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Redox Zonation and Oscillation in the Hyporheic Zone of the Ganges-Brahmaputra-Meghna Delta: Implications for the Fate of Groundwater Arsenic during Discharge

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Abstract

Riverbank sediment cores and pore waters, shallow well waters, seepage waters and river waters were collected along the Meghna Riverbank in Gazaria Upazila, Bangladesh in Jan. 2006 and Oct.-Nov. 2007 to investigate hydrogeochemical processes controlling the fate of groundwater As during discharge. Redox transition zones from suboxic (0-2 m depth) to reducing (2-5 m depth) then suboxic conditions (5-7 m depth) exist at sites with sandy surficial deposits, as evidenced by depth profiles of pore water ($n=7$) and sediment ($n=11$; diffuse reflectance, Fe(III)/Fe ratios and Fe(III) concentrations). The sediment As enrichment zone (up to ~ 700 mg kg⁻¹) is associated with the suboxic zones mostly between 0-2 m depth and less frequently between 5-7 m depth. The As enriched zones consist of several 5 to 10 cm-thick dispersed layers and span a length of ~ 5 -15 m horizontally from the river shore. Depth profiles of riverbank pore water deployed along a 32 m transect perpendicular to the river shore show elevated levels of dissolved Fe (11.6 ± 11.7 mg L⁻¹) and As (118 ± 91 μ g L⁻¹, mostly as arsenite) between 2-5 m depth, but lower concentrations between 0-2 m depth (0.13 ± 0.19 mg L⁻¹ Fe, 1 ± 1 μ g L⁻¹ As) and between 5-6 m depth (1.14 ± 0.45 mg L⁻¹ Fe, 28 ± 17 μ g L⁻¹ As). Because it would take more than a few hundred years of steady groundwater discharge (~ 10 m yr⁻¹) to accumulate hundreds of mg kg⁻¹ of As in the riverbank sediment, it is concluded that groundwater As must have been naturally elevated prior to anthropogenic pumping of the aquifer since the 1970s. Not only does this lend unequivocal support to the argument that As occurrence in the Ganges-Brahmaputra-Meghna Delta

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groundwater is of geogenic origin, it also calls attention to the fate of this As enriched sediment as it may recycle As into the aquifer.

Keywords

Arsenic; Meghna River; Groundwater discharge; Redox transition; Arsenic trapping

1. INTRODUCTION

Studies of hydrological and biogeochemical interactions in near-shore subsurface zones surrounding surface water bodies, the so-called hyporheic zones have illuminated the dynamics and fate of chemical and biological contaminants. In particular, the natural biogeochemical abilities of the near-shore zones to regulate and to remediate groundwater pollutants entering the surface water environment have received considerable attention. Within the context of fresh surface waters (Stanford and Ward, 1988), hyporheic processes regulate sediment respiration rates (Naegeli and Uehlinger, 1997), attenuate nutrients (Clavero et al., 1999), influence riparian vegetation regimes (Lambs, 2004) and, more broadly ecological health (Young and Huryn, 1996). Within the context of saline surface waters in coastal areas (Charette and Scholten, 2008), chemical loading from groundwater discharge to coastal waters has important implications for eutrophication (Valiela et al., 1990; Slomp and Van Cappellen, 2004), coastal zone management, and global-scale understanding of element cycles (Burnett et al., 2006). Attenuation of elements such as Fe, Mn, P, Ba, U, Th, and As that are reactive with freshly precipitated Fe-oxides in hyporheic zones known as “iron curtains” has been identified by a series of studies at Waquoit Bay (Charette and Sholkovitz, 2002; Charette et al., 2005; Bone et al., 2006; Charette and Sholkovitz, 2006). These studies underscored the role of geochemical processes in modifying chemical fluxes in groundwater discharge. Investigation of the behavior of As in hyporheic zones of Waquoit Bay has shown trapping of As by the “iron curtain” at ~1 m depth in the sediment (Bone et al., 2006; Jung et al., 2009). Recent studies have also reported that groundwater As is naturally immobilized by Fe(III) oxides formed in the hyporheic zone where groundwater interacts with lake water or stream water, and the removal of dissolved Fe and As varies seasonally depending on the hydrologic condition (Lee et al., 2014; MacKay et al., 2014; Baken et al., 2015). However questions remain regarding how aquifer heterogeneity influences the magnitude of the geochemical attenuation during discharge (Burnett et al., 2006).

The hydrological and biogeochemical processes resulting in elevated As content in shallow groundwater of the Ganges-Brahmaputra-Meghna Delta (GBMD) have been extensively investigated for more than a decade (Nickson et al., 1998; Harvey et al., 2002; Horneman et al., 2004; McArthur et al., 2004; Zheng et al., 2004; Polizzotto et al., 2005; Charlet and Polya, 2006; Stute et al., 2007; van Geen et al., 2008; Polya and Charlet, 2009; Fendorf et al., 2010; Mladenov et al., 2010; Neumann et al., 2010; Mailloux et al., 2013). There is broad consensus that microbial reduction of Fe(III) oxides containing As results in the mobilization of As into the dissolved phase in the presence of labile organic carbon, while the source of organic carbon and the impact of human activities on the enrichment of As in

groundwater still remain controversial. In addition, the vulnerability of low-As Pleistocene aquifer subject to various groundwater pumping scenarios has been extensively evaluated (Stollenwerk et al., 2007; Dhar et al., 2011; Radloff et al., 2011). The “discharge” of shallow groundwater through irrigation pumping and its associated risks of seasonal accumulation and release of As in rice paddy fields have also caught considerable attention (van Geen et al., 2006b; Dittmar et al., 2007; Roberts et al., 2007; Roberts et al., 2010). However, what happens to the groundwater As during discharge to rivers and its implications for As cycling in the GBMD are only beginning to be understood (Datta et al., 2009; Jung et al., 2012). Enrichment of As in shallow subsurface riverbank sediment along the Meghna River has been attributed to redox trapping of groundwater As by Fe(III) oxyhydroxides precipitated in the hyporheic zone during the dry season when the hydraulic gradient drives groundwater flow from the aquifer to the river (Datta et al., 2009; Jung et al., 2012). However the spatial and temporal variations in groundwater As trapping and sediment As enrichment along the Meghna Riverbank have not been addressed.

To evaluate the spatial variability and heterogeneity in the redox trapping of groundwater As in the hyporheic zone of GBMD, a comprehensive suite of depth profiles of riverbank pore water and sediment samples, as well as shallow well groundwater, river water, and seepage water samples were obtained along the Meghna River in January 2006 (the middle of the dry season) and October–November 2007 (the beginning of the dry season). The characteristics and efficiency of the natural reactive barrier in a heterogeneous deltaic flood plain, as well as the role of the reactive barrier in attenuating the chemical fluxes of reactive elements and its implications on the geogenic nature of As occurrence and cycling in GBMD aquifer are discussed.

