Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Applied Geochemistry 19 (2004) 201–214
Applied Geochemistry
www.elsevier.com/locate/apgeochem

Redox control of arsenic mobilization in Bangladesh groundwater

Y. Zheng[a,b,*], M. Stute[b,c], A. van Geen[b], I. Gavrieli[b,d], R. Dhar[a], H.J. Simpson[b,e], P. Schlosser[b,e,f], K.M. Ahmed[g]

[a]*Queens College, City University of New York, Flushing, NY 11367, USA*
[b]*Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964, USA*
[c]*Barnard College, New York, NY 10027, USA*
[d]*Geological Survey of Israel, Jerusalem 95501, Israel*
[e]*Department of Earth and Environmental Science, Columbia University, New York, NY 10027, USA*
[f]*Department of Earth and Environmental Engineering, Columbia University, New York, NY 10027, USA*
[g]*Department of Geology, University of Dhaka, Dhaka 1000, Bangladesh*

Abstract

Detailed hydrochemical measurements, $\delta^{34}S_{SO4}$ and ^3H analyses were performed on 37 groundwater samples collected during February 1999, January and March 2000 from 6 locations in eastern and southeastern Bangladesh to examine redox processes that lead to As mobilization in groundwater. The study sites were chosen based on available nation-wide As surveys to span the entire spectrum of As concentrations in Bangladesh groundwater, and to represent 3 of 5 major geological units of the Ganges-Brahmaputra Delta: uplifted Pleistocene terrace, fluvial flood plain and delta plain. Arsenic was found to be mobilized under Fe-reducing conditions in shallow aquifers (<35 m depth), presumably of Holocene age. It remained mobile under SO_4-reducing conditions, suggesting that authigenic sulfide precipitation does not constitute a significant sink for As in these groundwaters. The redox state of the water was characterized by a variety of parameters including dissolved O_2, NO_3^-, Mn^{2+}, Fe^{2+} concentrations, and SO_4^{2-}/Cl^- ratios. High dissolved [As] (> 50 μg/l; or > 0.7 μM) were always accompanied by high dissolved [HCO_3^-] (> 4 mM), and were close to saturation with respect to calcite. Groundwater enriched in As (200–800 μg/l; or 2.7–10.7 μM) and phosphate (30–100 μM) but relatively low in dissolved Fe (5–40 μM) probably resulted from re-oxidation of reducing, As and Fe enriched water. This history was deduced from isotopic signatures of $\delta^{34}S_{SO4}$ and ^3H_2O (^3H) to delineate the nature of redox changes for some of the reducing groundwaters. In contrast, As is not mobilized in presumed Pleistocene aquifers, both shallow (30–60 m) and deep (150–270 m), because conditions were not reducing enough due to lack of sufficient O_2 demand.

1. Introduction

Arsenic is a highly toxic and ubiquitous metalloid (Cullen and Reimer, 1989), and realization is growing that water-borne As now poses a significant threat to human and ecosystem health worldwide (Nriagu, 1994). The recent decision by the US Environmental Protection Agency that the Maximum Contamination Level (MCL) for As in drinking water will be lowered from 50 μg/l (0.7 μM) to 10 μg/l (0.1 μM) reflects re-evaluation of health risks associated with ingestion of this metalloid (NRC, 1999). Because of this threat, it is critically important to understand the factors controlling As

* Corresponding author. Tel.: +1-718-997-3329; fax: +1-718-997-3299.
E-mail address: yan_zheng@qc.edu (Y. Zheng).

0883-2927/$ - see front matter
doi:10.1016/j.apgeochem.2003.09.007

mobilization, both to assess risks posed by As-enriched natural waters and to design more effective remediation.

A striking and tragic example of the threat that As can pose is provided in the Ganges Brahmaputra Delta (GBD) region of Bangladesh (Dhar et al., 1997) and West Bengal, India (Chakraborty and Saha, 1987; Bagla and Kaiser, 1996). In the past 30 years, millions of tube wells have been drilled to provide reliable, mostly pathogen-free domestic water to villagers. Groundwater has also been used extensively for irrigation (Ravenscroft et al., 2002), greatly increasing agricultural productivity in the region. Unfortunately, the groundwater is often laden with As of natural origin, and chronic As poisoning is now widespread in the local population (Smith et al., 2000). Arsenic concentrations above 50 μg/l (0.7 μM), the current MCL in Bangladesh, are found in over 30% of the wells (Fig. 1), placing an estimated 20–50 million people (BGS and DPHE, 2001) at risk of developing cancer and other serious diseases (Chen and Lin, 1994; Chen et al., 1997). About 50% of the wells tested so far exceed the World Health Organization (WHO) MCL of 10 μg/l (0.1 μM; BGS and DPHE, 2001).

A detailed analysis by the British Geological Survey (BGS) has shown that water from shallow aquifers with recent alluvial sediments carries distinctly higher (As) than does water from deeper aquifers with presumed pre-Holocene sediments: only 1% of wells in the depth range of 150–200 m have aqueous As above 50 μg/l (0.7 μM; BGS, 1998). The BGS study reveals relationships between the occurrence of aqueous As, the geology, geomorphology and hydrogeology of the area, as well as land and water use. Together, these observations demonstrate that As concentrations in groundwater are controlled by a complex set of conditions and processes.

Of several proximate sources proposed for elevated As in GBD groundwater, two that appear most plausible are: (1) As-rich materials that occur in discrete layers, as suggested by As-rich pyrite particles found in aquifer sediments (Chatterjee et al., 1995); and (2) dispersed As associated primarily with Fe oxyhydroxides (Bhattacharya et al., 1997; Nickson et al., 1998). The first is known as the ‘‘oxidation hypothesis’’, whereby As-rich Fe-sulfide may be dissolved through oxidation driven partly by increased groundwater withdrawal. The second is known as the ‘‘reduction hypothesis’’, whereby the reduction of As-rich Fe-oxides results from increased O_2 demand possibly related to human disturbances, or buried peat (McArthur et al., 2001) and other organic deposits. The solid phase As is generally believed to be of natural origin. Because dissolved As, Fe, and HCO_3 are positively correlated in some groundwaters, and because organic C is abundant in GBD sediments, reduction of Fe oxyhydroxides and release of As may be coupled with organic C oxidation (Nickson et al., 2000). Although the correlation of aqueous As and Fe in some wells is an important consideration, elevated As levels could possibly be the result of additional source materials and release mechanisms as well (McArthur et al., 2001).

In this study, the authors report a number of observations that extend examination of As mobilization processes beyond the broad categories of ‘‘oxidation’’ and ‘‘reduction’’ hypotheses. By analyzing a suite of constituents in samples covering a wide range of groundwater conditions at 6 locations (Fig. 1), it is confirmed that redox processes, particularly reduction of Fe-oxyhydroxides, play a key role in the release of As to groundwater. To the authors' knowledge, this study is the first to measure $\delta^{34}S_{SO4}$ in GBD groundwater. Tritium concentration data are also presented. It is demonstrated that hydrological factors and the nature of the GBD sediments are closely linked to the dynamic redox processes of groundwater that control As mobilization, and warrant further investigation.

2. Materials and methods

2.1. Study sites

The study sites located in eastern Bangladesh, were chosen based on a nation-wide As survey to span the entire spectrum of observed As groundwater concentrations (Fig. 1), hence presumably a wide range of redox conditions. The Sripur and Dhaka sites are located within the uplifted Pleistocene Madhupur tract (Morgan and McIntire, 1959). The Araihazar and Sonargaon sites are located on the margin of the Holocene Mehgna fluvial floodplain where the transition occurs from the Madhupur tract to much younger, incised Meghna river channel deposits from west to east, resulting in a thicker sequence of Holocene deposits to the east of the study area. The Ramganj and Senbag sites are on the Holocene GBD delta plain (BGS and DPHE, 2001). Although the total number of samples is relatively small, they represent major geologic units found in large areas of Bangladesh, with the exception of the Sylhet Basin and the Mountain Front Fan Delta in the northern part of the country.

