



Biogeochemical Controls on the Release and Accumulation of Mn and As in Shallow Aquifers, West Bengal, India

Michael A. Vega¹, Harshad V. Kulkarni², Natalie Mladenov³, Karen Johannesson⁴, Ganga M. Hettiarachchi⁵, Prosun Bhattacharya^{6,7}, Naresh Kumar⁸, Joseph Weeks⁵, Madhubhashini Galkaduwa⁵ and Saugata Datta^{1*}

¹ Department of Geology, Kansas State University, Manhattan, KS, United States, ² Department of Civil Engineering, Kansas State University, Manhattan, KS, United States, ³ Department of Civil, Construction, and Environmental Engineering, San Diego State University, San Diego, CA, United States, ⁴ Department of Earth and Environmental Sciences, Tulane University, New Orleans, LA, United States, ⁵ Department of Agronomy, Kansas State University, Manhattan, KS, United States, ⁶ KTH-International Groundwater Arsenic Research Group, Department of Sustainable Development, Environmental Science and Engineering, KTH Royal Institute of Technology, Stockholm, Sweden, ⁷ International Center for Applied Climate Science, The University of Southern Queensland, Toowoomba, QLD, Australia, ⁸ Department of Geological Sciences, Stanford University, Stanford, CA, United States

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*Correspondence:

Saugata Datta
sdatta@ksu.edu

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HIGHLIGHTS

- Manganese and arsenic concentrations are elevated in Murshidabad groundwater.
- Manganese release appears to be independent of dissolved organic matter quality.
- Mineral precipitation and dissolution reactions impact fate of manganese.
- Arsenic concentrations are related to dissolved organic matter quantity and quality.

The prevalence of manganese (Mn) in Southeast Asian drinking water has recently become a topic of discussion, particularly when concurrent with elevated arsenic (As). Although Mn groundwater geochemistry has been studied, the link between dissolved organic matter (DOM) quality and Mn release is less understood. This work evaluates characteristics of DOM, redox chemistry, and the distribution of Mn within Murshidabad, West Bengal, India. Shallow aquifer samples were analyzed for cations, anions, dissolved organic carbon, and DOM properties using 3-dimensional fluorescence excitation emission matrices followed by parallel factor modeling analyses. Two biogeochemical regimes are apparent, separated geographically by the river Bhagirathi. East of the river, where E_h and nitrate (NO_3^-) values are low, humic-like DOM coexists with high dissolved Mn, As, and Fe. West of the river, lower dissolved As and Fe concentrations are coupled with more protein-like DOM and higher NO_3^- and E_h values. Dissolved Mn concentrations are elevated in both regions. Based on the distribution of available electron acceptors, it is hypothesized that groundwater east of the Bhagirathi, which is more reducing and enriched in dissolved Fe and Mn but depleted in NO_3^- , is chemically dominated by Mn(IV)/Fe(III) reduction processes. West of the river where NO_3^- is abundant yet dissolved Fe is absent, NO_3^- and Mn(IV) likely buffer redox conditions such that E_h values are not sufficiently reducing to release Fe into the dissolved phase. The co-occurrence of humic-like

DOM with dissolved As, Fe, and Mn in the more reducing aquifers may reflect complex formation between humic DOM and metals, as well as electron shuttling processes involving humic DOM, which may enhance metal(loid) release. Saturation indices of rhodochrosite (MnCO_3) suggest that precipitation is thermodynamically favorable in a greater proportion of the more reducing sites, however humic DOM–Mn complexes may be inhibiting MnCO_3 precipitation. Where dissolved arsenic concentrations are low, it is postulated that Mn(IV) reduction is oxidizing As(III) to As(V), increasing the potential for re-adsorption of As(V) onto relatively stable, un-reduced or newly precipitated Fe-oxides. Manganese release appears to be independent of DOM quality, as it persists in both humic and protein-like DOM environments.

Keywords: manganese, organic matter, West Bengal, arsenic, shallow aquifer

INTRODUCTION

Throughout the Bengal Basin, elevated levels of manganese (Mn) and arsenic (As) have adversely impacted groundwater quality, prompting serious concerns to human health (Bhattacharya et al., 1997; Nickson et al., 1998; BGS and DPHE, 2001; Buschmann et al., 2008; Datta et al., 2009, 2011; Frisbie et al., 2009; Farooq et al., 2011; Sankar et al., 2014; Datta, 2015; Shrivastava et al., 2015; Kshetrimayum and Hegeu, 2016). Further, groundwater is the primary source of drinking water in many of these regions due to surface waters being contaminated by anthropogenic waste (McArthur et al., 2012a).

Although Mn is an essential trace nutrient, it has been reported to cause negative health effects when consumed in excess, including adverse impacts on maternity and birth outcomes (Yazbeck et al., 2006; Barrett, 2007; Hafeman et al., 2007; Grazuleviciene et al., 2009; Ljung et al., 2009; Spangler and Spangler, 2009; Wood, 2009; Zota et al., 2009), inhibiting the intellectual development of children (Woolf et al., 2002; Wasserman et al., 2006, 2008, 2011; Bouchard et al., 2011; Khan et al., 2012) and neurological problems associated with Parkinson's-like symptoms (Barceloux, 1999; Ono et al., 2002; Bouchard et al., 2007; Avelino et al., 2014). Many of these ailments have been documented in the Bengal Basin (Wasserman et al., 2006, 2008, 2011; Barrett, 2007; Hafeman et al., 2007; Ljung et al., 2009; Khan et al., 2012).

The Bureau of Indian Standards (BIS) has enforced an Acceptable Limit for Mn in drinking water of 0.1 mg L^{-1} , and 0.3 mg L^{-1} in the absence of an alternative drinking water source (BIS, 2012); however, it has been suggested that the Mn limit may be practically difficult to achieve, given the naturally occurring concentrations of Mn in groundwater. Further, the World Health Organization (WHO, 2011) revoked the guideline for acceptable Mn in drinking water of 0.4 mg L^{-1} because it was well above concentrations of Mn normally found in drinking water. Ljung and Vahter (2007) argued that 0.4 mg L^{-1} was originally too high, and numerous studies have suggested a re-evaluation of the guideline for Mn is required (Biswas et al., 2012a,b; Frisbie et al., 2012; McArthur et al., 2012b).

Manganese (II) is the most common Mn species in acidic to circumneutral pH groundwater, as it is more soluble than Mn(III) or Mn(IV) (Tebo et al., 2007). Whereas the precipitation

of insoluble Mn(III)—Mn(IV)—oxy (hydroxides) at higher pH (Hem, 1985) is thermodynamically favorable, the activation energy is high and hence the reaction is slow in nature (Gounot, 1994). The biological oxidation of Mn(II) (Tebo et al., 1997), however, is kinetically favorable and has been shown to produce stable Mn(IV) bio-oxides (Tebo et al., 2004) that predominate in natural systems. Such Mn oxides are known to strongly adsorb As species in a similar fashion to Fe oxides (Morgan and Stumm, 1964; Young and Harvey, 1992; Manning et al., 2002; Deschamps et al., 2003; Foster et al., 2003; Toner et al., 2006; Wu et al., 2015). Furthermore, Mn(IV)—oxides can oxidize As(III) to As(V), limiting As mobility and toxicity (Golden et al., 1986). Arsenic—Mn precipitates have also been shown to form under such biogeochemical conditions (Tournassat et al., 2002).

Thermodynamically, Mn(IV) is a more favored terminal electron acceptor than Fe(III) by anaerobic microorganisms (Stumm and Morgan, 1981; McGuire et al., 2002; Bethke et al., 2011), and Mn(II) is mobilized as a result of reductive dissolution of Mn(IV)—oxides (Appelo and Postma, 2005; Buschmann et al., 2007). Further, the mobility of Mn(II) can be influenced by the precipitation of carbonate, sulfide, or phosphate phases (Nickson et al., 2000; McArthur et al., 2001; Buschmann et al., 2007; Nath et al., 2009; Sankar et al., 2014), sorption of Mn(II) onto sediment surfaces (Wersin et al., 1989), as well as complexation with dissolved organic matter (DOM) (Marshall, 1979; Gavin et al., 2001; Graham et al., 2002).

