Geochemical Evaluation of Arsenic and Manganese in Shallow Groundwater and Core Sediment in Singair Upazila, Central Bangladesh

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Abstract Geochemical characteristics of shallow groundwaters and core sediments are studied to better understand the sources and transportation process responsible for As and Mn enrichment in Singair Upazila of Manikgonj District in Bangladesh. Results demonstrate that the groundwater is mostly of Ca-HCO$_3$ and Ca-Mg-HCO$_3$ types. Concentrations of As in groundwater ranged from 1 to 159 µg/L, with about 59 % of these exceeded the WHO drinking water guideline of 10 mg/L. In addition, all groundwater samples had higher concentrations of Mn (0.6–5.7 mg/L) and Fe (0.9–16.5 mg/L) than the WHO drinking water guidelines (0.4 and 0.3 µg/L, respectively). Most groundwaters contained both As(III) and As(V) species in which the concentration of As(III) was generally higher than that of As(V). High concentration of As (23 mg/kg) with elevated levels of FeO, MnO and TOC were found within the upper 15 m of silty clay sediments. Multivariate geostatistical analysis showed that

dissolution of the Fe–Mn oxides was the dominant process of As and Mn release in groundwater. Geochemical modeling suggested that the concentrations of As, Mn, Fe and PO$_4^{3-}$ in groundwaters were also influenced by secondary minerals phases in addition to redox processes.

الخلاصة

تمت دراسة الخصائص الجيوكيميائية للمياه الجوفية الضحلة والرواسب الأساسية لفهم أفضل لمصادر وعملية النقل المسؤولة عن إغناء الزرنيخ والمنغنيز في سينجير أوبازيلا من منطقة مانيكيجنو في بنغلاديش. وأوضحت النتائج أن المياه الجوفية هي في معظمها من أنواع بايكربونات الكالسيوم وبايكربونات الكالسيوم ـ المغنيسيوم. وتراوحت تراكيز الزرنيخ في المياه الجوفية من 1 إلى 159 مايكروغرام/لتر، مع حوالي 59٪ من هذه التراكيز قد تجاوزت المبادئ التوجيهية الخاصة بمياه الشرب لمنظمة الصحة العالمية التي هي من 10 مايكروغرام/لتر. بالإضافة إلى ذلك، كان لجميع عينات المياه الجوفية تراكيز منغنيز (0.6 إلى5.7 ملغم/لتر) وحديد (0.9 إلى 16.5 ملغم/لتر) أعلى من المبادئ التوجيهية لمنظمة الصحة العالمية الخاصة بالمياه الصالحة للشرب (0.4 ملغم/لتر و 0.3 ملغم/لتر، على التوالي). ومعظم المياه الجوفية تحوي أنواع أيونات الزرنيخ(3) والزرنيخ(5) التي كان فيها تركيز أيونات الزرنيخ(3) أعلى من أيونات الزرنيخ(5). ووُجد أن التراكيز العالية من الزرنيخ (23 ملغ/كلغ) مع مستويات مرتفعة من أكسيد الحديد، وأكسيد المنغنيز والكربون العضوي الكلي TOC كانت أعلى في أعلى 15 متراً من الرواسب الطينية الغرينية. وأظهر التحليل متعدد المتغيرات الجيوإحصائي أن تحلل أكاسيد الحديد ـ المنغنيز كان العملية المهيمنة لإطلاق الزرنيخ والمنغنيز في المياه الجوفية. وتقترح النمذجة الجيوكيميائية أن تراكيز الزرنيخ، والمنغنيز، والحديد والفوسفات في المياه الجوفية قد تأثرت أيضا بمراحل المعادن الثانوية، إضافة إلى عمليات الأكسدة.

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1 Introduction

Groundwater contamination with geologically released arsenic represents a serious global environmental problem since

groundwater is increasingly being used as a significant drinking water source worldwide. Long-term ingestion of inorganic As causes kidney, liver, lung, skin and bladder cancers, and other chronic diseases including neurological disorders, cardiovascular diseases, diabetes, gastrointestinal and renal disorders. The toxicity of As depends on its oxidation states (+5, +3, 0, −3), and inorganic As is more toxic than organic arsenicals [1]. Inorganic As species in groundwater are predominantly arsenite [As(III)] and arsenate [As(V)] [2], where As(V) is at least 10-fold less toxic than As(III) [3]. Due to this adverse effect on human health, the World Health Organization (WHO) has set a guideline value of 10 µg/L for As in drinking water [4].

Naturally occurring As is responsible for elevated groundwater As concentrations in Bangladesh where mobilization from As-enriched minerals is the dominating process [5,6]. Several recent studies [7–9] suggested that As was derived from the weathering of Himalayan rocks and released As was subsequently strongly adsorbed by stream sediments and oxides under aerobic conditions when transported by surface water. Sediments with sorbed As were then deposited with organic matter in alluvial settings. Subsequently, Fe(III)-reducing bacteria present in alluvial sediments released sorbed As to groundwater under moderately reducing conditions [10]. However, the presence of high arsenic in sediments was not associated with primary As-bearing minerals, mostly appears to be secondary minerals origin [11]. Moreover, ions competing with As species for surface binding sites, especially phosphate, can lead to high concentrations in groundwater [12,13]. Harvey et al. [14] suggested that the mobilization of As may also be associated with recent inflow of organic carbon due to large-scale irrigation pumping, and although feasible, this hypothesis needs further investigation.

Manganese is another potential hazardous groundwater contaminant. Elevated levels of Mn are particularly harmful to newborns children since exposure to elevated Mn levels in drinking water during pregnancy may hamper the intellectual development of the child. Bouchard et al. [15] reported that Mn exposures associated with drinking water was also significantly positively related with hyperactive classroom behaviors in a study of 46 children in Québec. Due to effect on human health, the Department of Environment (DoE), Ministry of Environment and Forest, Bangladesh has set 0.4 mg/L guideline for Mn in drinking water [16], although the USA already had an even lower health reference level of 0.3 mg/L [17]. Exposure to Mn concentrations below the WHO guideline value could still result in adverse health effects, with children most vulnerable. Accordingly, Bouchard et al. [15] recommend that further research was required to establish adequate guidelines for Mn in drinking water. The occurrence and elevated concentration of Mn in groundwater are controlled by many factors, the main ones being sediment geochemistry, water chemistry and microbial activity. Manganese occurs mainly as reduced soluble Mn(II) at lower pH (<7), but is oxidized forming precipitates in the presence of oxygen at higher pH. Complexation with humic substances also inhibits Mn oxidation and precipitation in groundwater [18]. Moreover, the reduction of solid Mn oxides to the dissolved form in anaerobic conditions is generated by microbial degradation of organic matter [19].

Understanding the release mechanism of As and Mn may elucidate the predominant As and Mn species in groundwater and help in planning for proper mitigation steps in affected areas. Considering the present scenario, the geochemical characteristics of groundwaters and core sediments from shallow aquifers of Singair Upazila in Manikgonj District of Bangladesh are examined (1) to elucidate the magnitude of As and Mn contamination, (2) to determine the nature of As species in groundwater and (3) to better understanding the geochemical processes and factors responsible for the elevated groundwater concentrations.

2 Materials and Methods

2.1 Study Area

The study area Singair Upazila lies approximately 40 km west of Dhaka city to the east of the confluence of the rivers of the Ganges (Padma) and the Brahmaputra (Jamuna) (Fig. 1). Geographically, the study area is confined within 23°42′ to 23°52′ N latitudes and 90°04′ to 90°16′ E longitudes and covers an area of about 217 km^2. The study area is covered with alluvial silt and clay (Fig. 1). The landscape in this area is typically characterized by meander channels and scrolls, natural levees and back swamps formed by the river system. The low-lying landscape is naturally flooded each year during the monsoon due to overflow of the adjacent rivers.

