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A Hydrochemical Characterization & Quality Assessment of Groundwater and River water at Kaptai-Lichubagan Roadcut Section, Kaptai Upazila, Rangamati Hill District, Bangladesh

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ABSTRACT: The people living in the Kaptai-Lichubagan roadcut area of Kaptai Upazila in Rangamati Hill District, Bangladesh, rely on groundwater for drinking. This study aims to investigate the hydrochemistry of groundwater and river water, associated hydrochemical processes and to assess drinking water quality. In total, 26 water samples were collected for laboratory analysis; 22 from groundwater at depths ranging from 9 to 198 meters, and 4 from Karnaphuli river. Both groundwater and river water pH levels suggest acidic to neutral water. Electrical conductivity (EC) values indicate mostly fresh groundwater and river water, and EC of groundwater varies both spatially and vertically. The total hardness (TH) of groundwater suggests moderately hard to very hard water, whereas the river water is mostly soft. Most groundwater samples are either Ca-Mg-HCO_3 type or mixed Ca-Na-HCO_3 and Ca-Mg-SO_4-Cl type. In contrast, all the river water samples are Ca-Mg-HCO_3 type. Groundwater exhibit variable polygonal shapes in stiff diagrams, characterized by relatively low to moderate major ions. However, there is one sample which shows higher cations suggesting anthropogenic influence. River water show similar patterns but smaller shapes characterized by relatively low major ions. Groundwater is primarily influenced by water-rock interaction and silicate weathering is the dominant controlling factor of groundwater chemistry, followed by carbonate dissolution. Groundwater samples are mostly undersaturated with minerals - calcite, dolomite, gypsum, and siderite, which possess the potential for dissolution. None of the samples exceed the Bangladesh drinking standard (BDS) for As (50 µg/L). River water is also As safe. While As shows no spatial variability, Fe^{Total} shows significant spatial variability in the study area. Water Quality Index (WQI) indicates about 90% water samples including most groundwater and all river water samples are of excellent quality for consumption. Routine monitoring of the water quality in this area is recommended to ensure its continued safety.

Keywords: Groundwater; River Water; Electrical Conductivity; Total Hardness; Hydrogeochemistry; Drinking Water Quality; Hill District; Bangladesh

INTRODUCTION

Access to contaminant-free safe drinking water is fundamental to human health, and groundwater plays a crucial role in this regard. The primary objective of analyzing water quality is to confirm its safety for consumption. Also, it aids in identifying potential issues or deterioration in water quality that may cause adverse health or environmental impacts. More than 90% of water requirements in Bangladesh come from groundwater, which provides water to nearly 160 million people (UN-DESA 2017) and the country secure secured the sixth position among top groundwater user countries (Ahmed 2021). However, the groundwater occurrence is not uniform throughout the country, and there is also temporal variation. The Chittagong Hill Tracts in the eastern part of the country are considered as complex geological terrain composed of a series of anticlines and synclines (Khan 1991) and fall under Zone VI, a hydrogeological zone (Ahmed *et al.* 2003) where no straightforward exploration of groundwater applies. Local people in the hilly region face water scarcity, which becomes severe during the dry season when streams and local springs become dry (Chakma *et al.* 2020; Chakma *et al.* 2021). However, where groundwater is available, it offers a year-round water supply. Groundwater from different aquifers of different

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formations in the Kaptai-Lichubagan roadcut section of Kaptai Upazila of Sitapahar anticline provides drinking water to most of its population, whereas some other dependent on spring and Karnaphuli river.

Facies analysis and depositional environment of the Bhuban Formation of Sitapahar anticline in Kaptai have been conducted (Ali *et al.* 2020), and application of geomorphology and ongoing tectonism of the Sitapahar anticline have also been studied (Khan *et al.* 2017). Ali et al. (2020) and some other studies focus on the petroleum prospect of the anticline. Bacteriological and physicochemical characteristics of Kaptai lake water was studied (Barua *et al.* 2016; Rubel *et al.* 2019) and a Water quality assessment of the Kaptai reservoir was carried out (Karmakar *et al.* 2011). However, the water of this reservoir is not used for drinking purposes to the extent the aquifer underneath is used. Similarly, water quality index (WQI) analysis was done for Karnaphuli river draining the area, and suggestions have been made to use it for irrigation purposes (Hossen *et al.* 2019), although a good number of inhabitants in the study region use it for drinking purposes. Hydrogeochemical characterization and quality assessment of groundwater has been carried out in the nearby district (Khagrachhari Sadar Upazila) (Nawrin *et al.* 2022). Unfortunately, no study has been carried out on the hydrogeological viewpoint of the area, let alone hydrochemical studies, despite the presence of a productive aquifer composed of sandstone. Despite huge dependency on groundwater and river water for potable and domestic purposes, groundwater, and river water quality issues, along with the hydrochemistry of the aquifer and river, are frequently overlooked and merit attention to secure good quality water for the local inhabitants. To this extent, for the first time, an attempt has been made in this study to understand the hydrochemical characteristics of groundwater and river water and the geochemical behavior of the aquifer. Therefore, the primary objective of this research is the investigations of hydrochemistry and the assessment of water quality to determine its suitability for drinking uses and its interactions with host geological formations.

STUDY AREA

The Kaptai-Lichubagan roadcut section is located in one of the prominent anticlinal structures named Sitapahar in the Rangamati hill district of south-eastern Bangladesh (Ali *et al.* 2020) . It is about 75 kilometers northeast of the Chittagong metropolis. The regional strike runs in the NNW-SSE direction. The study area lies between 22.4781° N to 22.5094° N latitude and 92.1267° E to 92.2097° E longitude (Figure 1). Kaptai upazila has a total area of 258.99 km^2 and has 13,515 households, and a population of 59,693 (BBS 2011). The climate of the region can be classified as tropical to subtropical. The annual average rainfall in the nearby district named Khagrachari is 3031 mm (Nawrin *et al.* 2022). Karnaphuli River, the main river in the study area, is antecedent in origin and cuts through the Sitapahar folded rock (Valdiya 2015) (Figure 1). A giant reservoir named "Kaptai lake" is also situated here which was built to produce hydroelectricity for this region (Karmakar *et al.* 2011). Generally, there are several streams which are locally named as "Chora". Additionally, a large network of seasonal, intermittent, and permanent streams and streamlets drains the land. They are dendritic in pattern and are tributaries of Karnaphuli. The important perennial charas in the Kaptai region are Chitmoram Chari, Chandra Chari, Shil Chari, Barai Chari, Sita Chari etc.

Table 1 presents the stratigraphic succession of the Chittagong-Tripura Fold Belt (CTFB). Bhuban and Bokabill Formations of the Surma Group of the Miocene age consist of gray to brownish gray massive sandstone-siltstone, black shale, yellowish-gray to light-yellow medium to fine-grained sandstone with conglomerates, and yellowish-gray sandstone-siltstone with gray to bluish-gray mudstone (Gani and Alam, 1999; Khan 1991; Alam et al., 2003). Tipam sandstones of middle Miocene to Pliocene are coarse-grained, pebbly, cross-bedded sandstone, and Plio-Pleistocene Dupi Tila formation are coarse ferruginous sandstone with layers of quartz pebbles and sandstone with lignitic fragments and petrified wood (Khan, 1991).

The rock sequences exposed in Sitaphar anticline are the Bhuban, Bokabill, Tipam Sandstone, Girujan Clay, Dupi Tila, and Dihing Formation (Ali et al., 2020). Figure 1 shows the exposed rock in the study area. In the hill tracts, sedimentary rocks form aquifers; rainfall and geology control the regional hydrogeology. Bangladesh is divided into six hydrogeologic zones based on geology. The study area falls within Zone VI, which is a complex geology region (Ahmed et al., 2003).

