



Contribution of sedimentary organic matter to arsenic mobilization along a potential natural reactive barrier (NRB) near a river: The Meghna river, Bangladesh

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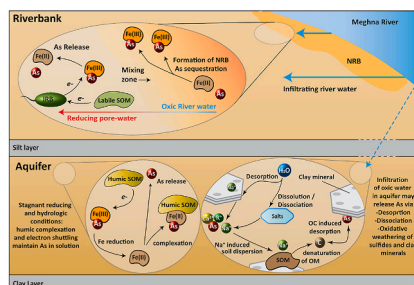
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HIGHLIGHTS

- Sediment from an As-contaminated aquifer and riverbank were geochemically studied.
- Infiltrating oxic river water into riverbank hyporheic zone leads to solid-phase As enrichment.
- Organic matter in aquifer sediments was highly humic-like and recalcitrant.
- Organic matter in riverbank sediments was protein-like and biologically labile.
- Fe and As are immobilized during the dry season when oxic river water moves laterally into the riverbank due to tides.

GRAPHICAL ABSTRACT



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ABSTRACT

Elevated dissolved arsenic (As) concentrations in the shallow aquifers of Bangladesh are primarily caused by microbially-mediated reduction of As-bearing iron (Fe) (oxy)hydroxides in organic matter (OM) rich, reducing environments. Along the Meghna River in Bangladesh, interactions between the river and groundwater within the hyporheic zone cause fluctuating redox conditions responsible for the formation of a Fe-rich natural reactive barrier (NRB) capable of sequestering As. To understand the NRB's impact on As mobility, the geochemistry of riverbank sediment (<3 m depth) and the underlying aquifer sediment (up to 37 m depth) was analyzed. A 24-hr sediment-water extraction experiment was performed to simulate interactions of these sediments with oxic river water. The sediment and the sediment-water extracts were analyzed for inorganic and organic chemical parameters. Results revealed no differences between the elemental composition of riverbank and aquifer sediments,

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which contained 40 ± 12 g/kg of Fe and 7 ± 2 mg/kg of As, respectively. Yet the amounts of inorganic and organic constituents extracted were substantially different between riverbank and aquifer sediments. The water extracted 6.4 ± 16.1 mg/kg of Fe and 0.03 ± 0.02 mg/kg of As from riverbank sediments, compared to 154.0 ± 98.1 mg/kg of Fe and 0.55 ± 0.40 mg/kg of As from aquifer sediments. The riverbank and aquifer sands contained similar amounts of sedimentary organic matter (SOM) ($17,705.2 \pm 5157.6$ mg/kg). However, the water-extractable fraction of SOM varied substantially, i.e., 67.4 ± 72.3 mg/kg in riverbank sands, and 1330.3 ± 226.6 mg/kg in aquifer sands. Detailed characterization showed that the riverbank SOM was protein-like, fresh, low molecular weight, and labile, whereas SOM in aquifer sands was humic-like, older, high molecular weight, and recalcitrant. During the dry season, oxic conditions in the riverbank may promote aerobic metabolisms, limiting As mobility within the NRB.

1. Introduction

Dissolved arsenic (As) concentrations in the shallow aquifers of Bangladesh commonly exceed both the national standard of $50 \mu\text{g/L}$ and the WHO guideline of $10 \mu\text{g/L}$, threatening the health of an estimated 22 and 45 million people, respectively (BGS&DPHE, 2001; Flanagan et al., 2012; Mukherjee and Bhattacharya, 2001; Smith et al., 2000; Yu et al., 2003). The spatial distribution of As concentrations is highly heterogeneous across the shallow alluvial aquifers of Bangladesh. This is influenced by regional groundwater flow (Aziz et al., 2008; Chakraborty et al., 2015; van Geen et al., 2006), the local stratigraphy (Bibi et al., 2006; Chakraborty et al., 2022; Hoque et al., 2009; McArthur et al., 2004; Weinman et al., 2008), and the extent and duration of surface inundation (Connolly et al., 2021). Consequently, the biogeochemical conditions leading to elevated As concentrations are linked to both past and currently active hydrologic processes including those that operate at the groundwater-surface water interface (Berube et al., 2018; Jung et al., 2015).

Exchanges between the groundwater and surface water within riverbank sediment occur within the hyporheic zone (HZ). This zone often experiences groundwater upwelling and downwelling and bidirectional flow between the river and the aquifer over a scale that typically extends from a few centimeters to tens of meters (Boano et al., 2014; White, 1993). Therefore, the HZ represents an area of transition in the riverbank, where the pore water has features of both river water and groundwater. Whereas surface waters are saturated with oxygen, the dissolved oxygen (DO) in the subsurface decreases with both depth and distance from the surface water body, resulting in a redox gradient (Krause et al., 2013; Triska et al., 1993). The transport of DO into the HZ determines the spatial extent of the redox gradient and is controlled by the interaction between flow rate and the rate of its consumption (Shuai et al., 2017a). The residence time of river water within hyporheic pore spaces can range from minutes to years (Cardenas, 2008b; McCallum and Shanafield, 2016; Zarnetske et al., 2011). The flow rate and residence time is controlled by the hydraulic conductivity of the riverbank sediment (Boano et al., 2014; Findlay, 1995), river sinuosity, the prevailing magnitude and direction of groundwater flow (Cardenas, 2008a, 2009), as well as the periodicity of river stage fluctuations (Berube et al., 2018; Shuai et al., 2017a).

The mixing of the two chemically distinct water sources within the HZ produces an area of high reactivity, generating a broad range of redox conditions and highly diverse microbial communities capable of filtering OM and nutrients (Boulton et al., 1998; Nogaro et al., 2013; Zhu et al., 2020). For example, the HZ processes labile dissolved organic matter (DOM) from infiltrating surface water (Findlay et al., 1993; Marmonier et al., 1995), and is capable of metabolizing the majority of OM from the discharging groundwater (Fiebig, 1995). Furthermore, the mixing of iron (Fe)-rich reduced groundwater with oxygen-rich surface waters often precipitates Fe-oxides on mineral surfaces, which may adsorb As and trace metals that would otherwise discharge into the river or be drawn down into the aquifer (Datta et al., 2009; Gandy et al., 2007). The ability to attenuate organic and inorganic contaminants from both the surface water and groundwater has earned the HZ the title “liver of the river” (Fischer et al., 2005).

Recently, the role of seasonal inundation and mixing from ocean tides that propagate up freshwater rivers in HZs have been recognized to drive key hydrological and biogeochemical processes that regulate the mobility of contaminants and OM (Bianchin et al., 2011; Musial et al., 2016; Shuai et al., 2017a). The infiltration of oxic river water into the riverbank under losing conditions in the river may create an Fe-oxide-rich zone, or natural reactive barrier (NRB), within the sediment which may act as a sink of As and other oxyanions (Bone et al., 2006; Charette and Sholkovitz, 2002, 2006; Charette et al., 2005; Jung et al., 2009). Charette and Sholkovitz (2002) first described similar Fe-accumulation accompanied by distinct redox changes in the shallow sediments lining the banks of estuaries which were deemed “subterranean estuaries”. This phenomenon was termed as an “iron curtain” (Charette and Sholkovitz, 2002). Since then, studies have investigated the formation and behavior of an Fe-rich NRB along fresh water-groundwater interfaces (Charette et al., 2005; Roy et al., 2010, 2013; Snyder et al., 2004; Spiteri et al., 2008). A NRB may function as a biogeochemical hotspot within the riverbank with increased reaction rates relative to the areas outside the mixing zone (McClain et al., 2003). Such biogeochemical hotspots have been attributed to As mobilization in the HZ of rivers in southeastern Asia where active deposition provides a continuous input of labile OM and reactive As-bearing Fe-oxides (Stahl et al., 2016; Wallis et al., 2020).

The formation of a NRB has been observed along the tidally and seasonally fluctuating Meghna River in Bangladesh when the hydraulic gradient drives reduced groundwater towards the river, which mixes with infiltrating oxic river water resulting in an enriched zone of freshly precipitated Fe^{3+} oxides (Berube et al., 2018; Datta et al., 2009; Jung et al., 2012). The resulting NRB may extend to various depths and distances from the river depending on the seasonal variation in the position of the shoreline and the direction of flow between the river and the aquifer (Berube et al., 2018). In the early dry season, rapidly discharging groundwater may diminish the extent of the seasonal NRB as the As-bearing Fe^{3+} minerals are dissolved (Baken et al., 2015; Berube et al., 2018; Datta et al., 2009). The fate of this re-mobilized As remains uncertain, although there is evidence that a fraction of the mobilized As may be re-adsorbed onto the remaining Fe^{3+} oxides within the NRB (Berube et al., 2018; Jung et al., 2012), or released into the river (Datta et al., 2009). Under persistently losing river conditions the mobilized As may be transported back into the aquifer (Polizzotto et al., 2005; Stahl et al., 2016; Wallis et al., 2020) where the As may then be immobilized by Fe-oxide minerals along the flow path (Johannesson et al., 2019). Although the hydrologic and biogeochemical processes responsible for elevated As concentrations in the shallow aquifers of Bangladesh have been thoroughly investigated (Bhattacharya et al., 2002, 2009; Fendorf et al., 2010; Harvey et al., 2002; Horneman et al., 2004; Huq et al., 2020; Mailloux et al., 2013; Mladenov et al., 2010; Neumann et al., 2010; Nickson et al., 1998; Polizzotto et al., 2005), the variable processes controlling the fate and cycling of As in HZs of fluctuating rivers in the Bengal Basin are not well defined.

