5$ mm, and form in globular or colliform concretions. At high magnification (2700X) the concretions exhibit discrete laminated rhombohedral crystals typically < 10 μm across (Fig. 14).

Energy Dispersive Spectroscopy

In addition to imaging, nine qualitative and five quantitative EDS analyses were performed to provide quantitative elemental composition data (Table 1). Concretions were isolated at high magnification (2700X) in the SEM so that the electron beam

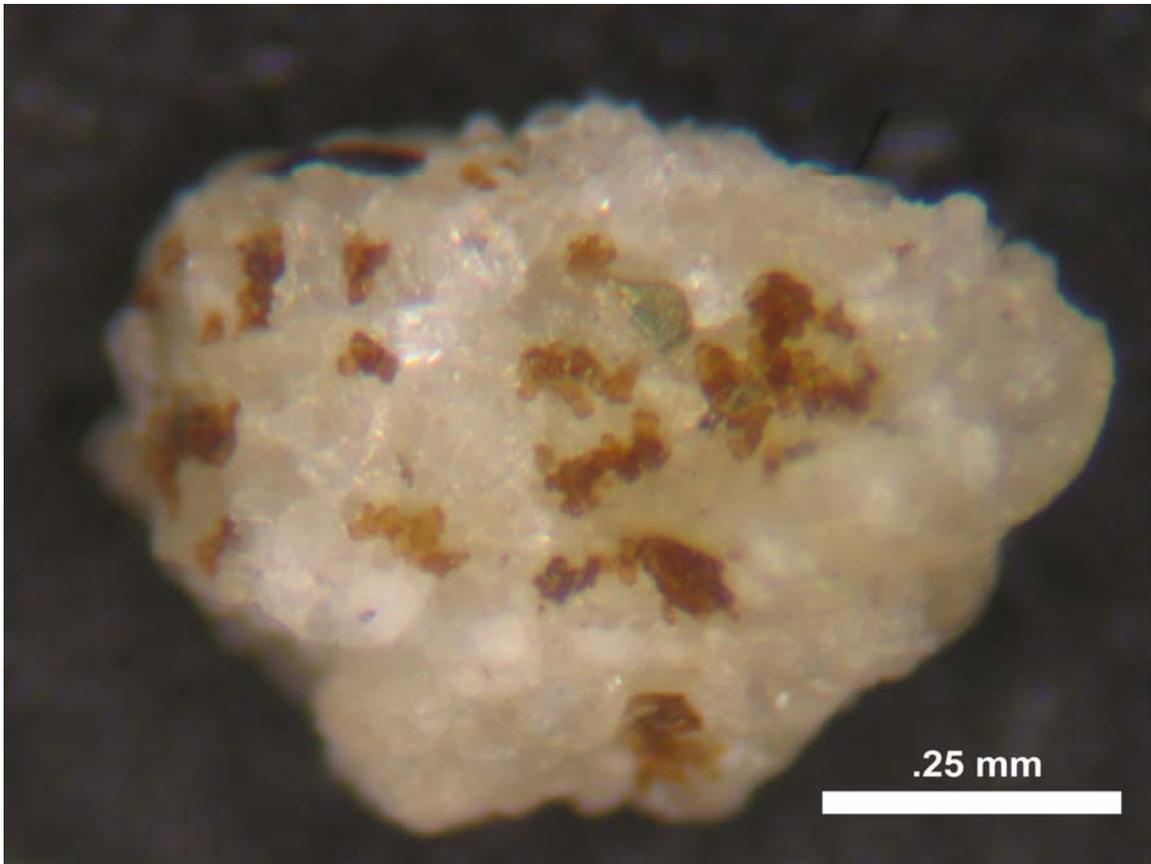


Figure 12. Siderite concretions on a quartz grain. This grain was photographed through a binocular microscope, and exhibits a typical example of concretions on quartz found in the Department of Public Health and Engineering well core at 500 feet.

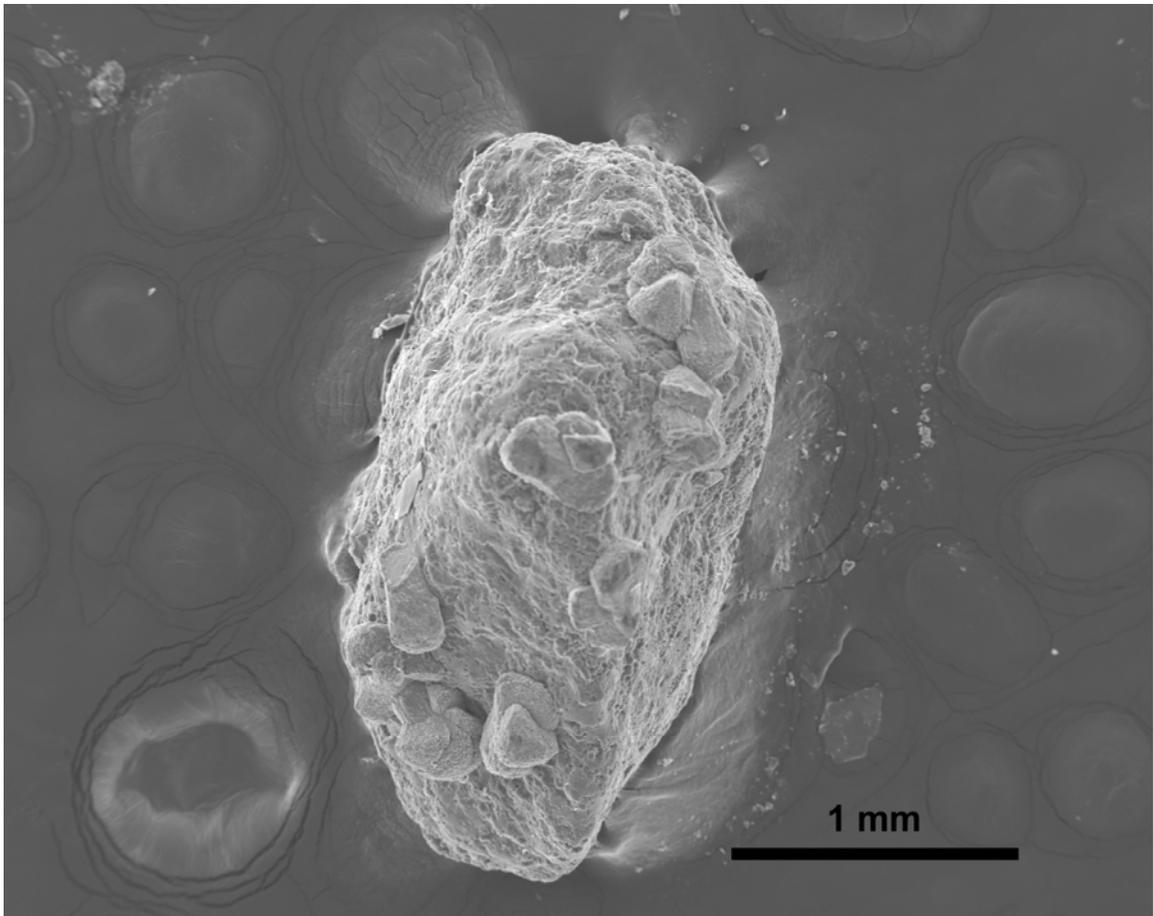


Figure 13. SEM image (75X) of authigenic siderite concretions on quartz grain Sample IV from Department of Public Health and Engineering well core. This is a typical grain found in the 400 foot core interval. EDS analysis was performed at high magnification on these and other concretions to determine elemental composition.

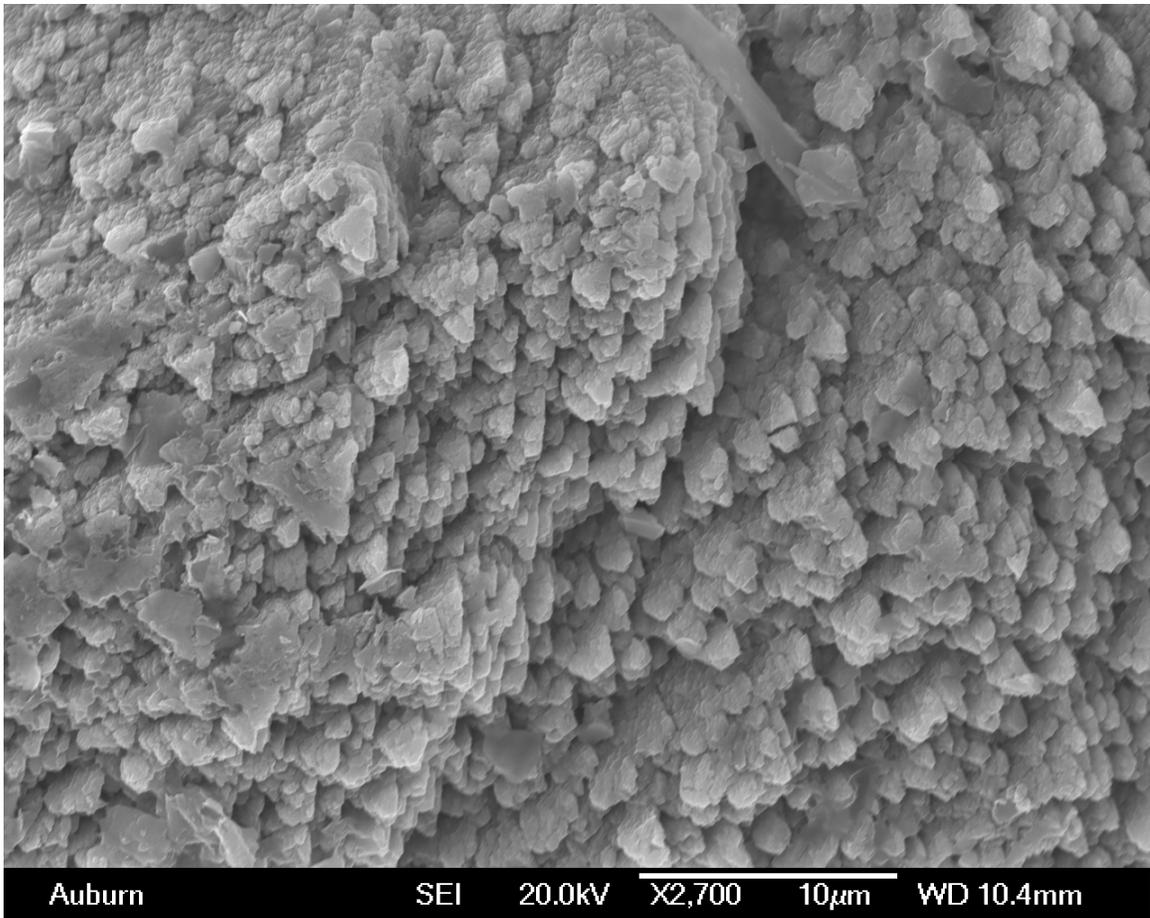


Figure 14. SEM image at 2700X of a siderite concretion on Sample IV. EDS results were obtained from a small area about 2 µm across from the middle of the field of view.