Table 1: Simplified Stratigraphy of the Chittagong-Tripura Fold Belt (CTFB) (Hossain et al. 2019), Modified after (Reimann, 1993; Gani and Alam, 1999; Alam et al., 2003)

Age (approx.)	Group	Formation	Lithologic description
Holocene		Alluvium	
		Dupitila	Coarse ferruginous sandstone with layers of quartz pebbles and siltstone with lignitic fragments and petrified wood.
Plio-Pleistocene		Girujan Clay	Clay and siltstone
	Tipum	Tipum Sandstone	Coarse grained , pebbly, cross-bedded sandstone.
Miocene Late Miocene		Boka Bil	Dark grey pyrite-bearing shale, sandy shale and sandstone.
Miocene Middle Miocene	Surma	Bhuban	Sandstone and pebbly sandstone at the top and sandy shale at the botton

Unfortunately, no lithologic information from boreholes is available to delineate the aquifers in the region. Sandstones of different groups, i.e. Dupi Tila, Tipam and Surma in the study area, might act as aquifers as this is an anticline and groundwater is mainly tapped from these aquifers. These aquifers are recharged with rainwater during monsoon and by the Kaptai reservoir all year round. In this region, no groundwater level data exists as no monitoring prevails.

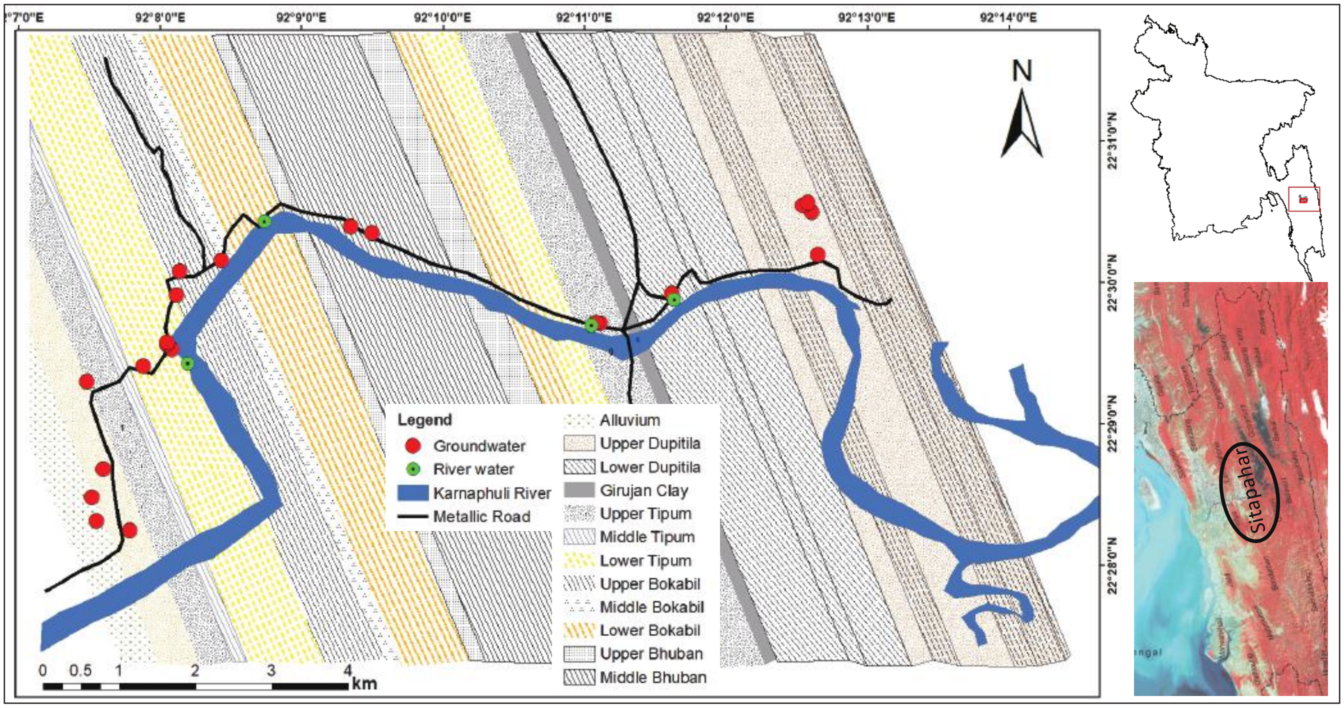

Figure 1: Geological Map Shows Exposed Tertiary Sediments at Sitapahar Anticline, Kaptai-Lichubagan Road Cut Section Modified after (Ali et al., 2020) Showing the Location of River Water and Groundwater Sampling. Inset, the Location of Study Area is Shown in the Map of Bangladesh and Sitapahar Anticle is Shown along with NNW-SSE Trending Anticlines of Chittagong Hill Tracts in a Satellite Image

MATERIALS AND METHODS

Water Sample Collection and Laboratory Analysis

The water sampling was conducted in January 2023, and 26 samples were collected, of which 22 were from wells (ring well, tube well and dug well) and 4 from Karnaphuli river (Fig. 1). Water samples were collected in 70 mL plastic bottles and rinsed at least three times with the water used for sampling. Suspended particles are filtered out by using a 0.45 µm membrane filter. An acidified (with concentrated HNO_3^-) and a non-acidified sample were collected separately from each location and labelled correctly. The samples were then brought to the Geochemistry Laboratory of the Department of Geology, University of Dhaka, for chemical analyses and were preserved at a controlled temperature.

Onsite parameters, including EC, pH, Redox potential (Eh), and Temperature, were measured using a pocket EC meter (HANNA, model DIST HI 198300/4) and pH meter (HANNA. model HI 98127). These instruments were calibrated beforehand with the specific calibration solutions. Sample ID, GPS location, type of water source, well depth and type of well, in case of groundwater, were documented along with onsite field parameters. In the geochemistry laboratory, the acidified water samples were analyzed for cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{Total}, Mn^{2+}) using an Atomic Absorption Spectrometer (AAS) (GBC Australia, model-SavantAA∑) and anions (Cl^-, SO_4^{2-}, NO_3^-, F^-) using Ion Chromatography (US, model-DIONEX ICS 1100). The non-acidified water samples were analyzed for HCO_3^- ion using the titration method with the aid of sulfuric acid. Arsenic (As) was not tested in the field but analyzed in the laboratory of Bangladesh Water Development Board (BWDB) using Thermo Scientific's iCE 3500 Series Atomic Absorption Spectrometer (AAS).

The total hardness (TH) in mg/L as $CaCO_3$ was calculated from the concentrations of Ca^{2+} and Mg^{2+} in mg/L by using the following equation (1) (Todd 2008).

$$TH = 2.5\,(Ca^{2+}) + 4.1\,(Mg^{2+}) \qquad (1)$$

The ionic balance was calculated to estimate the accuracy of chemical analysis. The ionic charge balance error (ICBE) equation was used for this purpose; concentrations of all the ions were converted from mg/L to meq/L unit.

$$ICBE\,(\%) = \frac{\sum Cations - \sum Anions}{\sum Cations + \sum Anions} \times 100 \qquad (2)$$

The ionic balance for all ten water samples was within ±10%, usually considered an acceptable range (Domenico and Schwartz 1998; Appelo and Postma 2005).

Data Processing, Data Visualization and Mapping

Physicochemical parameters and hydrochemical data were stored, organized and processed using Microsoft Excel and simple computation and conversion of units with the help of equation was done by this software. The excel spreadsheet with location information was imported in GIS software (ArcGIS 10) which was also used to create location map and spatial distribution map of different parameters. This software was used for digitization and geological map of the study area is reproduced. The Rockworks software can be used to analyze several types of data including stratigraphy, lithology, hydrochemistry etc. and to present them graphically. Rockworks 16 was used to prepare stiff and piper diagrams for geochemical interpretation.