2. MATERIALS AND METHODS

2.1. Study Area

The study area is located in Gazaria Upazila (23.6 °N and 90.6 °E) approximately 25 km southeast of Dhaka, Bangladesh (Fig. 1). Shallow groundwater (<25 m) from the southern GBMD aquifers is typically reducing with high dissolved Fe and As concentrations (BGS&DPHE, 2001; Zheng et al., 2004) (Fig. 1). In the GBMD, a distinct seasonal pattern of groundwater recharge and discharge has been inferred from several meters of seasonal water table fluctuation (BGS&DPHE, 2001; Zheng et al., 2005; Harvey et al., 2006; Stute et al., 2007). With the onset of the monsoon starting in late April, a rise of river level drives a rapid rise in groundwater table, resulting in little hydraulic gradient between the river and the shallow aquifer during the wet season. Following the end of the monsoon in late October, river water level rapidly declines while groundwater level declines at a slower rate, resulting in a hydraulic gradient that drives groundwater discharge during the dry season from November to April (Fig. 2A). The combination of substantial hydraulic gradient in the dry season and a heterogeneous sedimentary environment in a flood plain that has locations where sandy sediments are exposed near surface (Aziz et al., 2008; Weinman et al., 2008) results in considerable groundwater discharge.

The Meghna Riverbank study area (Fig. 1B) was chosen for two reasons. First, groundwater As and Fe are elevated, averaging $192 \pm 112 \mu\text{g L}^{-1}$ and $3.81 \pm 4.56 \text{ mg L}^{-1}$ in existing

shallow wells (< 30 m; n=5) (BGS&DPHE, 2001). Second, our previous study has found highly enriched sediment As along the Meghna Riverbank (Datta et al., 2009). Sites along the Meghna River lie in an area that is 0-3 m above sea level, and are subject to annual flooding and daily tide with amplitude of ~0.5 m (Barua, 1990; Goodbred and Kuehl, 2000; Zheng et al., 2005). The Meghna River plain consists of alluvial sediments with multiple layers of sand, silt, and clay. Usually below a few m thick surface clay and silt unit, the upper shallow aquifer of very fine to fine sand extends to 40-60 m depth below ground surface (Bibi et al., 2008).

2.2. Water Sample Collection

Sampling took place between Jan. 17 and Jan 25, 2006 and between Oct. 27 and Nov. 4, 2007. Four types of aqueous samples were collected: groundwater (n=22), riverbank pore water (very shallow groundwater, n=43), seepage water (n=5), and river water (n=9) (Fig. 1B).

Groundwater—Groundwater samples were collected from shallow tube wells with depth ranging between 14 and 24 m in villages located within ~10 km and ~1 km from the riverbank sampling sites in Jan. 2006 (n=11) and Oct.-Nov. 2007 (n=11), respectively. Water samples were collected after pumping continuously for 15-30 min until the temperature, conductivity, pH and ORP reading monitored by a HORIBA multiprobe (U22XD) had stabilized. Samples were not filtered but acidified to 1% HCl (Fisher Optima) for cation analysis, while not acidified for anion analysis.

Sediment pore water—Pore water samples were collected from ~1 to ~7 m depth using a “needle sampler” (van Geen et al., 2004) in Jan. 2006 at sites S (n=3) and J (n=8) and by a drive point piezometer system (Charette and Allen, 2006) in Oct.-Nov. 2007 at site J (n=32). Needle sampler was evacuated and attached to the extension rods, inserted into the PVC pipe after deepening the drill hole by the “hand-flapper” method to the desired depth, and then pushed into the sediment. Pore water and some sediment collected in the evacuated chamber through the long needle was immediately filtered through a 0.45 µm membrane filter (Whatman), and acidified to 1% HCl (Fisher Optima) in 20 mL scintillation vials (Wheaton Science).

A total of 7 pore water profiles with a depth resolution of 0.2-1.0 m were obtained from ~1 to ~6 m depth at 5 locations of site J (Fig. 1) along a ~30 m transect perpendicular to the shore using a stainless steel drive point piezometer system (“Retract-A-Tip”, AMS Inc). At each depth, water was drawn to the surface through acid-cleaned nylon tube using a peristaltic pump at a flow rate of 500 mL min⁻¹. After a minimum 3-fold flushing of the tube volume and stabilization of the readings of the oxidation reduction potential (ORP), pH, dissolved oxygen, and temperature monitored by a YSI 600XLM in a flow cell (YSI Inc), samples filtered through an inline 0.45 µm Pall AquaPrep 600 filter were collected in 20 mL acid-cleaned high-density polyethylene (HDPE) liquid scintillation vials (Wheaton Science). An aliquot of water was also inline filtered through an As speciation cartridge packed with 2.5 g of aluminosilicate adsorbent (Meng et al., 2001; Hug et al., 2008) to separate As(III) from As(V).

Seepage water—Discharging groundwater (n=5) was collected in a thin-walled plastic bag attached to a seepage meter through a quick-connect fitting. See section 2.6 for methods of seepage meter construction and deployment. After deployment of ~3-5 hours during the receding tide, the seepage water from the bags was filtered through a 0.45 μm membrane filter into two 20-mL scintillation vials for cation (acidified to 1% HCl) and anion (not acidified) analyses.

River water—River water samples were collected in 20 mL scintillation vials for cation (acidified to 1% HCl) and anion (not acidified) analyses after filtration through a 0.45 μm membrane filter on a boat. Temperature, pH, conductivity, and ORP were measured using a HORIBA or YSI multiprobe.

2.3. Water Analysis

Field test—Dissolved oxygen (DO) was measured with a CHEMet kit (Chemetrics), and alkalinity was determined by Gran titration (Gran, 1952) using 120-180 mL of sample. Immediately after groundwater or pore water sample collection without acidification in the field, dissolved Fe(II) was measured by a ferrozine colorimetry method (Stookey, 1970).

Laboratory analysis—Concentrations of dissolved As(III), As, P, Fe, Mn, S, Sr, Ba, Ca, Mg, K, Na, Si were determined by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICP-MS) (Cheng et al., 2004). The method has a detection limit of ~0.1 $\mu\text{g L}^{-1}$ for As. For quality assurance, one or more laboratory control samples (LDEO) or NIST 1643E were included with each run. The results are within 5 to 10% of the long-term averages of LDEO or NIST 1643E for As, P, Fe, Mn, S, and other major ions. Anions (F^- , Cl^- , Br^- , NO_2^- , NO_3^- and SO_4^{2-}) were measured by Ion Chromatography (Dionex DX500) following a standard EPA protocol.

2.4. Sediment Core Collection

Between January 17 and 25 in 2006, a total of 13 riverbank sediment cores were obtained from the surface to 7 m depth at 4 different locations, where the surface of the riverbank was covered with either a sandy layer or a silty clay layer (Fig. 1B). At sites J and S with sandy surface deposit, 3 transects of sediment cores (RS20-RS21-RS19-RS34 at site J, RS16-RS30-RS31 and RS17-RS33 at site S) were collected from upland to river shore within a distance of 25 m from the river shore. Sediment cores have 0.3-0.6 m depth resolution at shallower depth (< 1 m) and ~1.0-1.5 m depth resolution at deeper depth (> 1 m). The cores were retrieved by a soil recovery probe (AMS Inc., USA) consisting of a probe (1.9 cm diameter and 30.5 cm length), extension rods (60 cm each section), and a slide hammer. Before collecting a sediment core sample at any depth, a drill hole was deepened with a 5-cm diameter PVC pipe using the so-called “hand-flapper” method used by the local drillers (Horneman et al., 2004). After washing the hole, the soil probe with a plastic liner connected to the extension rods was inserted in the PVC pipe and hammered into the sediment. The probe was then raised, the plastic liner with core immediately capped and stored in a Mylar bag with oxygen absorbents (SorbentSystems) and kept on ice. After returning from the field and sub-sampling of a small amount of sediment for field analyses of HCl-leachable Fe(III)/Fe, P, and As, the Mylar bags with core sections and oxygen absorbents were flushed

with N₂ and then placed in a second Mylar bag with oxygen absorbent flushed with N₂. Finally, samples in the Mylar bags were stored on ice upon returning to the United States, and then stored at 4°C prior to analysis.

