

# Hydrogeochemical comparison and effects of overlapping redox zones on groundwater arsenic near the Western (Bhagirathi sub-basin, India) and Eastern (Meghna sub-basin, Bangladesh) margins of the Bengal Basin

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## Abstract

Although arsenic (As) contamination of groundwater in the Bengal Basin has received wide attention over the past decade, comparative studies of hydrogeochemistry in geologically different sub-basins within the basin have been lacking. Groundwater samples were collected from sub-basins in the western margin (River Bhagirathi sub-basin, Nadia, India; 90 samples) and eastern margin (River Meghna sub-basin; Brahmanbaria, Bangladesh; 35 samples) of the Bengal Basin. Groundwater in the western site (Nadia) has mostly Ca–HCO<sub>3</sub> water while that in the eastern site (Brahmanbaria) is much more variable consisting of at least six different facies. The two sites show differences in major and minor solute trends indicating varying pathways of hydrogeochemical evolution. However, both sites have similar reducing, postoxic environments ( $p_e$ : +5 to –2) with high concentrations of dissolved organic carbon, indicating dominantly metal-reducing processes and similarity in As mobilization mechanism. The trends of various redox-sensitive solutes (e.g. As, CH<sub>4</sub>, Fe, Mn, NO<sub>3</sub><sup>–</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2–</sup>) indicate overlapping redox zones, leading to partial redox equilibrium conditions where As, once liberated from source minerals, would tend to remain in solution because of the complex interplay among the electron acceptors.

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## 1. Introduction

Geogenic, non-point source, carcinogenic arsenic (As) is now considered as one of the most serious natural contaminants in groundwater worldwide (Mukherjee and Bhattacharya, 2001; Bhattacharya et al., 2002a; Smedley and Kinniburgh, 2002; Mukherjee et al., 2007). The Bengal Basin, comprising most of Bangladesh and parts of the Indian state of West Bengal, is regarded to be the most acutely arsenic-affected geological province in the world. The basin, formed by the sedimentation of the rivers Ganges (6th largest in the world), Brahmaputra (4th largest in the world), and Meghna, along with their numerous tributaries and distributaries (hence also called GBM basin), is the world's largest fluvio-deltaic basin (Alam et al., 2003). More than 95% of the >120 million inhabitants (>2% of total world population) rely on groundwater for drinking, and ~70% of all irrigation in this region is groundwater-fed (Hasan et al., 2007). However, the presence of elevated dissolved As in groundwater has endangered the lives of ~35 million people in Bangladesh (Smedley and Kinniburgh, 2002) and ~15 million people in West Bengal (Mukherjee, 2006), and has contaminated ~25% to ~33% (Ahmed et al., 2004; McArthur et al., 2004) of ~11 million tube wells providing water in Bangladesh alone (Smedley, 2005). Arsenic concentrations in groundwater of the Bengal Basin vary widely, ranging from <5 µg/L to 4100 µg/L in West Bengal (Ghosh and Mukherjee, 2002) and to 4730 µg/L in Bangladesh (Rahman et al., 2006).

Data from various previous studies at different locations (mostly in Bangladesh) show that groundwater in the shallow grey sediments of the basin, supposedly of Holocene age, is most contaminated, whereas groundwater in the deeper, yellowish or brownish, supposedly deeper Holocene sediments is much less contaminated (e.g. von Brömssen et al., 2007). However, in the western part of the basin, such arsenic-free, yellowish or brownish colored aquifer sediments have not been identified (Mukherjee, 2006). Similarly, several authors (e.g. Swartz et al., 2004) have noted considerable heterogeneity in groundwater As concentrations in the Bengal Basin at scales of tens to hundreds of meters horizontally. Nonetheless, regional-scale studies have shown consistent spatial patterns in major and trace solute chemistry (including As) for aquifers at these scales (e.g. JICA, 2002; Dowling et al., 2003; Mukherjee and Fryar, 2008), with the possibility of differences existing between sub-basins with dissimilar geologic and geomorphic evolutionary histories (e.g. Mukherjee, 2006; Hasan et al., (2007)). Hence, it is apparent that basin geology, hydrogeology, scale of heterogeneity, and depositional facies have substantial

control on the hydrogeochemistry and therefore on the distribution of As in Bengal Basin aquifers.

There has been a large number of local-scale studies (e.g. Harvey et al., 2002; Zheng et al., 2004; von Brömssen et al., 2007) and regional reconnaissance studies (e.g. BGS/DPHE/MML, 2001; Dowling et al., 2003) in both Bangladesh and India, however, very few studies (e.g. Hasan et al., 2007; Metral et al., in review) have evaluated the hydrogeochemistry and As distribution and mobilization mechanisms simultaneously in hydrogeologically different parts of the basin. The present study builds upon previous hydrogeochemical studies conducted by Bhattacharya et al. (2006) and Hasan et al. (2007) in eastern Bangladesh and by Mukherjee (2006) and Mukherjee and Fryar (2008) in the deep aquifers of West Bengal. The present work [with new data from the shallow aquifers of the study site in West Bengal (72 new locations)] differs from the previous studies as it involves a comparison of the hydrogeochemistry (up to a depth of 300 m below ground level [bgl]) between two geologically distinct, sub-basinal scale study sites located along the eastern margin (Meghna sub-basin, Brahmanbaria in Bangladesh) and western margin (Bhagirathi sub-basin, Nadia in West Bengal) of the Bengal Basin. In the course of this hydrogeochemical comparison, we also investigate the applicability of the findings on chemical evolution processes and As dynamics from each area (e.g. Bhattacharya et al., 2006; Mukherjee and Fryar, 2008) to the other. We also investigated for presence of common mechanisms for the liberation and retention of As in solution in the two sites. The observations from this study lead to the proposition of hypothesis of overlapping redox zonation and partial redox equilibrium (which to our knowledge have not previously been discussed for As-affected areas of Asia) as major controlling factors for arsenic retention and mobilization in groundwater. The generalization, description and conclusions of this study are drawn at a sub-basinal scale and may not be valid for smaller-scale study sites because of local-scale complexities (e.g. aquifer architecture, land use, recharge patterns, surface water/groundwater interactions). Hence, evaluating local-scale variations in groundwater chemistry study sites is beyond the scope of the present study.

## 2. Summary of present knowledge on arsenic source and mobilization in Bengal Basin

Although the general nature of the processes controlling the fate of As in Recent alluvial aquifers has been hypothesized, no consensus has been reached as to the exact reactions controlling As mobilization and retention in solution. Similarly, the primary source sediments of As in

these aquifers are not known with certainty. In the Bengal Basin, solid-phase As in sediment varies with sediment size and is not particularly high (Swartz et al., 2004), ranging from 1 to 30 mg/kg (Bhattacharya et al., 2001; McArthur et al., 2001; Harvey et al., 2002; Ahmed et al., 2004). The As has been found associated with Fe-hydroxide (mineral phases in the aquitard clays (e.g. Chakraborti et al., 2001; Swartz et al., 2004). However, many studies (e.g. Breit et al., 2001; Kent and Fox, 2004) have found As enrichment in Fe-oxide coated sand grains in aquifers, phyllosilicates, Mn/Al oxides and hydroxides, and authigenic pyrite (Lowers et al., 2007). Initially, it was believed that oxidation of As-rich pyrite mobilized adsorbed As, attributed to groundwater pumping and water-table draw-down resulting in more oxidizing conditions (e.g. Mallick and Rajgopal, 1995). Acharyya et al. (1999) suggested that As may be mobilized by competitive displacement by  $\text{PO}_4^{3-}$ . However, further studies didn't find any proof of such reactions happening in Bengal sub-surface. However, currently, the mechanism for mobilizing sorbed As is generally thought to be reductive dissolution of metal oxides and hydroxides (mostly FeOOH or hydrous ferric oxide [HFO], also Mn oxides/hydroxides). The process is largely driven by bacterially catalyzed oxidation of natural organic matter (e.g. Bhattacharya et al., 1997; McArthur et al., 2001). As a modification of the previous reductive dissolution hypothesis, Zheng et al. (2004) mentioned and Mukherjee (2006) elaborated that although the primary mobilization mechanism is reduction of HFO and similar phases, there might be some local re-oxidation and re-mobilization of sequestered As from adsorbed phases due to complex Fe–As–S biogeochemical cycles.

### 3. Geologic, physiographic and hydrogeologic setting

Although the present study focuses on similarities and differences between two sub-basinal scale study sites, it is important to understand these basins within the broader basinal-scale geologic/hydrogeologic framework.

#### 3.1. Bengal Basin

The Bengal Basin is a peripheral foreland basin formed by the subduction of the Indian plate beneath the Eurasian (Tibetan) and Burmese plates. It is bounded by the Precambrian Peninsular shield of India and the mid-Mesozoic Rajmahal basaltic hills in the west, Mio-Pliocene Tripura and Chittagong Hills in the east and southeast, and the Precambrian Shillong Plateau in the north. At present, about 1–8 km of Permian to Recent clastic sediments are thought to rest on the western part

of the basin (Imam and Shaw, 1985) and 16–22 km of Tertiary to Quaternary alluvial sediments in the active delta area in the eastern part of the basin (Alam et al., 2003).