Much of the aquifer system in the GBD has not been stratigraphically classified in detail, but basin-wide stratigraphic reconstructions suggest that the uppermost 30–100 m thick strata mostly consists of a coarse to fine sandy deposit underlying a fine-grained silty or clayey surface floodplain deposit. This sequence has accumulated within the last 11 ka (Umitsu, 1993; Goodbred and Kuehl, 2000), with rapid transgression advancing the delta seaward during the mid-Holocene climatic optimum period (Goodbred et al., 2003). In addition to sea level changes, other factors influenced the thicknesses of the Holocene strata: (1) tectonic activities favoring fine-grained sediment deposition; and (2) high-energy

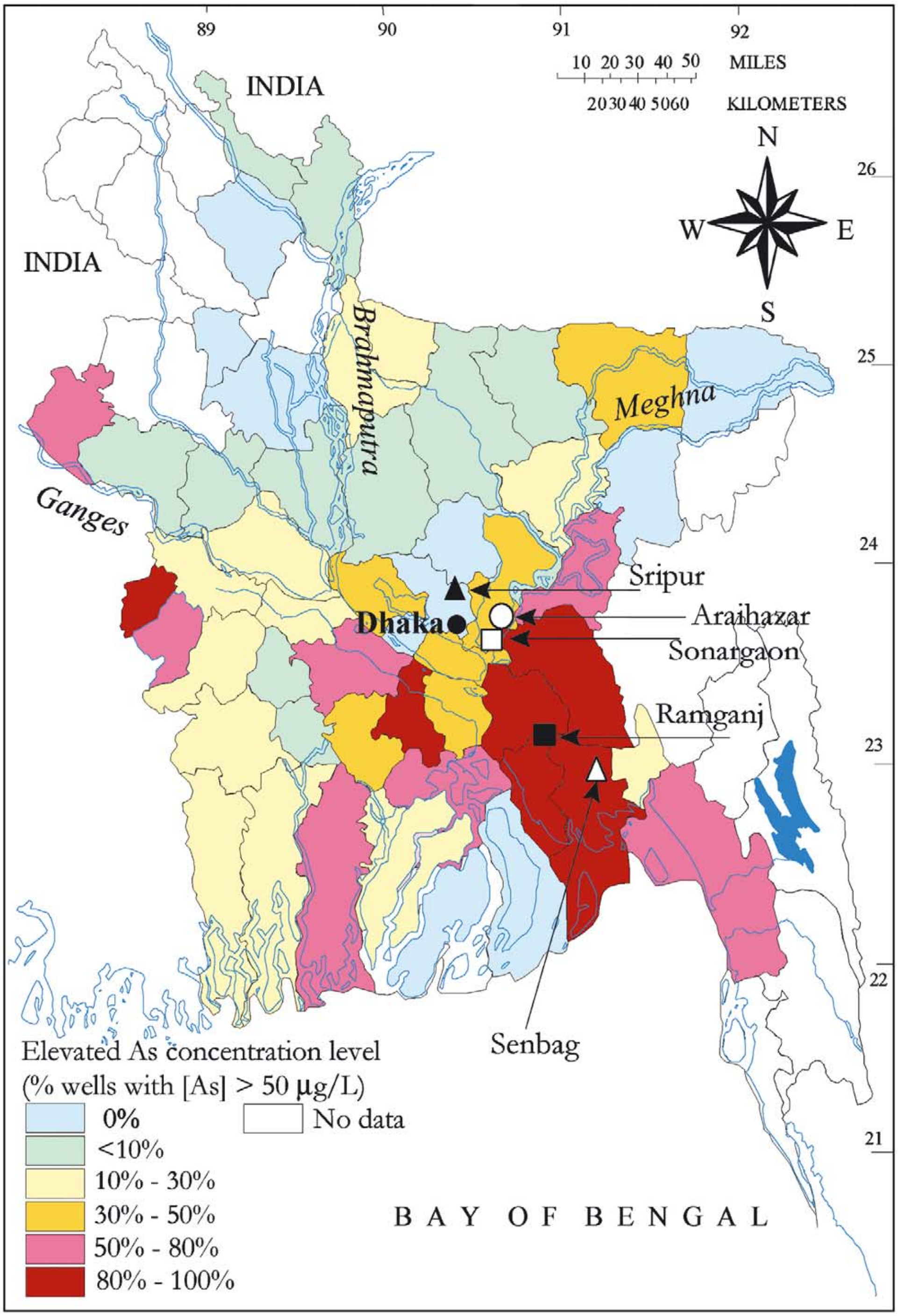

Fig. 1. Locations of 6 sampling sites representing a range of As concentrations in groundwater. The Sripur and Dhaka sites are located within the uplifted Pleistocene Madhupur tract (Morgan and McIntire, 1959). The Araihazar and Sonargaon sites are located on part of the Holocene Mehgna fluvial floodplain, where the transition from the Madhupur tract to incised Meghna river channel deposits from west to east occurs. The Ramganj and Senbag sites are on the Holocene GBD delta plain (BGS and DPHE, 2001). Color-coding reflects As levels in Bangladesh well waters based on a survey of ~6000 samples in 60 districts (Chakraborti et al., 1999). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

fluvial events favoring coarse-grained deposits, led to variable thickness of Holocene strata in the GBD (Goodbred and Kuehl, 2000). These basin-scale stratigraphic reconstructions suggest that shallow groundwater samples from Araihazar (<32 m), Sonargaon (<23 m), Ramganj (9 m) and Senbag (<35 m) are from the Holocene strata. Deep groundwater samples from Araihazar (152 m) and Ramganj (274 m) are most likely from Pleistocene, or perhaps even Pliocene strata. It is difficult to determine the age of strata from Sonargaon (91 m) from which two samples were obtained.

2.2. Sampling and field analysis protocols

Thirty-seven groundwater samples were collected from existing tube wells (locations determined with a GARMIN handheld GPS unit, depths obtained through interviews because it is time-consuming to remove the hand-pump) in Sripur ($n=2$), Dhaka ($n=3$), Araihazar ($n=17$), Sonargaon ($n=9$), Ramganj ($n=2$) and Senbag ($n=4$) upazilas. Groundwater was siphoned during steady pumping from the hand-pump head, after blocking the flow at the tube well outlet to minimize dissolved gas loss. After pumping continuously for 15–30 min until the temperature, conductivity, pH and oxidation/reduction potential (ORP) reading had stabilized, the following steps were performed:

1. Dissolved O_2 was measured with a CHEMet kit (Cole-Parmer).
2. Alkalinity was obtained by Gran titration (Gran, 1952) using ~120–180 ml of sample.
3. Inorganic As speciation was obtained following an anion exchange method (Ficklin, 1983) using ~120 ml of groundwater filtered with a 0.45 μm membrane syringe filter (Gelman Acrodisc).
4. Dissolved Fe(II) was determined by a ferrozine method (Stookey, 1970).
5. Hydrochemical samples: a set of 4 samples were collected in 60 ml HDPE bottles, that were (1) filtered and acidified (to 1% HCl with Fisher Optima), (2) filtered but not-acidified, (3) not-filtered and acidified, and (4) not-filtered and not-acidified. Dissolved ions including Ca^{2+}, Mg^{2+}, Na^+, K^+, SiO_2, As, Fe, Mn, PO_4^{3-} and SO_4^{2-} were measured on the acidified samples. Dissolved NO_3^- and Cl^- were measured on the not-acidified samples. Initially, both filtered and not filtered samples were measured, but little difference was found between the filtered and not filtered samples for all ions except for Fe and PO_4^{3-}. Filtration often resulted in rapid ferrihydrite precipitation that removed PO_4^{3-} but not As; hence the not-filtered sample results are reported for Fe and PO_4^{3-}, and filtered sample results for other ions including As.
6. For $\delta^{34}S_{SO4}$ analysis, up to 4 l of groundwater samples were collected in HDPE bottles and acidified to 1% HCl (Fisher Optima). Sample containers were then vigorously shaken, and in most cases purged with N_2 gas to eliminate any dissolved sulfide.
7. Samples for ^3H analysis were collected in 250 ml glass bottles or ~1 cm O.D., 50 cm long Cu tubes with stainless steel pinch-off clamps (Weiss, 1968).

2.3. Laboratory analytical methods

Conventional methods were applied for dissolved ion concentrations. Arsenic was determined by graphite furnace atomic absorption spectrometry, with a subset of samples also analyzed by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICP-MS). Dissolved Fe was determined by flame atomic absorption spectrometry, and dissolved Mn by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Dissolved Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} were determined by ion chromatography. Dissolved Ca^{2+}, Mg^{2+}, K^+, Na^+ were measured by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Dissolved SiO_2 was determined by colorimetry and ICP-AES. Standard calibrations were based on standard addition for all dissolved ions analyzed. A NIST Standard Reference Material 1640 (Trace Elements in Natural Water) were analyzed and results were found within 5–10% of the certified values for As, Fe, Mn and other dissolved ions. The measurement precision differed for different methods, but usually was within 5–10% based on repeated analysis of several internal laboratory standards, including an Evian water internal standard spiked with trace elements, and several Bangladesh groundwater samples.

