Evaluation of Hydrogeochemical Processes in Groundwater Using Geochemical and Geostatistical Approaches in the Upper Bengal Basin

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Overexploitation of groundwater for irrigation and radical changes of river morphology in the Bengal basin has posed difficulties to sustainable management of this resource. Forty groundwater samples were collected from tube wells of the pre-monsoon and post-monsoon seasons in 2020, and the water parameters were analyzed. The hydrogeochemical studies, bivariate plots, and multivariate techniques were used to evaluate the rock-water interactions, influencing factors, and contamination pathways. The principal component analysis (PCA) was used to extract several directions in the data space and understand the different geochemical processes. Q-mode hierarchical cluster analysis coupled with the post hoc ANOVA test of variance was also used to divide the sampling sites based on the geochemical water facies. The PHREEQC-3v software was used to measure the partial pressure of CO₂ in groundwater and elucidate the chemical reactions controlling the water chemistry. Near-neutral pH (7.4) and high EC (813.2 μS/cm), TDS (507.35 mg/L), and total hardness (383.45 mg/L) characterize the groundwaters of the study area. The research revealed that the order of abundance of cations was Ca²⁺ > Mg²⁺ > Na⁺ > K⁺ and of anions was HCO₃⁻ >> Cl⁻ > SO₄²⁻ > NO₃⁻ > PO₄³⁻. The PCA revealed that the chemical properties of the groundwater are derived from rock-water interactions. Hierarchical cluster analysis showed that two distinct groundwater zones were affected by neighboring river flow and irrigation return flow. Several diagrams suggested that the water was mainly of Ca-HCO₃ type originating from chemical weathering of rock-forming minerals with advanced water-rock interaction. The analyzed groundwater was supersaturated with calcite and partially saturated with dolomite. As a result, the chemical features of groundwater in the study area were largely dependent on the water-rock interaction, local lithological conditions, and neighboring river morphology. This study can be helpful for the improvement of water resource management, especially for drinking and irrigation purposes.

1. Introduction

Groundwater chemistry is affected by many issues, i.e., the quality of infiltrated water, the geological nature of the aquifer rocks, the decay of organic matters, partial pressure of soil carbon dioxide (stated as log₁₀ p CO₂), and various anthropogenic factors [1, 2]. The chemistry of groundwater is a function of the dealings between water and the mineralogical structure in the aquifer basement [3, 4]. Geochemical processes taking place inside this system include dissolution, percolation, precipitation, and cation exchange [4]. These phenomena happen together with the groundwater flow direction and depend on the residence time and recharging capacity that controls the chemical composition of the groundwater system [5]. Also, climate change and frequent extreme weather conditions overstress the severity of water scarcity. In this study, several techniques are used to investigate, evaluate, and illustrate the chemical features in groundwater and assess the rock-water interactions processes.

The Himalayan and non-Himalayan rivers drain to the Bay of Bengal as a joint river, transport the major alluvial sediment load; and create the largest delta basin in the world. This area is highly populated and covered by very fertile arable land. The study considered the western upper part of this
basin as a study area sited in the Kushtia district of Bangladesh. The previous study assumed that the hydrogeologic and aquifer condition in the study area were frequently chanced [6–8]. The watercourse of two main rivers, the Ganges and Brahmaputra, impeded significantly in the dry season in Bangladesh territory due to the upstream withdrawal for irrigation and other purposes [9, 10]. During the dry period, these rivers became almost dead, and this situation seriously impacted the neighboring groundwater composition. The morphology of the river and river banks has a changing trend that could harm the river ecosystem in the catchment areas. People heavily depend on groundwater systems for domestic, agricultural, and industrial activities living in that region. Thus, vast monitoring is vital for groundwater quality, healthy aquatic ecosystems, agriculture, and human health management.