Physiographically, the Bengal Basin can be divided into two major units, the Pleistocene uplands and Holocene lowlands (Morgan and McIntire, 1959). The Pleistocene uplands probably represent paleo-GBM plains. The Holocene lowlands are mostly comprised of alluvial fans, and the GBM flood and delta plain, which form at least 80% ( $\sim 10^5 \text{ km}^2$ ) of the total basin. The plain is formed by channel–interchannel and overbank deposits of the mega-rivers and their various tributaries and distributaries, with visible presence of numerous paleochannels, ox-bow lakes, and inland lakes. The Recent sedimentation has been largely controlled by Holocene sea-level change from the Pleistocene Ice age maximum leading to several phases of scouring of the alluvial plains and formation of marshes and wetlands with remnant mangrove vegetation and peat swamps in the south. (e.g. Ravenscroft, 2003). Moreover, orogeny along the Himalayan and Burmese front has generated vertically displaced regional sedimentary blocks, dividing the basin into numerous poorly connected sub-basins (e.g. Sylhet sub-basin, Atrai sub-basin) with divergent lithofacies evolution (Goodbred et al., 2003).

The aquifers of the basin are highly productive (except for a few localities), with generally shallow water tables (< 15 m bgl). Hydraulic heads tend to be similar each year at the beginning of the irrigation season, which suggest sufficient recharge replenishing the groundwater systems (BGS/DPHE/MML, 2001). The aquifer systems have been variously classified according to lithologic (e.g. UNDP, 1982) and stratigraphic/hydrostratigraphic models (e.g. Ravenscroft, 2003; Mukherjee et al., 2007). The groundwater flow systems in the basin have been conceptualized (Ravenscroft et al., 2005) as consisting of i) local-scale shallow flow systems (< 1 to few kilometers long) between local topographic features, ii) intermediate-scale flow systems (a few to tens of kilometers long) between major topographic features, and iii) regional or basinal-scale flow between basin boundaries. Current recharge has been estimated to be,  $\sim 0.6 \text{ m/year}$  and groundwater flux to the Bay of Bengal to be  $\sim 1.5 \times 10^{11} \text{ m}^3/\text{year}$  ( $\sim 19 \%$  of total surface water flux of  $1.07 \times 10^{12} \text{ m}^3/\text{year}$ ) (Dowling et al., 2003).

#### 3.2. Study areas

The study areas for the present work include two severely As-affected localities in the Bengal Basin: a) the

Nadia district of West Bengal, India, in the River Bhagirathi sub-basin (western site), and b) the Brahmanbaria Sadar Upazila of Bangladesh, in the River Meghna sub-basin (eastern site) (Fig. 1). The River Bhagirathi (also known as the River Bhagirathi-Hoogly) is the main

distributary of the Ganges river in India and the Meghna is the main tributary to the combined Ganges and Brahmaputra rivers. The two sites are ~260 km apart and are near the western and eastern margins of the Bengal Basin, respectively. The western site lies ~50 km east of

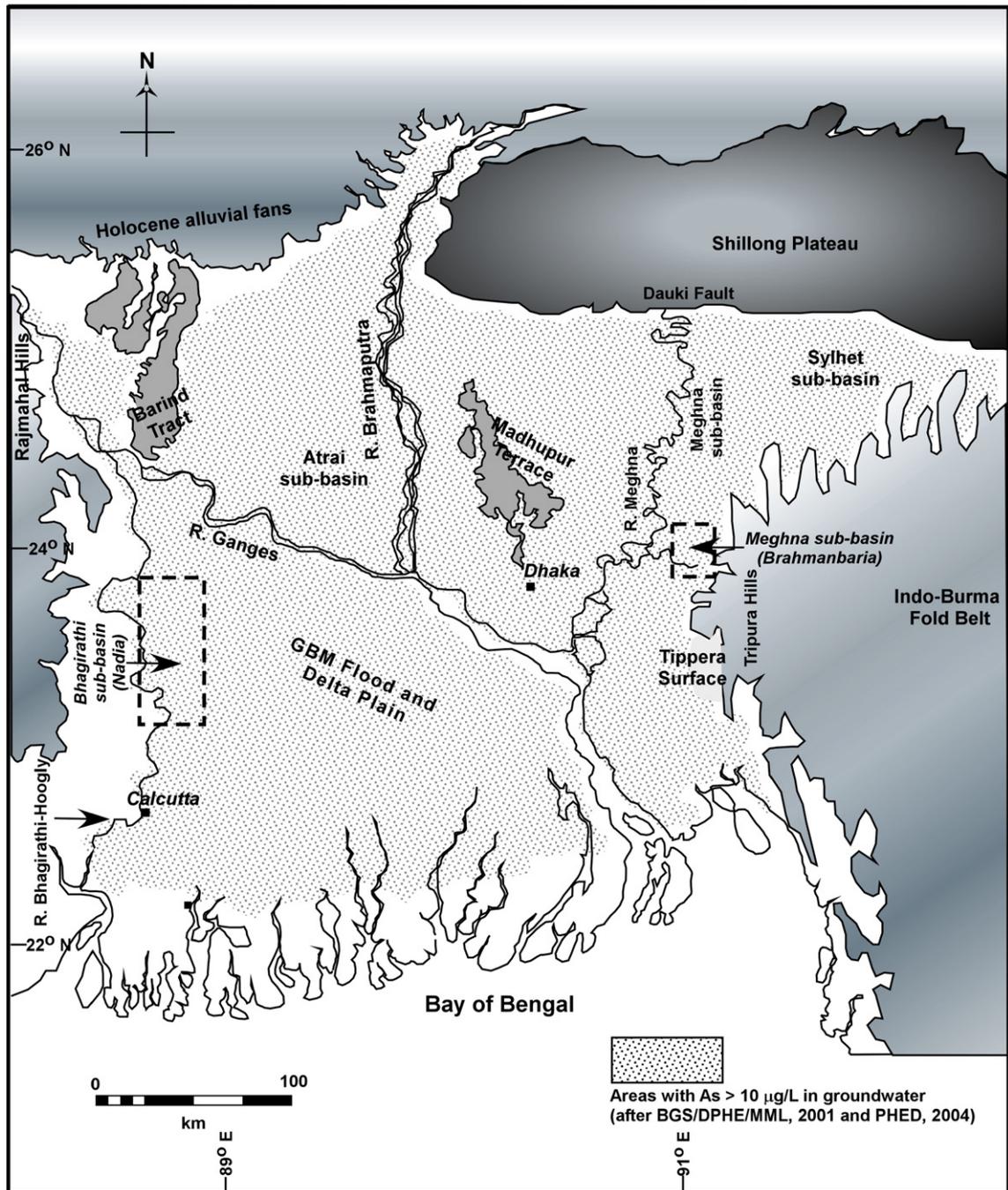


Fig. 1. Physiographic map of the Bengal Basin showing the two study areas and the arsenic-affected areas (as mapped by BGS/DPHE/MML, 2001 and PHED, 2004). The physiographic boundaries were drawn from the SRTM-90 digital elevation model of NASA.

the Indian Precambrian shield and southeast of the Rajamahals Hills, whereas the eastern site is adjacent to the Tripura Hills. The two sub-basins have distinctly different sediment provenances, geology, and geomorphology. The eastern site is mostly an alluvial flood plain, whereas the western site is at a lower elevation, closer to the Bay of Bengal, and dominated by deltaic deposits with some flood plain deposits.

The northern and central parts of the western site have been designated as the older delta and part of the Murshidabad Plain, whereas some of the southern part forms the modern delta and has been designated as the East Bhagirathi Plain (CGWB, 1994). The uppermost sediments consist of Holocene Bengal Alluvium, underlain by the Pleistocene Barind Group and Pliocene Debagram and Ranaghat formations of the Bhagirathi Group (Biswas, 1963). Most of the sediments in the western site were transported from the Himalayas by the Ganges and then by the Bhagirathi-Hoogly before discharging to the Bay of Bengal. The Rajamahals Hills and Indian shield probably serve as secondary sediment sources via western tributaries of the Bhagirathi-Hoogly (e.g., the rivers Damodar and Ajoy). Recent hydrostratigraphic delineation by Mukherjee et al. (2007) shows that most of the western site is underlain by a semi-confined single aquifer (Sonar Bangla aquifer), with a basal confining layer (Murshidabad aquitard) and discontinuous aquitard lenses (Fig. 2a). There are also some isolated aquifers within the basal aquitard, mostly >200 m deep. The hydraulic head is near surface (<10 m), with greatest drawdown during irrigation [May–June; up to ~10 m bgl (Fig. 2b)] and annual fluctuation amplitude of 3–6 m (Mukherjee et al., 2007). Groundwater samples were collected mostly from the Sonar Bangla aquifer at depths of 4.6 to 278.6 m bgl (between 23.92° N and 23.01° N).

The study area in the eastern site covers the Ashuganj and Brahmanbaria Sadar Thana areas and is part of the Chandina flood-delta plain deposits of the Chandina Formation, bounded by the Lalmai deltaic plain in the east and Meghna flood plain in the west. The Chandina is overlain by Meghna alluvium and underlain by the Pleistocene Madhupur Clay and Pliocene Dupi Tila Formation. The Meghna and its tributaries transport most of the sediments from the Shillong plateau and the eastern hills, including the Tripura Hills. Shifting of channels of the Meghna and Brahmaputra have largely influenced formation of the confined to semi-confined, multilayered aquifer system in the area. However, the hydrostratigraphy of the area is not well known, except along a short transect (Fig. 2a). No sampled wells were found to be tapping groundwater from depths of 76 m to

189 m bgl, probably indicating hydrostratigraphic control (Fig. 2a). Groundwater occurs near the surface in Holocene aquifers with maximum drawdown during April–May (up to ~7 m bgl) and annual amplitude of 2–5 m bgl (Fig. 2b).