The influence of DOM on the geochemistry of trace metals has been documented extensively (Lovley and Phillips, 1988; Nealson and Saffarini, 1994; Lovley et al., 1996; Nickson et al., 2000; Smedley and Kinniburgh, 2002). Microbially mediated reductive dissolution of Mn(IV)/Fe(III) oxides in the presence of labile organic carbon has been shown to cause elevated levels of dissolved Mn(II), As(III), and Fe(II) in the groundwater of the Bengal Basin (Dowling et al., 2002; Smedley and Kinniburgh, 2002; Lovley et al., 2004; McArthur et al., 2004). Recently, multiple roles of biologically refractive (humic-like) DOM such as aqueous complexation (Sharma et al., 2010; Liu et al., 2011) and electron shuttling (Lovley et al., 1996, 1998, 1999; Scott et al., 1998; Kappler et al., 2004; Jiang and Kappler, 2008; Wolf et al., 2009; Mladenov et al., 2010, 2015) have been implicated in the mobilization of redox sensitive elements such as Fe and As. Formation of Mn—humic complexes have been shown to inhibit

the adsorption of Mn in near surface environments (Gavin et al., 2001; Graham et al., 2002). Lovley et al. (1996) showed that the model humic substance (AQDS) was capable of shuttling electrons from anaerobic microorganisms to Fe(III)—oxides, and it was suggested that these findings were similar for Mn(IV)—oxides, yet no study to date has directly confirmed this. In addition, Mn(IV)—oxides have been shown to oxidize phenols to produce humic-like substances (Vodyanitskii, 2009), and lyse high molecular weight (HMW) biologically refractive humic and fulvic acids into low molecular weight (LMW) biologically labile organic compounds such as pyruvate, which can serve as an electron donor for microorganisms (Sunda and Kieber, 1994).

Absorbance and fluorescence spectroscopic techniques have been widely used to characterize chromophoric DOM sources and transformations. Three-dimensional excitation emission matrices (EEMs) contain fluorophores associated with DOM derived from both microbial and higher plant sources. In addition to evaluation of fluorescence peaks (Coble, 1996) and indices (Parlanti et al., 2000; Ohno, 2002; Zsolnay, 2003; Cory and McKnight, 2005; Hansen et al., 2016) found in the EEMs, fluorescence data can be further analyzed using a parallel factor (PARAFAC) multivariate modeling analysis. PARAFAC modeling of large EEM datasets identifies the underlying fluorescence components that comprise an EEM. PARAFAC models also provide concentrations and relative distributions of each modeled component in each sample. These techniques have been used to discriminate unique fluorescence components and investigate potential sources of DOM (Stedmon et al., 2003; Stedmon and Bro, 2008; Williams et al., 2013).

The quality of DOM and its potential roles in As mobilization have been investigated using a range of fluorescence and absorbance spectroscopic techniques in Bangladesh (Mladenov et al., 2010, 2015). Further, a PARAFAC model developed using samples from the same sites as in this study (West Bengal, India) identified four unique components, namely terrestrial humic-like, humic-like impacted by agriculture, protein-like, and microbial humic-like (Kulkarni et al., 2016). The association of DOM with Mn mobilization from aquifer sediments has not been examined to date. The objective of this study was therefore to highlight associations between Mn and As biogeochemistry in conjunction with DOM quality in the shallow groundwater of West Bengal, India.

MATERIALS AND METHODS

Study Site

A total of 51 groundwater and 16 sediment samples were collected from 2 sites located on the west side (Nabagram and Kandi) and 4 sites located on the east side (Hariharpara, Beldanga, Naoda, and Khidirpur) of the North-South flowing river Bhagirathi in Murshidabad to investigate the biogeochemistry of Mn (Figure 1). Murshidabad is a district (~5,500 km²) in north-central West Bengal with a population of ~7.1 million (Census of India, 2011).

Distinct geological settings on the east and west sides of the river Bhagirathi have been previously discussed in Datta et al. (2011), Sankar (2013), Sankar et al. (2014), and Kulkarni et al.

(2016). Briefly, the geology of the sites located east of the river Bhagirathi consists of young Holocene sediments (~7,000 years before present), whereas Pleistocene sediments (12,300–48,600 years before present) occur to the west of the river (Acharya et al., 2000; Mukherjee et al., 2007; Neidhardt et al., 2013). The permeability of Holocene sands east of the river Bhagirathi is reported to be 40–60 m d⁻¹, whereas the permeability of the Pleistocene sediments to the west are reported to be slightly lower (i.e., 20–30 m d⁻¹; Mukherjee et al., 2007). The lower permeability of the Pleistocene sediments is attributed to the presence of secondary clays and iron oxides, which are thought to clog pore spaces within the sands (Ravenscroft et al., 2005).

Several studies have reported higher Fe and As concentrations in groundwater from the Holocene aquifers (Mukherjee and Bhattacharya, 2001; Bhattacharya et al., 2002; Datta et al., 2011; Sankar, 2013; Sankar et al., 2014), whereas lower Fe and As concentrations have been observed in groundwater from the Pleistocene aquifers (Datta et al., 2011; Hoque et al., 2011; Sankar et al., 2014; Kulkarni et al., 2016). The contrasting DOM quality at Hariharpara, Beldanga, Nabagram, and Kandi sites has been discussed in Kulkarni et al. (2016), who demonstrated the presence of more humic-like DOM in Hariharpara and Beldanga compared to Nabagram and Kandi.

Sample Collection and Storage

Groundwater samples were collected at various depths from drinking water tube wells at Nabagram ($n = 8$, 27–43 m depth), Kandi ($n = 6$, 21–37 m depth), Hariharpara ($n = 12$, 12–25 m depth), Beldanga ($n = 13$, 18–40 m depth), Naoda ($n = 10$, 18–40 m depth) and Khidirpur ($n = 2$, 8 m depth) in January of 2010 (Sankar et al., 2014) and later in January of 2015. After pumping and purging each well for ~15 min, groundwater samples were collected in acid washed HDPE bottles pre-rinsed three times with the collected sample.

Field parameters such as pH, E_h (Ag/AgCl adjusted to standard hydrogen electrode (SHE)), temperature, electrical conductivity, salinity, and total dissolved solids (TDS) were measured immediately after the sample was collected in a clean 5-gallon HDPE bucket using portable probes (HACH HQ11D and Mettler Toledo SG3). The samples were filtered using a 0.45 μm nitrocellulose membrane filter and acidified in the field using Optima Grade HNO₃ (0.2% v/v) for the analysis of cations (Mn_T, Fe_T, As_T, Ca²⁺, Mg²⁺) by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). Filtered and unacidified samples were used for the analysis of anions (Cl⁻, Br⁻, F⁻, SO₄²⁻, NO₃⁻, and PO₄³⁻) by ion chromatography (IC). All collected samples were placed immediately on ice and preserved throughout transport to Kansas State University.

Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) concentrations were determined using a thermic oxidation method on a Shimadzu TOC/TN 5050A analyzer. The samples were filtered in the field using pre-combusted (4 h, 450°C) 0.7 μm glass fiber filters (GFF) to avoid the risk of leaching organics from filters (such as nitrocellulose filters). Filtered samples were acidified in the field using Optima Grade HCl (0.2% v/v) to inhibit microbial activity (Burdige and Homstead, 1994; Tupas et al., 1994; Burdige

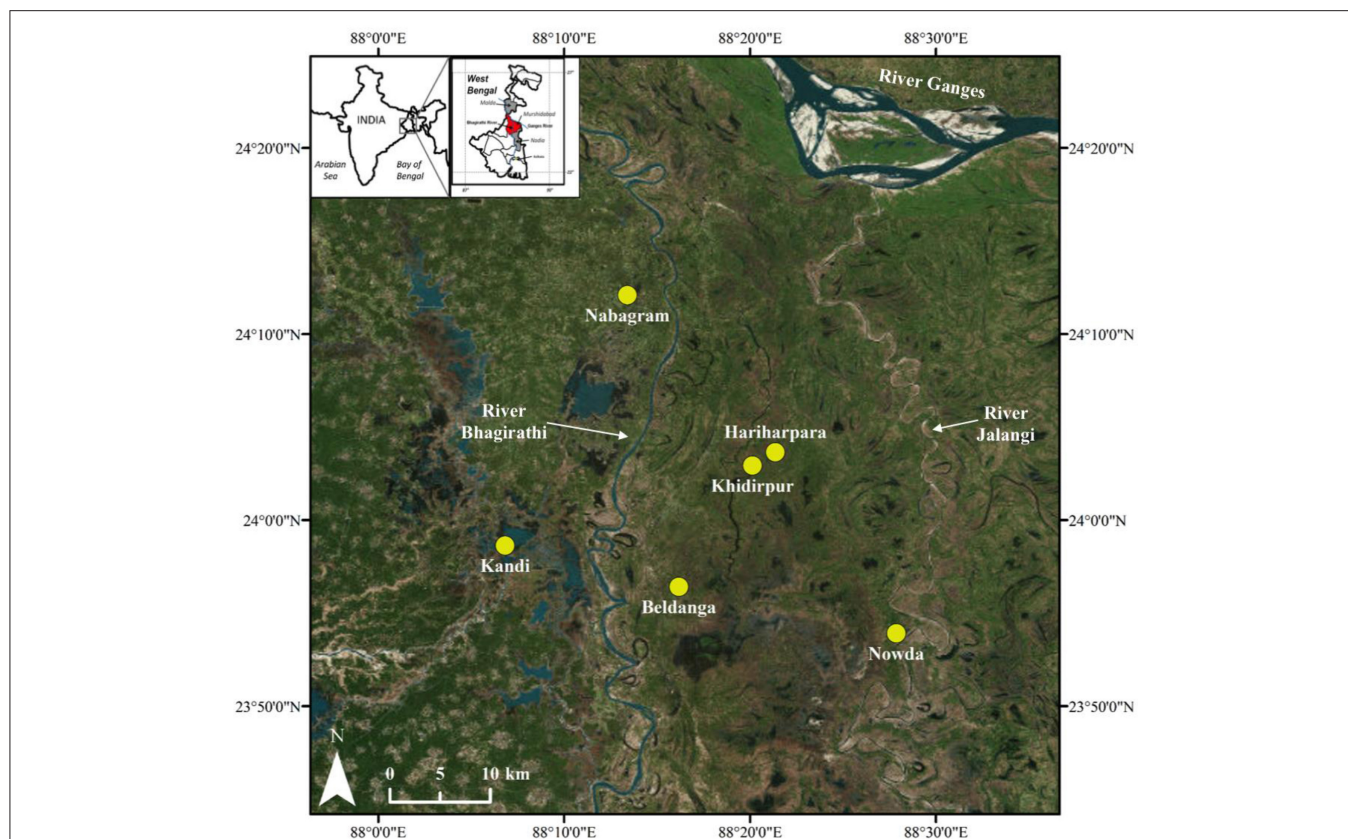


FIGURE 1 | Map of the study area, including sampling sites. Nabagram and Kandi are west of the river Bhagirathi (HMLA); Hariharpara, Beldanga, and Naoda are east of the river Bhagirathi (HMHA); Khidirpur is east of the river Bhagirathi, but an HMLA site.

