

Processes conducive to the release and transport of arsenic into aquifers of Bangladesh

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Arassic is a contaminant in the groundwater of Holocene aquifers in Bangladesh, where ≈57 million people drink water with arsenic levels exceeding the limits set by the World Health Organization. Although arsenic is native to the sediments, the means by which it is released to groundwater remains unresolved. Contrary to the current paradigm, ferric (hydr)oxides appear to dominate the partitioning of arsenic in the near surface but have a limited impact at aquifer depths where wells extract groundwater with high arsenic concentrations. We present a sequence of evidence that, taken together, suggest that arsenic may be released in the near surface and then transported to depth. We establish that (i) the only portion of the sediment profile with conditions destabilizing to arsenic in our analysis is in the surface or near-surface environment; (ii) a consistent input of arsenic via sediment deposition exists; (iii) retardation of arsenic transport is limited in the aquifers; and (iv) groundwater recharge occurs at a rate sufficient to necessitate continued input of arsenic to maintain observed concentrations. Our analyses thus lead to the premise that arsenic is liberated in surface and near-surface sediments through cyclic redox conditions and is subsequently transported to well depth. Influx of sediment and redox cycling provide a long-term source of arsenic that when liberated in the near surface is only weakly partitioned onto sediments deeper in the profile and is transported through aquifers by groundwater recharge.

redox | Ferric (hydr)oxides

Resolving the processes responsible for high concentrations of dissolved arsenic is essential for addressing the human health calamity within Bangladesh and West Bengal, India (1), where we are witnessing the largest mass poisoning in history. Furthermore, deciphering the processes and conditions responsible for arsenic partitioning to the aqueous phase within the Ganges-Brahmaputra Delta may also help diminish arsenic-induced hazards within deltas throughout subtropical and tropical regions of Asia. Although important work has been done to this end, numerous observations conflict with the prevailing theory that reductive dissolution of iron (hydr)oxides at well depth (i.e., 30–50 m) results in the high concentration of arsenic within drinking water (2–6). Although iron (hydr)oxides have been detected in oxidized upper sediments (7), as well as in orange Pleistocene sediments (8, 9), they do not appear widespread in the gray Holocene aquifer at depths of (and below) the highest arsenic concentrations (6, 8, 9). Moreover, proxies for active bacterial metabolism, namely redox potential (refs. 4, 5, and 10 and www.bgs.ac.uk/arsenic/Bangladesh), concentration of dissolved electron acceptors (e.g., sulfate, Fig. 1) and their products (e.g., methane), and molecular hydrogen (4), are all inconsistent with ongoing ferric-iron reduction at well depths of 30 to 40 m. Finally, solid-phase arsenic concentrations in the aquifer sediments are relatively low (typically <3 mg/kg) compared to world averages of sedimentary basins (11); if reductive dissolution of iron (hydr)oxides were the sole cause of arsenic release, one would expect As concentrations to have declined as Fe(III) minerals were consumed and aquifers flushed. However,

arsenic concentrations are highest at well depths where reactive ferric (hydr)oxides appear exhausted (8, 9). Accordingly, to help understand the processes controlling arsenic in Bangladesh groundwater, we evaluated the hydrologic and biogeochemical setting, conducted spectroscopic examinations of Holocene aquifer sediments, and performed arsenic release batch experiments incorporating sediments from depths where arsenic groundwater concentrations are highest. Our findings reveal that arsenic must be released upgradient and transported to the aquifer at well depth, a scenario we postulate is maintained by release in the surface or near-surface soils/sediments through cyclic, seasonal redox cycles.