2.5. Sediment Analysis

A suite of analyses including diffuse reflectance and Fe(III)/Fe ratios, As and P concentrations in HCl leachate of sediment was carried out either immediately after sampling in the field or at night on the same day of the sediment core collection. A few grams of sediment were extruded from the liner and homogenized aliquots of appropriate sizes were used for analyses.

Diffuse reflectance—An aliquot of ~1 g of sediment was wrapped with clear polyethylene cling-wrap (Glad, USA) and the diffuse reflectance spectrum was measured in triplicate using a CM 2005d spectrophotometer (Minolta Corp., USA) according to established methods (Horneman et al., 2004).

Fe(III)/Fe ratio in HCl leach—A second aliquot of ~1 g of wet sediment was weighed and placed in a 15 mL centrifuge tube (Corning) to which 10 mL of 1.2 N HCl was added. The sample tube was placed in a hot water bath (~80°C) for 1 hour and was shaken intermittently. A 10 µL aliquot of supernatant leachate was added to a 1% HCl solution containing 0.1 g of Ferrozine/L and buffered to pH ~5 with acetic acid and ammonia to determine Fe(II) concentration. Another 10 µL of aliquot of leachate was added to the same solution in which 2 g L⁻¹ of the hydroxylamine hydrochloride was also added to determine total Fe concentration (Stookey, 1970; Viollier et al., 2000). Concentrations of Fe(II) and total Fe in the leachate were determined by the absorbance reading at 562 nm using a portable single-beam Hach DR 2010 UV-Vis spectrophotometer with a 1-cm cell. The concentration of Fe(III) in the leachate was determined by the difference between total Fe and Fe(II) concentrations. The hot HCl leaches reactive phase of Fe and adsorbed or coprecipitated elements from amorphous and relatively labile crystalline Fe oxyhydroxides (Horneman et al., 2004).

As and P in HCl leachate—Concentrations of As and PO₄ in the same HCl leachate were determined in Bangladesh following the protocols of Dhar et al (2004) with slight modifications (Dhar et al., 2004). The HCl leachate was diluted 100 times before analyses. The absorbance of arsenomolybdate and phosphomolybdate complex at 880 nm was read on a spectrophotometer (Hach DR 2010) with a 1-cm cell. Thus the detection limit is 10 mg kg⁻¹ for P and 5 mg kg⁻¹ for As, respectively. The leachates were filtered through 0.45 µm filters and returned to US for further analyses of Mn, S, P, and As by HR ICP-MS (Cheng et al., 2004).

Grain size—Approximately 3 g of sediment was pre-treated with 10 mL of 10% HCl at 25 °C for 10 minutes to remove inorganic carbonate. After careful washing of samples with distilled water and drying at 60°C for 12 hours, sediment was washed through a 63 µm stainless steel sieve to separate sand particles from silt and clay particles (Sheldrick and Wang, 1993).

High-depth-resolution sediment core analysis—Three sediment cores (RS30, RS33 and RS34) of 1.2–6 m length was extruded and homogenized over ~2 to 5 cm interval for bulk As concentration measurement by an Innov-X alpha series environmental analyzer, a handheld X-ray Fluorescence (XRF) spectrometer with a detection limit of ~10 mg kg⁻¹ of As. Approximately 10 g of homogenized sediment was wrapped with clear polyethylene cling-wrap (Glad, USA), and a consistent sample thickness (~1 cm) was maintained for each measurement (measurement time: 300 seconds). A USGS shale SDO-1 with a reported As concentration of 68.5 mg kg⁻¹ gave a value of 68 ± 14 mg kg⁻¹ (n=4). Bulk concentrations of Fe, Mn, Sr, Zr and Ba were also determined. In general, the handheld XRF measurements were within <20% of certified concentrations of Fe, Mn, As, Sr, Zr, and Ba for USGS reference sample, SDO-1.

2.6. Seepage meter deployment

Six seepage meters were constructed by cutting 55-gallon plastic drums (diameter: 60 cm) to be 20 cm in height and by drilling a 2.2-cm vent hole on top of the drum (Lee, 1977). Several meters are deployed ~5 m away from the river shore, arranged in a line parallel to shore with the distance between meters being ~5 m. A total of 19 deployments were made between Oct. 31 and Nov. 4, 2007. The vent hole was left open initially during deployment into the riverbed sediment for quick equilibration of pressure with the water, and then a thin plastic bag was attached via a quick-connect fitting to collect discharging groundwater. Each bag was pre-filled with 1 L of river water to prevent under-filling (Shaw and Prepas, 1989) and to allow for measurement of inflow to the sediments. The bags were collected after deployment of ~3–5 hours during the receding tide, and the change in water volume over the deployment period was measured using a 500 mL or a 2000 mL cylinder.

2.7. Aqueous geochemical equilibrium modeling

Saturation indices (SI) of Meghna Riverbank pore water with respect to calcite, hydroxyapatite, rhodochrosite, siderite, and vivianite were calculated using Visual MINTEQ (version 2.53) (Gustafsson, 2007) (see Appendix 1 for thermodynamic database).

3. RESULTS

3.1. Groundwater Discharge

A hydraulic gradient is estimated to be 0.01 ± 0.004 based on the average head difference of 0.50 ± 0.20 m during the dry season between November and April for three years along 50 m distance from a groundwater monitoring station (MUN002) to Meghna River (river level monitoring station: SW275-5, Figs. 1B and 2A). Based on this gradient and a representative hydraulic conductivity (K) value of ~15 m d⁻¹ for fine sand aquifers in GBMD (BGS&DPHE, 2001), the groundwater discharge rate on an annual basis is estimated to be ~27 m y⁻¹ although much of the actual discharge occurs primarily during the dry season. On average, daily groundwater discharge rate based on 19 deployments of seepage meters in Oct. 31–Nov. 4, 2007 is 6.1 ± 1.8 cm d⁻¹. Assuming the same discharge rate for the 6-month dry season, annual groundwater discharge rate is estimated to be 11 ± 3 m y⁻¹ (Fig. 2B and Appendix 2).

3.2. Properties of Riverbank Sediment

In the study area, the surface of riverbank sediment was covered with either a fine grained silty-clay layer or a sand layer. Visual inspection revealed that the riverbank sediment cores of RS14 and RS15 (Fig. 1) consisted of silty-clay layer between the surface and ~1.5 m depth and sand layer between ~1.5 m and ~6 m depth. In contrast, sediment cores from sites S and J are comprised primarily of sand (about 60-100%; Appendix 6) from the surface to ~7 m depth.

Sediment cores of RS 14 and 15 displayed neither obvious redox transition nor HCl leachable sediment As enrichment (Fig. 3 and Table 1). Vertical profiles of HCl-leachable and bulk sediment As, reflectance, sediment Fe(III) concentrations and Fe(III)/Fe ratios reveal that sites S and J with sandy surface layers display a strong redox gradient between 0–2 m depth with significant sediment As enrichments (Fig. 3 and Table 1).