Geochemical Modeling

The geochemical model PHREEQC interactive 3.0 for Windows (Parkhurst and Appelo 1999) has been used to determine the saturation indices (SIs) of the minerals - calcite, dolomite, gypsum and siderite of the analysed water samples. The phreeqc.dat database was used during this geochemical modelling. The SI can be identified by the following equation: SI = log (IAP)/K, where IAP is the ion activity product, and K is the equilibrium constant. The SI was classified based on equilibrium conditions (SI = 0), oversaturation (SI > 0), and undersaturation (SI < 0).

Water Quality Index (WQI) for Drinking

Water Quality Index (WQI) has been calculated (Table 2) by assigning weightage for each parameter (pH, TDS, TH, Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe^{2+}, Mn^{2+}, As, HCO_3^-, SO_4^{2-}, Cl^-, F^-, Br^-, NO_3^-, NO_2^- and PO_4^-) depending on their significance for risk related to health issue. For instance, a value of 5 posing a high risk to human health, 3 concerning aesthetics and moderate risk to human health, and 1 posing low risk to human health and less concerning aesthetics (Table 2) (WHO, 2017).

Table 2: Water Quality Parameters According to the Bangladesh Drinking Water Quality Guidelines (DPHE 2024) and Their Assigned and Calculated Relative Weights Used to Evaluate WQI

Chemical parameter	Unit	Standard	Weight (wi)	Relative Weight (Wi)
NO_3^-	mg/l	10	5	0.106
As	µg/l	50	5	0.106
F^-	mg/l	1	5	0.106
TDS	mg/l	1000	3	0.064
Total Hardness*	mg/l	200 - 500	3	0.064
pH*	-	6.5 – 8.5	3	0.064
SO_4^{2-}	mg/l	400	3	0.064
Cl^-	mg/l	600	3	0.064
Ca^{2+}	mg/l	75	3	0.064
Mg^{2+}	mg/l	35	3	0.064
$Fe^{(total)}$	mg/l	1	3	0.064
Mn	mg/l	0.1	3	0.064
Na^+	mg/l	200	3	0.064
HCO_3^-	mg/l	200	1	0.021
K^+	mg/l	12	1	0.021
Total			47	1.000

*pH standard 7 and TH standards 350 mg/l have been considered for the WQI calculation.

The calculation of WQI has been summarized in (Horton, 1965; Nawrin et al., 2022).

RESULTS AND DISCUSSIONS

Physicochemical Characterization of Groundwater and River Water

Physicochemical parameters including temperature, pH, Eh, EC were measured in the field which are documented in table 3 along with depth information and TH calculated using equation 1. Groundwater temperature and variations in groundwater quality are related (Bonte et al., 2013). Groundwater temperature in the study area varies from 22.4 ^{0}C to 26 ^{0}C and river water temperature varies from 22.7 ^{0}C to 24 ^{0}C. The maximum EC value of groundwater was 900 µS/cm, which is safe as the maximum safe value is 1500 µS/cm (WHO, 2002). River water EC is around 100 µS/cm (Table 4). There is significant spatial variation of EC in the study area and the value of EC is the highest in the middle portion of the study area which decreases toward east and west (Fig. 2). EC also displays vertical variability (Fig. 2). Table 4 classifies the water according to EC values. pH is another fundamental parameter that demonstrates the water's acidity and alkalinity levels. The accepted pH range for drinking water is 6.5 to 8.5 (WHO, 2002). 77% of groundwater samples are acidic, and 23% are neutral. There is no alkaline groundwater in the collected samples. Half of river water samples are acidic, and half are neutral. The redox potential (Eh) indicates whether an aquifer is in an oxidizing or reducing condition (Hem 1985). In the study area, relatively oxidizing conditions prevailed in the aquifers, as shown by positive Eh values in groundwater ranging from 16 to 307 mV. However, at two locations, negative Eh values (-17, -36) were seen, indicating a slightly reduced condition in the aquifers. River water had positive Eh (range: 145–256 mV), suggesting oxidizing conditions (Mukherjee and Fryar, 2008). The maximum and minimum values for TH of groundwater were 222 mg/l and 12.32 mg/L. River waters are soft because the range of TH is 59.9 to 66.47 mg/l. Generally, soft water, in combination with acidic water, corrodes metal wells and pipes (WHO, 2017). As nearly 40% of groundwater samples and 100% of river water samples are soft water, the chance of corrosion of water supply equipment is higher. Therefore, routine monitoring is required for those wells and connection pipes.

Table 3: Onsite Field Parameters of River water and Groundwater Samples

Sample No	Latitude	Longitude	Depth (m)	pH	Eh (mv)	Temp ^{0}C	EC (µS/cm)	TH (mg/L as CaCO3)
1	22.47	92.12	45.72	4.91	307	25.6	52	21.02
2	22.47	92.12	9.44	5.26	260	24.1	105	32.12
3	22.47	92.12	18.28	5.6	197	24.5	59	20.34
4	22.47	92.12	36.57	5.52	238	25	43	12.32
5	22.48	92.12	36.57	5.36	90	25.2	106	36.90
6	22.49	92.13	60.96	5.64	16	25.3	235	95.97
7	22.49	92.13	12.19	5.36	20	25.7	362	172.36
8	22.49	92.13	79.24	4.9	205	24.5	160	78.77
9	22.49	92.13	76.2	5.44	23	24.2	315	160.6
10	22.49	92.13	45.72	6.04	40	25.8	392	119.39
11	22.50	92.13	60.96	6.1	242	23.3	444	132.1
12	22.50	92.14	18.28	6.11	140	24.8	245	102.91
13	22.50	92.14	River	7.53	233	22.7	105	61.58
14	22.50	92.15	12.19	5.05	342	26	356	131.65
15	22.50	92.15	60.96	5.54	176	26	298	147.66
16	22.49	92.18	45.72	5.26	-17	25.8	504	112.21
17	22.49	92.18	121.92	6.15	-36	25.5	433	221.9
18	22.49	92.18	River	6.71	145	24	106	60.52
19	22.49	92.19	85.34	6.06	69	25.8	900	117.62
20	22.49	92.19	River	5.75	253	23.7	108	66.47
21	22.50	92.21	198.12	6.68	156	25.6	475	36.81
22	22.50	92.21	198.12	6.31	216	24.4	361	90.24
23	22.50	92.20	182.88	7.29	93	24.5	362	123.42
24	22.50	92.20	9.14	8.26	25	24.6	325	72.77
25	22.49	92.13	River	5.92	256	22.7	108	59.93
26	22.49	92.13	33.52	5.42	58	22.4	296	155.75

**Note: Gray shaded rows and river water*

Table 4: Classification of Water Samples Based on EC

Classification Parameter and Range EC (µS/cm) (Wilcox 1955)	Water type	Groundwater		River water	
		No. of samples	% of samples	No. of samples	% of samples
<250	Excellent	8	36	4	100
250-750	Good	13	59	0	0
750-2000	Permissible	1	5	0	0
2000-3000	Doubtful	0	0	0	0
>3000	Unsuitable for Drinking	0	0	0	0