During the past decades, interest in the hydrogeochemistry of groundwater has increased, which is becoming a firm part of local hydrogeological studies. Previous studies employed graphical representations (Piper, Gibbs, Chadha, Stiff, Schoeller, etc.) in visually describing differences in major ion chemistry of groundwater and classifying water compositions into recognizable groups, which are typical of similar genetic history [9, 11, 12]. Lately, using geoenvironmental datasets and multivariate statistical techniques for the geochemical evaluation of groundwater has been applied with remarkable success as a tool in the study of groundwater chemistry [13]. The application of multivariate statistics to datasets has facilitated the unveiling of hidden structures and helped resolve the geoenvironmental problems at various scales [13, 14]. This technique of geochemical data operation on the concept that each aquifer region has its single groundwater quality signature, based on the chemical makeup of the sediments that comprise it [15, 16]. In addition, the thermodynamic calculations of $pCO_2$ through PHREEQC-3v software were used to identify the specific rocks that controlled the water equilibrium reaction in the solid phase [1, 2, 17]. This paper pursues to apply for the multivariate statistical technique and programs as a tool for a complete geochemical evaluation of groundwater that facilitates the unveiling of hidden structures in the datasets and assists in defining the factors responsible for the deviation of groundwater quality.

The main objective of this study was to assess the physical and chemical characteristics of groundwater and the processes controlling its chemistry. The spatial and temporal variability of major ions in groundwater is a widely accepted tool that provides information on sustainable water uses and periodic changes in groundwater quality [18, 19]. The study applied different statistical methods including the correlation matrix, principal component analysis, and cluster analysis, for assessing the correlation, association, and classification of the water variables. Some graphical bivariate plots and computer programs were considered for the evaluation of water type and identification of rock sources. The primary issue addressed by this study was to estimate natural and anthropogenic sources of solutes in the water system by evaluating the general groundwater chemistry and then exploring rock weathering evolution.

2. Methods and Materials

2.1. Study Area. The study area is geographically located at 23°42′ and 24°12′ north latitudes and 89°20′ east longitudes. The total sampling area is 1621 km$^2$ and is bounded by the Ganges River (Padma River), and the other three-branch rivers create a large deltaic alluvial plain (Figure 1). The population of that zone is around 2 million, and the maximum of the people are involved in agricultural activities [20]. The soil in the study area is good enough fertile as the district lies in the floodplain of the Ganges River; also, the physiographic situation belongs to the higher Ganges flood plain. The soil surface is characterized by uniform geomorphology, which seems to level a landscape with an elevation of around 9 m above sea level, but in some places, it consists of shallow depressions and somewhat higher ridges [21]. The study area is covered by a subtropical humid climate with a warm and rainy monsoon and a pronounced dry season in the winter months. The maximum temperature is mainly observed in May-June and the lowermost in December-January. The area received total rain of 1167 mm/y [20]. Around 95% of mining groundwater is used for agricultural activities and the remaining for consumption as drinking water. So, groundwater quality should be assessed as the most efficient in terms of irrigation purposes in the study area.

The primary aquifer comprises unconsolidated alluvial-sediments, which are spread over the surface by permeable sand, silt, and clayey soil (Figure 2). According to subsurface hydrogeological information, most of the good-quality aquifers of this area occurred between 20 and 100 m depth from the surface. The thickness of the local aquifer differs because of the effects of basement rock depth and the crosswise extent of the aquifer. The groundwater flow direction is typically from east-north to west-south.

