Hydrogeochemistry and Usability of Groundwater at the Tista River Basin in Northern Bangladesh

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Abstract

Objectives: A study on groundwater of Lalmonirhat Sadar Upazila, Bangladesh has been conducted to explore the groundwater hydrochemistry and suitability for potable water and agricultural uses. **Methods/statistical analysis:** During the dry season, fifty groundwater samples were collected from different shallow tube wells adjacent to Tista River, Bangladesh. Water samples were analysed according to the standard procedures. We calculated some parameters required for assessing irrigation water quality. The correlation matrix, hierarchical cluster analysis (HCA), and principal component analysis (PCA) were used for better understanding of groundwater chemistry and categorizing the water samples. **Findings:** The Ca^{2+}–Mg^{2+}–CO_3^{2-}–HCO_3^- was the dominant water type, and carbonate weathering was the main hydro geochemical process in the study area. The contributions of ion exchange and reverse ion exchange were almost equal. Groundwater characteristics were influenced by precipitation and not affected by seawater intrusion. The results of all the measured and calculated parameters clearly indicated the suitability of all ground water samples for irrigation. Based on all analysed parameters including hardness, all waters were suitable for drinking and domestic uses. **Applications:** The groundwater of the study area might be suitable for irrigation, drinking and domestic uses until the waters are otherwise polluted.

Keywords: Hydrogeochemistry, Groundwater, Irrigation, Drinking, Bangladesh

1. Introduction

For sustainable development, groundwater is a ubiquitous source of water for agricultural, domestic, and drinking purposes. At present, the uses of groundwater in the Earth for irrigation and domestic purposes are 40% and 70%, respectively. The declining quality of surface water resources has forced the people to become more dependent on groundwater. Consequently, the over-exploitation and deterioration of groundwater has been observed worldwide.[1,2] In Bangladesh, groundwater is the prime source for 75% irrigation[3] and 90% drinking uses[4] and these demands could be increased day by day. However, groundwater chemistry is controlled by the geological make-up, weathering of rocks, recharge water quality, and other sources.[5,6] Water quality related to geology, climate, sources, and uses can be explained by the chemical analysis of water.[7] Especially, major ions in water can help explain the geochemical processes influencing groundwater quality.[8,9]

For successful crop production, water quality is an important component for irrigation. Because the ionic concentrations in irrigation water have a direct or indirect effect on plant nutrition or soil characteristics. The concentrations of different anions and captions may increase in groundwater due to chemical fertilizers, industrial, and domestic wastes.[10] The changes in groundwater quality can be easily explained by its chemistry. Some research in other regions has investigated the irrigation water quality on crop production or

soil properties.[11] Studies in Bangladesh[3,4] showed that HCO_3^-, Na^+, Ca^{2+}, Mg^{2+}, and Cl^- were the prevalent ions in groundwater collected from different regions. In Bangladesh, farmers face acute shortage of irrigation water during dry season and use groundwater sources for irrigation. Besides this, water of desirable quality is necessary for drinking and domestic purposes. Thus the water quality assessment is the most significant aspect of water management irrespective of its utility.

Lalmonirhat Sadar Upazila is a densely populated area compared to the other Upazilas of Lalmonirhat district. There is no systematic study on the groundwater quality of Lalmonirhat Sadar Upazila for irrigation and drinking purposes. The investigation on groundwater quality is an important task for safety and survival of human population. In Bangladesh, arsenic contamination of groundwater at shallow aquifer is from geogenic sources[12] and irrigation with this water increases the arsenic uptake in field crops causing ultimate deposition of arsenic in the human body. But the people are using the groundwater for both the irrigation and drinking purposes. A systematic investigation of the groundwater of this Upazila is, however, necessary for assessing the geochemistry of groundwater and its suitability for various purposes. Therefore, the objectives were to characterise the physicochemical properties of groundwater, assess the processes controlling the groundwater chemistry, and evaluate suitability for irrigation, drinking, and domestic uses.

2. Materials and Methods

2.1. Geological Settings

In Bangladesh, the aquifer systems have not been divided stratigraphically. However, the aquifers are 1) upper shallower aquifer, 2) main aquifer, and 3) deep aquifer.[13] We collected the waters from the main aquifer. This aquifer occurs at depths from 5 m to 75 m and is the main water bearing zone. This zone is mainly semi-confined or leaky, stratified interconnected and unconfined. Medium and coarse grained sediments inter bedded with gravel is around 140 m from the ground surface.

2.2. Collection of Groundwater Samples

The groundwater samples were collected in the month of March–April 2016 from Lalmonirhat Sadar Upazila in the district of Lalmonirhat adjacent to Tista River,

Bangladesh. Water levels are very low in these months. Fifty samples were collected from different shallow tube wells in the study area. Figure 1 shows the information of water sampling sites. Water samples were collected in 2 L plastic bottles. The bottles and glassware were washed with P-free detergent, and rinsed three times with ultra-pure water. After soaking in 10% (v/v) HCl for 24 h, the bottles and glassware were again rinsed three times with ultra-pure water. All water samples were collected directly at the wellhead. Before sampling, plastic bottles were again rinsed 3–4 times with water to be sampled. The samples were analysed as quickly as possible on arrival at the laboratory.

