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GEOLOGICAL SURVEY OF CANADA

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Report of Activities
2003-2005

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Phase 1: Naturally occurring arsenic in groundwater:
a preliminary investigation of sources and release mechanisms,
Gotra, West Bengal, India.

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Summary

In April 2003, Natural Resources Canada and the Ministry of Mines of the Republic of India signed a Memorandum of Understanding (MOU) that led to the initiation of a joint project between the Geological Survey of Canada, the Geological Survey of India and the University of British Columbia. The project is aimed at identifying the mechanisms responsible for the release of arsenic from sediments into groundwater. This information will be useful to mitigation strategies aimed at reducing the level of arsenic in drinking water in West Bengal. This report describes the results of a 2004 preliminary field investigation in which groundwater samples were collected in the village of Gotra at a number of domestic wells and along two vertical profiles using a push-type sampling device. Two sediment cores were also collected and analyzed for total elemental abundances. The report concludes with recommendations for full-scale field investigations at the Gotra site.

Introduction

The presence of arsenic in groundwater at concentrations exceeding the 0.01 mg/l World Health Organization (WHO) recommended threshold for human consumption was brought to the notice of Government of West Bengal in 1978. Studies carried out by various agencies, including the Geological Survey of India (GSI), have established that arsenic is present at concentrations above WHO thresholds in the groundwater of eight districts, covering 830 villages in 57 blocks, spread over an area of 37,493 sq. km. It has been estimated that about 1.75 million people are consuming arsenic-contaminated water and around 200,000 people are suffering from arsenic-related diseases. The arsenic-affected area extends to the Bangladesh part of the Ganga-Brahmaputra River basin.

The arsenic-affected areas form a part of the Ganga-Brahmaputra deltaic tract, broadly confined between the Bhagirathi and Padma channel courses and comprise unconsolidated sediments of Late Quaternary age, ranging from sand and silt to clay. The arsenic-bearing aquifers are mostly confined to a depth of 20 to 80 m below ground level and conform to a regional slope towards the southeast. Work carried out to date has indicated that arsenic generally occurs as the absorbed form in the limonitic coating on clay particles. A few detrital grains of arsenical pyrite have also been reported in the arsenic-affected aquifers; however these are not considered a significant source for the arsenic.

The GSI has carried out investigations in selected areas of six districts of West Bengal in three phases (1988-90, 1992-96 and 2003-present). The later phase was in conjunction with NRCan. These investigations have helped in the delineation of the areas having arsenic-contaminated groundwater and recognized its geological cause. The purpose of the studies has been to identify relatively arsenic-free aquifers on the basis of their geomorphic expressions. Complementing this work is the need to identify the processes which are responsible for the release of arsenic.

Study Area

The study area is located approximately 56 km northeast of Kolkata in the village of Gotra in Nadia District, West Bengal, (2546396N 662938E UTM, 88.59° N, 23.018° E). The village is approximately 1 km long and 0.52 km wide, oriented on a south-east to north-west trend. The village is bounded to the south west by a line of south-east to north-west trending ponds created when causeways were filled across an abandoned channel. The north-east limit of the village is defined by four ponds that trend on a similar orientation, but it is less clear if these ponds were dug or are abandoned channels.

The near-surface sediments in the study area consist of fine sands, silts and clays deposited by the Hooghly River, a distributary of the Ganga. The Google satellite image in Figure 1 centered on the village of Gotra shows the numerous abandoned channels and ponds that dominate the surface in the area. The effects of channel migration and sea-level variations over the Holocene have produced a complex subsurface stratigraphy of laterally discontinuous clay and sand bodies (Ahmed et al., 2004; Ravenscroft et al., 2005). Wells in the area tend to be completed in the nearest-to-surface transmissive sand units. The sands are typically bound above and below by low-permeability clays, which can sometimes be distinguished in drill cuttings by subtle variations in color and texture.

The study site was selected based upon earlier field work by the GSI (Mukherjee et al., 2001; Mukhopadhyay et al., 2006; Pal et al., 2002a; Pal et al., 2002b). The GSI tested groundwater from village wells for arsenic using a portable Merck kit. This testing identified both low and high arsenic groundwater zones within the village. An objective of the study was to investigate conditions in both high and low arsenic zones in an attempt to identify and understand release mechanisms.



Figure 1: Google satellite image centered on Gotra, Nadia District, West Bengal

Methods

Field Methods

Samples of sediment and groundwater were collected from the region in and surrounding Gotra from both high and low arsenic zones. Sediment samples were obtained from two continuous cores. Water samples were collected from both pre-existing domestic and irrigation wells, and at several depths along two vertical profiles.

Two continuous cores, borehole 19 (low arsenic zone) and borehole 20 (high arsenic zone), were collected to 40 m depth below ground surface. The 6 cm diameter cores were collected by pounding a 50 cm long corer through the bottom of the borehole. The core barrel contained PVC sleeves, which were removed from the corer and capped immediately upon retrieval at the surface (Figure 2). After each core segment was collected, the borehole was advanced by over drilling the cored interval. The process was repeated until 40 m depth was reached.

Groundwater samples were collected from 48 domestic and irrigation tube wells in Gotra and surrounding countryside, and in two vertical profiles using a push-in water profiler. Well locations were determined using a portable GPS unit (Figure 4, 5). Before sample collection, the domestic tubewells were first purged by removing approximately 15 L of water using the pre-existing hand pumps found on all the wells. Irrigation wells were sampled directly from the outflow.



Figure 2: Core segments.

Samples of groundwater were also collected along two vertical profiles using the Waterloo profiler, a push-in sampling device (Figure 3). The profiler consists of a steel tip with six 5 mm diameter ports connected to ¼ inch tubing that runs to the surface. The profiler was attached to AW drilling rods and pushed into the ground

using a mobile cone-penetrometer rig. To collect a sample, the tip was first pushed to the desired sampling interval. To prevent clogging of the sampling ports, distilled deionized water was pumped out the ports using a peristaltic pump as the profiler was pushed downwards by the rig. When the desired sampling depth was reached, the peristaltic pumping direction was reversed and formation water drawn up to the surface into a flow-through cell where temperature, pH and specific conductance were monitored. The pH was measured using an Orion 250A pH meter equipped with an Orion 9107BN temperature-compensated probe. Specific conductance was measured with a HACH sension5 meter using a model 51975 four-electrode probe that has a cell constant of 0.45. The pH meter was calibrated at least once a day using pH 4 and 7 buffers.

Water samples were collected from the profiler after the deionized water had been removed from the lines and the pH and specific conductance measurements had stabilized, typically after several hundred milliliters of sample had been purged. Note that pH, temperature and specific conductance were not measured on groundwater from domestic wells.

Four distinct 60 mL water samples were collected from each domestic well. Each sample was filtered to 0.45 μm using polysulfonate syringe filters. One sample was preserved to pH < 2 using trace-element-grade nitric acid (for cations). One sample was preserved using trace-element-grade HCl (for arsenic speciation) and one sample was preserved using EDTA (for arsenic speciation) resulting in a 1.25 mM EDTA concentration in the sample. A fourth sample was collected and stored without any preservation. At each profiling point and at a few domestic wells filtered samples were collected for field alkalinity and ammonia analysis. One additional unfiltered sample (for dissolved + colloidal cations) was collected at each profiling point and preserved to pH < 2 using trace-element-grade nitric acid.



Figure 3: Waterloo Profiler tip connected to 1/4 inch polyethylene tubing shown with section of AW rod and coupler.

Dissolved oxygen was measured at profile points using Chemetrics model 7553 low-range (100 – 1200 ppb) self-filling Vacu-vial ampoules. The discharge tube from the profiler was connected to a small sampling funnel which was allowed to fill with water from below, minimizing exposure of the sample to atmospheric oxygen. The Vacu-vial tip was then placed at the bottom of the sampling funnel and snapped open to entrain the sample. The dissolved oxygen was determined quantitatively by measuring absorbance at 555 nm using a HACH 2400 field spectrophotometer.

Alkalinity and dissolved ammonia were measured in the field within 20 minutes of sample collection. Alkalinity was measured by titration of 12, 20 or 25 mL of filtered sample with 0.2 N sulfuric acid (obtained from the laboratories of GSI). The acid was titrated using a 2 mL Gilmont microburet. The pH was measured with an ORION 250A meter connected to an ORION model 9107BN temperature-compensated probe. The pH versus acid added titration data was analyzed using the Gran-plot method. The straight-line portion of the Gran plot was regressed onto a linear equation using EXCEL, and the equivalence point determined by solving the regression equation for the intercept.

Dissolved ammonia was measured in the field using HACH method 10031 Test 'N Tube vials which utilize the salicylate reagent. Unlike the Nessler approach, the reagents for the salicylate method do not contain cadmium and have an indefinite shelf life. The ammonia concentration was determined quantitatively by measuring absorbance with a HACH DR2400 spectrophotometer.

Sediment cores were shipped to the Geological Survey of Canada (GSC) in Ottawa. Borehole 19 core was received intact, but some caps on Borehole 20 core had dislodged during shipping and the samples disturbed. Water samples were taken directly to Ottawa for analysis by the GSC.

Analytical methods

Sub-samples of sediment were taken from both cores at intervals of 0.5 m and were sent to Acme Labs of Vancouver for analysis. The 133 distinct analyses followed a modified version of Acme's 1F-MS protocol. 15 g of wet sample was placed in a beaker along with 90 mL of HCl-HNO₃-H₂O aqua regia solution and digested for one hour at 95 C. After cooling, the extraction solution was brought to a final volume of 300 mL with the addition of 5% HCl. The extraction solution was analyzed for a suite of elements by inductively coupled plasma mass spectrometry (ICP-MS) and inductively couple plasma atomic emission spectroscopy (ICP-AES). After correcting for the initially wet state of the sediments, the results are expressed in parts per million (ppm) solid/solid. Standard materials and duplicate samples were also analyzed for quality control.

Minor and trace elements in water samples were analyzed at the GSC on an X Series quadrupole-based ICP-MS from Thermo Corporation, while major elements including iron, sulfur and phosphate were analyzed on a Perkin Elmer 3000 DV (dual view) ICP-AES. The HCl - and EDTA - preserved samples were analyzed for inorganic arsenic species using an ion-chromatography-ICP-MS

methodology. The arsenic (III) and (IV) species were separated in a Dionex AS7 column and measured by ICP-MS. Dissolved organic carbon (DOC) was measured using a Shimadzu 5000 TOC instrument. The sample was first acidified to drive off the dissolved inorganic carbon as CO₂. The sample was then catalytically oxidized at 680 C and the resulting CO₂ measured by infrared detection.

Results

Figure 4 shows the locations of the wells sampled in the Gotra regional area. Figure 5 shows the sample locations within the village of Gotra, and the location of the two vertical water profiles named BH17 and BH18, and the two cores, BH19 and BH20. The vertical profile BH17 and the sediment core BH19 were collected within 2 m horizontal separation of each other in a low-arsenic zone on the northern edge of the village, approximately 10 m south of a pond. Vertical profile BH18 was collected to the south east, in a higher arsenic zone. The sediment core BH20 was collected from the middle of a manmade causeway that straddles either side of an abandoned-channel pond, such that BH20 penetrates through the middle of the abandoned channel.