The subsurface geology of the study area is characterized by fining-upward sedimentary sequences. Color of sediments varies from gray (silty clay) to brown (very fine sand, fine to medium sand). Aquifers of the study area are formed mostly by Quaternary alluvial sands, and these are separated from each other by aquitard units, which are formed by clay and silty clay deposits of variable thickness. The uppermost aquifer system starts at approximately 10 m below the surface, and the average thickness of this upper shallow aquifer system is approximately 15–20 m [11]. Recharge to groundwater aquifers occurs primarily from direct percolation of rainwater through the low permeable surficial silty clay unit. Seasonal groundwater level elevations range between 1.5 and 6 m within the upper shallow aquifers (Bangladesh Water Development Board, unpublished data). The Dhaleshwari and Kaliganga are the major rivers flowing along the eastern and southern border of the study area, respectively (Fig. 1).
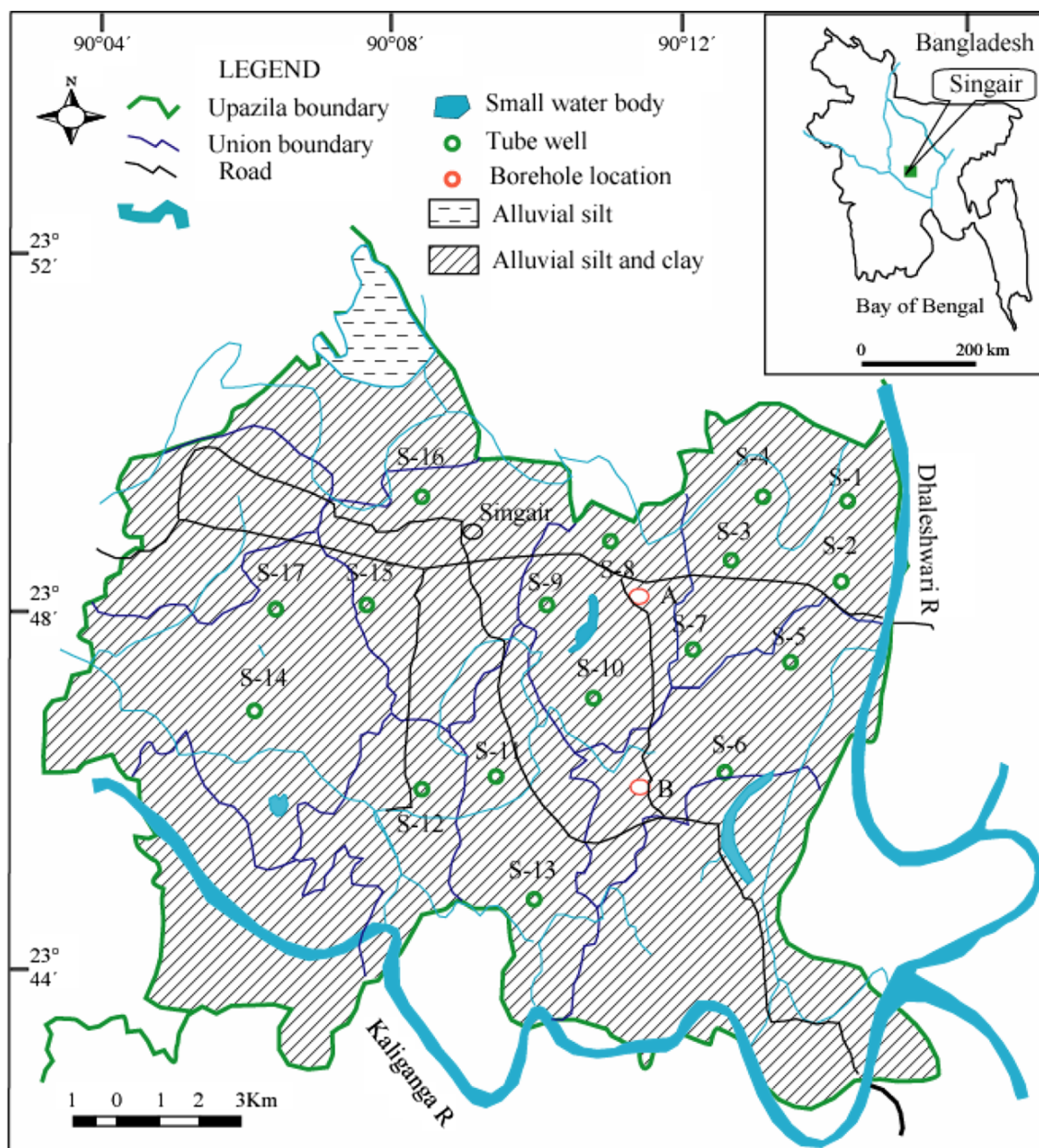
Fig. 1 Map showing groundwater sampling points, borehole positions and surface geological units in the study area of Bangladesh

2.2 Groundwater and Sediment Sampling

Groundwater samples were collected from 17 drinking water tube-well sites at different depths (10.7–56.4 m) from the study area in Bangladesh during February–March, 2008 (Fig. 1; Table 1). Samples were collected in high density polypropylene (HDPP) bottles following the procedure outlined by Bhattacharya et al. [20]. Before collection of water samples, wells were continuously pumped for 15–30 min until the temperature, electrical conductivity (EC) and pH stabilized. During sampling, the exposure of sampled water to air was minimized to prevent oxidation, and thus, the

risk of aeration was minor for sampled water. Each sample was immediately filtered on site through 0.45 μm cellulose acetate filters. To avoid any precipitation filtrate for cations, trace metals and dissolved organic carbon (DOC) analyses were transferred into polyethylene bottles and immediately acidified with supra pure 7 N HNO₃ (Merck, Darmstadt, Germany) to obtain a pH <2. Samples for anions including phosphate analyses were collected without acidification. Field blanks (Milli-Q water) were collected to insure the integrity of field sampling methods. Samples analyzed for inorganic arsenic species [As(III) and As(V)] were filtered with a 0.45-μm-membrane syringe filter and were collected

Table 1 Geochemical variables and their statistical summary in groundwater samples collected from Singair of the Manikgonj District, Bangladesh

	Depth (m)	pH	T (°C)	EC (µS/cm)	HCO_3^-	Cl^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	Na^+	K^+
S-1	20	6.8	28.3	792	234	30.46	1.04	60.44	3.04	11.9	10
S-2	46	6.8	26.4	761	135	36.96	1.60	31	0.42	21.4	7.48
S-3	56	6.9	26.4	646	184	30.07	6.48	0.56	2.51	26	6.07
S-4	11	6.9	26.3	395	110	10.16	1	23.62	0.83	11.3	4.65
S-5	12	7.0	26.0	360	123	11.67	0.69	10.56	0.14	10.4	4.55
S-6	17	7.0	27.0	692	221	38.68	0.27	52.24	1.55	12.6	9.42
S-7	15	6.9	26.1	456	184	9.43	0.72	12.82	5.31	15.7	5.48
S-8	18	6.9	27.0	588	160	7.69	2.3	0.36	5.38	13.8	7.20
S-9	11	6.9	26.7	272	73	11.56	0.57	14.35	0.31	4.7	9.05
S-10	14	6.9	26.5	597	49	21.86	1.08	1.66	4.34	7.9	6.53
S-11	15	6.7	27.5	632	295	3.03	1.2	0.98	3.98	14.1	4.49
S-12	15	6.8	26.1	480	184	11.25	1.31	3.32	2.21	17.9	7.08
S-13	15	7.0	26.1	985	258	365.5	3.94	269.7	0.41	225.7	37.9
S-14	14	6.9	25.9	556	184	34.35	2.4	1.15	7.28	27.9	8.70
S-15	15	6.8	26.0	632	209	4.85	9.64	0.48	4.01	11.8	6.46
S-16	15	6.9	26.3	783	271	12.71	1.29	11.06	2.78	14.5	9.55
S-17	11	7.0	25.3	432	160	7.78	0.31	7.11	0.49	6.6	5.01
Minimum	10.7	6.7	25.3	272.0	49	3	0.3	0.4	0.1	4.7	4.5
Maximum	56.4	7.0	28.3	985.0	295	365.5	6.5	69.7	7.3	225.7	37.9
Average	18.8	6.9	26.5	591.7	179	38.1	1.4	17.7	2.6	27.3	8.8
Median	15.2	6.9	26.3	597.0	184	11.7	1	10.6	2.5	14.1	7.1

	Mg^{2+}	Ca^{2+}	NH_4^+	DOC	Mn	Fe	Ba	As (III)	As (V)	As (total)
S-1	27.18	76.6	0.11	1.28	2	6.93	0.45	8.61	26.46	39.11
S-2	33.28	39.1	0.14	0.64	1.68	1.8	0.39	A	A	1.33
S-3	24.78	42.3	0.55	2.61	1.34	5.47	0.51	7.01	42.00	55.64
S-4	11.41	57.3	0.45	0.99	1.96	1.99	0.35	A	A	6.26
S-5	21.25	38.5	0.16	1.03	1.56	0.97	0.34	A	A	1.03
S-6	23.07	77.4	0.02	1.42	2.84	2.05	0.41	A	A	3.59
S-7	20.64	48.9	0.37	1.6	2.49	8.1	0.41	6.08	22.11	25.75
S-8	13.76	52.6	0.63	4.43	2.15	15.43	0.47	88.54	18.27	113.6
S-9	12.31	28.1	0.1	0.57	0.73	0.9	0.36	A	A	1.06
S-10	20.96	89.5	0.42	2.02	2.09	12.4	0.38	86.25	33.35	122.5
S-11	24.87	87.3	0.96	2.93	1.00	12.36	0.46	42.85	19.36	62.71
S-12	37.57	1.12	0.22	1.15	0.59	9.56	0.42	6.95	29.39	36.95
S-13	208.4	218.2	0.68	1.1	1.38	1.37	0.48	A	A	1.4
S-14	60.96	199.8	1.15	5.57	5.65	16.49	0.43	132.63	29.93	159.2
S-15	26.28	80.6	1.05	2.55	5	13.88	0.43	43.07	90.49	134.5
S-16	34.71	115.4	0.21	1.23	0.82	10.08	0.45	1.18	40.47	45.8
S-17	17.02	35.9	0.55	1.26	2.11	1.07	0.54	A	A	1.68
Minimum	11.4	28.1	0.02	0.57	0.59	0.9	0.34	1.2	18.3	1.03
Maximum	208.4	218.2	1.2	5.57	5.65	16.49	0.54	132.6	90.5	159.2
Average	36.4	72.3	0.5	1.91	2.08	7.11	0.43	42.3	35.2	47.77
Median	24.8	57.3	0.4	1.28	1.96	6.93	0.43	25.7	29.7	36.95

Here in the table all the analytical results are given in mg/L except the values of As(III), As(V) and As(total). The values of As(III), As(V) and As(total) are given in µg/L

A Not detected

in 10 mL opaque polyethylene bottles. EDTA was added to the filtrate to eliminate the precipitation of metal oxyhydroxides and reduce the effects of microbial activity [21,22]. All the samples were shipped to Japan and stored in a refrigerator at 4 °C until the analysis was performed.