and Gardner, 1998). Spectral characterization (absorbance and fluorescence) of DOM was conducted on a Jobin Yvon Horiba Aqualog benchtop fluorometer, using 0.7 μm GFF filtered but unacidified samples to avoid fluorescence quenching effects at pH lower than the natural pH of the sample (Spencer et al., 2007).

Sediment cores were collected at the time of sampling by locally hired drillers using the percussion hand drilling method. Samples were collected in PVC tubes in incremental depths ranging between ~ 10 and 40 m, followed by preservation in O_2 -impermeable Remel[®] bags (Mitsubishi Gas Company, Remel[®], Cat no. 2019-11-02), along with O_2 absorber pouches (Mitsubishi Gas Company, AnaeroPouch[®] Anaero; Cat no. 23-246-379), flushed with high-purity N_2 gas, sealed, and shipped on ice to Kansas State University. Bulk Mn, As, and Fe concentrations in sediments were acquired via a bulk digestion method modified from Premarathna et al. (2010). Briefly, ~ 0.5 g of finely homogenized (< 2 mm) sediments were treated in glass digestion tubes with 2.5 mL of 30% H_2O_2 for 10 min, followed by an additional 0.5 mL of 30% H_2O_2 , and allowed to react for 12 h. The samples were then digested at 90°C until the volume reduced to ~ 1 mL. To this, 2.5 mL of freshly prepared aqua regia (1:3, HNO_3 : HCl) was added and left to react for 12 h. Samples were heated to 75°C (30 min), 90°C (30 min), 110°C (30 min) and then to 140°C until the total volumes were reduced to ~ 1 mL. Samples were diluted to 10 mL using Optima Grade

0.1% HNO_3 , filtered through 2.5 μm (Whatman 42) filter paper and analyzed for Fe_T and Mn_T by a Varian 720-ES Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) and for As_T by Varian GTA 120 Graphite Tube Atomizer w/ AA 240Z Zeeman Atomic Absorption Spectrometer (GTA-AAS). Three NIST standards (Montana II) were digested and yields of 101% (As), 84% (Fe), and 88% (Mn) obtained. To minimize potential losses, 30 cm digestion tubes with constricted necks were utilized. Lower Fe and Mn yields were probably attributed to Fe and Mn binding to siliceous materials, which are not readily dissociated by aqua regia (Loeppert and Inskeep, 1996).

Fluorescence Analyses of DOM

Spectral acquisition for fluorescence analyses was performed using an excitation range of 240–450 nm in 3 nm increments and an emission range of 300–600 nm in 3.28 nm increments (instrument default) with an integration time of 0.25 seconds. Absorbance was simultaneously measured on the same instrument from 300 to 600 nm in 3 nm increments. Filtered samples were brought to room temperature prior to fluorescence and absorbance measurements. Ultrapure water (18.3 $\text{M}\Omega\text{-cm}$ Milli-Q) was used for Raman normalization (emission intensity at 350 nm) and for blank subtraction. Inner filter effect corrections were done using the absorbance of each sample. Detailed information on instrumental parameters and data

processing is described elsewhere (Kulkarni et al., 2016). Corrected EEMs of 51 samples were fitted to a four component PARAFAC model which was validated by split half analysis and random initialization technique using the DOMFluor toolbox (Stedmon and Bro, 2008).

Indices based on fluorescence and absorbance properties are useful in deciphering the quality of DOM in aqueous environments. The absorbance at 254 nm (Abs_{254}) provides insight regarding the degree of aromaticity of DOM, particularly when normalized to DOC concentration and the path length of incident light as specific UV absorbance ($SUVA_{254}$) (Weishaar et al., 2003). The ratio of the absorption spectral slopes between 275 and 295 nm ($S_{275-295}$) and 350 and 400 nm ($S_{350-400}$), or S_R , was calculated to determine whether DOM was marine-like ($S_R < 1$) or terrestrially dominated with high chromophoric dissolved organic matter (CDOM) ($S_R > 1$) (Helms et al., 2008). Freshness index ($\beta: \alpha$) was calculated as the ratio of emission intensity at 380 nm to the maximum intensity between 420 and 435 nm at an excitation wavelength of 310 nm (Parlanti et al., 2000); lower values signify a greater extent of DOM decomposition (Wilson and Xenopoulos, 2008; Fellman et al., 2010). Fluorescence index (FI), the ratio of fluorescence intensities at 470 and 520 nm emission and at an excitation wavelength of 370 nm, was calculated to understand the source of DOM. Higher FI's (~1.7–1.9) represent microbial derivation pathways and lower FI's (~1.3–1.4) imply a terrestrial origin (McKnight et al., 2001; Cory and McKnight, 2005). To measure the extent to which DOM has undergone humification, the humification index (HIX) was computed as the ratio of peak area under the emission spectra at 435 to 480 nm to the peak area from 300 to 345 nm at an excitation wavelength of 254 nm (Zsolnay, 2003).

Equilibrium Chemical Speciation and Modeling

Aqueous geochemical modeling was performed using Visual MINTEQ ver. 3.1 to calculate the equilibrium distribution and relevant saturation indices for Mn and Fe species. Arsenic speciation from groundwater within the same sites as this study was assessed previously by passing acidified samples through anion exchange columns, analyzing the eluent ($H_3AsO_3^0$) via HR-ICP-MS as As(III), then back-calculating from AsT to obtain As(V) (Sankar et al., 2014).

Statistical Analyses

Correlations were assessed by computing two-tailed Pearson correlation coefficients and the Mann-Whitney-Wilcoxon (MWW) U test was used to delineate statistically significant variability among groups due to a non-parametric distribution of parameters and a relatively small sample size. All statistical analyses were performed using SPSS Statistics Software. Parenthetic values represent the mean \pm 95% confidence interval, and only correlations of statistical significance ($p < 0.05$) are presented.

RESULTS

Hydrochemistry of Dissolved Mn, As, and Fe in Groundwater

Of the 51 tube wells sampled, 73% contained total dissolved Mn (Mn_T) > 0.4 mg L^{-1} (revoked (WHO, 2011) guideline), 78% contained total dissolved As (As_T) > 10 $\mu g L^{-1}$ (WHO, 2011 guideline), and 57% exceeded both of these guidelines (Figure 2, Figure S1). Only 6% of wells had $Mn_T < 0.4$ mg L^{-1} and $As_T < 10$ $\mu g L^{-1}$. Typically, high Mn_T (0.83 ± 0.14 mg L^{-1}) and high As_T (330 ± 97 $\mu g L^{-1}$) concentrations were observed in the tube wells located to the east of the river Bhagirathi and these sites are termed as HMHA sites for further discussion (Table 1). Conversely, high Mn_T (1.1 ± 0.29 mg L^{-1}) and low As_T (9.0 ± 2.1 $\mu g L^{-1}$) concentrations were observed (Table 1) in the tube wells located to the west of the river (HMLA). The total Fe concentrations (Fe_T) at HMHA sites (3.6 ± 0.93 mg L^{-1}) were significantly higher than at HMLA sites (0.31 ± 0.10 mg L^{-1}) (Table 1). The difference between As_T and Fe_T concentrations at the HMHA and HMLA sites was found to be statistically significant, but insignificant for Mn_T concentrations (Table 1). Nitrate (NO_3^-) and sulfate (SO_4^{2-}) values were significantly higher in HMLA (2.8 ± 3.0 mg $NO_3^- L^{-1}$; 16 ± 9.7 mg $SO_4^{2-} L^{-1}$) groundwater than in HMHA (0.21 ± 0.30 mg $NO_3^- L^{-1}$; 5.0 ± 2.8 mg $SO_4^{2-} L^{-1}$) groundwater (Table 1). Khidirpur, despite being east of the river Bhagirathi, showed exceptionally low As_T

TABLE 1 | Distribution of groundwater hydrogeochemical parameters within all sites, HMHA sites, and HMLA sites.