Table 1. Quantitative EDS results of Sample IV. KeV and KRatio are plotted above in Figure 15. Weight % and Atomic % values affirm the concretions are siderite.

Element	Line	keV	KRatio	Wt%	At%	At Prop	ChiSquared
O	KA1	0.523	0.1333	32.47	53.65	0	5.22
Al	KA1	1.487	0.0033	0.69	0.68	0	10.05
Si	KA1	1.74	0.006	0.99	0.93	0	10.05
Ca	KA1	3.691	0.0263	2.77	1.83	0	15.12
Mn	KA1	5.898	0.0178	1.88	0.9	0	104.93
Fe	KA1	6.403	0.3538	37.95	17.97	0	104.93
Au	MA1	2.121	0.0871	13.12	1.76	0	10.05
C	KA1	0.277	0.0219	10.12	22.28	0	4.03
Total			0.6495	100	100	0	39.57

focused on an area on the concretion surface < 5µm across. Results (Fig. 15) show that siderite concretions typically contain varying levels of Fe (24-38%), O (32-40%), C (10-13%), Ca (2-3%) and Mn (1-2%), which is consistent with United States Geological Survey (USGS) findings (George Breit, USGS, pers. comm.).

Organic Carbon

Organic carbon contents range from low to relatively high (0.125 to 4.00 weight %) in sediment samples from the Department of Public Health and Engineering well core (Table 2). Silty dark gray samples have higher organic carbon contents than sandy, lighter colored intervals.

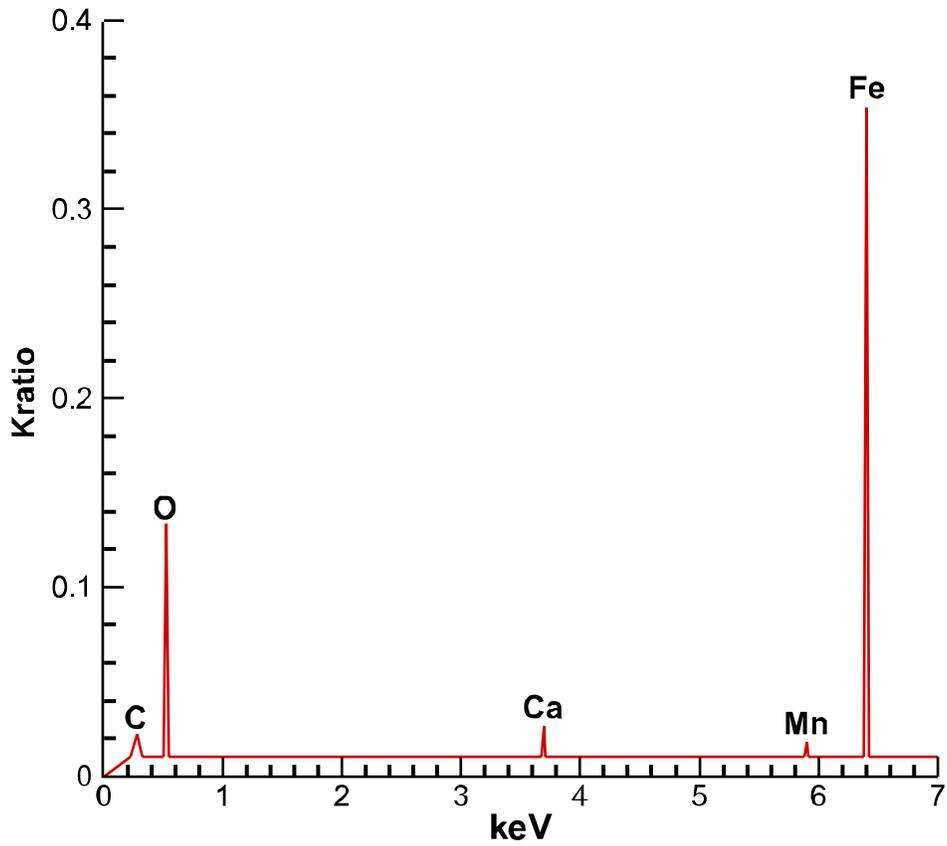


Figure 15. Emitted x-ray energy versus relative counts of the detected x-rays. Qualitative EDS results of the center concretion on Sample IV shown above in figure 13. Fe, C, and O peaks show that the predominant constituent of the concretion is siderite (FeCO_3). Minor amounts of Mn suggest the possible presence of rhodocrosite (MnCO_3). Nine samples were analyzed, and this is a typical representation of the results.

Table 2. Organic carbon contents in sediments extracted from the Department of Public Health and Engineering well core.

Sample	Depth Interval (ft)	Carbonate Digested Samples		Raw Sediment samples	
		Sample wt. (g)	Organic C %	Sample wt. (g)	Organic C %
JT1	2--4	0.2550	1.5500	0.2152	1.650
JT2	14--16	0.2803	0.9160	0.2097	1.410
JT3	22--24	0.2866	2.6100	0.2544	2.850
JT4	30--32	0.2758	0.9750	0.2192	0.936
JT5	50--52	0.2506	2.8900	0.2034	3.000
JT6	70--72	0.4664	0.2660	0.2267	0.325
JT7	78--80	0.2498	0.2680	0.2137	0.296
JT8	90--92	0.4398	0.1880	0.2280	0.210
JT9	98--100	0.2570	0.2540	0.2278	0.269
JT10	110--112	0.2784	0.1710	0.2022	0.166
JT 11	200--202	-	-	0.3681	0.172
JT 12	300--302	-	-	0.3389	4.000
JT 13	400--402	-	-	0.3738	0.125
JT 14	500--502	-	-	0.3319	0.276

GEOCHEMICAL RESULTS

The following sections present and discuss observed data on major ions, trace elements, dissolved H₂ gas, $\delta^{13}\text{C}$, and organic carbon. Results presented include both new data, collected from 15 tubewells in January 2005, and pre-existing data collected from 51 tubewells in 2002 by Sadia Arafin of University of Dhaka. Relationships and correlations between the geochemical data, field parameters, carbon isotopic signatures, and H₂ gas provide evidence that elevated concentrations of As, Mn, and Fe are associated with high organic carbon content, high alkalinity, and anaerobic microbial activity.

Field Parameters

ORP, pH, conductivity, latitude/longitude, temp., H₂S level, and well depth of tubewells are shown in Tables 3 and 4. In the study area, groundwater pH values range from 6.11 to 7.14. In circum-neutral pH range and moderately reducing conditions, As is mobilized and As(III) is the dominant aqueous As phase (see geochemical modeling section). Measured ORP values ranged from -125 to +103 mV. Of the 15 sampled wells, only 2 had positive ORP, one of which was adjacent to a shallow, large-diameter dug well which recharged the tubewell. Arsenic and trace metal concentrations are very low in the two wells with positive ORP values, and conversely, elevated As and trace metal concentrations are associated with negative ORP values.

Table 3. Field parameters and location of sampled tubewells in Manikganj.

Sample ID#	pH	ORP (mV)	Conductivity (μ S)	lat/long	well depth (m)	temp °C	H ₂ S (ppm)
M/L-08	6.89	54	1580	23.52.24.8/90.00.21.0	229	25.2	< .1
M/L-19	7.07	-101	1855	23.52.25.7/89.59.37.0	36	24.6	< .1
M/L-37	7.02	-99.4	1664	23.51.28.0/89.59.35.8	36.6	24.4	< .1
M/L-39	7.01	-100.7	2200	23.51.47.6/89.59.41.8	45.3	25.7	< .1
M/L-60	7.13	-103	1431	23.52.48.4/89.59.32.1	25	25	< .1
M/L-61	6.91	-96	2110	23.52.50.3/89.59.32.8	24.8	24.8	< .1
M/L-62	6.93	-106	1850	23.51.26.7/89.58.31.1	39.6	25.1	< .1
M/L-63	6.87	-104.8	2290	23.51.25.7/89.58.31.2	22.9	25.6	< .1
M/L-64	6.8	-108	1812	n/a	24.3	24.8	< .1
M/L-65	7	-125	1906	23.52.51.7/89.59.31.5	24.6	24.6	< .1
M/L-66	6.88	-70.7	2500	23.52.51.4/89.59.31.0	18.2	24.3	< .1
M/L-67	7.14	103	2280	23.52.50.0/89.59.33.0	10	23.2	< .1
M/L-68	7.05	-114	2300	23.52.26.6/89.59.35.0	28.9	23	< .1
M/L-69	7.03	-103	1836	23.52.24.4/89.59.36.5	73.2	23.3	< .1
M/L-70	7.05	-104.9	1265	23.52.49.3/89.59.31.9	22.9	24.2	< .1

Table 4. Field parameters and location of previously sampled wells in Thana Manikganj (Arafin, 2003). ORP and H₂S data were not collected.