Materials and Methods

Sediment Samples. Sediment samples were obtained from the Munshiganj district of Bangladesh, 30 km south of Dhaka and 7 km north of the Ganges River. Our field site is located centrally in Bangladesh with geological and hydrological conditions typical of the areas worst affected by arsenic; geochemical conditions are similar to those sites with high dissolved arsenic as discussed in the Bangladesh-wide British Geological Survey study (ref. 10 and www.bgs.ac.uk/arsenic/Bangladesh). The site encompasses 16 km² and is thus considerably larger than the dominant scales of spatial heterogeneity (tens to hundreds of meters) in dissolved arsenic in the worst-affected areas, yielding findings of widespread utility. The subsurface at our location consists of a surficial clay, a Holocene aquifer of gray sand, a clay aquitard, and a deep, burnt-orange sandy Pleistocene aquifer.

Core extraction procedures and groundwater aqueous chemistry were summarized previously (9). Arsenic concentrations in the groundwater increase with depth to a maximum at ≈30 m and then decrease with increasing depth; solid-phase arsenic concentrations in the Holocene aquifer are below 3 mg/kg (4). Sediment subsamples for spectroscopic analyses were collected from one core at depths of 5, 10, 15, 22, 30, and 60 m and put into crimp-sealed serum vials under an N₂ atmosphere. The samples were shipped from Bangladesh and stored at 4°C on arrival.

X-Ray Microprobe and X-Ray Absorption Spectroscopic (XAS) Analyses. Spatial distributions of As, Fe, Cu, and Zn were determined by using x-ray fluorescence (XRF) spectroscopy, and XAS was used to elucidate oxidation and chemical states of arsenic. Experiments were conducted on undulator beamline 13-ID-C at the Advanced Photon Source, Argonne National Laboratory (Argonne, IL). The ring operated at 7 GeV, and current was maintained at ≈100 mA through periodic electron injection. Energy selection was performed by a Si (111) monochromator.

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Abbreviations: XAS, x-ray absorption spectroscopy; μ -XANES, micro-x-ray absorption near-edge structure.

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All sample preparation was conducted under anaerobic conditions ($N_2:H_2$, 95:5) in a polyethylene glovebag. Sediments were spread on polycarbonate slides and sealed with Kapton tape. Slides were rastered in 5- to 15- μm steps around a $5 \times 6 \mu\text{m}$ x-ray beam, and 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. Iron XAS was collected and analyzed as described previously to determine the solid-phase speciation (12); detection limits of this approach are $\approx 5\%$ of the total iron within the system.

Multiple x-ray fluorescence maps were made on sediments from each depth, and thousands of points were analyzed. Areas of arsenic concentration in the elemental maps were analyzed with micro-x-ray absorption near-edge structure (μ -XANES) spectroscopy to determine arsenic speciation. The sample spectra were collected from -50 to $+100$ eV about the As K_{α} edge of 11867 eV, and speciation was determined through a spectral analysis of first-derivative peaks from the XANES spectra of As standards. Arsenic concentrations within grains were determined by comparison to a thin-film standard. The proportion of total arsenic bound in sulfide form in the sediments was approximated by considering spheres of sulfide minerals (as determined by μ -XANES) with volumes based on radii in the 2-dimensional maps; the density of pyrite was used, and arsenic was assumed to be 1% of the total sulfide mass.

Arsenic Displacement Experiments. Arsenic release from 30-m sediments was examined in batch experiments with 5 g of sediment and 10 ml of solution in 20-ml serum vials. Solutions of 18 M Ω water and 1.5 mM dissolved organic carbon (DOC) (as lactate) were autoclaved and made anoxic by boiling and cooling under a stream of O_2 -free N_2 . Ferrihydrite-coated sand was

synthesized according to previous methods (12) and added to some vials with the natural sediments to give 0.04 and 0.20 total weight percent Fe(III). Sediment and Fe-coated sand samples for abiotic controls were sterilized by gamma irradiation (2,855 R/min for 14 h; 1 R = 0.258 mC/kg). All glassware was autoclaved before experimentation, and sterile techniques were used. Reactions were initiated and sampled under anaerobic conditions ($N_2:H_2$, 95:5) in a glovebag. Sediment slurries including water, lactate, or Fe(III)-oxide and water were sealed and shaken (140 rpm in a VWR orbital shaker) in darkness, and separate sets of experiments were run for 2 and 16 days. Aqueous samples were acidified with concentrated trace-metal grade hydrochloric acid (to achieve 0.17 M acidity) and stored at 4°C until analysis.