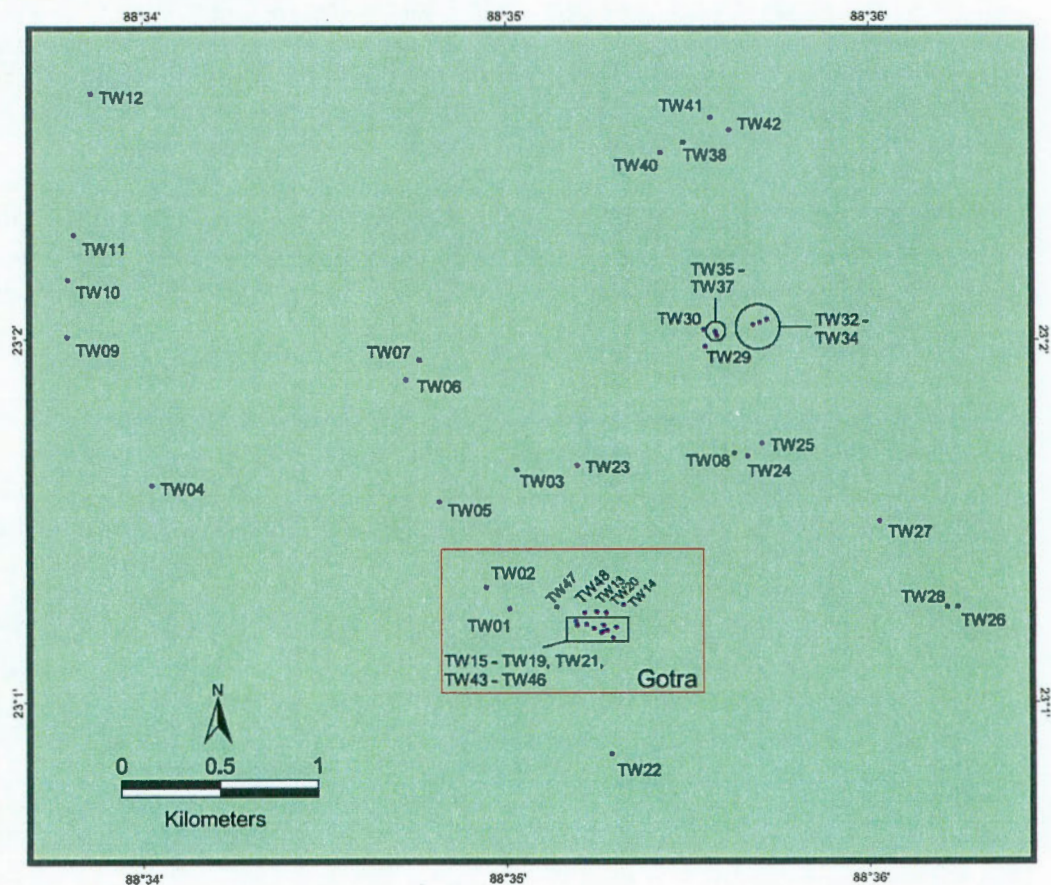


Figure 4: Well locations in the Gotra regional area. Area within rectangle is shown in more detail in Figure 5.

Subsurface Geology

Two boreholes (BH-17 & BH-18) were drilled (each of 40 meter) for the purpose of collecting water samples from different depths through the profiler. To observe whether there is any correspondence between arsenic values in water samples from different depths on the one hand and sediment arsenic values from those depths on the other, soft sediment core drilling (each of 40m depth) was carried out at two sites. BH-19 (N23001'14. 8"E88035'16.3") is immediately adjacent to BH-17 and BH-20 (N23001'19. 08" E88035'19.1") in the southern extreme of Gotra village, located on a man-made embankment created to divide an abandoned fluvial channel into several ponds at the south of Gotra village. BH-1 (N23001'11.1", E88035'14.8") (drilled earlier by GSI) is located near well, BH-18, in which water samples were collected by profiler. For comparison, another soft sediment borehole, BH-2 (N23001'09.9"E88035'27.7"), located at about 100m east of BH-1, is also shown here.

One of the purposes of such an approach was to investigate the relation between the level of As in sediments and aqueous As at equivalent depths.

The subsurface logs of all the boreholes start with a top soil, followed by clayey silt, to soft clay, to silty sand, to fine sand and to fine-medium sand at a 40 m depth. In BH-20 a horizon of 28 m thick soft bluish grey soft clay rich in carbonaceous matter has been intersected. The depth and thickness of soft clay varies across the area from one borehole to another.

The constituent sediments are the product of migrating meander belts with components of channel lag, point bar, levee and back swamp deposits. The sequence created by each stream is arranged laterally across the composite upper delta plain, forming a single aquifer with different lithologies juxtaposed at the same horizontal plain. In a vertical section it is composed of festoons with fining upward sequence of variable thickness. The sandy lithofacies is dominantly channel fill and the finer muddy (Clay) lithofacies is overbank flood plain or channel lag deposits. In BH-2 the volume of soft clay is less compared to BH-1 and BH-20, and aquifer sand encountered in this borehole is brown to grayish brown in nature in contrast to the grey sand in BH-1 and BH-20. Near BH-2, the concentration of As in groundwater in one tube well is below detection limit whereas the concentration of As is very high in two tube wells proximal to BH-1 and BH-20.

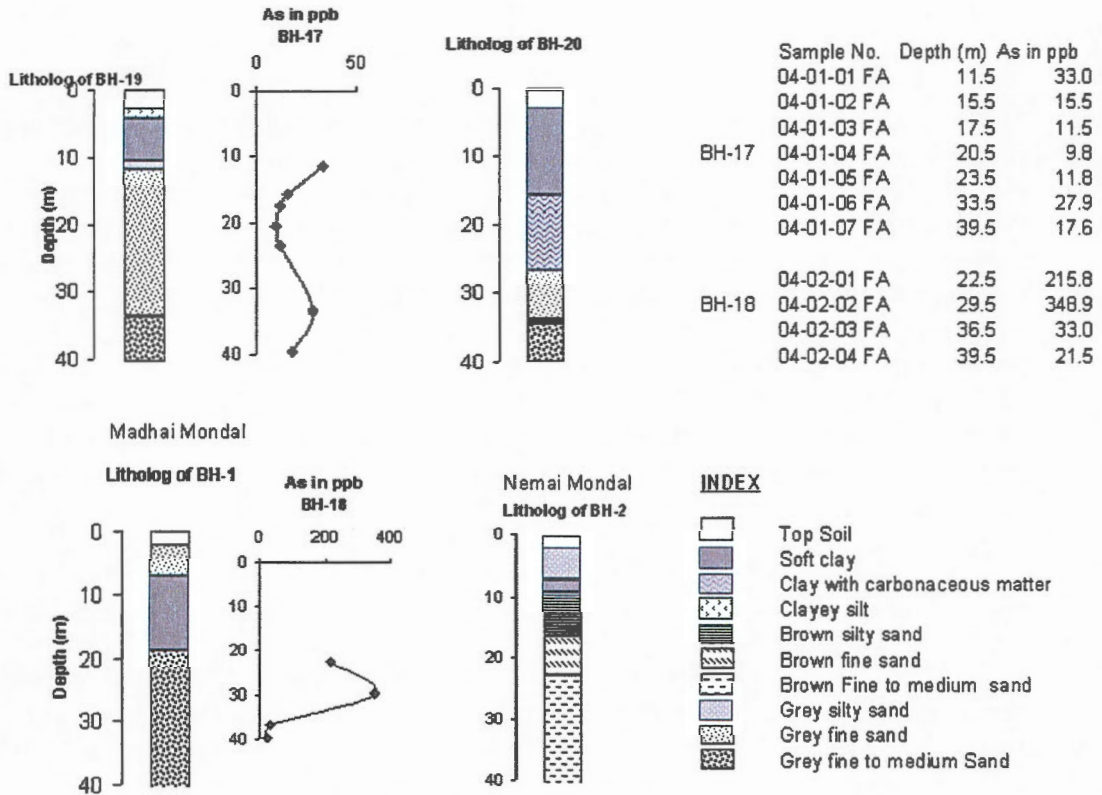


Fig. 4a : Lithologies of BH-1 and BH-2, BH-19 & BH-20 along with variation of arsenic in subsurface water (collected through profiler at points BH-17 & BH-18).

In BH-19 soil and soft clay is encountered up to 10 meters from the top. They are followed downwards by a thin unit of silty sand further followed by thick units of grey fine sand and grey fine to medium sand. Water has been collected from all three sandy units. Maximum As (aqueous) is recorded from a silty sand unit immediately below the soft clay unit. There is a uniform decrease in the fine sand unit up to a depth of 20 meters followed by increase once again with the peak at 35 meters within the fine to medium sand unit.

In BH-1, a soft clay unit separates two sand units. This is a scenario observed sporadically in several other bore holes in the Gotra-Ghetugachi area. The bottom of the clay unit here is around 20 meters. Profiler samples were collected in this site for depths below 20 meters (BH-18), because of difficulty in collecting water samples from the upper clay unit. Water samples could not be collected from the sand unit overlying clay. It is felt that results of any sample collected from this overlying unit would be very significant to understand the depth-wise variation of aqueous arsenic. From 20 meters down the arsenic values increased and peaked at 30 meters and then decreased to very low values around 40 meters. The high values at this site are higher than those in BH-17.

Water chemistry

Groundwater in the study area exhibited a wide range of arsenic concentrations. The maximum arsenic concentration of 531 ppb was recorded in well TW46, located about 20 m north of the southern ponds in the Gotra village (Figure 5). Eight of the 48 tubewell samples had arsenic concentrations less than the WHO guideline value of 10 ppb. Figure 6 shows the spatial distribution of the measured total arsenic from all depths superimposed upon a false-color satellite image. Arsenic was highest in Gotra village, with isolated hot spots in the surrounding region. Figure 7 shows the arsenic versus depth for all wells in the survey. The plot shows that the highest arsenic values are located approximately 20 to 30 m below ground surface and that shallower and deeper wells tend to have lower, yet often still significant arsenic. This is a widely observed pattern in other studies in the Bengal Basin (McArthur et al., 2001; Ravenscroft and McArthur, 2004; Van Geen et al., 2003).

The spatial distributions in Figure 6 and Figure 7 must be interpreted with caution, as the wells are located in a variety of lithologic packages deposited in different parts of the fluvial system over a limited period of time. Most domestic wells are placed in the shallowest productive unit encountered, and therefore it is difficult to determine a vertical profile of arsenic concentration from domestic wells.