Parameter	All ($n = 51$)	HMHA ($n = 35$)	HMLA ($n = 16$)
Mn_T (mg L^{-1})	0.92 ± 0.20 (0.03 – 4.2)	0.83 ± 0.14 (0.13 – 2.2)	1.1 ± 0.29 (0.03 – 4.2)
As_T ($\mu g L^{-1}$)	229 ± 90 (0.26 – 1,264)	330 ± 97 (0.88 – 1,264)	9.0 ± 2.1 (0.26 – 25)
Fe_T (mg L^{-1})	2.6 ± 0.88 (0.0 – 14)	3.6 ± 0.93 (0.01 – 14)	0.31 ± 0.10 (0.0 – 1.0)
NO_3^- (mg L^{-1})	1.0 ± 0.92 (0.0 – 21)	0.21 ± 0.30 (0.0 – 0.99)	2.8 ± 3.0 (0.0 – 21)
SO_4^{2-} (mg L^{-1})	8.4 ± 3.5 (0.0 – 52)	5.0 ± 2.8 (0.0 – 35)	16 ± 9.7 (0.0 – 52)
DOC (mg L^{-1})	1.7 ± 0.16 (0.58 – 3.3)	1.8 ± 0.15 (0.58 – 3.3)	1.3 ± 0.13 (0.62 – 2.3)
TDN (mg L^{-1})	3.8 ± 1.3 (0.0 – 24)	4.0 ± 1.4 (0.0 – 15)	3.3 ± 3.7 (0.13 – 24)
E_h (mV)	$+207 \pm 34$ (+99 – (+)363)	$+163 \pm 26$ (+99 – (+)276)	$+285 \pm 47$ (+151 – (+)363)
pH	7.3 ± 0.12 (6.5 – 8.3)	7.3 ± 0.13 (6.5 – 7.8)	7.4 ± 0.30 (6.8 – 8.3)
Alkalinity (mg L^{-1} as $CaCO_3$)	399 ± 29 (148 – 648)	415 ± 30 (270 – 648)	357 ± 64 (148 – 560)
Well Depth (m)	(8.0 – 43)	(12 – 40)	(8.0 – 43)

HMHA, High Mn, High As; HMLA, High Mn, Low As. Upper values indicate 95% confidence interval; values in parentheses denote ranges. Shaded cells indicate statistically significant differences between HMHA and HMLA sites for that parameter ($p < 0.05$). E_h , pH, and alkalinity values are based on $n = 23, 45$, and 47 (of 51 total), $n = 14, 34$, and 35 (of 35 HMHA), and $n = 9, 13$, and 13 (of 16 HMLA), respectively. Well depth values represent ranges among the respective sites.

concentrations ($3.4 \pm 0.26 \mu\text{g L}^{-1}$) and is therefore discussed as an HMLA site.

Based on Visual MINTEQ speciation modeling, the dominant species of Mn in all studied sites was Mn^{2+} (~73–89 % of Mn_T), with MnHCO_3^+ and $\text{MnCO}_3(\text{aq})$ comprising the remaining ~4–17 % and ~7–9 % of Mn_T , respectively (Figure S4A). There was no significant difference in the percentages of Mn^{2+} , MnHCO_3^+ , and $\text{MnCO}_3(\text{aq})$ between the HMHA ($\text{Mn}^{2+} = 81.6 \pm 2.78\%$; $\text{MnHCO}_3^+ = 7.52 \pm 0.60\%$; $\text{MnCO}_3(\text{aq}) = 10.7 \pm 2.66\%$) and HMLA ($\text{Mn}^{2+} = 83.3 \pm 4.90\%$; $\text{MnHCO}_3^+ = 7.42 \pm 1.05\%$; $\text{MnCO}_3(\text{aq}) = 9.03 \pm 4.04\%$) sites (Table S4A), and all dissolved Mn species were of the oxidation state Mn(II). Iron speciation was more variable, with the dominant species being Fe^{2+} (~30–95 % of Fe_T), $\text{Fe}(\text{OH})_2^+$ (~0–67 % of Fe_T), FeHCO_3^+ (~2–7 % of Fe_T), and FeOH^+ (~0–1 % of Fe_T) (Figure S4B). Thus, Fe(II) and Fe(III) were present in proportions of ~32–99 % and 0–67 % of Fe_T , respectively. There was significantly more Fe^{2+} in HMHA ($87.4 \pm 6.31\%$ of Fe_T) than in HMLA ($49.9 \pm 19.9\%$ of Fe_T) sites, and there was significantly less $\text{Fe}(\text{OH})_2^+$ (the only dominant Fe(III) species) in HMHA ($6.87 \pm 6.48\%$ of Fe_T) relative to HMLA ($46.2 \pm 21.7\%$ of Fe_T) sites (Table S4B). Percentages of FeHCO_3^+ were not significantly different between HMHA ($5.16 \pm 0.48\%$ of Fe_T) and HMLA sites ($3.23 \pm 1.79\%$ of Fe_T) (Table S4B). Analytically determined As speciation by a previous study of these same sites demonstrated that 55–98 % of As_T was As(III) in HMHA sites, whereas the only sample analyzed from HMLA sites was 36 % As(III) (Sankar et al., 2014).

Physical parameters (e.g., pH, E_h , alkalinity, depth) were not significantly different between HMHA and HMLA sites, excluding E_h , which was significantly lower in HMHA ($+163 \pm 26 \text{ mV}$) relative to HMLA ($+285 \pm 47 \text{ mV}$) sites (Table 1). Correlations of physical parameters with Mn_T , As_T , and Fe_T are presented in Tables S1–S3. A weak positive correlation was observed between Mn_T and As_T in HMHA groundwater, however, a significant positive correlation between Mn_T and As_T in Naoda was observed (Figure S2, Tables S1, S2). At Hariharpara, a positive correlation between Fe_T and As_T was apparent (Figure S2, Tables S2, S3). In all HMLA sites, As_T and Fe_T were positively correlated (Figure S2, Tables S2, S3). Positive correlations between Mn_T and As_T and between As_T and Fe_T were observed in groundwater from the Nabagram location (Tables S1–S3).

Dissolved Organic Matter Quality

Dissolved organic carbon (DOC) concentrations at the HMHA sites ($1.8 \pm 0.15 \text{ mg L}^{-1}$) were significantly higher than at HMLA sites ($1.3 \pm 0.13 \text{ mg L}^{-1}$). Total dissolved nitrogen concentrations (TDN) at HMHA sites ($4.0 \pm 1.4 \text{ mg L}^{-1}$) and HMLA sites ($3.3 \pm 3.7 \text{ mg L}^{-1}$) were not significantly different (Table 1). At the HMHA sites, groundwater DOC was positively correlated with Mn_T (Figure S2, Table S1) and also with As_T (Figure S2, Table S2), but not with Fe_T (Figure S2, Table S3). By contrast, in HMLA groundwater, no significant correlation of DOC with Mn_T , As_T or Fe_T (Figure S2, Tables S1–S3) was found. Isolating just Kandi samples revealed a significant positive

correlation between Mn_T and DOC concentrations, however (Table S1).

Absorbance at 254 nm (Abs_{254}) intensities for groundwater from the HMHA sites (0.047 ± 0.006) were significantly higher than for groundwater from the HMLA sites (0.029 ± 0.007) (Table 2). Specific ultraviolet absorbance at 254 nm (SUVA_{254}) values at HMHA sites ($2.60 \pm 0.28 \text{ L mg}^{-1} \text{ m}^{-1}$) and HMLA sites ($2.43 \pm 0.39 \text{ L mg}^{-1} \text{ m}^{-1}$) did not vary significantly (Table 2). It should be noted that ferric iron concentrations can artificially enhance Abs_{254} and SUVA_{254} values due to similar absorbance spectra (Weishaar et al., 2003), and that the variability of Fe concentrations between HMHA and HMLA sites (Table 1) may influence the observed variability in Abs_{254} (Table 2); therefore, SUVA results should be interpreted with caution. Spectral slope ratios (S_R) at HMHA sites (1.16 ± 0.11) and HMLA sites (1.44 ± 0.29) were not significantly different (Table 2). Within HMLA groundwater, significant positive correlations were observed between SUVA_{254} and As_T (Table S2) and SUVA_{254} and Fe_T (Table S3). SUVA_{254} was also positively correlated with As_T (Table S2) and Mn_T (Table S1) in groundwater from Nabagram. In Beldanga, only As_T exhibited a positive correlation with SUVA_{254} (Table S2).

TABLE 2 | Distribution of groundwater dissolved organic matter parameters within all sites, HMHA sites, and HMLA sites.