2.3. Measurements of Physicochemical Parameters

Using portable meters (Thermo, Orion), we measured electrical conductivity (EC), pH, and temperature. After filtration (0.45 μm), alkalinity was measured by titration with 0.02 N H_2SO_4 until the pH reached at 4.3. Hydrochloric acid was used to acidify the samples to maintain the pH <2 for analysis of cations and silica, and all the samples were stored at a temperature of 4 °C. Total dissolved solids (TDS) was measured by drying and
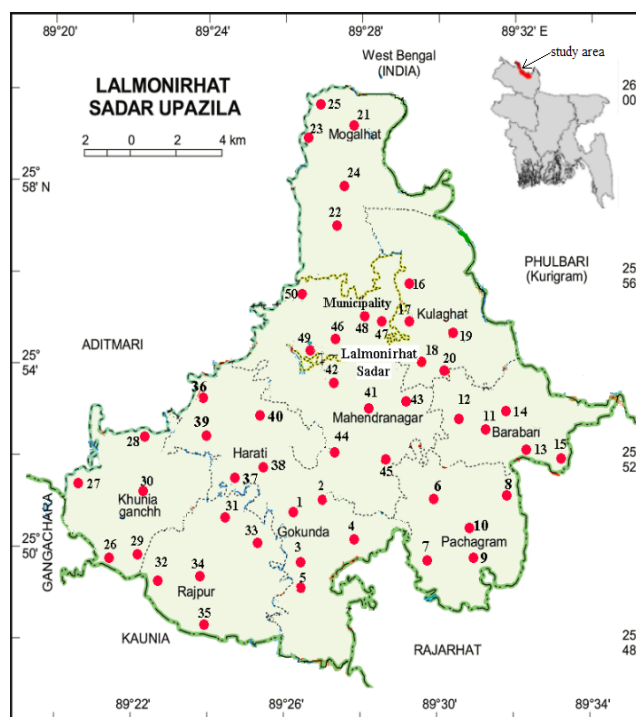

Figure 1. Map of Lalmonirhat Sadar Upazila indicating the groundwater sampling sites (red circles) along with the

weighing method. Zn^{2+}, Cu^{2+}, Mn^{2+}, As^{3+}, and Fe^{3+} were determined by atomic absorption spectrophotometry.[14] Ca^{2+} and Mg^{2+} were measured by complexometric titration. K^+ and Na^+ were analysed by flame emission spectrophotometry. Boron (B) and silicon dioxide (SiO_2) were analysed using spectrophotometer (DR 2800). SO_4^{2-} was determined turbid metrically. CO_3^{2-} and HCO_3^- were analysed titrimetrically. PO_4^{3-} and NO_3^- were determined colorimetrically.[14] Chloride was estimated by argentometric titration.[14] Fluoride (F^-) was estimated by ion chromatography. After treating the sample with $KMnO_4$ and NaOH, and digestion, the chemical oxygen demand (COD_{Mn}) was estimated titrimetrically.

2.4. Quality Assurance and Quality Control

For any analysis, accuracy is very important for explaining the experimental result. Standard procedures were used for measuring all parameters. The accuracies of chemical analyzes were checked by means of externally supplied standards with known standards added to samples and reagent blanks, and also calibration check standards. The precision of measurements was checked taking three replicates of the sample. All reagents used in chemical analysis were from Merck Company. The differences between the sum of cations and the sum of anions and the measured or calculated TDS to EC ratio were used for detecting discrepancies. The sum of anions and cations expressed as meq/L must be balanced because all potable waters are electrically neutral. The difference between the anion and caption sums fell between acceptable limits (5–10%) and the percentage of difference is calculated on the basis of the following equation:

$$\% \text{ difference} = \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \times 100$$

The ratios of calculated or measured TDS to EC were from 0.55 to 0.70 which are quite acceptable for chemical analysis of water.

2.5. Evaluation of Water Quality

The equations related to the irrigation water class rating and hydrochemistry of groundwater were as follows:
a) Sodium adsorption ratio (SAR)

$$SAR = \frac{Na+}{\sqrt{\dfrac{Ca^{2+} + Mg^{2+}}{2}}}$$

b) Residual sodium carbonate (RSC)

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+})$$

c) Hardness or total hardness (H_T)

$$H_T = 2.5 \times Ca^{2+} + 4.1 \times Mg^{2+}$$

d) Permeability index (PI) $= \dfrac{Na^+ + \sqrt{HCO_3^-}}{Ca^{2+} + Mg^{2+} + Na^+}$

e) Potential salinity; $PS = Cl^- + (\dfrac{SO_4^{2-}}{2})$

f) Gibbs ratio for cation; $GRFC = \dfrac{Na^+ + K^+}{Na^+ + K^+ + Ca^{2+}}$

g) Gibbs ratio for anion; $GRFA = \dfrac{Cl^-}{Cl^- + HCO_3^-}$

h) Chloroalkaline index I (CAI-I) and chloroalkaline index II (CAI-II)

$$CAI\text{-}I = \frac{Cl^- - (Na^+ + K^+)}{Cl^-}$$

$$CAI\text{-}II = \frac{Cl^- - (Na^+ + K^+)}{SO_4^{2-} + HCO_3^- + CO_3^{2-} + NO_3^-}$$

i) Kelly's ratio; $KR = \dfrac{Na^+}{Ca^{2+} + Mg^{2+}}$

j) $\%Na = \dfrac{Na^+ + K^+}{Ca^{2+} + Mg^{2+} + Na^+ + K^+} \times 100$

Ion concentration units are in meq/L in all cases except hardness (mg/L).

2.6. Multivariate Statistical Analysis

The correlation matrix, hierarchical cluster analysis (HCA), and principal component analysis (PCA) were used for better understanding of groundwater chemistry. The Kaiser–Mayer–Olkin (KMO) measure evaluates the applicability of PCA. In this study, the KMO was 0.646. To interpret the factors of high significance, factor rotation using varimax was employed. HCA links the similar observations systematically and can easily identify different hydrochemical characteristics. For cluster analysis, Ward's method with squared Euclidean distance was applied and is the best option for dendrogram preparation.[15] The relations among different water parameters were detected by correlation studies. All the statistical calculations were carried out by SPSS 22.