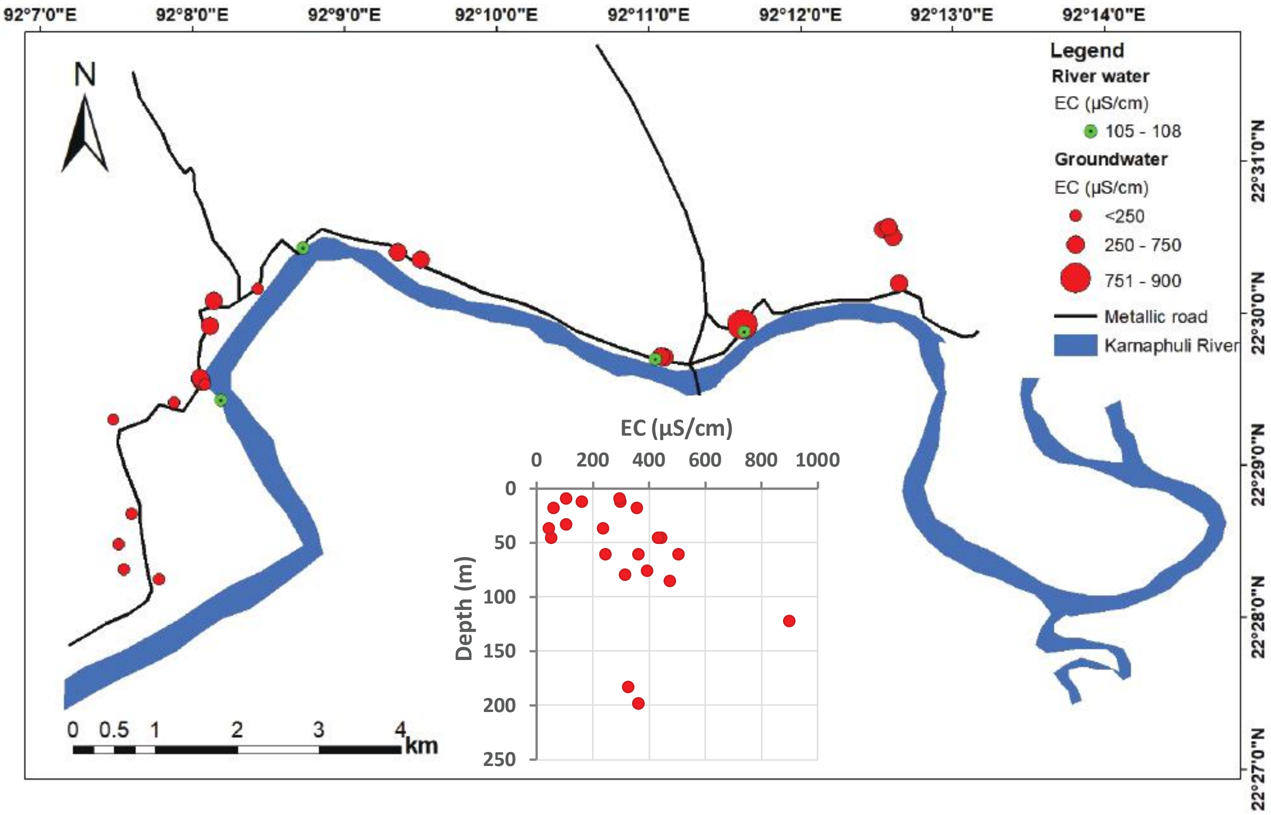

Figure 2: Spatial Distribution of EC in Both Groundwater and River Water within the Study Area, Along with a Depth Profile of EC in Groundwater Samples

Hydrochemical Parameters of Groundwater and River Water

Table 5 presents the results of laboratory analysis of hydrochemical parameters, including major cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) and anions (HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, F^-) with trace elements (Fe^{Total}, As and Mn^{2+}).

Table 5: The Laboratory Analysis Results of Groundwater and River Water Samples

Sample ID	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	Fe^{Total}	As	Mn^{2+}
	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	mg/L	(µg/L)	(mg/l)
1	6.41	1.18	2.14	0.14	7.6	0.17	3.04	0.91	4.5	bdl*
2	10.45	1.41	11.75	0.45	30.5	0.13	17.25	0.55	4.3	bdl
3	6.74	0.82	1.98	0.29	22.9	0.18	1.74	0.65	3.3	bdl
4	4.42	0.29	3.21	0.3	15.3	0.4	1.46	0.85	4.1	bdl
5	28.36	5.98	12.45	1.45	99.1	15.31	4.79	3.75	5.0	0.27
6	55.58	7.91	10.75	0.98	236.4	1.28	4.88	1.43	2.5	0.20
7	25.80	3.37	8.64	1.68	76.3	13.33	4.23	0.91	5.2	bdl
8	52.08	7.19	16.85	1.26	198.3	3.25	0.99	1.67	5.7	0.22
9	30.68	10.25	36.74	3.69	251.6	10.82	1.92	0.64	4.6	bdl
10	38.83	8.36	68.45	7.64	297.4	11.25	2.1	0.81	4.2	bdl
11	25.70	9.29	13.05	2.45	91.5	5.84	23.12	0.74	5.7	bdl
12	39.22	8.01	32.98	1.45	91.5	12.45	52.48	0.76	4.8	bdl
13	17.62	4.19	11.64	0.53	83.9	0.45	2.01	0.84	6.3	bdl
14	43.30	9.41	18.46	0.48	176.4	3.15	1.98	1.16	5.2	bdl

15	23.42	12.95	74.12	2.36	312.6	5.65	21.12	5.09	42.9	0.13
16	71.92	9.96	16.95	1.89	320.3	7.45	18.87	1.63	2.6	0.33
17	38.66	4.95	305.3	0	427.0	3.46	256.78	1.04	6.2	bdl
18	16.71	4.49	7.46	0.78	76.2	0.17	1.78	0.86	5.6	bdl
19	12.69	1.18	95.69	6.98	289.8	1.45	16.78	1.09	3.9	bdl
20	18.54	4.81	7.98	0.89	114.4	0.21	1.85	0.61	4.3	bdl
21	31.17	2.87	72.48	2.38	236.4	2.01	15.65	0.97	4.8	bdl
22	41.56	4.58	73.48	1.98	327.9	1.95	16.01	1.02	4.5	bdl
23	25.73	1.95	73.98	2.00	259.3	1.75	14.98	0.99	4.0	bdl
24	50.7	6.86	19.78	1.25	198.3	2.01	7.1	1.42	4.2	0.14
25	16.66	4.38	6.98	0.69	76.3	0.21	1.67	0.94	4.1	0.22
26	10.15	2.76	9.15	0.36	76.3	1.34	1.41	1.81	0	0.006

**Note: Gray shaded rows indicate river water and bdl means below detection limit*

The box plots (Fig. 3) show the statistics of the concentration of different hydrochemical parameters and present visuals of basic statistics. These plots also include Bangladesh Drinking Water Standards (BDS) for each parameter (DPHE, 2024) so that a comparison of their concentrations can be made with allowable drinking limits.