A conventional method of isotope ratio gas mass spectrometry was employed for $\delta^{34}S_{SO4}$ analyses on samples containing >2 mg/l SO_4, after precipitating the SO_4 as $BaSO_4$ and converting it to SO_2 on a S vacuum line (Coleman and Moore, 1978). The reproducibility on a frequently run internal laboratory standard is ±0.2‰, similar to the precision of the analyses as determined on NBS-127. Samples with low SO_4 content (<2 mg/l) were analyzed by thermal ionization mass spectrometry (TIMS). The TIMS procedure is based on the method of Paulsen and Kelly (1984) as modified by Gavrieli for groundwater that allows analysis of less than 100 μg of SO_4. Measured ratios were corrected for mass fractionation based on comparison with the NBS-127 standard, which was loaded on filaments and run under the same conditions. The external reproducibility based on the NBS-127 standard (2σ; $n=7$) is better than 0.7‰.

The ^3H analysis was performed on either $\sim$40 cm^3 of water collected in glass bottles or on $\sim$16 cm^3 of water collected in Cu tubes using the ^3He in-growth technique (Bayer et al., 1989; Ludin et al., 1998). The precision of the ^3H data is about $\pm$2–3%.

3. Results and discussion

3.1. Chemical composition of GBD groundwater

The total dissolved ion concentrations based on electrical conductivity (EC) varied by a factor of 35, ranging from a minimum EC value of 60 μS/cm in Sripur to a maximum EC value of 2070 μS/cm in Senbag (Fig. 2). This large range of total dissolved ions primarily reflects the variations of Cl^- (0.03–10.7 mM) and HCO_3^- ($\sim$0.5–11 mM) concentrations, with a very strong linear correlation (not shown; $R^2 = 0.97$) between conductivity and $[HCO_3^-]+[Cl^-]$. But $[HCO_3^-]$ are, on average, about 10 times greater than $[Cl^-]$ in samples with EC values of $<$1000 μS/cm, suggesting that the increase of $[HCO_3^-]$ contributes more to the EC increases (up to 1000 μS/cm) than does the increase of $[Cl^-]$. Waters with low dissolved $[HCO_3^-]$ were also found to be under-saturated with respect to calcite (Fig. 3a). These samples frequently contained dissolved O_2 (Fig. 3b, samples with non-detectable dissolved O_2 concentrations were plotted with assigned values of 0.01 mg/l, the detection limit of the CHEMet oxygen kit). Samples from Senbag, which display the highest $[HCO_3^-]$ but also show detectable amounts of O_2, will be discussed later (Section 3.2).

Concentrations of dissolved HCO_3^- reflect the degree of water–rock interaction in groundwater systems as well as integrated microbial degradation of organic matter. Groundwater alkalinity, or HCO_3^-, originates from weathering of silicate and calcite minerals by atmospheric or respired CO_2 that leads to secondary mineral formation (Garrels, 1967). With the exception of one sample at 91 m from Sonargaon, samples with high dissolved $[HCO_3^-]$ ($>$ 4 mM) are O_2 free, suggesting that the source of dissolved inorganic C includes a component of respired CO_2 derived from the oxidation of organic matter either during infiltration through soil or along the flow path of the water. The rather negative $\delta^{13}C$ values in other GBD groundwater samples reported by McArthur et al. (2001) support this concept. Respired CO_2 from oxic and anoxic organic matter degradation then reacted with primary silicate minerals or calcite to release Ca^{2+}, Mg^{2+}, Na^+ and K^+ to the water (data not shown).

Most of the samples from shallow depths ($<$35 m) are characterized by high $[HCO_3^-]$, close to saturation with respect to calcite, and low in dissolved O_2 (Fig. 3). They frequently contain detectable amounts of ^3H (Fig. 4). Tritium concentrations are mostly $<$20 TU (Fig. 4) as expected from reconstructions of ^3H concentrations in precipitation in Bangladesh (Stute, 2001), with the exception of one sample with a value of 462 TU, which was probably due to contamination. Tritium is an anthropogenic tracer primarily released to the atmosphere by atmospheric bomb tests that began in the early 1950′s and peaked around 1963 (IAEA, 1992). Tritium becomes part of the water molecule and when detected in groundwater generally indicates recharge during the past 40 a. Together, these characteristics suggest that O_2 demand and consumption in shallow groundwaters ($<$35 m) is high despite a residence time of less than 40 a.

In contrast, several deep ground water wells in Araihazar (152 m), Dhaka (168 m) and Dhaka (274 m) are not as chemically evolved, with less than 4 mM dissolved $[HCO_3^-]$ (Fig. 3), despite isolation of these samples from the atmosphere for longer periods of time, as indicated by not-detectable ^3H concentrations (Fig. 4). These deep waters contain readily detectable amounts of dissolved O_2 (Fig. 3), suggesting that O_2 demand, or the labile organic matter content is low along the flow path from recharge. Samples from Dhaka (76 m, 146 m) and Sripur (32 m, 67 m) containing detectable amounts of ^3H (Fig. 4) and high dissolved O_2 concentrations ($>$ 1 mg/L), can also be explained by low O_2 demand and consumption during infiltration and transport, which presumably does not generate enough respired CO_2 to yield chemically mature water in the relative short time since the water has been recharged. It is also noted that two samples collected at 91 m in Sonargaon have distinctly higher dissolved $[HCO_3^-]$ than waters from a comparable depth range (76–274 m) in other locations. At present the authors do not have an explanation for this difference, except to note that the age of the strata of these samples is not well constrained and that these two samples also have distinctly higher Na^+/Ca^{2+} ratios, which may imply marine influence as discussed below.

Elevated $[Cl^-]$ and higher proportions of Na^+ relative to other cations (Ca^{2+}, Mg^{2+}, K^+) in groundwater suggest that these samples are influenced by a source of Na^+ and Cl^-. The highest Cl^- concentration ($\sim$10 mM) observed in Senbag is $\sim$270 times higher than the average $[Cl^-]$ of the Brahmaputra and Meghna Rivers (0.04$\pm$0.02 mM; Sarin et al., 1989; Galy and France-Lanord, 1999). It is unlikely that evapotranspiration can increase recharge water $[Cl^-]$ to $>$ 1 mM because extensive evaporation in Bils on Barind tracts (an uplifted Pleistocene terrace in northeastern Bangladesh) elevates Bil water $[Cl^-]$ to $\sim$0.7 mM (Ahmed and Burgess, 1995). Bils are saucer-shaped depressions that are perennially flooded, with some becoming completely dessicated towards the end of the dry season. Furthermore, $\delta^{18}O$ and ^2H variations of groundwater in the region were shown to closely follow that of the meteoric water line, suggesting recharge during the wet season without