2.2. Sampling Strategy and Analysis. Selection of sampling points, collection, transportation, parameters, and analytical methods of the samples are the important factors for the rational sampling and analytical strategy. The present sampling area is rural and peri-urban, and we involved the community in the sampling process. This study was divided into two categories of sampling field, i.e., groundwater for drinking, and irrigation purposes. The potential pollution sources are different in the two sampling fields, while the nonpoint pollution sources are the most common compared to point sources in both sampling fields. Nonpoint source pollution is the leading cause of water pollution in Bangladesh because it is challenging to regulate this widespread source rather than one specific source of pollutants. In the study area, run-off and over flooding that has accumulated contaminants in the sediment, surface pollutants, nutrients, pesticides, fertilizer, inorganic pollutants, livestock wastes, human excreta, etc., into water bodies. Most of the portions of these matters are leached into the subsoil and finally reach the ground aquifers. With other causes, the overall water quality of the study area is deviated by the above external sources. Table 1 represents the sampling descriptions and probable pollution sources of the group of sampling stations.
For physical and chemical analysis of groundwater, two sampling periods, i.e., May-June (premonsoon) and October-November (postmonsoon) 2020, were selected. Groundwater was collected from the first aquifer, which was up to 100 m below the surface, less than 100 years old, and continuous recharge by rainwater and river stream [22, 23]. It was collected randomly from the selected hand pump to cover the topographical extension of the study area and the key geologic sceneries. The samples were collected from two different fields, i.e., residential and agricultural areas, and the depth of sampling wells ranged from 22 to 105 m (Table 1). According to the standard procedure [24], samples were collected in prewashed and high-density polythene bottles after five (5) min of pumping to get clean water and avoid any debris. All samples were collected directly at the well-head. The pH, temperature, electrical conductivity (EC), and total dissolved solids (TDS) were measured in situ using the portable multimeters. Anions such as Cl\(^-\), SO\(_4\)\(^{2-}\), NO\(_3\)\(^-\), and PO\(_4\)\(^{3-}\) were measured by a UV-Vis Spectrophotometer. Ca\(^{2+}\), Mg\(^{2+}\), HCO\(_3\)\(^-\), and total hardness (TH) were determined using the titrimetric method. Na\(^+\) and K\(^+\) were measured from preacidified stored water samples using the flame photometer. Analyzed water variables are stated in Table 2. Quality control was kept in spectrometric analyses as stated by individual instruction manuals, and method precision was more than 95% in confidence interval (CI) with the correlation coefficient, \(r \approx 1\) of respective calibration curves. Cation and anion charge balance was added as proof of the accuracy of the data and was determined by the following equation:

\[
\text{Charge balance error (CBE)} = \frac{\sum M_c |N_c| - \sum M_a |N_a|}{\sum M_c |N_c| + \sum M_a |N_a|} \times 100,
\]

(1)

where \(M_c\) and \(N_c\) are molar concentration and charge of cation; similarly, \(M_a\) and \(N_a\) are the same for the anion. All calculated ionic balance errors are within ±5%.

2.3. Data Analysis. At first, Piper, Chadha’s, and Gibb’s plots were used to determine the water classification and solutes source of the groundwater solution. Then, the following statistical methods, i.e., correlation matrix, principal component analysis (PCA), hierarchical cluster analysis (HCA), linear regression, and bivariate plots, were applied to determine the correlation and association within water variables and some information about sources of solutes in the groundwater. All the statistical calculations were performed using IBM-SPSS v-26. Data screening showed that the data are generally skewed. Therefore, the data were log-transformed and corresponded more closely to normally distributed data. Then, all variables were standardized by

![Figure 1: Location of groundwater sampling.](image-url)
calculating their standard scores (z-scores). In this way, each variable has equal weight in the statistical analysis [25]. The strength of a linear correlation between two variables or the degree of association was assessed by Pearson’s correlation coefficient, r. Once the two variables were considered concurrently, multiple linear regression analyses were used to assess their interdependence [26]. For multiple regression, as a quantity of the degree of association, the coefficient of determination, the $R^2$ value is more easily explainable than correlation coefficient, r, because $R^2$ is equivalent to the part of the total variability in the dependent variable that may impose the effects of the independent variables [27].

Principal component analysis (PCA) is a powerful and flexible method that can be applied broadly and work...
Table 2: Summary of the analyzed data of the groundwater in the premonsoon (PRM) and postmonsoon (POM) of the 2020 sampling campaign, with basic statistics.