Reflectance—It has been reported that sediment reflectance (R), the first derivative transformation of the diffuse reflectance at 520 nm, usually shows an inverse correlation with the sediment Fe(II)/Fe in HCl leachates (Horneman et al., 2004; van Geen et al., 2006a). For sediments from sites S and J, the reflectance rapidly decreases from 0.34 ± 0.16 ($n=25$) at the shallowest depth interval between 0 and 1 m to 0.21 ± 0.11 ($n=12$) for depth interval between 1 and 2 m, and remains low with 0.14 ± 0.08 ($n=17$) between 2 and 5 m depth and 0.18 ± 0.12 ($n=9$) between 5 and 7 m depth (Table 1 and Fig. 3). This decrease corresponds with shallow brown sediments becoming increasingly gray or black with depth.

Iron and Manganese—Consistent with the depth profiles of R , sedimentary Fe(III)/Fe ratio at sites S and J decreases from 0.52 ± 0.23 ($n=25$) between 0-1 m depth, to 0.37 ± 0.20 ($n=12$) between 1-2 m depth, and then to 0.24 ± 0.12 ($n=17$) between 2-5 m depth, while it increases slightly to 0.28 ± 0.15 ($n=9$) between 5-7 m depth. The variation of sedimentary Fe(III)/Fe ratios with depth corresponds to the variation of HCl leachable Fe(III) concentrations (Fig. 3 and Table 1). Depth trend in HCl-leachable total sedimentary Fe concentrations (average 1.05 ± 0.38 wt. %, $n=63$) is however not observed (Fig. 3). These Fe contents leached by hot 1 N HCl for 1 hour are lower than Fe contents of As-enriched Holocene alluvial sediments (2.9-12.8 wt. % Fe) leached by cold 0.5 N HCl (Breit et al., 2004), but higher than those from reducing Holocene aquifer sediment (< 0.5 wt. %) extracted using cold 1 N HCl for 1 hour or 0.2 M oxalate for 2-4 hours (BGS&DPHE, 2001; Ahmed et al., 2004; Swartz et al., 2004). Depth profiles of RS14 and RS15 sediment cores show lower Fe(III)/Fe ratios and Fe(III) concentrations but similar total Fe content compared to sediments from sites S and J (Table 1).

Concentrations of Fe and Mn are correlated (Fig. 4). First, bulk sedimentary Fe and Mn concentrations determined by hand-held XRF are correlated for three sediment cores (RS30, 33, and 34, $n=112$) from sites S and J (Fig. 4A). The bulk Fe and Mn concentrations are on average 2.1 ± 0.6 wt.% and 372 ± 103 mg kg⁻¹, respectively, and have a similar Mn to Fe molar ratio (0.018 ± 0.003) to that in the HCl-extract (0.022 ± 0.004). The HCl-extractable Fe and Mn concentrations in 7 sediment cores (RS16, 17, 19, 20, 21, 30, and 33; $n=38$) from sites S and J are strongly correlated (Fig. 4B). For suboxic sediments with Fe(III)/Fe > 0.3 ,

HCl-leachable Mn correlates better with HCl-leachable Fe(III) ($R^2 = 0.90$, $n=26$) than with Fe(II) ($R^2 = 0.19$) (Fig. 4C). For reducing sediments with Fe(III)/Fe < 0.3, HCl-leachable Mn correlates better with Fe(II) ($R^2 = 0.76$, $n=12$) than with Fe(III) ($R^2 = 0.07$) (Fig. 4D).

Arsenic—The HCl leachable As is significantly higher at depth < 2 m or 5-7 m depth than at 2-5 m depth at sites S and J (Table 1). Average sediment As is $99 \pm 203 \text{ mg kg}^{-1}$ (1 to 709 mg kg^{-1}) between 0-1 m depth, $119 \pm 195 \text{ mg kg}^{-1}$ (1 to 506 mg kg^{-1}) between 1-2 m depth, and $115 \pm 232 \text{ mg kg}^{-1}$ (1 to 629 mg kg^{-1}) between 5-7 m depth, whereas it is $9 \pm 21 \text{ mg kg}^{-1}$ (1 to 87 mg kg^{-1}) between 2-5 m depth (Table 1). The As enrichment (> 50 mg kg^{-1} As) was found at depth shallower than 2 m or deeper than 5 m, whereas no As enrichment was identified at depth between 2-5 m, except for one sample with 87 mg kg^{-1} As at 4.6 m depth. P-extractable sediment As (e.g. sorbed As) concentration was also elevated between 0 and 2 m depth, showing 46 to 600 mg kg^{-1} As (Jung et al., 2012). In RS 14 and RS 15 sediment cores covered with silty-clay layer, the HCl leachable As concentrations were less than 5 mg kg^{-1} at all depths (Table 1).

3.3. Chemistry of Waters

Well water—The chemical characteristics of shallow groundwater (Table 2; 14-23 m depth) are comparable to those of 5 wells sampled in 1998 by BGS and DPHE (2001). Groundwater has circumneutral pH, is of Ca(Mg)-HCO₃ type, and is reducing with DO typically < 0.05 mg L^{-1} (Table 2). Consistent with the observed sulfate depletion, nitrate/nitrite, Fe, Mn, As, and P compositions are in agreement with those observed for anoxic GBMD groundwater (Zheng et al., 2004).

River water—River water also has circumneutral pH, but is oxygenated, contains nitrate and displays at least 100 times less electrical conductivity (EC) compared to well water (Table 2). Major ion and Si concentrations are comparable with previous reports for the Ganges-Brahmaputra rivers (Sarin and Krishnaswami, 1984; Galy et al., 1999). Although river water is still of Ca(Mg)-HCO₃ type, Cl⁻ and SO₄²⁻ are more important in relative terms compared to well water or riverbank pore water (Table 2). Elements such as Sr, Ba, Fe, Mn, and P are found at trace levels, while As displays a low but consistent level of ~2 $\mu\text{g L}^{-1}$.

Riverbank pore water—Five high resolution depth profiles (~1-6 m depth) of chemical composition of riverbank pore waters from site J (Fig. 5) indicate three distinct redox zones with a reducing zone between 2-5 m depth and two suboxic zones above (0-2 m) or below (> 5 m). Water from suboxic zone at 0-2 m depth has pH of ~6.2 and is 2.5 times fresher although it has twice as much Cl⁻ and >10 times of SO₄²⁻ compared to well water (Table 2). Only ~50% of As is in the reduced form of As(III), consistent with the mixed As(III) and As(V) speciation of sediment As as shown by phosphate extraction and XAS analysis (Jung et al., 2012). Water from 2-5 m depth is the most reducing and has composition most similar to well water except that average As and P concentrations are 2 or 3 times less (Table 2). As(III) is the dominant As species accounting for ~90% of As, which is associated with lower DO (< ~0.2 mg L^{-1}). Water from 5-6 m depth is similar to well water in terms of major cation and Si composition but appears to be less reducing with lower concentrations

of Fe and Mn (Table 2). NO_3^- was below the detection limit (0.1 mg L^{-1}) at all depths, although NO_2^- of $\sim 0.4\text{--}0.6 \text{ mg L}^{-1}$ was detected from 13 samples out of 32 samples. The changes in concentrations of redox reactive species (e.g. Fe, Mn, As, SO_4^{2-}) between 0–2 m depth and 2–5 m depth are orders of magnitude higher than the changes in non-redox sensitive properties (e.g. EC, sum of major cations, and Si). The depth profiles of Fe, Mn and SO_4^{2-} suggest concurrent Fe, Mn and sulfate reduction between 2 and 5 m (Fig. 5), although at depth $> 5 \text{ m}$, sulfate levels increase again. Sulfate reduction can decrease dissolved As concentration through coprecipitation of As with sulfide minerals (Kirk et al., 2004; Omoregie et al., 2013; Burton et al., 2014). However, dissolved As is elevated in the reducing zone with sulfate reduction probably because authigenic sulfide precipitation was not sufficient to remove As due to initially low dissolved sulfate concentration (BGS&DPHE, 2001; Zheng et al., 2004).