Parameter	All (n = 51)	HMHA (n = 35)	HMLA (n = 16)
Abs_{254} (a.u.)	0.041 ± 0.005 (0.007 – 0.097)	0.047 ± 0.006 (0.014 – 0.097)	0.029 ± 0.007 (0.007 – 0.051)
S_R	1.25 ± 0.12 (0.54 – 2.54)	1.16 ± 0.11 (0.65 – 2.15)	1.44 ± 0.29 (0.54 – 2.54)
SUVA_{254} ($\text{L mg}^{-1} \text{ m}^{-1}$)	2.53 ± 0.29 (0.37 – 4.73)	2.60 ± 0.23 (0.96 – 4.27)	2.43 ± 0.39 (0.37 – 4.73)
FI	1.72 ± 0.02 (1.47 – 1.93)	1.72 ± 0.02 (1.53 – 1.89)	1.72 ± 0.04 (1.47 – 1.93)
$\beta:\alpha$	0.79 ± 0.04 (0.63 – 1.20)	0.73 ± 0.01 (0.63 – 0.88)	0.93 ± 0.04 (0.66 – 1.20)
HIX	9.30 ± 1.62 (1.87 – 30.24)	11.1 ± 1.63 (1.87 – 30.24)	5.32 ± 0.89 (2.19 – 13.46)
C1 (%)	43.3 ± 2.71 (20.0 – 56.2)	47.9 ± 1.01 (41.4 – 56.2)	33.1 ± 3.13 (20.0 – 50.6)
C2 (%)	36.6 ± 1.68 (21.0 – 55.0)	37.5 ± 0.94 (30.0 – 43.2)	34.7 ± 2.57 (21.0 – 55.0)
C3 (%)	9.91 ± 1.14 (0.00 – 22.0)	9.09 ± 1.04 (4.15 – 22.0)	11.7 ± 1.17 (0.00 – 18.1)
C4 (%)	10.2 ± 3.44 (0.00 – 47.6)	5.47 ± 1.39 (0.00 – 17.7)	20.5 ± 4.67 (0.00 – 47.6)
Humic:Protein	10.3 ± 1.12 (3.54 – 23.1)	11.5 ± 1.12 (3.54 – 23.1)	7.56 ± 0.64 (4.54 – 11.9)
Terr:Microb	5.84 ± 0.91 (0.73 – 14.7)	6.74 ± 0.76 (3.07 – 14.7)	3.62 ± 0.97 (0.73 – 11.7)

^{C1} Terrestrial, humic-like; ^{C2} Humic-like, impacted by agriculture, marine humic; ^{C3} Protein-like, tyrosine and tryptophan; ^{C4} Microbial humic-like (Kulkarni et al., 2016). HMHA, High Mn, High As; HMLA, High Mn, Low As. Upper values indicate 95 % confidence interval; Values in parentheses denote ranges. Shaded cells indicate statistically significant differences between HMHA and HMLA sites for that parameter ($p < 0.05$).

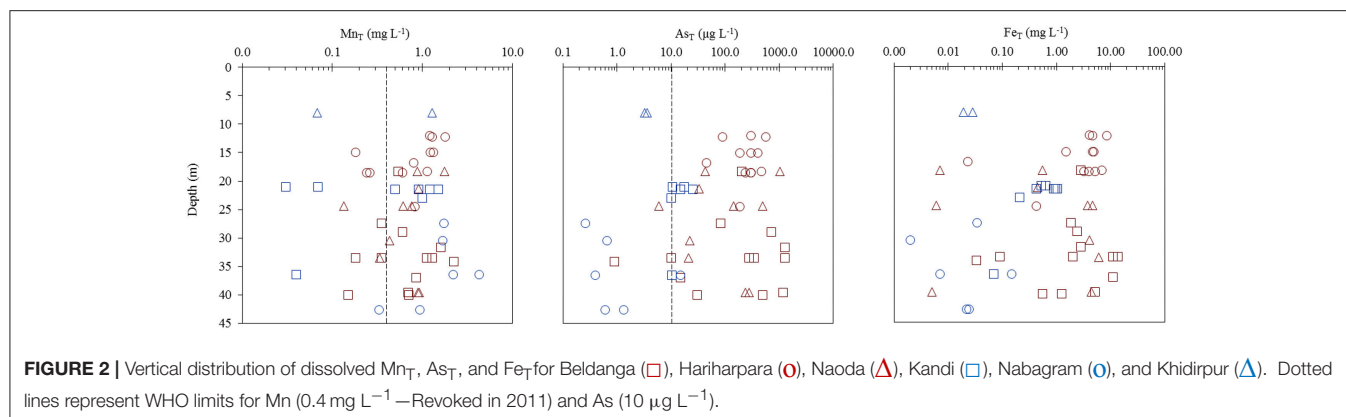


FIGURE 2 | Vertical distribution of dissolved Mn_T , As_T , and Fe_T for Beldanga (\square), Hariharpara (\circ), Naoda (\triangle), Kandi (\square), Nabagram (\circ), and Khidirpur (\triangle). Dotted lines represent WHO limits for Mn (0.4 mg L^{-1} —Revoked in 2011) and As ($10 \text{ } \mu\text{g L}^{-1}$).

Fluorescence index (FI), freshness index ($\beta:\alpha$) and humification index (HIX) at HMHA sites were 1.72 ± 0.02 , 0.73 ± 0.01 , and 11.1 ± 1.63 , respectively, whereas they were 1.72 ± 0.04 , 0.93 ± 0.04 , and 5.32 ± 0.89 , respectively, at the HMLA sites (Table 2). Fluorescence index (FI) did not vary significantly between HMHA and HMLA groundwater, whereas $\beta:\alpha$ was significantly lower in HMHA groundwater than in HMLA groundwater, and HIX was significantly higher in HMHA groundwater than in HMLA (Table 2).

A negative correlation was observed in all sites between As_T and $\beta:\alpha$ (Table S2) and between Fe_T and $\beta:\alpha$ (Table S3), whereas a positive correlation was observed between As_T and HIX (Table S2). At the HMLA sites, a negative correlation was found between Mn_T and $\beta:\alpha$ (Table S1), whereas As_T and Fe_T were positively correlated with $\beta:\alpha$ (Tables S2, S3). In Nabagram, As_T was negatively correlated with $\beta:\alpha$ (Table S2). A positive correlation was observed between FI and Fe_T in Naoda (Table S3), and in Beldanga FI was negatively correlated with As_T , and As_T with $\beta:\alpha$ (Table S2).

The PARAFAC model identified 4 fluorescence components (Table 2, Figure 3, Table S5): (1) a terrestrial humic-like (C1) component; (2) a humic-like component influenced by agricultural and wastewater activities (C2); (3) a protein-like component similar to tryptophan and tyrosine (C3); and (4) a microbial humic-like (C4) component. The four components identified were similar to components C1–C4 found in an earlier study in this region (Kulkarni et al., 2016). On average, the % C1 in groundwater from the HMHA sites ($47.9\% \pm 1.01$) was significantly higher than % C1 in groundwater from the HMLA sites ($33.1\% \pm 3.13$) (Table 2). In all sites and within HMLA sites, % C1 was positively correlated with As_T concentrations (Table S2), and also with Fe_T concentrations at HMLA sites (Table S3). The component % C2 in groundwater from the HMHA sites ($37.5\% \pm 0.94$) and at the HMLA sites ($34.7\% \pm 2.57$) was not significantly different (Table 2). Groundwater from HMLA sites shows positive correlations between % C2 and As_T (Table S2) and with Fe_T (Table S3). Component C3 (%) was significantly higher in groundwater from the HMLA sites ($11.7\% \pm 1.17$) than in groundwater from the HMHA sites ($9.09\% \pm 1.04$) (Table 2). Positive correlations between As_T and

% C3 at all sampled locations (Table S2) and between As_T and % C3 at Beldanga (Table S2) were observed. The proportion of the DOM pool attributed to Component C4 (% C4) was significantly higher in groundwater from the HMLA sites ($20.5\% \pm 4.67$) than in groundwater from the HMHA sites ($5.47\% \pm 1.39$) (Table 2). A positive correlation between As_T and % C4 in groundwater from the HMLA sites was observed (Table S2). No significant correlations were observed between Mn_T and any of the proportions of the total DOM pool (Table S1).

Bulk Sediment Geochemistry

Bulk sediment concentrations of Mn ($278 \pm 67.5 \text{ mg kg}^{-1}$), As ($6.61 \pm 1.84 \text{ mg kg}^{-1}$) and Fe ($21.9 \pm 4.82 \text{ g kg}^{-1}$) at the HMHA sites were not significantly different than Mn ($420 \pm 122 \text{ mg kg}^{-1}$), As ($4.72 \pm 0.36 \text{ mg kg}^{-1}$) and Fe ($19.2 \pm 3.24 \text{ g kg}^{-1}$) contents of the sediments from the HMLA sites (Table 3, Figure 4). Bulk As and Fe contents of sediments were positively correlated within all sites, within HMHA sites, and at Hariharpara (Table S4, Figure S3). Sediment Mn and Fe concentrations were positively correlated within the HMHA sites, at Hariharpara, and at Beldanga (Table S4, Figure S3). Similarly, sedimentary Mn and As were positively correlated at Hariharpara (Table S4, Figure S3).