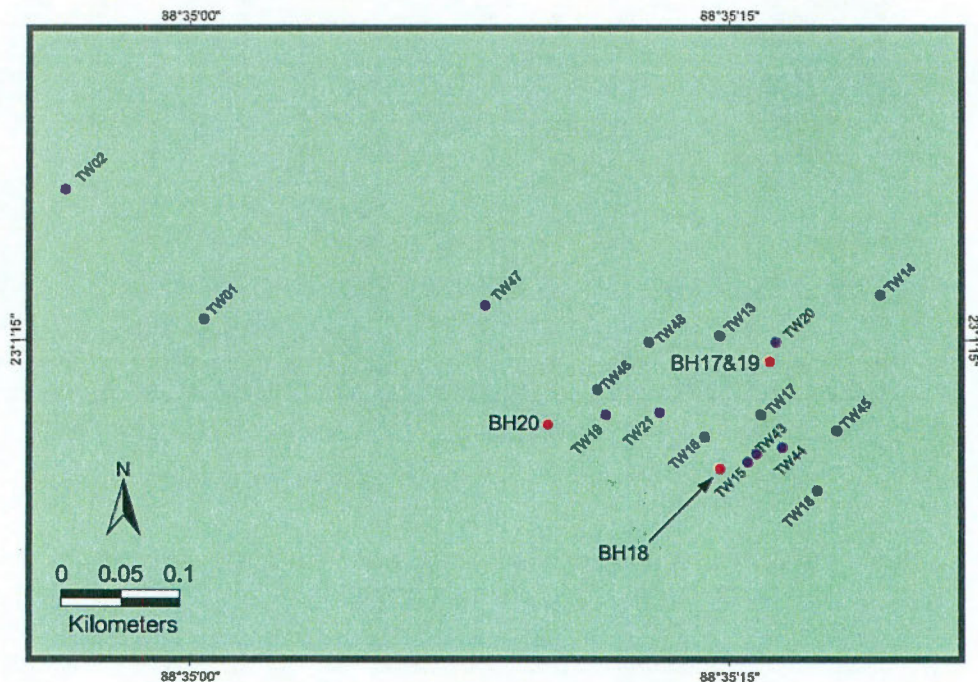


Figure 5: Wells and boreholes in Gotra Village (2004 numbering convention).

The elemental abundances in groundwater measured by ICP- AES and ICP-MS are given in tabular form in an accompanying spreadsheet. The major-ion chemistry of the groundwater was dominated by the cations calcium, sodium and magnesium and the anion bicarbonate. The measured pH was circumneutral,

between 6.87 and 7.13 and specific conductance ranged from approximately 500 $\mu\text{S}/\text{cm}$ to almost 1400 $\mu\text{S}/\text{cm}$. One sample, profiler water sample 04-02-03, had an anomalous pH of 7.7 and specific conductance of only 167 $\mu\text{S}/\text{cm}$. These values are probably not representative of formation conditions, and more likely reflect the effects of carbon dioxide degassing and dilution of the sample with the distilled water used to keep the profiler ports open while advancing the tool. Indeed, the flow rate from the profiler during that sample collection was very slow and the elemental concentrations are all consistently low compared to the other samples.

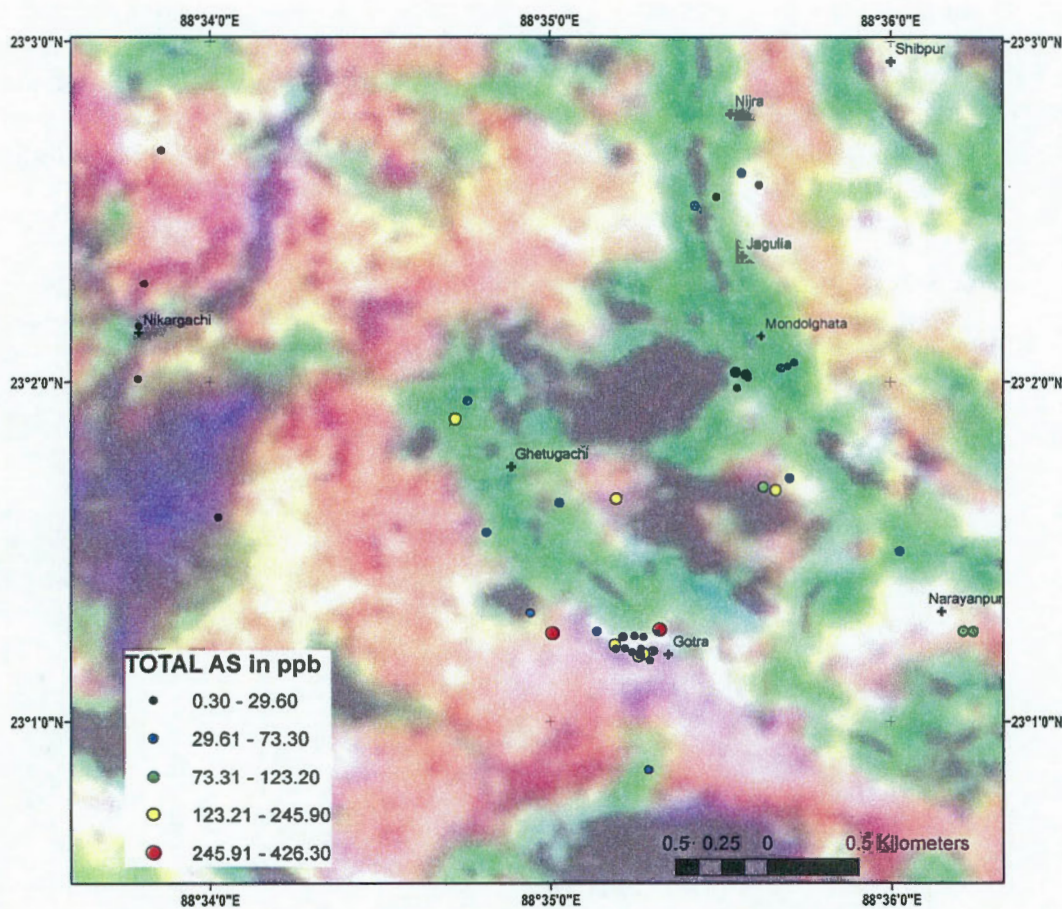


Figure 6: Total arsenic shown on a false-color satellite image.

A visual summary of the water-chemistry variability is provided by the plot in Figure 8, which shows the aqueous concentration of the most abundant elements in solution (except carbon) for every sample analyzed, where each sample is plotted as a distinct line. The major element water chemistry is fairly stable among the samples, while the minor and trace element chemistry shows considerable variability. As shown later by PHREEQC modeling, elements with a relatively tight range of variability such as silicon and perhaps strontium, are likely controlled by mineral solubility constraints. The molar ratio of calcium to magnesium ranges from 1.2 to 3.9 and averages 2.7. Iron shows a large variability and its concentration may be an indication of redox conditions, with high iron corresponding to reducing conditions and low iron corresponding to

oxidizing conditions, although other work in Bangladesh suggests that arsenic release is not necessarily coincident with ferrous iron release (Horneman et al., 2004; Pedersen et al., 2006; 2004). The sulfur measured by ICP-AES is most likely in the form of sulfate, as the high iron concentrations preclude sulfur in the form of sulfide. Phosphorous, almost surely found as phosphate, reaches a maximum of approximately 2.4 ppm.

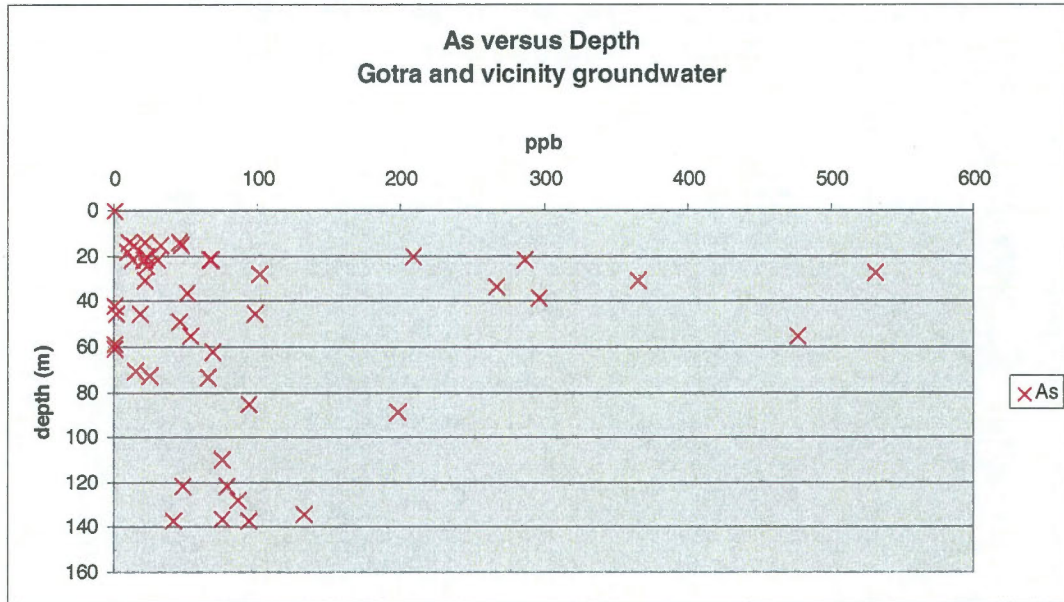


Figure 7: Total arsenic versus depth for all tubewells in Gotra and surrounding region.

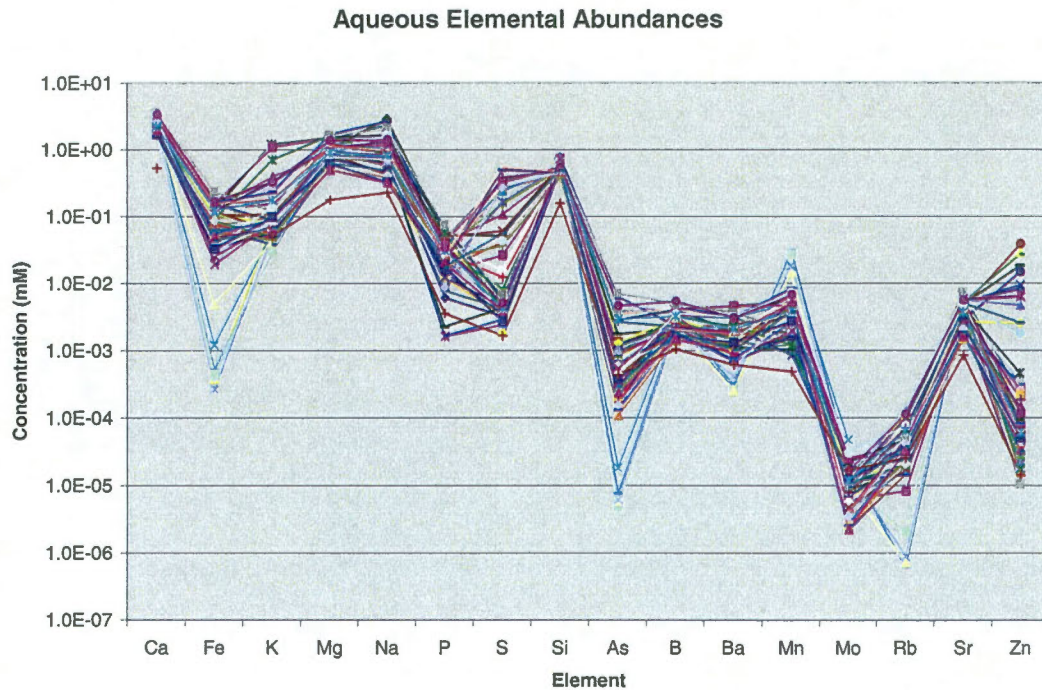


Figure 8: Elemental abundances of water samples as determined by ICP-AES and ICP-MS. Each line represents a distinct sample.