Labile OM has been attributed to the mechanistic release of As through the reductive dissolution of Fe^{3+} minerals, where iron reducing bacteria utilize the OM as the preferred electron donor (Bhattacharya et al., 2001; Glodowska et al., 2020; Hasan et al., 2007; McArthur et al.,

2001; Nickson et al., 1998, 2000; Qiao et al., 2020; Zheng et al., 2004). However, recent discoveries reveal that relatively recalcitrant OM, such as humic and fulvic acids, may also enhance As mobilization (Mladenov et al., 2010). Relatively recalcitrant OM can enhance As mobility by shuttling electrons between labile OM, the microbial cell, and Fe^{3+} minerals (Kulkarni et al., 2018b; Lovley et al., 1996, 1999; Mladenov et al., 2010, 2015), participating in ligand complexation reactions under reducing conditions (Buschmann et al., 2006; Chin et al., 1998; Liu et al., 2011; Sharma et al., 2010; Warwick et al., 2005; Wu et al., 2019), and competing with As for available oxide adsorption sites (Bauer and Blodau, 2006; Gustafsson, 2006; Redman et al., 2002; Simeoni et al., 2003). However, the influence of OM characteristics in a redox cycling HZ of fluctuating riverbanks have not been evaluated to the author's knowledge.

To understand the riverbank processes responsible for elevated solid-phase As concentrations and its mobility within a NRB, we compare the biogeochemical characteristics of sediment from a potential riverbank NRB and the underlying Holocene aquifer, both with substantial aqueous As and Fe concentrations which are common in the region. Specifically, this study aims to: (1) identify the specific inorganic and organic chemical properties of the sediment that drive As mobilization; and (2) investigate the chemical composition of the extracted dissolved components from the sediment when exposed to oxygenated water. This is done to identify the respective processes operating in the riverbank and aquifer which may regulate the mobility of bioavailable As when conditions become oxidizing.

2. Materials and methods

2.1. Study area

The study area is located along the banks of the Meghna River in the Nayapara village (23.7°N, 90.7°E) approximately 30 km east of Dhaka (Fig. 1). Nayapara is part of the Khagkanda union within the Araihaaz upazila (sub-district) and Narayaganj district. The Meghna River floodplain in this region consists of meandering channels with remnants of infilled channels, scroll bars, and levees, which are prominent controls on the distribution of dissolved As concentrations in the shallow (<60 m) aquifer (Aziz et al., 2008; Weinman et al., 2008). The shallow aquifer sediments in the region consist of very fine to medium grain unconsolidated sands with an occasional thin (1–3 m) silt, clay, or fine sand unit (Bibi et al., 2008; Weinman et al., 2008). Previous studies have reported high dissolved As and Fe concentrations in the shallow aquifer (<30 m) (BGS&DPHE, 2001; van Geen et al., 2014; van Geen et al., 2003) along with the enrichment of solid-phase Fe and As within the Meghna riverbank (Berube et al., 2018; Datta et al., 2009; Jung et al., 2015). Short-term fluctuations in groundwater flow direction in the riverbank are influenced by river stage fluctuations owing to 12 h (semidiurnal) and 14-day (neap-spring) tidal cycles in the Bay of Bengal, however, prevailing flow directions vary with season in the monsoonal climate. Although the river is generally gaining for most of the year, it is most strongly gaining in the early dry season and most weakly gaining or slightly losing during the early wet season (Berube et al., 2018). The



Fig. 1. Location of study site in Bangladesh (a, b). Sampling locations for riverbank sediment cores (circles) and aquifer sediment from monitoring wells (squares) along the Meghna River (c).

river stage fluctuates between 3 and 7 m above sea level annually (Shuai et al., 2017b). The site along the Meghna River was chosen for its proximity to the previously reported elevated sedimentary As concentrations in the riverbank (Berube, 2017) and the presence of sandy surficial sediments, which should permit extensive mixing between surface water and groundwater.

2.2. Sample collection and analyses

A total of 50 sediment samples were collected from the aquifer and the bank of the Meghna River during the dry season in January 2020 along a line that was oriented orthogonal to the shoreline. Aquifer sediment samples were collected from a transect of 3 boreholes up to a maximum depth of 37 m below ground level (bgl) (Fig. 1). The boreholes were drilled using the hand flapper method (Horneman et al., 2004) and labeled MW-1, MW-2, and MW-3 at 131 m, 87 m, 42 m from the dry season, low tide river edge, respectively. Upon collection, samples were immediately placed in oxygen impermeable Mylar Remel® bags (Mitsubishi Gas Company, Remel®) flushed with N₂ containing an O₂ absorbent pouch (Mitsubishi Gas Company, AnaeroPouch®). Six sediment samples were chosen from each borehole for analyses based on grain size and depth (n = 18). Nine sediment cores (up to a maximum depth of 3 m bgl) were collected along a transect up to 83 m inland from the riverbank (C1, C2, C3, C4, C5, C6, C7) and 6 m into the river from the subaqueous riverbank (C8, C9) (Fig. 1). The cores were collected using a direct push sediment probe (AMS Inc., USA) and a slide hammer loaded with clear plastic liners (2.5 cm diameter and 60 cm length) to obtain undisturbed sediment profiles. Upon extraction, sediment cores were immediately capped and sealed with electrical tape. After returning from the field, the sediment cores remained frozen until shipped to labs in the U.S. Sediment samples from the cores were collected at ~0.6 m intervals for analyses (n = 32) and were preserved using Mylar Remel® bags and O₂ absorbent pouches (See Fig. S1 for sampling diagram). All samples were stored in a freezer at -7 °C until analysis. The sediment collected from the borehole drillings and sediment probes are referred herein as aquifer and riverbank samples, respectively. Bulk elemental composition of the aquifer and riverbank sediment was determined by X-Ray Fluorescence (XRF) on a Rigaku Primus II Wavelength Dispersive XRF spectrometer. Loss on Ignition (LOI) was calculated prior to the XRF analysis to measure the volatiles present in the samples and to serve as a proxy of the total sedimentary OC (Beaudoin, 2003; Davies, 1974; Heiri et al., 2001). Detailed descriptions of the LOI procedure and XRF methodology are described in the Supplementary Text. Bulk particle size analysis was determined using Horiba CAMSIZER® P4 and Malvern Mastersizer (at the University of Texas at Austin) to determine the proportion of sand to silt and clay. Low levels of inorganic carbonates were determined to be present following LOI, therefore the sediment was not treated with HCl or hydrogen peroxide to remove inorganic carbonate prior to bulk particle size analysis.

2.3. Sediment-water extractions and analyses

To determine the water-extractable constituents in the riverbank and aquifer sediments (n = 50), a 1 g aliquot of sediment was powdered using an agate pestle and mortar and was leached with 40 mL of DI water (18.3 Mohm, pH = 7.11, conductivity = 1.04 µS/cm) for 24 h (table shaker, 60 rpm) in a 50 mL centrifuge tube at ambient temperature under oxic conditions. After 24 h, the slurry was centrifuged (12,000 rpm, 6 min), pH and electrical conductivity (EC) were measured using a probe (Sension + PH31, Hach), and the supernatant was filtered through a 0.2 µm syringe filter (polypropylene, Whatman). To accommodate for the analytical method requirements, three separate aliquots of the supernatant were preserved for further analyses: unacidified, HCl acidified (0.2% v/v), and HNO₃ acidified (0.2% v/v). The major cations (Na⁺, K⁺, Mg²⁺, Ca²⁺) in HNO₃ acidified samples and anions (Cl⁻, SO₄²⁻, NO₃⁻, PO₄³⁻) in unacidified samples were measured by Ion Chromatography

(IC, Dionex DX500, Thermo Fisher). The concentrations of major elements (Fe, Mn) and trace elements (As, Co, Cr, Cu, Ni, V, Zn) were measured in the HNO₃ acidified sample aliquots by inductively coupled plasma mass spectrometry (ICP-MS, Agilent ICP-MS 7500cx) at the University of Nebraska, Lincoln. The ICP-MS measurements were conducted in a single quadrupole cell in reactive collision mode with an argon flow rate between 13 and 14 L/min. The flow rates for the auxiliary, carrier, and makeup gases were 1 L/min each. The samples were placed on a 96-well plate autosampler (Elemental Scientific, Inc.) and were injected by a peristaltic pump into a Micromist nebulizer at a rate between 50 and 60 µL/min. To normalize the results, the mass of the water-extractable constituents, M_e (mg/kg), was calculated from the aqueous concentrations measured in the extracts. The mass was calculated as

$$M_e = \frac{C_p * V_w}{m_s} \quad (\text{EQ.1})$$

where C_p is the concentration of the measured parameter in the extract (mg/L or µg/L), V_w is the volume of water, and m_s is the mass of sediment used.

Sediment-water extraction experiments have previously been used to characterize water-extractable SOM from an As contaminated aquifer in China using Fourier transform-ion cyclotron resonance-mass spectrometry techniques (Wang et al., 2021; Zhao et al., 2022). In this study, we characterize bulk and spectroscopic properties of water-extractable SOM. Dissolved Organic Carbon (DOC) and Total Dissolved nitrogen (TDN) were measured in 0.2 µm filtered HCl acidified samples by thermic oxidation (TOC/TN Analyzer, Shimadzu). The characterization of OM was done on the unacidified sample aliquots by simultaneous UV-Vis measurement of absorbance (from 240 nm to 450 nm) and fluorescence (from 300 nm to 600 nm) using a benchtop fluorometer (Aqualog, Horiba), following the methods previously described in Kul-karni et al. (2017). The fluorescence spectroscopy data from these wavelengths was used to generate an excitation-emission matrix (EEM) for each sample. Size exclusion chromatography (SEC) using a high-performance liquid chromatography (HPLC) system (Agilent 160 Infinity system II, USA) with variable wavelength (VWD) at 254 nm was used to determine the molecular weight distribution of water-extractable SOM at Auburn University, following similar methods described elsewhere (Kawasaki et al., 2011). Details of these methods are described in the Supplementary Text.