Calcium (Ca^{2+}) occurs from carbonate minerals (limestone, dolomite), anhydrite, gypsum, plagioclase, pyroxenes, amphiboles, and fluorite (Hounslow, 1995). The concentration of Ca^{2+} in groundwater ranges between 4.4 and 743 mg/l, and no systematic depth variation is observed. The concentration of Ca^{2+} in river water is less than 20 mg/l. Magnesium (Mg^{2+}) comes from dolomite, ferromagnesian minerals such as olivine, pyroxenes, dark-colored mica, and amphiboles (Hounslow, 1995). The Concentration of Mg^{2+} in groundwater is between 0.29 to 140 mg/l and no systematic depth variation is observed. The concentration of Mg^{2+} in river water is nearly 4 mg/l. Sodium (Na^+) is a common groundwater cation that comes from halite and feldspar; other sources include sea spray, silicates, hot springs, brines, and ion exchange (Hounslow, 1995). Most groundwater samples show Na^+ concentrations ranging from negligible amounts to 100 mg/l, and only one sample (no 17) exceeds 300 mg/l. All the river water samples have a concentration of <10 mg/l. Depth variation is not that significant for Na^+. Potassium (K^+) in groundwater is caused by the gradual weathering of minerals containing K^+, i.e. feldspar, mica, clay minerals, illite. K^+ concentration in groundwater varies from 0.14 to 44 mg/l and no systematic depth variation of K^+ is observed. All the river water samples have a concentration of <1 mg/l. Bicarbonate (HCO_3^-) is the primary groundwater anion, indicating alkalinity and may come from dolomite, calcites, fossil carbon, or silicate minerals (Saha et al., 2019a). Organic matter breakdown causes high HCO_3^- in water. The range of HCO_3^- in groundwater is 7.6 mg/L to 427 mg/L; the maximum value is found at 198m depth. There is a significant spatial variation of HCO_3^- concentration in groundwater. However, they don't show any significant variation with depth. The concentration of HCO_3^- in river water ranges between 76 and 115 mg/L and does not vary spatially. Groundwater usually has low chloride (Cl^-) and high Cl^- indicates salinity. Cl^- sources are halite, sea sources, and water intrusion. The range of Cl^- in groundwater is 0.99 mg/L to 256.78 mg/L, and it does not vary with depth. The concentration of Cl^- in river water ranges from 1.67 to 2.01 mg/l. Pyrite, gypsum, and sulfate reduction are primary sources sulphate (SO_4^{2-}). The range of SO_4^{2-} in groundwater is 0.13 mg/L to 105 mg/L and does not vary with depth. The concentration of SO_4^{2-} in river water is <0.5 mg/L. Nitrate (NO_3^-) enters groundwater from fertilizers, septic tanks, and manure. The range of NO_3^- in groundwater is bdl to 15.44 mg/L. The nitrate concentrations in groundwater is higher in the western part of the study area. The river water does not have any detectable NO_3^-. The concentration of fluoride (F^-) in groundwater is 0.15 to 5.4 mg/L and the no detectable

F^- is found in river water.

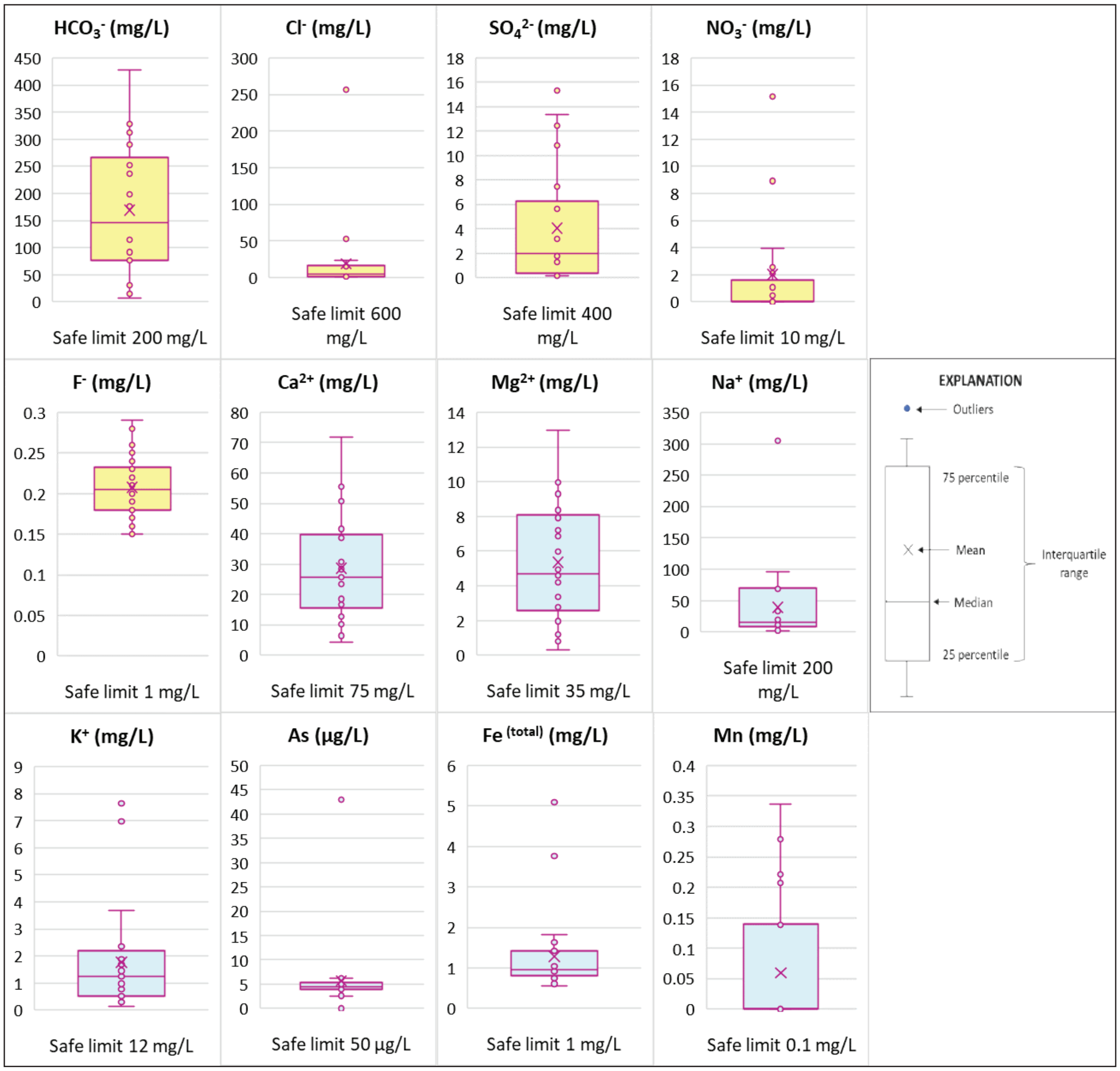

Figure 3: Box and Whisker plots of the Concentrations of Hydrochemical Data (Yellows are Anions and Blues are Cations) along with Their Safe Limits (DPHE 2024)

The range of Fe^{Total} concentration in groundwater is 0.556 mg/L to 5.09 mg/L; the range in river water is 0.61 mg/L to 0.94 mg/L. The concentration of iron in groundwater shows significant spatial variability, whereas its concentration in river water samples is uniform (Fig. 4, left). Fe^{Total} concentration in groundwater does not vary with depth (Fig. 4, left). Arsenic (As) is a carcinogen and can lead to many serious illnesses (Fazal et al., 2001). As is detected in the present study and the range of As in groundwater is 2.4 µg/L to 42.9 µg/L, and the mean value is 5.85 µg/L. Arsenic concentration in groundwater does not vary spatially and vertically (Fig. 4, right). The concentration of As in river water is nearly uniform (4.1 -6.3 µg/L) and is within WHO limit. The concentration of manganese (Mn) in groundwater is bdl to 0.33 mg/L and the range in river water is bdl to 0.22 mg/L.