Sample ID#	pH	ORP (mV)	Conductivity (μS)	lat/long	well depth (m)	temp °C	H ₂ S (ppm)
M/L-01	6.62	-	710	23.51.55/90.00.05	178.30	26.6	-
M/L-02	6.95	-	690	23.51.55/90.00.04	45.00	26.6	-
M/L-03	6.84	-	560	23.50.52/90.00.11	79.52	26.6	-
M/L-04	6.93	-	520	23.51.02/90.00.15	-	28.8	-
M/L-05	6.93	-	510	23.51.06/90.00.14	105.89	26.6	-
M/L-06	6.92	-	500	23.51.12/90.00.15	-	26.4	-
M/L-07	6.94	-	560	23.52.10/90.00.06	137.16	26.4	-
M/L-08	6.95	-	480	23.52.22/90.00.31	228.60	26.3	-
M/L-09	6.48	-	510	23.50.47/90.01.02	73.15	26.2	-
M/L-10	6.28	-	580	23.50.53/90.00.53	36.58	26.2	-
M/L-11	6.18	-	750	23.50.49/90.00.56	18.29	26.0	-
M/L-12	6.48	-	580	23.50.59/90.00.55	73.15	26.1	-
M/L-13	6.54	-	620	23.50.44/90.01.20	36.58	26.1	-
M/L-14	6.22	-	670	23.50.41/90.01.21	27.43	26.2	-
M/L-15	6.35	-	490	23.50.45/90.01.22	73.15	26.2	-
M/L-16	6.11	-	760	23.51.57/89.59.52	22.86	26.6	-
M/L-17	6.3	-	520	23.52.01/89.59.51	15.24	26.1	-
M/L-18	6.86	-	550	23.52.19/89.59.46	73.15	27.1	-
M/L-19	7.02	-	650	23.52.23/89.59.46	36.58	26.6	-
M/L-20	6.9	-	510	23.52.24/89.59.47	18.29	26.5	-
M/L-21	6.96	-	490	23.51.10/90.01.49	73.15	26.0	-
M/L-22	6.94	-	470	23.51.16/90.01.32	22.86	26.3	-
M/L-23	6.95	-	530	23.51.06/90.01.36	36.58	26.0	-
M/L-24	6.96	-	460	23.51.23/89.58.58	73.15	26.0	-
M/L-25	6.81	-	600	23.51.16/89.58.55	36.58	25.8	-
M/L-26	6.3	-	800	23.51.27/90.01.55	22.86	26.0	-
M/L-27	6.23	-	560	23.51.26/90.01.57	36.58	26.2	-
M/L-28	6.35	-	610	23.51.41/90.02.00	73.15	25.4	-
M/L-29	6.6	-	520	23.51.29/90.02.01	15.24	25.7	-
M/L-30	6.42	-	640	23.51.48/90.00.53	21.35	25.5	-
M/L-31	6.5	-	440	23.51.51/90.00.55	18.29	24.9	-
M/L-32	6.22	-	590	23.51.37/90.01.02	37.19	25.7	-
M/L-33	6.57	-	530	23.52.02/90.01.30	73.15	26.3	-
M/L-34	6.37	-	870	23.52.01/90.01.30	22.86	26.2	-
M/L-35	6.46	-	550	23.52.07/90.01.31	45.72	26.1	-
M/L-36	6.45	-	520	23.51.24/89.59.47	73.15	25.9	-
M/L-37	6.48	-	610	23.51.27/89.59.46	36.58	26.1	-
M/L-38	6.5	-	870	23.51.19/90.00.00	21.34	26.6	-
M/L-39	6.49	-	740	23.51.45/89.59.52	45.72	26.1	-
M/L-40	6.39	-	510	23.52.19/90.01.01	73.15	26.1	-
M/L-41	6.56	-	560	23.52.18/90.01.01	18.29	26.2	-
M/L-42	6.52	-	520	23.52.07/90.01.09	37.19	26.4	-
M/L-43	6.63	-	710	23.50.40/90.01.36	73.15	26.2	-
M/L-44	6.38	-	500	23.50.40/90.01.37	45.72	26.2	-
M/L-45	6.39	-	920	23.50.40/90.01.19	18.29	26.0	-
M/L-46	6.78	-	1810	23.50.26/89.59.12	202.69	26.6	-
M/L-47	6.53	-	420	23.52.20/89.58.25	192.02	25.8	-
M/L-48	6.22	-	490	23.52.37/89.59.08	185.93	28.2	-
M/L-49	6.4	-	540	23.52.45/89.59.44	185.93	26.3	-
M/L-50	6.45	-	550	23.52.41/90.01.16	195.07	26.2	-
M/L-51	6.45	-	630	23.51.41/90.00.03	137.16	26.1	-

Trace Metals and Major Ions

Elevated concentrations of trace metals As, Fe, Mn, Sr, Ba (Tables 5, 6) are present in groundwater in the shallow alluvial aquifers in the study area. Arsenic concentrations ranged from 2.66 to 105.9 µg/L in the study area. 37 of the 66 wells sampled had As concentrations exceeding the WHO drinking water standard of 10 µg/L. Fe concentrations in this study ranged from 0.07 to 4.94 mg/L in filtered samples. Arafin (2003) measured Fe concentrations ranging from 0.03 to 26.98 mg/L as unfiltered concentrations. In general, Fe concentrations are very high in the study area. Several tubewells sampled had visible Fe-colloids in suspension. Mn concentrations ranged from 0.23 to 4.16 mg/L, Sr from .06 to 5.11 mg/L, and Ba from .06 to 1.42 mg/L. SO₄ concentrations ranged from below the detection limit (0.06 mg/L) to high concentrations (73.42 mg/L) over short distances.

ORP - Fe, As, and Mn

Figure 16 shows that As and Fe levels are very low in the two shallow wells with positive ORP (54-104 mV). In contrast, elevated concentrations of As and Fe are observed in tubewells under moderately reducing conditions, particularly with ORP values around -100 mV. Fe concentrations are much higher than As concentrations in the study area, but in Fe-reducing zones precipitation of authigenic siderite preferentially removes Fe from solution relative to As. Elevated Mn levels are also found around -100 mV, and are well correlated with elevated As (Fig. 17). These data support the hypothesis that Mn- and Fe- reductive dissolution in anaerobic groundwater is responsible for elevated As, Mn, and Fe concentrations.

Table 5. Selected major ion and trace metal concentrations of sampled tubewells. 6 of the 15 wells sampled had arsenic levels exceeding the WHO drinking water standard of 10 ppb, and are shown below in red.

Sample ID#	As ppb	Ca ppm	Mg ppm	Mn ppm	SO ₄ ppm	Na ppm	K ppm	Fe ppm	Sr ppm	Ba ppm
M/L-08	2.66	63.3	-	0.62	0.25	-	3.08	0.08	0.35	0.10
M/L-19	22.4	89.1	26.2	0.27	0.13	-	3.47	0.20	0.34	0.90
M/L-37	3.55	76.0	27.7	0.90	8.18	12.9	9.45	0.15	0.22	1.42
M/L-39	5.90	141.0	42.4	1.00	30.8	22.7	5.37	0.18	4.34	1.34
M/L-60	12.3	63.4	27.7	0.37	0.06	13.3	2.96	0.13	3.18	0.06
M/L-61	8.81	108.0	30.7	-	1.85	12.5	1.70	0.13	3.39	0.07
M/L-62	5.22	83.5	29.4	0.95	4.18	19.2	7.98	0.32	3.27	0.13
M/L-63	6.49	111.0	40.5	-	9.26	18.2	5.83	0.15	2.93	1.01
M/L-64	6.10	84.0	24.5	0.44	0.06	14.0	2.99	1.15	-	1.10
M/L-65	11.1	82.6	30.9	-	0.06	19.2	4.10	1.53	3.91	0.07
M/L-66	4.43	133.0	45.5	-	18.2	27.6	2.48	1.88	5.11	0.11
M/L-67	4.83	118.0	29.0	-	9.89	16.4	6.92	1.49	3.58	0.10
M/L-68	58.1	120.0	35.9	0.36	26.1	-	5.93	4.94	5.04	0.18
M/L-69	20.8	78.2	27.1	0.23	0.06	-	4.14	2.61	3.20	0.14
M/L-70	12.5	49.2	20.4	0.49	0.06	15.2	3.69	2.45	2.62	0.06

Table 6. Selected major ion and trace metal concentrations of tubewells sampled by Sadia Arafin (2003). Shown below in red, 31 of 51 wells sampled exceed the WHO drinking water standard for arsenic.