The plots in Figure 10 show the aqueous concentration of elements in groundwater samples cross plotted against each other. The plots show that arsenic has a weak inverse correlation with sulfur and manganese, and a weak positive correlation with iron and phosphate. Zinc, which has a rather wide range of variability, is anti-correlated with sulfur, manganese and iron. Phosphate has a fairly strong correlation with dissolved iron. Note that dissolved chloride was not measured in any samples and dissolved ammonia was measured in the profiler water samples only.

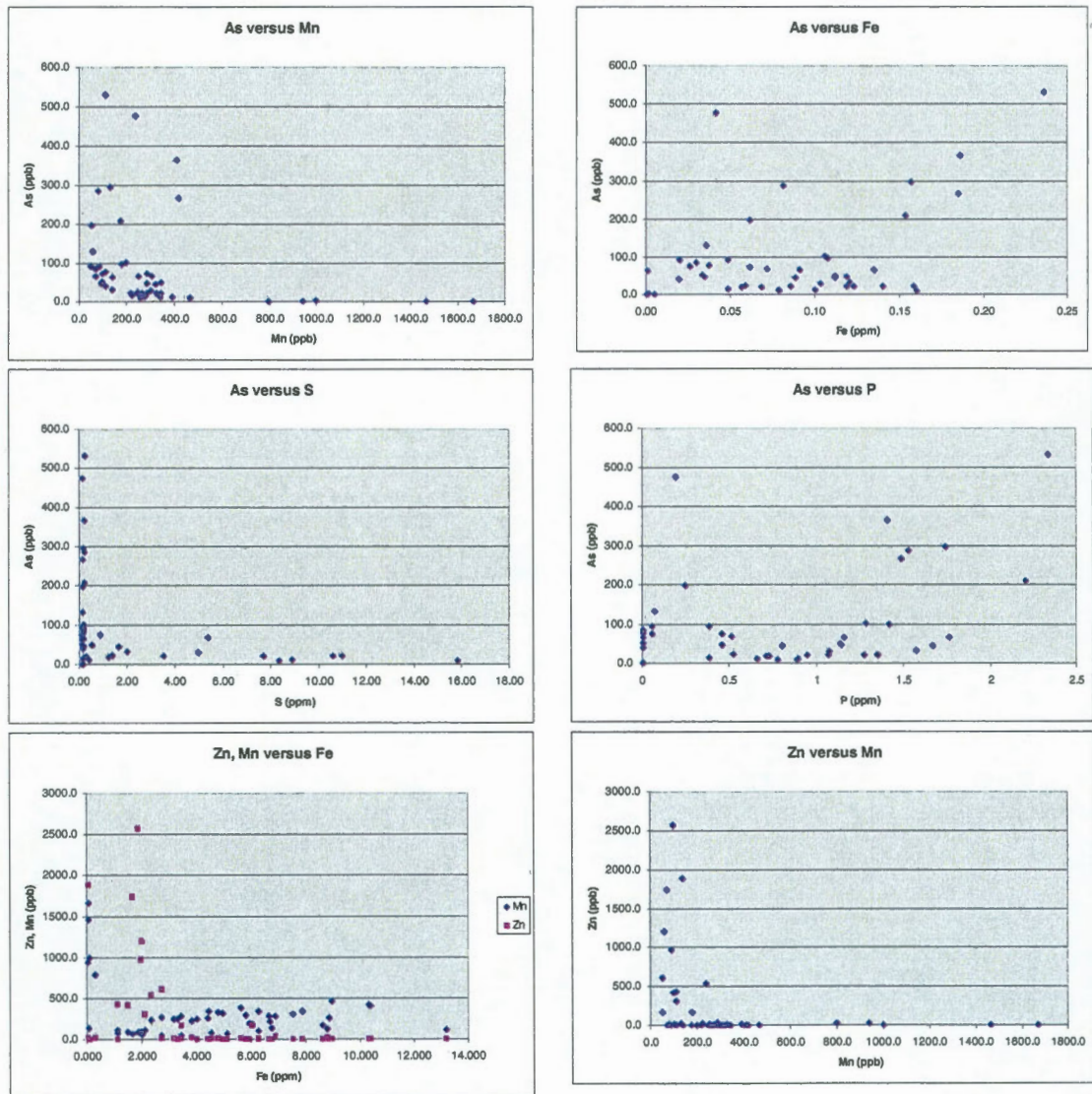


Figure 9: Dissolved element cross plots.

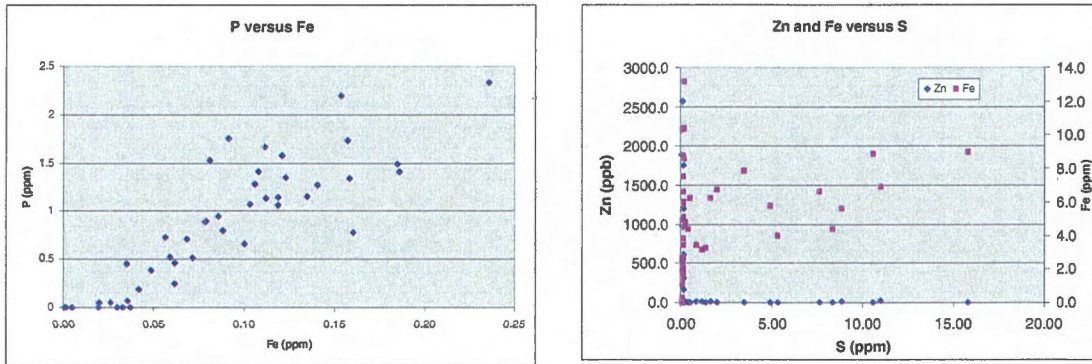


Figure 10: Dissolved element cross plots.

Profiles of water chemistry with depth from samples collected using the Waterloo profilers are shown in Figure 11. The profiler was most successful at BH17. There, the arsenic concentration is highest, just over 30 ppb, at the shallowest sampling point, then drops to a minimum of 10 ppb at 20 m depth. Alkalinity, sodium, magnesium, and calcium more or less steadily decrease with depth. Iron is fairly constant with a peak at approximately 18 m depth, whereas manganese peaks at the top and bottom of the profile and is at a minimum at 20 m depth. Ammonia is fairly constant through the profile except at the shallowest sampling point, where it reaches a maximum of approximately 7 ppm. Note that concentrations of Mg Ca and Fe (not shown) from unfiltered samples were almost identical to the filtered samples, suggesting very little colloidal sediment in the profiler samples.

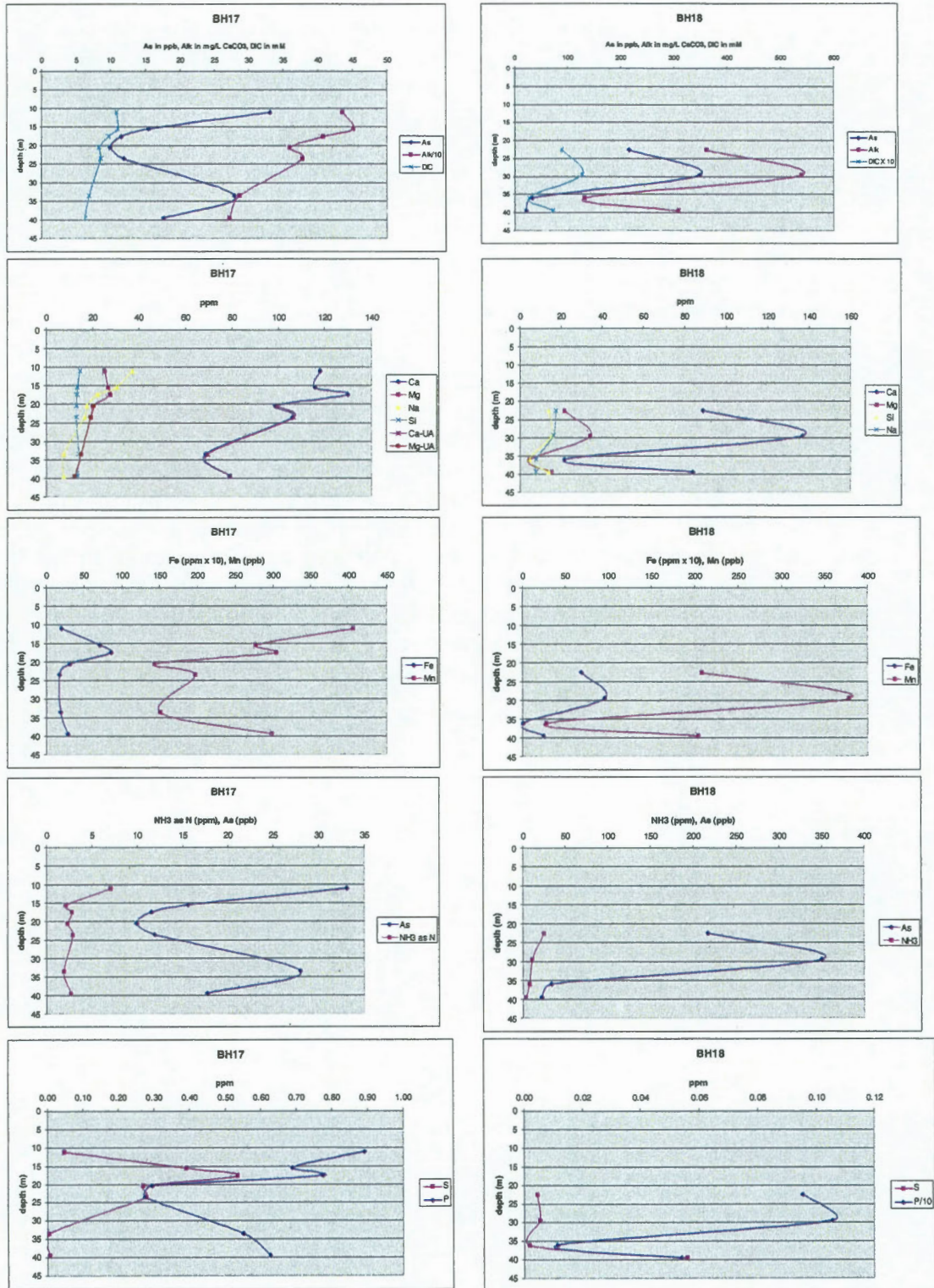


Figure 11: Aqueous chemistry from vertical profiles collected using the Waterloo Profiler. BH17 - low As zone; BH18 - high As zone.