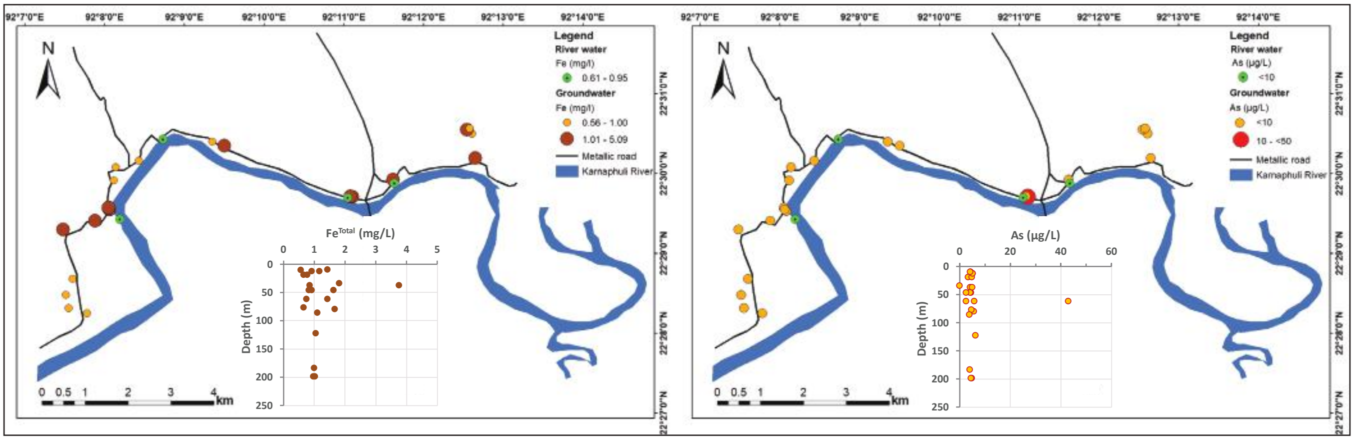

Figure 4: Left; Spatial Distribution of Fe^{Total} Concentrations in Both Groundwater and River Water within the Study Area, Along with a Depth Profile of Fe^{Total} in Groundwater Samples. Right; Spatial Distribution of As Concentrations in Both Groundwater and River Water within the Study Area, Along with a Depth Profile of As in Groundwater Samples

Hydrochemical Facies and Water Types

In the diamond Piper plot (Piper, 1944) (Fig. 5), it is observed eleven groundwater samples and all four river water samples are Ca-Mg-HCO_3 type waters which are labelled as 1; four groundwater samples are mixed Ca-Na-HCO_3 type water labelled as 3; two groundwater samples are mixed Ca-Mg-SO_4-Cl type water labelled as 4; one groundwater sample is Na-Cl-SO_4 type water labelled as 2, one groundwater sample is Ca-Cl type water labeled as 5 and one groundwater sample is Na-HCO_3 water types labeled as 6. The prevalence of Ca-Mg-HCO_3 type water gives indication of carbonate weathering in the aquifer system. When groundwater percolates through the CO_2 enriched sediments, carbonate ($CaCO_3$) dissolution occurs quite readily and releases Ca^{2+} and HCO_3^- into groundwater (Foster, 1950; Hem, 1985).

The stiff diagram is a graphical representation where major ions form a polygon; cations appear on the left, and anions on the right, both in meq/l. It is useful for quickly visually comparing water samples with high ion concentrations (Stiff Jr, 1951). In the study area, groundwater samples exhibit variable polygonal shapes, characterized by relatively low to moderate concentrations of cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) and anions (Cl^-, HCO_3^-, and SO_4^{2-}) (Fig. 7). Sample no 19 shows excessive Na^+ and K^+. Note that EC value of that sample is also high (900 µS/cm from 85 m depth) and probably results from anthropogenic activities. However, the river water samples (13, 18, 20 and 25) show a similar and relatively smaller pattern characterized by relatively low cations and anions compared to groundwater samples (Fig. 6). In groundwater samples, higher concentrations of HCO_3 than other ions are observed, as the wells draw water from different sandstone aquifers. Therefore, the interaction of water with carbonate and silicate minerals results in increased HCO_3^- concentrations (Foster, 1950).

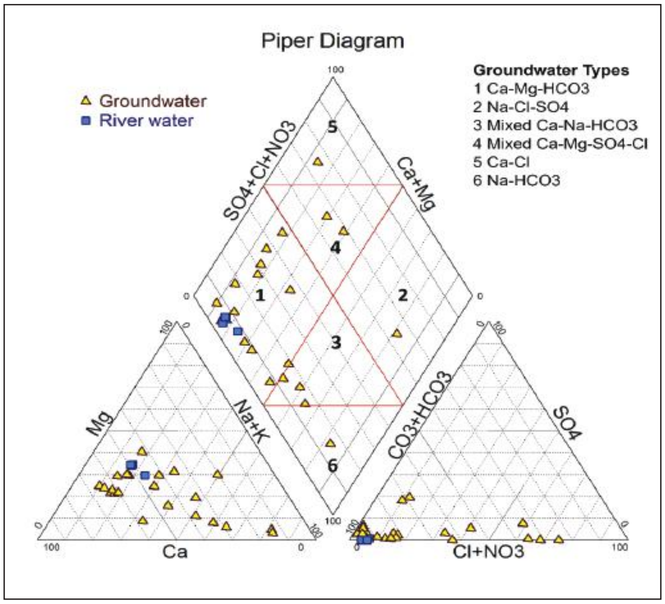

Figure 5: Piper Diagram Showing the Water Types for River Water and Groundwater

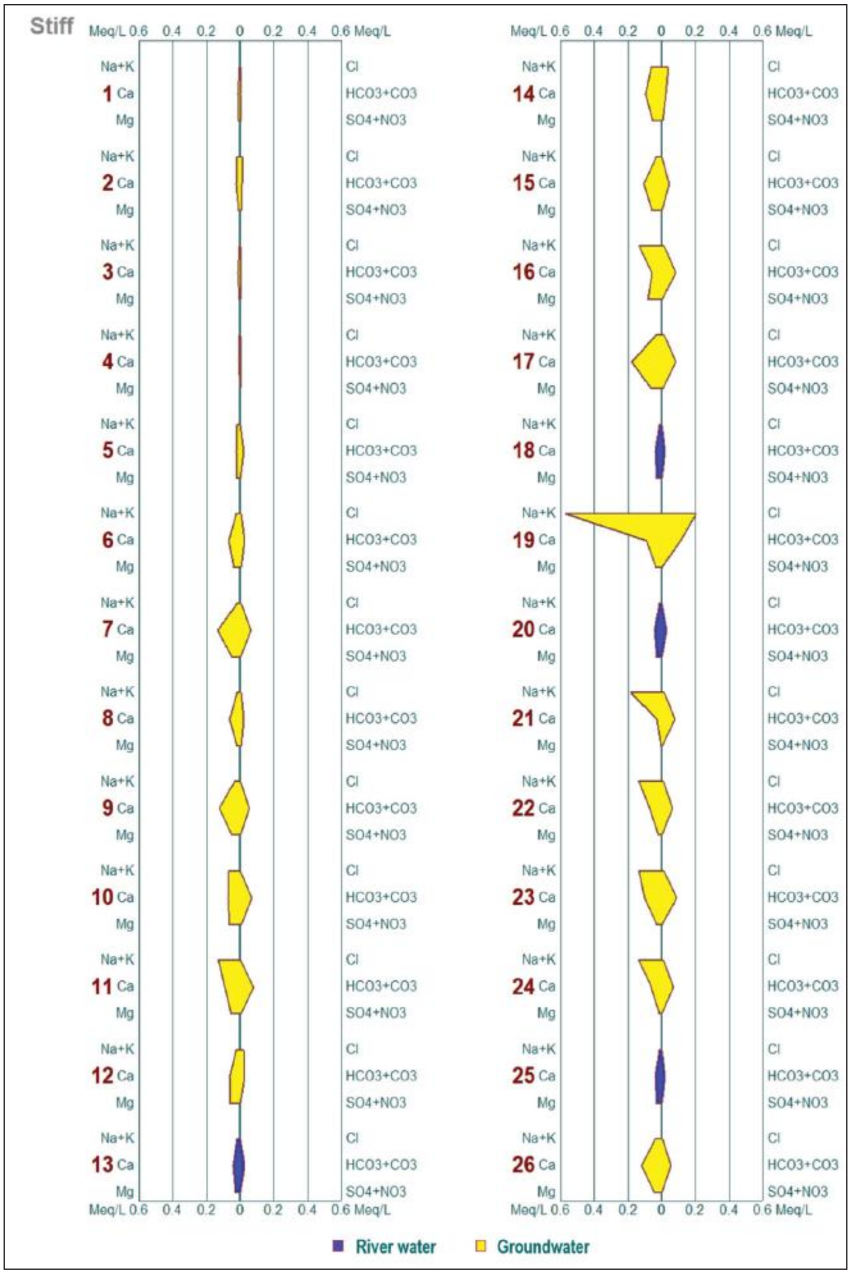

Figure 6: Stiff Diagram Showing the Concentrations of Major Cations and Anions of River Water and Groundwater Samples