Solution-phase arsenic concentrations were analyzed by hydride generation inductively coupled-plasma optical emission spectroscopy (HG-ICP-OES). To reduce any arsenate to arsenite, 3 ml of sample was mixed with 3 ml of concentrated trace-metal grade hydrochloric acid, 1 ml of 8% urea, and, after 10 min of reaction time, 1 ml of 16% KI. The mixture was allowed to sit for at least 1 h and then further reacted with 6 M HCl and 0.6% $NaBH_4/0.5\%$ NaOH. The resulting arsine gas was measured by ICP-OES. Detection limits were 5 μg /liter for arsenic.

Results and Discussion

The current paradigm within Bangladesh and West Bengal is that Fe(III) (hydr)oxides remain the dominant host of arsenic even at well depth (i.e., 30 to 50 m) within contaminated aquifers, and that organic carbon derived either from the surface (4) or from detrital material (2, 3, 6) is stimulating reductive dissolution of the iron phases and concomitant release of arsenic. Here we explore operative redox processes impacting arsenic partitioning between the solid and aqueous phase by using multiple lines of data, inclusive of detailed spectroscopic measurements, batch experiments, and field observations.

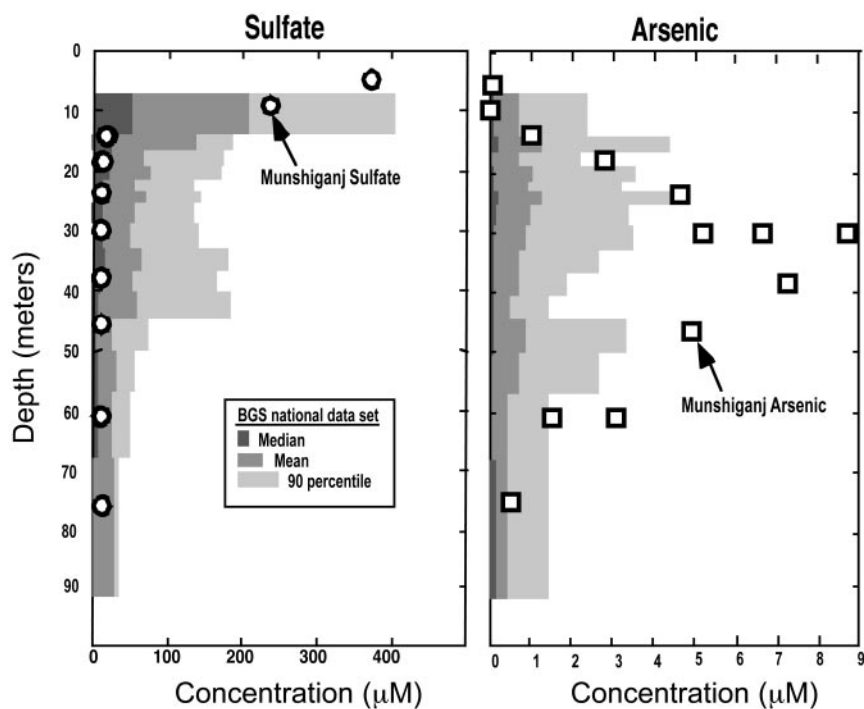


Fig. 1. Sulfate and arsenic concentrations measured at our study site (4) (circular and square data points), and mean, median, and 90th-percentile of the shallowest 2,848 samples from the country-wide British Geologic Survey report (ref. 10 and www.bgs.ac.uk/arsenic/Bangladesh) (shaded areas), binned into depth intervals of ≈ 200 samples each. Similar dissolved arsenic peaks have been described at other sites (6), although the country-wide data does not display a clear peak.