DISCUSSION

The distribution of dissolved Mn_T and As_T in groundwater of this study area appears to be controlled by redox processes as has been noted in previous studies in other regions of the Bengal Basin (Bhattacharya et al., 2002; McArthur et al., 2004, 2008; Buschmann et al., 2007; von Brömmssen et al., 2007; Sankar et al., 2014). Elevated Mn_T was prevalent throughout all surveyed sites, yet As_T and Fe_T were constrained to groundwater with lower E_h and dissolved NO_3^- concentrations. Greater quantities of DOC and humic-like, terrestrial DOM coincided with low E_h , high As_T and Fe_T groundwater. By contrast, lower DOC concentrations and protein-like DOM were present within high E_h and low As_T and Fe_T groundwater. The distribution of Mn_T was seemingly unaffected by both DOC quantity and DOM quality, as Mn_T concentrations were consistently high. It should be noted here that E_h is employed as a qualitative measure of the general redox

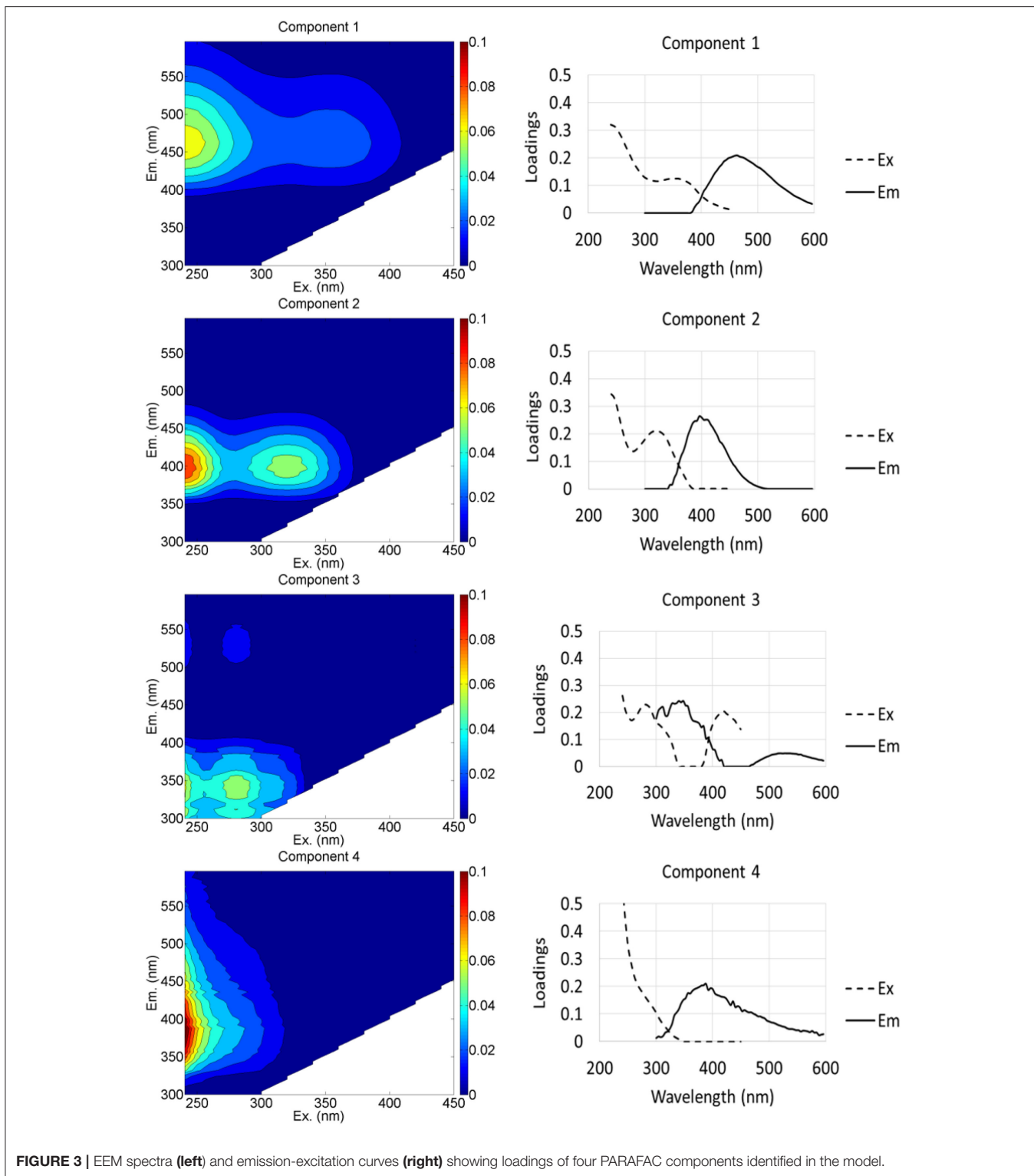


FIGURE 3 | EEM spectra (left) and emission-excitation curves (right) showing loadings of four PARAFAC components identified in the model.

state of groundwater, as it is a difficult parameter to quantify due to the inherent redox disequilibrium in natural waters (Lindberg and Runnells, 1984; Stefansson et al., 2005). The discussions

herein will attempt to correlate the release and accumulation of Mn, As, and Fe species with redox chemistry, carbonate chemistry and DOM properties.

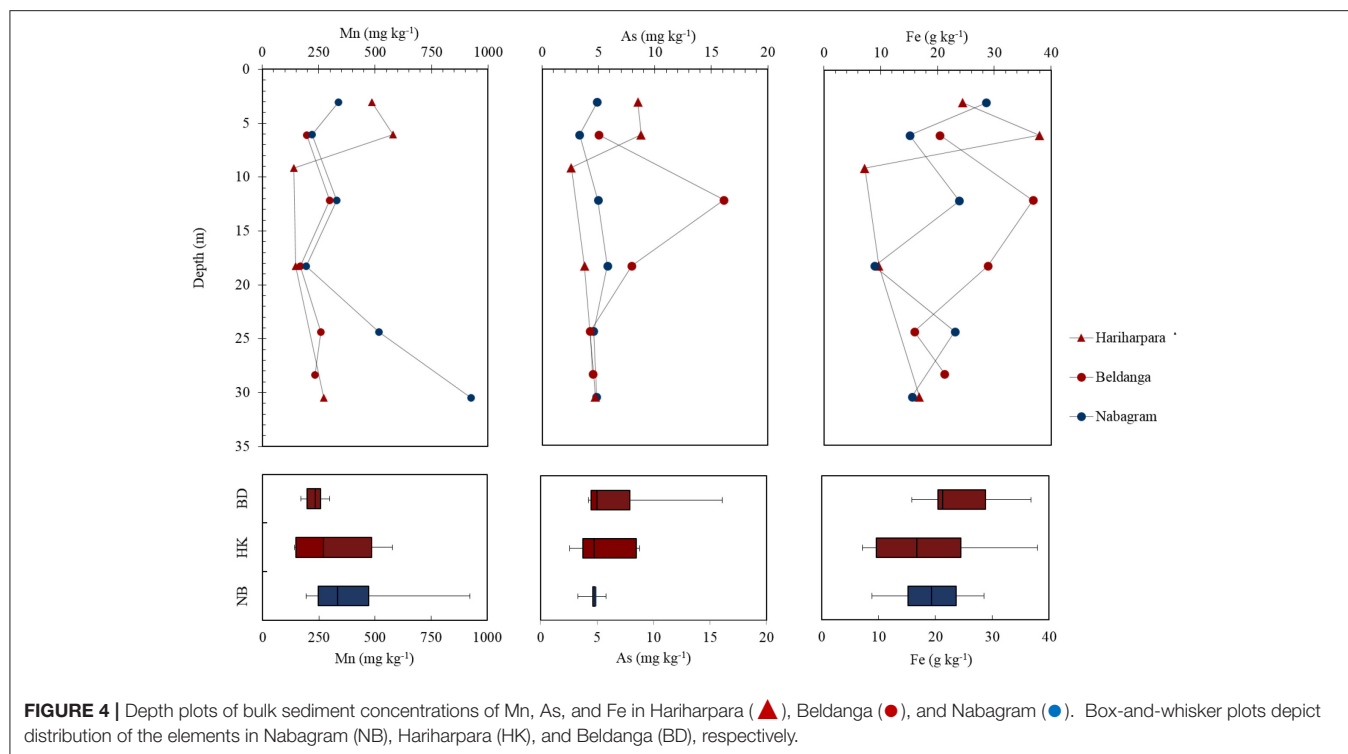


TABLE 3 | Distribution of bulk sediment concentrations of Mn, As, and Fe within all sites, HMHA sites, and HMLA sites.

Parameter	All ($n = 16$)	HMHA ($n = 10$)	HMLA ($n = 6$)
Mn (mg kg^{-1})	331 ± 97.6 (141 – 924)	278 ± 67.5 (141 – 578)	420 ± 122 (194 – 924)
As (mg kg^{-1})	5.90 ± 1.54 (2.59 – 16.1)	6.61 ± 1.84 (2.59 – 16.1)	4.72 ± 0.36 (3.31 – 5.78)
Fe (g kg^{-1})	20.9 ± 4.34 (7.16 – 38.0)	21.9 ± 4.82 (7.16 – 38.0)	19.2 ± 3.24 (8.87 – 28.6)

HMHA, High Mn, High As; HMLA, High Mn, Low As. Upper values indicate 95% confidence interval; Values in parentheses denote ranges. Absence of shaded cells indicates that no statistically significant differences between HMHA and HMLA sites were observed ($p < 0.05$).

