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Full Length Research Paper

Nature of arsenic enrichment in groundwater and to assess the main geochemical factors controlling arsenic mobilization in Pabna, Bangladesh

Humayun Ali Hasan, Ziaur Khan , Surya Hamid* and Monica Bhashani

Department of Geology and Mining, University of Rajshahi, Bangladesh.

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Arsenic (As) in the groundwater of Bangladesh is a serious natural calamity and a public health hazard. Groundwaters (to a depth of 70 m) from the study area of Pakshi Union in the southwestern part of Bangladesh were collected to determine arsenic concentration and geochemical analyses. Groundwater geochemical conditions changed from oxidized form to a successively more reduced form. Groundwater is characterized by circum-neutral pH with a moderate to strong reducing nature. The analysis reveals that groundwater arsenic concentrations in the uppermost aquifer (10-70 m of depth) range from 7.0 to 168.2 μgL^{-1}. The dominant groundwater type is Ca-Mg-HCO_3 type with high concentrations of As, Fe and Mn but low levels of NO_3^- and SO_4^{2-}, and other parameters were also below the desirable limit. Correlation analysis shows that As is closely associated with Fe and Mn which suggest that reductive dissolution of MnOOH and FeOOH mediated by anaerobic condition represents an important mechanism for releasing arsenic into the groundwater from arsenic rich sediments. Poor correlation of Mn and Fe suggests that siderite and rhodochrosite were precipitated on the surface of sediments.

Key words: Arsenic, groundwater, sediment, aquifer.

INTRODUCTION

Arsenic (As) enrichment in Bangladesh groundwater is considered to be one of the greatest current environmental disasters in the world. Arsenic-contaminated groundwater has caused endemic arsenic poisoning among millions of people in many countries such as Bangladesh, Indian, Vietnam, Cambodia, Argentina, Chile, the United States and China (Charlet and Polya, 2006). The main sources of arsenic in arsenic-contaminated aquifers worldwide are naturally occurring arsenic, either from clay/organic-rich aquitards containing arsenic rich minerals (for example, arsenopyrite, arsenian pyrite, and enargite) or from aquifers containing iron and manganese oxides (Smedley and Kinniburgh, 2002). As ingestion through crops grown with groundwater containing high As has become a matter of serious concern (Correll et al., 2006), various studies demonstrate that enrichment of groundwater by As is restricted mainly to the Holocene alluvial and deltaic plains of the Bengal Basin, whereas groundwater abstracted from the older Plio-Pleistocene aquifers are characteristically low in As (Zheng et al., 2005). Mobilization of As into the groundwater of shallow alluvial aquifers in the Bengal Basin through natural processes involving reductive dissolution of Feoxyhydroxide is widely accepted as the principal mechanism (Anawar et al., 2003). Apart from Fe(III)-oxyhydroxides, other solid phases such as Mn/Al-oxyhydroxides and phyllosilicates may also play an important role in As cycling and mobilisation (Saunders et al., 2005).

The study area, Pakshi union, belongs to Iswardi upazilla under Pabna district. The study area lies between latitude 24°03′N to 24°08′N and longitude 89°00′E to 89°04′E. It is bounded by Sara union and Ishwardi paurashava in the north, Silimpur and Sahapur union in the east, Lakshmikunda union in the west and the Ganges river in the South. The location map of the

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*Corresponding author. E-mail: surya.hamid@yahoo.com.