Sample ID#	As ppb	Ca ppm	Mg ppm	Mn ppm	SO ₄ ppm	Na ppm	K ppm	Fe ppm	Sr ppm	Ba ppm
M/L-01	31.20	68.24	25.85	0.87	3.42	58.82	4.50	4.59	0.68	0.13
M/L-02	43.90	88.06	32.47	0.26	6.35	16.15	3.81	17.74	0.39	0.16
M/L-03	17.60	71.30	25.83	0.29	2.40	27.18	4.25	9.11	0.33	0.13
M/L-04	46.90	64.74	23.97	0.12	1.86	22.70	4.19	0.07	0.30	0.08
M/L-05	64.80	61.41	25.15	0.22	-	22.71	4.54	7.32	0.30	0.11
M/L-06	33.10	65.11	21.62	0.28	-	19.85	3.87	7.72	0.29	0.16
M/L-07	4.10	62.39	24.65	0.75	-	45.07	3.25	0.77	0.40	0.16
M/L-08	18.10	54.39	20.75	0.69	1.89	34.99	3.08	0.90	0.38	0.10
M/L-09	3.60	62.21	23.44	0.61	4.26	18.58	3.86	11.60	0.24	0.17
M/L-10	28.40	71.71	32.24	0.20	26.22	13.20	2.76	14.82	0.24	0.19
M/L-11	22.30	102.41	28.51	1.60	2.47	26.44	2.43	14.35	0.32	0.09
M/L-12	17.10	67.59	28.50	0.59	-	15.25	3.27	15.95	0.28	0.16
M/L-13	14.10	82.06	30.19	0.53	8.52	17.64	7.23	7.54	0.35	0.24
M/L-14	59.50	75.17	34.47	1.23	40.16	18.14	13.97	13.15	0.20	0.26
M/L-15	4.00	61.30	20.96	0.33	3.35	13.70	4.21	10.37	0.27	0.16
M/L-16	4.80	78.83	26.44	0.04	49.92	46.30	39.97	0.16	0.12	0.06
M/L-17	43.50	71.61	20.92	0.54	12.62	14.84	8.67	0.25	0.13	0.04
M/L-18	105.90	67.61	24.37	0.21	-	25.16	3.36	6.55	0.34	0.17
M/L-19	102.00	85.52	25.93	0.36	-	16.69	3.72	10.16	0.42	0.19
M/L-20	55.30	68.63	21.83	0.35	1.84	12.80	3.09	8.67	0.33	0.14
M/L-21	35.30	58.79	24.73	0.51	43.03	14.33	3.65	9.27	0.26	0.15
M/L-22	69.40	57.98	21.55	1.43	-	8.20	2.98	16.54	0.24	0.11
M/L-23	78.60	68.43	21.16	0.30	-	10.78	3.62	13.25	0.29	0.15
M/L-24	60.20	56.92	19.87	0.41	-	11.67	4.27	7.95	0.24	0.13
M/L-25	12.20	71.37	21.28	0.52	-	10.74	3.03	26.98	0.21	0.20
M/L-26	51.20	116.05	30.25	4.16	17.65	12.52	3.23	2.23	0.37	0.11
M/L-27	27.60	57.55	25.74	0.66	1.96	12.84	4.23	18.92	0.26	0.15
M/L-28	5.80	71.37	24.98	0.71	-	16.35	3.64	15.13	0.29	0.20
M/L-29	1.20	71.85	20.01	1.12	-	11.20	3.67	0.71	0.23	0.09
M/L-30	3.90	95.06	19.75	0.60	41.70	13.12	3.75	0.21	0.22	0.09
M/L-31	9.80	51.04	19.58	0.44	14.32	12.79	12.21	0.19	0.06	0.06
M/L-32	0.80	55.68	23.49	0.87	22.34	7.52	2.41	10.55	0.20	0.09
M/L-33	16.40	56.26	22.55	0.66	-	11.86	28.63	2.46	0.23	0.25
M/L-34	9.40	91.07	43.70	0.94	73.42	21.57	4.38	8.06	0.29	0.20
M/L-35	63.70	58.11	23.94	0.88	12.41	13.80	18.36	-	0.22	0.18
M/L-36	38.90	70.37	22.58	0.28	12.33	11.68	6.08	6.67	0.27	0.15
M/L-37	2.30	73.56	27.76	1.04	13.91	10.90	10.20	5.69	0.25	0.20
M/L-38	58.80	135.18	34.51	0.94	41.68	18.19	0.67	-	0.31	0.09
M/L-39		93.47	40.07	0.76	18.87	10.47	5.62	0.60	0.42	0.14
M/L-40	24.00	62.04	18.58	0.88	1.81	12.68	3.73	0.01	0.25	0.16
M/L-41	11.10	72.94	28.99	2.05	19.12	11.53	3.91	0.16	0.28	0.09
M/L-42	4.10	47.78	28.14	0.75	1.87	18.96	20.83	-	0.14	0.17
M/L-43	21.20	86.22	43.89	0.90	47.17	22.03	4.26	0.03	0.29	0.14
M/L-44	14.90	51.45	28.55	0.79	75.73	18.92	21.40	7.79	0.15	0.20
M/L-45	0.50	125.38	38.45	3.36	4.20	22.00	1.81	0.19	0.38	0.20
M/L-46	9.20	142.97	33.81	1.23	1.85	18.94	0.82	3.51	0.31	0.12
M/L-47	0.40	41.71	20.09	0.38	2.90	36.09	3.66	0.40	0.28	0.12
M/L-48	0.50	58.67	21.64	0.73	-	31.37	3.32	0.32	0.37	0.14
M/L-49	0.50	64.33	28.77	0.89	1.76	36.15	3.01	-	0.44	0.16
M/L-50	8.90	54.31	20.97	0.63	2.25	56.11	3.09	-	0.37	0.16
M/L-51	8.9	39.25	15.95	0.31	1.73	98.82	3.32	-	0.26	0.12

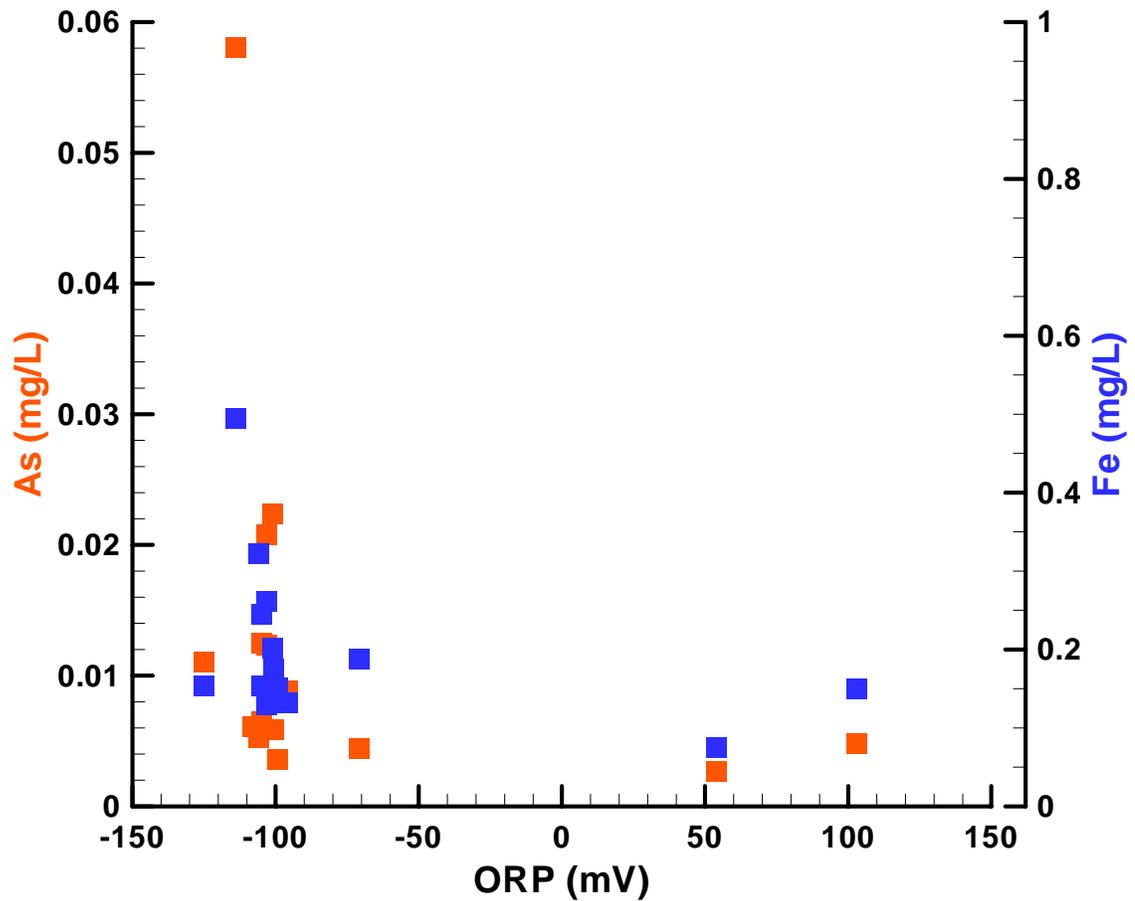


Figure 16. ORP vs. As and Fe plot shows that elevated levels of As and Fe correlate with $ORP \approx -100$ mV, levels associated with Fe-reducing conditions. HFO is reduced by Fe-reducing bacteria to soluble Fe(II), simultaneously releasing sorbed As into solution. As concentrations are low in the shallow dug wells under oxidizing conditions, in which As is strongly sorbed by HFO.

As - Fe, Mn

Data presented by Arafin (2003) also reveals a correlation between As and Fe (Fig. 18). Specifically, in samples with Fe concentrations < 1 mg/L, As levels are consistently below 0.02 mg/L. Samples with Fe exceeding 5 mg/L have elevated As concentrations ranging up to 0.1059 mg/L. Arafin's (2003) results do not provide a strong correlation between As and Mn (Fig. 19). However, elevated amounts of both As and Mn are found throughout the study area.

As - SO_4^{2-}

An inverse relationship is found between As and SO_4^{2-} in the study area. Geochemical data from this study show that wells with high As concentrations (> 0.01 mg/L) generally have low SO_4^{2-} concentrations (< 2 mg/L) (Fig. 20). Wells containing < 0.01 mg/L arsenic have variable concentrations of sulfate ranging from below the detection limit (0.06 mg/L) to > 30 mg/L. Data from Arafin (2003) shows a similar, although less distinct inverse relationship between As and SO_4^{2-} , where tubewells with elevated SO_4^{2-} levels generally have low As (Fig. 21). This relationship is possibly due to the natural precipitation of Fe-sulfides such as pyrite, mackinawite, and pyrrhotite in the aquifers, which preferentially removes Fe and As from solution by co-precipitation or sorption (see General Arsenic Geochemistry section). However, this biogenic sulfate reduction is probably limited by low SO_4^{2-} concentrations. Only a fraction of As can be removed by iron sulfide solids even when all sulfate ions are consumed.

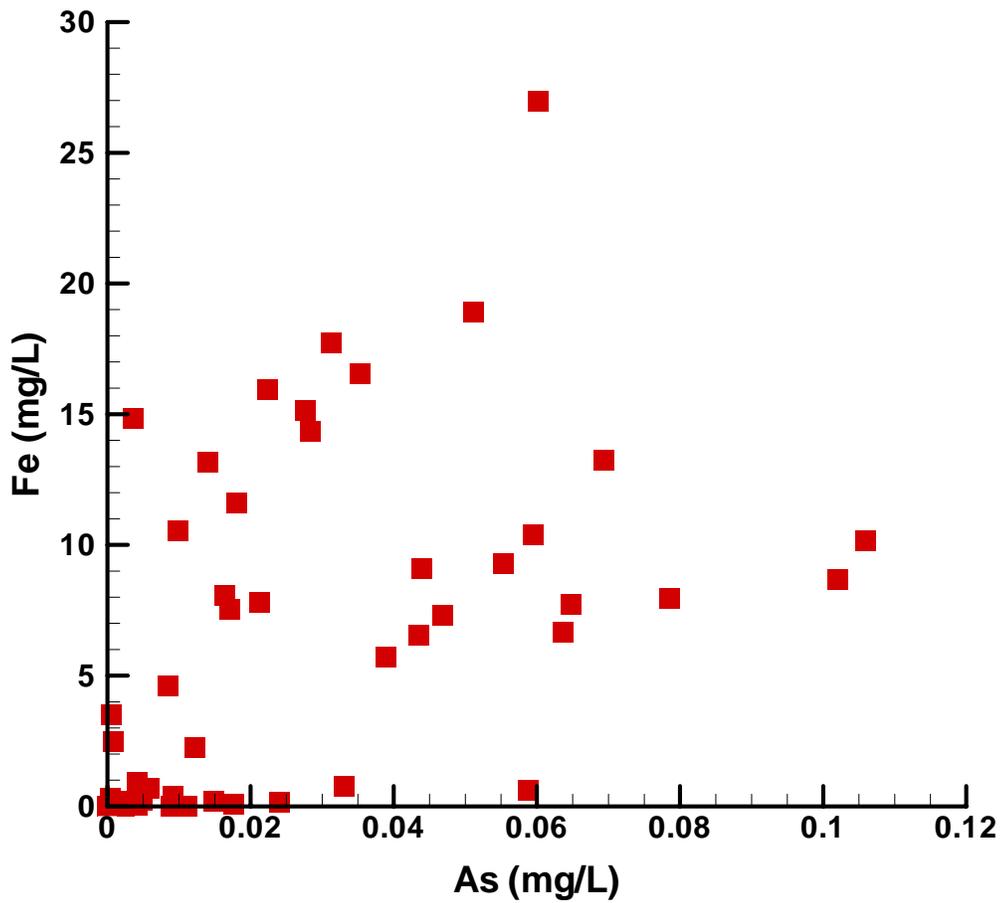


Figure 18. Existing data (Arafin, 2003) shows correlation between increased levels of As and Fe in Manikganj groundwater. Where Fe levels are < 1 mg/L, As levels are below 0.02 mg/L.