It was much more difficult to collect samples with the Waterloo profiler at the last two sampling points of BH18. Indeed, the second deepest point from BH18 plot is the sample that was likely diluted by the distilled water used to keep the profiler ports open, and it is possible that the deepest point was similarly diluted. The arsenic concentrations in BH18 peak at nearly 350 ppm at 30 m depth. The elemental concentrations in BH18 are more strongly correlated to each other than those in BH17, perhaps because dilution with purge water overprints the natural chemistry.

Figure 12 shows the speciation results as determined by the IC-ICP-MS approach. Dissolved arsenic was dominantly in the As(III) valence state; although some of the lower-arsenic samples had a higher proportion of As(IV). The data shows that higher total As samples tended to be dominantly reduced arsenic, whereas the low As samples tended to contain more oxidized arsenic. This is consistent with the stability of iron oxides that would immobilize As under the oxic conditions. The EDTA speciation was not successful, likely because the 1.25 mM EDTA concentration was too weak for the high dissolved load in these groundwater samples.

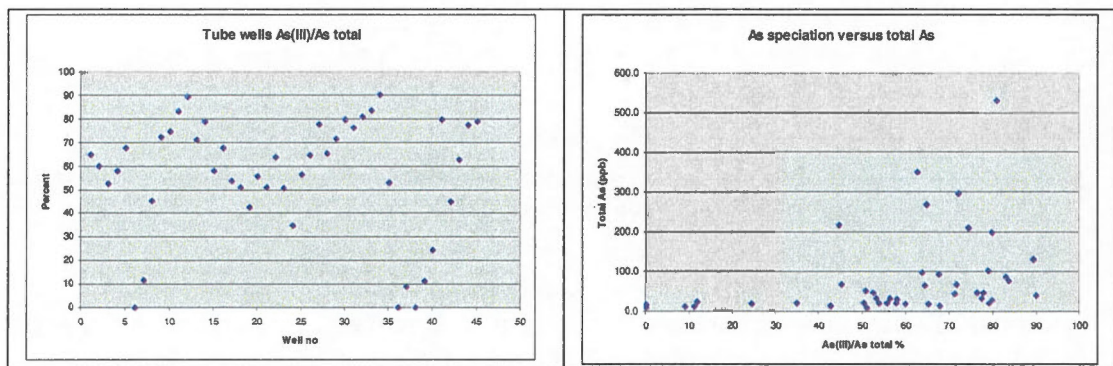


Figure 12: Arsenic speciation in aqueous samples. Percent of As found as As(III) and total arsenic versus percent As(III).

Figure 13 shows that the field kit predictions were generally good, although the color scale is somewhat indeterminate in the middle range between 200 and 400 ppb.

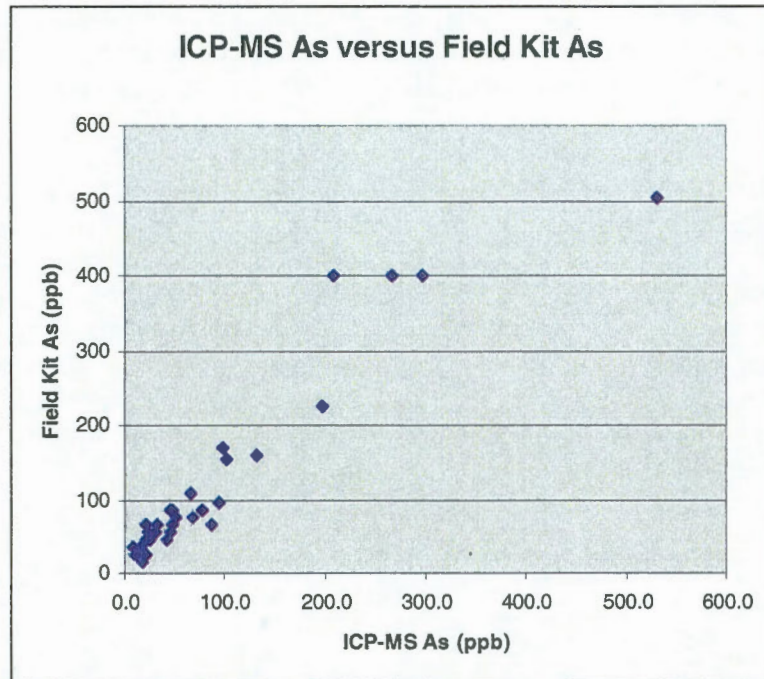


Figure 13: Dissolved total arsenic measured by ICP-MS versus that measured by Merck field kit. Each point represents a distinct groundwater sample.

The dissolved oxygen (DO) measured in profiler samples ranged between 400 and 900 ppb in BH17 and was several mg/L at two points in BH 18. Since the samples also contained high dissolved iron and manganese, which is incompatible with oxygen, it is likely that the measured oxygen is a result of contamination. The low DO in BH17 is possibly from diffusion across the polyethylene sampling line. Similarly, the very high oxygen levels in BH18 samples probably came from air that was incompletely purged from the sample line.

Dissolved organic carbon (DOC) was below detection of 2 ppm in all samples except the shallowest profile point in BH17 (2 ppm), the second deepest profile point in BH18 (2 ppm), and six domestic wells with (4 at 2 ppm, 1 at 3 ppm and 1 at 4 ppm). Regrettably, the DOC was measured on unpreserved samples. Consequently, it is likely that the measurements underrepresented the actual DOC in the groundwater, as DOC in unpreserved samples can oxidize after contact with atmospheric oxygen in the sample bottle headspace.

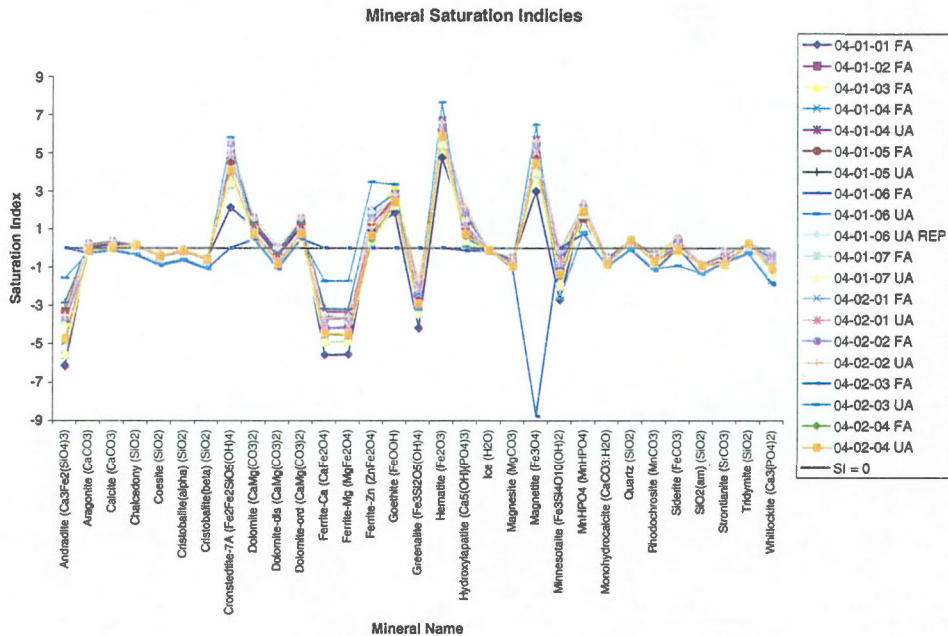


Figure 14: Saturation indices computed for profiler waters using PHREEQC and the Lawrence Livermore National Laboratory thermodynamic database.

The aqueous geochemistry from the profiler water samples, for which alkalinity and field pH were available, were analyzed using PHREEQC and the Lawrence Livermore National Laboratory (LLNL) thermodynamic database. The phosphorous and sulfur measured by ICP-OES was assumed to be in the form of phosphate and sulfate respectively. Indeed, the high iron concentration and volatile nature of sulfide precluded the retention of sulfide in the samples during transport to the laboratory. Field pH was used and a formation temperature of 26 C assumed. Charge balance errors were generally excellent, all between a fraction of a percent and 5 %, except one sample which had a 16% error.

The PHREEQC-computed saturation state of selected minerals from the LLNL database are plotted in Figure 14. Many more minerals are in the database, but are not plotted here as they are strongly undersaturated. The carbonates dolomite, siderite and aragonite are supersaturated in all waters, while calcite is just at or above saturation. Iron oxides are all supersaturated as is the mixed-valence magnetite. The phosphate minerals hydroxylapatite and MnHPO_4 are also supersaturated. Most of the amorphous or weakly crystalline silica species are at saturation, explaining the low variability seen for silicon in Figure 8. No arsenic bearing minerals are computed to be at saturation, and therefore dissolved arsenic is likely controlled by surface geochemical processes such as sorption. Future analytical work based on selective leaches would provide further insight.