Mobilization of Mn and As from Sediments to Groundwater

The solid phase concentrations of Mn, Fe, and As (Table 3) suggest that there are abundant metal(loid) concentrations in the shallow aquifers of Murshidabad. Hering and Kneebone (2002) experimentally showed that even 1.8 mg kg^{-1} of sedimentary As was enough to cause dissolved concentrations $>10 \mu\text{g L}^{-1}$ under reducing conditions in the presence of sufficient labile organic carbon. Previously, we showed that both the HMHA and HMLA sites have substantial sedimentary organic matter ($\sim 10\text{--}20\%$ by weight) (Datta et al., 2011; Sankar, 2013; Mohajerin et al., 2014; Kulkarni et al., 2016), which could drive microbial reductive dissolution of both Mn and Fe minerals. Elevated dissolved concentrations of Fe_T and As_T in groundwater from other regions of the Bengal Basin have been described

previously, and are thought to be the result of microbial reductive dissolution of Fe minerals under anoxic conditions (McArthur et al., 2001, 2004; Bhattacharya et al., 2002; Dowling et al., 2002; Roychowdhury et al., 2002; Horneman et al., 2004; Ravenscroft et al., 2005; Sankar et al., 2014). By contrast, relatively higher E_h values in HMLA sites may explain lower Fe_T ($\sim 0.31 \text{ mg L}^{-1}$) and As_T ($\sim 9.0 \mu\text{g L}^{-1}$) concentrations. The average Mn_T and Fe_T concentrations in groundwater from the HMHA sites were 0.83 and 3.6 mg L^{-1} (i.e., $\text{Mn}_T < \text{Fe}_T$), whereas HMLA groundwater had average Mn_T and Fe_T concentrations of 1.1 and 0.31 mg L^{-1} , respectively (i.e., $\text{Mn}_T > \text{Fe}_T$). These observations were consistent with the stoichiometry that 1 mole of acetate (simplest electron donor) would produce 8 moles of Fe(II) but only 4 moles of Mn(II) (e.g., Lovley and Phillips, 1988). Assuming that the same organic matter was used as an electron donor for both Fe(III) and Mn(IV) reduction, groundwater from the HMHA sites was apparently reducing enough to be dominated by Fe(III) reduction, releasing greater Fe(II) than Mn(II). In contrast, groundwater from the HMLA sites was less reducing. This may have led to Mn(IV) reduction remaining dominant and thus greater amounts of Mn(II) being released to solution relative to Fe(II).

Based on thermodynamics, it is suggested that after O_2 and NO_3^- are reduced, Mn(IV) is commonly the next electron acceptor utilized by respiratory bacteria (Champ et al., 1979; Stumm and Morgan, 1981; Rittman and McCarty, 2001; McGuire et al., 2002; Bethke et al., 2011). Microbial Fe(III) reduction typically occurs after Mn(IV) is reduced. However, in natural systems, these zones are not sharply defined but rather overlap substantially [e.g., simultaneous $\text{Fe(III)}\text{--SO}_4^{2-}$

reduction or simultaneous SO_4^{2-} reduction— CH_4 generation] (Chapelle and Lovley, 1992; Postma and Jakobsen, 1996; Jakobsen and Postma, 1999; Kirk et al., 2004; Bethke et al., 2011). The abundance of electron acceptors also determines the prevalence of specific redox reactions by competitive exclusion of microbial communities (Lovley and Goodwin, 1988). For example, in aquifers with abundant Fe(III) but limited SO_4^{2-} , iron-reducing bacteria would outcompete SO_4^{2-} reducing bacteria by limiting the concentration of electron donor such that SO_4^{2-} reduction cannot proceed (Chapelle and Lovley, 1992; Kirk et al., 2004).

Despite consistent TDN values between HMHA and HMLA sites, our analyses show that NO_3^- concentrations were predominantly below detection (i.e., $< 0.1 \text{ mg L}^{-1}$) in groundwater from the HMHA sites ($\sim 0.21 \text{ mg L}^{-1}$; $n = 28$), yet significantly higher ($\sim 2.8 \text{ mg L}^{-1}$; $n = 13$) in groundwater from the HMLA sites (also observed at Nabagram site, Sankar et al., 2014). This supports the notion that under sufficiently reducing conditions with an abundance of Fe(III) and Mn(IV) minerals and adequate supply of labile carbon, Mn(IV) and Fe(III) reduction can occur simultaneously, releasing Mn(II), Fe(II), and adsorbed As_T into HMHA groundwater. In contrast, higher concentrations of NO_3^- were coupled with relatively higher E_h , abundant Mn(IV) or Fe(III) bearing minerals and sufficient sedimentary labile carbon in HMLA sites. This may suggest that simultaneous NO_3^- and Mn(IV) reduction maintained the electron donor capacity to such a low level that Fe(III) reduction could not proceed, resulting in high dissolved Mn(II) but low Fe(II) and As_T concentrations. Contrasting regimes of high and low As_T groundwater (i.e., as in HMHA or HMLA in this study) are widespread throughout the Bengal Basin and other fluviodeltaic plains (Buschmann et al., 2007; von Brömssen et al., 2008; Bhattacharya et al., 2009; Bundschuh et al., 2010; Hug et al., 2011).

In the HMLA sites, it is expected that Mn(IV)—oxide bound As_T would accumulate in the aqueous phase upon reductive dissolution of Mn(IV)—oxides; however, this is not the case in the current study. Lower As_T concentrations may be attributed to the re-adsorption of As_T onto clay minerals, carbonate minerals, or incompletely reduced Fe(III)—oxides (Manning and Goldberg, 1997; McArthur et al., 2004; Guo et al., 2007; Bhattacharya et al., 2009).

The possibility that PO_4^{3-} effectively competes with As_T for adsorption sites is considered negligible for groundwater from the HMLA sites because PO_4^{3-} concentrations were below detection (i.e., $< 0.1 \text{ mg L}^{-1}$; Jain and Loeppert, 2000; Dixit and Hering, 2003; Stollenwerk et al., 2007). Mn(IV)—oxides have been shown to oxidize Fe(II) even in the presence of Fe(III) reducing microorganisms (Lovley and Phillips, 1988), which could precipitate Fe(III)—oxides. This provides additional sorption sites for As_T and maintains low Fe(II) and As_T concentrations in groundwater, as was shown experimentally by Wu et al. (2015). Several studies have reported the oxidation of As(III) by Mn(IV) and subsequent adsorption of As(V) onto Mn and Fe bearing minerals, specifically oxides (Oscarson et al., 1981; Sun et al., 1999; Manning et al., 2002; Amirbahman et al., 2006; Stollenwerk et al., 2007; Ehlert et al., 2014, 2016; Bai et al., 2016). Hence, the higher Mn(II) and lower Fe(II) and As_T

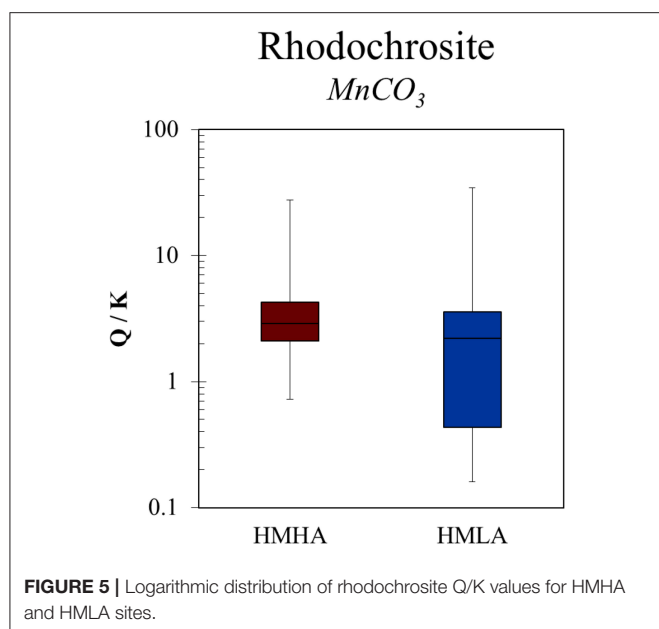
concentrations in groundwater from the HMLA sites may be a product of Mn(IV) reduction and the associated oxidation of Fe(II) and As(III).