3. Results and Discussion

3.1. Quality Characteristics of Groundwater

The summary results of groundwater of our study are shown in Table 1. The water temperature ranged from 22.5 to −27.1 °C during the study period. The pH of water varied from 6.4 to 8.0 and indicated that the waters were slightly acidic to slightly alkaline (Table 1). The COD of the study water ranged from 1.2 to 3.9 mgO_2/L. The alkalinity and hardness values varied from 12 to 81 mg/L

Table 1. Different measured and calculated parameters of the water samples collected from different sampling sites in the Lalmonirhat Sadar Upazila, Bangladesh

Parameters	Unit	Min	Max	Mean	SD	Standard limit[43]
Depth	m	13	80	29	15	–
pH	–	6.4	8.0	7.25	0.40	6.5–8.0
Temp	°C	22.5	27.1	24.5	1.1	Ambient
COD_{Mn}	mgO_2/L	1.2	3.9	2.5	0.66	–
EC	µS/cm	131	686	325	146	750
TDS	mg/L	64	343	160	69	500
Hardness	mg/L	40	226	99	40	500
Alkalinity	mg/L	12	81	31	14	–
Cl^-	mg/L	4	53	23	12	250
HCO_3^-	mg/L	49	207	101	37	200
SO_4^{2-}	mg/L	0.18	11.72	1.97	2.03	200
NO_3^-	mg/L	1.25	7.21	4.20	1.45	50
PO_4^{3-}	mg/L	0.003	0.019	0.011	0.004	–
F^-	mg/L	0.130	0.52	0.269	0.089	0.6–1.5
SiO_2	mg/L	5.00	33.00	18.08	6.86	–
B	mg/L	0.028	0.096	0.061	0.018	–
Ca^{2+}	mg/L	5.61	37.68	14.69	6.39	75
Mg^{2+}	mg/L	5.83	32.08	15.19	6.16	30
Na^+	mg/L	5.00	20.00	9.60	3.40	200
K^+	mg/L	2.40	14.00	6.51	3.24	30
Zn^{2+}	mg/L	0.025	0.067	0.048	0.011	–
Cu^{2+}	mg/L	0.011	0.148	0.030	0.029	1
Fe^{3+}	mg/L	0.064	1.190	0.474	0.310	0.1
Mn^{2+}	mg/L	0.030	0.710	0.298	0.146	0.05
As^{3+}	mg/L	0.011	0.042	0.027	0.009	0.010
SAR	–	0.21	0.74	0.36	0.10	–
%Na	–	12.53	37.85	23.47	6.36	–
RSC	meq/L	−1.41	0.38	−0.35	0.40	–
PI	–	0.48	1.16	0.74	0.16	–
PS	meq/L	0.11	1.56	0.66	0.33	–
Kelly's ratio	–	0.11	0.43	0.23	0.07	–
Cl/å anions	–	0.08	0.44	0.26	0.08	–
Na/ Na + Cl	–	0.20	0.71	0.42	0.11	–
SO_4^{2-}/Cl^-	–	0.006	0.70	0.082	0.106	–

and 40 to 226 mg/L, respectively. We found significant variability in EC values, with the values ranging from 131 to 686 µS/cm. The amount of TDS varied from 64 to 343 mg/L with an average of 160 mg/L (Table 1).

The concentration of K was comparatively low than that of Na in all waters (Table 1), because K minerals have low ability in migration[16] and are resistant to decomposition.[17] However, Na^+ ranged from 5 to 20 mg/L with a mean of 9.60 mg/L. Na^+ usually comes from the dissolution of evaporites and silicates.[8] Ca^{2+} and Mg^{2+} are the results of carbonate dissolution in general and varied from 5.61 to 37.68 and 5.83 to 32.08 mg/L, respectively. The concentrations of As^{3+}, Fe^{3+}, Zn^{2+}, Mn^{2+} and Cu^{2+} ranged from 0.011 to 0.042 mg/L, 0.064 to 1.190 mg/L, 0.025 to 0.067 mg/L, 0.030 to 0.710 mg/L, and 0.011 to 0.148 mg/L, respectively.

The concentrations of CO_3^{2-} were negligible compared with HCO_3^-. The sources of CO_3^{2-} and HCO_3^- are the dissolution of carbonate rocks resulting in eventual precipitation of CO_2.[16] Sedimentary rocks and chloride salts are the sources of Cl^-.[17] The dominant natural sources of SO_4^{2-} include rock weathering and biochemical processes.[18] Weathering of muscovite, biotite, fluorite, and fluoroapatite is the main cause of fluoride in groundwater. However, the concentrations of HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, F^-, B, and SiO_2 ranged from 49 to 207 mg/L, 4 to 53 mg/L, 0.18 to 11.72 mg/L, 1.25 to 7.21 mg/L, 0.003 to 0.019 mg/L, 0.13 to 0.52 mg/L, 0.028 to 0.096 mg/L, and 5 to 33 mg/L, respectively. Fertilizer application can alter the major ion concentrations in groundwater in the study area.

3.2. Mechanisms Controlling Groundwater Chemistry

Relations among the different anions and cations are able to explain the mechanisms that control groundwater chemistry. It can be explained by the following headings.