<table>
<thead>
<tr>
<th></th>
<th>Depth</th>
<th>Temp.</th>
<th>pH</th>
<th>EC</th>
<th>TDS</th>
<th>TH</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Cl⁻</th>
<th>HCO₃⁻</th>
<th>SO₄²⁻</th>
<th>NO₃⁻</th>
<th>PO₄³⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Premonsoon (PRM), n = 40</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Min.</td>
<td>22</td>
<td>27.5</td>
<td>6.65</td>
<td>366</td>
<td>219</td>
<td>122</td>
<td>56.6</td>
<td>13.0</td>
<td>5.10</td>
<td>0.30</td>
<td>12.0</td>
<td>271.5</td>
<td>2.91</td>
<td>0.80</td>
<td>0.21</td>
</tr>
<tr>
<td>Max.</td>
<td>105</td>
<td>33.0</td>
<td>7.80</td>
<td>1035</td>
<td>675</td>
<td>562</td>
<td>151.4</td>
<td>63.8</td>
<td>71.6</td>
<td>2.90</td>
<td>562</td>
<td>703</td>
<td>45.7</td>
<td>14.3</td>
<td>2.90</td>
</tr>
<tr>
<td>Mean</td>
<td>50.03</td>
<td>30.5</td>
<td>7.02</td>
<td>669.6</td>
<td>413.2</td>
<td>362.2</td>
<td>95.64</td>
<td>32.62</td>
<td>14.12</td>
<td>1.27</td>
<td>31.2</td>
<td>418.6</td>
<td>16.46</td>
<td>4.14</td>
<td>0.99</td>
</tr>
<tr>
<td>Median</td>
<td>31.0</td>
<td>29.0</td>
<td>7.00</td>
<td>647.0</td>
<td>404.0</td>
<td>362.0</td>
<td>94.75</td>
<td>31.45</td>
<td>11.65</td>
<td>1.10</td>
<td>29.4</td>
<td>381.0</td>
<td>15.45</td>
<td>2.05</td>
<td>0.85</td>
</tr>
<tr>
<td>SD (±)</td>
<td>31.9</td>
<td>0.07</td>
<td>0.22</td>
<td>172.5</td>
<td>113.2</td>
<td>93.52</td>
<td>22.46</td>
<td>12.3</td>
<td>11.7</td>
<td>0.72</td>
<td>9.29</td>
<td>110.8</td>
<td>9.29</td>
<td>3.81</td>
<td>0.61</td>
</tr>
<tr>
<td>Skewness</td>
<td>0.96</td>
<td>1.32</td>
<td>2.10</td>
<td>0.36</td>
<td>0.21</td>
<td>-0.07</td>
<td>0.21</td>
<td>0.75</td>
<td>3.36</td>
<td>0.72</td>
<td>0.80</td>
<td>1.36</td>
<td>1.19</td>
<td>1.11</td>
<td>1.27</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Depth</th>
<th>Temp.</th>
<th>pH</th>
<th>EC</th>
<th>TDS</th>
<th>TH</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Cl⁻</th>
<th>HCO₃⁻</th>
<th>SO₄²⁻</th>
<th>NO₃⁻</th>
<th>PO₄³⁻</th>
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<tr>
<td><strong>Postmonsoon (POM), n = 40</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Min.</td>
<td>22</td>
<td>25.0</td>
<td>7.0</td>
<td>662</td>
<td>450.5</td>
<td>225</td>
<td>67.2</td>
<td>14.0</td>
<td>3.90</td>
<td>0.20</td>
<td>12.9</td>
<td>248.5</td>
<td>2.95</td>
<td>0.80</td>
<td>0.20</td>
</tr>
<tr>
<td>Max.</td>
<td>105</td>
<td>30.0</td>
<td>8.91</td>
<td>1708</td>
<td>1109</td>
<td>615</td>
<td>187.8</td>
<td>52.6</td>
<td>51.6</td>
<td>2.90</td>
<td>41.8</td>
<td>817</td>
<td>41.7</td>
<td>18.3</td>
<td>2.10</td>
</tr>
<tr>
<td>Mean</td>
<td>50.03</td>
<td>27.0</td>
<td>7.83</td>
<td>956.8</td>
<td>601.5</td>
<td>404.7</td>
<td>114.4</td>
<td>28.96</td>
<td>11.56</td>
<td>1.013</td>
<td>27.09</td>
<td>448.8</td>
<td>15.14</td>
<td>3.7</td>
<td>0.91</td>
</tr>
<tr>
<td>Median</td>
<td>31.0</td>
<td>28.1</td>
<td>7.90</td>
<td>923.5</td>
<td>566.8</td>
<td>382.5</td>
<td>111.7</td>
<td>28.8</td>
<td>9.20</td>
<td>0.85</td>
<td>26.95</td>
<td>440.7</td>
<td>10.85</td>
<td>2.00</td>
<td>0.80</td>
</tr>
<tr>
<td>SD (±)</td>
<td>31.9</td>
<td>0.08</td>
<td>0.22</td>
<td>206.1</td>
<td>156.2</td>
<td>94.03</td>
<td>26.87</td>
<td>9.44</td>
<td>8.73</td>
<td>0.68</td>
<td>7.61</td>
<td>124.5</td>
<td>9.25</td>
<td>3.64</td>
<td>0.51</td>
</tr>
<tr>
<td>Skewness</td>
<td>0.96</td>
<td>1.16</td>
<td>0.02</td>
<td>1.31</td>
<td>0.00</td>
<td>0.59</td>
<td>0.54</td>
<td>0.70</td>
<td>2.90</td>
<td>0.87</td>
<td>0.32</td>
<td>0.61</td>
<td>1.33</td>
<td>2.01</td>
<td>0.71</td>
</tr>
</tbody>
</table>