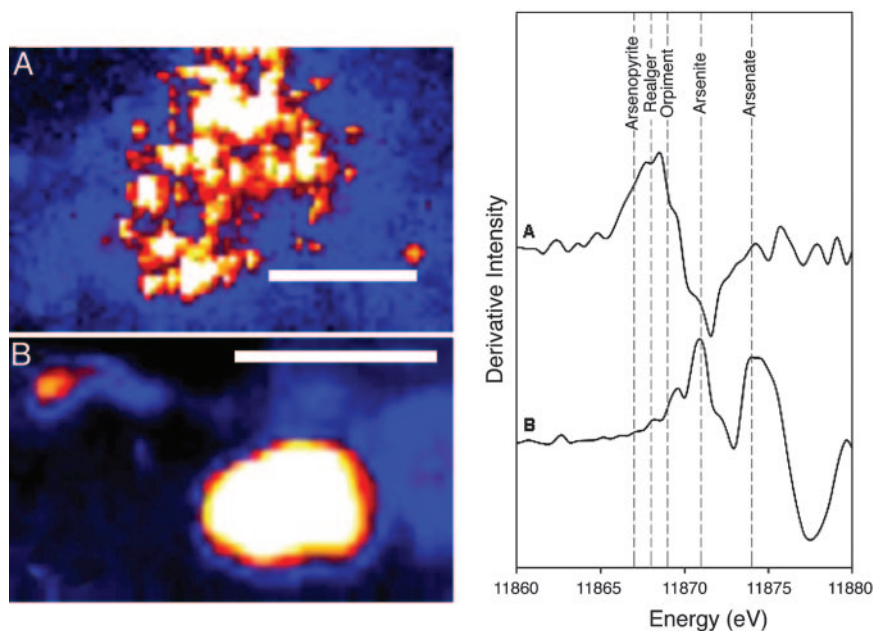


Fig. 2. X-ray fluorescent images (Left) and corresponding XANES spectra (Right) of arsenic-bearing grains from 30 m depth of the Holocene aquifer. Light intensity corresponds with the highest arsenic concentrations in the image (Left), and the scale bars represent 100 μm . (A) Arsenic concentrations within the grain range from 1% to 5.6% and are distributed within sulfide complexes (as noted by the first-derivative peak maxima between 11,867 and 11,869 eV). (B) A weathered As-bearing sulfide grain containing $\approx 0.7\%$ arsenic composed of 17% orpiment-like, 55% arsenite-like, and 28% arsenate-like phases. White-line positions of arsenopyrite (FeAsS), realgar (AsS), orpiment (As_2S_3), arsenite (AsO_3^{3-}), and arsenate (AsO_4^{3-}) standards are depicted at 11,867 eV, 11,868 eV, 11,869 eV, 11,871 eV, and 11,874 eV.

Aquifer Redox Processes. Aqueous arsenic concentrations in Bangladesh aquifers often reach a maximum within the first 50 m below the surface, and at our site we find a distinct peak at ≈ 30 m depth (Fig. 1, ref. 10, and www.bgs.ac.uk/arsenic/Bangladesh). Groundwater at 30 to 40 m depth often has high methane concentrations (>1 mM) and very low redox potentials (refs. 4, 5, and 10 and www.bgs.ac.uk/arsenic/Bangladesh), and at our field site in the Munshiganj district of Bangladesh 10 nM H_2 was observed at 38 m depth (4). Given that dissimilatory iron reduction, the primary means of iron reduction, precedes methane generation in sediment diagenesis (or aquifer redox profiles), active iron reduction occurred at an earlier stage in diagenesis (13) as opposed to the present time. Furthermore, the H_2 concentration at 38 m is 10 to 100 times higher than representative of dissimilatory Fe(III) reduction and is instead indicative of CO_2 reduction to methane, consistent with the high methane values recorded (13).