#### 4. Methods

One hundred twenty-five groundwater samples (90 from western site and 35 from eastern site) were collected from hand-pumped tube wells and public water supply wells from 2000 to 2005. The total depth intervals of the samples are similar for both areas (western site: 15–279 m; eastern site: 18–235 m), but samples were taken from a wider distribution of depths intervals in western site than in eastern site, where no samples were available between the depths of 75.6 and 189.6 m bgl.

The groundwater sample collection and field measurements were done following standard procedures. In-line flow cells with platinum redox electrode (Orion 9678BN, MC408 pt) under minimal atmospheric contact were used to measure the redox potential (later corrected with reference  $H_2$  electrode for  $E_H$ ). Temperature probe (CD22, Orion 917005), pH electrode (8165BN, pH C2401-7), and a specific conductance (EC) meter (CD22, Orion 130) were simultaneously used to measure those parameters. Fe(II) was measured in the field at 18 sites in western site by CHEMets® (Chemetrics, Calverton, USA) field kit using the 1,10-phenanthroline method (Tetlow and Wilson, 1964). Groundwater samples were collected through high capacity in-line Sartorius or QED 0.45- $\mu$ m filters after purging for several well volumes. Samples for cations (major and trace, including As(III), and excluding  $NH_4^+$ ) were collected and preserved by acidification with  $HNO_3$  in the field to pH ~2. Samples for As(III) were collected in 18 wells of western site and all wells of eastern site after extraction through disposable ion exchange resins (Supelco/Sigma-Aldrich, Bellefonte, PA, or Metalsoft Center, PA, USA) (Bednar et al., 2002). Anion and  $NH_4^+$  samples were collected unpreserved or by adding  $CHCl_3$  in the field. Presence or absence of sulfide (as  $HS^-$ ) was determined by odor or taste. In case of detection, sulfide was sampled as ZnS by addition of Zn acetate and NaOH. Dissolved organic carbon (DOC) samples were collected after addition of 50%  $H_2SO_4$  in the field to eliminate inorganic carbon.  $CH_4$  samples, collected at 18 locations in Western site, were sampled in glass vials without headspace. Alkalinity was analyzed within 48 h by titration by inflection point method to pH ~4.

The samples were analyzed in the laboratories of the Royal Institute of Technology and Stockholm University (Sweden) and University of Kentucky (USA).

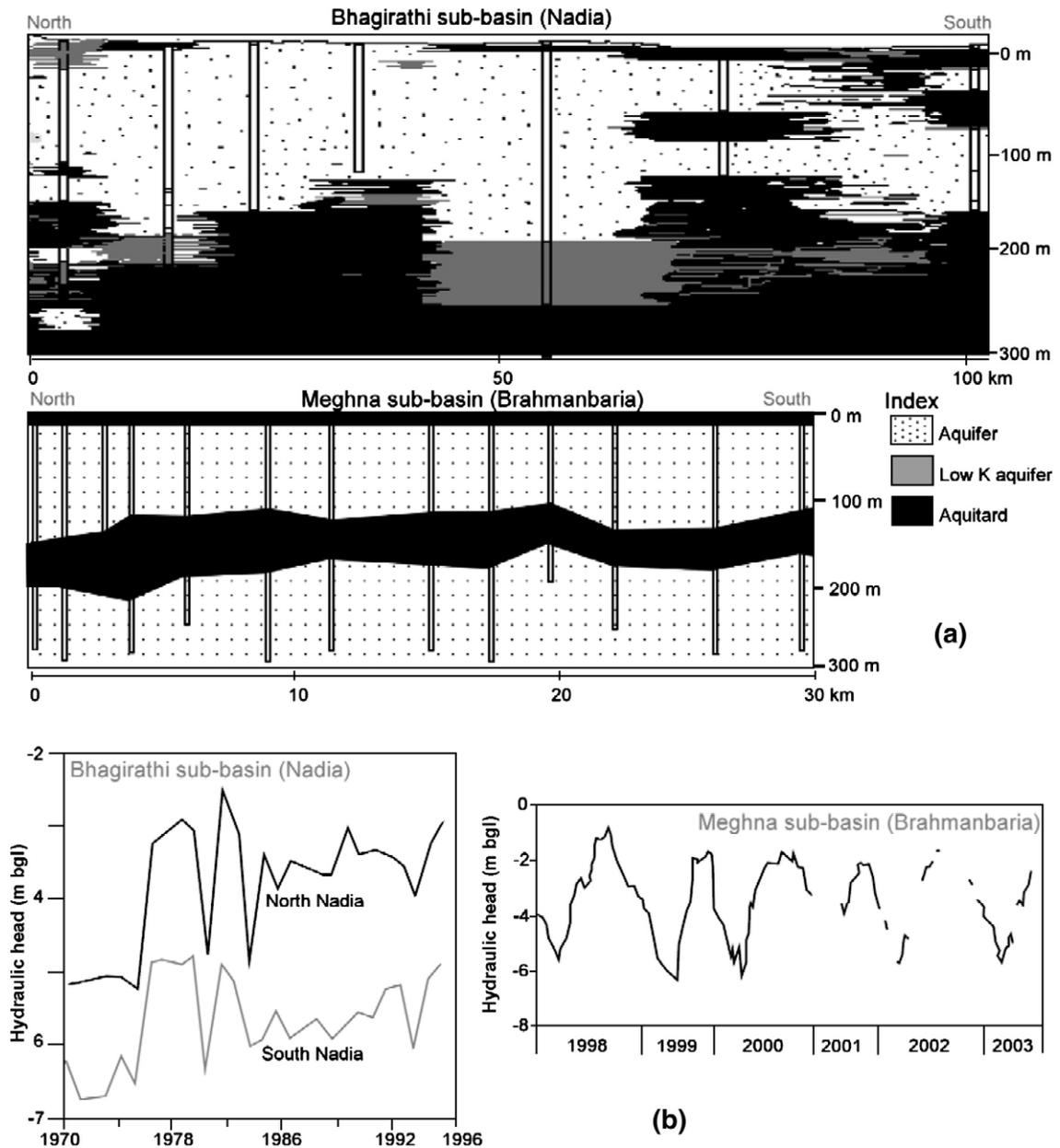


Fig. 2. a) Hydrostratigraphy along a regional-scale (~100 km) north–south transect in Nadia (redrawn after Mukherjee, 2006) and a local-scale (~30 km) transect in Brahmanbaria; b) plots of hydraulic head over time from north and south Nadia (redrawn from CGWB, 1997), and Brahmanbaria (redrawn from Hasan et al., 2007).

Major and trace metals and metalloids (except  $\text{NH}_4^+$  and As) were measured by multi-element scans using an inductively coupled plasma-optical emission spectrometer (ICP). Y and Sc were used as internal standards. The As samples (total and As[III]) were analyzed by atomic absorption spectrophotometer with a graphite furnace (AAS-GF). The precision of analyses was

generally better than 5%. Anions were measured using ion chromatography systems (Dionex ICS-2000, 2500, DX-120 with IonPac 14 and 18), autoanalyzer (Bran-Luebbe AAIH) and spectrophotometer (Tecator Aquattec 5400). The error was generally <6% for the IC and <3% for the autoanalyzer. The  $\text{CH}_4$  samples were analyzed using a gas chromatograph with flame

Table 1

Summary statistics of pH, Eh and common solutes observed in the samples collected from Nadia and Brahmanbaria