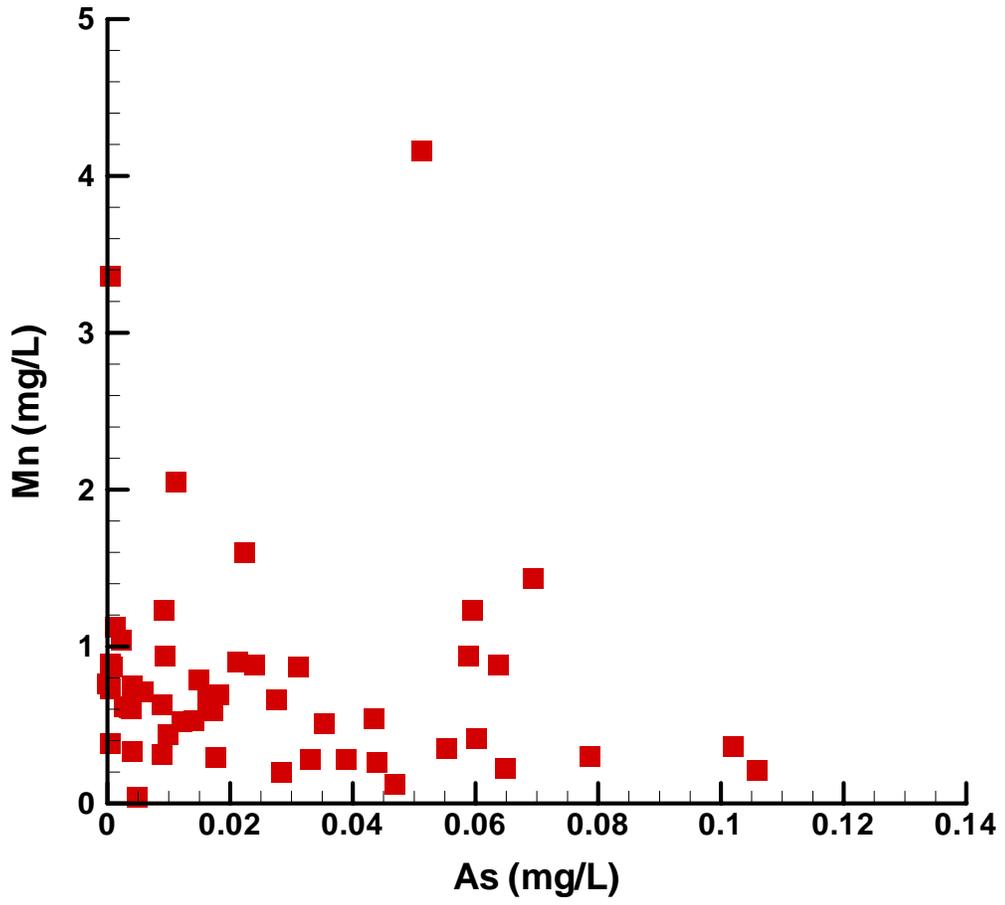


Figure 19. Arafin's (2003) data reveals a poor correlation between As and Mn concentrations.

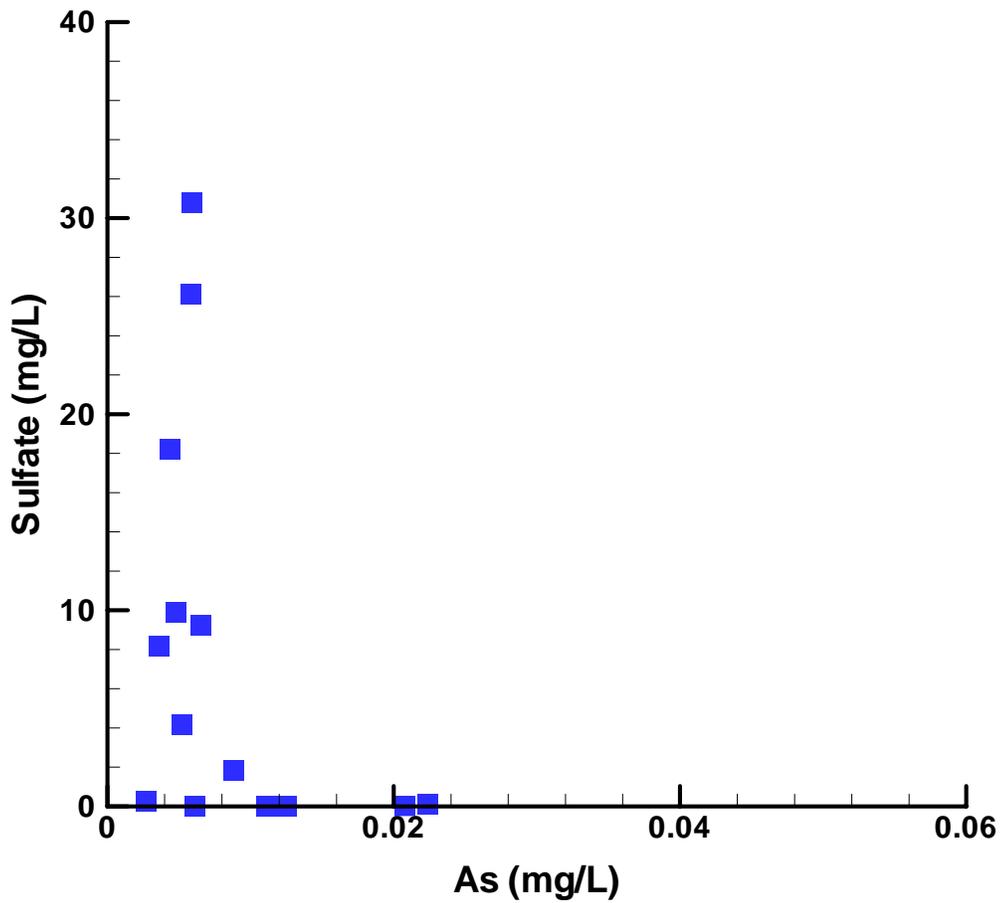


Figure 20. Arsenic levels are elevated only in samples where sulfate content is below 2 mg/L. Wells containing < .01 mg/L arsenic have variable concentrations of sulfate, from below the detection limit (.06 mg/L) to > 30 mg/L.

As – HCO₃⁻ - pH

Groundwaters in the study area are characterized by high alkalinity (as HCO₃⁻, in mg/L) (Figs. 22, 23). As discussed earlier (equations 2, 3, 6, 7, see General Arsenic Geochemistry section), anaerobic bacterial reduction of Fe(III)-oxides and Mn(IV)-oxides releases reduced Mn²⁺ and Fe²⁺, as well as HCO₃⁻ into solution. All groundwaters in the study area had circum-neutral pH values, ranging from 6.11 to 7.14. According to the geochemical modeling section, As(III) is the dominant aqueous species in neutral pH water under moderately reducing conditions. According to equations 2, 3, 6, and 7, bacterial Fe-reduction would release Fe and As and raise alkalinity at the expense of H⁺. Thus elevated As concentrations are found in groundwaters with high concentrations of HCO₃⁻ (120 to 500 mg/L) and pH values > 6.

δ¹³C

δ¹³C values for dissolved inorganic carbon (DIC) range from -3.32‰ to 4.07‰ relative to the Vienna PeeDee Belemnite standard (VPDB), indicating a relatively heavy isotopic signature for DIC in Manikganj groundwater (Table 7). All these values fall within the range reported by the British Geological Survey (BGS) special study, although most of the Manikganj values are heavier than the results reported from throughout Bangladesh. BGS data shows that DIC is about 50 times as abundant as DOC in As-rich Bangladesh groundwaters, but much of the DIC in most samples is derived from bacterial respiration of organic matter in sediments (George Breit, USGS, pers. comm.). δ¹³C