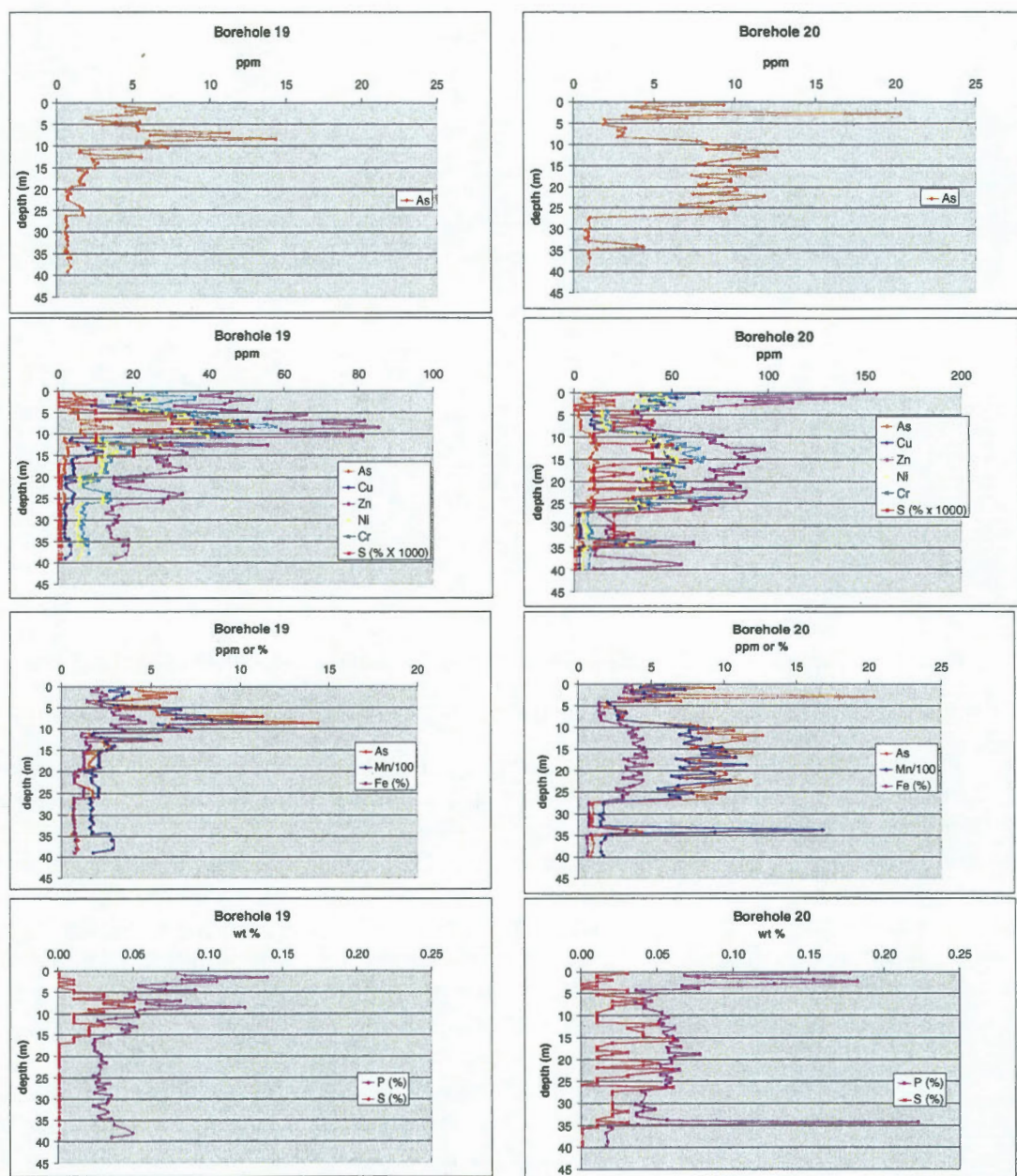


Figure 15: Sediment extraction profiles from the two sediment cores. All results expressed as ppm in dried sediment, except Fe, which is in weight %. BH19 corresponds to a low dissolved arsenic zone while BH20 corresponds to a high dissolved arsenic zone.

The results of geochemical extractions from cored sediments are shown in Figure 15 as vertical profiles of elemental abundance versus depth and in Figure 16 as cross plots of elemental abundances. Sediment core BH19 is directly adjacent to the vertical water chemistry profile BH17 plotted above in Figure 11. Sediment core BH20 is in a zone of relatively high arsenic, although not adjacent to a vertical water chemistry profile.

The sediment arsenic concentrations in the two cores are within the range of those observed elsewhere in the Bengal Basin, from 1 to 20 ppm. BH19 shows arsenic levels in the 4 – 5 ppm range at the surface, followed by a spike up to 14

ppm at 7 m depth. The arsenic concentration is then somewhat erratic to 15 m depth and then gradually declines to approximately 1 ppm in the silty sand aquifer found below 25 m. At time of writing, detailed stratigraphy and grain-size data for the cores was not available.

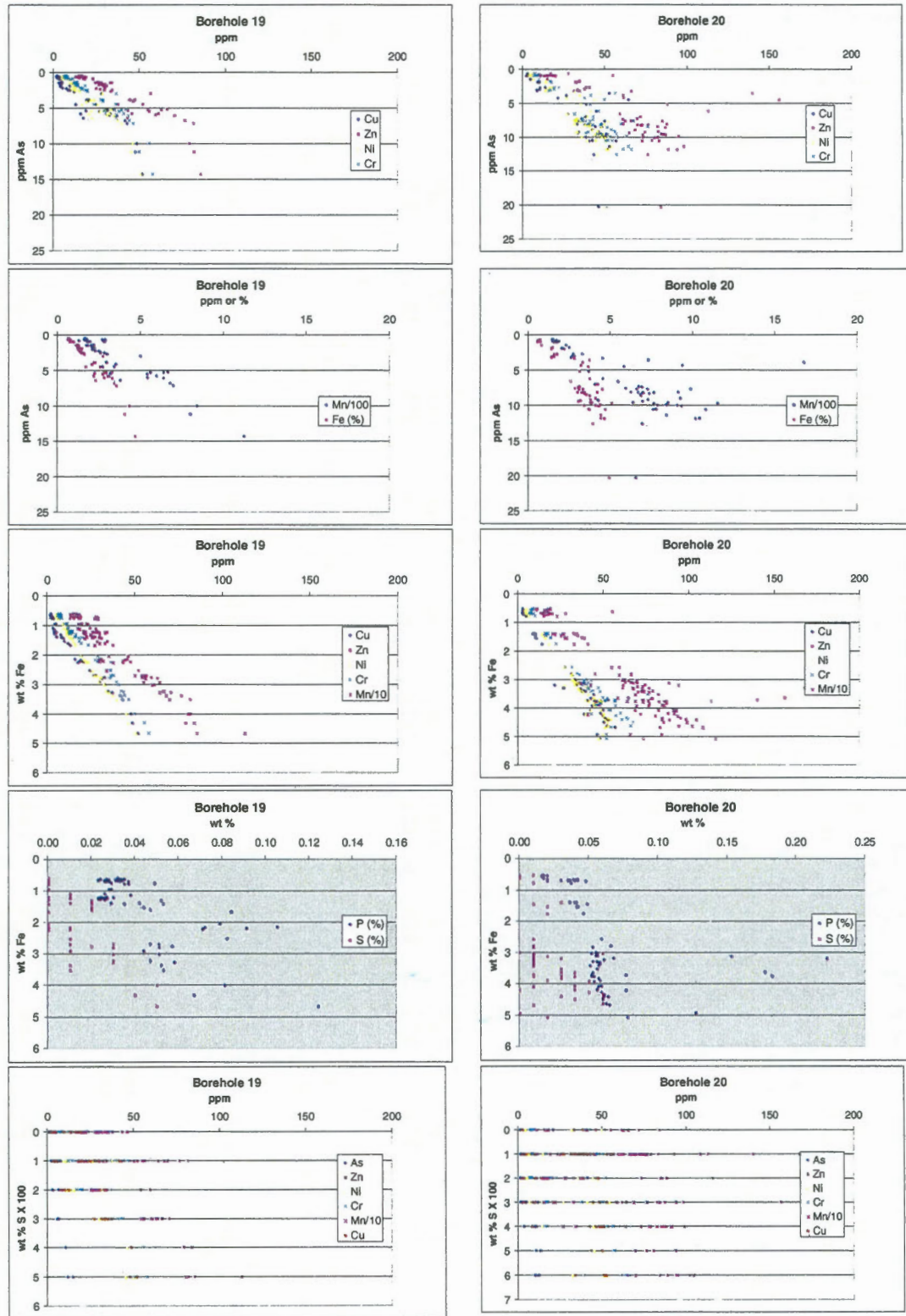


Figure 16: Sediment extraction results from the two cores. Cross plots of elemental concentrations in either ppm or wt %.

The sediment arsenic in BH20 increases to 20 ppm at approximately 3 m below ground surface. This core was collected on a man-made causeway in the middle of a pond formed by an abandoned channel, and the 3 m depth may correspond to the pond bottom. The arsenic in the silty – sand found between 5 to 7 m depth is in the 2 – 3 ppm range. The thick clay sequence that follows from 10 to 25 m depth shows a relatively high arsenic concentration, fluctuating between 7 and 12 ppm. Except for a small spike at 34 m depth, the As concentration drops to less than 2 ppm in the silty sand found below 27 m depth.

The other metals as well as iron and manganese are elevated in the clay zones and lower in the silty-sand aquifer sediments. Sulfur seems to show a poor correlation with stratigraphy, although appears slightly elevated in shallow silty sand in BH 19.

The cross plots of solid-phase abundances in Figure 16 show that arsenic is fairly tightly correlated with iron, and somewhat less strongly correlated with manganese. Arsenic also strongly co-varies with other weakly sorbing metals Cu, Ni, Zn, and the oxyanion Cr. The correlations are very strong in the low-dissolved-arsenic zone (BH19) and weaker in the high-arsenic-zone (BH20). These elements are however more strongly correlated with iron than with arsenic, although again the correlation is strongest in the low-dissolved-arsenic zone (BH19). It has been suggested that sulfides may be responsible for a fraction of the arsenic found on the solids (Pal et al., 2002b; Polizzotto et al., 2006; Swartz et al., 2004). The cross plots in the bottom panel of Figure 16 show a relatively poor correlation between sulfur and metals, including As, although the sediment sulfur content was close to the detection limit of 0.01 wt % S.

Discussion

The Acme Labs extraction methodology used in this research can be considered a near - total digestion (Chen and Ma, 2001; Hudson-Edwards et al., 2004; Pavlickova et al., 2003). According to the ALS-Chemex website, aqua regia will dissolve most base metal sulphates, sulphides, oxides and carbonates but will not completely dissolve most rock-forming elements and refractory elements. It is highly unlikely that these recalcitrant phases will play any significant role in the geochemistry of the water, especially for arsenic and major-element chemistry. While the method's use of ICP-MS gives it good detection levels for minor and trace elements such as arsenic, the aqua-regia leach is too strong to be able to characterize the weakly sorbed and iron- and manganese-bound arsenic, which current hypotheses place at the centre of the arsenic debate.

The sediment extraction data from BH 19 and 20 suggest that solid-phase arsenic is primarily associated with iron oxides, dominantly in a sorbed state. The solid-phase element cross plots in Figure 16 show a strong correlation between solid-phase iron and arsenic and a good correlation between arsenic and manganese, although this last correlation is distinctly weaker in BH20. There is no correlation with sulfur. Pal et al., (2002b) performed detailed separations and electron microscopy of aquifer sands from a core collected a few kilometers north of Gotra, and found that arsenic was dominantly associated with four fractions:

iron oxide/hydroxide with residual magnetite and ilmenite (10-40 mg/kg), illite (10-41 mg/kg), iron oxyhydroxide-coated sand grains (30 mg/kg), and biotite (9 mg/kg).

The solid phase sulfur determined by the Acme extractions is almost surely in the form of sulfides. Indeed, Pal et al., (2002b) observed authigenic sulfides, often associated with siderite, in sediments from the Gotra-area aquifer sands. Pal et al., (2002b) did not perform sequential extractions and were not able to estimate the sulfide As content of the sediments. Similarly, with the near-total digestion used in this research, it is not possible to determine whether the sulfides are detrital or authigenic, or what proportion of the total solid-phase arsenic is contained in sulfides. The strong association of solid-phase Cr, typically found as an oxide, with solid-phase As, Zn and Cu, suggests that some of the As, along with these other elements, are in a sorbed state since Cr does not incorporate into pyrite or sulfides (Morse and Luther, 1999).