Parameters	Nadia						Brahmanbaria					
	<i>n</i>	Maximum	Minimum	Average	Median	Standard deviation	<i>n</i>	Maximum	Minimum	Average	Median	Standard deviation
Depth (m bgl)	90	278.6	4.6	57.7	26.2	61.9	35	234.7	18.3	63.7	32.0	67.3
As ( $\mu\text{M}$ )	90	3.6	bdl	0.8	0.5	0.9	35	5.9	bdl	1.5	1.1	1.4
As(III) ( $\mu\text{M}$ )	18	0.9	bdl	0.3	0.2	0.3	35	4.0	bdl	Q	0.3	0.9
As(III)%		100.0	34.6	82.5	97.3	22.5		99.4	bdl	50.3	51.7	33.3
B ( $\mu\text{M}$ )	90	374.5	bdl	8.1	0.5	43.9						
Ba ( $\mu\text{M}$ )	90	5.7	bdl	1.7	1.3	1.3						
Ca ( $\mu\text{M}$ )	90	4890.5	494.2	2509.4	2407.8	685.4	35	2328.0	286.9	1160.5	1070.4	560.8
Fe (total) ( $\mu\text{M}$ )	90	286.3	0.2	63.3	51.8	55.8	35	184.5	bdl	37.4	23.7	41.6
Fe(II) ( $\mu\text{M}$ )	18	93.7	0.2	19.6	15.2	21.5						
Fe(II)%		100.0	87.3	98.7	100.0	3.8						
K ( $\mu\text{M}$ )	90	1067.8	30.9	112.1	85.4	135.9	35	3325.0	20.5	270.4	168.8	548.6
Mg ( $\mu\text{M}$ )	90	2971.2	346.0	994.6	949.1	406.1	35	3015.8	176.9	1114.5	835.2	720.1
Mn ( $\mu\text{M}$ )	90	86.3	0.1	6.6	3.7	10.5	35	22.2	0.1	3.1	0.8	5.6
Na ( $\mu\text{M}$ )	90	56468.8	265.3	2162.8	819.9	7618.4	35	24967.7	200.1	3837.9	1304.9	5370.6
NH <sub>4</sub> ( $\mu\text{M}$ )	36	1078.1	bdl	141.5	30.9	231.3	31	944.0	bdl	251.4	176.1	253.3
Si ( $\mu\text{M}$ )	71	833.2	92.6	555.3	550.8	120.8	30	717.7	5.4	104.1	38.3	149.9
Sr ( $\mu\text{M}$ )	90	43.1	0.4	3.9	3.3	4.4	30	3.4	0.1	1.1	0.8	0.8
Zn ( $\mu\text{M}$ )	90	23.9	0.1	3.9	2.0	5.3	30	1.6	bdl	0.4	0.3	0.4
V ( $\mu\text{M}$ )	18	3.6	0.7	1.7	1.4	0.7						
Br ( $\mu\text{M}$ )	18	92.1	bdl	8.1	0.0	21.8						
Cl ( $\mu\text{M}$ )	90	80642.7	bdl	2340.0	662.6	9581.2	35	14639.2	112.8	2301.2	984.4	3274.1
NO <sub>3</sub> -N ( $\mu\text{M}$ )	90	547.4	bdl	21.7	2.2	76.4	35	51.0	bdl	3.4	1.0	9.6
SO <sub>4</sub> ( $\mu\text{M}$ )	90	4818.1	bdl	348.3	45.0	837.2	35	2456.0	bdl	288.0	21.4	613.3
PO <sub>4</sub> -P ( $\mu\text{M}$ )	90	27.5	0.1	8.7	7.5	7.4	35	171.6	1.1	36.9	28.4	41.6
HCO <sub>3</sub> ( $\mu\text{M}$ )	89	12736.6	2620.7	6917.7	6959.0	1813.8	35	10865.8	1212.8	5282.4	6293.3	3143.2
DOC ( $\mu\text{M}$ )	90	586.5	0.9	213.7	193.2	130.3	35	1816.4	19.4	444.5	298.1	420.3
CH <sub>4</sub> ( $\mu\text{M}$ )	18	68216.9	6.4	7762.8	199.9	17391.7						
HS <sup>-</sup> ( $\mu\text{M}$ )				not detected			5	32.8	bdl	4.7	29.7	7.8
pH	81	8.4	6.0	7.2	7.1	0.4	34	7.6	6.4	6.9	6.9	0.3
Eh (mV)	58	206.0	-160.0	106.5	154.0	99.1	35	299.0	184.0	206.3	184.0	37.4

ionization detector (Shimadzu GC-14A with Chromatopac C-R5A). DOC was measured using Phoenix 8000 UV-Persulfate and Shimadzu 5000 TOC analyzers.

Saturation indices ( $SI = \log[IAP K_T^{-1}]$ , where IAP is the ion activity product and  $K_T$  is the equilibrium solubility constant of a mineral phase at ambient temperature) were calculated for representative groundwater samples of both the locations using PHREEQC version 2.8 (Parkhurst and Appelo, 1999) with thermodynamic values of the mineral phases from the MINTeQ database (Allison et al., 1990). The  $p_c$  was set to Fe(II)/Fe(III) or As(III)/As(V) couples, where available, or was allowed to be calculated by the program from an initial default value. Multivariate statistics (principal component analyses [PCA]) were used to investigate relationships among the samples. PCA was performed on the concentrations of As<sub>tot</sub>, Ca, Fe<sub>tot</sub>, K, Mg, Mn, Na, NH<sub>4</sub><sup>+</sup>, Sr, Zn, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>-N, PO<sub>4</sub><sup>3-</sup>-P, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, DOC, pH

and  $E_H$  for each location. Below detection level (bdl) concentrations were replaced by  $dl \times 0.55$  (Sanford et al., 1993) for calculation. PCA was done on the original data set following Güler et al. (2002) and Dreher (2003) using the statistical software package SPSS version 14 (SPSS Inc., Chicago, IL). The component axes were rotated using a varimax algorithm for simplified visualization.

## 5. Results and discussion

### 5.1. Trends and comparison among the two sites

#### 5.1.1. Major solute chemistry

Major solute chemistry of groundwater in the two study sites are distinctly different. Lack of samples for the entire depth interval in eastern site (as noted above) makes detailed depth-wise comparison between the two sites infeasible. Measured pH in the western site has a wider

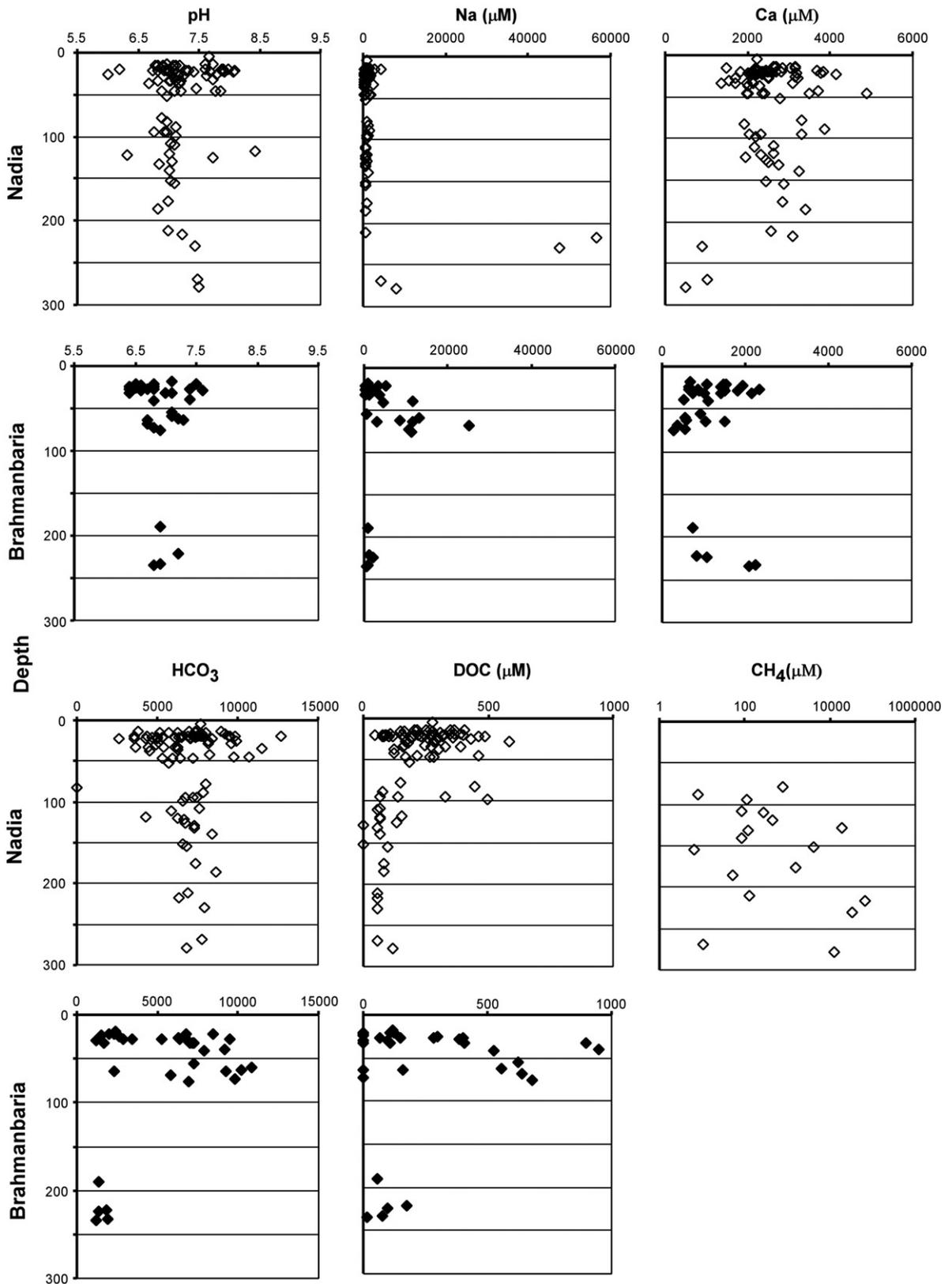


Fig. 3. Depth trends of pH and selected major species for Nadia and Brahmanbaria.