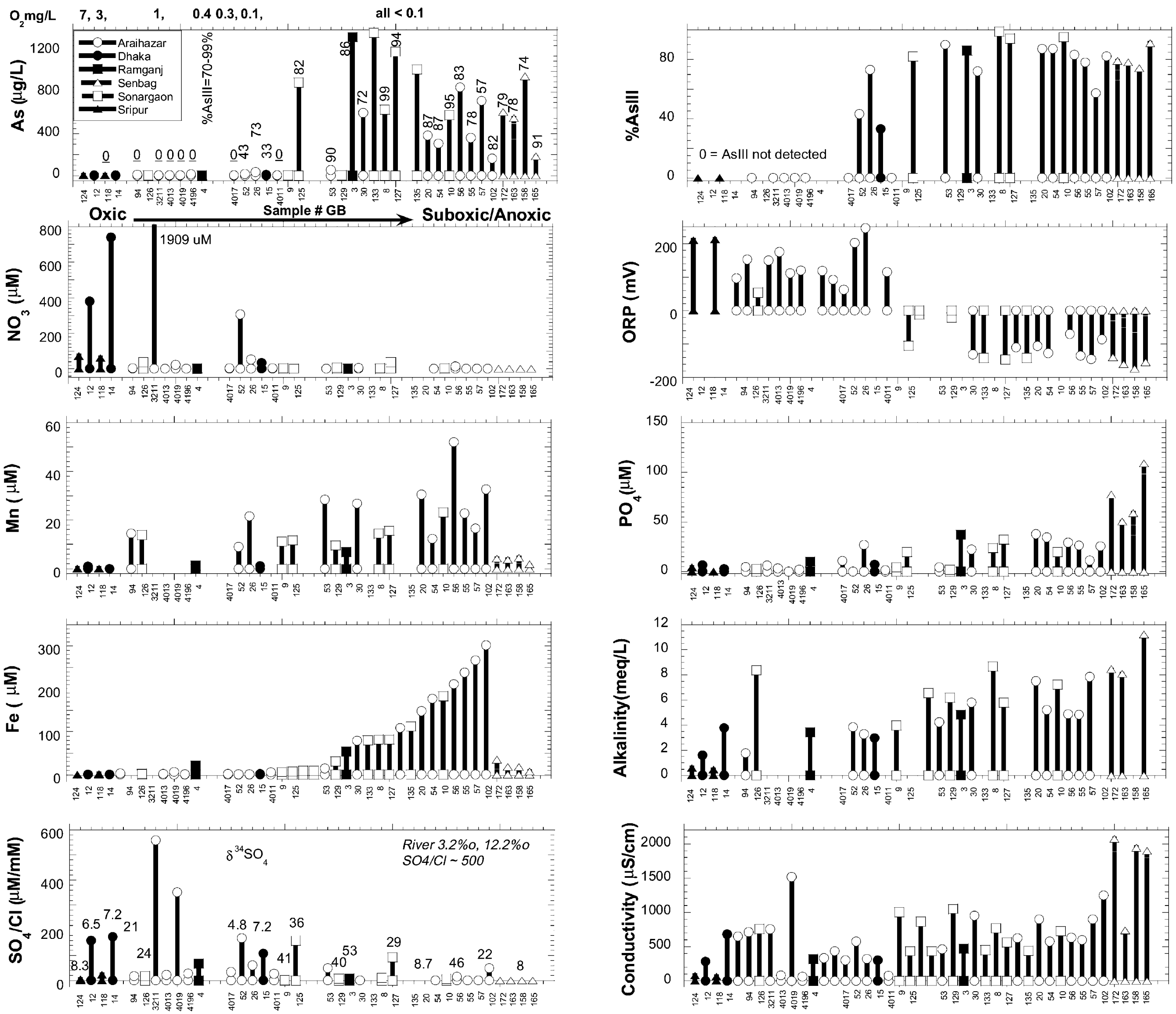

Fig. 2. Redox chemistry of groundwater samples collected in 6 locations (Fig. 1) spanning a wide range of redox conditions existing in the GBD. Samples were ordered in a sequence of decreasing O_2, and for $O_2 < 0.1$ mg/l, increasing dissolved Fe, except for samples from Senbag (triangles). Senbag samples were assessed as the most reducing based on the presence of CH_4 and were ranked by decreasing Fe concentrations. The same symbols for each site were used for Figs. 3–5.

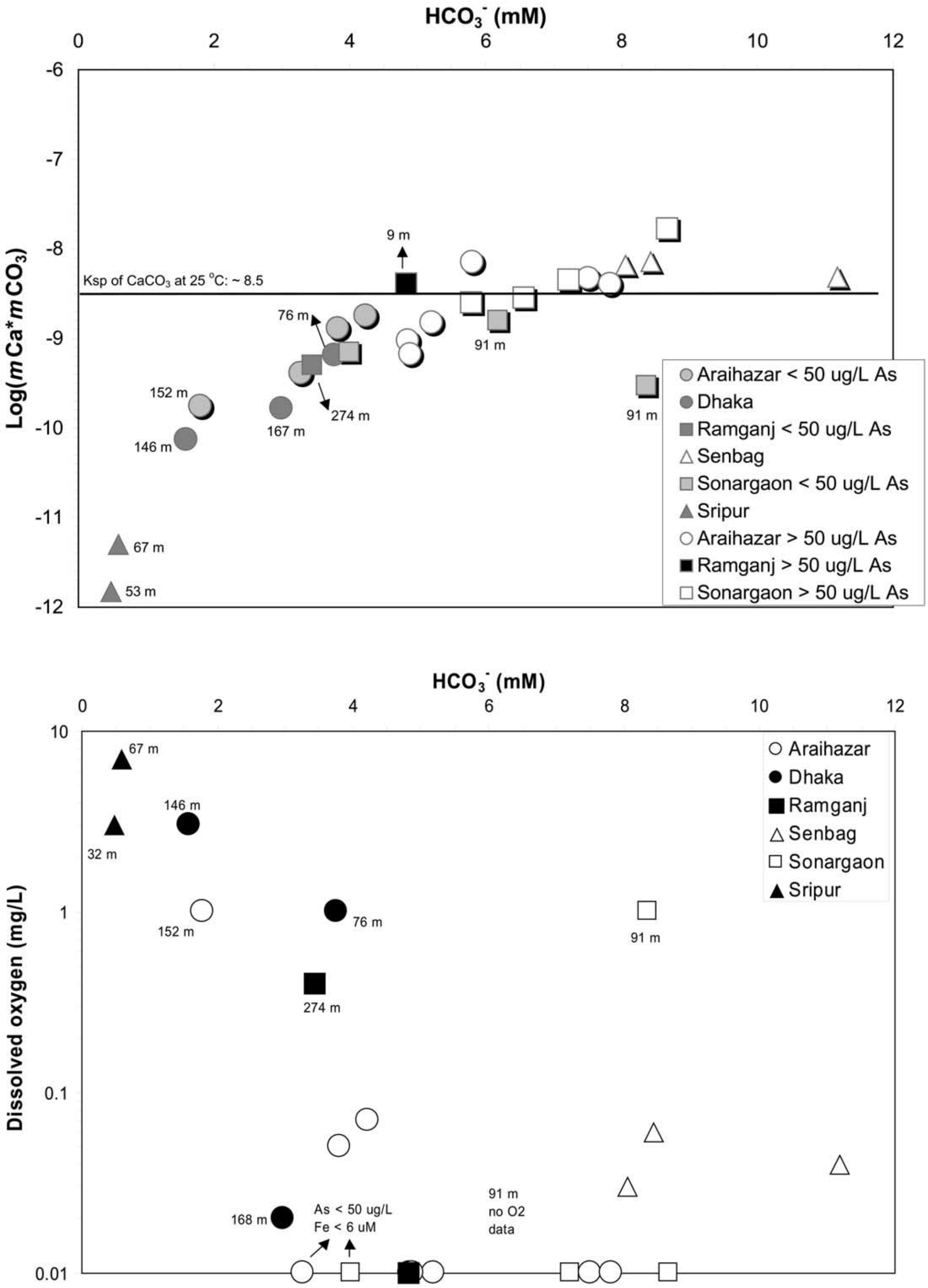

Fig. 3. Plot of log ($m\text{Ca}^{2+}m\text{CO}_3^{2-}$) (upper panel) and dissolved O_2 (lower panel) versus dissolved [HCO_3^-]. In the upper panel, samples with <50 μg/l As are shown in gray, and samples with > 50 μg/l are shown with open symbols except for Ramganj (black). The horizontal line indicates the temperature dependent Log(Ksp) of calcite (~8.5 at 25 °C). The temperature range of groundwater samples in the GBD is 24.3–28.2 °C, and thus does not change the Log(Ksp) of calcite significantly, i.e, 8.48–8.50.