(a) n: number of samples; EC: electrical conductivity; TDS: total dissolved solids; TH: total hardness. (b) All parameters’ unit is in mg/L except EC in μS/cm, depth in m, temperature in °C, and pH.

Geofluids
organic matters [35, 36]. The slightly alkaline nature of the groundwater in the POM season was the cause of mineralization of cations and dissolution of carbonates/bicarbonates [37, 38]. The higher pH values with the elevated HCO$_3$ concentration (448.8 mg/L) in the POM season indicated the free H$^+$ bond to the buffering agent HCO$_3$. Bicarbonate controlled the acidic and alkaline nature in water solution through equilibrium conditions. The EC values of the water samples were varied from 366 to 1035 and 662 to 1708 μS/cm in the PRM and POM, respectively. A higher EC value found in the POM season compared to the PRM may be due to the weathering processes during surface run-off and percolation in the rainy season [39]. The large variations in EC values (±SD: 172.5 and 206.1) are mostly attributed to the geochemical activities viz. exchange of ions, percolation and infiltration of rainwater, evaporation, and sediment dissolution [40]. The TDS value of water typically depends on the EC. During the rainy season, the surface run-off of rainwater enters the soil through percolation and infiltration and finally reached the aquifer with a higher mineral concentration. The results showed that EC and TDS values are relatively lower at the recharge zone and higher at the discharge zone. When the water moved through the recharge to discharge zone, then it dissolved extra ingredients along its flow path. For this reason, more ions or electrolytes in the groundwater were added and led to a higher EC as well as the TDS value. The analysis results showed that the higher EC and TDS values were found in the POM (just after the rainy season) season compared to the PRM period due to the mineralization of the groundwater [17]. The elevated values of EC are attributable to the impact of geology and anthropogenic events [27, 41].