3.2.1. Carbonate Weathering

In carbonate weathering, the molar ratio of Ca^{2+} + Mg^{2+}: HCO_3^- (Figure 2Af) had greater than unity suggesting the dominancy of carbonate weathering and the source of high HCO_3^-. The possible causes are the dissolutions of gypsum, anorthite, and calcium montmorillonite and cation exchange. On the other hand, the formation of $CaCO_3$ can decrease Ca^{2+} concentration with
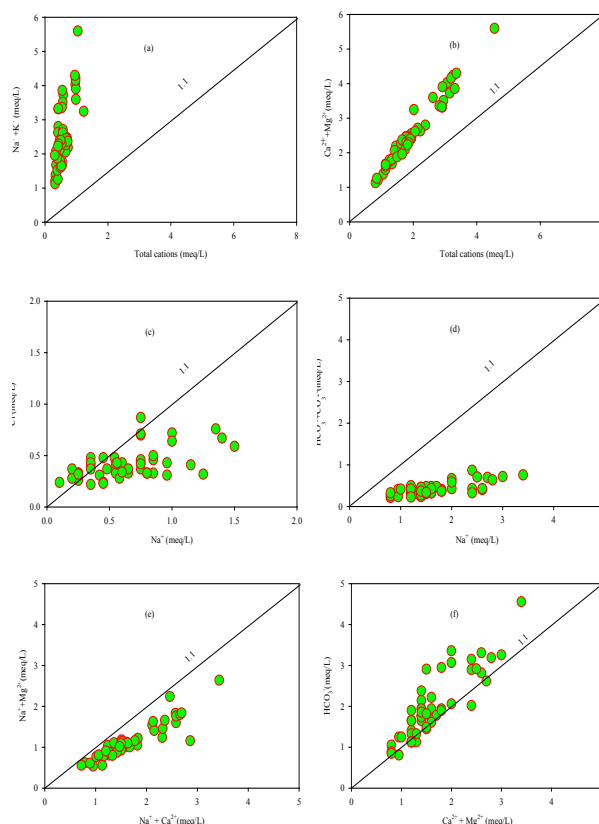

Figure 2A. Stoichiometric relations of the major cations and anions of the study water.

a proportional increase of Na^+. Consequently, the Mg^{2+}:Ca^{2+} ratio were greater than 1 (Figure 2Ae). With elevated Na^+ ions, Mg^{2+} is dominant over Ca^{2+} in the increased clay-rich soil.[19] Dominance of Na^+ + Mg^{2+} over Na^+ + Ca^{2+} in groundwater can have a greater Na^+ hazard.[19]

The HCO_3^-:Na^+ > 1 indicates carbonate weathering while its lower value suggests silicate weathering.[20] In this study, the ratios of HCO_3^- + CO_3^{2-}: Ca^{2+} (Figure 2Bi) and HCO_3^- + CO_3^{2-}: Mg^{2+} (Figure 2Bj) were close to the unity reflecting the dominancy of Ca and Mg-containing minerals. However, the influences of Na-containing minerals are less because the ratio of HCO_3^- + CO_3^{2-}: Na^+ (Figure 2Ad) was far below the unity. In most cases, the ratios of Ca^{2+} + Mg^{2+}: total cations were close to unity (Figure 2Ab). The ratios of Na^+ + K^+: total cations indicate lower concentrations of these two cations over Ca^{2+} and Mg^{2+} (Figure 2Aa). The Ca^{2+} + Mg^{2+} vs HCO_3^- + SO_4^{2-} relations of most samples were approaching unity (Figure 2Bg) reflecting dominancy of carbonate weathering.[21]
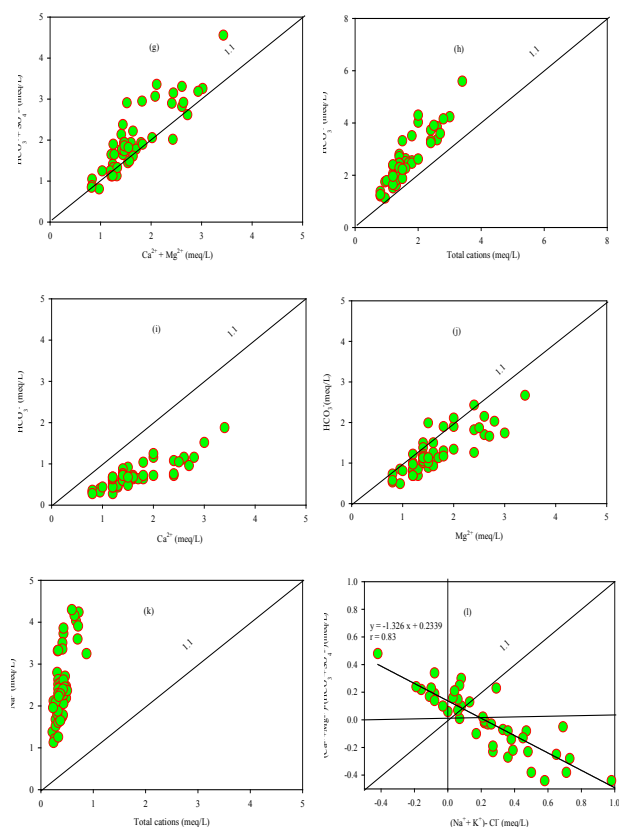
Figure 2B. Stoichiometric relations of the major cations and anions of the study water.