To compare the spectroscopic properties of the SOM in the extracts, 44 water samples were collected for the characterization of DOM from the riverbank pore water and aquifer groundwater. In the riverbank, a transect of drive-point piezometers (0–83 m from the river) were installed to depths up to ~5 m bgl, along a trajectory similar to that of the riverbank sediment cores. Water samples collected from the riverbank piezometers are referred to as riverbank porewater (n = 21). Groundwater samples from the shallow aquifer were collected from nearby household wells (n = 14) and from the monitoring wells which were installed using the hand flapper method (n = 9). Specifications on the depth and location of the water samples is provided in Table S1. All monitoring wells and piezometers were pumped continuously for 1 h before collecting the samples. The samples were filtered through a 0.2 µm polypropylene syringe filter (Whatman) into a sterile 50 mL centrifuge tube. Samples for bulk dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) measurements were acidified using 0.2% v/v HCl, and the samples for fluorescence and size exclusion chromatography were kept unacidified. All water samples were stored at 4 °C until analysis.

2.4. Statistical analyses

Geochemical data were analyzed using JMP Pro 14. Principal Components Analysis (PCA) was performed separately on the sediment

geochemical data and the extract data to help explain the relationships among the variables. The PCA was constructed from a correlation matrix with z-score standardized data to give a value between -1 and 1 (mean = 0 and SD = 1) for each variable. The relevant PCs were selected based on eigenvalues >1 (Kaiser's rule). Exploratory factor analysis was then performed on the correlation matrix to supplement the PCA findings by providing the rotated factor loadings (varimax rotation) and contributions of each variable. Riverbank and aquifer samples were not split into separate groups for these assessments. However, to determine the statistical differences between the riverbank and aquifer samples, the geochemical parameters of the sediment and water extracts were calculated by a non-parametric Mann-Whitney U test using a 0.05 p -value for significance.

3. Results

3.1. Physical and elemental composition of riverbank and aquifer sediments

The riverbank sediment cores (0 – 3 m depth bgl) contained a homogeneous distribution of fine sands. Drill cuttings obtained from the boreholes revealed a silt layer at a depth of ~ 5 m– ~ 6 m bgl which separates the riverbank sands from the underlying aquifer (Fig. 2). Resistivity measurements were conducted orthogonal to the river at this site and confirmed the presence of a silt layer between ~ 3 and ~ 7 m bgl (Pedrazas et al., 2021). A basal clay layer at ~ 36 m bgl marks the bottom of the shallow aquifer at the site. From the clay layer ~ 36 m bgl, grain size increases from fine to medium sand up to ~ 25 m. Between a depth of ~ 25 m bgl and the silt layer at ~ 6 m, there is a fining upward sequence of medium to fine sands, typical of a fluvial depositional environment (Ahmed et al., 2004). The LOI in the aquifer silt (4.8 ± 0.2 wt%, $n = 3$) and aquifer clay samples (7.7 ± 1.0 wt%, $n = 2$) were significantly higher than the LOI measured in the aquifer and riverbank sand samples (2 ± 0.6 wt%, $n = 45$) (Fig. 2a). Sedimentary concentrations were similar in the riverbank and aquifer sands for all measured elements except for Ca and Na, which had higher values in the riverbank and aquifer, respectively (Table 1). Despite the differing Ca and Na concentrations in the riverbank and aquifer sands, there was no correlation between depth or grain sized observed for either element. In both the riverbank and aquifer sediment, the bulk Fe and manganese (Mn) concentrations were strongly correlated ($R^2 = 0.93$), averaging 40 ± 12 g/kg and 0.7 ± 0.2 g/kg, respectively. Both Fe and Mn were negatively correlated with grain size ($R^2 = 0.93$ and 0.87 , respectively). Consequently, the concentrations of Fe and Mn in the aquifer sediments were lower in the aquifer sands (33 ± 13 and 0.6 ± 0.3 g/kg, respectively) than the silt (67 ± 1 and 1.1 ± 0 g/kg, respectively) and clay (58 ± 8 and 1.0 ± 0.3 g/kg, respectively) layers. Bulk As concentrations were similar in the aquifer and riverbank sands averaging 7 ± 2 mg/kg ($n = 45$) and showed a weak negative correlation with grain size ($R^2 = 0.47$) with slightly higher concentrations in the aquifer silt (9 ± 0.3 mg/kg) and clay layers (12 ± 0.1 mg/kg). Concentrations for all measured inorganic parameters are given in Table S2. The sedimentary PCA using the bulk elemental concentrations of the riverbank and aquifer samples revealed that redox sensitive elements, including As and Fe, were partitioned based on grain size. The redox sensitive elements were similarly distributed within the sediment as shown by the high degree of association along PC1 of the loadings plot (Fig. 3a) and were typically associated with finer grain sediment as shown in the score plot (Fig. 3b). In PC1, Al was the most dominant contributor to the model and was positively correlated with redox sensitive elements, including Fe and As (Table S3, Fig. S2). A more detailed explanation of the sedimentary PCA, including results and interpretation, is described in the Supplementary Text.

In the riverbank sediment, Fe concentrations were enriched in core C3 (40 m from the river) averaging 48 ± 6 g/kg, relative to the remaining riverbank sediment samples averaging 38 ± 5 g/kg (Fig. 4a).

Despite the overall strong correlation between Mn and Fe, Mn is not enriched in C3, although higher Mn concentrations are found at distances >40 m from the river in the unsaturated zone (Fig. S3). The bulk concentrations of As in the riverbank sediment ranged between 5 and 10 mg/kg, with a zone of As enrichment found between 10 and 40 m from the river with higher concentrations than at distances >40 m (7.4 and 6.3 mg/kg, respectively) ($p = 0.024$) (Fig. 4a). Siderophile elements Co and Ni and chalcophile element Zn, which are strongly influenced by the distribution and speciation of Fe minerals, also showed enrichment within the riverbank between 10 and 40 m (Kabata-Pendias, 2000; Liu et al., 2022; Rinklebe and Shaheen, 2017). The average concentrations of Co, Ni, and Zn within this 10 – 40 m zone (17.1 , 43.7 , and 74.6 , respectively) were higher than the average concentrations of Co, Ni, and Zn for distances >40 m (14.7 , 39.1 , and 69.3 , respectively) ($p < 0.05$) (Fig. S3). The bulk sediment concentrations of Fe, Mn, and As in the riverbank are comparable to previously reported concentrations measured using XRF in the Meghna Riverbank (Berube et al., 2018; Jung et al., 2015; Datta et al., 2009).

3.2. Characteristics of sediment-water extracts

3.2.1. Chemical composition of riverbank and aquifer sediment extracts

The mean electrical conductivity of the aquifer water extracts was 180 $\mu\text{S}/\text{cm}$, dominated by monovalent cations Na^+ and K^+ (1836 ± 293 mg/kg, 93 ± 34 mg/kg, respectively). Riverbank extracts had a lower mean conductivity of 11 $\mu\text{S}/\text{cm}$ with higher proportions of divalent cations Ca^{2+} (19 ± 10 mg/kg) and Mg^{2+} (12 ± 7 mg/kg) and lower Na^+ (42 ± 21 mg/kg) (Fig. 5a). The concentrations of cations in the aquifer extracts are representative of evaporite dissolution whereas the cations in the riverbank extracts suggest the products of both silicate and carbonate weathering (Fig. 5b) (Vega et al., 2020). All ions except Mg^{2+} , Cl^- , and NO_3^- were significantly higher in the aquifer extracts compared to the riverbank extracts (Table S2). The pH of the aquifer extracts (average = 7.31 ± 0.22) was lower than that of the riverbank extracts (average = 7.67 ± 0.44). There was a strong correlation between DOC and Na^+ in all the samples, although this correlation is better observed in the aquifer extracts due to the wider range of Na^+ and DOC concentrations (Fig. 5c).

The aquifer sands contained higher water extractable concentrations of the redox-sensitive elements Fe (174.3 mg/kg), As (0.48 mg/kg), and Mn (1.9 mg/kg) than the riverbank extracts (6.4 mg/kg, 0.03 mg/kg, 0.7 mg/kg, respectively) (Fig. 2b, Table 1). Furthermore, water-extractable Fe, As, and Mn, as a fraction of the bulk sediment concentrations were higher in the aquifer samples (0.5% , 7.1% , and 0.3% respectively) than the riverbank samples (0.02% , 0.4% , and 0.1% respectively) (Table S2). The PCA results on the extracts showed that the positive axis of PC1 contained high loadings and large contributions from DOC, Na^+ , As, and Fe (Fig. 3c, Table S3). However, as shown in the score plot, riverbank and aquifer samples are primarily differentiated along the PC1 axis (Fig. 3d). Riverbank samples are tightly grouped along the negative X axis (negative PC1) and aquifer samples plot on the right side of the score plot (positive PC1). Furthermore, there was no correlation among As, Fe, or Mn measured in the extracts. Although these elements are often associated together in reducing groundwaters within Bangladesh aquifers, the oxic conditions used in this experiment did not promote the simultaneous reduction of As bearing Mn and Fe oxides. Rather, the water-extractable concentrations of As and Fe were correlated to the organic properties such as DOC ($r = 0.74$ and $r = 0.80$, respectively) (Fig. S2). A more detailed explanation of the extract PCA, including results and interpretation, is described in the Supplementary Text.