The concentrations of Na$^+$, K$^+$, and Cl$^-$ in the groundwater of the study areas are lower compared to those of the southern and other parts of the country [37, 42–46]. While the concentrations of Ca$^{2+}$, Mg$^{2+}$, and HCO$_3$ are significantly high and contained more than 95% of total ions in groundwater during the sampling periods. These are the dominating ions of the collected samples indicating the water quality was very hard. It might be due to the overmining of groundwater, cation exchange, excess weathering of carbonate rocks, lower river flow, soil erosion, and dissolution of carbonic acid [34, 47]. Generally, earth metal ions come from carbonate minerals (aragonite, calcite, and/or dolomite), which are boosted by breathed CO$_2$ from oxic and anoxic organic matter degradation [48]. Calcite/aragonite (CaCO$_3$) and dolomite (CaMg(CO$_3$)$_2$) react with CO$_2$ resulting in elevation of Ca$^{2+}$, Mg$^{2+}$, and HCO$_3$ concentrations in groundwater. In the rainy season, CO$_2$ in rainwater can facilitate carbonate mineral dissolution. For this reason, the concentration of Ca$^{2+}$, Mg$^{2+}$, and HCO$_3$ in the POM was relatively higher than that in the PRM period. Besides, Infante et al. [49] pointed out that alluvial deposits (main deposition in the study area) developed Ca-rich calcrite nodules. The levels of other anions like SO$_4^{2-}$, NO$_3^-$, and PO$_4^{3-}$ were found in relatively lower ranges of concentration.

The multivariate statistical analysis utilizes normally distributed data [17]. The data for most chemical parameters skewed positively (Table 3). In statistics and probability theory, skewness is a measure of the asymmetry of the probability distribution of a random variable about its mean [16]. If it is between 0.5 and 1, it indicates that the data are moderately skewed [50]. Other statistical tests such as the goodness of fit test are necessary to verify which statistical model describes the observations. Univariate nonparametric tests (Mann–Whitney U-test) assess the null that both samples are drawn from the same population, and the test bases its calculations on the ranks of the data. In this study, this test delivered significant differences between the PRM and POM sampling periods for some water variables (Figure 3). It also analyzed and signified both the seasonal and coincidental variations. The values of EC, TDS, Ca$^{2+}$, and Cl$^-$ do

Table 3: Pearson’s correlation matrix of analyzing groundwater quality parameters in PRM (left side) and POM (right side).