Other workers have examined sediments in affected areas of Bangladesh and India (Acharyya, 2002; Pal et al., 2002b; Polizzotto et al., 2005). On the basis of the large 100 μm grain size, the oxidation state observed with micro-x-ray adsorption near edge spectroscopy and the correlation with chalcophiles Cu and Zn, Polizzotto et al., (2006; 2005) suggest that some of the sulfide from Munshiganj, Bangladesh is detrital. However, authigenic pyrite can have a variety of trace-element elemental substitutions such as Cu and Zn (Morse and Luther, 1999). Pal et al., (2002b) state that they could find not a single detrital sulfide grain in isodynamic separations from over 360 m of core. Acharyya (2002) similarly reports that separate arsenic minerals are rare or absent in West Bengal, although authigenic pyrite is associated with woody sediments and or on heavy minerals such as magnetite as a cement-like coating. Swartz et al., (2004), analysis of the same Munshiganj sediments that were analyzed by Polizzotto et al., (2006; 2005) used sequential extractions to show that As is found in several pools, the largest of which was sulfide-hosted As, although, similar, to Pal et al., (2002b), the magnetic separates also showed high As. Polizzotto et al., (2006; 2005) find that sulfide As constitutes over 60% of the total As, compared to 15% that is weakly sorbed.

Anawar et al., (2003) found that of the total As in the sediments they analyzed, 10 – 20 % was associated with organic matter, ~40 % was associated with oxides and 30 – 50 % associated with sulfides. Similarly, Akai et al., (2004) used sequential extractions to determine that As was found principally in the following forms: (1) acid soluble form (As mainly fixed in carbonates), (2) reducible form (As fixed in Fe- and/or Mn-oxides), (3) organic form, (4) insoluble form (As fixed mainly in sulfide and rarely in silicate minerals).

Recently, Meharg et al., (2006) have proposed that the iron-oxide association is secondary to a stronger organic carbon control of arsenic. Specifically, their results suggest that arsenic is highest where organic carbon is high. They speculate that in turn iron oxides may be formed by root plaques on the plants. Their argument has a few gaps. Specifically, Meharg et al., (2006) do not explain how the Fe(III) oxides and OC survive together over geologic time and they do not present groundwater data to show that the As-rich organics are associated

with high dissolved As. The conventional wisdom is that OC and iron react, with the reduction of the iron causing dissolution of the iron oxides. If sulfur is present, then sulfate reduction may occur and authigenic pyrite can form. Recent calculations show pyrite can contain up to 5% As in its crystal structure (Reich and Becker, 2006). Through sulfate reduction high solid-phase As can be associated with low dissolved As and organic carbon can be associated with arsenic fixation. Organic carbon was not characterized in BH19 and BH20 samples so we cannot examine this issue. An extraction targeted at arsenic sorbed onto or in association with organic matter may be worthwhile (Ahmed et al., 2004; Hudson-Edwards et al., 2004).

Before interpreting the aqueous geochemical data, it is valuable to review the dominant terminal electron accepting processes (TEAPs) and their effects on groundwater geochemistry. Although not well characterized, organic matter is the only reasonable reductant driving the redox processes in the subsurface (McArthur et al., 2001). The conventional understanding is that labile organic matter enters the aqueous phase, carried in with surface water (Harvey et al., 2002) or from sediment organic matter such as peat (McArthur et al., 2004; McArthur et al., 2001) or leached from organic matter contemporaneously deposited with the sediment (Meharg et al., 2006). The DOC is then partially oxidized by one of a number of possible TEAPs. It is well accepted that microbes mediate almost all of these subsurface redox reactions (Lovley and Chapelle, 1995).

The most probable TEAPs that are viable under the anaerobic conditions found in Gotra area groundwaters are presented in Table 1 (nitrate reduction, manganese reduction, iron reduction, sulfate reduction, and methanogenesis) (Lovley and Chapelle, 1995). Nitrate reduction probably also occurs at the surface from anthropogenic nitrate. This list is given in order of decreasing energy yield to bacterial per mole of DOC oxidized, and was earlier thought to be the sequence in which TEAPs exclusively occur in the subsurface. That is with an excess of organic carbon, first nitrate is reduced until exhausted, then only manganese will be reduced until the solid-phase manganese is exhausted, then iron will be reduced, followed by sulfate and finally methanogenesis. It is now believed that many TEAPs can coexist, and they are not clearly segregated in space or time (Lovley and Chapelle, 1995; Pedersen et al., 2006) although the local supply of electron acceptors may lead one TEAP to dominate in a particular region. At the Gotra site, the products of each of these TEAPs can probably be expected throughout the profile.

and many results are at or below this level. The 7 m solid-phase S peak corresponds to a peak in aqueous As at that depth in Figure 11 and a low in aqueous sulfur, consistent with sulfate reduction in that zone. There is likely no sulfate reduction at 20 m depth in BH17 and the adjacent BH19, where the solid-phase arsenic is at the detection limit and the dissolved arsenic is at a local minimum. At the MIT Munshiganj field site, acid-volatile sulfides, that is amorphous or weakly crystalline authigenic sulfides, peaked in a zone at 30 m depth, where sulfate was lowest and dissolved arsenic peaked (Harvey et al., 2002; Swartz et al., 2004). If As is being sequestered in sulfides at that site, then the high dissolved As is difficult to reconcile with the apparent active sulfate reduction at the 30 m depth.

The argument for sulfate reduction at Gotra based upon the water-well data is more tenuous. The dissolved-element cross plots in Figure 10 show a strong inverse correlation between dissolved sulfur and dissolved arsenic, as well as sulfur and zinc, however not for sulfur and iron. If sulfate reduction were occurring, one may expect that where sulfate is low, then elements like iron, zinc and arsenic would also be low as they would be fixed in sulfides. This may not occur simply because sulfur is overwhelmed by iron. However, as others have convincingly argued, (McArthur et al., 2004; McArthur et al., 2001), the As versus S plot implies that sulfide oxidation is not the process responsible for As release, as then high As would be associated with high sulfur.

Methane was not measured at the Gotra site, but it would be hardly surprising to find it. Methanogenesis can be expected in the high DOC zones, and is well-known to be associated with paddy fields. At the MIT field site, gas collected from groundwater was flammable, but methane has not been quantified. Arsine gas, indicative of strongly reducing conditions, was detected by colleagues at EWAG in Switzerland (Hug, personal communication 2004) from a sample of gas exsolved from Munshiganj groundwater, although others have questioned whether the gas sample would survive the several weeks between collection and analysis.

The anaerobic oxidation of DOC by any of the TEAPs in

Table 1 will produce CO₂ and (except for methanogenesis) alkalinity in addition to products specific to the TEAP. The CO₂ then can be partially consumed by mineral weathering reactions, producing more alkalinity and base cations (Ca, Mg, Na, K). De-amination of amino acids in organic matter during fermentation and oxidation can also produce ammonia, which will accept a proton at pH less than 9.2, thus also increasing alkalinity. The concentrations of alkalinity, base cations and ammonia are therefore indicators of the quantity of DOC that has been oxidized through any of these anaerobic TEAPs. The correspondence will however not be perfect, as other reactions, notably secondary mineral precipitation, may remove these oxidation products from solution.

The vertical water-chemistry profiles in Figure 11 show that in the high As profile BH18, alkalinity and arsenic peak at the same depth, whereas in the low arsenic BH17, the arsenic peak is associated with the second highest alkalinity. Both profiles have similar, very high alkalinity in the range of 400 ppm as calcite

Denitrification
$CH_2O + \frac{1}{2}NO_3^- \rightarrow HCO_3^- + \frac{1}{2}NH_4^+ + \frac{1}{2}H_2O$
Manganese reduction
$CH_2O + 2MnO_2 + 3H^+ \rightarrow 2Mn^{2+} + HCO_3^- + 2H_2O$
Iron reduction
$CH_2O + 4FeOOH + 7H^+ \rightarrow 4Fe^{2+} + HCO_3^- + 6H_2O$
Sulfate reduction
$CH_2O + \frac{1}{2}SO_4^{2-} \rightarrow HCO_3^- + \frac{1}{2}HS^- + \frac{1}{2}H^+$
Methanogenesis
$CH_2O + \frac{1}{2}H_2O \rightarrow \frac{1}{2}HCO_3^- + \frac{1}{2}CH_4(aq) + \frac{1}{2}H^+$

Table 1: List of anaerobic Terminal Electron Accepting Processes (TEAPs).

The most favorable anaerobic TEAP from a bacterial perspective is probably manganese reduction, followed by iron reduction. During the reduction of manganese and iron, low – solubility solid-phase Mn(IV) and Fe(III) oxides are reduced to soluble manganese Mn(II) and iron Fe(II). The cross plot of dissolved Mn versus Fe in Figure 10 shows that the highest Mn concentrations occur where Fe is low. This could be explained by an abundance of solid-phase Mn in those sample locations, and accordingly, Mn reduction is excluding Fe reduction. At higher Fe concentrations, dissolved Mn is relatively low, but shows an increasing trend with Fe. This proportion may be explained by simultaneous Mn and Fe reduction, or perhaps the release of Mn(II) that was sorbed onto Fe(III) oxides, and then released upon iron reduction.

Dissolved iron and manganese are only weakly correlated with dissolved arsenic (Figure 10). If arsenic is principally sorbed on the iron and manganese oxides, then a stronger correlation may be expected. However, Horneman et al., (2004), Van Geen et al., (2004; 2006b) and more recently Pedersen et al., (2006) have argued that the reduction of iron oxides and perhaps manganese does not necessarily coincide with the release of Fe(II) and Mn(II) to solution, as much appears to be re-adsorbed by the remaining oxide or perhaps deposited as a secondary mineral phase such as siderite. In the Gotra groundwaters, both siderite and magnetite are supersaturated (see Figure 14) and may take up Fe(II) from groundwater. Mn(II) could perhaps also be resorbed by Fe(III) oxides, although the strong peak of dissolved Mn at low dissolved Fe concentrations seems inconsistent with this hypothesis.

There is evidence of possible sulfate reduction in both the dissolved-element profiles and in the cross plots. Some of the well waters show sulfur up to 15 ppm S (equivalent of 45 ppm as sulfate), while the samples from vertical profile BH 17 are all below 0.6 ppm S and the samples from the high – As vertical profile BH18 are essentially below the ICP-AES detection limit of 0.05 ppm S (Figure 11). There is a small peak in solid-phase sulfur and arsenic at 7 m depth in core BH19 in Figure 15, although the solid-phase sulfur detection limit is 0.01% (or 100 ppm)

(approximately 655 ppm as bicarbonate). In both cases, the highest alkalinity is near the top of the profile. Ammonia displays a similar pattern with the peak near the top of the profile near the arsenic peak, and a lower concentration at depth. Ammonia may possibly also convert over to N_2 gas by oxidation by nitrite or in combination with methane oxidation in newly recognized anaerobic oxidation processes (Kuypers et al., 2003; Raghoebarsing et al., 2006). While ammonia is not associated with any secondary minerals, it may be lost from solution by sorption. A peak in ammonia may correspond to ammonia production, an ammonia source via groundwater flow or, possibly, ammonia desorption. The association of As with high alkalinity and ammonium suggests that organic matter oxidation is associated with As release.