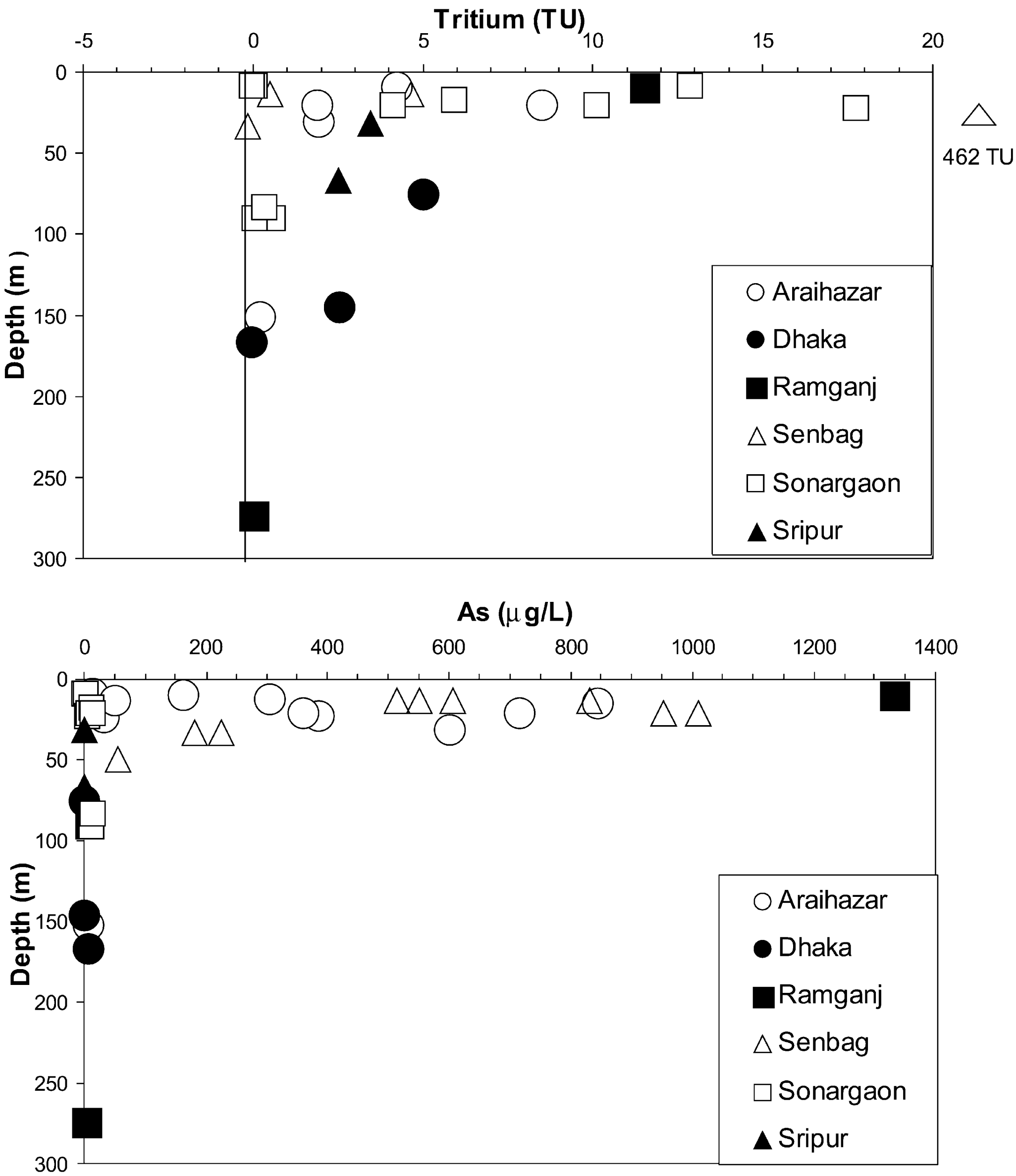

Fig. 4. Depth profiles of ^{3}H and [As] of groundwaters collected in 1999 and 2000. Expected bomb-^{3}H concentrations in GBD groundwater range from 0 to 25 TU (Stute, 2001). One extremely high ^{3}H concentration of 462 TU probably was due to a local contamination source.

much evaporation (Ahmed and Burgess, 1995). Thus, this groundwater must gain some of its Cl^- from water–rock interaction, and possibly from NaCl if excess Na^+ is also found relative to other cations.

Water–rock interaction, weathering of either silicate or calcite minerals, generates groundwater that is more enriched in Ca^{2+} and Mg^{2+} relative to Na^+ (Garrels, 1967). Samples from Senbag, and two 91 m samples from Sonargaon show Na^+/Ca^{2+} molar ratios that are distinctly higher than that of the trend expected from silicate mineral weathering, which ranges from 1 to 10 and decreases with increasing HCO_3^-/SiO_2 ratio (Garrels, 1967). The samples with Na^+/Ca^{2+} molar ratios of >10 also display $Na^+/(Na^+ + 2Ca^{2+} + 2Mg^{2+} + K^+)$ molar ratios greater than 0.4 (not shown), as well as high Cl^- concentrations ($>$ 1 mM, Fig. 5). Since these samples are from relatively shallow depths (14 and 34 m), it is possible that seawater intrusion, sea salt aerosol deposition, or remnant seawater could have caused the elevated Na^+ and Cl^- concentrations.

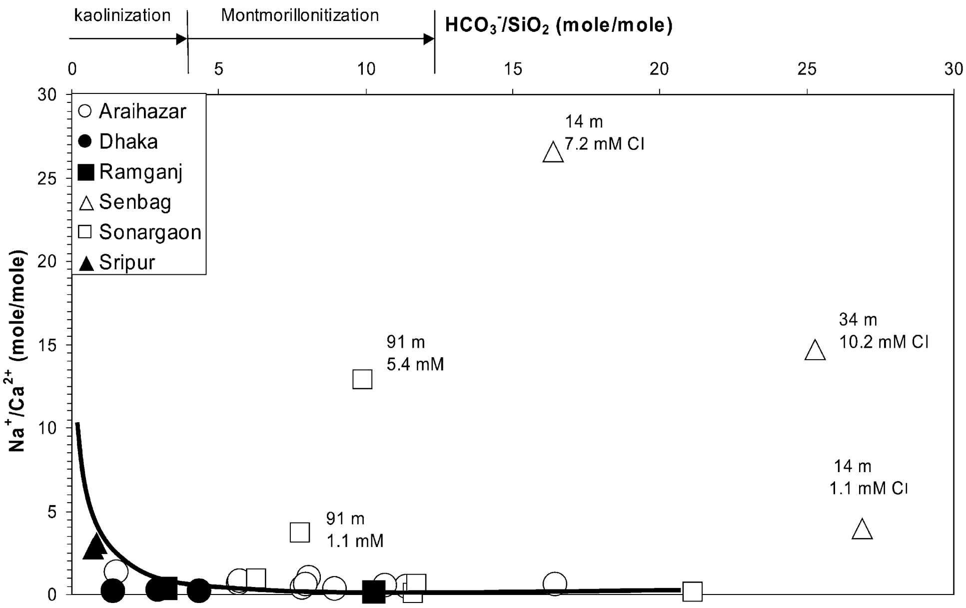

Fig. 5. Molar ratio of Na^+ to Ca^{2+} plotted versus molar ratio of HCO_3^- to SiO_2. Most samples follow the trend expected from general water-rock interaction (indicated by the thick line) with decreasing Na^+/Ca^{2+} ratios with increasing HCO_3^-/SiO_2 ratios (Garrels, 1967), except for those with distinctly high Na^+/Ca^{2+} ratios, probably having inputs of marine salts.

3.2. Conditions under which As is mobilized

Arsenic in natural waters occurs primarily as the inorganic oxyanions of As(V), or arsenate, and As(III), or arsenite, although metallic and methylated forms are also known (Cullen and Reimer, 1989). Aqueous As is controlled primarily by sorption and precipitation: adsorption of As(V) onto Fe oxyhydroxides appears to control both As mobility in lake sediments (Takamatsu et al., 1985; Edenborn et al., 1986; Aggett and Kriegman, 1988; Belzile and Tessier, 1990) and diel cycles of dissolved As in stream water (Fuller and Davis, 1989). The extent of adsorption is strongly influenced by the As oxidation state and the inorganic and organic solutes present (Wilkie and Hering, 1996; Hering et al., 1997). Under sufficiently reducing conditions, however, precipitation of As sulfides such as arsenopyrite can control aqueous As levels (Moore et al., 1988; Vink, 1996). In light of the above, it is understandable that redox reactions involving As, Fe, and S appear to be essential factors in As fate and transport both in the GBD region and in numerous other As-contaminated environments (Kuhn and Sigg, 1993; Spliethoff et al., 1995).

Redox processes, particularly the reduction of Fe-oxyhydroxides (Nickson et al., 2000; Bhattacharya et al., 2001), play a key role in the release of As to groundwater as shown by a suite of constituents in samples covering a wide range of groundwater chemical conditions at 6 locations (Fig. 1). High aqueous As concentrations are accompanied by reducing conditions, particularly those in which reduced Fe is high as well (Fig. 2). The reasons for water containing high As but little Fe (e.g., GB 125, 158, 165, 163 and 172; Fig. 2) are discussed later in this section. In contrast to previous observations (Nag et al., 1996), samples with high As concentrations were dominated by As(III) (70–100%) and contained <0.1 mg/l dissolved O_2. Samples from Araihazar and Sonargaon were assayed by ferrozine colorimetry, hence the high concentration of dissolved Fe (up to 270 μM) was Fe(II). The data show that the onset of NO_3^- and Mn(IV) reduction, as reflected in their respective decrease and increase (MnII) in concentrations, is insufficient to mobilize As. Samples with high As also displayed elevated PO_4^{3-} concentrations (20–100 μM, Fig. 2), possibly as a result of reduction of Fe-oxyhydroxides onto which both arsenate and phosphate had been adsorbed. Competitive sorption of PO_4^{3-} onto limited Fe-oxyhydroxides surface may also contribute to the release of As under certain conditions and is discussed later in this section.