In the riverbank extracts, elevated concentrations of Fe were found at 40 m from the river and 55 m from the river at depths of 0.5 m and ~ 1.6 m bgl respectively. Whereas the highest water-extractable As amounts were observed in the riverbank sediment between 0 m and 10 m from the river (Fig. 4b). Unlike the concentrations of water-extractable As,

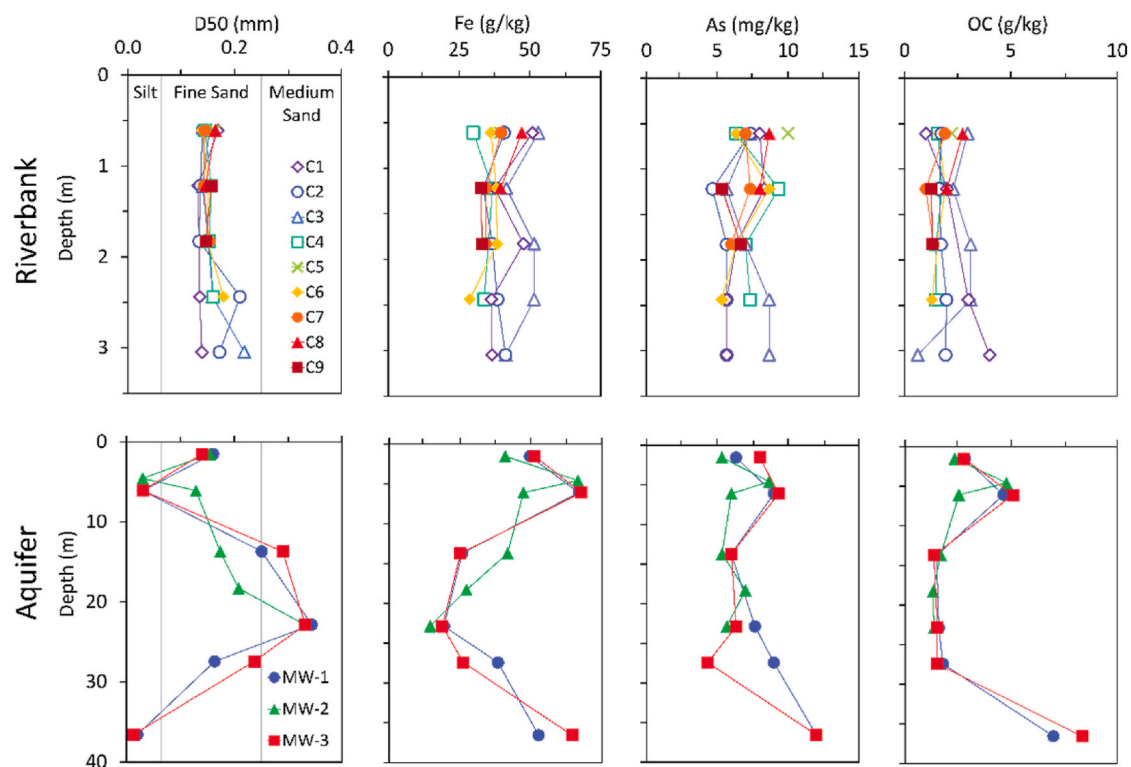
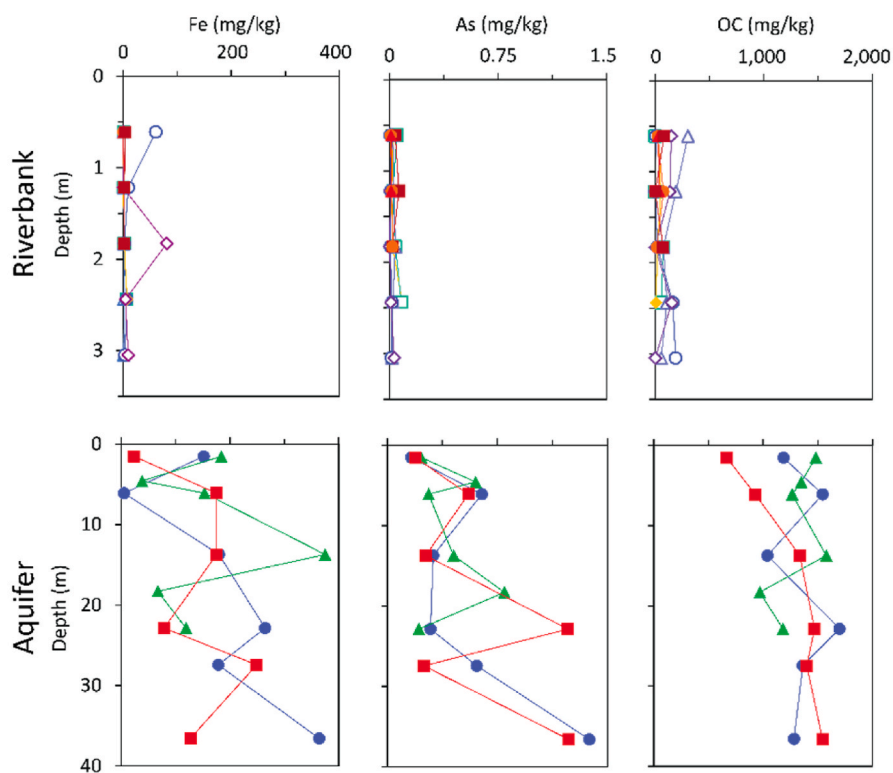
a**Sediment****b****Water Extracts**

Fig. 2. Depth profiles of sediment and extract properties for the Meghna Riverbank sediment and aquifer sediment. The colors denote different well or core locations, which are shown in Fig. 1. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 1

Results showing the properties of sediment and extract parameters in the riverbank and underlying aquifer. Average values for parameters $\pm$ standard deviation with the ranges given in parentheses.

Analysis Type	Parameter	Riverbank Sand (n = 32)	Aquifer Sand (n = 13)	MWW Test (p value)
Sedimentary Concentrations	Fe (g/kg)	40 $\pm$ 6 (29–53)	33 $\pm$ 13 (14–51)	0.123
	Mn (g/kg)	0.7 $\pm$ 0.1 (0.5–0.9)	0.6 $\pm$ 0.3 (0.3–0.9)	0.299
	As (mg/kg)	7 $\pm$ 1 (5–10)	6 $\pm$ 1 (4–9)	0.199
	LOI (g/kg)	19 $\pm$ 7 (6–33)	18 $\pm$ 6 (13–28)	0.507
	Na (g/kg)	19 $\pm$ 0.5 (18–21)	21 $\pm$ 1.4 (18–24)	0.0001
	Ca (g/kg)	22 $\pm$ 2 (16–25)	19 $\pm$ 5 (12–29)	0.0323
Water-Extractable Concentrations	Fe (mg/kg)	6.4 $\pm$ 16.0 (0.1–73.1)	174.3 $\pm$ 86.2 (65.5–350.7)	0.0001
	Mn (mg/kg)	0.7 $\pm$ 1.2 (0.1–7)	1.9 $\pm$ 0.7 (0.9–3.3)	0.0001
	As (mg/kg)	0.03 $\pm$ 0.02 (0.00–0.09)	0.48 $\pm$ 0.33 (0.21–1.25)	0.0001
	DOC (mg/kg)	67.4 $\pm$ 72.3 (0.4–301.3)	1330.3 $\pm$ 226.6 (969.9–1698.9)	0.0001
	Na ⁺ (mg/kg)	41.6 $\pm$ 21.1 (16.4–102.2)	1963.4 $\pm$ 293.3 (1552.9–2434.2)	0.0001
	Ca ²⁺ (mg/kg)	18.9 $\pm$ 9.5 (4.1–49.5)	57.7 $\pm$ 13.3 (36.2–78.8)	0.0001

Bold values denote statistically significant ($p < 0.05$) difference between the riverbank and aquifer samples based on a non-parametric Mann-Whitney-Wilcoxon (MWW) Test.

other redox sensitive trace elements (V, Co, Ni, Zn), were distributed similarly to the water-extractable Fe concentrations in the riverbank (Fig. S3).

3.2.2. Characteristics of water-extractable sedimentary organic matter

Significantly higher concentrations of water-extractable DOC were found in the aquifer sediment (1294 mg/kg) relative to the riverbank sediment (67 mg/kg). This was not primarily driven by grain size since similar amounts of water-extractable DOC were measured in the aquifer sand (1330 mg/kg), silt (1274 mg/kg), and clay (1412 mg/kg). Amongst these, however, aquifer sands contained a higher average water-extractable fraction of DOC per mass of LOI (8%) than the aquifer silt (3%) and clay samples (2%) (Fig. 6). Furthermore, all measured optical properties of the SOM were significantly different between the riverbank and aquifer extracts ($p < 0.05$, Table S4). The water-extractable SOM from riverbank sands (0–3 m bgl) exhibited a strong protein-like fluorescence, and prevalence of chromophoric apparent molecular weight (AMW) peaking at 100 Da (Daltons), followed by fractions of $\sim$ 830 Da (Fig. 6). In comparison, the water-extractable SOM from aquifer sands (6–36 m bgl) showed the presence of both humic-like and protein-like fluorophores, and chromophoric AMW predominantly peaking at 1500 Da, followed by fractions of 4500 Da and 27,000 Da. The silt (5 m bgl) and clay (37 m bgl) contained water-extractable SOM which showed a strong humic-like fluorescence, and chromophoric AMW peaking at 1600 Da and 1800 Da respectively. Both riverbank and aquifer sediments had trace amounts of SOM with chromophoric AMW peaking at 100,000 Da. The groundwater and riverbank pore water contained similar amounts of DOC, averaging 3 ± 1 mg/L, with similar chromophoric AMW peaks at $\sim$ 1600 Da. However, the fluorescence signature in the groundwater samples exhibited a strong humic-like signature (humic:protein ratio of 8 ± 5), whereas the riverbank pore water exhibited a mixed humic and protein-like fluorescence signature (humic:protein ratio of 3.3 ± 2.7) (Fig. S4, Table S4).