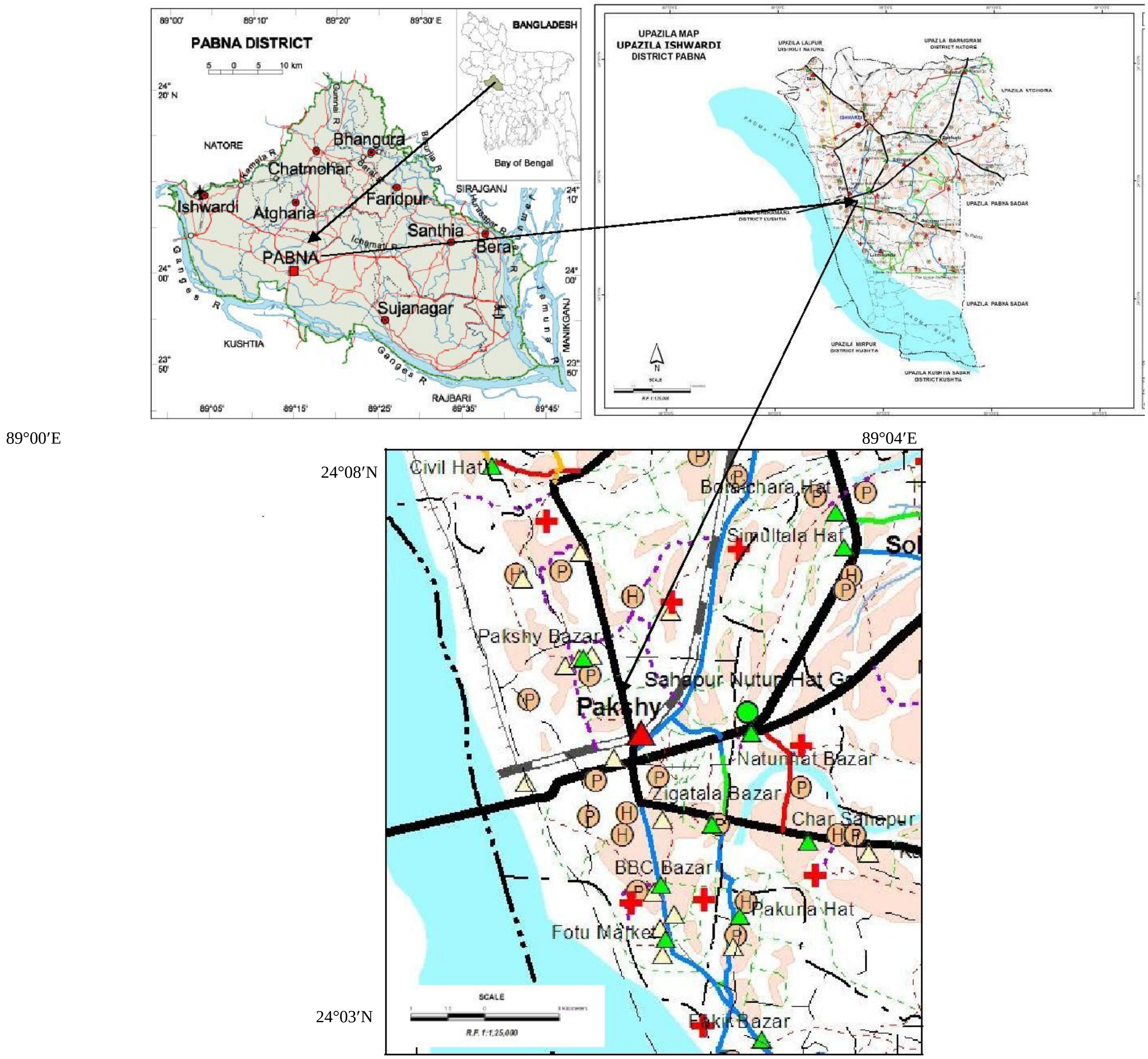

Figure 1. Location map of the study area. Figure 1: Location Map of the Study Area

study area is shown in Figure 1. The study area is well communicated with Pabna and other districts by means of national high way.

In the study area, arsenic related diseases like arsenicosis is one of the major problems. Arsenicosis is caused due to access of arsenic in groundwater (Selinus, 2005). Some other problems may exist in the study area which is related to water quality.

Bangladesh comprises a major part of the Bengal Basin. Bengal Basin was formed during the Tertiary period as the Indian plate breaks away from Gondwanaland in the late Cretaceous and moved towards a collision with Eurasian plate. Several scientific articles have already been published regarding the regional Geology of the Bengal Basin and its surrounding area (Morgan and McIntire, 1959). Bangladesh is divided into two major tectonic units, one is the Precambrian platform in the northwest and the other is the Bengal Foredeep on the southeast separated by the Calcutta, Pabna and Mymensing Hinge Zone. The study area is a part of Bengal Foredeep which is a significant tectonic feature of Bangladesh.

Rashid (1991) subdivided Bangladesh into 24 physiographic sub regions and 54 units by refining the previous works. These are based mainly on topographical features, drainage patterns, soil associations and geomorphology. Physiographically, the study area belongs to the Ganges flood plain (Reimann, 1993). The surface geology consists entirely of sedimentary formations of alluvial sand, silt and clay,

Table 1. Physical parameters of hand tubewell water samples in the study area.

Sample No.	Temperature (°C)	pH (pH meter)	EC (μs/cm)	TDS (mgl^{-1})
1	24	8.1	806	515.84
2	28	8.1	1097	702.08
3	25	7.8	944	604.16
4	25	8.0	783	501.12
5	24	8.1	802	513.28
6	24	8.0	902	577.28
7	26	8.0	870	556.80
8	25	8.0	1182	756.48
9	27	8.1	777	497.28
10	27	8.0	882	556.48
11	26	8.0	882	564.48
12	25	8.1	735	470.40

which are mainly of riverine origin.

The main objectives of this paper are to characterize the hydrogeochemical setting of the study area, to evaluate the nature and the extent of arsenic enrichment in groundwater and to assess the main geochemical factors controlling arsenic mobilization.