The depth and establishment year of the wells were noted from the record preserved by the well owners. The geographical locations of the tube wells were accurately determined using a GARMIN handheld global positioning system (GPS). Temperature, electrical conductivity and pH were measured in the field using portable instruments. Groundwater pH was measured using a B-212, HORIBA pH meter, while electrical conductivity and temperature were measured using a ES-14, HORIBA conductivity meter. Total alkalinity (as HCO_3^-) was determined on-site by the point inflection method using a digital titrator, pH meter and 1.6 N H_2SO_4 cartridges.

Sediment core samples were collected from two boreholes (A and B), which were drilled in the study area by a split-spoon sampler with a rotary drill rig in February–March, 2008 (Fig. 1). The depths of cores A and B were 31 and 29.25 m, respectively. Sediment samples were collected with a continuous core recovery in plastic PVC tubes. The samples were maintained at ambient temperature and shipped to Kyushu University, Japan for analysis.

2.3 Groundwater Analysis

2.3.1 Chemical Composition

The concentrations of anions (Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+) in groundwater samples were measured using ion chromatography (Compact IC, 761, Metrohm). The instrument was linearly calibrated with standards (Wako Pure Chemicals Industries Ltd., Japan) in Kumamoto University, Japan.

Concentrations of As, Fe, Mn and Ba (Table 1) were measured by inductively coupled plasma and mass spectrometry (ICP-MS, 7500C, Agilent), which was linearly calibrated from 10 to 100 µg/L with custom multielement standards (SPEX CertiPrep, Inc., NJ, USA). Dissolved organic carbon was measured by a high-temperature catalytic oxidation method using a Shimadzu Corporation TOC 5000 analyzer with a detection limit of 0.5 mg/L. All analyses were performed at the Center of Advanced Instrumental Analysis, Kyushu University, Japan.

2.3.2 Arsenic Speciation

Speciation of inorganic arsenic as As(III) and As(V) (Table 1) in groundwater samples was carried out using high-performance liquid chromatography (HPLC, 1100 series, Agilent) coupled to an inductively coupled plasma and mass spectrometry (ICP-MS 7500C, Agilent) in the Fukuoka Insti-

tute of Health and Environmental Sciences, Japan. A HPLC column Excel Pak SEC-W12 (7.8 × 300 mm) was used for As speciation (Table 1). An ICP-MS was used as a detector, which was operated in the He mode for As determination to eliminate the possibility of an isobaric interference with ArCl. System was linearly calibrated with 10, 20, 50 and 100 µg/L mixed standard solutions of As(III) and As(V). The relative standard deviation for these species was within ±3%.

2.4 Sediment Analysis

Total contents of major metal oxides (Al_2O_3, CaO, FeO, K_2O, MgO, MnO, P_2O_5, SiO_2 and TiO_2) and trace elements (As, Ba, Cu, Mo, Nb, Pb, Rb, Sr, Y, Zn and Zr) in core sediments were measured by the powder press method using a wavelength dispersive X-ray fluorescence spectrometer (WD-XRF) (Rigaku, Japan) (Table 2). The sampled sediments were air-dried at room temperature to constant weight, and powdered samples were mixed well to form pellets prepared by a hydraulic press of sediments with binder (steric acid: sample at a ratio of 1:10). Standards used in analyses were from the Geological Survey of Japan (GSJ) stream sediments (JSD) series. Total organic carbon (TOC) was measured by a dry combustion method [23]. An aliquot of the powdered sample (1 g) was placed in a porcelain crucible, moisture was determined by oven-drying for 24 h at 105 °C, and then, the crucible was placed in a muffle furnace and heated to 550 °C for 4 h to combust organic carbon. The weight loss was calculated as organic carbon content.

2.5 Statistical Analysis and Geochemical Modeling

Hydrochemical data for groundwater samples were used for Spearman rank-order correlation coefficient, principal component analysis (PCA) and cluster analysis (CA) using the program STATISTICA 8 for Windows [24]. In factor analysis, a varimax normalized rotation was applied to minimize the variances of the factor loadings across variables for each factor and all principal factors with eigenvalues greater than 1.0 taken into account. The mineral saturation indices for groundwater samples were calculated using PHREEQC [25] with the thermodynamic database of MINTEQA2 [26].

3 Results and Discussion

3.1 Major Groundwater Composition

The physicochemical variables determined in groundwater samples are summarized in Table 1. Groundwater pH was near neutral and varied between 6.7 and 7.0 with an average

Table 2 Concentrations of major metal oxides, total organic carbon (TOC) and trace metals of core sediments (Borehole A and Borehole B)

	Depth (m)	Concentration of major metal oxides (wt%)									TOC (mg/kg)
		SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	K_2O	P_2O_5	
Core A											
A1	1.0	62.3	1.0	16.3	6.4	0.12	3.5	2.8	3.3	0.15	3.6
A2	2.5	63.3	1.0	15.2	6.1	0.1	3.3	2.5	3.3	0.14	4.0
A3	4.0	61.7	1.1	16.9	6.7	0.14	3.6	3.2	3.4	0.17	2.9
A4	5.5	61.3	1.0	16.6	6.6	0.17	3.4	2.3	3.3	0.14	4.0
A5	7.0	66.0	0.9	14.5	5.4	0.11	3.0	3.1	3.1	0.16	2.7
A6	8.5	63.8	1.0	15.4	6.0	0.12	3.3	2.5	3.3	0.12	3.2
A7	10.0	61.8	1.0	16.4	6.4	0.12	3.5	2.8	3.4	0.16	3.7
A8	11.5	68.5	0.9	14.1	4.4	0.09	2.6	2.2	3.0	0.12	2.1
A9	13.0	62.2	1.0	16.5	6.3	0.13	3.4	2.2	3.4	0.13	3.4
A10	14.5	68.0	0.8	14.8	3.9	0.06	2.8	2.4	3.0	0.12	2.8
A11	16.0	67.9	0.9	14.6	4.3	0.08	2.8	2.5	3.1	0.12	2.3
A12	17.5	70.6	0.7	13.4	3.3	0.06	2.2	2.5	2.8	0.12	2.4
A13	19.0	70.6	0.8	13.0	4.2	0.08	2.5	2.4	3.2	0.12	0.9
A14	20.5	72.7	0.6	12.7	3.2	0.06	2.1	2.0	3.1	0.10	0.8
A15	22.0	74.1	0.6	11.8	3.2	0.07	2.0	2.1	2.9	0.10	0.8
A16	23.5	75.1	0.6	11.4	2.9	0.06	1.9	2.1	2.9	0.11	0.8
A17	25.0	72.8	0.7	12.0	3.7	0.08	1.9	2.2	2.7	0.13	0.4
A18	26.5	73.8	0.8	11.5	3.6	0.09	2.2	2.0	2.6	0.12	0.8
A19	28.0	68.8	0.8	14.5	4.2	0.08	2.9	2.1	3.5	0.10	1.1
A20	29.5	73.8	0.6	12.1	3.3	0.06	1.9	2.0	3.2	0.1	1.0
A21	31.0	74.3	0.7	11.7	3.2	0.08	2.0	2.5	3.0	0.2	0.7
Minimum		61.3	0.6	11.4	2.9	0.1	1.9	2.0	2.6	0.1	0.4
Maximum		75.1	1.1	16.9	6.7	0.2	3.6	3.2	3.5	0.2	4.0
Average		68.3	0.8	14.1	4.6	0.1	2.7	2.4	3.1	0.1	2.1
Median		68.5	0.8	14.5	4.2	0.1	2.8	2.4	3.1	0.1	2.3

	Concentration of trace metals (mg/kg)														
	V	Cr	Co	Ni	Cu	Zn	Pb	As	Mo	Rb	Sr	Ba	Y	Zr	Nb
Core A															
A1	140	101	7	66	48	108	25	15	5	182	177	588	40	245	19
A2	130	110	14	57	37	101	24	9	3	182	187	602	36	254	18
A3	141	112	14	70	50	112	26	14	3	189	179	619	42	247	19
A4	134	119	25	66	46	111	25	23	4	182	173	665	38	238	19
A5	124	110	14	51	32	80	19	11	6	156	184	566	39	303	18
A6	124	116	20	59	37	93	18	14	3	174	187	587	38	272	17
A7	133	119	23	68	46	106	20	15	5	186	181	653	42	262	19
A8	107	102	21	41	17	57	22	9	7	138	197	538	39	328	15
A9	129	125	11	63	40	100	27	15	5	175	181	607	39	308	18
A10	109	95	21	38	19	55	21	12	8	132	213	495	34	294	14
A11	109	100	7	42	18	58	18	13	3	135	203	533	40	320	15
A12	89	82	12	31	14	41	14	12	5	118	200	490	30	296	13
A13	99	69	22	34	8	47	17	8	7	141	229	520	35	326	15
A14	76	56	12	28	8	31	15	6	4	123	210	500	24	161	10
A15	76	87	12	27	8	34	14	7	4	118	210	454	27	191	11
A16	76	50	0	23	9	37	19	6	4	118	198	474	25	185	11
A17	87	97	17	25	2	32	13	7	6	102	210	448	38	249	13