4. Discussion

4.1. Potential natural reactive barrier along Meghna riverbank

A study along the Meghna River by Berube et al. (2018) on a bank of the river located 5 km upstream and on the opposite (eastern) side of our study site noted a zone of aged river water (seasonal mixing zone) mixing up to approximately 50 m from the dry season river edge. The zone of aged river water mixing was attributed to inundation of the riverbank during the wet season and characterized by a progressive dilution in major ions and conductance towards the river. At this site, the sedimentary Fe concentrations (40 g/kg) at the 50 m seasonal mixing zone were enriched relative to the average riverbank concentrations (30 g/kg) (Berube, 2017). Likewise, the Fe enrichment 40 m from the river at our site reflects the current extent of the spring tide mixing zone and may indicate a dry season NRB maintained by the ongoing river water-groundwater mixing (Fig. 4a). Two lines of evidence further suggest the sediment in this stretch of the riverbank (0–40 m) hosts seasonally driven hyporheic exchange: 1) The sedimentary concentrations of As and other elements which are strongly influenced by redox cycling of Fe (Co, Ni, Zn) show solid phase enrichment within distances < 40 m from the river relative to their concentrations in sediment at distances > 40 m (Fig. S3) (Kabata-Pendias, 2000). Here, the immobilization of redox sensitive elements in the riverbank may be maintained by the periodic infiltration of river water from combined semidiurnal and neap-spring tides and alternating saturation conditions. Within this zone, the infiltration of river water and periods of aeration may maintain Fe³⁺-oxides in the mineral form, providing sorption sites for As and other trace metals (Bone et al., 2006); and 2) The homogeneous riverbank sands promote river water infiltration and mixing within the riverbank, excluding the notion that the contrasting zones of As (< 40 m) and Fe accumulation (40 m) are mainly attributed to the grain size. It should be noted that the samples taken for this study represent a point in time during the life cycle of a NRB that may change seasonally. Ocean tides operate most strongly during the dry season, the tidal mixing would diminish during the early wet season when the riverbank is submerged (Berube et al., 2018). During complete submersion by river water, the riverbank may turn more deeply reducing which may dissolve much of the iron oxides in the sediment.

4.2. Geochemical processes influencing as mobility

The bulk sedimentary concentrations of the riverbank and aquifer sediments were similar. The sedimentary PCA demonstrated that Fe exerts a strong influence on the distribution of trace metals and is enriched in sediment containing clay minerals as seen by the strong associations in PC1 (Fig. 3a). The co-occurrence of these elements relates to the partitioning of redox sensitive elements within organic rich phyllosilicate and Fe-bearing minerals (Fig. 3b). Similarly, the positive association of As with PC1 suggests that As is associated with OM or phyllosilicate and clay minerals in the sediment (Fig. 3a). Despite similar sedimentary concentrations, the average water-extractable concentrations of As in the aquifer sands (0.5 mg/kg), silts (0.6 mg/kg), and clays (1.3 mg/kg) were substantially higher than the riverbank sands (0.03 mg/kg) (Table 1). Previous studies have shown that the water-extractable fraction of As from certified reference soils and contaminated sediments is generally less than 2% of the total As in the sample (Cappuyns et al., 2002; Montperrus et al., 2002; Shiohata et al., 2001; Van Herreweghe et al., 2003; Wan et al., 2017). Interestingly, the water-extractable fraction of sedimentary As in the aquifer sands, silts, and clays reported in this study (7.5%, 6.9%, 11.2%, respectively) are substantially greater than the values typically reported for the certified reference sediment and contaminated sediments, and that of the riverbank sands (0.37%). However, the water extractable fraction of sedimentary As in these aquifer sediments are similar to previously reported values from a nearby site in Araihaazar (15 km north

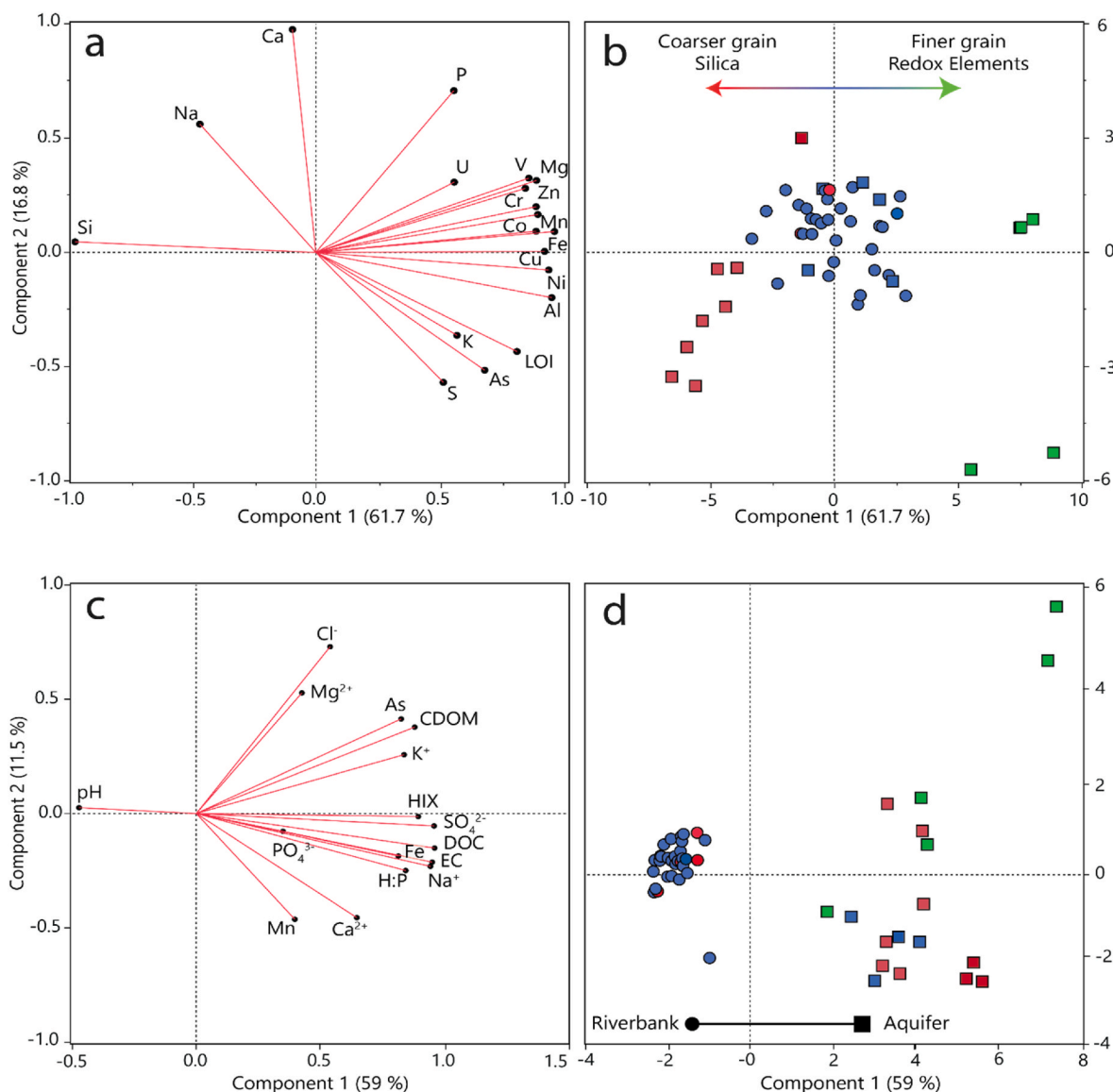


Fig. 3. PCA graphs depicting the spatial relationships among organic and inorganic chemicals in solid-phase and extracted with water: (a) Loadings plot of solid-phase elemental concentrations, (b) score plot of the samples, (c) Loadings plot of chemicals and ions extracted from sediments with DI water, (d) score plot of the samples. Circles are riverbank samples and squares are aquifer samples. Colors represent the grain size of the sample: red is medium grain sands, blue is fine sand, and green is silt and clay samples. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

of our site) which ranged between 0.46 and 34.4% (Radloff et al., 2017).

Exposing the aquifer material to oxic water that was initially undersaturated for all minerals likely resulted in the release of As through one or more oxidative pathways (Huyen et al., 2019; Polizzotto et al., 2006). For example, Masuda et al. (2010) proposed that the oxidative weathering of clay minerals in solution can release substantial amounts of As, enough to maintain elevated levels of As in the Holocene aquifers of Bangladesh that are poor in Fe-oxide minerals. Sulfide oxidation is of prominent importance in aquifer systems subjected to temporal redox changes (Appelo and Postma, 2004; Battistel et al., 2021; Prommer and Stuyfzand, 2005; Wallis et al., 2010). However, little SO_4^{2-} was produced during the experiments, therefore, the majority of As extracted was likely from desorption processes. The desorption of As and other constituents is controlled by changes in pH, ion-exchange effects, and the presence of competing ligands that exchange with sorbed As to re-establish equilibrium with the pore-waters (Smith et al., 1998). Under oxic conditions and above circumneutral pH, the desorption of As from mineral hosts may be promoted despite the presence of Fe-oxide minerals (Johannesson and Tang, 2009). In the case of this study, the DI

water thermodynamically favored desorption until equilibrium concentrations of As were established.