Associations of Arsenic in the Solid Phase. In sediments from 30 m depth, the approximate depth of the maximum dissolved As at our field site and the average well depth in the region (4), we find arsenic within sulfide grains exceeding 100 μm in diameter (Fig. 2). Grain size, association with copper and zinc (chalcophiles), and weathering progress of the sulfides suggest detrital origin. For example, analysis of a 150- μm grain illustrates sulfidic arsenic (Fig. 2A), with local arsenic concentrations as high as 50 g/kg (5%) within the grain. Another large grain (Fig. 2B) exhibiting oxidation, as indicated by arsenate and arsenite species, is in association with sulfidic arsenic (Fig. 2B), and Cu and Zn correlate strongly with arsenic (R^2 values of 0.77 and 0.82, respectively); occlusion in quartz or other primary silicates may be, in part, responsible for their preservation. Sulfidic grains with arsenic concentrations of $\approx 1\%$ and diameters of 15 to 35 μm occur throughout the Holocene sediment borehole samples obtained at our field site, including depths ranging from 5 to 60 m, and are likely of authigenic origin. Although we observe

concentrated arsenate- and arsenite-bearing grains within aquifer sediments, arsenic-bearing sulfides (detrital and authigenic) represent the largest solid-phase arsenic fraction within the investigated aquifer sediments, accounting for up to 60% of the total arsenic (based on spatial analysis using x-ray microprobe/XAS and supported by chemical extractions; ref. 9). Additionally, small framboidal pyrite, presumably diagenetic, was observed in surficial (<9 m) Holocene sediments (3), and we find acid volatile sulfides at our field site in Munshiganj (4).

Arsenic Desorption from Aquifer Sediments. A paucity of ferric (hydr)oxides has been observed in extraction (9) and reflectance (8) experiments, and, albeit with detection limits restricted to $\approx 5\%$ of the total Fe within the sampled region, we did not detect iron (hydr)oxides in Holocene aquifer sediments by using both bulk- and micro-XAS. Most importantly, current redox conditions are inconsistent with dissimilatory iron reduction being the dominant electron accepting process. Thus, because reactive Fe(III) (hydr)oxides are predominantly depleted from the Holocene aquifer, adsorption of aqueous arsenic is limited to phases such as the silicate and carbonate minerals, which have a low surface area and a relatively weak affinity for arsenic. Laboratory batch experiments (ours in Fig. 3 and others' in ref. 14) and previous *in situ* injection-withdrawal tests (4) both reveal rapid desorption of arsenic from the sediments, indicating that arsenic is more labile than would be expected if it were bound to ferric (hydr)oxides. Arsenic is released from gray Holocene sediment solids by the simple addition of water, and thus amendment with labile organic carbon [e.g., lactate (Fig. 3) or acetate (14)] is not necessary to invoke rapid desorption of arsenic. In contrast, arsenic remains in the solid phase with the addition of ferric (hydr)oxide to sediment incubations (Fig. 3). Consequently, the weakly adsorbed (labile) phase of arsenic within the Holocene aquifer, constituting $\approx 20\%$ of the initial solid-phase