Table 2 continued

	Concentration of trace metals (mg/kg)														
	V	Cr	Co	Ni	Cu	Zn	Pb	As	Mo	Rb	Sr	Ba	Y	Zr	Nb
A18	91	85	0	26	7	32	16	5	6	100	207	418	42	323	16
A19	89	88	9	38	7	48	18	7	4	143	215	543	26	194	12
A20	71	68	25	28	9	37	19	6	3	142	212	545	24	171	11
A21	84	62	36	23	6	31	15	6	6	104	203	410	33	271	13
Minimum	71.0	50	0.0	23	2.0	31.0	13.0	5.0	3.0	100	173	410	24.0	161	10
Maximum	141.0	125	36.0	70	50.0	112.0	27.0	23.0	8.0	189	229	665	42.0	328	19
Average	105.6	93	15.3	43	22.3	64.3	19.3	10.5	4.8	145	198	536	34.8	259	15
Median	107.0	97	14.0	38	17.0	55.0	19.0	9.0	5.0	141	200	538	38.0	262	15

	Depth (m)	Concentration of major metal oxides (wt%)									TOC (mg/kg)
		SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	K_2O	P_2O_5	
Core B											
B1	1.0	66.3	0.9	14.0	5.4	0.1	3.0	2.48	3.2	0.19	2.8
B2	2.3	63.2	1.0	15.3	6.1	0.1	3.2	2.19	3.3	0.17	4.0
B3	3.8	60.8	1.0	16.1	6.9	0.1	3.6	2.11	3.5	0.19	4.4
B4	5.3	63.1	1.0	15.4	6.0	0.1	3.4	2.26	3.3	0.17	3.8
B5	6.8	63.7	1.0	15.1	6.0	0.1	3.4	2.32	3.4	0.18	3.4
B6	8.3	62.6	1.0	15.6	6.0	0.1	3.4	2.3	3.3	0.19	4.2
B7	9.8	64.7	1.0	14.9	5.6	0.1	3.3	2.47	3.2	0.19	3.0
B8	11.3	58.1	1.0	17.9	8.2	0.1	3.4	2.98	3.5	0.23	5.7
B9	12.8	59.3	1.1	16.4	7.0	0.1	3.6	2.7	3.4	0.21	5.8
B12	17.3	61.1	1.0	16.2	6.6	0.1	3.5	2.03	3.4	0.19	4.5
B13	18.8	68.7	1.0	12.8	4.7	0.1	2.7	1.93	2.9	0.17	2.2
B14	20.3	64.6	1.0	15.2	5.4	0.1	3.3	2.36	3.3	0.17	3.1
B15	21.8	70.1	0.7	13.0	4.1	0.1	2.6	2.02	3.2	0.16	1.7
B16	23.3	70.7	0.8	12.3	3.8	0.1	2.4	1.9	2.9	0.15	1.9
B17	24.8	69.7	0.8	12.4	4.3	0.1	2.6	1.92	3.0	0.175	2.1
B18	26.3	70.0	0.8	12.7	4.2	0.1	2.6	2.09	3.0	0.16	1.7
B19	27.8	57.3	1.2	16.3	8.8	0.2	4.2	2.91	3.8	0.22	4.8
B20	29.3	62.7	1.0	15.5	6.5	0.1	3.6	2.18	3.7	0.18	3.0
Minimum		57.3	0.7	12.3	3.8	0.1	2.4	1.9	2.9	0.2	1.7
Maximum		70.7	1.2	17.9	8.8	0.2	4.2	3.0	3.8	0.2	5.8
Average		64.3	1.0	14.8	5.9	0.1	3.2	2.3	3.3	0.2	3.4
Median		63.5	1.0	15.3	6.0	0.1	3.3	2.2	3.3	0.2	3.3

	Concentration of trace metals (mg/kg)														
	V	Cr	Co	Ni	Cu	Zn	Pb	As	Mo	Rb	Sr	Ba	Y	Zr	Nb
Core B															
B1	122	88	17	44	23	72	14	13	5	147	207	553	42	364	17
B2	127	118	8	60	38	90	21	10	3	169	181	538	39	264	18
B3	133	106	20	66	49	109	26	13	4	184	178	552	39	246	19
B4	108	100	11	57	40	95	23	11	4	166	180	547	36	239	17
B5	124	100	25	54	34	88	18	12	5	169	192	570	38	267	17
B6	132	109	15	62	37	100	21	13	6	165	181	574	39	255	18
B7	115	101	26	52	33	80	19	10	5	154	195	549	41	313	17
B8	143	118	34	77	56	118	26	19	1	195	148	649	37	171	18
B9	146	122	12	69	52	114	25	14	2	185	164	592	39	222	19

Table 2 continued

| | Concentration of trace metals (mg/kg) | | | | | | | | | | | | | | |
	V	Cr	Co	Ni	Cu	Zn	Pb	As	Mo	Rb	Sr	Ba	Y	Zr	Nb
B12	133	108	12	64	47	109	24	11	3	184	167	621	40	235	18
B13	108	84	17	37	14	58	16	9	9	128	215	446	51	545	16
B14	109	87	20	47	24	71	19	8	4	153	199	517	37	290	16
B15	94	65	20	32	9	42	23	7	6	135	222	479	34	304	14
B16	88	79	0	31	7	42	14	8	6	120	226	404	36	337	13
B17	112	75	20	33	11	47	15	10	7	128	226	468	39	379	14
B18	101	74	24	34	9	47	19	9	6	127	226	466	36	345	14
B19	157	123	14	81	50	142	26	14	1	232	172	627	33	219	20
B20	132	107	20	55	30	85	23	10	5	187	196	612	37	357	17
Minimum	88.0	65	0.0	31	7.0	42.0	14.0	7.0	1.0	120	148	404	33.0	171	13
Maximum	157.0	123	34.0	81	56.0	142.0	26.0	19.0	9.0	232	226	649	51.0	545	20
Average	121.3	98	17.5	53	31.3	83.8	20.7	11.2	4.6	163	193	542	38.5	297	17
Median	123.0	101	18.5	55	33.5	86.5	21.0	10.5	5.0	166	194	551	38.5	279	17

of 6.9. Temperatures varied from 25.3 to 28.3 °C with an average of 26.5 °C.

Electric conductivity (EC) values were relatively low, with an average of 591.7 μS/cm and ranging between 272 and 985 μS/cm. Bicarbonate is the most dominant anion in the study area and its concentration in groundwater ranged from 49 to 295 mg/L with an average of 179 mg/L. Chloride, which ranged from 3.0 to 365.5 mg/L with an average of 38.1 mg/L, was the second major anion. The order of relative abundance of major anion is $HCO_3^- > Cl^- > SO_4^{2-} > PO_4^{3-} > NO_3^-$ (on an mg/L basis). Relatively high concentration of HCO_3^- coupled with low concentrations of SO_4^{2-} (average of 17.7 mg/L) and NO_3^- (average of 1.4 mg/L) in the groundwater aquifers may be due to process resulting from microbially mediated reduction in the presence of organic matter [27,28]. On contrary, the concentration of PO_4^{3-} in the groundwater varied from 0.1 to 7.3 mg/L with an average value of 2.6 mg/L. This variation of PO_4^{3-} concentrations may be due to application of P-enriched fertilizers in the adjoining agricultural land to increase food production. Phosphate is sorbed strongly onto solid phases, including Fe and Al oxides in soils [29]. However, the amount of P released into water is related to the concentration of PO_4^{3-} that exceeds the capacity of Fe to create insoluble Fe phosphate [30]. In contrast, PO_4^{3-} may also release into groundwater due to microbially mediated reductive dissolution of Fe(III)-oxyhydroxide [29,31,32]. Apatite may also be another potential source of P that is contributed to increase concentration of PO_4^{3-} in groundwater.

The dominant cations in the groundwater samples were Ca^{2+} (average of 72.3 mg/L) and Mg^{2+} (average of 36.4 mg/L), and their order on relative abundance was $Ca^{2+} >$

$Mg^{2+} > Na^+ > K^+ > NH_4^+$ (Table 1). To classify the major ions for groundwater and to summarize the major contrasts in hydrogeochemical composition between different water sources, Piper diagrams are widely used. Major ion compositions plotted on a Piper diagram (Fig. 2) indicated that all groundwater samples were clustered near the left corner of the central diamond except sample # S-13. In general, the groundwater was compositionally evolved, characterized as Ca–HCO₃, Ca–Mg–HCO₃ and Mg–Ca–Na–Cl type. High concentrations of Mg^{2+}, Ca^{2+}, Na^+, Cl^- and SO_4^{2-} and low concentrations of NO_3^- were found in sample # S-13. Agricultural activities directly or indirectly affect the concentrations of a large number of inorganic chemicals (for example, NO_3^-, N_2, Cl^-, SO_4^{2-}, H^+, P, C, K^+, Mg^{2+} and Ca^{2+}) in groundwater [33]. High concentrations of Mg^{2+}, Ca^{2+}, Na^+, Cl^- and SO_4^{2-} in sample # S-13 may be influenced by agricultural activities. Moreover, low concentrations of NO_3^- in sample # S–13 may be due to denitrification and/or nitrate reduction in presence of organic matter [34]. In addition to the agricultural activities, a number of reasons including domestic pollution (latrines) and evaporation are potential sources of these ions in sample # S-13. Sodium and Ca^{2+} in groundwater can be derived from halite and the incongruent dissolution of plagioclase feldspars [35]. The major cation Ca^{2+} may also come from carbonate minerals such as calcite and dolomite, whereas Mg^{2+} can be derived from biotite, carbonate and chlorite minerals. Potassium may also come from orthoclase and clay minerals [28]. Release of Ca^{2+}, Mg^{2+}, Na^+ and K^+ into groundwater from silicate and carbonate mineral weathering is normally enhanced by respired CO_2 from oxic and anoxic degradation of organic matter. In addition to carbonate and silicate mineral weathering, cation exchange may be another process to release these