3.2.2. Silicate Weathering

The ratio of Na^+: total cations (TC) indicates the levels of silicate weathering process.[22] Groundwater samples had Na^+: TC< 0.25 (Figure 2Bk) indicating that there was less silicate weathering. The ratio of $Na^+ + K^+$: TC was 0.25 (Figure 2Aa). This implies that silicate weathering is less responsible to the supply of cations in groundwater. When carbonate and silicate minerals are the major contributors for groundwater chemistry, the HCO_3^-: TC value would be one.[23] This study did not correspond well to the above-mentioned mechanism (Figure 2Bh). The plotting of $Ca^{2+} + Mg^{2+}$ versus HCO_3^- (Figure 2Af) further infers that the groundwater did not have an excess of HCO_3^-. This HCO_3^- was not balanced by Na^+ (Figure 2Ad), as the silicate weathering was not a prime mechanism to release the Na^+ and HCO_3^- into the groundwater. The ratio of Na^+:Cl^- in most samples was lower than unity (Figure 2Ac). The dissolution of NaCl generates a 1:1 ratio of Na^+:Cl^- while the release of Na^+ from silicate weathering produces a wide ratio.[24]

3.2.3. Saline Water Intrusion

Salinity and saline water intrusions are related to Na–Cl relationship.[25] The equations of Cl^-/Σ anions > 0.8 and $Na^+/(Na^+ + Cl^-)$ < 0.5 suggest seawater intrusion into groundwater.[26] In this study, the average value of Cl^-/Σ anions ratio was 0.26 and also $Na^+/(Na^+ + Cl^-)$ ratio was 0.42 (Table 1). A significant correlation ($r = 0.56$) exists between Na^+ and Cl^- suggesting that they might be originating from the same sources (Table 3). The cation exchange process may also increase Na^+ concentration in addition to the dissolution of halite.[27] Figure 2Ac shows the deviations of the expected Na^+:Cl^- (1:1) relation indicating that a fraction of Na is associated with another anion. In the study area, the ratio of Na^+/Cl^- < 1 meaning another source is contributing chloride to the groundwater.

3.2.4. Ion Exchange

In aquifer, the clay minerals in unconsolidated deposits adsorb cations in their pore spaces. Ion exchange with clay materials is responsible for ionic concentration in groundwater.[28] In this study, the majority of the samples showed an excess of Mg^{2+} over Ca^{2+} (Figure 2Ae), which could be the dissolution of Mg-containing minerals in addition to dolomite. The exchange of Na^+ in water by Ca^{2+} or Mg^{2+} in clay material can cause an excess of Ca^{2+} or Mg^{2+} in groundwater and vice versa.[29] An excess of $HCO_3^- + SO_4^{2-}$ over $Ca^{2+} + Mg^{2+}$ indicates ion exchange process, while an excess of $Ca^{2+} + Mg^{2+}$ over $HCO_3^- + SO_4^{2-}$ supports reverse ion exchange.[30] In this study, the ratio of $(Ca^{2+} + Mg^{2+})/(HCO_3^- + SO_4^{2-}) > 1$ indicates the reverse ion exchange process (Figure 2Bg). If the dissolutions of calcite, dolomite, and gypsum are dominant in water, the relationship between $Ca^{2+} + Mg^{2+}$ and $SO_4^{2-} + HCO_3^-$ would be close to 1:1.[28] The role of ion exchange in groundwater can be evaluated by plotting $(Ca^{2+} + Mg^{2+}) - (HCO_3^- + SO_4^{2-})$ against $(Na^+ + K^+) - Cl^-$. The $(Ca^{2+} + Mg^{2+}) - (HCO_3^- + SO_4^{2-})$ relation implies that excess Ca and Mg were originated by the influences of other processes, whereas the $(Na^+ + K^+) - Cl^-$ indicates that K and Na were from the sources other than their respective chlorides. In case of the dominancy of ion exchange process, the graphical representations of the samples will form a line with a slope of –1.[31] Figure 2Bl shows that samples had a slope of –1.326, indicating cation exchange influences the groundwater chemistry in the study area.

Table 2. Correlation matrix of the water quality parameters with depth

	Depth	EC	TDS	Cl⁻	HCO₃⁻	NO₃⁻	SO₄²⁻	F⁻	Ca²⁺	Mg²⁺	Na⁺	K⁺	SAR
Depth	1.00												
EC	−0.04	1.00											
TDS	−0.03	0.94	1.00										
Cl⁻	0.02	0.74	0.66	1.00									
HCO₃⁻	−0.03	0.88	0.90	0.55	1.00								
NO₃⁻	−0.18	−0.27	−0.22	−0.21	−0.18	1.00							
SO₄²⁻	0.06	0.19	0.16	0.14	0.00	−0.03	1.00						
F⁻	−0.20	0.05	0.06	−0.06	0.17	0.05	−0.04	1.00					
Ca²⁺	−0.05	0.87	0.84	0.78	0.87	−0.28	0.07	0.13	1.00				
Mg²⁺	0.10	0.81	0.79	0.81	0.84	−0.11	0.10	0.09	0.88	1.00			
Na⁺	−0.09	0.86	0.81	0.56	0.73	−0.26	0.18	−0.01	0.66	0.54	1.00		
K⁺	−0.33	0.69	0.66	0.48	0.54	−0.14	0.07	0.07	0.47	0.36	0.76	1.00	
SAR	−0.15	0.41	0.38	0.09	0.25	−0.14	0.14	−0.14	0.09	−0.02	0.80	0.62	1.00

Values are significant at $p = 0.05$ where $r \geq 0.28$.

3.2.5. Chloroalkaline Index

Two chloroalkaline indices (CAI-I and CAI-II) suggested by Schoeller[32] were used to identify the specific ion exchange between the groundwater and its surroundings.[33] In general, Na⁺ and K⁺ in groundwater are exchanged with Ca²⁺and Mg²⁺ in aquifer matrix. An exchange between Na⁺ or K⁺ in water with Mg²⁺ or Ca²⁺ in rock indicates a direct ion exchange. Na⁺ or K⁺ will decrease in water and both the above indices will be positive. Conversely, the reverse ion exchange will produce negative indices.[33] The negative and positive values for both indices suggest the contribution of direct ion exchange and reverse ion exchange in the system (Figure 3). Results show that 68%

is negative and 32% is positive in CAI-I while in CAI-II, 22% is negative and 78% is positive. On an average, the contribution of direct ion exchange and reverse ion exchange reaction is almost equal.