In the aquifer extracts, Na^+ dominates the ionic composition of the solution. In the context of typical hydrochemical processes, a high ratio of Na^+ relative to other cations suggests the solution chemistry is dominated by evaporite dissolution (Fig. 5a and b) (Gaillardet et al., 1999; Mukherjee and Fryar, 2008; Vega et al., 2020). However, because the sediment-water extracts are not natural water samples, this idea was only used as a heuristic tool to explain the solution chemistry in the riverbank and aquifer samples. Furthermore, Na^+ lacks correlation with Cl^- , which would otherwise suggest a sodium chloride source. In this case, the source of Na^+ in the aquifer extracts must be desorbed from the mineral surfaces comprising the aquifer sediment or dissolved from alternative evaporite mineral hosts. The strong correlation between DOC and dissolved Na^+ suggests that easily exchangeable DOC and Na^+ in the aquifer sediments are concurrently mobilized (Fig. 5c). High Na^+ concentrations have been linked to enhanced DOC mobilization due to the ability of Na^+ to denature the supra-molecular structures of humic substances (Amrhein et al., 1992; Pontoni et al., 2019). The mobilized

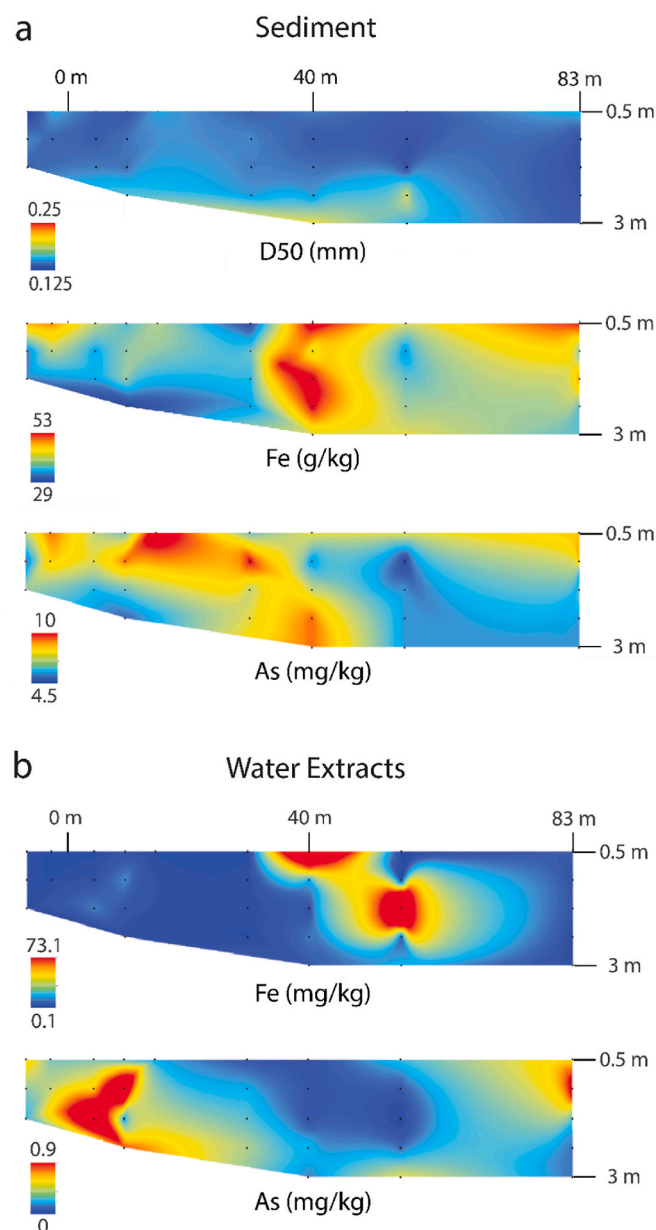


Fig. 4. Spatial distribution of D50 and the solid phase Fe and As concentrations in the riverbank sediments (a) and the Fe and As concentrations in sediment-water extracts (b), interpolated using inverse distance weighting (IDW) method. Although a homogenous layer of fine sand was observed in 0–3 m bgl in the riverbank sediments, these interpolations may not take into account minute-scale spatial geochemical variations and should be interpreted with caution.

DOC may then compete with As for sorption sites, suppressing the sorption abilities of clay and oxide minerals promoting further desorption of As (Keller & da Costa, 1989; Lin and Puls, 2000; Wang and Mulligan, 2006a, 2006b; Xue et al., 2019). In the extract PCA, high loading values of DOC, Fe, K^+ , Ca^{2+} , Na^+ , and As in PC1 suggest these constituents are co-mobilized and link the effects of clay minerals (i.e., illite, chlorite, smectite, vermiculite) to As desorption and the overall extract chemistry (Table S3). Prior studies in the Bengal basin have also highlighted the important role of clay minerals to act as either a sink or source of exchangeable As (Acharyya et al., 2000; Charlet et al., 2007; Masuda et al., 2010). In a similar leaching experiment as this study, using aquifer sediment from the Mekong Delta and DI water, Huyen et al. (2019) found that As release from aquifer sediment under oxic

conditions was attributed to DOC enhanced desorption from clay minerals and the dissolution of As-bearing salts.

Despite exhibiting similar sedimentary concentrations of OM and major and trace elements, the riverbank extracts contained much lower elemental and DOC concentrations (Table 1). These differences may be attributed, in part, to higher flushing rates in the riverbank sediments, frequent oscillations in the redox state of riverbank sediments, the presence of older and recalcitrant organic matter in the aquifer sediments compared to riverbank sediments, the availability of sorption sites, and the differing methods used to sample the riverbank and aquifer sediment. The primary factor contributing to the lower concentrations in the riverbank sediment is likely from the periodic flushing and redox cycling in the riverbank from tidal and seasonal inundation. The flushing rate, in this case the amount of time it takes to replace the pore water volume, is controlled by the local hydrology and stratigraphy and exerts a prominent control on the groundwater As concentrations by removing the exchangeable As and other solutes from the system (Choudhury et al., 2018; van Geen et al., 2008). Frequent tidal fluctuations and seasonal inundation lead to relatively high flushing rates in the riverbank compared to the adjacent aquifer. Furthermore, tidal and seasonal inundation may promote anoxic conditions deeper in the riverbank as oxygen is consumed with depth in the sediment column, such inundated parafluvial zones have been linked to elevated As concentrations in the underlying and adjacent aquifers (Connolly et al., 2021). In environments where the fluctuations in redox conditions have a short half cycle, the transformation of amorphous Fe^{3+} minerals, such as ferrihydrite, is impeded and the amorphous Fe^{3+} minerals can accumulate in the sediment (Tomaszewski et al., 2016). Along the tidally fluctuating Meghna River, the frequent shifts in redox conditions may similarly promote the accumulation of amorphous Fe^{3+} minerals in the sediments. For example, Jung et al. (2012) found ferrihydrite accounted for 49% of the Fe^{3+} minerals within the top 2 m of the riverbank sediments during the dry season. These amorphous Fe-hydroxides are commonly formed in the presence of DOC and have a larger As-attenuation capacity than crystalline Fe^{3+} minerals (Bigham et al., 2002; Dixit and Hering, 2003; Dzombak and Morel, 1991). However, during the monsoon season, prolonged periods of anoxic conditions may promote dissolution of the amorphous Fe-hydroxides in the riverbank sediments and release substantial amounts of the accumulated As, which may then advect into the river during subsequent flushing episodes. Furthermore, the riverbank extracts have a cationic signature with high proportions of Mg^{2+} and Ca^{2+} , typically indicative of carbonate mineral dissolution in groundwater (Fig. 5a). The presence of divalent ions, Mg^{2+} and Ca^{2+} , create favorable electrostatic conditions for As adsorption on the surface of clay minerals (Fakhreddine et al., 2015) and oxides (Wang et al., 2019; Wilkie and Hering, 1996), at much higher rates than when monovalent counter ions such as Na^+ are dominant (Masue et al., 2007; Smith et al., 2002). The low concentrations of As in the riverbank extracts relative to that of the aquifer extracts may be partially explained by the higher relative dominance of divalent cations (Fig. 5b) and absence of anions competing for sorption sites such as SO_4^{2-} , PO_4^{3-} , and DOC.

The riverbank sediment that released the highest proportion of Fe to the solution simultaneously contained the lowest water-extractable fractions of As (Fig. 4b). For example, the riverbank extracts with the highest amounts of As were found within the 40 m mixing zone whereas the highest concentrations of water-extractable Fe were found at distances ≥ 40 m from the river (Fig. 4b). This is likely due to the re-adsorption of As in the during the experiment onto the remaining Fe minerals in the solution (Gruebel et al., 1988; Kheboian and Bauer, 1987; Wenzel et al., 2001). In the case of the riverbank samples taken from distances ≥ 40 m from the river, where sedimentary Fe concentrations were higher, any liberated As could re-adsorb onto these Fe minerals during the extraction procedure resulting in the lower extractable concentrations of As. Despite the low water-extractable amount of Fe and As in the riverbank sediment (0.02% and 0.37%,