Fig. 2 Piper diagram illustrating the major hydrochemical features of the groundwater. The *red square* and *yellow circle* denote Mg–Ca–Na–Cl and Ca–HCO$_3$/Ca–Mg–HCO$_3$ type waters, respectively
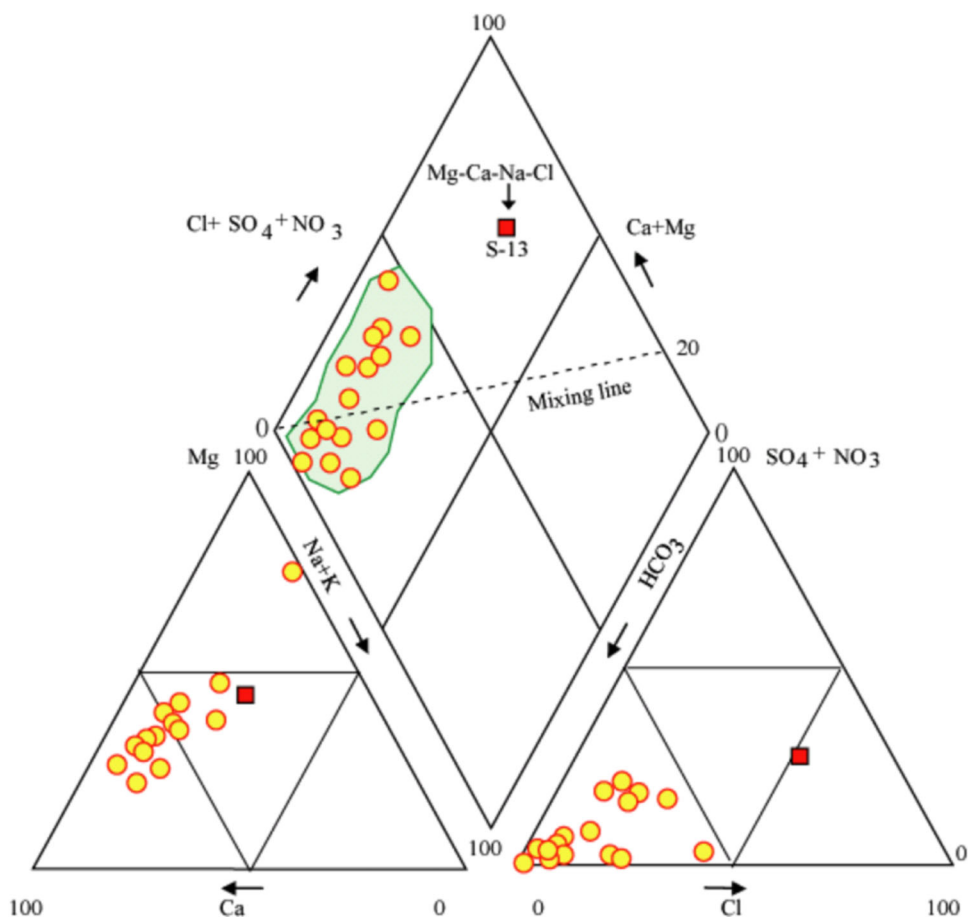
major cations in groundwater. Presence of NH_4^+ was also observed in all groundwater samples ranged from 0.02 to 1.2 mg/L (average of 0.5 mg/L). The NH_4^+ is likely a product of the decomposition of organic matter. Dissolved organic carbon in groundwater samples varied from 0.6 to 5.7 mg/L with an average of 2.1 mg/L (Table 1).

The concentration of total As in groundwater varied between 1.03 and 159.2 µg/L with an average value of 47.77 µg/L (Table 1). The average concentration of As(III) (varied from 1.2 to 132.6 µg/L with a mean of 42.3 µg/L) was higher than the value of As(V) (varied from 18.3 to 90.5 µg/L with a mean of 35.2 µg/L) (Table 1). Moreover, the dominance of As(III) was observed in all groundwater samples with high DOC concentrations (Table 1). The total As concentrations in about 59 % groundwater samples exceed the World Health Organization (WHO) guideline value for safe drinking water of 10 µg/L [4]. The recent studies [29] in the Bengal Basin show high levels of As present in shallow aquifers (<100 m), and As concentration in groundwater generally decreases with increasing well depth (Fig. 3a).

Elevated level of Mn (between 0.59 and 5.65 mg/L with an average of 2.08 mg/L) and Fe (between 0.9 and 16.49 mg/L with an average value of 7.11 mg/L) was found in groundwater samples (Table 1). All groundwater samples contained both Mn and Fe above the WHO [4] guideline values for drinking water (0.4 and 0.3 mg/L for Mn and Fe, respectively) (Fig. 3b, c). In comparison, Ba concentrations ranged from 0.34 to 0.54 mg/L (average of 0.43 mg/L) in all groundwater samples, which were lower than the WHO [4] drinking water guidelines (0.7 mg/L) (Table 1). Therefore, the findings of this investigation indicated that people in the study area may be exposed not only to As but also to Mn and Fe from groundwater, and may experience possible adverse health effects.

3.2 Mobilization of As and Mn in Groundwater

3.2.1 Multivariate Geostatistical Analysis

Multivariate geostatistical analysis including correlation coefficient matrix, principal component analysis and cluster analysis of all groundwater parameters was carried out in order to evaluate the relationships of As with other valuables. Arsenic shows a strong positive correlation with Fe ($r = 0.95$, $p < 0.001$), DOC ($r = 0.86$, $p < 0.001$) and NH_4^+ ($r = 0.62$, $p < 0.01$), a moderate correlation with Mn ($r = 0.38$) and a negative correlation with SO_4^{2-} ($r = -0.69$,
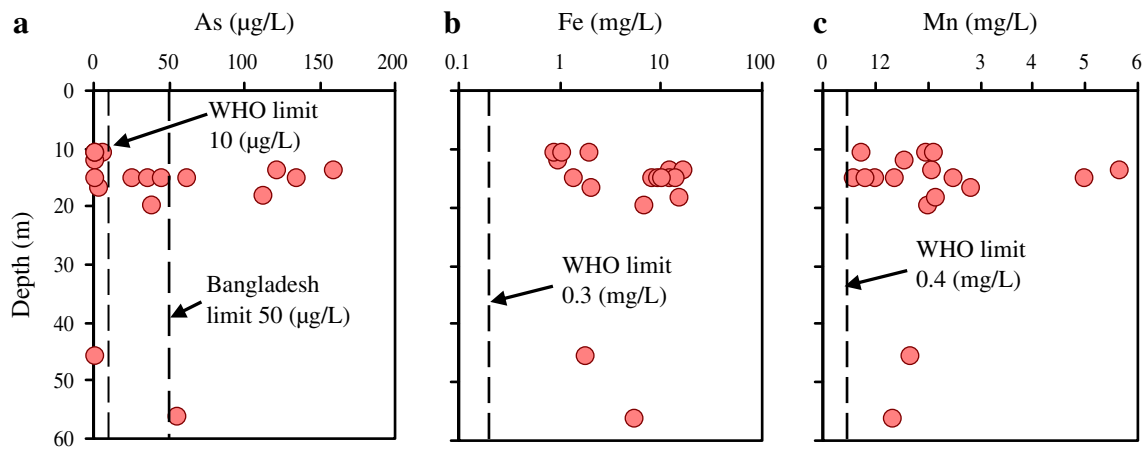
Fig. 3 Depth distributions and drinking water guideline limits of **a** As; **b** Fe and **c** Mn in groundwater

Table 3 Spearman rank-order correlation for physicochemical parameters of groundwater samples

	pH	HCO₃	Cl	NO₃	SO₄	PO₄	Na	K	Mg	Ca	NH₄	As	Mn	Fe	Ba	DOC
pH	1.00															
HCO₃	−0.21	1.00														
Cl	0.28	0.08	1.00													
NO₃	−0.22	0.15	0.16	1.00												
SO₄	0.10	0.06	0.60	−0.08	1.00											
PO₄	−0.34	0.25	−0.28	0.02	−0.57	1.00										
Na	−0.10	0.31	0.50	0.61	−0.05	0.32	1.00									
K	0.02	0.32	0.68*	0.15	0.49	−0.03	0.30	1.00								
Mg	−0.22	0.63	0.49	0.30	0.11	0.08	0.68*	0.49	1.00							
Ca	−0.13	0.59	0.25	0.14	0.00	0.48	0.48	0.37	0.51	1.00						
NH₄	−0.05	0.22	−0.36	0.13	−0.62	0.49	0.32	−0.31	0.19	0.43	1.00					
As	−0.37	0.28	−0.25	0.09	−0.69*	0.90**	0.33	−0.04	0.20	0.57	0.62	1.00				
Mn	0.18	−0.05	−0.01	−0.54	−0.15	0.52	−0.05	−0.02	−0.14	0.22	0.29	0.38	1.00			
Fe	−0.43	0.31	−0.26	0.11	−0.64	0.93**	0.38	0.01	0.26	0.58	0.54	0.95**	0.39	1.00		
Ba	0.11	0.59	−0.10	0.33	−0.30	0.25	0.28	0.14	0.31	0.25	0.51	0.00	0.24	1.00		
DOC	−0.07	0.35	−0.24	0.00	−0.70*	0.86**	0.30	−0.15	0.10	0.43	0.62	0.86**	0.51	0.81**	0.49	1.00

* Significant at $p < 0.005$ and ** significant at $p < 0.001$

$p < 0.005$) (Table 3), which typically characterizes anoxic aquifers where reductive dissolution of Fe and/or Mn phases releases surface bound As (and phosphate) and is the principal source of dissolved As in groundwater. Elevated level of PO_4^{3-} and Fe due to biodegradation of organic matter [14,32] is also indicated by the significant positive correlation between DOC and PO_4^{3-} ($r = 0.86$, $p < 0.001$) and Fe ($r = 0.81$, $p < 0.001$) (Table 3). A significant positive correlation of As and PO_4^{3-} ($r = 0.90$, $p < 0.001$) also supported a release mechanism caused by reductive dissolution of sediment minerals because PO_4^{3-} and AsO_4^{3-} have similar chemical structures and therefore tend to be bound to (and to be released from) the same mineral surfaces [36]. Manganese was also positively correlated with DOC ($r = 0.51$),

Fe ($r = 0.39$) and PO_4^{3-} ($r = 0.52$) demonstrating that As and Mn may release by bacterial reductive dissolution of Mn oxide/oxyhydroxide [20,37].