Because samples have been acidified by HCl for total dissolved S analysis, the molar ratio higher than ~ 1 especially in the reducing riverbank pore water at 3–5 m depth (Table 2 and Fig. 5) may reflect a dissolved organic S component (McArthur et al., 2001). The molar ratio of S to SO_4^{2-} is ~ 1 for oxic river water and seepage water ($n=10$), suggesting that SO_4^{2-} is the dominant S species. The elevated concentrations of Cl and Na+K at shallower depth could result from the infiltration of river water that dissolved salt precipitated in the preceding dry seasons. While the concentrations of As, P and Mn all increase with pore water Fe concentration, the correlation is stronger for Mn ($n=32$, $R^2=0.89$) than for As and P ($n=32$, $R^2=0.72$ for both) (Fig. 6). Although such a strong coupling between these elements and Fe has not been commonly observed from shallow well groundwater in the GBMD aquifers, it may simply reflect less heterogeneous conditions in the riverbank sediment than in a typical GBMD shallow aquifer sediment given that the scale of the sampling is only $\sim 30 \text{ m}$ in horizontal distance and $\sim 6 \text{ m}$ in depth. Dissolved sulfate is present only in suboxic water with low dissolved Fe concentration (Figs. 5 and 6).

Seepage water—Chemical composition of seepage waters (Table 2) is reported after correction for the contribution of 1 L of pre-filled river water using average chemical composition of river waters. The chemistry of seepage water must be interpreted with caveats, as it is a mixture of river water and discharging groundwater water inside the seepage meter, subject to artifacts of deployment. The measured EC ($0.071 \pm 0.002 \text{ mS cm}^{-1}$) was slightly higher than that of the river water ($0.062 \pm 0.001 \text{ mS cm}^{-1}$), suggesting a groundwater input. Whereas it is not entirely obvious based on the major cation and anion compositions how to un-mix the two end-members, the redox sensitive components also suggest groundwater influence of seepage water. Dissolved Fe, P, and As are 2 to 4 folds higher in seepage water (680 , 13 , and $3 \text{ } \mu\text{g L}^{-1}$) than in river water, while they are comparable or slightly higher in seepage water than in suboxic riverbank pore water (Table 2). Dissolved Mn is ~ 60 folds higher in seepage water ($610 \text{ } \mu\text{g L}^{-1}$) than in river water, and comparable to suboxic riverbank pore water ($580 \text{ } \mu\text{g L}^{-1}$). This is noteworthy because these elements are expected to experience some loss upon entering the oxygenated environment. The seepage meter water did not appear to have become artificially anoxic due to the deployment because the concentrations of nitrate were comparable to river water.

4. DISCUSSION

4.1. Non-conservative Behavior from Redox Reactions

To evaluate the redox reaction driven non-conservative behavior of reactive elements during groundwater discharge, the concentration changes are compared between the reactive elements such as Fe, Mn, P, and As and the sum of the major cations (SMC) or Si. The rationale to choose SMC and Si are as follows. First, major cations and Si do not undergo redox changes, and that their affinities to Fe-oxyhydroxide are weak under circumneutral pH condition (Swedlund and Webster, 1999). Second, silicic acid (H_4SiO_4) is an extremely weak acid with a $\text{pK}_{\text{a}1}$ of 9.83 at 25 °C, thus, it is a non-charged species at neutral pH. This implies that ion exchange reactions will not involve Si. For this reason, Si is likely a better conservative reference because Na^+ and K^+ can exchange with NH_4^+ and H^+ from clay surfaces and Ca^{2+} is influenced by hydroxyapatite precipitation (see section 4.2). Finally, the weathering rates of silicate minerals are significantly slow when compared to the transport of Si in subsurface environment, and Si remains under-saturated with respect to authigenic silicate precipitation. Dissolved [Si] in shallow aquifer (< 25 m depth) also shows a low degree of variability with average concentration of $18.6 \pm 4.1 \text{ mg L}^{-1}$ (Table 2), similar to reducing riverbank pore water between 2-5 m depth ($22.7 \pm 5.2 \text{ mg L}^{-1}$ on average). Using average Si concentration in the reducing riverbank pore water ($22.7 \pm 5.2 \text{ mg L}^{-1}$) and river water ($5.4 \pm 0.4 \text{ mg L}^{-1}$) in Oct.-Nov. 2007 as two end members, the calculation indicates that shallow suboxic pore water (0-2 m depth, average dissolved Si of $8.9 \pm 1.2 \text{ mg L}^{-1}$) consists of 73% river water and 27% reducing pore water.

Based on the mixing ratio determined above from Si concentration, if the hydrologic mixing was the only factor for the lower concentrations of Fe, Mn, P, and As observed in the shallow suboxic pore water at 0-2 m depth, the concentrations of these reactive elements should have decreased to 3252, 1044, 210, and $33 \mu\text{g L}^{-1}$, respectively. Likewise, the less reactive SMC and Sr should have decreased to 1.47 meq L^{-1} and 0.11 mg L^{-1} . While the estimated concentrations of SMC and Sr are similar to the observed concentrations of 1.66 meq L^{-1} and 0.12 mg L^{-1} , respectively, the calculated Fe, Mn, P, and As are significantly higher than the observed concentrations of 128, 576, 25, and $1 \mu\text{g L}^{-1}$, respectively. This suggests that further removal of reactive elements occurs by chemical reactions in addition to hydrologic mixing in the shallow suboxic zone. After accounting for the mixing, the chemical removal rates for Fe, Mn, P, and As are 96, 45, 88, and 96%, respectively in the 0-2 m suboxic zone. Therefore the redox-controlled immobilization processes in the hyporheic zone can significantly influence the estimation of chemical fluxes of reactive elements from the aquifer to the river in GBMD that at present are not accounted for (Dowling et al., 2003; Charette and Sholkovitz, 2006).