METHODOLOGY

Twelve groundwater samples were collected from Pakhshi, Ishardi, Pabna District (Figure 1). The water samples were collected in 500 ml plastic bottles, which were corked immediately to make them airtight. Samples were acidified with concentrated nitric acid (HNO_3) for determination of trace elements to prevent any reaction. The physical parameters such as pH, EC, and temperature were measured in the field. A rapid determination of total dissolved solids (TDS) was made simply by multiplying the measured EC values (μS/cm) by the constant 0.64 (Todd, 1980).

Na^+ and K^+ of groundwater samples were analyzed using flame photometer. Ca^{2+}, Mg^{2+}, Mn and Fe of groundwater samples were measured using flame atomic absorption spectrometer. Arsenic of groundwater samples were analyzed using hydride vapor generation atomic absorption spectrometer (Model: Varian, AA 220 FS; Method: APHA 3114.C and APHA 3112.C) in the Central Laboratory, Rajshahi University. Some anions such as NO_3^-, SO_4^{2-} and Cl^- were determined using Ion-Chromatograph (Shimadzu, CTO-20 AC SP; Method: APHA 4110.B). Alkalinity, HCO_3^- was measured using titration method. A total of 12 samples including blank, spike, duplicate, quality control and check samples were measured sequentially. All calibrated standard, quality control standard and check standard are traceable to National Institute of Standards and Technology (NIST), USA. Recovery of quality control spiked sample, duplicate sample and quality control sample were observed. Then the collected and determined data were analyzed and interpreted by using Statistical Software.

RESULTS AND DISCUSSION

The groundwater quality analysis was carried out on the basis of physical parameters and chemical analysis.

Physical parameters

The physical parameters such as hydrogen ion concentration (pH), electrical conductance (EC), temperature (°C) were measured in the field. These physical parameters gave idea about the present quality of groundwater.

Hydrogen ion concentration

The pH is one of the most important characteristics of water. Water may be acidic, neutral or alkaline. A neutral solution has a hydrogen ion concentration of pH = 7.0, acidic has pH = 5 and alkaline has pH = 9. The pH value in the study area ranges from 7.8 to 8.1; it indicates almost neutral water (Table 1) and is suitable for drinking and irrigation purposes.

Specific electrical conductance (EC)

Electrical conductance of all groundwater samples was measured in the field by a portable EC meter (HANNA pocket EC meter). Electrical conductance is directly related to the abundance of charged ionic species, that is, higher electrical conductance is the reflection of higher ionic concentration and this is especially true in case of chloride (Cl^-) concentration (Hem, 1989). The EC values of groundwater samples in the study area ranged from 735 to 1182 μS/cm (Table 1). The EC value indicates total dissolved solids (TDS) present in water. However,

Table 2. Results of chemical analyses of groundwater samples in the study area.

Sample No.	Cation (in mg/l)				Anion (in mg/l)				Trace Element (μg/l)			
	Ca^{2+}	Mg^{2+}	Na^{*}	K^{+}	HCO^{-}_{3}	Cl^{-}	SO_4^{2-}	NO_3^{-}	As	Mn	Fe	Cd
HTWS 1	51.75	3.06	12.52	0.1705	301.08	32.11	8.34	1.70	80.66	492.2	128.0	13.9
HTWS 2	48.6	2.88	9.32	0.1832	302.7	98.09	9.12	7.88	20.78	1411.2	220.5	15.2
HTWS 3	42.7	1.69	7.88	0.1701	318.5	31.12	5.92	4.15	58.62	579.4	277.4	21.6
HTWS 4	118.66	1.22	11.70	0.1405	410.0	36.31	16.72	2.08	95.6	468.8	192.9	13.5
HTWS 5	85.32	1.02	10.22	0.1333	305.02	46.39	0.89	1.72	23.0	690.0	209.8	20.8
HTWS 6	103.2	0.96	6.12	0.1345	383.6	27.98	1.30	0.48	168.2	1072.2	168.9	23.4
HTWS 7	61.32	0.88	5.10	0.1225	334.3	41.17	3.82	2.18	53.8	792.1	208.0	23.4
HTWS 8	62.92	1.01	7.12	0.1496	350.6	38.02	2.18	0.16	34.3	691.2	236.5	19.9
HTWS 9	63.2	3.50	13.61	0.1436	358.6	26.96	6.02	8.12	153.6	972.5	152.9	26.3
HTWS 10	68.13	1.82	8.96	0.1231	310.6	37.96	15.58	0.58	57.8	602.2	152.9	18.3
HTWS 11	70.12	1.76	8.32	0.1049	320.1	32.50	8.25	0.16	7.0	274.1	310.3	23.0
HTWS 12	72.18	0.98	6.56	0.1155	366.5	19.88	6.18	0.08	101.5	270.5	146.7	31.8

the temperature of the study area ranges from 24 to 28°C.

Results of chemical analysis data

Water samples were collected from different hand tube wells of the study area which is analyzed for detailed description of the hydrochemical changes in hand tubewell water chemistry. Results of the chemical analyses of groundwater samples from different wells are shown in Table 2.