Principal component analysis (PCA) suggested that just four factors (PCs) were able to account for 81 % of the variance of all variables in groundwater (Fig. 4). Among these, PC 1 showed the highest positive loadings of EC, Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} explained 35 % of variance. In contrast, PC 2, which had high positive loading with Mn, Fe, As, PO_4^{3-} and DOC, accounts for 29.6 %. This result suggested that the distribution of these positive loading variables in PC 2 may be controlled by the biodegradation of organic matter combined with precipitation–dissolution processes [9,32,38]. Presence of organic matter and peat in aquifer sed-
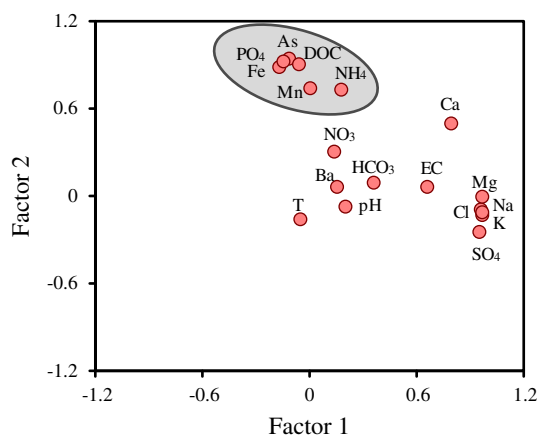
Fig. 4 Principal component analysis based on physiochemical properties of groundwater. Elevated concentrations of As, Fe, Mn, DOC, PO_4 and NH_4 are closely associated with each other suggesting origin from similar sources
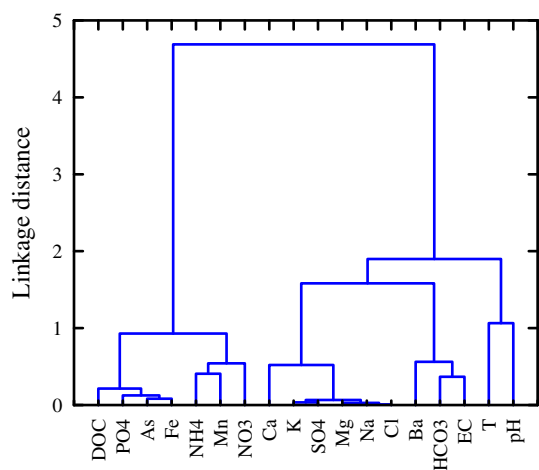

Fig. 5 Dendrogram showing the behavior of geochemical variables in groundwater. Cluster analysis was performed using Person and Ward's method

iments of Bengal Basin had been reported in several studies [8,9,39]. Degradation of these organic matter and peat could drive the sequence of redox reactions in the aquifer [31,40]. Aiken [41] pointed out that the DOC had produced through the biodegradation of organic matter in the aquifer. A significant portion of the refractory DOC remains for a longer time in groundwater phase. Bacteria mediate the release of As in younger sediments into groundwater under reducing conditions. Enhanced microbial activity accelerates the diagenetic process, involving mobilization of As from sediments with high organic matter [42].

Cluster analysis was also carried out to visualize the groupings in measured variables of groundwater data sets (Fig. 5). Parameters belonging to the same cluster are likely to be originated from a common source. In this study, the geochemical variables are divided into four distinct clusters, namely (1) DOC, PO_4^{3-}, As, Fe, NH_4^+, Mn and NO_3^-, (2) Ca^{2+}, K^+, SO_4^{2-}, Mg^{2+}, Na^+ and Cl^-, (3) Ba, HCO_3^- and EC, and (4) temperature and pH. Each of the last three clusters was decoupled from one another, and redox sensitive parameters were loaded in the first cluster. These findings further support that As and Mn release are likely promoted during microbial metabolization of dissolved organic compounds coupled with reductive dissolution of Fe-Mn oxides/oxyhydroxides where NH_4^+ is produced as a reduction product of organically bound nitrogen and/or dissimilatory nitrate reduction [43].

3.2.2 Arsenic Speciation

Generally in groundwater, two important As species are available as oxyacids arsenite (H_3AsO_3) and arsenate (H_3AsO_4). Arsenate reduction occurs through thermodynamically favored processes combined with organic matter oxidation. Iron and Mn oxides/oxyhydroxides can easily be reduced under the anaerobic condition. Biodegradation of buried peat deposits could drive extreme degrees of reduction of Fe-oxyhydroxide and supply high concentrations of As to groundwater [40]. The role of other secondary Fe-phases in sequestering As, particularly As(V), is also significant as evidenced by reductive transformation of Fe(III)-oxyhydroxides to magnetite by microbial degradation [44,45]. In the study, concentration of As (III) was significantly positively correlated with that of dissolved Fe ($r = 0.77$, $p < 0.01$), DOC ($r = 0.78$, $p < 0.01$), PO_4^{3-} ($r = 0.69$, $p < 0.05$) and Mn ($r = 0.62$, $p < 0.05$) (Fig. 6a, b) while not any relationship between As(V) and either Fe, Mn, PO_4 or DOC was observed. These findings further suggest that As, Fe and Mn may release to the groundwater through the predominant process of reductive dissolution of solid phase Fe–Mn oxides/oxyhydroxides in the aquifer, and this reduction is coupled with the microbial degradation of organic matter in the sediments.

3.2.3 Geochemical Modeling

Geochemical modeling was performed in order to calculate the saturation indices (SI) for selected minerals in groundwater samples. More than 80 % groundwater samples were supersaturated with respect to siderite ($FeCO_3$), while 60 % of the samples were supersaturated with respect to vivianite ($Fe_3(PO_4)_2 8(H_2O)$). The results comply with the statement that siderite and vivianite are potential precipitates because of elevated concentrations of carbonate and phosphate reported for Bangladesh groundwater [46]. Moreover, all groundwater samples were supersaturated with respect to $MnHPO_4$, while 50 % of the samples were supersaturated with respect

Fig. 6 Bivariate plots showing the relationships of **a** As(III) with Fe and DOC and **b** As(III) with PO$_4$ and DOC in groundwater
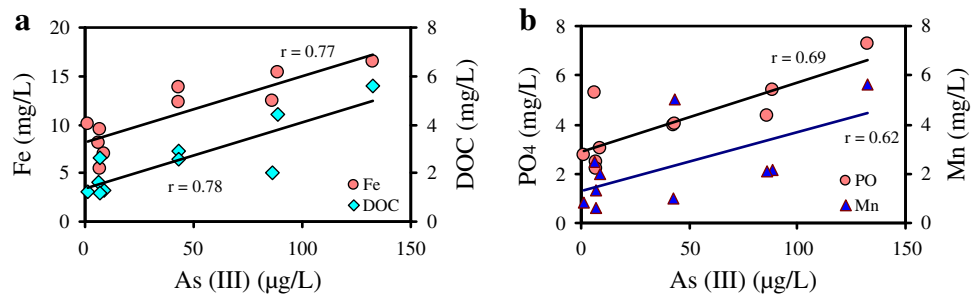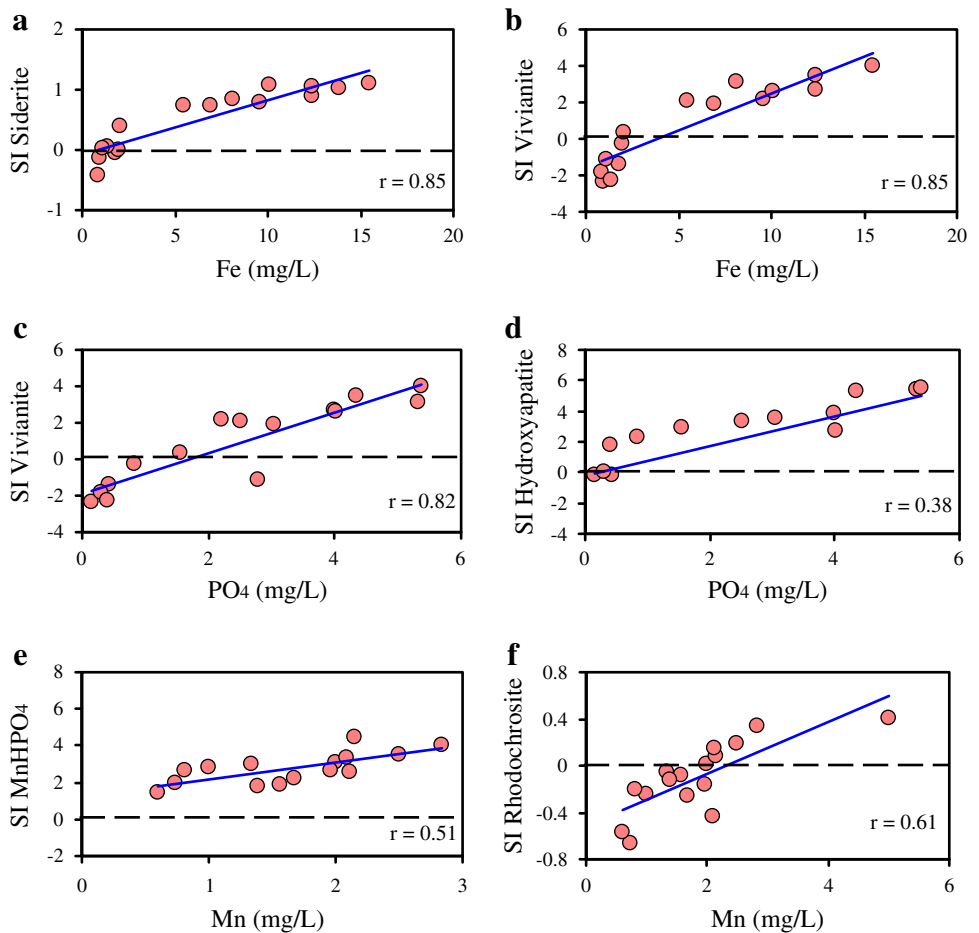