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>EC</th>
<th>TDS</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>B</th>
<th>TH</th>
<th>Cl</th>
<th>HCO$_3$</th>
<th>SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
<th>PO$_4^{3-}$</th>
<th>Dep.</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>-0.41*</td>
<td>-0.20</td>
<td>-0.39*</td>
<td>-0.38*</td>
<td>-0.37*</td>
<td>-0.47*</td>
<td>0.29</td>
<td>-0.44*</td>
<td>0.03</td>
<td>-0.47*</td>
<td>-0.04</td>
<td>-0.10</td>
<td>-0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td>-0.12</td>
<td>0.85**</td>
<td>0.64**</td>
<td>0.33*</td>
<td>0.37*</td>
<td>0.32</td>
<td>-0.12</td>
<td>0.59**</td>
<td>0.33*</td>
<td>0.52**</td>
<td>0.60**</td>
<td>0.48**</td>
<td>0.05</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>TDS</td>
<td>-0.22</td>
<td>0.96**</td>
<td>0.50**</td>
<td>0.17</td>
<td>0.21</td>
<td>0.10</td>
<td>-0.15</td>
<td>0.41*</td>
<td>0.33*</td>
<td>0.42*</td>
<td>0.57**</td>
<td>0.51**</td>
<td>-0.1</td>
<td>-0.11</td>
<td></td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>-0.15</td>
<td>0.78**</td>
<td>0.77**</td>
<td>0.54**</td>
<td>0.43*</td>
<td>0.45*</td>
<td>-0.28</td>
<td>0.94**</td>
<td>0.36*</td>
<td>0.81**</td>
<td>0.54**</td>
<td>0.10</td>
<td>0.01</td>
<td>-0.05</td>
<td></td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.03</td>
<td>0.50**</td>
<td>0.46*</td>
<td>0.45*</td>
<td>0.13</td>
<td>0.37*</td>
<td>-0.13</td>
<td>0.80**</td>
<td>0.09</td>
<td>0.45*</td>
<td>0.34*</td>
<td>-0.21</td>
<td>0.06</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>Na$^+$</td>
<td>-0.27</td>
<td>0.43*</td>
<td>0.45*</td>
<td>0.25</td>
<td>0.08</td>
<td>0.73**</td>
<td>-0.07</td>
<td>0.36*</td>
<td>0.25</td>
<td>0.28</td>
<td>0.28</td>
<td>0.22</td>
<td>-0.02</td>
<td>-0.01</td>
<td>-0.01</td>
</tr>
<tr>
<td>K$^+$</td>
<td>-0.11</td>
<td>0.55**</td>
<td>0.54**</td>
<td>0.44*</td>
<td>0.41*</td>
<td>0.62**</td>
<td>0.20</td>
<td>0.48*</td>
<td>0.34*</td>
<td>0.36*</td>
<td>0.28</td>
<td>0.01</td>
<td>0.09</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>TH</td>
<td>-0.1</td>
<td>0.58**</td>
<td>0.55**</td>
<td>0.65**</td>
<td>0.52**</td>
<td>-0.03</td>
<td>0.15</td>
<td>0.02</td>
<td>0.29</td>
<td>0.76**</td>
<td>0.53**</td>
<td>-0.02</td>
<td>0.02</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.04</td>
<td>0.39*</td>
<td>0.31</td>
<td>0.30</td>
<td>0.12</td>
<td>0.22</td>
<td>-0.21</td>
<td>0.30</td>
<td>0.27</td>
<td>0.15</td>
<td>0.20</td>
<td>0.13</td>
<td>-0.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCO$_3$</td>
<td>-0.1</td>
<td>0.76**</td>
<td>0.78**</td>
<td>0.80**</td>
<td>0.46*</td>
<td>0.09</td>
<td>0.34</td>
<td>-0.08</td>
<td>0.68**</td>
<td>0.17</td>
<td>0.55**</td>
<td>0.12</td>
<td>0.02</td>
<td>-0.17</td>
<td></td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>-0.25</td>
<td>0.76**</td>
<td>0.80**</td>
<td>0.66**</td>
<td>0.35*</td>
<td>0.32</td>
<td>0.47*</td>
<td>0.21</td>
<td>0.52**</td>
<td>0.18</td>
<td>0.61**</td>
<td>0.27</td>
<td>0.13</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>-0.16</td>
<td>0.29</td>
<td>0.34*</td>
<td>0.18</td>
<td>0.05</td>
<td>0.31</td>
<td>0.17</td>
<td>-0.16</td>
<td>0.22</td>
<td>0.28</td>
<td>0.10</td>
<td>0.38*</td>
<td>0.09</td>
<td>-0.25</td>
<td></td>
</tr>
<tr>
<td>PO$_4^{3-}$</td>
<td>0.11</td>
<td>0.13</td>
<td>0.02</td>
<td>0.06</td>
<td>0.05</td>
<td>-0.05</td>
<td>0.22</td>
<td>-0.1</td>
<td>0.15</td>
<td>0.27</td>
<td>-0.05</td>
<td>0.11</td>
<td>0.03</td>
<td>-0.06</td>
<td></td>
</tr>
<tr>
<td>Depth</td>
<td>-0.24</td>
<td>-0.12</td>
<td>-0.15</td>
<td>-0.03</td>
<td>0.07</td>
<td>0.06</td>
<td>-0.07</td>
<td>0.28</td>
<td>0.12</td>
<td>-0.21</td>
<td>-0.20</td>
<td>-0.01</td>
<td>-0.19</td>
<td>-0.05</td>
<td></td>
</tr>
</tbody>
</table>

**Correlation is significant at the p = 0.01 level with 95% CI (2-tailed, bold). *Correlation is significant at the p = 0.05 level with 95% CI (2-tailed).
not show significant differences while significant differences were found for the rest of the variables in both sampling rounds at \( p < 0.05 \).