Groundwater geochemistry

Major cations such as Ca^{2+} (42.70 - 118.66 mgl^{-1}), Mg^{2+} (0.88 - 3.50 mgl^{-1}), Na^{+} (5.10 - 13.61 mgl^{-1}) and K^{+} (0.1049 - 0.1832 mgl^{-1}) show significant variations with depth as well as region. Major anion composition is dominated by HCO_3^{-} (301 - 410 mgl^{-1}) and Cl^{-}(19.88 - 98.09 mgl^{-1}). Concentration of SO_4^{2-} (<10 mgl^{-1}) and NO_3^{-}(≤0.89 mgl^{-1}) are generally low, except for some local variations. Concentration of trace elements such as As (7.0 - 168.2 μgL^{-1}), Fe (128.0 - 310.3 μgl^{-1}), Mn (270.5 - 1411.2 μgl^{-1}) and Cd (13.5 - 31.8 μgL^{-1}) in the groundwater samples both has a function of depth and region.

The chemical characteristics of the groundwater samples of this study fall in different subdivisions of diamond shaped field of the Piper Diagram. Figure 2 shows that all the samples fall in field-1 suggesting that alkaline earths exceed alkalis. These entire samples also fall in field-3 indicating that weak acids exceed strong acids. Finally, all the samples fall in field-5 implying that the groundwaters have an excess of 50% carbonate hardness (secondary alkalinity). It may be concluded that the groundwater samples of the study area is the dominance of alkaline earth (Ca^{2+} and Mg^{2+}) and weak acids. From the piper diagram (Piper, 1953), it shows that ground waters are generally Ca-HCO_3 or Ca-Mg-HCO_3 type (Figure 2).

From the calculated saturation indices of mineral in aquifer using FREEQUE Software, the common rock forming minerals were obtained as: Anhydrite, Aragonite, Arsenolite, Calcite, Claudetite, Dolomite, Goethite, Gypsum, Hematite, Magnesite, Magnetite Manganite, Rhodochrosite and Siderite. Most of the minerals were precipitated and the others were dissolved (Table 3).

Arsenic enrichment and mobilization

Arsenic (As) is derived from the weathering of Himalayan rocks in tectonically active areas (Bhattacharya et al., 2002). Released As is strongly adsorbed by stream sediments and oxides under aerobic conditions when it is transported by surface water. Sediments with sorbet As are then deposited with organic matter in alluvial settings. Subsequently, Fe(III), reducing bacteria present in alluvial sediments causes the release of absorbed As to groundwater under moderately reducing conditions (Reza et al., 2010).

The main source of As in groundwater is postulated to be geogenic deposits associated with fine-grained, clay rich sediments. The two most possible mechanisms for the release of As from sediments to groundwater are oxidation of sulfides and reduction of Fe and Mn oxyhydroxides. The hydrogeochemical process of As enrichment is the main characteristics of this groundwater as the Holocene alluvial sediments are rich in organic matter and reactive minerals, though water is mostly of Ca-Mg HCO_3 and Ca-Na-HCO_3 type (Bhattacharya et al., 2002).

Arsenic is widely distributed as a trace constituent in rocks and weathered soils. It may be derived from the weathering of rocks exposed along the Himalayan