range (Table 1, Fig. 3, ESM Table 1) (6.0–8.4, mean: 7.2), increasing at depths >200 m. The eastern site has circum-neutral water (6.4–7.6, mean: 6.9), with no change in pH with depth. However, in both sites the greatest variation in pH was found within the upper 50 m zone. Piper plots show that groundwater in the western site is predominantly Ca–HCO<sub>3</sub> facies, with subordinate Mg–Ca–HCO<sub>3</sub> (Fig. 4). A few samples, which are mostly from deeper (generally >200 m) isolated aquifers (Mukherjee and Fryar, 2008) were found to have Na as the dominant cation. In contrast, groundwater from the eastern site is characterized by six hydrochemical facies with no dominant facies. Although the largest number of samples is of Ca–HCO<sub>3</sub> facies (~40%) is this not the dominant facies then?, many samples are of Ca–Na–HCO<sub>3</sub> (~20%) and Mg–Ca–Cl (~20%) type. Most groundwater to 50 m depth bgl is Ca–HCO<sub>3</sub> facies, whereas groundwater samples from 50 to 150 m bgl are typically Mg–Cl or Mg–Ca–Cl facies. Deeper samples (>150 m) mostly have Na+Ca and HCO<sub>3</sub> as the major ions. Differences in major-ion chemistry in the eastern site could not be attributed to variations in hydrostratigraphy because of lack of lithologic data. In the western site, Na enrichment at depths >200 m bgl in isolated aquifer samples (which are relatively alkaline) has been attributed to cation exchange, indicating long residence time (Mukherjee and Fryar, 2008). Similar deeper, supposedly older, Na-enriched water has not been detected in the eastern site, although samples from 50 to 75 m bgl show a trend of increasing Na and decreasing Ca; however, the underlying cause is not understood. High HCO<sub>3</sub> is

ubiquitous in Bengal Basin groundwater, and has been thought to play an important role in hydrochemical evolution and trace metal mobilization. Zheng et al. (2004) identified relatively low HCO<sub>3</sub> concentrations (<4000 μM) in deeper aquifers in their study sites in Bangladesh, which were attributed to limited hydrogeochemical evolution in older (probably pre-Holocene) aquifers. The few deeper samples available from the eastern site support this observation. However, in the western site, HCO<sub>3</sub> concentrations are ~7500 μM from 50 m to ~300 m bgl, suggesting there is a major difference in the processes or pathways of hydrochemical evolution between these two locations, probably as a manifestation of depositional environment and hydrologic flow regime. Mukherjee et al. (2007) showed that in western site, regional groundwater flow (from north to south) has largely been distorted by irrigational abstraction. In the eastern site, such impact of irrigation on flow paths have not yet been studied, but local flow paths are probably dominant at shallow depths (Ravenscroft, 2003), which suggests the possibility of intra sub-basinal water and solute exchanges.

#### 5.1.2. Redox conditions

The groundwater samples collected from both areas indicate moderately reducing conditions. We converted the measured  $E_H$  values (which are essentially the resultant values of various redox-sensitive parameters) to  $p_e$  (where  $p_e = 16.9E_H$  at 25 °C) and plotted them against the equilibrium  $p_e$  (at 25 °C) of the possible redox-sensitive species present in the groundwater of the study

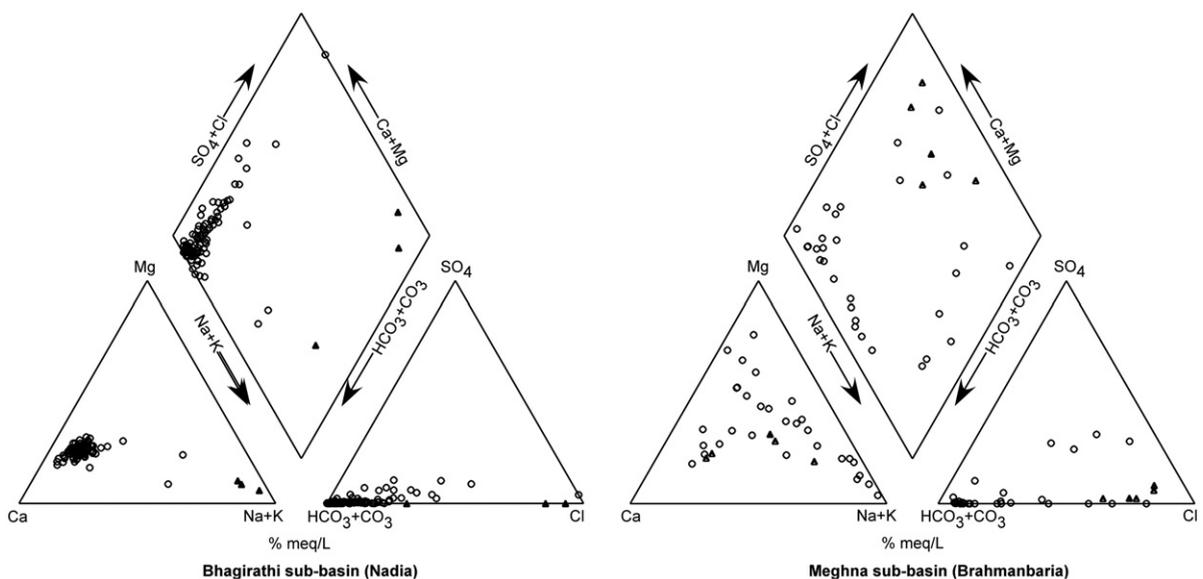


Fig. 4. Piper plots of groundwater samples collected from Nadia and Brahmanbaria. Triangular symbols indicate samples >100 m bgl depth.

sites (redrawn after Parkhurst et al., 1996). The samples from eastern site fall around the Fe(III)–Fe(II) transition point ( $p_e \sim 5$ ), whereas the samples for western site have a wider range of  $p_e$  values, starting from values close to Fe(III)–Fe(II) and extending close to values of V(IV)–V(III) ( $p_e \sim -3.2$ ) (Fig. 5). Barcelona et al. (1989) observed that the mean  $E_H$  value in reducing groundwater is frequently dominated by the equilibrium value of Fe(II)/Fe(III). All of our samples fall in the postoxic subgroup of anoxic environment of Berner (1981), and the mean  $p_e$  values are lower than Fe(III) reduction and higher than for As(V) reduction. Therefore, a resultant metal-reducing condition appears to be the dominant redox environment in both study sites. However, as noted later, the co-existence of various redox indicators suggests that the system may not have attained equilibrium.

Based on the Fe(II)/Fe<sub>tot</sub> ratios of samples, where measured, from the western site, and according to measured  $E_H$  values, Fe(II) is the dominant Fe species in the western site and is likely dominant in the eastern site also. The western site has higher As(III)/As<sub>tot</sub> ratios (median:  $\sim 0.8$ ) than the eastern site ( $\sim 0.5$ ) (Table 1), which is also expected based on the measured  $E_H$  values. Concentrations and variability of all of the redox-sensitive solutes (NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, Fe, As, and Mn) were found to be highest within the upper  $\sim 50$  m bgl. All these solute concentrations decrease sharply with

depth (Fig. 6), possibly along natural vertical flow paths in local flow cells (Ravenscroft, 2003) or induced flow paths caused by pumping (Mukherjee et al., 2007). However, some deep ( $>200$  m) samples from the eastern site have Fe, Mn and SO<sub>4</sub><sup>2-</sup> concentrations, which indicate a return to metal mobilization (less reducing) conditions at those depths or mixing of groundwater from different sources. This finding is critical for evaluation of sustainability of deeper groundwater at this site, and needs detailed future sampling of the deep water. HS<sup>-</sup> was detected in the eastern site at five locations within 60 m bgl, but was not detected in the western site. Elevated concentrations of CH<sub>4</sub> were detected in several locations of the western site and were found to increase with depth. CH<sub>4</sub> was not measured in eastern site, but there are some reports of its detection in adjoining areas (e.g. Ahmed et al., 1998).

## 5.2. Chemical dynamics and multivariate relationships

### 5.2.1. Thermodynamic calculations

Saturation index calculations for groundwater from both western site and eastern site show higher-than-atmospheric  $P_{CO_2}$  values (Fig. 7). High groundwater  $P_{CH_4}$  values relative to atmospheric values in the western site suggest active methanogenesis. Groundwater at both sites is generally near equilibrium with respect to carbonate phases

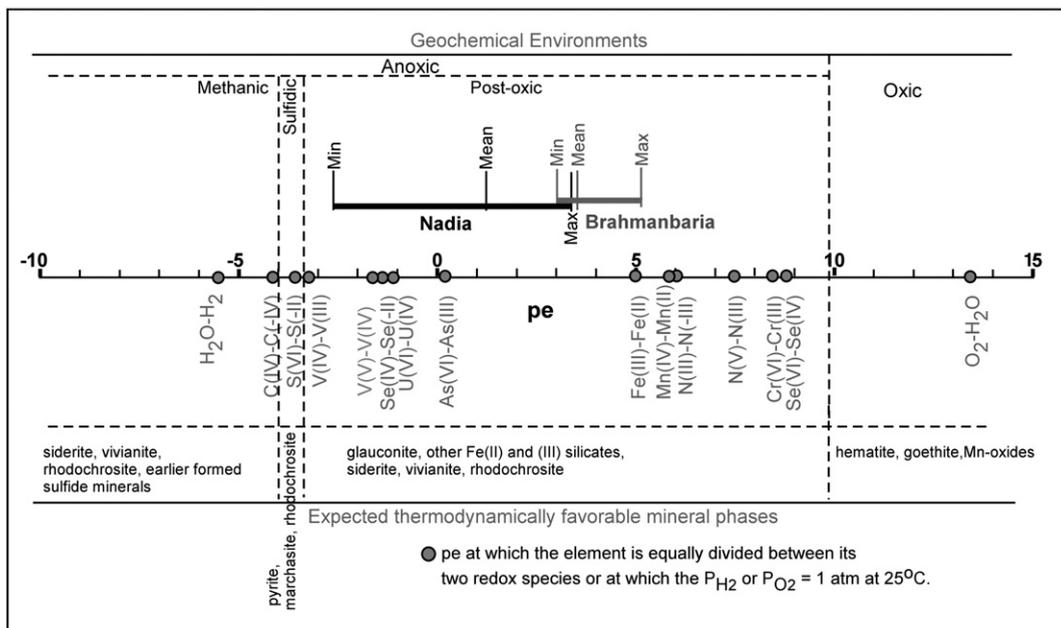


Fig. 5. Plot of range of  $p_e$  (calculated from observed Eh values) for Nadia and Brahmanbaria in comparison to the equilibrium points of the various redox couples as documented by Parkhurst et al. (1996). The plot also shows the relative position of the geochemical (redox) environments and some of the thermodynamically favorable mineral phases expected in them (after Berner, 1981).