4.2. Non-Conservative Behavior from Precipitation-Dissolution Reactions

The behaviors of Fe and Mn are further influenced by precipitation-dissolution reactions. Although the riverbank pore water is oversaturated with respect to siderite (average SI: +0.2) and vivianite (average SI: +2.7) in the 2-5 m reducing zone (Fig. 7), the dissolved Fe concentration is slightly higher in the reducing riverbank pore water ($11.6 \pm 1.7 \text{ mg L}^{-1}$) than in shallow well water ($9.8 \pm 5.4 \text{ mg L}^{-1}$). To compensate the “loss” of dissolved Fe by

vivianite and siderite precipitation, additional mobilization of Fe from the riverbank sediment by reductive dissolution of Fe(III)-oxyhydroxides is suspected. This is more evident for Mn because dissolved Mn concentration increases from $1.8 \pm 0.4 \text{ mg L}^{-1}$ in groundwater to $3.8 \pm 2.4 \text{ mg L}^{-1}$ in reducing pore water at 2-5 m depth although the precipitation of rhodochrosite (average SI: +0.2) is likely (Fig. 7). Additionally, the HCl-extractable Mn-Fe(III) (Fig. 4C, $R^2 = 0.90$, $n=26$) and Mn-Fe(II) (Fig. 4D, $R^2 = 0.76$, $n=12$) correlations supports that Mn is incorporated into Fe(III) minerals such as goethite in the suboxic zones and into Fe(II) minerals such as siderite in the reducing zone. Mn has been shown to replace up to half of the Fe in the structure of synthetic goethite (Ebinger and Schulze, 1990), although naturally occurring Mn-substituted goethite is rarely observed in part due to their different loci of formation because soluble Mn is seldom present in the stable oxidizing zones in which crystalline Fe(III) oxides form. The redox oscillation (section 4.3) in the suboxic zone may facilitate co-loci of Mn and Fe(III). The Mn-Fe(II) correlation indicates the precipitation of both MnCO_3 and siderite (FeCO_3) or Mn^{2+} substituting for Fe^{2+} in siderite (Wersin et al., 1989).

Pore water Ca may be regulated by precipitation-dissolution reactions involving calcite and hydroxyapatite (Rakovan and Hughes, 2000). Pore waters are under-saturated with respect to calcite with an average SI of -0.9 in reducing pore water and an average SI of -2.3 in suboxic pore water (Fig. 7). Reducing pore waters are supersaturated with respect to hydroxyapatite with an average SI of $+1.4$ (Fig. 7).

4.3. Redox Oscillation of the Natural Reactive Barrier

Several lines of evidence suggest that temporal redox oscillation is a key feature of the natural reactive barrier consisting of Fe(III) oxyhydroxides at the Meghna riverbank (Jung et al., 2012; Lee et al., 2014; MacKay et al., 2014). The sandy riverbank sediment may undergo temporal redox oscillation due to the $\sim 4\text{-}5 \text{ m}$ seasonal fluctuation in the groundwater table and river water level (Fig. 2A) between dry and rainy seasons (BGS&DPHE, 2001; Stute et al., 2007), as well as tide with daily amplitude of $\sim 0.5\text{-}1 \text{ m}$ (Barua, 1990) that can affect oxygen flux to the subsurface (Williams and Oostrom, 2000). Although the sampling of this study did not target specifically such redox oscillations, the mixed sediment As speciation [As(III) and As(V)], as well as a mixture of reactive Fe(III) oxyhydroxides ($49 \pm 8\%$ of Fe minerals) and Fe(II) minerals ($26 \pm 5\%$ of Fe minerals; fit as siderite) (Jung et al., 2012) are supportive of cycles of reducing and oxidizing conditions in response to seasonal water level changes and possibly, tidal influences. In addition, sediment As enrichment in the shallow redox transition zone between 0-2 m ($n=10$) is associated with a wide range of sediment Fe(III)/Fe ratio (0.11-0.79), not just oxidized sediment with high Fe(III)/Fe (Fig. 8). Sediment As enrichment at depth $> 5 \text{ m}$ ($n=2$) is also associated with low Fe(III)/Fe ratios (Fig. 8).

Despite the seasonal oxidation-reduction influence on reactive Fe minerals, most As appear to have been retained in the riverbank sediments because pore water As concentrations in the oxic-suboxic zone between 0-2 m depth are only $1 \text{ } \mu\text{g L}^{-1}$ for both Jan. 2006 and Oct.-Nov. 2007 (Table 2). Recent studies suggest that reductive transformation of ferrihydrite does not necessarily lead to mobilization of As, and in some cases could enhance As

retention (Kocar et al., 2006; Pedersen et al., 2006; Tufano and Fendorf, 2008). This may be attributed to either the formation of an amorphous aggregates of Fe(II)-As(III) (Thoral et al., 2005) or adsorption on or incorporation into secondary solid phases (Kocar et al., 2006). Coker et al (2006) showed that As(III) and As(V) adsorbed on ferrihydrite were not released during mineralogical transformation to magnetite, which caused incorporation of As(V) within the magnetite structure (Coker et al., 2006). Therefore, even with seasonal redox transformation of Fe minerals at the Meghna Riverbank, it would not necessarily result in a significant mobilization of As.

4.4. Heterogeneous As Enrichment in the Hyporheic Zone

Sediment As enrichment along the Meghna riverbank is found to be heterogeneous at various spatial scales. At a regional scale of ~10 km encompassed by our study area, sediment As enrichment is frequently found from riverbank (sites J and S) where sandy deposits extended to the surface, and in turn, where redox zonation develops within < 10 m depth. Sediment HCl-leachable As concentrations are elevated ($> 50 \text{ mg kg}^{-1}$) for one or more sampling depths in 7 cores out of 11 cores taken at sites J and S (Fig. 3). In contrast, HCl-leachable As concentrations were all below 5 mg kg^{-1} in sediment cores RS14 and 15, which were covered with a fine grained silty clay layer. At the local scale of the riverbank sediment coring sites, high resolution depth profiles of bulk sediment As reveal that the As enrichment is formed within thin (~5-10 cm) sediment layers (Fig. 3 and Appendix 7). In RS30 of site S, 34-207 mg kg^{-1} of As was detected from 79 cm to 90 cm depth. In RS33 of site S, it was from 27 to 30 cm, and again at 150 cm. In RS34 of site J, it was from 136 to 142 cm. The horizontal extent of As enriched layer estimated from 3 transects perpendicular to the river shore (Fig. 3) is approximately 5-15 m from river shore towards upland. At site J along a 23 m transect of RS20-21-19-34, high As sediment ($>50 \text{ mg kg}^{-1}$) at the shallow depth (< 2 m) spans ~15 m. At site S, along a 10 m transect of RS16-30-31, the horizontal extent of As enrichment is approximately 5 m. Also at site S, enrichment found in two cores RS17-33 suggests a minimum 5 m length. The vertically thin and horizontally extensive As enriched layers may result from rapid kinetics of adsorption onto or co-precipitation with Fe(III) oxyhydroxides precipitated at the redox interface between reducing groundwater and oxic river water (Fuller et al., 1993; Waltham and Eick, 2002; Jung et al., 2012).

Based on the spatial patterns and the heterogeneity of As enrichment in the hyporheic zones of the Meghna River, a conceptual model delineating how preferential groundwater flow facilitates the redox trapping of discharging groundwater As is proposed (Fig. 9). Hydrological models of groundwater discharge have shown that the groundwater discharge tends to concentrate along a narrow zone near the shore where the flow paths converge (McBride and Pfannkuch, 1975; Pfannkuch and Winter, 1984; Trefry et al., 2007). This was the case for Canning River of Western Australia where a strong seasonal hydraulic gradient between the aquifer and the river exists due to precipitation seasonality (Trefry et al., 2007). Therefore we may expect that any dissolved conservative species originating from the upgradient region and advecting along groundwater streamlines would preferentially discharge to the river along a quite narrow zone of the riverbank. We add to this by suggesting that conditions favoring trapping of groundwater As, a redox-sensitive species, are met in the high permeability area with sandy surficial deposits where discharging

reducing groundwater readily interacts with infiltrating oxic river water to form the reactive barriers of Fe(III) oxyhydroxides (Fig. 9A). Conditions are not favorable for sediment As enrichment in areas with less permeable silty-clay surficial deposits because the interaction between discharging groundwater and infiltrating river water is limited (Fig. 9B). However further investigation of less permeable areas will be helpful because only 2 cores were subjected to partial analysis in this study.