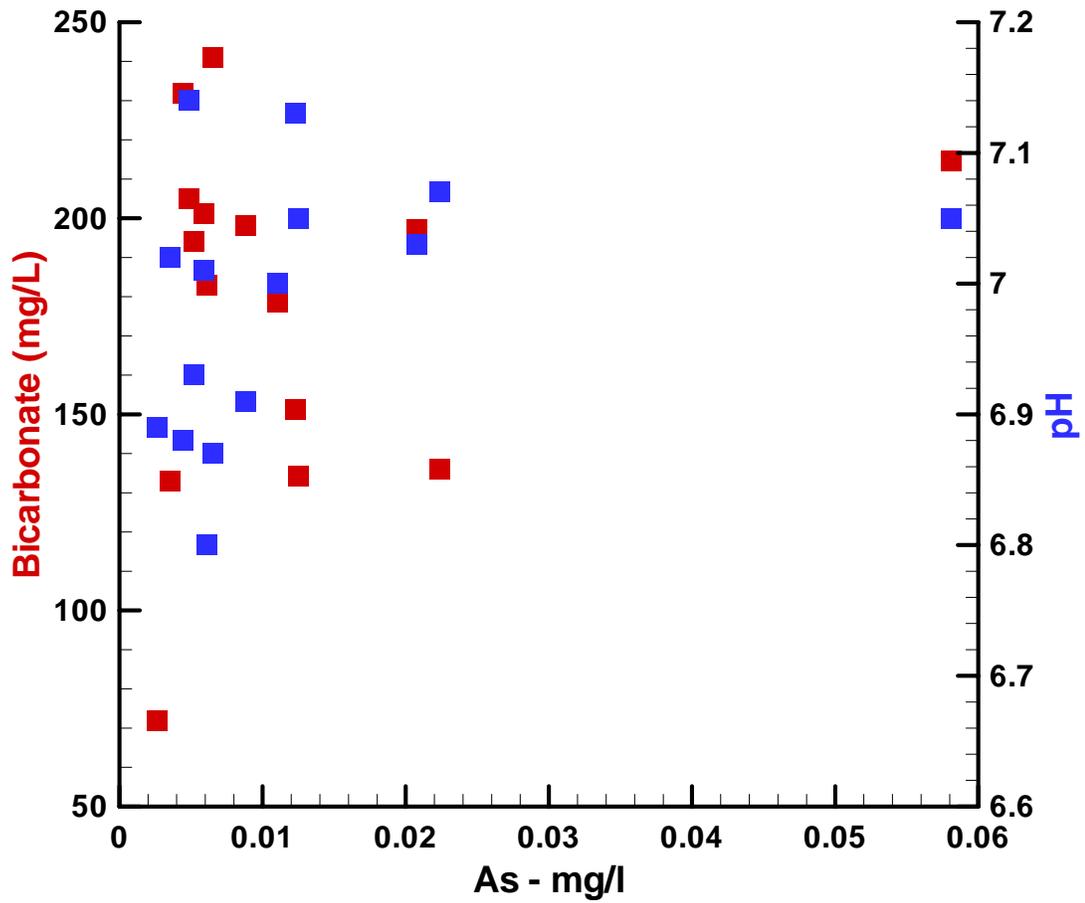


Figure 22. As-rich groundwaters in Manikganj have relatively high alkalinity and circum-neutral pH. Wells with elevated As concentrations had > 120 mg/L HCO_3^- .

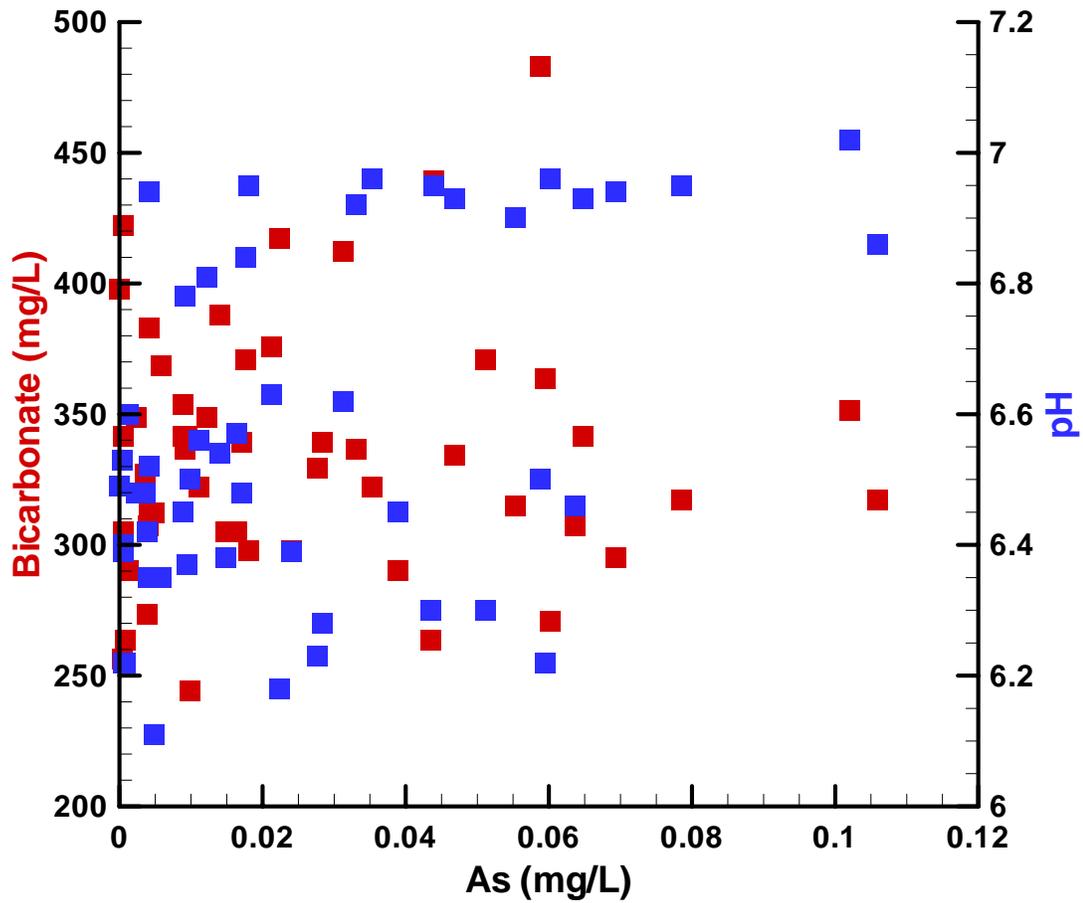


Figure 23. Existing data also shows that elevated As concentrations are found in groundwater with high alkalinity and pH between 6.1 and 7.14. Arafin's (2003) data shows that As concentrations exceeding the drinking water standard are found in wells with HCO_3^- concentrations ranging from 240-500 mg/L.

Table 7. $\delta^{13}\text{C}$ values for DIC and DOC in Manikganj groundwater.

	DIC samples			DOC samples
	$\delta^{13}\text{C}$ (‰)PDB	standard deviation	Total DIC (mg C/L)	$\delta^{13}\text{C}$ (‰)PDB
M/L-08	-0.87	0.01	33	-23.6
M/L-19	0.54	0.01	23	-22.8
M/L-37	-1.63	0.04	31	-24.5
M/L-39	-0.92	0.05	31	-24.3
M/L-60	3.41	0.07	33	-24.6
M/L-61	-1.56	0.02	45	-23.8
M/L-62	1.03	0.02	47	-24.2
M/L-63	-1.22	0.02	79	-24.2
M/L-64	-0.29	0.02	45	-23.0
M/L-65	2.36	0.04	29	-23.3
M/L-66	-0.84	0.02	48	-23.9
M/L-67	-3.32	0.02	33	-24.9
M/L-68	-0.90	0.02	51	-25.0
M/L-69	1.77	0.02	45	-23.6
M/L-70	4.07	0.02	22	-24.0

values for dissolved organic carbon (DOC) range from -22.8‰ to -25.0‰ (VPDB), significantly lighter than those of DIC.

Elevated As and Fe concentrations correlate with isotopically heavy $\delta^{13}\text{C}$ DIC levels in groundwater (Fig. 24, 25). Isotopic fractionation may be caused by bacterial respiration of lighter ^{12}C from organic matter in aquifer sediments. When bacterial Fe(III)-reduction takes place, groundwater is simultaneously enriched in heavier $\delta^{13}\text{C}$, Fe, and associated desorbed As. Alternatively, degassing of CO_2 and CH_4 , methanogenesis, and formation of biogenic, isotopically-light carbonate minerals would cause further enrichment in ^{13}C of DIC. Moreover, de-watering and fluid expulsion of deep-crustal rocks associated with tectonic collision in the Himalayas could have contributed CO_2 (and perhaps other metals) that is isotopically heavier than atmospheric CO_2 .

H₂ gas

Dihydrogen is produced as a by-product of microbial metabolism. H_2 concentrations of 0.2 to 0.8 nM have been cited as a marker for Fe-reduction, 1 to 4 nM imply SO_4^{2-} reduction, and levels > 5 nM indicate that reductive methanogenesis is the dominant metabolic process (Chapelle et al., 1995, Kirk et al., 2004). H_2 levels in 6 Manikganj tubewells range from 1.3 to 2.4 nM, and the concentrations increase with increasing As and Fe levels (Fig. 26). No sulfate is present in wells with H_2 concentrations > 2.1 nM, and in wells with H_2 concentrations < 1.4 nM, sulfate concentrations range up to 31 mg/L, indicating that locally, some groundwaters are under sulfate reducing conditions, and some H_2 may be generated by bacterial sulfate reduction.

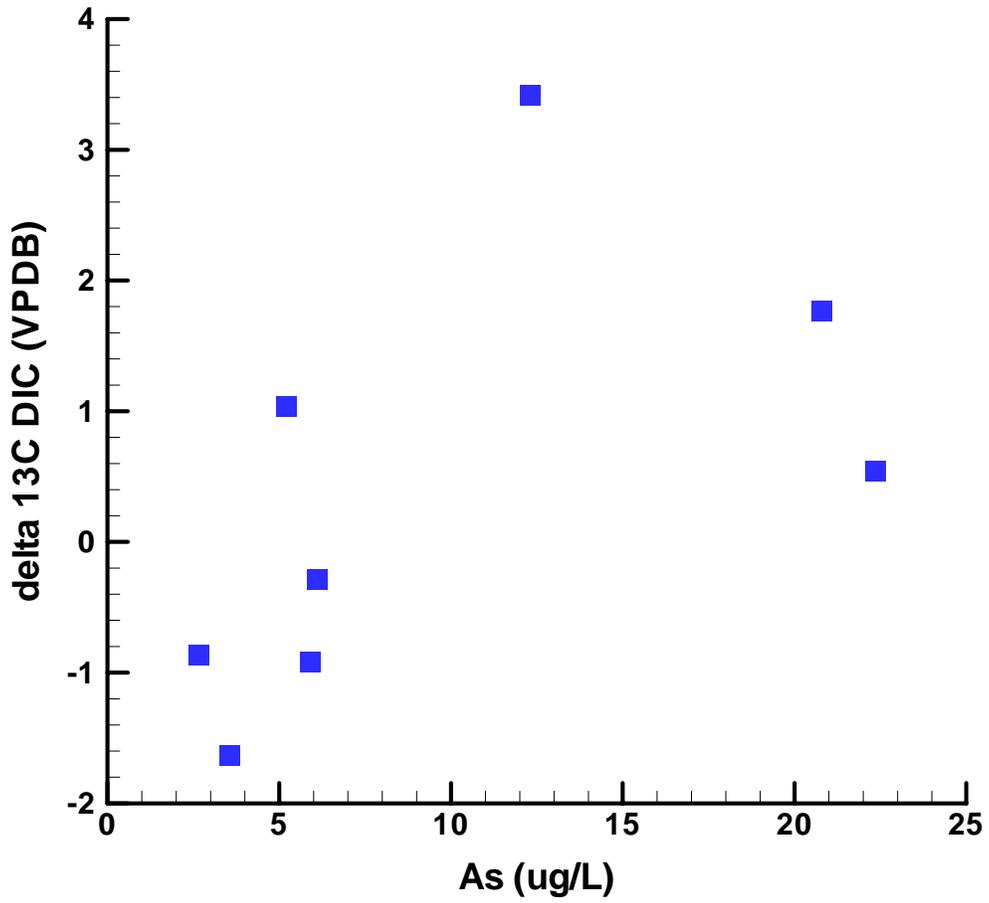


Figure 24. Elevated As concentrations correlate with isotopically heavy $\delta^{13}\text{C}$ DIC levels in groundwater. Isotopic fractionation may be caused by bacterial respiration of lighter ^{12}C from organic matter in aquifer sediments.