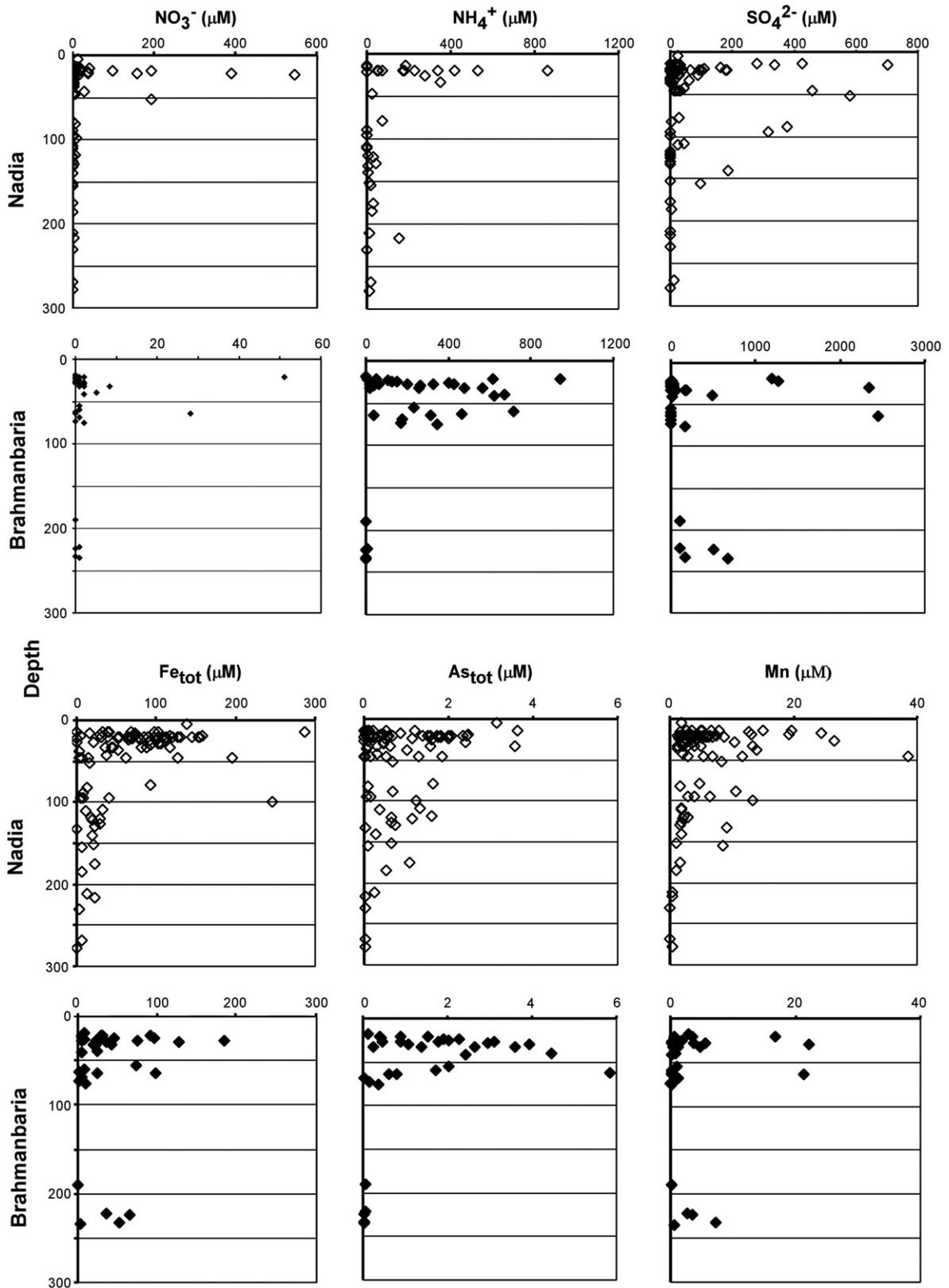


Fig. 6. Depth trends of redox-sensitive parameters for Nadia and Brahmanbaria. Please note that the x-axis of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are different between the two locations.

such as calcite ( $\text{CaCO}_3$ ) and dolomite ( $\text{MgCa}(\text{CO}_3)_2$ ), suggesting that the high  $\text{HCO}_3^-$  values in Bengal Basin groundwater cannot be totally attributed to carbonate dissolution and may have a significant input from natural organic matter (NOM) oxidation (Ahmed et al., 2004).

Groundwater at both sites is highly undersaturated with respect to major As phases (e.g. arsenolite,  $\text{As}_2\text{O}_5$ , and  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ), similar to most studies and indicating that As should generally remain dissolved after mobilization. Groundwater is also highly undersaturated with respect to Mn oxide phases (e.g. birnessite, bixbyite, manganite, nsutite, and pyrolusite) and slightly undersaturated to near equilibrium with rhodochrosite ( $\text{MnCO}_3$ ). Mn may be removed from groundwater by precipitation of rhodochrosite or by incorporation as solid solutions in other carbonate minerals such as siderite, as expected in the postoxic environment (Fig. 5).

In both areas, there is no significant complexation of Fe with other inorganic anions and the principal aqueous species is  $\text{Fe}^{2+}$ . Groundwater is supersaturated with respect to magnetite ( $\text{Fe}_3\text{O}_4$ ), hematite ( $\text{Fe}_2\text{O}_3$ ), and goethite ( $\text{FeOOH}$ ) and slightly supersaturated to near equilibrium with ferrihydrite ( $\text{Fe}(\text{OH})_3$ ), indicating that precipitation of Fe(III) phases from groundwater is thermodynamically favorable. Detection of  $\text{HS}^-$  in some locations in the eastern site shows active  $\text{SO}_4^{2-}$  reduction, indicating possible sulfide precipitation (consistent with high SI values for sulfide phases) and sequestration of Fe (II) and other trace solutes such as As from groundwater.

### 5.2.2. Relationships among solutes

Statistical associations do not necessarily demonstrate cause–effect relationships; however, they allow to simultaneously evaluate variability of different parameters within a sample or suite of samples. Therefore, multivariate statistical results presented in this section should be regarded only as possible indicators of hydro-

geochemical evolution processes, which may or may not have any actual geochemical significance. PCA results for groundwater chemistry from the two sites show some complex relationships (Fig. 8). The first four factors explain a large percentage of the variance expressed by the data matrix (western site: 82.3%; eastern site: 74.3%). High factor loading in absolute values in the same axis may indicate a close relationship among the respective hydrochemical components (Stüben et al., 2003), whereas inverse loading between components may indicate lack of a relationship. The principal component (PC) 1 of the western site was expressed by very high loading of major solutes ( $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) probably resulting from water rock interaction. In contrast, in the eastern site, PC1 is dominated by positive loading of  $\text{As}_{\text{tot}}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{HCO}_3^-$  and DOC, and negative loading of  $\text{Ca}^{2+}$ ,  $\text{Fe}_{\text{tot}}$  and  $\text{Mn}^{2+}$ , which are generally associated with redox-dominated processes, with some input from mineral dissolution.  $\text{HCO}_3^-$  in the western site has a high to very high loading in the first two PCs, with an inverse relation to DOC in PC1 and a positive relation in PC2, indicating that  $\text{HCO}_3^-$  in the western site may have been introduced into groundwater both from oxidation of NOM and dissolution of detrital carbonates. However, in the eastern site, a positive relation between  $\text{HCO}_3^-$  and DOC in all four PCs, suggests an apparent genetic relationship. Elevated  $\text{NH}_4^+$  concentrations in groundwater at both sites may reflect dissimilatory nitrate reduction catalyzed by microbial degradation of NOM (and hence production of  $\text{HCO}_3^-$ ); thereby, also potentially subsequently mobilizing  $\text{PO}_4^{3-}$  (as shown by similar loading of  $\text{NH}_4^+$ , DOC, and  $\text{PO}_4^{3-}$ ). Some  $\text{NH}_4^+$  may also have been introduced into groundwater along with NOMs.

Although  $\text{Fe}_{\text{tot}}$  and Mn are correlated in both the western (Pearson Correlation  $r=0.47$ ) and eastern ( $r=0.63$ ) sites, there seems to be basic differences in the

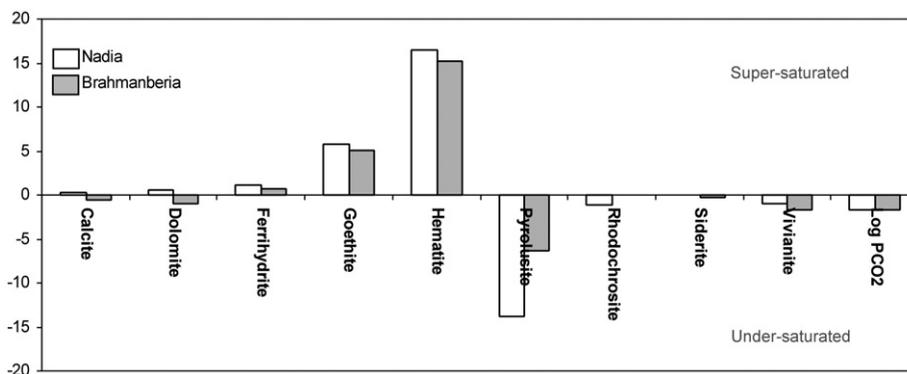


Fig. 7. Plot of mean saturation index (SI) values for Nadia and Brahmanberia.