The infiltration of oxic river water can occur not only through the permeable riverbank sediment but also through the permeable riverbed sediment (Winter et al., 1998), which may have caused suboxic conditions at depths deeper than 5 m. The elevated sediment As concentrations at 5-7 m depth may result from the accumulation of As on Fe(III) oxyhydroxides formed along the deeper redox interface under transient oxidizing conditions immediately after the rainy season (Jung et al., 2009).

4.5. History of Arsenic Trapping and Implications for Arsenic Occurrence and Cycling

How long did it take to accumulate 400 mg kg^{-1} sediment As, the average value observed in this study, by the natural reactive barrier in the hyporheic zone of the Meghna River? Assuming that groundwater As, with an average concentration of $\sim 100 \mu\text{g L}^{-1}$, is completely trapped by a 5-10 cm thick natural reactive barrier with a porosity of 0.25 and a bulk density of 2 g cm^{-3} , and that groundwater flow rate is $\sim 10 \text{ m y}^{-1}$, it would only require ~ 40 to 80 years to accumulate $\sim 400 \text{ mg kg}^{-1}$ As. This however ignores the fact that As transport is retarded within the aquifer. The solute velocity of groundwater As (and thus the rate at which it is delivered to the As enrichment zone) is dependent on K_d (distribution coefficient), which is likely to be $\sim 1\text{-}4 \text{ L kg}^{-1}$ in reducing GBMD aquifers (van Geen et al., 2008; Jung et al., 2012). For K_d of 1 or 4 L kg^{-1} , the retardation factors and solute velocities are calculated to be 9 to 33 and 1.2 to 4.4 m y^{-1} , respectively, based on the following (Fetter, 2001);

$$\text{Solute Velocity} = \text{Average linear velocity} / \text{Retardation factor} = \text{Average linear velocity} / [1 + (\text{Bulk density} / \text{Porosity}) \times K_d]$$

Thus, approximately 350-700 years (for K_d of 1) to 1300-2600 years (for K_d of 4) are required to trap $\sim 400 \text{ mg kg}^{-1}$ As in the riverbank sediment at 5-10 cm of thickness. This is a reasonable time scale given that the Holocene sediment in GBMD has been deposited since $\sim 10,000$ years B.P.

That hundreds of years are required to form As-enriched sediments along the Meghna Riverbank suggests that mobilization and immobilization processes of groundwater As have been occurring naturally prior to extensive installation of shallow tube wells since 1970-80s. This supports the view that elevated groundwater arsenic has probably been present well before the GBMD aquifer system was highly modified by extensive groundwater pumping (Mailloux et al., 2013). Although seasonal fluctuation of groundwater table does not seem to have mobilized As from the riverbank sediment to any significant extent, the infiltration of river water containing labile dissolved organic carbon (DOC) as the result of increasing sewage discharge, could induce reduction of riverbank sediment, and subsequently mobilize sediment As through reductive dissolution of Fe(III) oxides (Jung et al., 2012). Mobilized

As could discharge to the river or migrate back to the aquifer if the hydraulic gradient is reversed toward the floodplain because of extensive irrigation pumping (Klump et al., 2006). Over longer periods of time, the As enriched sediment can be redistributed by tectonic events or with river channel migration (Goodbred et al., 2003), and act as a source of As to shallow aquifer as the sediment is reduced in subsurface after deposition.

5. CONCLUSION

Distinct redox zonation with a shallow oxic-suboxic zone (0-2 m), a reducing zone (2-5 m) and a deeper suboxic zone (5-7 m) develops in the hyporheic zone of the Meghna River in Bangladesh characterized by sandy surficial deposits where the reducing shallow groundwater interacts with oxic river water upon discharge during the dry season. In contrast to Si, Sr, and major cations that displayed mostly conservative behaviors, many elements exhibit non-conservative behaviors because of redox reactions (Fe, Mn, As, P, and S) in the suboxic zone and/or precipitation-dissolution reactions (Fe, Mn, Ca and P) in the reducing zone. Seasonal fluctuations of river water level and groundwater table result in the formation of natural reactive barriers consisting of a mixture of Fe(III) oxyhydroxides and Fe(II) minerals in the shallow oxic-suboxic zone. In both shallow and deeper suboxic zones, frequent enrichment of sediment As up to $\sim 700 \text{ mg kg}^{-1}$ has been attributed to trapping of discharging groundwater As by the natural reactive barriers at a flow rate of about 10 m yr^{-1} over hundreds of years. The As enriched sediment layers are vertically thin ($\sim 5\text{-}10 \text{ cm}$) and spans $\sim 5\text{-}15 \text{ m}$ horizontal distance from the river shore where groundwater discharge flow lines are presumed to converge. Neither redox zonation nor As enrichment has been observed in areas with less permeable silty-clay surficial deposits, reflecting the heterogeneous groundwater discharge patterns of a floodplain setting. Several lines of evidence suggest that As mobilization and immobilization processes have been naturally occurring for at least hundreds of years before the perturbation of the Ganges-Brahmaputra-Meghna Delta aquifer by extensive irrigation pumping. Highly elevated sediment As in the riverbank may be mobilized or redistributed by natural processes or human activities, thus becoming a “recycled” source of As for shallow aquifer in the Ganges-Brahmaputra-Meghna Delta.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights

1. The hyporheic zone in the sandy Meghna riverbank displays a redox transition.
2. Sediment As is enriched in two suboxic zones at depths of 0-2 m and 5-7 m.
3. The As enriched sediment layers are only 5 to 10 cm thick but are 5 to 15 m long.
4. Hundreds of years of groundwater As discharge is required for the As enrichment.

Fig. 1.

A: Location of the study site, Gazaria Upazila (Red square) in Bangladesh. Circles with different colors represent shallow well groundwater As concentrations (BGS & DPHE, 2001). Circles with dots in the center indicate the locations of sediment sampling along the Meghna River by Datta et al (2009). **B:** Locations of riverbank sediment cores (yellow crossed circle), shallow well groundwater (solid square: Jan. 2006, solid triangle: Oct.-Nov. 2007, and solid circle: BGS & DHPE, 2001), riverbank pore water and seepage water (Site J and Site S), river water (reverse triangle; green for Jan. 2006 and orange for Oct.-Nov. 2007), a monitoring well (MUN002, yellow open circle) and a river level monitoring station (SW275-5; yellow star) at the Meghna Riverbank.

Fig. 2.

A: Hydrograph of groundwater table from MUN002 (23.6° N, 90.6° E; depth of well: 38.1 m) and river stage at SW275-5 (23.7° N, 90.7° E) maintained by the Bangladesh Water Development Board. Groundwater table is higher than river water level during the dry season. **B:** Estimated annual groundwater discharge rate (m yr^{-1}) based on seepage meter measurements in Oct. 31-Nov. 4, 2007 at site J, assuming the same discharge rate for the 6-month dry season.