3.2.6. Gibbs Ratio

Gibbs[34] proposed two diagrams known as Gibbs diagrams that explain the major mechanisms governing water chemistry. These diagrams are widely used in groundwater studies[8,33] in addition to surface water. In our study, the water samples fell in the precipitation dominance area of Gibbs diagram (Figure 4). Due to high evapotranspiration and restricted fresh water exchange in the study area, salt layers may form in the evaporating surface.[35] On the other hand, human activities can also change the groundwater chemical composition.

3.2.7. Piper Diagram

Piper diagram[36] can easily classify and compare the water types. The concentrations of majoranions and cations build this diagram. Groundwater samples are classified as Ca²⁺–Mg²⁺–CO₃²⁻–HCO₃⁻ type (Figure 5). This signifies that the dissolution of carbonates is a predominant process releasing substantial amount of Ca²⁺ and Mg²⁺ into the groundwater of the study area. Piper's diagram confirms that all the groundwater's are characterised as alkaline earth's (Ca²⁺ + Mg²⁺) exceeds alkalies (Na⁺ + K⁺) and are described as weak acids (CO₃²⁻ + HCO₃⁻) exceed strong acids (SO₄²⁻ + Cl⁻ + F⁻).
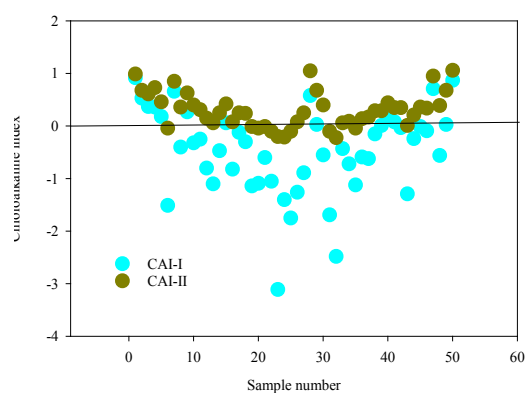

Figure 3. Variation of index of Base Exchange (CAI-I and CAI-II) against sample site numbers of the groundwater in the study area.
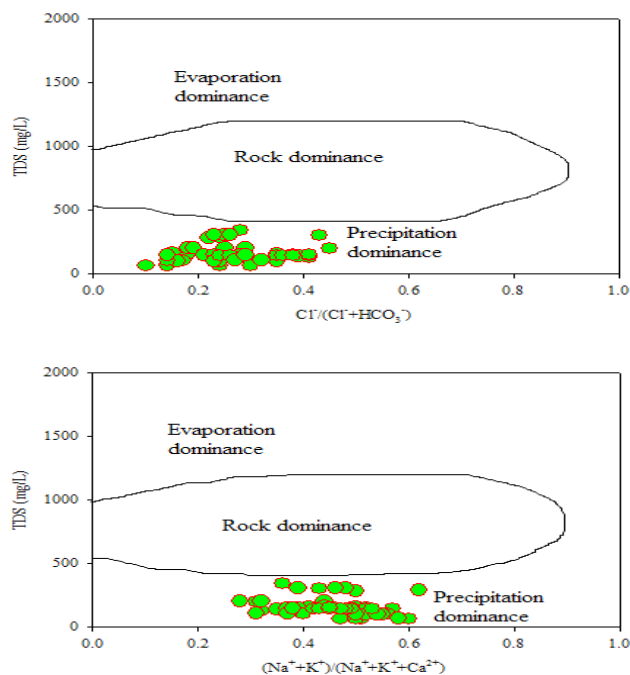
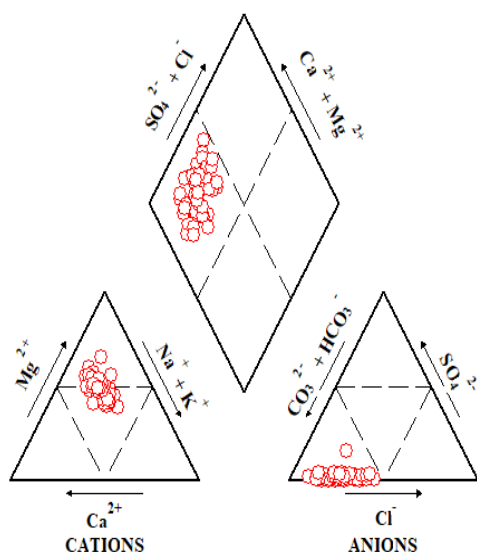**Figure 4.** Gibbs diagram of groundwater in the study are

Figure 5. Piper diagram of the groundwater samples in the study area showing Ca^{2+}–Mg^{2+}–CO_3^{2-}–HCO_3^- type.

3.3. Multivariate Statistical Analysis

In this study, a Pearson correlation matrix was used to determine the relationships between variables (Table 2). There were few significant relationships among

the measured concentrations with depth. The high correlations between Cl^- and HCO_3^- ($r = 0.55$), Cl^- and Na^+ ($r = 0.56$), K^+ and HCO_3^- ($r = 0.54$), Na^+ and K^+ ($r = 0.76$), and Na^+ and HCO_3^- ($r = 0.73$) indicate that they most likely derive from the same sources of water (Table 2). The relation between Ca^{2+}–HCO_3^- ($r = 0.87$) and Ca^{2+}–Na^+ ($r = 0.66$) might represent the contributions of carbonate and silicate weathering.

PCA was applied to the 24 physicochemical parameters, but only eight PCs with eigenvalue greater than 1 are considered to be the most important (Table 3). The high eigenvalue indicates the greater contribution to the variability of the groundwater chemistry. The PC loadings were categorised into strong, moderate, and weak corresponding to the absolute loading values of >0.75, 0.75–0.50, and 0.50–0.30, respectively.[37] A total of eight factors were accredited responsible for groundwater chemistry in the study area accounting 76.80% of the total variance (Table 3). Factor-1 has the highest loading (33.33%) and the contributors include Ca^{2+}, HCO_3^-, Cl^-, Mg^{2+}, Na^+, K, EC, TDS, hardness, and alkalinity. These major ions might be due to bedrock dissolution arising from rock–water interaction.