Fig. 7 Bivariate plots showing the dependency of the geochemical modeled saturation index values for **a** Fe vs siderite; **b** Fe vs vivianite; **c** PO$_4^{3-}$ vs vivianite; **d** PO$_4^{3-}$ vs hydroxyapatite; **e** Mn vs MnHPO$_4$; and **f** Mn vs rhodochrosite

to rhodochrosite (MnCO$_3$). In these samples, supersaturation of Fe and Mn species could result in preferential precipitation of secondary siderite, vivianite and rhodochrosite during their transportation into different environments. In contrast, the groundwater samples, which were undersaturated with respect to these minerals, probably came from an environment where Fe^{2+} and Mn^{2+} existed in other forms. Moreover, von Brömssen et al. [47] observe low concentrations of dissolved Mn^{2+} in groundwater from Bangladesh, and this is likely because the concentration of Mn(II) is controlled by the precipitation of Mn(II) minerals (e.g., rhodochrosite and MnHPO$_4$). Thus, above statement complies with the observed results discussed herein.

Dissolved Fe was significantly correlated with the SI values of siderite ($r = 0.84$, $p < 0.001$) and vivianite ($r = 0.85$, $p < 0.001$), suggesting that these two minerals may exert an important role in controlling Fe concentrations in groundwater, in addition to redox processes (Fig. 7a, b). The average SI values for hydroxyapatite and MnHPO$_4$ are approximately 2.4 and 2.7, respectively, which indicates the crystalline phase of these minerals may present in the aquifer. The positive relationships of PO$_4^{3-}$ with vivianite ($r = 0.82$, $p < 0.001$), hydroxyapatite ($r = 0.42$) and MnHPO$_4$ ($r = 0.45$, Figure not shown) suggest that the concentration of PO$_4^{3-}$ in groundwater may also be controlled by these three minerals (Fig. 7c, d). Moreover, a significant correlation
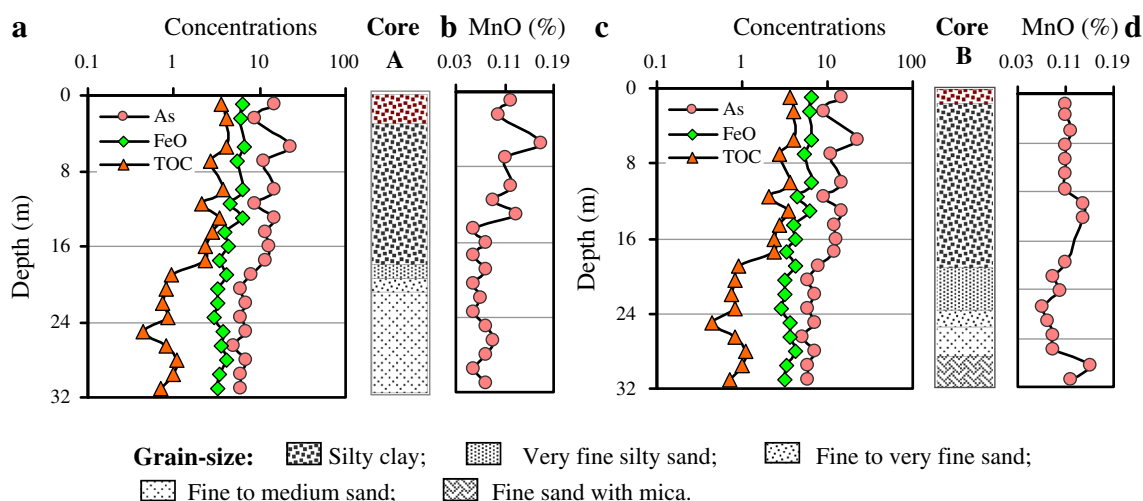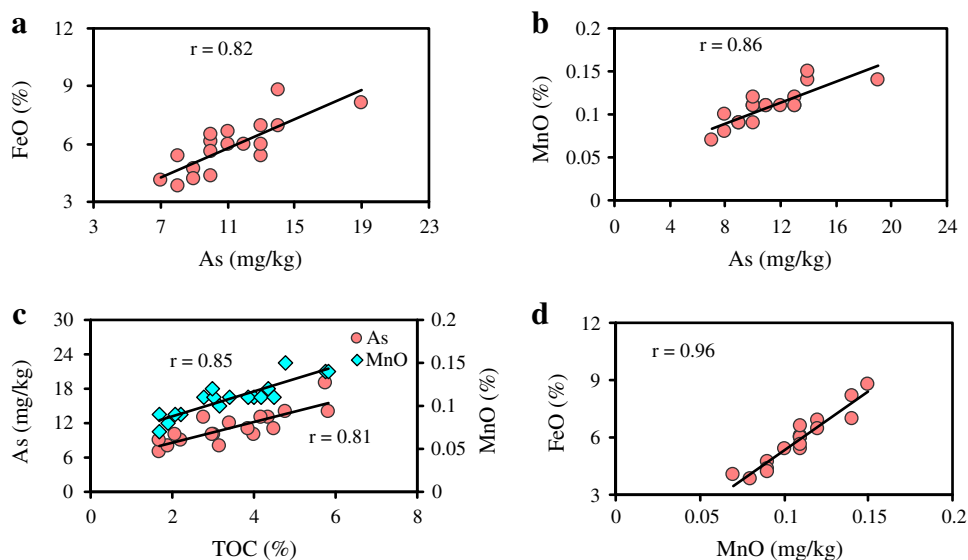
Fig. 8 Distributions of As (mg/kg), FeO (wt%), MnO (wt%) and TOC (wt%) at different depths in sediment samples of cores A and B

Fig. 9 Bivariate plots showing the correlations of **a** As with FeO; **b** As with MnO; **c** TOC with As and MnO; and **d** MnO with FeO in sediment samples of core B

between As and PO_4^{3-} was observed. Thus, the geochemical modeling results help to conclude that the competing ion PO_4^{3-} containing these secondary mineral phases coupled with microbial-mediated reductive dissolution of Fe–Mn oxides/oxyhydroxides results in the high content of As in groundwater. Similarly, dissolved Mn is strongly correlated with SI values of MnHPO₄ ($r = 0.51$) and rhodochrosite ($r = 0.61$), indicating that these minerals are responsible for the high dissolved Mn concentrations, in addition to the reductive dissolution of Mn–oxyhydroxides (Fig. 7e,f).

3.3 Geochemistry of As and Mn in Sediments

Variations in geochemical composition of core sediments with depth are given in Table 2. The total concentrations of As in sediment samples ranged from 5 to 23 and 7 to 19 mg/kg with an average of 10.5 and 11.2 mg/kg in core

A and core B, respectively. The maximum concentrations of As were observed in a silty clay sediment samples of A4 (depth of 5.5 m) and B8 (depth of 11.25 m) of core A and core B, respectively, and gradually decreased with increasing depth, but increased in fine sand with mica at a depth of 27.8 m (sample B19) of core B (Fig. 8a, c), as they possess higher surface areas and thereby adsorb the bulk of As onto their surfaces [48,49]. The average concentrations of MnO in sediments were 0.1 wt% (varied from 0.1 to 0.2 wt%) and 0.11 wt% (varied from 0.07 to 0.15 wt%) in cores A and B, respectively, while the contents of FeO in these core sediments ranged from 2.9 to 6.7 wt% and from 3.8 to 8.8 wt% with an average of 4.6 wt% and 5.9 wt%, respectively. Contents of total organic carbon (TOC) in both cores A and B ranged from 0.4 to 4 wt% (mean value of 2.1 wt%) and from 1.7 to 5.8 wt% (mean value of 3.4 wt%), respectively, and the vertical distribution patterns of TOC were very similar to that

Table 4 Spearman rank-order correlation coefficients for geochemical variables in sediment samples at different depths of core B