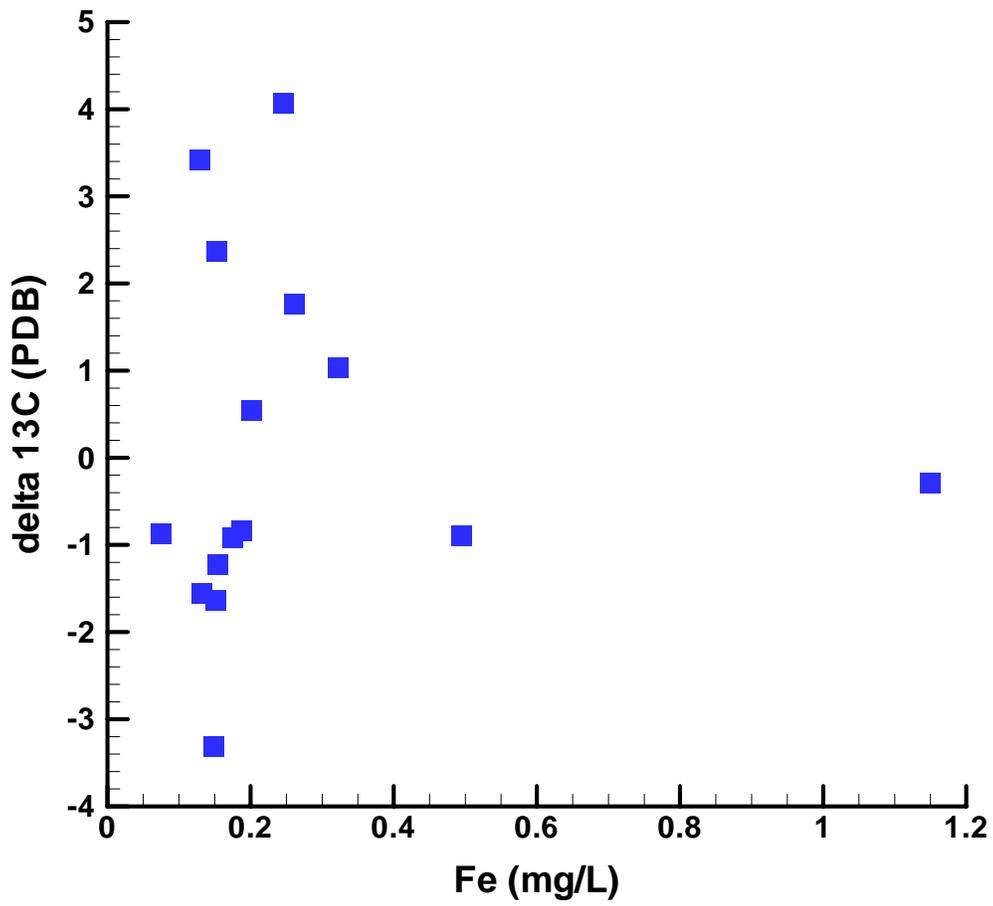


Figure 25. Heavy $\delta^{13}\text{C}$ DIC signature is associated with elevated Fe concentrations in Manikganj groundwater.

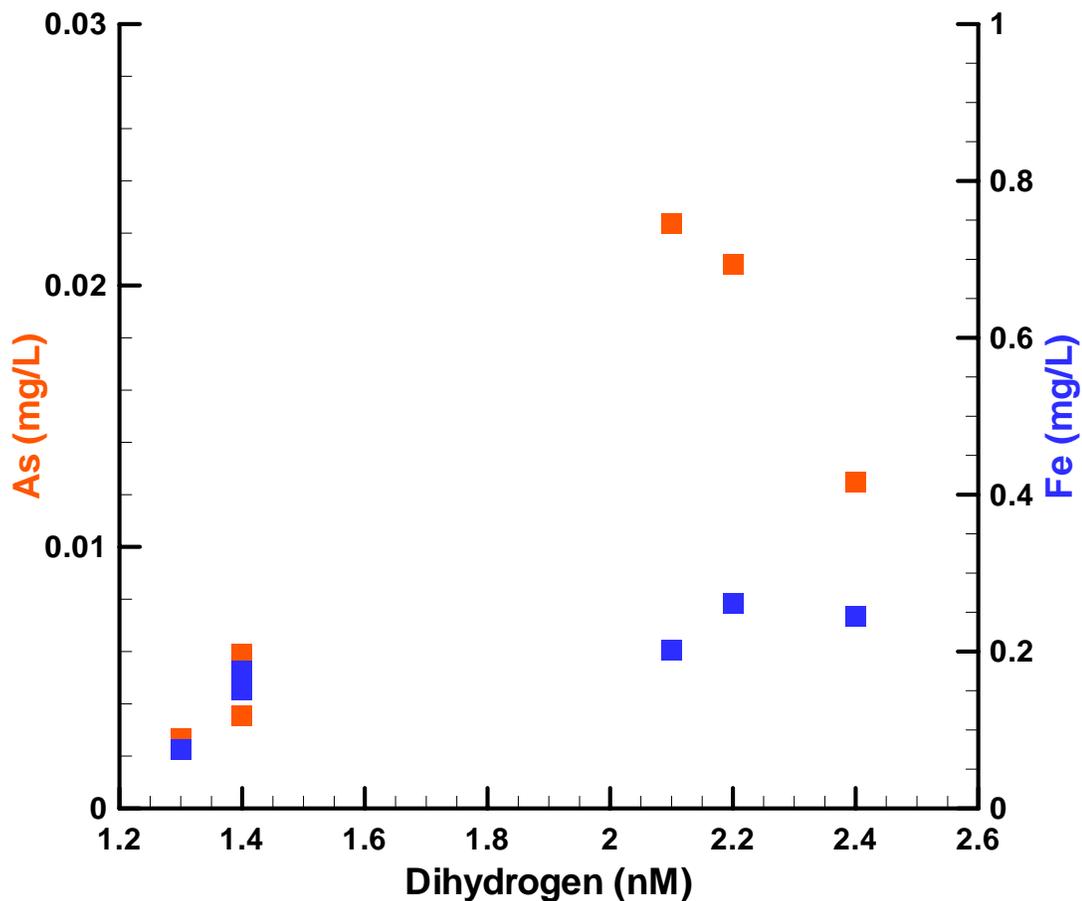


Figure 26. Elevated As and Fe concentrations correlate with elevated dissolved H₂ gas levels (>2 nM), indicating a probable input from Fe-reduction. Chapelle (1995) and Kirk et al. (2004) suggest H₂ levels from 0.2 to 0.8 nM indicate a geochemical zone of Fe-reduction, 1 to 4 nM indicates sulfate reduction, and >5 nM indicates reductive methanogenesis. Elevated Fe levels and low sulfate concentrations indicate likely simultaneous Fe-reduction, SO₄²⁻ reduction, and possibly methanogenesis are responsible for the H₂ levels, not solely sulfate-reduction.

However, H₂S (a by-product of sulfate-reduction reactions) concentrations were below the detection limit (0.1 mg/L) in all the tubewells. The stronger correlation between elevated concentrations of Fe, As, and H₂ suggests that H₂ is mainly generated by bacterial Fe-reduction.

Additionally, studies show that sulfate reduction is limited by low sulfate levels (Nickson et al., 2000). Elevated concentrations of Fe and As indicate that Fe-reduction is taking place (Fig. 27). It is possible that Fe-reduction, SO₄²⁻-reduction, and possibly methanogenesis are all adding dihydrogen to the system simultaneously (Kirk et al., 2004). This study suggests it is unlikely that elevated H₂ levels are produced solely by a zone of sulfate reduction due to the lack of H₂S. Future studies should be conducted to measure methane levels to further determine the sources of dihydrogen gas into the groundwater system.

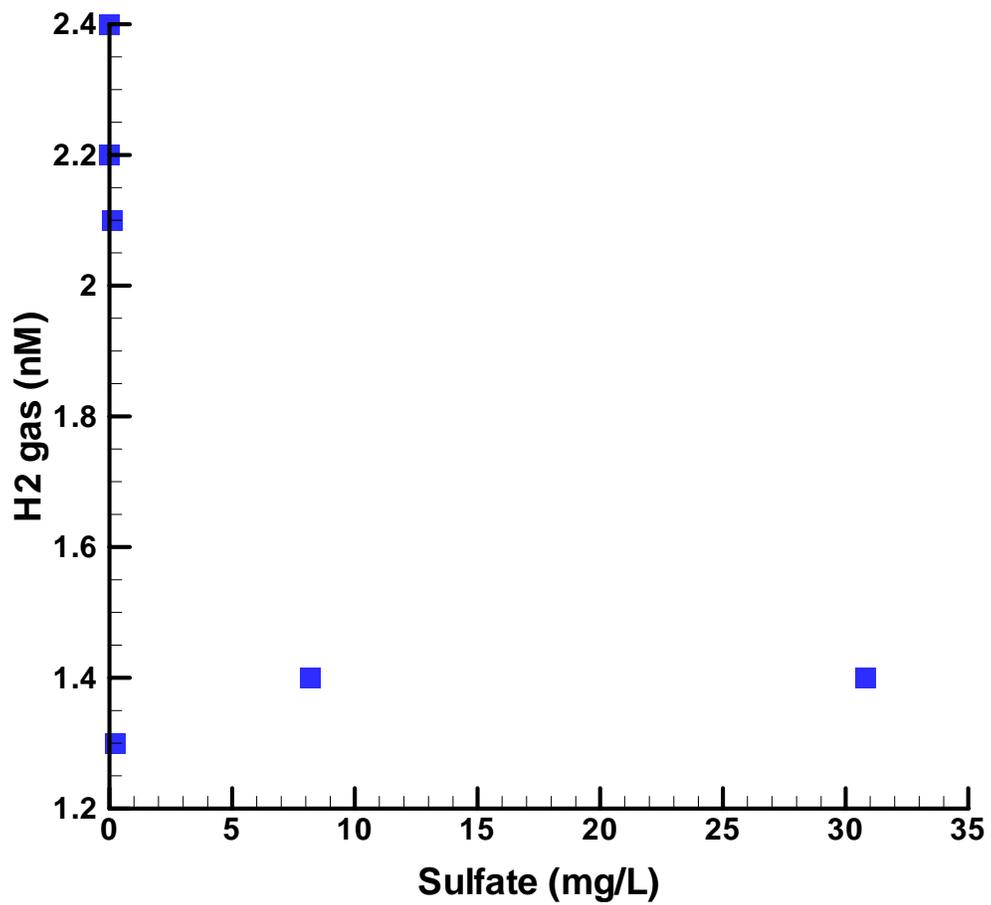


Figure 27. No sulfate is present in samples with dihydrogen concentrations > 2.1 nM. At dihydrogen concentrations ≤ 1.4 nM, sulfate ranges from 7 to 31 mg/L.