Site S **Site J** **RS14 & RS15** **Fig. 3.**

Depth profiles of sediment properties for the Meghna Riverbank sediment in Gazaria Upazila, Bangladesh. Sediment Fe and As data were obtained by hot 1.2 N HCl extraction. Site S: RS16, 17, 30, 31, 32, and 33 were collected at 12 m, 10 m, 9 m, 2 m, 4 m, 5 m from the river shore in Jan 2006, respectively. Site J: RS19, 20, 21, 34, and 35 were collected at 7 m, 25 m, 15 m, 2 m, and 35 m from the river shore in Jan 2006, respectively. RS 14 and RS 15 sediment cores were collected at ~10 m from the river shore in Jan. 2006. Redox transition and As enrichment are obvious for sediment cores from sites S and J, but not for RS 14 and 15 sediment cores.

Fig. 4.

A: XRF bulk Fe vs. XRF bulk Mn for RS30, 33, and 34 ($n=112$) from sites S and J. Correlations between **(B)** HCl leachable total Fe and Mn, **(C)** HCl leachable Fe(III) and Mn, and **(D)** HCl leachable Fe(II) and Mn for sediments ($n=38$) from sites S and J. For suboxic sediments with Fe(III)/Fe > 0.3, Mn correlates better with Fe(III) than with Fe(II), while for reducing sediments with Fe(III)/Fe < 0.3, Mn correlates better with Fe(II) than with Fe(III).

Fig. 5.

Depth profiles of chemical properties of Meghna Riverbank pore water collected from site J in Oct-Nov. 2007. PZ8, PZ6, PZ5&9, PZ7&10, PZ11 are located at 42 m, 30 m, 20 m, 15 m, and 10 m from the river shore of Jan. 2006. For the depth profile of molar ratio of S/SO_4 , SO_4^{2-} concentrations below the detection limit of IC (0.1 mg L^{-1} ; mostly at 3-5 m depth interval) are assumed to be 0.1 mg L^{-1} , hence are minimum S/SO_4 values for those depths shown for illustrative purpose only. The pore water depth profiles indicate three distinct redox zones with a reducing zone between 2-5 m depth and two suboxic zones above (0-2 m) or below ($> 5 \text{ m}$).

Fig. 6. Concentrations of As, P, Mn, and SO₄²⁻ vs. concentration of Fe for the Meghna Riverbank pore waters at site J. The concentrations of As, P and Mn all increase with increasing Fe concentration, while sulfate concentration decreases with increasing Fe concentration.

Fig. 7. Saturation indices (SI) with respect to vivianite, rhodocrosite, siderite, hydroxyapatite, and calcite in Meghna Riverbank pore water at site J. The pore water in the reducing zone at 2-5 m depth is oversaturated with respect to vivianite, rhodocrosite, siderite, and hydroxyapatite, but is undersaturated with respect to calcite.

Fig. 8. HCl leachable sediment As concentrations vs HCl leachable Fe(III)/Fe ratios. Sediment As enrichment in the redox transition zone is associated with a wide range of sediment Fe(III)/Fe ratio (0.11~0.79) due to temporal redox oscillation.

Fig. 9. Schematic model showing (A) the formation of the reactive barrier [Fe(III) oxyhydroxides] trapping As in discharging groundwater along the sand covered riverbank and (B) no formation of the reactive barrier along the silt-clay covered riverbank.

Table 1

Depth distribution of average chemical composition and diffuse reflectance of Meghna Riverbank sediments in Gazaria Upazila, Bangladesh.

Surface sediment type	Number of samples	Depth m	Reflectance at 520 nm	Fe(III)/Fe	Fe(III)		mg/kg			
					wt. %					
Sand	25	0-1	0.34	0.52	0.58	1.09	269	469	99	
	12	1-2	0.21	0.37	0.32	0.89	166	500	119	
	17	2-5	0.14	0.24	0.26	1.12	222	481	9	
	9	5-7	0.18	0.28	0.27	1.03	218	549	115	
Silty-clay	2	0-1	nd	0.31	0.42	1.32	nd	629	< 5	
	2	1-2	nd	0.12	0.12	0.83	nd	659	< 5	
	4	2-5	nd	0.15	0.14	0.98	nd	604	< 5	
	2	5-7	nd	0.20	0.14	0.71	nd	390	< 5	

Sediment samples with sandy surface layer are from sites S and J (RS 16, 17, 19, 20, 21, 30, 31, 32, 33, 34, and 35), and sediment samples with silty-clay surface layer (~1.5 m thickness) are from RS14 and RS15. nd = not determined.

Table 2

Average chemical composition of four types of water samples (well groundwater, riverbank pore water, seepage water, and river water) in Gazaria Upazila, Bangladesh.

Sample type	Sampling Date	Number of samples	Depth m	EC mS/cm	DO mg/L	pH	Na	K	Ca	Mg	Si	HCO ₃	SO ₄	Cl	F	Sr	Ba	NO ₃	NO ₂	Fe	Mn	S	As		P
																							µg/L		
mg/L																									
Well groundwater	Jan 2006	11	14-21				8.4	3.4	71.2	10.5	20.3							0.070		8.75	1.53	0.61	238	1875	
	Oct-Nov 2007	11	15-23	0.569	0.05	6.87	14.2	3.1	98.2	20.2	18.6	269.2	0.9	58.4	0.23	0.47		0.00	0.13	9.77	1.79	1.67	385	1258	
	* BGS&DPHE	5	13-27				19.1	4.6	99.7	24.3	18.0		2.0				0.29	0.085		3.81	1.00		192	1300	
River bank pore water		1	0-2				3.9	1.4	15.8	4.7	10.2							0.033		1.02	0.34	4.93	1	15	
	Jan 2006	5	2-5				3.9	2.1	107.1	16.3	24.4							0.081		5.46	3.54	0.89	99	420	
		5	5-7				4.0	1.8	80.7	13.3	23.7							0.059		1.25	2.56	0.36	78	278	
Seepage water		8	0-2	0.228	0.29	6.19	4.4	1.5	17.2	6.8	8.9	49.0	12.4	8.9	0.15	0.12		0.00	0.28	0.13	0.58	5.89	1	25	
	Oct-Nov 2007	18	2-5	0.482	0.12	6.55	4.1	1.9	60.0	15.3	22.7	194.6	2.6	4.5	0.18	0.35		0.00	0.09	11.57	3.84	1.26	118	760	
		6	5-6	0.401	0.19	6.56	3.6	1.2	39.3	11.7	21.2	129.7	1.9	3.3	0.14	0.24		0.00	0.28	1.14	1.52	0.90	28	211	
	Oct-Nov 2007	5		0.071			0.5	0.1	4.5	0.4	4.4		4.3	1.3	0.16	0.03		1.05	0.13	0.68	0.61	1.61	3	13	
River water	Jan 2006	3		0.011	8.74	6.28	3.2	0.8	11.1	2.3	5.4						0.013		0.04	0.07	1.48	2	9		
	Oct-Nov 2007	5		0.062	5.51	6.96	1.9	0.5	3.5	0.9	3.9	8.8	2.3	1.2	0.15	0.02		1.08	0.07	0.18	0.01	0.93	2	6	

Anions were analyzed only for samples collected in Oct.-Nov. 2007. EC, DO, and pH of well groundwater and riverbank pore water were not measured in Jan. 2006. Riverbank pore waters were collected from sites S and J in Jan. 2006, and from only site J in Oct.-Nov. 2007.

* BGS&DPHE shows shallow well groundwater data reported in BGS&DPHE (2001).