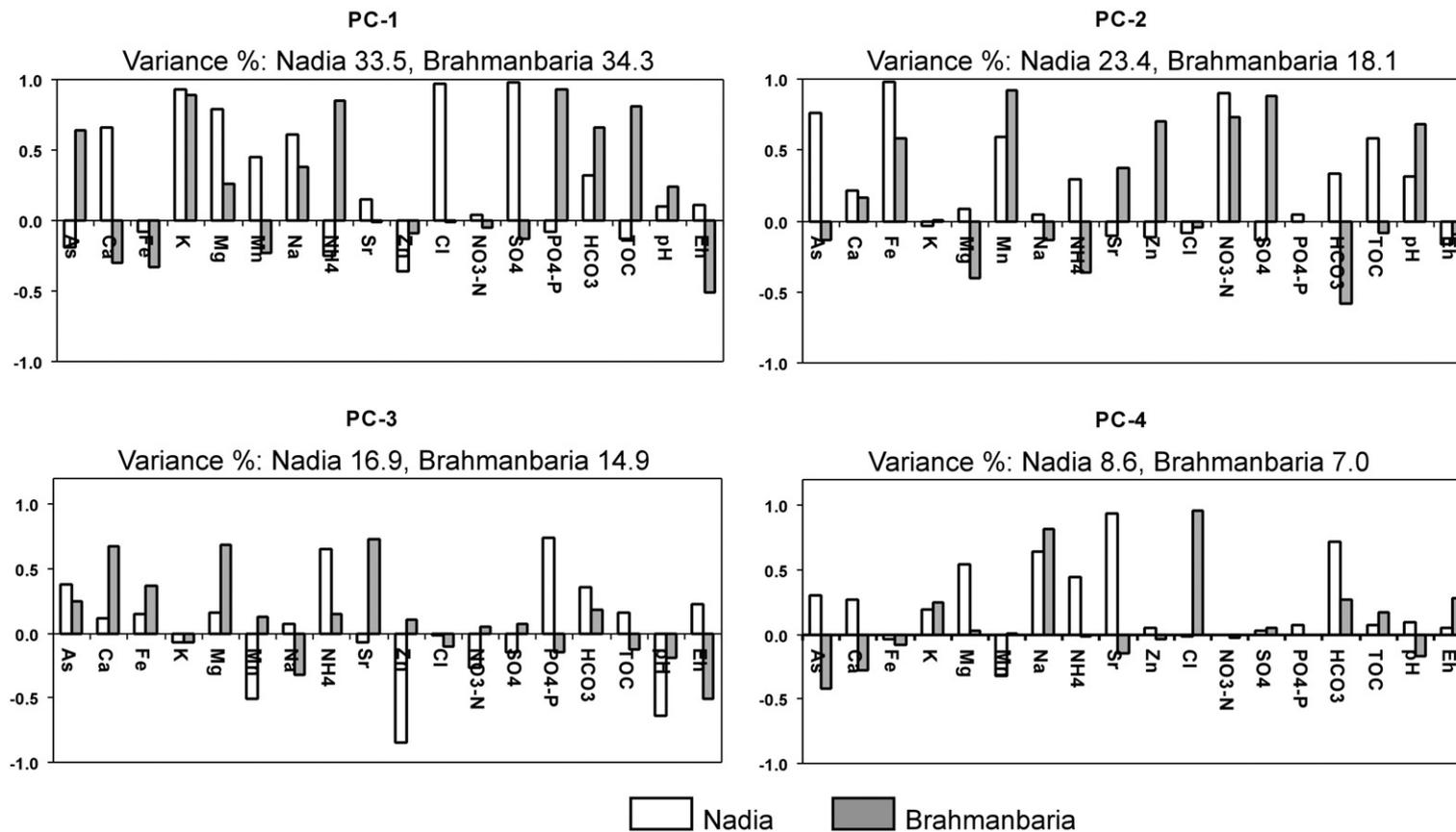


Fig. 8. Plot of the loading of the first four principal components obtained by PCA analyses of groundwater samples from Nadia and Brahmanbaria.

mobilization of Fe and Mn from source minerals and retention of those solutes in solution between the two sites.  $As_{tot}$  is strongly positively correlated with  $Fe_{tot}$  in the western site ( $r=0.81$ ) but weakly negatively correlated ( $r=-0.14$ ) with  $Fe_{tot}$  in the eastern site. Negative correlations between  $Fe_{tot}$  and  $HCO_3^-$  ( $r=-0.55$ ) and  $PO_4^{3-}$  ( $r=-0.23$ ) in the eastern site contrast with positive correlations ( $r=0.31$  and  $0.19$  respectively) in the western site. In the western site, Fe and Mn co-exist and are probably retained in solution once they are mobilized. In contrast, results from eastern site suggest non-conservative behavior of Fe and Mn, with possible precipitation of minerals like siderite, vivianite, and/or rhodochrosite. These minerals may act as a sink for  $Fe^{2+}$  and  $Mn^{2+}$  ions in anoxic groundwater with high  $HCO_3^-$  and  $PO_4^{3-}$  concentrations (e.g. Bhattacharya et al., 2002a).

### 5.3. Model of overlapping redox zonation and its effect on arsenic mobility

#### 5.3.1. Concept of redox zonation and equilibrium

Zonation of individual terminal electron accepting processes (TEAPs) during oxidation of organic matter (here simplified as  $CH_2O$ ) and their successive presence in sediments, proceeding from highest to lowest energy yield, have been invoked to explain occurrences of redox processes in sedimentary systems. These steps can be aggregated and summarized as (after Berner, 1981, Postma and Jakobsen, 1996, and Stumm and Morgan, 1996):

- $O_2 + CH_2O$  (organic matter)  $\rightarrow CO_2 + H_2O$  (aerobic respiration, free energy change:  $-475$  kJ/mol  $CH_2O$ )
- $4NO_3^- + 5CH_2O \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$  (denitrification,  $-448$  kJ/mol  $CH_2O$ )
- $NO_3^- + 2CH_2O + 2H^+ \rightarrow NH_4^+ + 2CO_2 + H_2O$  (dissimilatory nitrate reduction,  $-368$  kJ/mol  $CH_2O$ )
- $2MnO_2 + 3CO_2 + H_2O + CH_2O \rightarrow 2Mn^{2+} + 4HCO_3^-$  (Mn(IV)-reduction,  $-349$  kJ/mol  $CH_2O$ )
- $4Fe(OH)_3 + 7CO_2 + CH_2O \rightarrow 4Fe^{2+} + 8HCO_3^- + 3H_2O$  (Fe(III) reduction,  $-114$  kJ/mol  $CH_2O$ )
- $SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^-$  (sulfate reduction,  $-77$ )
- $2CH_2O \rightarrow CH_4 + CO_2$  (methanogenesis,  $-58$  kJ/mol  $CH_2O$ )

Likewise, processes have been classified into redox environments (e.g. oxic, postoxic, sulfidic, and methanic (Berner, 1981; Stumm and Morgan, 1996; Postma and Jakobsen, 1996) (Fig. 5). The reaction steps are initiated by fermentation of organic molecules like acetate and formate, with production of  $HCO_3^-$  and low energy yield

(Chapelle, 1993). Fermentation products are subsequently consumed by the TEAPs to continue the reaction steps along the groundwater flowpath (Potsma and Jakobsen, 1996). Such examples of redox zonation have been widely reported (e.g. Park et al., 2006). However, in a rate-limited fermentative system with TEAP steps faster than fermentative steps, the sequence of TEAPs and their related reactions may not be predictable, and the system would be in partial redox equilibrium (Postma and Jakobsen, 1996). This may be promoted by fast inorganic reactions between electron acceptors and reaction products, e.g. metal oxides and  $H_2S$  (Rickard, 1974). In such a fast reactive system, it is possible that redox zones overlap, and reactions can be concomitant (Jakobsen and Postma, 1999). In natural systems, partial equilibrium has been observed in several studies, e.g. Fe(III) reduction and methanogenesis (e.g. Berner, 1981),  $SO_4^{2-}$  reduction and methanogenesis (e.g. Parkes et al., 1990),  $SO_4^{2-}$  and Fe(III) reduction (e.g. Canfield et al., 1993), and Fe(III) reduction,  $SO_4^{2-}$  reduction and methanogenesis (e.g. Jakobsen and Postma, 1999). An extreme condition would be redox disequilibrium in an open system (e.g. Stefansson et al., 2005), where multiple redox zones would overlap, and oxidized and reduced species of the same element would co-exist.

#### 5.3.2. Effect of overlapping redox zonation on arsenic retention in solution

Given the measured postoxic conditions, relationships between As and other redox-sensitive or associated solutes (e.g. Fe(II), Mn,  $NH_4^+$ , DOC,  $PO_4^{3-}$ ,  $HCO_3^-$  etc.), and dominance of As(III) over As(V), microbial reduction of As(V) sorbed on surfaces of metal (Fe/Mn) oxyhydroxides in the sediments (Bhattacharya et al., 2006) seems to be the most plausible general mechanism for As mobilization in the present study areas and probably also in other parts of the Bengal Basin. However, the complex interactions among the (TEAPs) that result in initial liberation and subsequent retention of As in dissolved phases are not yet well understood.