Arsenic remained mobile under SO_4^{2-}-reducing conditions (Fig. 2) and perhaps into the methanogenesis field. Significant enrichment of $\delta^{34}S_{SO4}$ (up to 53‰) along with elevated As and Fe concentrations in several samples from Araihazar and Sonargaon (Fig. 1) suggest that the very low SO_4^{2-}/Cl^- ratios (mostly <10 μM/mM) result primarily from SO_4^{2-} reduction (Fig. 2) and are not due to recharge of low SO_4^{2-} water. Surface waters show SO_4^{2-}/Cl^- ratios ranging from hundreds to 3000 μM/mM (Sarin et al., 1989; Galy and France-Lanord, 1999). The $\delta^{34}S_{SO4}$ composition derived from monsoonal rains is ~10‰ (Jacks et al., 1994) whereas 2 samples collected from the Meghna River in Araihazar had low SO_4^{2-}/Cl^- ratios (170 μM/mM) with initial $\delta^{34}S_{SO4}$ compositions of ~3 and 12‰. Higher SO_4^{2-}/Cl^- ratios were inferred by Galy and Frace-Lanord (1999) to originate from oxidation of pyrite upstream of the Ganges and Brahmaputra Rivers, consistent with more depleted S isotopic compositions observed for river waters than that of rain water. Some of the oxic groundwater samples had S isotopic compositions ($\delta^{34}S_{SO4}$: 6.5, 7.2, 8.3‰; Fig. 2) similar to those expected for surface waters, indicating that extensive sulfide oxidation or SO_4^{2-} reduction had probably not occurred. Elevated As concentrations found in Senbag (Fig. 1) probably fall into the range of the most reducing conditions once achieved by these waters (Fig. 2) because wells from this region contain combustible gases, presumably reaching the methanogenesis state (Ahmed et al., 1998).

One plausible explanation of why As remained mobile in SO_4^{2-} reducing groundwater is because there was insufficient authigenic sulfide precipitation to remove all the As. This probably resulted from relatively low initial SO_4^{2-} content in the groundwater. Groundwater samples from Araihazar, Sonargaon and Senbag with low SO_4^{2-}/Cl^- ratios and enriched $\delta^{34}S_{SO4}$ all contained dissolved sulfide that was barely detectable by colorimetry (<1–2 μM). Therefore, the GBD aquifer system may represent a situation of limited S availability relative to an abundant supply of Fe. This contrasts wih the situation where trapping of As in reducing sediments in a reservoir on the Clark Fork River could occur where the SO_4 supply was not limited even though Fe was abundant (Moore et al., 1988).

Sulfur isotopes can also help to explain why not all As-rich waters are elevated in dissolved Fe. One valuable aspect of $\delta^{34}S_{SO4}$ is that it reflects the integrated effects of SO_4^{2-} reduction history. The authors envisage a re-oxidation scenario as follows: introduction of small amounts of O_2 to SO_4^{2-}-reducing groundwater with elevated Fe, As concentrations plus enriched $\delta^{34}S_{SO4}$ alters the redox state to mildly reducing, allowing dissolved Fe^{2+} oxidation and perhaps some arsenite oxidation. Re-oxidation could lead to As and PO_4 co-precipitation with or sorption onto newly formed Fe-oxyhydroxide when As and competing anions, most importantly PO_4, are not abundant relative to Fe (Hering et al., 1996). However, when the As and PO_4 to Fe ratio is relatively high such co-precipitation or sorption would not lead to immobilization of most of the As and PO_4 (Meng et al., 2000). The $\delta^{34}S_{SO4}$ signature would remain highly enriched as long as sedimentary sulfide was not oxidized. This interpretation is robust because oxidation of dissolved or sedimentary sulfide would introduce depleted S into the water, resulting in lower $\delta^{34}S_{SO4}$ values.

Re-oxidation followed by incomplete immobilization due to high abundance of dissolved As and PO_4 relative to Fe would explain why GB125 (21 m) contains ~800 μg/l, or ~11 μM of As, and ~30 μM PO_4, yet has only ~10 μM dissolved Fe (Fig. 2). The enriched $\delta^{34}S_{SO4}$ value of 36‰ is consistent with this water having reached reducing conditions capable of mobilizing As and Fe at one time. Additional evidence supporting the re-oxidation scenario is provided by the ^3H concentration in GB125, which, at 17 TU, is the 2nd highest of the entire data set (Fig. 4). Furthermore, this sample is the only one for which the authors observed a significant and gradual decrease from a positive ORP value (+151 mV) to a stable negative ORP value (−105 mV) after ~2 h of pumping at a rate of ~2 l/min, while all the other samples reached stable ORP reading after at most ~10 min of pumping at the same rate. Together, they suggest that water from GB125 has had recent, and perhaps even frequent periodic interaction with the atmosphere.

The re-oxidation scenario described above could also explain some of the characteristics of samples from Senbag (GB172, 163, 158, 165), which contain small amounts of dissolved Fe (5–40 μM), high As (200–700 μg/l; or 2.7–9.3 μM), and high PO_4 (50–110 μM), except that here the balance of evidence is more ambivalent. The SO_4 isotopic composition in Senbag is not enriched ($\delta^{34}S_{SO4}=8$‰). This could be reconciled if re-oxidation also oxidized authigenic sulfide that was depleted in $\delta^{34}S_{SO4}$, which would have shifted the isotopic signature of the water significantly towards less positive values due to very low concentrations of SO_4. Presence of CH_4 and very high dissolved $[HCO_3^-]$ (Fig. 3) are consistent with the notion that these waters were once reducing enough to release As. However, the presence of detectable amounts of dissolved O_2 (0.03–0.06 mg/l, Fig. 3) implies that these once very reducing waters have been slightly re-oxidized. At least in one sample (GB 163) ~5 TU ^3H was detected (Fig. 4); the highest ^3H concentration of 462 TU in GB158 was probably due to contamination in the field or during sample transport, because it exceeds any reasonable environmental ^3H concentration in precipitation for this region (Stute, 2001). Together, most of the evidence is consistent with a re-oxidation scenario.

These new observations allow the authors to postulate that a series of redox changes involving Fe-oxyhydroxide reduction, and subsequent oxidation, could be key controls of As concentrations in some GBD groundwater and explains why As can be enriched in reducing groundwater with elevated Fe concentrations, as well as in groundwater with only small amounts of Fe. Limited As-rich secondary sulfide precipitation also would allow groundwater [As] to remain high despite SO_4 reduction. It is important to note that the possible role of secondary sulfide formation indicated by the water SO_4 S-isotopic data goes beyond consideration of sulfides only as a primary source of As. Instead, these results suggest a coupled Fe–S–As cycle whereby the mobility of As can be influenced by the behavior of both Fe and S in the system.

3.3. Low As in deep groundwater

Although the cause of low [As] in deep groundwaters can qualitatively be attributed to these waters not being sufficiently reducing, this explanation is explored in more detail. The striking chemical differences discussed earlier (Section 3.1) between deep groundwaters (150–300 m) occurring in presumed Pleistocene or older formations and shallow groundwaters (9–35 m) occurring in presumed Holocene formations in Araihazar and Ramganj imply that the Pleistocene groundwater does not become reducing enough to mobilize As due to lack of O_2 demand, primarily liable organic matter. One line of evidence that supports this explanation is that, despite the absence of ^3H (Fig. 4), which indicates recharge more than 40 a ago, these waters remain chemically immature and oxic. Two 91 m groundwater wells in Sonargaon are not included in the discussion because their stratigraphic association cannot be constrained from regional stratigraphic reconstruction (Goodbred and Kuehl, 2000). Additional supporting evidence comes from order of magnitude calculations that address the amount of time that it might take to exhaust all reactive organic matter in a sedimentary aquifer with oxidants (dissolved O_2 and SO_4) supplied through recharge.

It is assumed that the rate-limiting step of organic matter oxidation is the supply of dissolved oxidants to the aquifer, i.e. the rate of organic matter consumption equals the rate of dissolved oxidants supply.