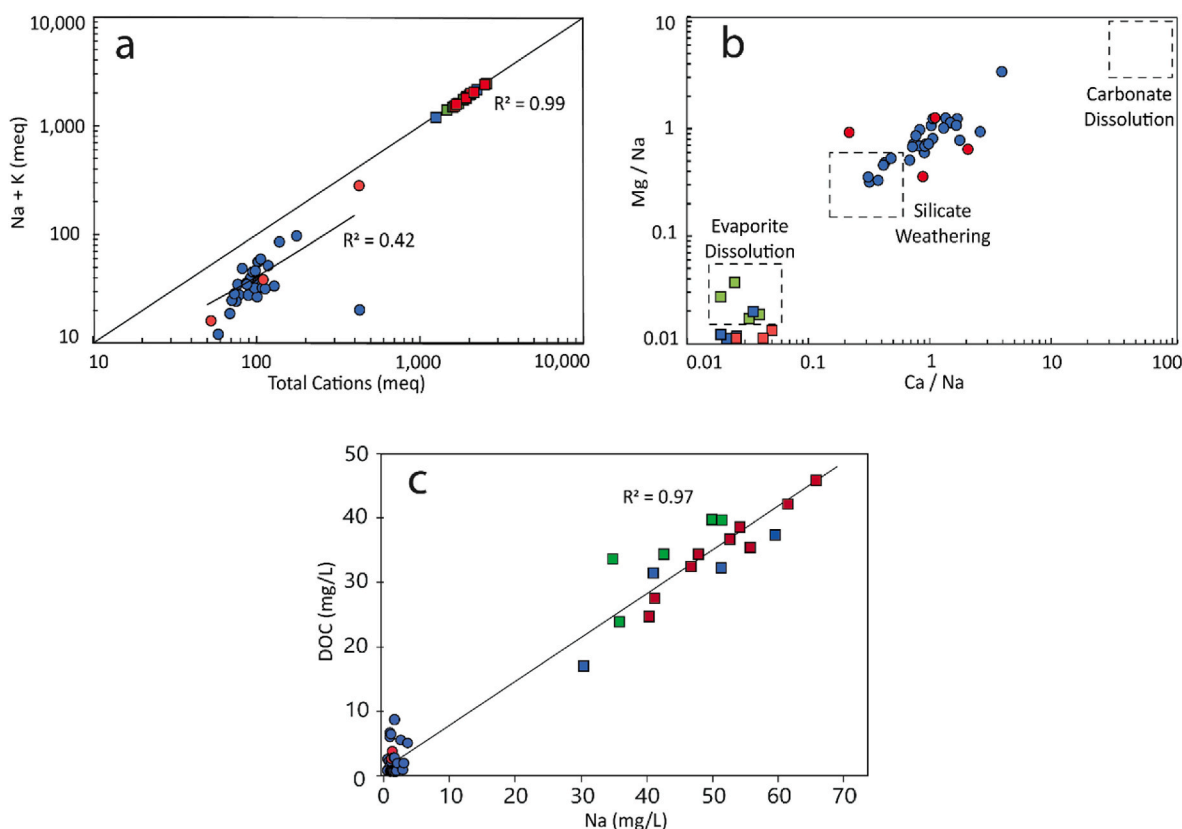


Fig. 5. Ionic composition of extracts: (a) Correlation between total cation concentration and monovalent cations, (b) Molar ratio of Ca/Na and Mg/Na representative of major geochemical processes affecting water chemistry. Dashed rectangles represent the predominant geochemical processes in natural waters (Gaillardet et al., 1999; Mukherjee and Fryar, 2008; Vega et al., 2020). (c) Correlation between Na^+ and DOC. Circles represent riverbank samples and squares represent aquifer samples. Colors represent grain size of the sample: red is medium grain sands, blue is fine sands, and green are silt and clay samples. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

respectively), these amounts may account for large portions of dissolved As and Fe in the riverbank porewater. Assuming an average bulk density in the riverbank sand of 1.45 g/cm^3 and a porosity of 0.45, the apparent porewater concentration can be calculated based on the following:

$$\text{Pore water concentration} = \frac{\text{mass of sample} \times \text{volume of water}}{\text{bulk density} \times \text{porosity}} \quad (\text{EQ. 2})$$

Based on this calculation, the water-extractable concentrations of Fe and As in the riverbank pore water would average 10.4 mg/L and $41.8 \text{ } \mu\text{g/L}$, respectively. These values are within the previously reported ranges measured in the Meghna riverbank pore waters for dissolved Fe ($0.1\text{--}20 \text{ mg/L}$) and As ($1\text{--}220 \text{ } \mu\text{g/L}$) (Berube et al., 2018; Jung et al., 2015). It is expected that a higher amount of As and Fe would be mobilized from the sediment under anaerobic conditions. However, as observed in this study, the riverbank sediment may also contribute significant proportions of Fe and As to the dissolved load under oxic conditions. Although the DI water was initially undersaturated for all elements and likely resulted in higher water-extractable concentrations under the experimental conditions, these findings illustrate the potential for the mobilization of substantial amounts of As from the riverbank sediment over time in an oxic environment. Further investigation into the processes promoting As release from the riverbank sediments under anaerobic conditions is warranted, as the reductive dissolution of redox sensitive minerals could exacerbate the release of As in the riverbank.

4.3. Role of sedimentary organic matter on as mobility in the riverbank hyporheic zone

The bulk content of SOM was estimated from % mass of LOI. Water-extractable DOC can be expressed as the fraction of SOM extracted by

the water during the batch experiment (Fig. 6). Both riverbank (0–3 m depth) and aquifer sands (6–36 m depth) contained 2% mass of LOI, which was significantly lower than that in silt (5%) and clay (8%) layers in the aquifer. This is consistent with prior studies that report high SOM content in silts and clays in Bengal basin aquifers (Anawar et al., 2002; Kulkarni et al., 2017; McArthur et al., 2004; Mihajlov et al., 2020; Sankar, 2013). The water-extractable portion of SOM is a crucial component in the biogeochemical processes as most heterotrophic microbial metabolisms require solubilized OM (Fenchel et al., 2012). However, some species of Fe-reducing bacteria utilize extracellular electron transport for the dissimilatory reduction of Fe minerals (Holmes et al., 2016; Richter et al., 2012). Upon the dissolution of the Fe-bearing minerals comprising the sediment, the SOM trapped in the sediment can be released (Kaiser and Guggenberger, 2000; Lalonde et al., 2012). Interestingly, the amount of water-extractable SOM, measured in the extracts as DOC, was significantly different in riverbank sands (67 mg/kg) than that in aquifer sands (1294 mg/kg). Prior evidence suggests that aquifer sediments in Bangladesh may preserve high molecular weight, recalcitrant humic-like SOM due to prolonged reducing conditions (Datta et al., 2011; McArthur et al., 2004; Mladenov et al., 2010; Neumann et al., 2014). In the reducing aquifer, the desorption of this accumulated SOM is unlikely to occur under prevailing reducing conditions as the desorption of SOM rarely occurs in conditions similar to those present during the time of initial sorption (Kaiser and Guggenberger, 2000; Kaiser and Zech, 1999). As a result, exposing the sediment to undersaturated oxic water facilitated the release of such SOM in aquifer sands in higher amounts of DOC as compared to the riverbank sands which experience natural periods of oxidation. These findings are consistent with the results from a microcosm experiment (Mladenov et al., 2010) showing that aquifer sediments (11 m depth) from a

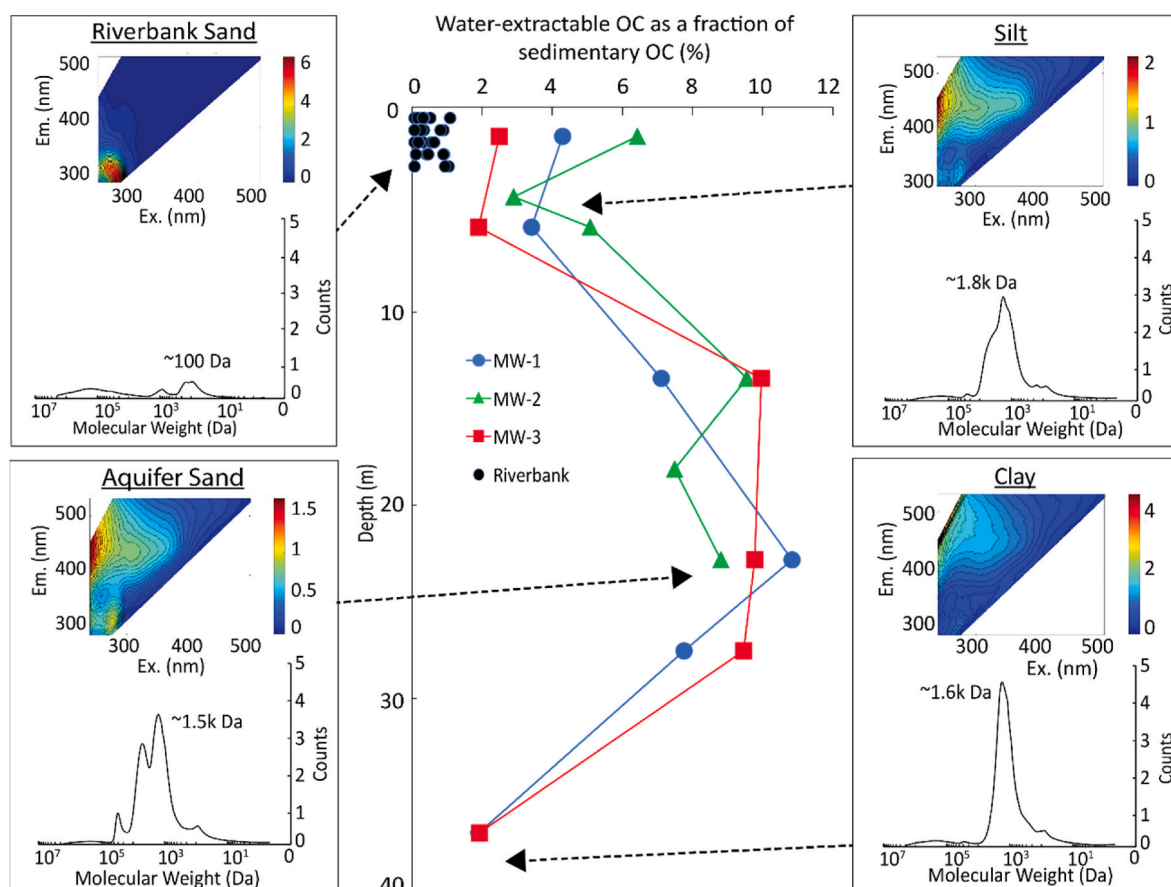


Fig. 6. Distribution of water-extractable organic carbon as a fraction of % loss on ignition (bulk OM content) in riverbank sands (0–3 m), a silt layer (5 m), aquifer sand (6–36 m), and a clay layer (37 m). A three-dimensional fluorescence excitation emission matrix (EEM) shows a representative fluorescence signature of water-extractable organic matter in respective sediments. Size exclusion chromatogram for each representative sediment type indicates the distribution of apparent molecular weight (AMW) of water-extractable chromophore SOM (254 nm) and the approximate peak centered average AMW in the respective sediment samples. Additional data is provided in the SI (absorbance and fluorescence indices in Table S4; molecular weight averages for individual samples in Table S5).

different site within Araihaazar (~15 km north of our study site) released humic-like SOM to solution, highlighting the presence of humic-like SOM trapped in these sediments that is mobilized upon prolonged interactions with groundwater. Comparatively, much lower release of DOC from riverbank sands may be attributed to fluctuating redox conditions in the riverbank which may partly oxidize the riverbank SOM.