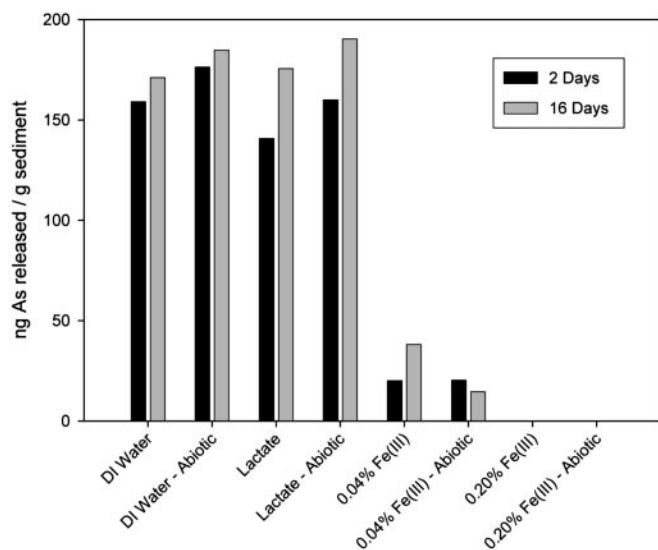


Fig. 3. Arsenic desorption from Holocene aquifer sediments of 30-m depth after batch incubation for 2 (black bars) or 16 (gray bars) days. Arsenic is released from sediments placed in deionized water and 1.5 mM dissolved organic carbon (as lactate). Aqueous arsenic concentrations are suppressed with the addition of 0.04% ferrihydrite and are below detection limits with the addition of 0.2% ferrihydrite. Agreement of nonsterile results with gamma-irradiated control experiments indicates that desorption of arsenic observed here is not controlled by biological activity, neither reduction of iron or arsenic.

arsenic in our experiments, can be easily liberated and transported during groundwater movement.

Groundwater Flow and Arsenic Transport. Groundwater tritium concentrations at our site (15), and across Bangladesh (16), indicate a residence time of typically <50 years in the upper 30 m, consistent with the rate of irrigation withdrawal (15, 17). Three scenarios therefore may explain the current aqueous arsenic concentrations: (i) groundwater flow was much slower in the past such that arsenic was not flushed from the Holocene aquifer, (ii) geochemical conditions have recently shifted to mobilize arsenic, or (iii) dissolved arsenic is provided by a source that is hydrologically upgradient of the sampling wells. Surface sediments, which typically have higher solid-phase arsenic concentrations than the aquifer materials (9, 18, 19), can provide a source of arsenic, potentially maintaining constant aqueous arsenic concentrations downgradient in areas where groundwater velocities and/or solid-phase arsenic concentrations are modest. Assuming a downward component of groundwater velocity of 1 m/yr (17), arsenic concentration of 1 μM [the approximate national average (ref. 10 and www.bgs.ac.uk/arsenic/Bangladesh)], sedimentation rate of 1 cm/yr, and 50 nmol of arsenic mobilized per gram of surface sediment [$\approx 1/4$ of typical surface sediment concentrations (9, 19)], the groundwater arsenic flux and input by sedimentation are comparable, both equal to 1 mmol As $\text{m}^{-2}\text{-y}^{-1}$. This calculation suggests that steady groundwater concentrations could be sustained by sediment deposition in areas where groundwater velocities and dissolved arsenic concentrations are modest. However, where arsenic concentrations are higher, such as our site in Munshiganj (8 μM) (4), or when sedimentation rates are lower, the observed arsenic concentrations suggest hydrologic or geochemical transience.

Our hydrologic data (17) reveal residence times on the order of 80 yr without irrigated agriculture; with irrigation pumping, residence times decrease to <40 yr—the recent onset of irriga-

tion pumping increases recharge rates by a factor of 2. The recent alteration in irrigation pumping has changed groundwater flow patterns, decreasing the residence time of groundwater and perhaps flushing arsenic (6, 15) from the Holocene aquifer. Dry season rice cultivation, now covering $\approx 25\%$ of the country (20), is irrigated with ≈ 1 m/yr of groundwater (17), which, assuming a porosity of 25%, causes an average downward component of groundwater velocity of ≈ 1 m/yr to the depth of well screens. The increased groundwater flow might explain current arsenic profiles but only if past groundwater residence times were sufficiently slow to impede even a single pore-volume of flushing since the inception of the aquifer. Therefore, if arsenic concentrations are to remain elevated, an upstream source must be present.

Arsenic Release Through Deposition Combined with Redox Cycling.