The supply of dissolved oxidant to the aquifer is:

$$C_{ox} \times F$$

Where C_{ox}: dissolved oxidant concentration, mol/l
F: flux of recharged water, l/a

The amount of organic matter that it can oxidize at a given time is:

$$\frac{\alpha \times C_{ox} \times F}{M} = \frac{\alpha \times C_{ox}}{t_{res}}$$

Where α: stoichiometric ratio of oxidants, mole reductant/mole oxidant
M: size of the aquifer, l^3
t_{res}: residence time of aquifer, $t_{res} = M/F$

Thus, the rate of organic matter consumption can be estimated by:

$$\frac{dC_{org}(t)}{dt} = -\frac{\alpha \times C_{ox}}{t_{res}}$$

Where C_{org}: concentrations of organic C, mol/l

Integration over time gives a linear decrease of the amount of C_{org} with time:

$$C_{org}(t) = C_{org}(0) - \frac{\alpha \times C_{ox}}{t_{res}} \times t$$

The dissolved oxidant concentrations include 0.2 mM of dissolved O_2 based on solubility equilibrium, and 0.1 mM of dissolved SO_4, a value representing the average composition of GBD river waters (Sarin et al., 1989; Galy and Frace-Lanord, 1999). Accordingly, with an initial labile organic matter content of 1 or 0.1%, the time it would take to exhaust labile organic matter is 60 or 2 ka if the groundwater residence time was 10 a, and is > 100 or 16 ka if the groundwater residence time was 100 a, respectively. In this calculation, an aquifer porosity of 30%, and particle density of 2 g/cm^3 are assumed. For simplicity, the stoichiometric ratio of oxidants, α, is assumed to be 1 in the case of O_2 reduction, and 2 in the case of SO_4 reduction.

Residence times of groundwaters in aquifers under the uplifted Pleistocene Madhupur terrace (Davis, 1994), such as sites in Sripur and Dhaka, are likely to be approximately 10–100 a based on the observation that groundwater in such systems contained detectable amounts of ^3H (Fig. 4). Whereas the concentration of reactive organic matter in such systems is not known, the assumption that the system has a homogeneously distributed concentration of 1% labile organic C is probably a reasonable upper limit case. Such a calculation illustrates that one prerequisite for low As concentrations in the Pleistocene or Pliocene aquifers is that these sediments probably need to have been previously high-standing relative to sea level for a considerable period of time to allow oxidation from relatively rapid flushing of oxygenated groundwaters through the system, i.e., water residence time <100 a. Such conditions clearly existed during the Pleistocene when sea levels were much lower than that of the present. Hydrological factors, such as recharge, infiltration and flow rates of aquifers, and the nature of the GBD sediments warrant more investigation to examine controls on redox conditions of groundwater on different time scales, and to investigate whether low [As] deep aquifers are likely to be a sustainable source of domestic water supply.

4. Conclusions

After characterizing redox states of groundwaters by a variety of parameters including dissolved O_2, NO_3^-, Mn^{2+}, Fe^{2+} concentrations, and SO_4^{2-}/Cl^- ratios, it is concluded that As in shallow groundwater (<35 m) from eastern Bangladesh was primarily mobilized under Fe-reducing conditions and remained mobile under SO_4-reducing conditions. The generally high Fe content of the aquifer system should lead to Fe-sulfide precipitation, resulting in sulfide concentrations of less than 1–2 μM even in the most reducing groundwater samples. Even if secondary sulfide constituted a sink for As, the relatively small amounts of sulfide generated from bacterial SO_4 reduction, which is limited by the initial low SO_4 content of the groundwater, could not immobilize much of the As. Most of the As in reducing groundwater was in the reduced form As(III).

Isotopic signatures of $\delta^{34}SO_4$ and ^3H_2O (^3H) can be used to delineate some aspects of the dynamic nature of redox processes in the aquifer. Groundwater samples enriched in As (200–800 μg/l; or 2.7–10.7 μM) and PO_4 (30–100 μM) but with relatively low dissolved Fe (5–40 μM), can be explained by a re-oxidation scenario. These waters were once reducing enough to mobilize As, as evidenced by enriched $\delta^{34}SO_4$ values (up to 40‰). Small amounts of O_2 (0.03–0.06 mg/l) and high concentrations of ^3H in some samples suggest that they have been in recent contact with the atmosphere.

Striking chemical differences exist between groundwater from the shallow (<35 m), presumed Holocene aquifer and from the deep (150–300 m), presumed Pleistocene aquifer. Deep waters containing low dissolved As (<50 μg/l; or 0.7 μM) are usually oxic, low in dissolved HCO_3^- concentration (<4 mM), and undersaturated with respect to calcite, with no detectable ^3H. In contrast, ^3H concentrations display a wide dynamic range (0–17 TU, with one value as high as 462 TU) in shallow (<35 m), presumed Holocene aquifers. These differences can be best explained by the nature of the aquifer sediments, whereby the once uplifted Pleistocene sediments are now depleted of labile organic C content due to previous flushing of the aquifer and therefore cannot produce sufficiently reducing conditions to mobilize As.

Acknowledgements

We thank Dr. I. Hussain of the National Institute of Preventive Medicine of Bangladesh for logistic assistance during our January and March 2000 field trips. We thank our field assistants Mohammed Shahnewaz, Mujibur Rahman, and Shahinur Islam for the long but enjoyable hours spent in the field. Queens College students, Jennifer Rommel, Bettina Ben-Elizer, Timothy Brutus and Ohinka Singh helped with sample analyses and preparation. Funding was provided by the US NIEHS/Superfund Basic Research Program P42ES10349. The Columbia University Earth Institute provided funding for initial fieldwork and other aspects of our research. Ratan Dhar is also supported by a CUNY graduate center science fellowship. This is Lamont-Doherty contribution 6372.

References

Aggett, J., Kriegman, M.R., 1988. The extent of formation of arsenic(III) in sediment interstitial waters and its release to hypolimnetic waters in Lake Ohakuri. Water. Res. 22, 407–411.

Ahmed, K.H., Burgess, W.G., 1995. Bils and the Barind Aquifer, Bangladesh. In: Brown, A.G. (Ed.), Geomorphology and Groundwater. John Wiley & Sons, New York, pp. 143–155.

Ahmed, K.M., Hoque, M., Hasan, M.K., Ravenscroft, P., Chowdhury, L.R., 1998. Occurence and origin of water well methane gas in Bangladesh. J. Geol. Soc. India 51, 697–708.

Bagla, P., Kaiser, J., 1996. India's spreading health crisis draws global arsenic experts. Science 274, 174–175.

Bayer, R., Schlosser, P., Boenisch, G., Rupp, H., Zaucker, F., Zimmek, G., 1989. Performance and blank components of a mass spectrometric system for routine measurement of helium isotopes and tritium by the 3He ingrowth method. Sitzungsberichte der Heidelberger Akademie der Wissenschaften, Mathematisch-naturwissenschaftliche Klasse, Jahrgang 5, 241–279.

Belzile, N., Tessier, A., 1990. Interactions between arsenic and iron oxyhydroxides in lacustrine sediments. Geochim. Cosmochim. Acta 54, 103–109.

BGS, 1998. Groundwater Studies for Arsenic Contamination in Bangladesh Phase I: Rapid Investigation Phase, Main Report. British Geological Survey and Mott MacDonald Ltd.

BGS and DPHE, 2001. Arsenic contamination of groundwater in Bangladesh. In: Kinniburgh, D.G., Smedley, P.L. (Eds.), British Geological Survey Report WC/00/19. British Geological Survey, Keyworth, UK.

Bhattacharya, P., Chatterjee, D., Jacks, G., 1997. Occurrence of arsenic-contaminated groundwater in alluvial aquifers from delta plains, eastern India: options for safe drinking water supply. Water Resour. Develop. 13, 79–92.

Bhattacharya, P., Jacks, G., Jana, J., Sracek, A., Gustafsson, J.P., Chatterjee, D., 2001. Geochemistry of the Holocene alluvial sediments of Bengal Delta Plain from West Bengal, India: implications on arsenic contamination in groundwater. In: Jacks, G., Bhattacharya, P., Khan, A.A. (Eds.), Groundwater Arsenic Contamination in the Bengal Delta Plain of Bangladesh, Proceedings of the KTH-Dhaka University Seminar, February 1999. KTH Special Publication, Stockholm, Sweden, Dhaka, Bangladesh, pp. 21–40.

Chakraborti, D., Biswas, B.K., Basu, G.K., Chowdhury, U.K., Chowdhury, T.R., Lodh, D., Chanda, C.R., Mandal, B.K., Samanta, G., Chakraborti, A.K., Rahman, M.M., Paul, K., Roy, S., Kabir, S., Ahmed, B., Das, R., Salim, M., Quamruzzaman, Q., 1999. Possible arsenic contamination free groundwater source in Bangladesh. J. Surf. Sci. Tech. 15, 179–187.

Chakraborty, A.K., Saha, K.C., 1987. Arsenical dermatosis from tubewell water in West Bengal. Indian J. Med. Res. 85, 326–334.

Chatterjee, A.D., Das, D., Mandal, B.K., Chowdhury, T.R., Samanta, G., Chakraborty, D., 1995. Arsenic in groundwater in 6 districts of West Bengal, India—the biggest arsenic calamity in the world. A. Arsenic species in drinking water and urine of the affected people. Analyst 120, 643–650.