Examination of Figure 6 led to the identification of three major clusters in the dendrogram labeled as cluster 1, cluster 2, and cluster 3. The majority of samples (28) were grouped in cluster 1. Their similarity could support the hypothesis of a common evolutional trend to the study area. The cluster 2 and cluster 3 include 12 samples and 10 samples, respectively. The linkage distance is highest in cluster 3 followed by cluster 1 and cluster 2.

3.4. Irrigation Suitability

For agricultural use, the suitable pH ranges from 6.0 to 8.5[38] and all waters were suitable. The permeability index (PI) ranging from 48 to 116% locates under Class I and Class II (Table 1). These two classes allow 75% or more permeability of irrigation waters. Groundwater with Kelly's ratio greater than one is not good for irrigation. In this study, Kelly's ratio ranged from 0.11 to 0.43 indicating the suitability of all the samples for irrigation (Table 1).

High EC values may relate to salinity hazard. Table 4 shows that out of 50 samples, 30% were as 'excellent' and 70% were rated as 'good' for irrigation.[39] According to Richards[40] waters were C1S1 (30%) and C2S1 (70%) categories. C1 indicates 'low' salinity (EC < 250 µS/cm),

Table 3. Varimax rotated factor loading of groundwater chemistry in Lalmonirhat

Variables	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 8
pH	−0.240	0.072	0.087	0.146	**−0.742**	0.132	0.078	0.166
Temp	0.090	−0.467	0.451	0.061	0.484	0.079	−0.099	−0.015
COD	0.144	0.033	−0.085	−0.088	−0.151	0.117	**0.859**	0.005
EC	**0.955**	0.063	0.062	−0.143	0.007	−0.059	−0.114	−0.002
TDS	**0.938**	0.019	0.047	−0.117	0.058	−0.003	−0.039	0.058
Hard	**0.950**	0.047	−0.022	0.192	0.013	−0.010	0.098	−0.033
Alka	**0.893**	0.007	0.049	0.139	0.026	0.018	0.075	0.064
Cl	**0.820**	−0.134	0.046	0.142	0.017	0.037	0.028	−0.270
HCO_3	**0.905**	0.176	−0.039	−0.047	0.020	−0.066	0.022	0.141
SO_4	0.109	0.002	**0.816**	−0.121	−0.124	0.228	0.015	−0.148
NO_3	−0.266	0.107	0.135	0.085	0.370	−0.228	0.541	0.003
PO_4	−0.047	0.147	0.188	−0.155	−0.131	**0.816**	0.054	−0.131
F	0.053	**0.715**	−0.028	−0.003	0.024	0.040	0.230	0.119
SiO_2	−0.052	0.211	0.650	0.147	−0.041	−0.394	−0.036	0.301
B	−0.085	0.196	−0.334	0.077	0.561	0.088	0.070	0.358
Ca	**0.938**	0.091	−0.014	0.146	0.018	−0.010	−0.080	−0.052
Mg	**0.912**	0.017	−0.026	0.211	0.009	−0.010	0.205	−0.020
Na	**0.792**	0.026	0.092	−0.361	0.031	−0.060	−0.230	0.028
K	**0.624**	0.199	0.089	−0.425	0.081	−0.005	−0.123	−0.032
Zn	−0.233	**−0.834**	−0.135	−0.050	0.010	−0.095	0.215	0.132
Cu	−0.065	−0.342	−0.174	−0.568	−0.293	0.002	−0.113	0.037
Fe	0.166	−0.078	−0.105	**0.728**	−0.220	−0.043	−0.166	−0.161
Mn	−0.060	0.014	−0.009	0.153	0.047	0.018	−0.008	**−0.860**
As	−0.119	−0.011	−0.179	0.333	0.086	**0.605**	−0050	0.357
Eigen values	8.000	1.775	1.593	1.584	1.451	1.363	1.346	1.319
% of variance	33.335	7.397	6.638	6.602	6.047	5.678	5.607	5.496
Cumulative %	33.335	40.733	47.370	53.972	60.019	65.697	71.304	76.801

Bold values indicate absolute values >0.5 of parameters with strong loading value

C2 indicates 'medium' salinity (EC= 250–750 μS/cm), and S1 indicates 'low sodium'. In this study, 30% samples were rated as 'excellent' and 70% samples were rated as 'good' according to %Na.[39] As for RSC values, all water samples were graded as 'suitable'. Based on hardness, 30% samples were classified as 'soft', 56% samples were grouped as 'moderately hard', and 14% samples were as 'hard' (Table 4).

All the waters were rated as 'fresh' (TDS < 1000 mg/L) suggested by Freeze and Cherry.[41] Based on major cations, all the study waters were below the permissible limits (Ca^{2+} = 80 mg/L, Mg^{2+} = 35 mg/L, Na^+ = 200 mg/L, K^+ = 30 mg/L).[42] The chloride concentration should be below 140 mg/L in irrigation water,[38] and all waters were suitable for irrigation. The groundwater NO_3^-–N did not exceed the maximum concentration (30 mg/L) as because most crops are relatively unaffected below this value.[38] The lower concentrations of Cu^{2+}, Zn^{2+}, Fe^{3+}, As^{3+}, and Mn^{2+} might be suitable for crop production and soil environment.