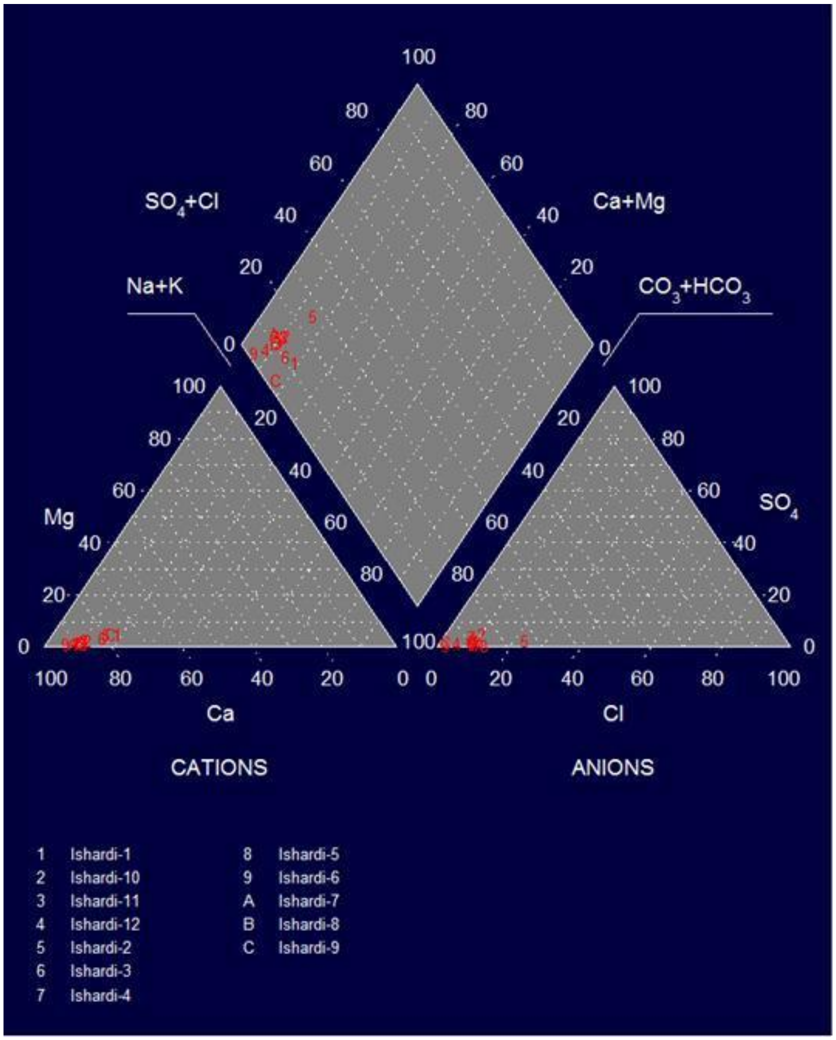

Figure 2. Piper diagram of groundwater samples.

Table 3. Calculated saturation indices of mineral in aquifer using FREEQUE Software.

Sample No. Mineral	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10	S-11	S-12
Anhydrite	-	-	-	-	-	-	-	-	-	-	-	-
Aragonite	+	+	+	+	+	+	+	+	+	+	+	+
Arsenolite	-	-	-	-	-	-	-	-	-	-	-	-
Calcite	+	+	+	+	+	+	+	+	+	+	+	+
Claudetite	-	-	-	-	-	-	-	-	-	-	-	-
Dolomite	+	+	+	+	+	+	+	+	+	+	+	+
Goethite	+	+	+	+	+	+	+	+	+	+	+	+
Gypsum	-	-	-	-	-	-	-	-	-	-	-	-
Hematite	+	+	+	+	+	+	+	+	+	+	+	+
Magnesite	+	+	-	-	-	-	-	-	+	-	-	-
Magnetite	+	+	+	+	+	+	+	+	+	+	+	+
Manganite	-	-	-	-	-	-	-	-	-	-	-	-
Rhodochrosite	+	+	+	+	+	+	+	+	+	+	+	+
Siderite	+	+	+	+	+	+	+	+	+	+	+	+

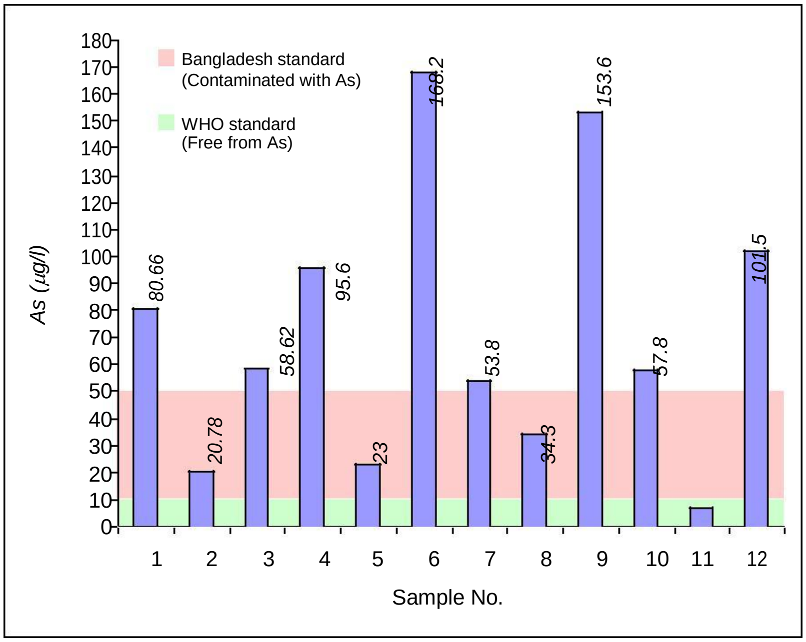

Figure 3. Comparison of arsenic concentrations in groundwater samples with WHO Standard and Bangladesh Standard.