Chen, C.-J., Lin, L.-J., 1994. Human carcinogenicity and atherogenicity induced by chronic exposure to inorganic arsenic. In: Nriagu, J.O. (Ed.), Arsenic in the Environment, Part II: Human Health and Ecosystems Effects. John Wiley & Sons, New York.

Chen, C.-J., Chiou, H.-Y., Huang, W.-I., Chen, S.-Y., Hsueh, Y.-M., Tseng, C.-H., Lin, L.-J., Shyu, M.P., Lai, M.S., 1997. Systematic non-carcinogenic effects and developmental toxicity of inorganic arsenic. In: Abernathy, C.O., Calderon, R.L., Chappell, W.R. (Eds.), Arsenic Exposure and Health Effects. Chapman and Hall, London.

Coleman, M.L., Moore, M.P., 1978. Direct reduction of sulfate to sulfur dioxide for isotopic analysis. Anal. Chem. 50, 1594–1595.

Cullen, W.R., Reimer, K.J., 1989. Arsenic speciation in the environment. Chem. Rev. 89, 713–764.

Davis, J., 1994. The hydrogeochemistry of alluvial aquifers in central Bangladesh. In: Nash, H., McCall, G.J.H. (Eds.), Groundwater Quality. Chapman & Hall, pp. 9–18.

Dhar, R., Biswas, B.K., Samanta, G., Mandal, B.K.D.C., Roy, S., Jafar, A., Islam, A., Ara, G., Kabir, S., Khan, A.W., Ahmed, S.A., Hadi, S.A., 1997. Groundwater arsenic calamity in Bangladesh. Curr. Sci. 73, 48–59.

Edenborn, H.M., Belzile, N., Mucci, A., Lebel, J., Silverberg, N., 1986. Observation on the diagenetic behavior of arsenic in a deep coastal sediment. Biogeochem. 2, 359–376.

Ficklin, W.H., 1983. Separation of arsenic(III) and arsenic (V) in ground waters by ion-exchange. Talanta 30, 371–373.

Fuller, C.C., Davis, J.A., 1989. Influence of coupling of sorption and photosynthetic processes on trace-element cycles in natural waters. Nature 340, 52–54.

Galy, A., Frace-Lanord, C., 1999. Weathering processes in the Ganges-Brahmaputra basin and the riverine alkalinity budget. Chem. Geol. 159, 31–60.

Garrels, R.M., 1967. Genesis of some ground waters from igneous rocks. In: Abelson, P.H. (Ed.), Researches in Geochemistry. John Wiley & Sons, New York, pp. 405–421.

Goodbred Jr., S.L., Kuehl, S.A., 2000. The significance of large sediment supply, active tectonism, and eustasy on margin sequence development: Late Quaternary stratigraphy and evolution of the Ganges-Brahmaputra Delta. Sed. Geol. 133, 227–248.

Goodbred Jr., S.L., Kuehl, S.A., Steckler, M.S., Sarker, M.H., 2003. Controls on facies distribution and stratigraphic preservation in the Ganges-Brahmaputra delta sequence. Sed. Geol. 155, 301–306.

Gran, G., 1952. A new method to linearize titration curves. Analyst 77.

Hering, J.G., Chen, P.-Y., Wilkie, J.A., Elimelech, M., 1997. Arsenic removal from drinking water during coagulation. J. Environ. Engineer. 800–807.

Hering, J.G., Chen, P.-Y., Wilkie, J.A., Elimelech, M., Liang, S., 1996. Arsenic removal by ferric chloride. J. Am. Water Works Assoc. 88, 155–167.

IAEA, 1992. Statistical Treatment of Data in Environmental Isotopes in Precipitation. IAEA, Vienna.

Jacks, G., Sharma, V.P., Trossander, P., Aberg, G., 1994. Origin of sulphur in soil and water in a Precambrian terrain, S. India. Geochem. J. 28, 351–358.

Kuhn, A., Sigg, L., 1993. Arsenic cycling in eutrophic Lake Greifen, Switzerland: influence of seasonal redox processes. Limnol. Oceanog. 38, 1052–1059.

Ludin, A., Weppernig, R., Bonisch, G., Schlosser, P., 1998. Mass Spectrometric Measurement of Helium Isotopes and Tritium. L-DEO Technical Report No. 98-6, Palisades, NY.

McArthur, J.M., Ravenscroft, P., Safiullah, S., Thirlwall, M.F., 2001. Arsenic in groundwater: testing pollution mechanisms for sedimentary aquifer in Bangladesh. Water Resour. Res. 37, 109–117.

Meng, X., Korfiatis, G.P., Christodoulatos, C., Bang, S., 2000. Treatment of arsenic in Bangladesh well water using a household co-precipitation and filtration system. Water Res. 34, 1255–1261.

Moore, J.N., Ficklin, W.H., Johns, C., 1988. Partitioning of arsenic and metals in reducing sulfidic sediments. Environ. Sci. Technol. 22, 432–437.

Morgan, J.P., McIntire, W.G., 1959. Quaternary geology of the Bengal Basin, East Pakistan and India. Geol. Soc. Am. Bull. 70, 319–342.

Nag, J.K., Balaram, V., Rubo, R., Alberti, J., Das, A.K., 1996. Inorganic arsenic species in groundwater: a case study from Purbasthali (Burdwan), India. J. Trace Elements Med. Biol. 10, 20–24.

Nickson, R., McArthur, J., Burgess, W., Ahmed, K.M., Ravenscroft, P., Rahman, M., 1998. Arsenic poisoning of Bangladesh groundwater. Nature 395, 338.

Nickson, R.T., McArthur, J.M., Ravenscroft, P., Burgess, W.G., Ahmed, K.M., 2000. Mechanisms of arsenic release to groundwater, Bangladesh and West-Bengal. Appl. Geochem. 15.

NRC, 1999. Arsenic in Drinking Water, National Research Council. National Academic Press, Washington DC.

Nriagu, J.O., 1994. Arsenic in the Environment: Part II: Human Health and Ecosystem Effects. John Wiley & Sons, New York.

Paulsen, P.J., Kelly, W.R., 1984. Determination of sulfur as arsenic monosulfide ion by isotope dilution thermal ionization mass spectrometry. Anal. Chem. 56, 708–713.

Ravenscroft, P., McArthur, J.M., Hoque, B.A., 2002. Geochemical and palaeohydrological controls on pollution of groundwater by arsenic. In: Chappell, W.R., Abernathy, C.O., Calderon, R.L. (Eds.), 4th Internat. Conf. Arsenic Exposure and Health Effects. Elsevier Science Ltd, Oxford.

Sarin, M.M., Krishnaswami, S., Dilli, K., Somayajulu, B.L.K., Moore, W.S., 1989. Major ion chemistry of the Ganges-Brahmaputra river system: Weathering processes and fluxes to the Bay of Bengal. Geochim. Cosmochim. Acta 53, 997–1009.

Smith, A.H., Lingas, E.O., Rahman, M., 2000. Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. Bull. W.H.O. 78, 1093–1103.

Spliethoff, H.M., Mason, R.P., Hemond, H.F., 1995. Interannual variability in the speciation and mobility of arsenic in a dimictic lake. Environ. Sci. Technol. 29, 2157–2161.

Stookey, L.L., 1970. Ferrozine—a new spectrophotometric reagent for iron. Anal. Chem. 42, 779–781.

Stute, M., 2001. ^{3}H in precipitation in Bangladesh. In: G. Jacks, P. Bhattacharya and A. A. Khan (Ed.), Groundwater Arsenic Contamination in the Bengal Delta Plain of Bangladesh, Proceedings of the KTH-Dhaka University Seminar, Feb. 1999. KTH Special Publication, Stockholm, Sweden, Dhaka, Bangladesh.

Takamatsu, T., Kawashima, M., Koyama, M., 1985. The role of Mn^{2+}-rich hydrous manganese oxides in the accumulation of arsenic in lake sediments. Water Res. 19, 1029–1032.

Umitsu, M., 1993. Late Quaternary sedimentary environments and landforms in the Ganges Delta. Sed. Geol. 83, 177–186.
Vink, B.W., 1996. Stability relations of antimony and arsenic compounds in the light of revised and extended Eh–pH diagrams. Chem. Geol. 130, 21–30.
Weiss, R.F., 1968. Piggyback samplers for dissolved gas studies on sealed water samples. Deep-Sea Res. 15, 695–699.
Wilkie, J.A., Hering, J.G., 1996. Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate-adsorbent ratios and co-occurring solutes. Colloids Surfactants A107, 97–124.