Hydrochemical Process and Origin of Mineralization

Groundwater chemistry is changed by a variety of processes as water moves through different geological formations of different geochemical settings from recharge to discharge. Physical processes that control the formation of an aquifer include the host's interaction, which depends on its characteristics, the amount of time that water is present, and chemical reactions that alter the precipitation or solution (Hamma et al., 2024). Three mechanisms that control natural water chemistry are precipitation, rock weathering, and evaporation (Apodaca et al., 2002). The control mechanisms of groundwater chemistry are analyzed by (Gibbs, 1970) and (Gaillardet et al., 1999) diagrams. Total dissolved solids (TDS) were plotted against [($Na^+ + K^+$)/ ($Na^+ + K^+ + Ca^{2+}$)] and against [Cl^-/($Cl^- + HCO_3^-$)] in figure 7 (top). Most groundwater samples fall at the rock-dominance zone, with few in between the zone of rock dominance and rainfall dominance region. All the river water samples fall in between the zone of rock dominance and rainfall dominance region. The ratios of [$(Na^+ + K^+)/(Na^+ + K^+ + Ca^{2+})$] and [$Cl^-/(Cl^- + HCO_3^-)$] do not rise with increasing TDS in these multi-layered aquifers in the anticline due to more or less similar groundwater residence time combined with rock-water interaction.

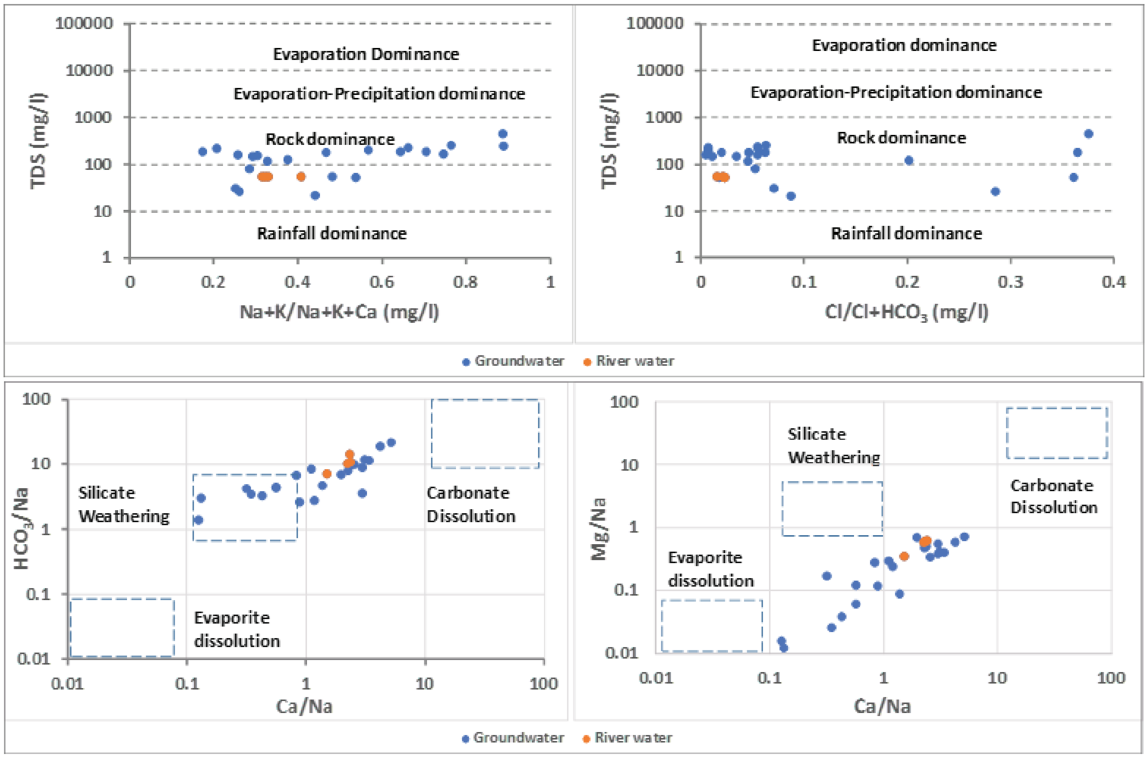

Figure 7: Gibbs Plots for Groundwater and River Water Samples (Top) and Gaillardet Plots for Groundwater and River Water Samples

The Gaillardet diagram in Figure 7, bottom (left) (Ca/Na)/(HCO_3/Na) indicates predominantly silicate weathering as the primary source of groundwater and river water chemistry followed by carbonate dissolution. Figure 7, bottom, right (Ca/Na)/(Mg/Na) illustrates most samples clustered between silicate weathering and evaporite dissolution zone, signifying that these processes and combined chemical reactions dominantly influence groundwater and river water chemistry in this area.

Geochemical Modeling

The saturation indices (SI) of some minerals calculated from the water chemistry data presented in Table 6 imply that the groundwater samples are under-saturated (negative SI) with respect to calcite, dolomite, gypsum, and siderite across all locations except sample no 24, where it is saturated (positive SI) for calcite, dolomite, and siderite. Therefore, these minerals possess the potential for dissolution for most of the samples (Appelo and Postma, 2005). Few portions of the aquifer sediments, which show negative SI for calcite or dolomite, might dissolve these minerals (Appelo and Postma, 2005). As a consequence, porosity might be increased. In contrast, other portions, where the SI is positive, mineral precipitation will reduce the porosity (Rao et al., 2013). As sample 24 is slightly saturated with siderite and it may be expected that siderite would slowly precipitate to establish a new equilibrium. All the river water samples (gray shaded rows) are under-saturated (negative SI) with respect to calcite, dolomite, gypsum, and siderite except sample no 13 where it is saturated (positive SI) for siderite.

River Water and Groundwater Interaction

Groundwater and surface water form essential components within any hydrological system. Precipitation and surrounding and host rocks impact groundwater quality before and after recharge, and this also impacts river water quality. Field parameters, including EC, pH, and TH of river water and groundwater of this area, are nearly similar and there is no significant change in the hydrochemical processes. This river water may be fed by groundwater because the sampling time was January 2023, which is a dry period. The spatial distribution of field parameters and similar concentrations of different ions suggest no significant variation between river water and groundwater as sampling locations of river water were close. Therefore, the connection between groundwater and the river may be predicted, and groundwater may discharge to the river from the aquifers in the region (Mukherjee and Fryar, 2008).