DISCUSSION

General groundwater geochemistry of the study area is similar to other As-contaminated regions in Bangladesh, as is evident in comparing the data presented in this research with results from previous studies (British Geological Survey, 1999, Nickson et al., 2000, Anawar et al., 2003, Van Geen et al., 2003, Ahmed et al., 2004, Akai et al., 2004). Implications presented in this research should be considered pertinent to similar As-contaminated Holocene alluvial aquifer settings in south Asia, and are not limited to Manikganj. The current study brought several questions to light that require further investigation to provide a better understanding of the complex mechanisms controlling elevated trace metal concentrations of As, Fe and Mn. Fortunately, collaborators of this research are currently conducting ongoing studies and arsenic remediation efforts in the study area. The ongoing research should answer some of the questions brought up during the current investigation. Results from the new study are still pending, and when available and coupled with this research should provide a more thorough understanding of the microbial processes controlling the groundwater geochemistry in the region.

An initial focus of this study was the pilot bioremediation experiment intending to stimulate bacterial sulfate reduction in a tubewell by adding sulfured molasses to remove dissolved As by co-precipitation with biogenic iron sulfide solids. After the injection, ORP dropped from 66.6 to -105 mV in the course of 3 months. Long-term monitoring

never detected $\text{H}_2\text{S} > 0.1 \text{ mg/L}$, which indicates that sulfate reduction wasn't rigorously stimulated by the addition of locally acquired sulfured molasses to the tubewell. It is possible that the locally-obtained sulfured molasses may not contain concentrations of SO_4^{2-} high enough to stimulate sulfate reduction in the sulfate-limited system.

Also, an effort was made in this research to analyze carbon isotopic signatures of groundwater and authigenic siderite concretions in order to determine the $\delta^{13}\text{C}$ biological fingerprint to elucidate carbon isotopic fractionation between groundwater, bacteria, and biogenic carbonate concretions. The sample set of siderite sent to be analyzed was dissolved in the lab, but the amount of siderite was not enough for any conclusive data. A laser-based ion microprobe analysis is needed in the future to measure the *in-situ* isotopic compositions of small biogenic carbonate concretions.

In December 2005, collaborators from Auburn University and Dhaka University successfully drilled a new tubewell in Manikganj and obtained semi-continuous drill core for further concurrent geochemical and microbiologic analyses of sediment and pore-water samples. This effort could shed light on isotopic fractionation between $\delta^{13}\text{C}$ DIC of groundwater and $\delta^{13}\text{C}$ signatures in authigenic carbonate minerals. Further studies should focus on understanding the processes that form authigenic Fe- and Mn- carbonate minerals, which control trace metal concentrations and possibly As mobility in groundwater (see geochemical modeling section). The forthcoming research will also provide additional groundwater geochemical data from 21 tubewells in Manikganj.

Another As-bioremediation effort was initiated, by the addition of sulfured molasses, in early November 2005 by students from Dhaka University. In December 2005, alcohol was smelled at the wellhead, indicating microbial respiration of the added

dissolved carbons. In late December 2005, a team from Auburn University added 3 lbs. of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (epsom salts) to the injection well to provide additional soluble sulfate. In the course of three weeks, a “rotten egg” smell was detected at the wellhead, indicating the presence of H_2S in the well and the successful stimulation of sulfate reduction. Results from weekly monitoring of the injection well will be forthcoming in future studies.

Microbiological investigations are also currently underway to determine the species of various anaerobic bacteria indigenous to the aquifer. Culture-independent DNA sequencing will be conducted, in collaboration with the University of Tennessee, on microbial samples collected from the new drill core and 21 water wells in Manikganj.

Investigations during this research raised interesting questions regarding the microbial source of H_2 gas. Previous investigations on H_2 concentrations in naturally As-contaminated aquifers (Chapelle et al., 1995, Kirk et al., 2004) delineates geochemical zones based on H_2 concentrations, e.g., Fe-reducing zones are characterized by 0.2 to 0.8 nM H_2 . However, Kirk et al. (2004) also states that overlap of anaerobic geochemical zones may be responsible for the same H_2 concentrations. H_2 concentrations from 1.3 to 2.4 nM were observed in this study, which indicates a geochemical zone of SO_4^{2-} reduction, but could alternately be derived from overlapping zones of Mn-reduction, Fe-reduction, SO_4^{2-} reduction, and possibly methanogenesis. Although results of the current study indicate that dihydrogen concentrations are consistent with natural sulfate reduction, as suggested by Kirk et al. (2004), little or no H_2S was detectable by colorimetric methods. Future studies should consider methanogenesis as a possible

contributor of H_2 to groundwater. More analyses should be conducted to establish the correlation between H_2 concentrations and As levels in the groundwater.

CONCLUSIONS

This study integrates hydrogeology, groundwater geochemistry, carbon isotope chemistry, geochemical modeling, and SEM and EDS analysis in order to understand the complex system responsible for elevated arsenic concentrations of Manikganj, Bangladesh groundwater. Geochemical correlations, $\delta^{13}\text{C}$ isotopic signatures, and high TOC (up to 4%) contents of sediment samples, and the presence of authigenic siderite in aquifer sediments support the hypothesis that elevated As, Fe, and Mn concentrations are derived from bacterial iron and manganese reduction. Furthermore, $\delta^{13}\text{C}$ isotopic signatures in Manikganj groundwater supports that Fe-reducing bacteria preferentially use light carbon (^{12}C) to form biogenic carbonate minerals, causing isotopic fractionation to leave the remaining water relatively heavy in ^{13}C and enriched in As, Mn^{2+} , and Fe^{2+} .

Geochemical modeling indicates that the precipitation and dissolution of various Mn- and Fe- minerals control the mobility of metals in groundwater. Geochemical data show that groundwater with elevated As concentrations are associated with high alkalinity, reducing ORP values, and elevated concentrations of Fe, Mn and dissolved H_2 . Conversely, groundwater with As concentrations below the drinking water standard are associated with positive ORP values and low concentrations of Fe and Mn.

Locally poor correlations among Fe, Mn, As, SO_4 , and alkalinity may be resulting from heterogenous precipitation of biogenic carbonates and, to a lesser degree, sulfide minerals. Lack of appreciable sulfate will limit the capacity of SRB to remove

significant amounts of As from reducing groundwaters. Local variability in concentrations of As and SO_4 and inverse relationships between As and SO_4 in Manikganj groundwater may be attributed to co-precipitation of As in Fe-sulfides by activities of SRB. Current studies are underway to examine microbial populations of Fe- and SO_4 reducing bacteria in Manikganj groundwater.

This research indicates that bioremediating As-contaminated groundwater may be possible by adding a solution of hydrous ferrous sulfate and a carbon electron donor (e.g., sucrose, molasses, methanol, ethanol, etc.) through injection wells. Elevated concentrations of Fe and organic carbon are already present in the aquifer, but SO_4 concentrations are generally very low due to the terrigenous source of aquifer sediments. Addition of soluble sulfates, Fe, and organic carbon to tubewells could locally stimulate sulfate-reduction and effectively remove Fe and As from solution.

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APPENDICES

APPENDIX A: *Geochemist's Workbench* input file for activity-activity plot of As(OH)_3 vs. H_2S

swap As(OH)_3 for As(OH)_4^-
swap e^- for $\text{O}_2(\text{aq})$
swap $\text{H}_2\text{S}(\text{aq})$ for SO_4^{--}
diagram As(OH)_3 on As(OH)_3 vs $\text{H}_2\text{S}(\text{aq})$
pH = 7
Eh = .1
x-axis from -10 to 0 increment 1
y-axis from -20 to 0 increment 2.5

APPENDIX B: *Geochemist's Workbench* input file for bacterially mediated reactions
controlling trace metal mobility

```
temperature = 25
swap e- for O2(aq)
swap Pyrolusite for Mn++
swap Hematite for Fe++
1 kg H2O
.7 Eh
.05 free gram Pyrolusite
.05 free gram Hematite
7.26 pH
balance on Cl-
116 mg/kg Cl-
585 mg/kg HCO3-
70.9 mg/kg SO4--
115 mg/kg Na+
41.5 mg/kg Mg++
22.2 mg/kg K+
141 mg/kg Ca++
slide Eh to -.15
react 500 umol of CH3COO-
react 500 umol of Na+
React> go
```

APPENDIX C: *Geochemist's Workbench* input file for arsenic adsorption-desorption to HFOs in oxidizing conditions

```
temperature = 25
decouple AsO4---
decouple Fe+++
swap Fe(OH)3(ppd) for Fe+++
swap e- for O2(aq)
1 kg H2O
1 free gram Fe(OH)3(ppd)
.1 Eh
7 pH
.001 mg/kg As(OH)4-
.05 mol Na+
balance on Cl-
.05 mol Cl-
.001 mg/kg AsO4---
slide pH to 10

suppress Hematite Goethite
React>
```