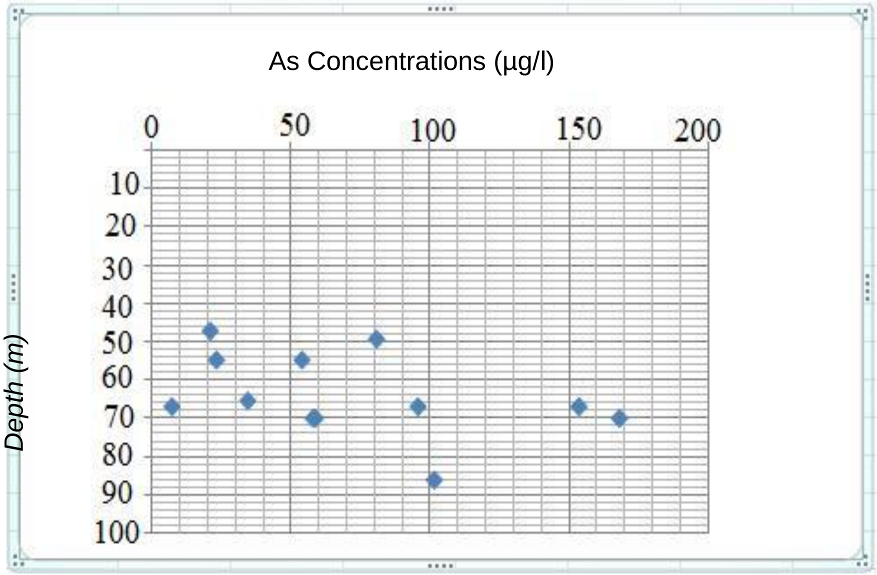

Figure 4. Distribution of As in groundwater with the depth of the aquifers in the study area.

orogeslic belt or oxidation of metal sulfides (Nickson et al., 2000). Poor correlation between dissolved sulfate and arsenic in groundwater argues against metal sulfides as the main source of As, as absorbed sediments are then deposited with organic matter in alluvial settings.

Arsenic concentration of groundwater in the study area ranges from 7.0 to 168.2 μgL^{-1} which exceeds the drinking water standard (DOE, 1997; WHO, 1984) (Figure 3).

The process of As mobilization in alluvial sediments is complex, in that it may occur as Fe and Mn oxides are reducing bacteria under moderately reducing conditions. Alternatively, arsenic may be mobilized by ionic competition of other ions (for example, nitrate, carbonate and silicate) on sorting sites of oxides.

BGS and DPHE (2001) reported that maximum As concentrations occur at depths between 20 and 50 m whereas samples shallower than 10 m and deeper than 150 m are basically As free (Figure 4). It is therefore apparent that the As distribution in groundwater is not only controlled

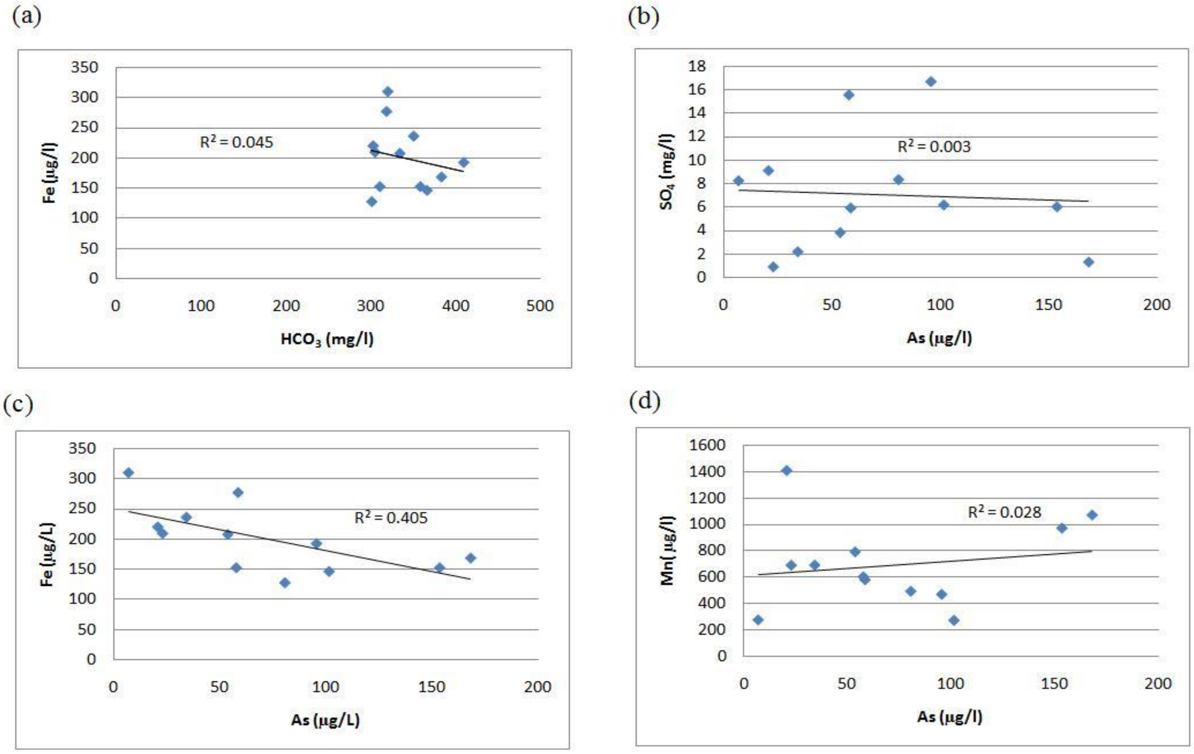

Figure 5. Correlations for (a) Fe versus HCO_3, (b) SO_4 versus As, (c) Fe versus As, and (d) Mn versus As in ground water of the study area.

by depth but also to a major extent by subsurface geology, that is, age and grain size of sediments. It has been established from the different studies that As is mobilized in tube wells placed in the fine grained Holocene aquifers, while those penetrating the coarser Holocene sediments and the Plio-Pleistocene (Dupi Tila) aquifers are found to be safe all over the country, thereby revealing that distribution of As in the wells is largely dependent on the facies characteristics of the alluvial deposits.