3.5. Drinking and Public Health Suitability

In this study, the pH (6.4–8.0) of all groundwater samples was safe (safe limit 6.5–8.5) for drinking water prescribed by WHO.[43] The recommended concentration of TDS is 500 mg/L,[43] and all waters were suitable for drinking. The Na^+ concentration should be below 200 mg/L.[43] People can feel
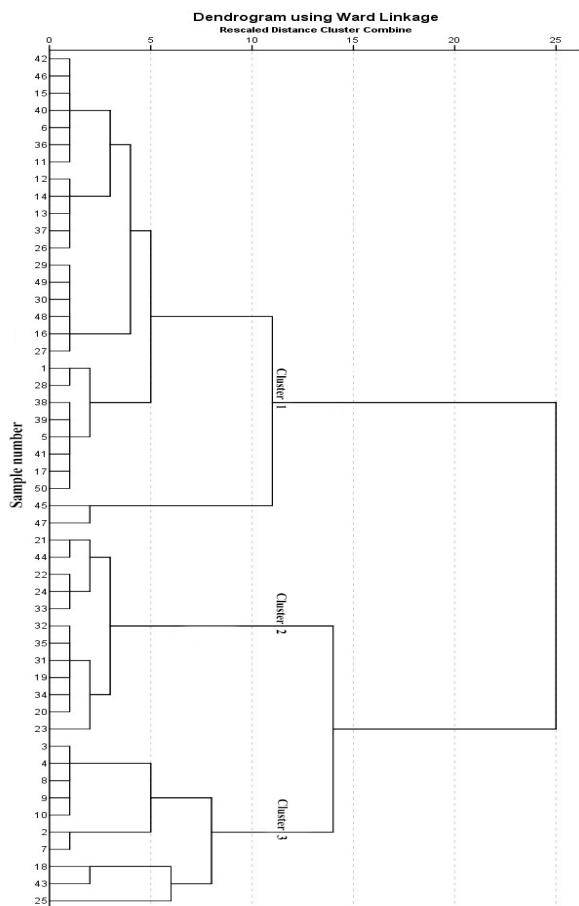
Figure 6. HCA analysis of the groundwater of the study sites.

Table 4. Water quality rating for irrigation in the study area

Parameters	Reference	Range	Category (%)
EC	39	<250 μS/cm	Excellent (30%)
		250−750 μS/cm	Good (70%)
SAR	40	<10	Excellent (100%)
TDS	41	0−1000 mg/L	Freshwater (100%)
Hardness	44	<75 mg/L	Soft (30%)
		75−150 mg/L	Moderately hard (56%)
		150−300 mg/L	Hard (14%)
RSC	45	<1.25 meq/L	Suitable (100%)
Kelly's ratio	46	<1	Suitable (100)
Percentage of Na	39	<20	Excellent (30%)
		20−40	Good (70%)
Alkalinity-salinity class	40	C1 < 250 μS/cm, S1 < 10	C1S1 (30%)
		C2 = 250−750 μS/cm	C2S1 (70%)

a salty taste if there is an excess of Cl^- present in drinking water. Hypertension, methemoglobinemia, and gastric cancer are the consequences of high NO_3^- concentration in drinking water. However, the concentrations of Cl^-, SO_4^{2-}, and NO_3^- of the studied groundwater samples were under the permissible limits. WHO[43] suggests the maximum permissible limit of Cl^-, SO_4^{2-}, and NO_3^- in drinking water should be 250 mg/L, 150 mg/L, and 10 mg/L, respectively. The content of As is above the WHO guideline for drinking water (<0.01 mg/L)[43] but below the Bangladesh limit (<0.05 mg/L). Concentration of Fe of almost all the samples exceeded the WHO permissible limit (<0.1 mg/L). The mean value of Mn (0.298 mg/L) was above the WHO guideline for drinking water (<0.05 mg/L). Exposure to high levels of manganese can cause a disease manganism characterised by a Parkinson-like syndrome showing weakness, muscle pain, apathy, and slow clumsy movement of limbs. Hard water may cause high incidence of urolithiosis,[43] anencephaly, parental mortality, and cardio-vascular disorders. This water also develops scales in distribution pipes and cooking utensils, and requires more soap for washing clothes.[35]

4. Conclusion

Groundwater quality of Lalmonirhat Sadar Upazila was measured for drinking and agricultural purposes. The findings of this study are as follows:

- The major cations in the study area were in the order of $Mg^{2+} > Ca^{2+} > Na^+ > K^+$. The anions were also arranged in decreasing order as $HCO_3^- > Cl^- > NO_3^- > SO_4^{2-}$.
- The dominant water type was $Ca^{2+}–Mg^{2+}–CO_3^{2-}–HCO_3^-$ and the study area is a precipitation dominance area.
- Based on Wilcox requirement and SAR, the groundwater might be suitable for irrigation without salinity hazard.
- Carbonate weathering was the main component for controlling groundwater chemistry followed by silicate weathering and ion exchange processes.

- The PCA and HCA explain the variations of different anions and cations and also the anthropogenic causes. Anthropogenic activities might cause the excess concentrations of some anions and cations.
- Accumulated salts on soil surfaces generated by irrigation can leach by recharge water and reach the water table, and could become a cause of groundwater pollution. And recycling of groundwater for irrigation can increase soil and groundwater salinity.
- According to the measured parameters such as pH, TDS, Na^+, Cl^-, SO_4^{2-}, NO_3^-, and semi-heavy metals (Cu, Zn, Fe, Mn, and As), all waters were suitable for drinking and domestic purposes.

Based on observed patterns, it can be concluded that all the groundwater samples of the Upazila, Bangladesh were suitable for irrigation, drinking, and domestic uses. However, continuous monitoring of groundwater in the study area would be useful for predicting the suitability for irrigation and drinking purposes in the upcoming days.

Acknowledgements

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