Spectroscopic and chromatographic analyses indicated the presence of fresh, protein-like, and predominantly low AMW (100 Da) water-extractable SOM in riverbank sands, compared to older, humic-like, and predominantly high AMW (1500 Da) water-extractable SOM in aquifer sands (Fig. 6). The riverbank SOM with a strong protein-like fluorescence signature and relatively low AMW indicates microbially labile and biodegradable SOM (D'Andrilli et al., 2015; Marschner and Kalbitz, 2003). This SOM may have formed via microbial metabolic processes or from the degradation of high AMW OM derived from the river (Mopper et al., 2007). Conversely, high AMW SOM in aquifer sands may be attributed to older, terrestrially-derived OM deposited during Holocene (McArthur et al., 2004; Rowland et al., 2006; Schittich et al., 2018), which is considered to be relatively recalcitrant (Mopper et al., 2007). Silt and clay layers in the aquifer at 5 m and 32 m depth, respectively, contained high mass % of LOI, exhibit a strong humic-like fluorescence signature and AMW of 1600 Da and 1800 Da respectively. This finding is consistent with many prior studies which suggested the clay layers (or clay lenses) in the aquifer are sources of DOC that promote As mobilization (Guo et al., 2019; Kulkarni et al., 2017, 2018a; Mihajlov et al., 2020; Mladenov et al., 2015; Mukherjee et al., 2007a, 2007b; Sankar, 2013).

The release of the humic-like SOM in the aquifer may facilitate the mobilization of As (Kulkarni et al., 2017, 2018a; Mladenov et al., 2015; Vega et al., 2017) via electron shuttling (Kulkarni et al., 2017, 2018b; Mladenov et al., 2010, 2015), competitive exchange processes (Wang and Mulligan, 2006a; Xue et al., 2019), or by forming mobile ternary complexes with Fe and As under oxic conditions (Mikutta & Kretzschmar, 2011; Sharma et al., 2010). Neumann et al. (2014) found that the SOM was readily mobilized by perturbations within the aquifer and could provide a substantial source of carbon within the aquifer. This water-extractable SOM in aquifer sediments may serve as a key source of energetic carbon to the groundwater to preserve Fe-reducing conditions (Zhao et al., 2022).

On the other hand, riverbank sands containing labile and low AMW SOM may support a wide range of microbial metabolisms such as aerobic, nitrate-reducing, and metal-reducing (Fe, Mn, As) as favored by the thermodynamics (Bethke et al., 2011). Although there are no obvious sources at our study site, some organic contaminants (e.g., PAH) also exhibit similar molecular weights (Hinga, 2003; Rojo-Nieto et al., 2013). The prevalence of a particular metabolism depends upon the availability of an electron acceptor (e.g., $O_{2(aq)}$, NO_3^- , or Fe^{3+} minerals). During the dry season, when conditions are periodically oxidizing in the riverbank, oxygen is likely to be the most favored electron acceptor promoting aerobic heterotrophic oxidation of labile SOM. During the wet season, however, microbially-mediated reductive dissolution of Fe^{3+} minerals is likely to prevail. Therefore, mineralization of labile SOM in the riverbank may continue under both oxidizing and reducing conditions, but the dissolution of Fe^{3+} minerals and mobilization of As would occur only

under reducing conditions.

We also compared the characteristics of DOM in riverbank pore water and groundwater with the SOM of the corresponding riverbank and aquifer sediment extracts (Table S4, Fig. S4). Comparison between the properties of DOM in groundwater and water-extractable SOM in aquifer sediments indicated that during our experiment, the SOM with a higher AMW of 4500 Da and 27,000 Da released in the aquifer extracts was not present in the groundwater DOM, which contained primarily ~1600 AMW Da (Table S5). These differences may be attributed to the oxic experimental conditions used in this study, compared to prolonged reducing conditions in the aquifer (Mladenov et al., 2010). For instance, high AMW SOM may not be released under reducing conditions as we observed under oxidizing conditions in this study. Similarly, in the case of riverbank pore water DOM and the water-extractable SOM from riverbank sands, the pore water DOM shows a higher AMW peak (~1600 Da) than found in the water-extractable SOM (peaks at ~100 Da and 830 Da) which is consistent with the lower water-extractable SOM content of these sediments. The trace amounts of 100,000 Da AMW in the riverbank and aquifer sediments resembles complex molecules, macromolecular assemblages, or aqueous complexes between humic and fulvic acids, clay minerals, and dissolved metals such as Fe (Docter et al., 2015; Leenheer and Croué, 2003).

The characterization of SOM in this study supported the role that SOM release plays in As mobilization within the aquifer through complexation and competitive exchange processes. However, the contrasting SOM properties revealed that the riverbank sediment may contribute to As mobilization through multiple pathways. The tidal and seasonal river stage fluctuations create a dynamic redox environment in the riverbank which likely affects the local microbial communities. The response of microbial gene expression to these recurrent redox changes within the riverbank hyporheic zone should be studied. However, more sediment sampling and analysis across all seasons and sediment-water interaction experiments under both reducing and oxic conditions are needed to comprehensively understand the role that SOM plays in the formation and demise of a riverbank NRB. Nevertheless, we hypothesize that during the dry season when reduced As and Fe-rich groundwater flows towards the river, the degradation of OM in the riverbank will not support the reductive dissolution of Fe, allowing for the formation of a NRB within the riverbank mixing zone. This NRB can exist where oxic conditions persist, allowing for the formation of a NRB unchallenged by microbially mediated OM degradation. However, during the wet season when the riverbank is flooded and conditions become reducing, the degradation of labile OM and microbially mediated reduction of Fe-oxides is promoted, which may deteriorate the previous extent of the NRB and potentially release large fluxes of Fe and As from within the NRB. When flooding recedes towards the end of the monsoon season and the riverbank is exposed once again, the NRB can become re-established within the river water-groundwater mixing zone. Here, spectroscopic characterization and molecular weight analysis of OM in the riverbank and aquifer sediment revealed contrasting roles that OM plays in the mobilization of As from the sediment in these settings.

4.4. Effects of sediment sampling methods on geochemical characterization

In this study, riverbank sediment samples were collected in the form of pristine cores (Berube, 2017), whereas, the aquifer sediments were collected during drilling of monitoring wells by hand-flapper method (Horneman et al., 2004; Sankar et al., 2014). The hand-flapper method may disturb the sediments compared to pristine coring, as it uses reverse circulation of native groundwater to extract the sediments. The mixing of the sediment and groundwater may be biased towards larger grain sizes (Horneman et al., 2004), this bias could have resulted in the underestimation of the sedimentary concentrations for the aquifer sediments in this study. A similar study collected aquifer sediment using both direct push coring and hand-flapper methods from Araihaazar,

Bangladesh (15 km north of our site), and found that the amounts of water extractable As were similar for each of these sampling methods (Radloff et al., 2017). However, our results showed contrasting differences between water-extractable constituents (inorganic and organic) of aquifer and riverbank sediments. While some of these differences may be attributed to the different sampling methods for the two types of sediments collected in this study (i.e. mixing during the drilling process for aquifer sediment), the differing in-situ processes in the riverbank and aquifer are likely the primary determinant on the observed sediment chemistry. Further, the analysis of aquifer sediments coincided with prior studies that report the presence of high AMW, humic-like SOM (Ghosh et al., 2015; Rowland et al., 2006), and similar bulk elemental composition (Sankar et al., 2014). This indicated that despite disturbances, the bulk characteristics of aquifer sediments were retained. Nevertheless, future studies are warranted to determine effects of varying sampling methods on the adsorption/desorption behavior of the sediments, specifically for the organic constituents.

5. Conclusion

This study investigated the solid phase and water-extractable geochemistry of the riverbank and its adjacent aquifer along the seasonally and tidally fluctuating Meghna River, Bangladesh and how these properties are related with the mobilization and immobilization of As. The results are interpreted within the context of a NRB. At this site, enrichment of sedimentary As was observed within 40 m from the river during the dry season maintained in the solid phase under intermittent oxidizing conditions. During the dry season, labile OM supports aerobic and nitrate-reducing metabolisms leading to the immobilization of Fe and As within the riverbank NRB. However, during the wet season when conditions become reducing, labile OM in the riverbank may promote the microbial reduction of Fe and Mn leading to the mobilization of As and Fe within the riverbank NRB. These findings suggest that the reactivity of SOM in the riverbank HZ plays a vital role in the formation of a NRB, including the solid-phase enrichment and mobilization of Fe and As. The presence of humic-like substances in the aquifer sediment are consistent with previous studies that have highlighted the role of humic substances in promoting As mobility. However, the high concentrations of DOC, As, and Na⁺ in the aquifer extracts suggests the co-mobilization of these constituents would be exacerbated if perturbations in the aquifer introduce oxic conditions. Aspects of the transport and reactions between the riverbank NRB of fluctuating rivers and shallow aquifers remain uncertain. These processes may have important implications for As cycling throughout the deltas of southeast Asia. This study improves our understanding of the hydrologic and biogeochemical controls on As mobility at the river water-groundwater interface.

Credit author statement

Thomas Varner: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization, Writing – review & editing. Harshad Kulkarni: Conceptualization, Software, Validation, Formal analysis, Data curation, Writing – review & editing, Visualization, Methodology – Organic Matter Characterization, Supervision. William Nguyen: Methodology – Particle Size Analysis. Kyungwon Kwak: Methodology – Water Analysis, Validation of Water Data, In Field Help. Bayani Cardenas: Conceptualization, Methodology, Validation, Investigation, Resources, Writing – review & editing, Visualization, Supervision, Funding acquisition. Peter Knappett: Conceptualization, Methodology, Validation, Investigation, Resources, Writing – review & editing, Visualization, Supervision, Funding acquisition. Ann Ojeda: Methodology – Organic Matter Characterization, Formal analysis, Validation, Writing – review & editing. Natalia Malina: Methodology – Organic Matter Characterization, Formal analysis, Validation, Writing – review & editing. Mesbah Uddin Bhuiyan: Methodology – Field Investigation. Kazi Matin Ahmed:

Methodology – Field Logistics, Preparation. Saugata Datta: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2022.136289>.

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