One potential upstream source of arsenic is the near-surface sediments, where, as noted above, sedimentation fluxes can sustain groundwater arsenic concentrations. Three pathways may lead to arsenic release within the surface and near-surface soils/sediments, all involving Fe and As reduction. First, recently deposited sediments containing As(V) associated with ferric (hydr)oxides will undergo reduction upon the following seasonal addition of organic carbon (surface-derived) and flood waters. Solid-phase arsenic is deposited in association with detrital sulfides and ferric (hydr)oxides. Ferric (hydr)oxides dissolve, as illustrated by increasing Fe(II)/Fe_{total} ratios with depth (8), in concert with As(V) reduction to As(III) as the sediments are buried to the depths of the gray aquifer material.

Second, seasonal cycling in aerobic/anaerobic conditions will lead to the destabilization of arsenic-bearing sulfides, which contain >10 g/kg of arsenic and are thus major repositories of this toxin. Seasonal water-table oscillations (refs. 4, 10, and 17 and www.bgs.ac.uk/arsenic/Bangladesh) establish an oxic-anoxic cycle in the surface and near-surface sediments. During the dry season, sulfide minerals will be oxidized, leading to the repartitioning of arsenic into ferric (hydr)oxides (21), followed then by reductive dissolution of iron and arsenic during the ensuing wet season. Cyclic redox conditions in the near-surface sediments would therefore accelerate sulfide weathering and release of arsenic, consistent with processes noted for mining impacted environments (22). The presence of both detrital and authigenic sulfides demonstrates, in fact, that redox cycling is occurring, and fluctuating redox conditions have been proposed based on $\delta^{34}\text{S}$ measurements (23).

Finally, a third means of arsenic liberation to the aqueous phase may result from changes in conditions that enhance the reducing intensity of the redox cycle, such as increased periods of field saturation. An area within the soil/sediment profile (down to depths of 80 m) consistently having arsenic concentrations >10 mg/kg exists within the upper 2 m of the surface, precisely where the greatest biogeochemical activity resides. Arsenic exists at concentrations in excess of 1,000 mg/kg (18) within iron bands created by past redox conditions (24). Moreover, microbial reductive mobilization of arsenic from sediments of the oxic-anoxic boundary has been observed (25), demonstrating the potential for arsenic release under the onset of reducing conditions at the near surface. Once partitioning into the aqueous phase, dissolved arsenic may then enter the aquifer during recharge.

Summary and Conclusions

Transport of carbon into the aquifer undoubtedly creates reducing conditions, and the high levels of dissolved molecular hydrogen and methane indicate that ferric iron no longer serves as a primary electron acceptor. High concentrations of young inorganic carbon correlate strongly with arsenic, ammonium, methane, and calcium and inversely with sulfate concentrations

in the Holocene aquifer in Munshiganj (4), implying that the most significant biological processes occur upgradient and mix during transport. Furthermore, the bell-shaped vertical profile of these solutes (4) is typical of plume migration from a surface source. After solute enters an aquifer, plume movement is dominated by lateral transport away from the surface source, but recharge also displaces the plume downwards, so local sources create bell-shaped vertical solute profiles. Groundwater flow has a large lateral component because the distance between discharge areas (irrigation wells and river channels) is greater than the aquifer thickness. We therefore suggest that both inorganic carbon and arsenic are signatures of biological processes upgradient, likely reflecting surface and near-surface processes (anaerobic-aerobic cycles induced by the influx of carbon-rich surface waters after dry-season draw-down), that are transported

along groundwater flow paths until reaching wells in the sandy aquifer. Organic carbon from the surface would be consumed rapidly, and arsenic, as arsenite, could easily be transported because of its low distribution coefficient in the sediments. Seasonal cycling in redox conditions coupled with annual deposition therefore could account for the liberation of arsenic to the aqueous phase. We therefore hypothesize that surface and near-surface biogeochemical processes mobilize arsenic in Bangladesh and that these processes, coupled with arsenic transport through the aquifer, should be the focus of further research.

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