	TiO$_2$	Al$_2$O$_3$	FeO	MnO	MgO	CaO	K$_2$O	P$_2$O$_5$	V	Cr	Co
TiO$_2$	1.00										
Al$_2$O$_3$	**0.84**	1.00									
FeO	**0.89**	**0.94**	1.00								
MnO	**0.87**	**0.89**	**0.96**	1.00							
MgO	**0.89**	**0.91**	**0.91**	**0.89**	1.00						
CaO	0.49	0.64	0.63	**0.74**	0.56	1.00					
K$_2$O	**0.75**	**0.89**	**0.87**	**0.83**	**0.92**	0.56	1.00				
P$_2$O$_5$	**0.76**	**0.78**	**0.81**	**0.86**	**0.75**	**0.72**	0.65	1.00			
V	**0.88**	**0.89**	**0.93**	**0.92**	**0.87**	0.61	**0.80**	**0.90**	1.00		
Cr	**0.86**	**0.89**	**0.91**	**0.90**	**0.82**	0.65	**0.73**	**0.78**	**0.91**	1.00	
Co	−0.04	−0.07	−0.05	0.02	−0.02	0.22	0.09	0.17	−0.01	−0.23	1.00
Ni	**0.88**	**0.96**	**0.97**	**0.92**	**0.88**	0.65	**0.83**	**0.81**	**0.92**	**0.93**	−0.10
Cu	**0.81**	**0.94**	**0.95**	**0.89**	**0.83**	0.66	**0.79**	**0.79**	**0.87**	**0.89**	−0.09
Zn	**0.85**	**0.95**	**0.96**	**0.92**	**0.87**	0.66	**0.81**	**0.83**	**0.91**	**0.92**	−0.12
Pb	**0.71**	**0.87**	**0.80**	0.70	**0.77**	0.39	**0.83**	0.55	0.69	0.67	0.00
As	0.68	**0.77**	**0.82**	**0.86**	0.70	0.70	0.62	**0.90**	**0.85**	**0.77**	0.00
Mo	−0.63	**−0.84**	**−0.85**	**−0.79**	−0.69	−0.69	**−0.79**	−0.6	−0.73	**−0.79**	0.15
Rb	**0.85**	**0.93**	**0.97**	**0.93**	**0.93**	0.62	**0.94**	**0.76**	**0.90**	**0.88**	0.01
Sr	**−0.79**	**−0.96**	**−0.93**	**−0.85**	**−0.83**	−0.63	**−0.79**	**−0.77**	**−0.84**	**−0.89**	0.13
Ba	**0.75**	**0.88**	**0.87**	**0.88**	**0.87**	0.69	**0.86**	**0.87**	**0.89**	**0.82**	0.10
Y	0.18	−0.02	0.04	0.04	−0.01	−0.01	−0.27	0.30	0.18	0.11	0.01
Zr	−0.57	**−0.86**	**−0.77**	−0.67	−0.67	−0.55	**−0.73**	−0.58	−0.67	**−0.74**	0.18
Nb	**0.86**	**0.90**	**0.93**	**0.90**	**0.85**	0.63	**0.75**	**0.82**	**0.92**	**0.93**	−0.17
TOC	**0.80**	**0.94**	**0.92**	**0.85**	**0.82**	0.64	**0.76**	**0.79**	**0.88**	**0.91**	−0.18

	Ni	Cu	Zn	Pb	As	Mo	Rb	Sr	Ba	Y	Zr	Nb	TOC
TiO$_2$													
Al$_2$O$_3$													
FeO													
MnO													
MgO													
CaO													
K$_2$O													
P$_2$O$_5$													
V													
Cr													
Co													
Ni	1.00												
Cu	**0.98**	1.00											
Zn	**0.99**	0.98	1.00										
Pb	**0.82**	0.79	**0.78**	1.00									
As	**0.83**	0.83	**0.87**	0.53	1.00								
Mo	**−0.83**	−0.86	**−0.82**	**−0.73**	−0.62	1.00							
Rb	**0.92**	0.90	**0.90**	**0.82**	**0.73**	**−0.83**	1.00						
Sr	**−0.96**	−0.99	**−0.97**	**−0.80**	**−0.79**	**0.86**	**−0.89**	1.00					
Ba	**0.85**	0.81	**0.86**	0.67	**0.81**	−0.72	**0.90**	**−0.82**	1.00				
Y	0.04	0.08	0.06	−0.29	0.17	0.14	−0.07	−0.07	0.03	1.00			

Table 4 continued

	Ni	Cu	Zn	Pb	As	Mo	Rb	Sr	Ba	Y	Zr	Nb	TOC
Zr	−0.85	−0.87	−0.85	−0.82	−0.65	**0.84**	−0.75	**0.90**	−0.68	0.27	1.00		
Nb	**0.96**	**0.93**	**0.96**	**0.74**	**0.84**	−0.78	**0.87**	−0.91	**0.80**	0.18	−0.77	1.00	
TOC	**0.96**	**0.97**	**0.97**	**0.73**	**0.81**	−0.84	**0.86**	−0.97	**0.80**	0.11	−0.88	**0.93**	1.00

Significant p values ($p < 0.001$) correspond to high coefficient values are marked in bold

of As, FeO and MnO in these core sediments (Fig. 8a–d). Vertical distributions of these variables (Fig. 8a) suggested that As was strongly sorbed by Fe–Mn-bearing minerals such as Fe–Mn oxides/oxyhydroxides, and they have strong affinity to organic matter present in the core sediments [49]. The concentrations of CaO (averages of 2.4 and 2.3 wt%) and P_2O_5 (average values of 0.1 and 0.2 wt%) in both cores A and B are slightly higher in the upper silty clay sediments and gradually decrease with increasing depth, suggesting that these clay sediments contain more Ca and P. Contents of other trace metals in sediments of core A and core B are also higher in the high As and Mn zones.

In order to examine the relationships of As with MnO and other variables, correlation coefficient analysis was performed based on core sediments geochemical data and the relationships showed significant positive correlations of As with FeO ($r = 0.82$, $p < 0.001$), MnO ($r = 0.86$, $p < 0.001$) and TOC ($r = 0.82$, $p < 0.001$) (Fig. 9a–c). Furthermore, core sediments As concentrations showed a strong correlation with Al_2O_3 ($r = 0.77$, $p < 0.001$), CaO ($r = 0.70$, $p < 0.005$), P_2O_5 ($r = 0.90$, $p < 0.001$) and other trace metals (at $p < 0.001$) such as V ($r = 0.85$), Cr ($r = 0.77$), Ni ($r = 0.83$), Cu ($r = 0.83$), Zn ($r = 0.87$) and Ba ($r = 0.81$) (Table 4). Similarly, MnO was significantly positively correlated with these geochemical variables, including FeO ($r = 0.97$, $p < 0.001$), TOC ($r = 0.85$, $p < 0.001$), CaO ($r = 0.76$, $p < 0.001$) and P_2O_5 ($r = 0.84$, $p < 0.001$) (Fig. 9d; Table 4).

These positive significant relationships and depth profiles of As, FeO and MnO (Fig. 7a–d) suggest that As is strongly associated with Fe and Mn oxides, and their dissolution (reductive) is involved in mobilization of As, Fe and Mn in groundwater [39,50]. Strong positive correlations of TOC with As, FeO and MnO in core sediments further indicate that organic matter plays a significant role in controlling the mobility of As, Fe and Mn in groundwater aquifers. Furthermore, concentration of P_2O_5 was also significantly correlated with CaO ($r = 0.72$, $p < 0.001$) (Table 4), indicating that P in the sediments was present in apatite or some other Ca-bearing minerals. As both P_2O_5 and CaO show strong correlation with As in the studied core sediment samples, these P and Ca-bearing mineral apatite/hydroxyapatite may exert an important role for transportation of As, in addition to the reductive dissolution of Fe–Mn oxides/oxyhydroxides as suggested by von Brömssen et al. [47].

4 Conclusions

The hydrogeochemical characteristics and As and Mn enrichment of groundwater and subsurface sediments of Singair Upazila in Bangladesh were evaluated to refine our understanding of the mechanisms of As and Mn release to groundwater. The results demonstrate that groundwaters are mostly of Ca-HCO_3 and Ca–Mg–HCO_3 types with the dominant anion of HCO_3^-, which is mostly contributed to the EC increases. Major cations Ca^{2+}, Mg^{2+} and Na^+ may release through the dissolution of carbonates, cation exchange and weathering of silicates enhanced by respired CO_2 from organic matter degradation.

This study revealed that 59 % of tubewells contained As in excess of the maximum WHO contaminant level of 10 µg/L while all groundwater samples had levels of Mn and Fe that exceeded the WHO standards of 0.4 and 0.3 mg/L, respectively. In addition, dissolved As(III) was found to be the dominant As species. Elevated levels of Fe, Mn, DOC and PO_4^{3-} coupled with low concentrations of NO_3^- and SO_4^{2-} suggested that aquifers of the study area were under reducing condition where sediments were deposited with abundant organic matter. Significant positive correlations of As(III) with dissolved DOC, Fe, PO_4^{3-} and Mn suggested that the biodegradation of organic matter present in sediments created a favorable reducing conditions, facilitating biotransformation of Fe(III) to Fe(II), Mn(IV) to Mn(II) and As(V) to As(III), thereby releasing As, Fe and Mn to groundwater. Geochemical modeling indicated that the concentrations of these variables in groundwater were also influenced by the formation of secondary minerals siderite, vivianite, hydroxyapatite, $MnHPO_4$ and rhodochrosite in addition to redox processes to create favorable environment for microbial reductive dissolution of Fe-Mn oxides/oxyhydroxides. Vertical distribution of geochemical variables suggested that silty clay sediments are rich in CaO, FeO, MnO and P_2O_5 minerals together with abundances of trace metals and organic matter containing As concentrations as high as 23 mg/kg.

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