The above discussion mostly conforms to typical HMHA and HMLA sites, which are underlain by Holocene and Pleistocene sediments, respectively. A possible outlier may be the site of Khidirpur (Figure 1), a low As_T yet high Mn_T site, which is $\sim 2 \text{ km}$ southwest of Hariharpara (HMHA site). Due to the patchy distribution of As_T observed in the Bengal Basin and other fluviodeltaic plains (van Geen et al., 2003; Fendorf et al., 2010), this is not entirely surprising. In this context, one possible control could be paleointerfluvial Pleistocene deposition beneath Khidirpur (McArthur et al., 2011), which may have led to groundwater chemistry similar to other HMLA sites, overlying Pleistocene sediments. Another possible explanation could be that shallower sampling depths at Khidirpur ($\sim 8 \text{ m}$) relative to nearby HMHA sites ($\sim 12\text{--}25 \text{ m}$ sampling depth) were related to higher E_h values observed in Khidirpur groundwater. It is possible that at $\sim 8 \text{ m}$ depth, a NO_3^- —Mn(IV) redox zone exists due to aeration induced by vertical mixing during the post-monsoon period. This is supported by the fact that the highest NO_3^- concentrations (average $\sim 12 \text{ mg L}^{-1}$) of all sampled wells ($n = 51$) were observed in Khidirpur, and Mn_T concentrations were also high (average $\sim 0.67 \text{ mg L}^{-1}$). The effects of vertical mixing on the geochemistry of shallow groundwater ($< 40 \text{ m}$) from the Nadia district ($\sim 160 \text{ km}$ south of the current study site) have been observed during the post-monsoon period (Majumder et al., 2016). However, further investigations with detailed sediment analyses at Khidirpur would be necessary to understand the mechanism of As_T immobilization.

Influence of Dissolved Organic Matter Quality on Mn and As Mobilization

Analyses of spectral properties of fluorescent DOM suggest that the DOM in groundwater from the HMHA sites contains more humic-like (higher Humic: Protein ratio), terrestrial (higher Terrestrial: Microbial), and decomposed (lower $\beta:\alpha$) organic compounds compared to the DOM in groundwater from the HMLA sites. These results are in agreement with previous investigations of DOM quality in West Bengal groundwater (Kulkarni et al., 2016).

Several studies have now demonstrated the important role of humic and biologically refractory DOM in mobilizing Fe_T and As_T via aqueous complex formation (Sharma et al., 2010; Liu et al., 2011). Formation of complexes between metals and DOM acts to keep those constituents in solution (Gavin et al., 2001). Another important role for humic substances in Bengal Basin groundwater is the ability of quinone moieties in humic DOM to shuttle electrons between Fe-reducing bacteria and Fe minerals (Lovley et al., 1996, 1998; Scott et al., 1998; Jiang and Kappler, 2008; Mladenov et al., 2010, 2015). By serving as electron shuttles, humic substances have the capability to accelerate reductive dissolution of Fe minerals, and the electron shuttling capacity has been shown to be very high in groundwater fulvic acids isolated from the Bengal Basin. This potential electron shuttling role by humic DOM is supported by higher concentrations of



dissolved Fe_T and As_T in groundwater from the HMHA sites compared to groundwater from the HMLA sites. By contrast, the less aromatic and humic DOM that characterizes groundwater from the HMLA sites is expected to contribute far less to electron shuttling or complexation reactions.

Graham et al. (2002) showed that humic substances in topsoil (0–15 cm) formed aqueous complexes with dissolved Mn(II) under reducing conditions and therefore maintained higher Mn(II) concentrations in solution. This was partially based on humic–Mn(II) complexation inhibiting the ability for Mn precipitation reactions, as evidenced by a previous investigation (Gavin et al., 2001). In our study, because more humic-like DOM is present in groundwater from the HMHA sites relative to the HMLA sites, substantially higher Mn_T concentrations could be expected in groundwater from the HMHA sites as a result of humic–Mn(II) complexation. However, saturation indices for the mineral rhodochrosite ($MnCO_3$) indicated supersaturation in $\sim 93\%$ of samples from the HMHA sites (Figure 5), suggesting precipitation (Lovley and Phillips, 1988) of Mn(II) with excess HCO_3^- that is present due to oxidation of organic matter (Ying et al., 2011). For HMLA groundwater, supersaturated conditions for rhodochrosite were observed in 63% of samples (Figure 5). Despite differences in rhodochrosite saturation calculations and DOM quality, Mn_T concentrations were similar in groundwater from the HMHA and HMLA sites. It is possible that humic DOM–Mn(II) complexation inhibits the precipitation of rhodochrosite in HMHA groundwater, resulting in comparable concentrations of dissolved Mn between the two regions. This is contrary to the expectation that greater Mn_T would be dissolved in HMHA groundwater based on: (i) humics acting as electron shuttles to catalyze Mn(IV) reduction, (ii) inherently lower E_h values, and (iii) a greater abundance of DOC for heterotrophic microbial metabolisms to catalyze Mn(IV) reduction.

Spatial Distribution of Dissolved Mn and As: Implications for Human Health

This study shows concentrations of groundwater Mn_T and As_T far exceed their recommended health limits in drinking water. The fact that 73% of the tube wells sampled exceed the revoked WHO limit of Mn_T in drinking waters of 0.4 mg L^{-1} substantiates the notion that the reimplementation of a guideline value is prudent. Geogenic Mn_T contamination of groundwater is widespread throughout West Bengal, as well as in groundwater from Bangladesh, the Mekong Delta, and some parts of Europe, and recent advances in understanding its neurotoxicity are receiving attention worldwide (Wasserman et al., 2006, 2008, 2011; Barrett, 2007; Bouchard et al., 2007, 2011; Hafeman et al., 2007; Grazuleviciene et al., 2009; Ljung et al., 2009; Spangler and Spangler, 2009; Wood, 2009; Zota et al., 2009; Khan et al., 2012). Furthermore, the co-occurrence of Mn_T with As_T in groundwater is of particular concern, where the release of both may be linked to the dissolution of metal-oxides under reducing conditions. Although regional studies such as Buschmann et al. (2008) and McArthur et al. (2004) have documented an inverse relationship between dissolved Mn and As in groundwater, it is important to note that such deductions are most often applicable to basin-wide investigations. Probing these relations within a single sampling site, or a constrained series of sites as in the current study, may reveal unique trends that are heterogeneous and difficult to generalize. Effectively assessing an area for Mn_T and As_T contamination requires both of these perspectives—knowledge of regional and local scale relationships—in order to predict or evaluate the quality of water in a given well.

This study affirms that elevated As_T does not exclude the possibility of elevated Mn_T , especially in reducing, geogenically derived systems rich in labile DOM. Likewise, elevated Mn_T does not imply the absence of As_T . Knowledge of redox conditions, most easily attained via sediment color (Biswas et al., 2012b), can be a useful tool in estimating whether high Mn waters may be afflicted with high As concentrations. Nonetheless, it is apparent that obtaining “safe” drinking water from subsurface aquifers in Murshidabad is a serious challenge. Oxidized sediments similar to those in HMLA regions, i.e., brown sand aquifers and paleointerfluves, have been posed as alternative drinking water sources in SE Asia, however, the prevalence of dissolved Mn_T in these systems has raised concerns (von Brömssen et al., 2007; McArthur et al., 2008, 2012b; Biswas et al., 2012b, 2014 and references therein). Other strategies such as filtration and rainwater have been implemented, but due to cost and maintenance their application is not practical at this time (Hossain et al., 2015). It is important that remediation strategies and alternative water sources continue to be developed so that the inhabitants of regions such as SE Asia may eventually have access to safe drinking water supplies.

CONCLUSION

Geogenic Mn_T contamination in West Bengal groundwater significantly exceeds the revoked WHO guideline of 0.4 mg L^{-1} , and only 6% of the surveyed tube wells met the guidelines

for both Mn_T and As_T . The release and accumulation of these metal(loid)s is strongly related to their redox chemistry, DOM characteristics, and the availability of electron acceptors and carbonate ligands. Relationships between Mn_T and DOM quality suggest that Mn_T release persists in conjunction with both protein-like and humic-like DOM, whereas dissolved As_T is strongly associated with humic-like, terrestrial DOM. Where E_h values are lower (e.g., HMHA), NO_3^- concentrations are negligible and Mn(IV) and Fe(III) are likely the dominant electron acceptors for microorganisms, leading to elevated Mn(II), Fe(II), and HCO_3^- in the groundwater. Saturation indices of rhodochrosite imply a net sink for aqueous Mn(II) in HMHA sites, yet Mn_T concentrations are not significantly higher than in the samples with higher E_h values (e.g., HMLA), detectable NO_3^- , and low As_T and Fe_T . It is postulated that humic–Mn(II) complexation was inhibiting rhodochrosite precipitation, yet further work is required to understand these mechanisms.

AUTHOR CONTRIBUTIONS

MV and SD are the principal executors of the field work, research and preparing this manuscript; MV is the principle researcher in this project; HK and NM contributed to the DOM modeling and interpretation and editing the manuscript; KJ, NK, PB contributed in data interpretation and shaping up of the manuscript; GH, JW, and MG contributed in data interpretation

and editing sediment analyses, GH also contributed in data interpretation of the sediment geochemistry.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <http://journal.frontiersin.org/article/10.3389/fenvs.2017.00029/full#supplementary-material>

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