Table 6: Saturation Indices (SIs) of Minerals of the Analyzed Water Samples (Gray Shaded Rows Indicate River Water Samples; White Rows are Groundwater Samples)

ID	Calcite	Dolomite	Gypsum	Siderite	logpP_CO2(g)	ID	Calcite	Dolomite	Gypsum	Siderite	logpP_CO2(g)
1	-4.66	-9.72	-5.09	-3.25	-0.95	14	-2.74	-5.83	-2.64	-2.22	-0.13
2	-3.54	-7.61	-5.04	-2.56	-0.80	15	-2.02	-4.35	-3.20	-1.39	-0.25
3	-3.52	-7.62	-5.04	-2.29	-1.22	16	-2.27	-4.46	-3.25	-0.78	0.19
4	-3.96	-8.77	-4.86	-2.42	-1.29	17	-0.89	-2.30	-2.69	-0.38	-0.70
5	-3.05	-6.32	-4.06	-1.57	-0.50	18	-1.56	-3.36	-4.76	-0.62	-1.81
6	-2.34	-5.01	-2.64	-0.99	-0.60	19	-1.20	-2.95	-3.38	-0.63	-0.49
7	-1.90	-4.30	-3.51	-1.31	-0.03	20	-2.26	-4.76	-4.64	-1.53	-0.74
8	-3.18	-6.91	-2.71	-2.40	-0.01	21	-1.15	-2.99	-4.05	-0.07	-1.24
9	-2.02	-4.56	-3.12	-1.33	-0.11	22	-1.27	-3.23	-3.53	-0.60	-0.93
10	-1.53	-3.19	-2.82	-1.03	-0.60	23	-0.03	-0.67	-3.46	0.49	-1.80
11	-1.31	-2.95	-2.73	-0.83	-0.64	24	0.66	0.55	-3.68	1.25	-2.91
12	-1.92	-3.94	-3.11	-1.23	-1.14	25	-2.38	-5.01	-4.67	-1.40	-1.02
13	-0.73	-1.74	-4.32	0.17	-2.58	26	-2.06	-4.65	-3.33	-1.42	-0.12

Water Quality Assessment

Hydrochemical analysis of groundwater and river water is crucial for assessing water quality. Hydrochemical study evaluates groundwater suitability for domestic and drinking use via physical and chemical parameters (Saha et al., 2019b). Higher concentrations of chemical parameters negatively impact public health and the environment (Anderson, 2014). Table 7 presents minimum and maximum values of water quality parameters of groundwater and river water and compare their concentrations with drinking water quality standards of WHO and BDS (WHO, 2017; DPHE, 2024). Concentrations of major cations including Na^+, K^+, Mg^{2+}, Ca^{2+} and anions including HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, F^- of groundwater and river water are within allowable limit of WHO and BDS. However, concentrations of Na^+ in only one groundwater sample (no. 17) exceeds allowable limit. Note that concentrations of Cl^- for this sample marginally exceeds WHO limit which requires further investigation.

Table 7: Drinking Water Quality Standards of WHO and BDS Along with the Observed Value

Drinking Water Quality Standards				Observed value			
				Groundwater		River water	
Parameters	Unit	WHO	BDS	Max	Min	Max	Min
As	µg/L	10	50	42.92	2.47	6.3	4.1
$Fe^{(total)}$	mg/L		0.3 to 1	5.09	0.55	0.94	0.61
Mn	mg/L	0.5	0.1	0.33	bdl	0.22	bdl
K^+	mg/L		12	7.64	0.14	0.89	0.53
Na^+	mg/L	200	200	305.3	1.98	11.6	7
Ca^{2+}	mg/L		75	71.92	4.42	18.5	16.6
Mg^{2+}	mg/L	50	30 to 50	12.95	0.29	4.8	4.1
HCO_3^-	mg/L	200 to 500		427	7.62	114.4	76.2
SO_4^{2-}	mg/L	250	400	105.67	0.13	0.45	0.17
NO_3^-	mg/L	50	10	15.44	bdl	bdl	bdl
Cl^-	mg/L	250	150 to 600	256.78	0.99	2.01	1.67
F^-	mg/L	1.5	1	0.29	0.15	bdl	bdl

Eleven samples exceed the allowable limit of Fe^{Total} in groundwater However, this is mainly an aesthetic concern and no concern related to health applies here. The Fe^{Total} concentration in river water is within BDS limit. Groundwater containing high levels of As is commonly found in shallow groundwater (<100 m) beneath the Quaternary-Recent Ganges, Brahmaputra and Meghna (GBM) floodplains (BGS and DPHE, 2001; Nickson et al., 2000; Smedley et al., 2002; van Geen et al., 2003; Hasan et al., 2007). No study has reported the presence of a relatively high concentration of As WHO limit (>10 µg/L) in the hill districts of Chittagong. However, As is detected in the study area. Although concentrations of As in groundwater are below the BDS level but in one location (sample 15), the maximum value was found (42.9 µg/L) at about 61 m depth which merits attention. River water As is within WHO limit. Concentrations of as in both groundwater and river water are well below the BDS and WHO limit and do not pose any health risk.

Water Quality Index (WQI) for Drinking

88.5% of water samples (19 groundwater and all the 4 river water samples) collected for this study fell in the excellent quality category for drinking and the rest 11.5% of groundwater samples (only 3 samples) fell in the good category.

CONCLUSIONS

Groundwater samples in the study area display pH values ranging from 5.93 to 7.53, indicating an acidic to neutral nature. The electrical conductivity (EC) values range from 43 to 900 µs/cm, indicating fresh groundwater which varies with depth. The middle part of study area has the highest EC value, which decreases towards the east and west with a vertical depth variation. The pH values of river water range from 4.9 to 8.6, and EC values range from 43 to 900 µs/cm. The total hardness (TH) of groundwater ranges from 12.3 to 221 mg/l, indicating that the samples are moderately hard to very hard. On the other hand, the TH of river water ranges from 59.9 to 66.47 mg/l. According to the Piper plot, half of groundwater samples and all river water samples are Ca-Mg-HCO3 type water. Groundwater samples exhibit variable polygonal shapes in stiff diagrams, characterized by relatively low to moderate cation and anion concentrations and one sample shows high concentration of Na^+ and K^+. The river water samples show a similar and relatively smaller pattern characterized by relatively low cation and anion concentrations.

The findings reveal that groundwater chemistry is mainly influenced by natural processes such as water-rock interaction. According to the Gaillardet diagram, silicate weathering is the primary factor that controls groundwater chemistry, followed by carbonate dissolution. Except for sample 24, which is saturated with calcite, dolomite, gypsum, and siderite, geochemical modelling shows that groundwater samples are typically lacking in these minerals. As a result, most of the samples have the potential for dissolution of these minerals. Almost all the river water samples are under-saturated for calcite, dolomite, gypsum, and siderite, which could lead to the dissolution of the host rocks. River water may be fed by groundwater in dry periods. Similar concentrations of ions and similar geochemical process prevailing both in groundwater and river water suggesting their interaction.

Concentrations of As do not show any spatial variability, whereas Fe^{Total} shows significant spatial variability. However, no vertical depth variability is seen for As and Fe^{Total}. The concentration of As in groundwater ranging from 2.48 µg/L to 42.93 µg/L where only one sample exceeds WHO limit. This is the first time higher concentrations of As in groundwater, such as 42.93 µg/L, have been reported in any Hill District of Bangladesh. The highest As concentration was observed at the site of negative Eh value, i.e. at reducing condition. Although, the sample is still within Bangladesh Drinking Water Standard (50 µg/L) but further investigation is required. River water As is safe according to both WHO and BDS limits. An evaluation of the WQI suggested that the nearly 90% water samples which includes 19 groundwater samples and all river water samples of the area is excellent for drinking uses. Although river water is chemically safe but microbial testing is recommended before consumption.

The lack of borelog data, rainfall, and groundwater level data in the study area prohibits to provide a detailed description of hydrology, subsurface geology, and aquifer condition. Additionally, the concentration of silicon (Si) could not be determined due to the unavailability of a laboratory instrumental kit. More samples analysis is needed for a better appraisal of water quality of the region. Routine monitoring of groundwater and surface water quality is required to protect this resources from contamination.

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