In reducing systems, such as the aquifers in the present study areas, availability of both natural and/or anthropogenically-derived organic matter (OM) can play a critical role in regulating concentrations of As and other trace metals in solution. Results from the two sites show that DOC concentrations are highest in shallow parts of the aquifers and decrease sharply with depth (Fig. 3). OM is generally common in recent fluvio-deltaic sediments, and may also exist as DOC infiltrating with recharge water (Harvey et al., 2005) or as peat, which can produce  $CH_4$  (e.g. Ravenscroft et al., 2001). Although peat has been found in the southernmost districts of Bangladesh and West

Bengal (e.g. McArthur et al., 2004), it has not been found in the northern areas of the basin (e.g. western site). Similarly, surface-derived NOM is more plausible as a driver for local-scale reduction and As mobilization than at the basin scale. Most probably, NOM in the Bengal Basin [0.1–5% (Bhattacharya et al., 2002b)] occurs as dispersed phases (lighter organic macromolecules), probably deposited with the sediments and later dissolved. NOM can also be transformed to labile phases by acid consumption during Fe (III)-oxide reduction (Jackobsen and Postma, 1999). However, because of the lack of sediment data in this study, it was not possible to deduce the amount and source of NOM in aquifer sediments available for oxidation.

High concentrations of  $\text{HCO}_3^-$  (up to 12,000  $\mu\text{M}$ ) in Bengal Basin groundwater warrant are commonly thought to result from NOM oxidation and lower  $\text{HCO}_3^-$  concentrations are thought to suggest less evolved groundwater (e.g. in deep aquifers of Bangladesh (Zheng et al., 2004)). However,  $\text{HCO}_3^-$  in Bengal Basin groundwater can also be produced by carbonate dissolution or silicate weathering (Mukherjee, 2006). Comparison of depth profiles of  $\text{HCO}_3^-$  and DOC in the western site (Fig. 3) suggests that they may be related at depths  $< \sim 50$  m. However, the sharp decrease in DOC, in contrast to the steady concentration

of  $\text{HCO}_3^-$  ( $\sim 6000$  to  $8000$   $\mu\text{M}$ ), and enrichment in  $\delta^{13}\text{C}_{\text{DIC}}$  (Mukherjee, 2006) suggest that NOM oxidation is not the sole  $\text{HCO}_3^-$  producing process. On the other hand, in the eastern site,  $\text{HCO}_3^-$  and DOC trends seem to track each other, suggesting the dominance of NOM oxidation. PCA results also support these observations. At various locations in the western site,  $\text{HCO}_3^-$  concentrations may also be limited by reduction to  $\text{CH}_4$ , although methanogenesis can also result from acetate fermentation (e.g. Hansen et al., 2001).

At equilibrium, redox reactions would be expected to segregate with distance along lateral and vertical flow paths. However, occurrence of highest concentrations of various redox-sensitive solutes within  $\sim 50$  m bgl indicates that reactions such as dissimilatory nitrate reduction [ $\text{NH}_4^+$  ( $\geq 1000$   $\mu\text{M}$ ), Table 1] and mobilization of metals and metalloids [Mn (up to 86  $\mu\text{M}$ ), Fe (up to 286  $\mu\text{M}$ ), As (up to 6  $\mu\text{M}$ ), Table 1] occur at shallow depths. The co-existence of various solutes with increasing depth [e.g.  $\text{SO}_4^{2-}$  (up to 4800  $\mu\text{M}$ , Table 1), Mn, Fe, As,  $\text{HS}^-$  (in the eastern site) and  $\text{CH}_4$  (in the western site)] further supports the idea of overlapping redox zones. Fig. 9 shows schematically how this could occur as a function of depth in both the study areas.

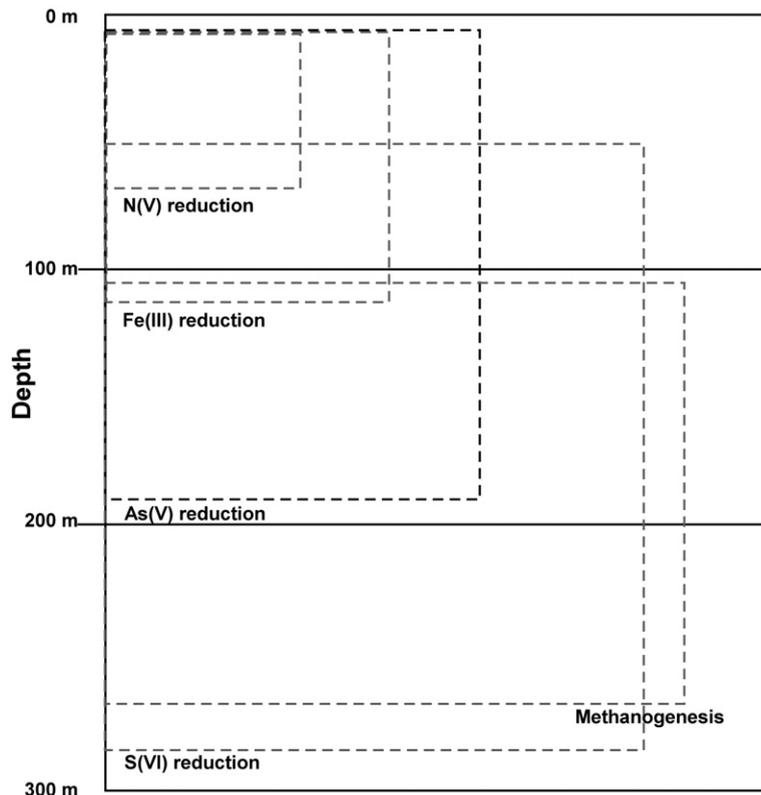


Fig. 9. Conceptual plot of the relative depths of the redox zones as observed from the trends of solutes in the two study areas.

Formation of arsenian pyrite within metal-reducing zones, which has been found at ~80 m depth in West Bengal (Das et al., 1995), is consistent with partial redox equilibrium.

In such a system, As is liberated by reductive dissolution of metal oxides and hydroxides. Once mobilized, As is retained in solution except to the extent that it is sequestered by other phases. Remnant Mn(IV) or Fe(III) oxides, which might re-adsorb some of the As from partially reduced HFOs (McArthur et al., 2004), would also be sequentially and/or simultaneously reduced, thereby remobilizing the As as As(III). Formation of authigenic Fe sulfides could partially scavenge the As, depending on the initial  $\text{SO}_4^{2-}$  concentrations (e.g. Lowers et al., 2007), thus regulating the concentration of As in the aquifer (Kirk et al., 2004). Arsenic exists in solution, even in sulfidic and methanogenic zones of the aquifers in the Bengal Basin, because of partial redox equilibrium and the possibility of limited  $\text{SO}_4^{2-}$  availability in deeper groundwater. Even in the presence of FeS, As(III) will have a lesser tendency to sorb and would behave more conservatively than As(V) (Wolthers et al., 2005). Moreover, introduction of small concentrations of  $\text{O}_2$  (e.g. as a result of pumping) could locally re-oxidize some of the sediments and hence re-liberate As sequestered in authigenic pyrite. Thus the presence of As in groundwater in different parts of the Bengal Basin (e.g. in the western site and eastern site) cannot be explained merely by mobilization mechanisms, but may also be a function of retention (and potential remobilization) mechanisms.

## 6. Conclusions

Hydrogeochemical comparison of groundwater chemistry in two geologically divergent sub-basins near the western margin (Nadia, Bhagirathi sub-basin, West Bengal) and the eastern margin (Brahmanbaria, Meghna sub-basin, Bangladesh) of the Bengal Basin was done to understand the controls of As occurrence in groundwater. Results shows that groundwater in the western site is mostly Ca– $\text{HCO}_3$  facies, while that in the eastern sub-basin consists of 6 different facies. Depth profiles of major solutes (Na, Ca and  $\text{HCO}_3^-$ ) show different trends in the two sub-basins; however, redox-sensitive solutes in both areas tend to behave similarly, strongly decreasing in concentration with depth, which suggests similarity in the redox processes along vertical flowpaths. In the eastern site, concentrations of Mn, Fe, and  $\text{SO}_4^{2-}$  in deeper aquifers are greater than in the western site, which may result from differences in hydrostratigraphy between the two sites.

Because As mobilization is mostly controlled by redox-dependent reactions, understanding these reactions in the two study areas is important. Field parameters and laboratory analyses suggest that the groundwater in both areas occurs under reducing (postoxic) conditions. Fe(II) and As(III) are the dominant Fe and As species in the groundwater. Field measurements, solute trends, multivariate statistical analyses and saturation index calculations suggest that As is liberated primarily by reductive dissolution of metal oxides in a microbially mediated environment with organic matter acting as the major electron acceptor, which is consistent with results from previous studies in the Bengal Basin. Spatial trends of different redox-sensitive solutes (e.g. Fe, Mn, As,  $\text{SO}_4^{2-}$ ,  $\text{CH}_4$ ) indicate the existence of concomitant redox processes at various depths suggesting an environment with overlapping redox zones (e.g. nitrate reduction, metal reduction, sulfate reduction, and methanogenesis) and can be best explained by a partial redox equilibrium model. Thus, As, once liberated from adsorbed solid phase would tend to remain in solution, and would not be sequestered even in highly reducing conditions.

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