Iron has moderately positive correlation with HCO_3^- (r^2 = 0.045; Figure 5a). Sulfate levels in groundwater are generally very low and there is no significant correlation with As (r^2 = 0.003; Figure 5b). Low SO_4 concentrations in many point to SO_4 reduction as having been an important process. Highest As concentrations are found in some of the most reducing (low SO_4) groundwaters and they indicate that development of strongly reducing conditions is likely to be a major control on As mobilization. The poor correlations among dissolved As, Fe and SO_4 concentrations in groundwater suggest that pyrite / sulfide oxidation is not the dominant process for arsenic release. Pyrite was rarely found in the sediment samples of the Ganges delta plain (Nickson et al., 2000), suggesting that alluvial aquifers are sulfur-limited systems. Locally, high sulfate concentrations in groundwater may result from weathering of sulfate and sulfide minerals. Iron has positive correlation with As (r^2 = 0.405; Figure 5c) and Manganese has also positive correlation in groundwater with As (r^2 = 0.028; Figure 5d), implying that reductive dissolution of FeOOH and MnOOH may be responsible for part of the dissolved As loads in the study area.

High concentration of arsenic, iron and bycarbonate reflect that the bacterial reductive dissolution of iron oxyhydroxides is the dominant process for arsenic mobilization in Bangladesh groundwater. Locally, the poor correlation between dissolved iron and arsenic may be caused by the loss of Fe by precipitation of siderite ($FeCO_3$) / Rhodochrosite ($MnCO_3$), implying that the other geochemical processes also control As and Fe levels in groundwater.

Distribution of As, Fe and Mn

The concentration of As in Rooppur is higher than the surrounding areas (Figure 6). The concentration of Fe is high in Pakshi Bazar and low in Rooppur (Figure 7). The concentration of Mn is low in Fotu Market and high in Shahapur (Figure 8).

Conclusions

The study reveals that environment sensitive index parameters like pH, EC, Eh, and temperature values of

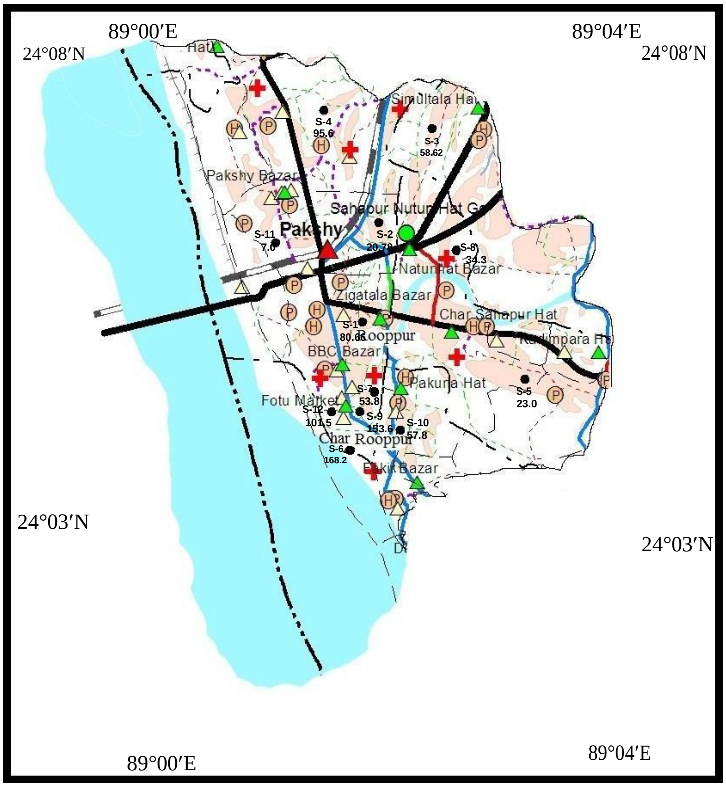

Figure 6. Distribution of As showing map of the study area.