The strong correlation between dissolved iron and phosphorous in the cross-plots in Figure 10 contrasts the much weaker correlation between dissolved Fe and As. Phosphorous is most likely in the form of phosphate, and is conventionally thought to originate from organic matter where it is found in proportions given by the Redfield ratio of 106:16:1 for C:N:P. Phosphate competes more strongly with arsenic for sorption sites than any other anion found commonly in Gotra groundwater. Accordingly, the strong dissolved Fe-P correlation suggests sorption control of phosphorous through iron oxides. The weak correlation between dissolved As and P may indicate that sorption is not the only control on arsenic or at least that phosphorous does not control As.

The distribution of solid-phase arsenic in the vertical profiles closely follows that of both P and Fe. However, at depths of 2.5 m and 8.5 m in BH19 and at 34 m in BH20, the ratio of P to Fe is much greater than average, suggesting perhaps P accumulation in those zones. PHREEQC modeling (Figure 14) shows that hydroxylapatite is supersaturated in the profiler waters, and could accumulate in zones where calcium or phosphate is released into solution. Dissolved calcium in the vertical water profile in BH17 (Figure 11), adjacent to the core BH19, does not correspond well with solid phase P.

A satisfactory interpretation of the arsenic found in groundwater will require an understanding of hydrologic pathways, connecting recharge areas to arsenic – rich zones. No hydraulic head data was collected during the 2004 investigations, so conventional flow net analysis or similar is not possible. Instead, we can only speculate about flow patterns by applying basic groundwater flow theory.

The geology of the site consists of a package of sand and clay units that are discontinuous laterally. The clay units are much more impermeable than the fine-sand aquifers. Given the vertical – to horizontal dimensions of the units, flow-line refraction requires that groundwater flows for the most part horizontally along the sand bodies and orthogonal to the sand – clay boundaries in the clays, that is, mostly in the vertical direction in clays. In the unsaturated zone, we can expect water to flow vertically, essentially straight downward. These observations imply that in clays we can expect vertical transport, either upward or downward into the aquifers. These simple observations have implications for observed dissolved arsenic peaks. In aquifers where horizontal flow dominates, a “peak” in a dissolved constituent must be transported from a lateral, upstream location. High

dissolved As at a location in an aquifer that is confined by clay units does not necessarily correlate with an As source at the sample location.

One hypothesis is that clay units, which are relatively high in solid-phase arsenic, are a source of the dissolved arsenic in the aquifers. There are, however, very few data of pore-water-arsenic concentrations in the clay units, principally because it is very difficult to sample water from clays using wells. Clearly, given the slow rate at which water can be released from clay, a large volume of source clay, or at least a very large clay-aquifer interface area would be required to sustain large volumes of arsenic-contaminated water. In addition, the required large interfacial area seems to contradict the smaller, local hot spots that are observed.

An understanding of the water balance and the flow rate through the aquifers is required to fully explore the leakage from clay hypothesis. A water balance model for the MIT Munshiganj field site suggests that about two-thirds of the aquifer recharge comes through surface clays that underlie ponds and rice paddies, and that about one third comes through more permeable connections along river channels (Harvey et al., 2006). It is not clear if these conclusions transfer to the Gotra area, which does not flood every year, in contrast to the Mushiganj site.

Current understanding

There is yet to be published a satisfactory explanation for the observed arsenic in groundwater in the Bengal Basin. Any theory must explain these observations:

- 1) Why is the arsenic occurrence so patchy over relatively short scales, when the sediment geochemistry appears fairly homogeneous over these scales, although Pal et al., (2002b) note variations in arsenic-bearing phases?
- 2) Why is there generally a peak in As at approximately 20-30 m depth?
- 3) If reduction of iron oxides is occurring, why is there so little iron-oxide in the aquifer (Polizzotto et al., 2006; Polizzotto et al., 2005)?
- 4) Why has the arsenic not been flushed out over the Holocene lifetime of the sediments?

There is sufficient As in the sediments to explain elevated dissolved As. Indeed, 1 ppm solid phase arsenic is equivalent to 6.7 mg/L dissolved As, assuming 30 % porosity ($1 \text{ g As}/10^6 \text{ g solid} \times 2000 \text{ kg solid} / \text{m}^3 \text{ aquifer} \times 1 \text{ m}^3 \text{ aquifer} / 300 \text{ L water}$). Groundwater flow requires a steady flux of As to sustain the aqueous phase concentrations. If the source is sedimentary, then eventually the As will be flushed from the system.

Many workers now seem to favor some surface-related hypothesis to explain the As release. Harvey et al., (2002) proposed surface-water derived organic matter was driving iron oxide reduction. Ravenscroft et al., (2005) and Polizzotto et al., (2006; 2005) propose a near-surface oxidation-reduction sequence, where arsenic is first released from sulfides, and segregated from sulfate. Arsenic is then released in a subsequent reduction. The Columbia group has collected extensive data (Van Geen et al., 2004; Van Geen et al., 2006b; Zheng et al., 2005) and now seem to favour some sort of near-surface release mechanism

(van Geen et al., 2006a). The 2004 Gotra results are consistent with a reduction mechanism, although the data are principally from the aquifer and below the water table.

The Gotra results provide some of the most highly resolved sediment geochemistry data from the Bengal Basin. The promise of coincident highly resolved water chemistry was not however achieved with the Waterloo Profiler because of unanticipated deployment problems. While the profile from BH17 was excellent, the second last point on BH18 was probably compromised by purge water. The profiler suffered from extremely low flow rates and excessively long sampling times. Subsequent to the field work, the low flow rates were explained by the unexpectedly deep water table at Gotra, which is generally 5 to 7 m below ground surface. This deep water table requires close to the maximum lift that can be achieved with the vacuum-based peristaltic sampling method used in Gotra in 2004. A gas-drive sampling approach would likely overcome the deep water table problem, although it would be difficult to collect water from clays using any borehole-based method, including the profiler. The survey of local wells revealed a patchiness in arsenic levels over relatively short (100's m) spatial scales, in agreement with what has been observed elsewhere (Acharyya et al., 2005; Hossain and Sivakumar, 2006; McArthur et al., 2001; Pal et al., 2002a; Ravenscroft et al., 2005; Van Geen et al., 2003), although field chemistry parameters were only collected for profiler points.

Conclusion

In the 2004 joint field investigations conducted by the GSI, GSC and UBC, naturally occurring arsenic in the village and region surrounding Gotra, Nadia District, West Bengal, India was studied by collecting and analyzing two 40 m sediment cores, two vertical profiles of groundwater and water samples from 48 domestic and irrigation wells. The groundwater geochemistry showed highly variable arsenic values between sample locations, although there was no clear distinction in major – element chemistry between high-dissolved-arsenic and low-dissolved-arsenic zones. The sediment cores showed arsenic values between 1 ppm As in sandy zones up to 20 ppm As in finer-grained material. Sediment arsenic peaks did not coincide with dissolved-arsenic peaks although the highest dissolved and sediment arsenic was observed near the surface. High dissolved arsenic was correlated with high alkalinity, ammonia but was weakly correlated with dissolved iron and inversely correlated with dissolved sulfur. The sediment geochemistry showed that solid-phase arsenic was strongly correlated with solid-phase iron, manganese and the metals copper, nickel, chromium and to a slightly lesser extent zinc. The correlation was stronger in the low-dissolved-arsenic zone than in the high-dissolved-arsenic zone. There was a poor correlation between solid-phase arsenic and sulfur, although any correlation could have been masked by the high solid-phase sulfur detection limits. The solid-phase data suggest that arsenic is associated with oxide minerals, and thus a reductive or desorption process may be responsible for arsenic release, although there is also evidence that arsenic may be sequestered as sulfides in some zones.

Future directions

The 2004 preliminary field investigations conducted jointly by the GSI, the GSC and UBC have confirmed the suitability of the Gotra site for project objectives. They have allowed the parties to test and refine groundwater and sediment sampling methodologies while generating useful initial data. Based on the 2004 experience and the results obtained, the following recommendations are proposed for future follow-up field work conducted by the parties under the MOU between NRCan and the MoM of India:

Future efforts should focus on Gotra and build upon the understanding developed through the 2004 preliminary investigation and earlier work conducted by the GSI. The Gotra site has many advantages: there are both low and high dissolved As zones in a small geographic area, there is excellent pre-existing well control from village wells, and the two cores provide detailed sediment and stratigraphic observations. Future efforts should focus upon understanding groundwater flow directions, rates and water balance, as well as near-surface processes and the quantification of recharge processes. Ideally, water and sediment geochemistry should be traced along flow paths to track the evolution of water and sediments. Indeed, a fundamental line of inquiry is to follow a water flow path from rain or low-arsenic surface water, into the subsurface as it picks up its dissolved load. This suggests a phase approach where the hydrogeology is first constrained and then used to guide locations for detailed geochemical investigation. Of course, in a low gradient environment, geochemical data may itself be the best constrain on flow paths.

Hydrogeology

Groundwater flow and recharge are not well understood at the Gotra site, or at any other site in the Bengal Basin. Hydraulic heads were not measured in 2004 because domestic and irrigation wells were closed off by either hand pumps or distribution manifolds and no project-dedicated wells were installed. Quantifying groundwater hydrology using passive hydraulic head data will be very challenging given the low gradients, the complex stratigraphy and the interferences of multiple irrigation wells (Harvey et al., 2006).

Given sufficient spatial and temporal observations, pumping tests will likely be able to elucidate hydrologic connections below the water table. Existing irrigation wells could be used for pumping wells, although domestic wells are impractical from groundwater head monitoring and dedicated observation wells would be required. It is likely that most irrigation wells are completed in the same horizon, which will constrain the inferences that can be made.

It is much more difficult to constrain recharge, given that it is spatially and temporally variable. Recharge should be hydrologically distinct between unconfined zones with permeable sediments to surface and confined zones or unconfined zones with relatively impermeable sediments above. When relatively high permeability sediments connect the water table to the surface then relatively fast recharge is possible, for example during the onset of the monsoon. If the relatively high permeability zone is localized, then local mounding of groundwater

may be observed. Accordingly, water level monitoring may be useful, particularly given the dynamic nature of recharge through high-permeable pathways. Where clay is near the surface, probably the most common situation in the Bengal Basin, then recharge will be vertically downwards and spatially distributed. No local mounding of the water table would be observed and hydraulic head monitoring will be less useful.

Geochemistry

Relatively little is known about the processes and geochemistry in the unsaturated zone above the water table and below the surface clays. MIT is currently studying the surface clay and rice paddy hydrology at their site in Munshiganj. There, the water table is very close to surface and the site floods to several meters depth annually. Questions that arise include: i) what is the geochemistry of water and solids in the unsaturated zone, particularly those of iron, sulfur, organic carbon and arsenic? ii) how does the geochemistry of this zone change in response to water-table rise during the monsoon? iii) what is the rate at which water leaks to the aquifer from the overlying clay? At Gotra, the geochemical questions could be addressed by collecting unsaturated soil-zone water samples using soil-water solution profilers and sediment samples by coring. It is more challenging to determine leakage rates, since hydraulic heads are not informative under gravity drainage and the soils hydraulic conductivity varies with water content. Natural or introduced tracer studies are potentially useful, although such a study would present considerable logistical challenges.

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