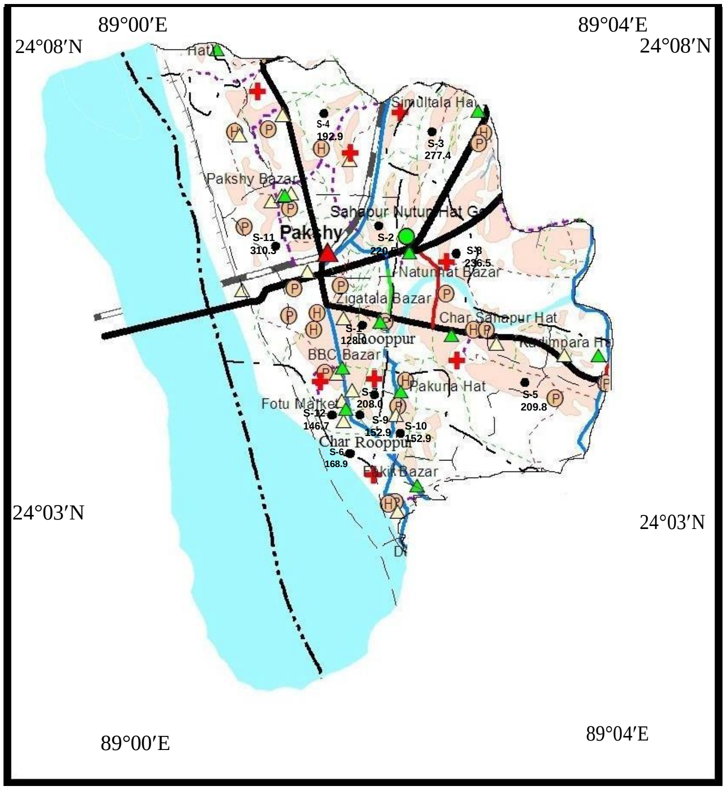

Figure 7. Distribution of Fe showing map of the study area.

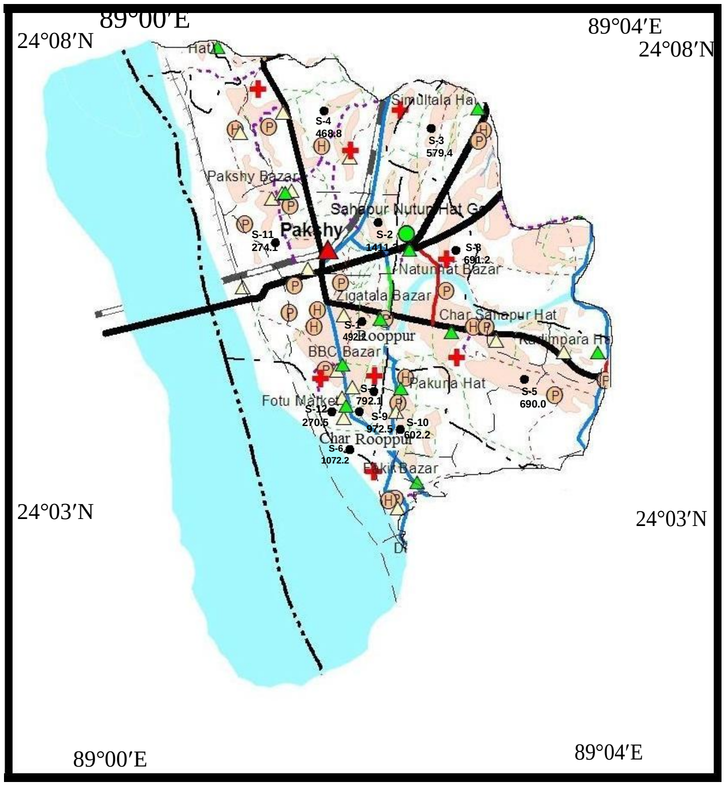

Figure 8. Distribution of Mn showing map of the study area.

groundwater samples in the study area fall within permissible limit. It changes season to season. Concentrations of cation and anion of all the samples are within permissible limit. All the values of trace elements concentration are below the allowable limit of WHO standards except As. Arsenic concentrations of groundwater in the uppermost aquifer between 10 and 70 m depth ranges from 7.0 to 168.2 μgL^{-1} in the study area which exceeds the drinking water standards. For highly enriched As, an alternative water source is thus needed for drinking and domestic water supply. Possible solutions are to install tube wells in the deeper Pleistocene aquifers or use clean surface water sources such as reservoirs or rain water. Correlations analysis showed that As, Fe and Mn are positively correlated in groundwater. These correlations along with results suggest that reductive dissolution of MnOOH and FeOOH mediated by anaerobic bacteria is the primary mechanism for releasing As into the groundwater. Positive correlation between As, Mn and Fe in groundwater suggests that reductive dissolution of MnOOH and FeOOH may be responsible for part of the dissolved As loads in the study area. Sometimes, the poor correlation between As and Fe in groundwater is perhaps due to the precipitation of dissolved Fe as siderite solids ($FeCO_3$) or rhodochrosite ($MnCO_3$) under reducing conditions.

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