3.2. Water Classification. The study plotted Piper’s and Chadha’s diagrams to explore the water classification of the groundwater in the areas [51, 52]. Based on the symbolic area in the piper diagram, maximum water samples are categorized as absolutely Ca and HCO\(_3\) type and water class denoted as Ca-HCO\(_3\) (Figure 4(a)). But for PRM season, a little number of samples lay in no dominant type area. These samples may classify roughly as Ca-Mg-HCO\(_3\) type. From Chadha’s classification diagram (Figure 4(b)), the linear plots of \([\text{HCO}_3^- (\text{Cl + SO}_4^- + \text{NO}_3^- + \text{PO}_4^{3-})]\) vs. \([\text{Ca + Mg}^- (\text{Na + K})]\) shows strongly positively correlated \( R^2 = 0.6902 \) in PRM and \( R^2 = 0.9714 \) in POM. It indicates the prevalence of Ca-HCO\(_3\) facies that reveals the alkaline earth metals (Ca\(^{2+}\) and Mg\(^{2+}\)) significantly exceed the alkali metals (Na\(^+\) and K\(^+\)) and strong conjugate base (HCO\(_3^-\)) dominates over a weak conjugate base (Cl\(^-\), SO\(_4^{2-}\), NO\(_3^-\), and PO\(_4^{3-}\)). So, both diagrams

Figure 3: Boxplot illustrations of the upper and lower quartiles (box); median (black line within the box); 1.5 \times \text{interquartile range (IQR)} (cross mark in the box); and outliers (circles) for designated variables in the two sampling seasons PRM (green) and POM (red). As stated by Mann–Whitney \( U \)-test, letters “a” and “b” in each panel signify suggestively different data deliveries at \( p < 0.05 \) (in two-tailed).
represent the Ca-HCO₃ type of water class in the groundwater samples.

The Gibbs diagram is widely used to demonstrate the relationship between aquifer lithology and water chemistry [53]. Two plots show the relation between TDS and Na/(Na+Ca) and/or Cl/(Cl+HCO₃) (Figures 5(a) and 5(b)). The figures showed that all water samples of both periods fell under the rock-weathering dominance region. The cation (a) and anion (b) plots describe the occurrence of weathering reactions in the study area.

3.3. Multivariate Statistical Analysis. Pearson’s correlation matrix of the analyzed geochemical variables in both periods is presented in Table 3. Among all the variables, the value of TDS, Ca²⁺, Mg²⁺, TH, SO₄²⁻, and HCO₃⁻ of the samples were highly correlated with EC ($r > 0.5$, $p = 0.01$, at 95% confidence interval) in both seasons. The high value of EC is mainly caused by the divalent cation (Ca²⁺ and Mg²⁺) and elevated concentration of HCO₃⁻, but not with univalent ions such as Na⁺, K⁺, Cl⁻ and NO₃⁻. Total hardness (TH) was strongly correlated with Ca²⁺, Mg²⁺, HCO₃⁻, and SO₄²⁻, indicating its Ca-Mg-HCO₃-type temporary hardness (SO₄²⁻ concentration found very low). So, Ca²⁺ and Mg²⁺ appear to be the main donors to TH, stemming from the weathering of calcite by CO₂-charged precipitation. pH shows a weak negative correlation with carbonate components (Ca²⁺, Mg²⁺, and HCO₃⁻). It has a significant rule of low pH on the calco-carbonic equilibrium and potentiality of carbonate mineral/rock weathering. A moderate positive correlation was detected between Ca²⁺ and Mg²⁺ that suggested the ions were involved in several physicochemical reactions (ion exchange or oxidation-reduction) in the aquifer system [54, 55]. But Na⁺, K⁺, and Cl⁻ show a weak correlation with Ca²⁺, Mg²⁺, HCO₃⁻, and SO₄²⁻. This was attributed to the effect of leaching and dissolution of rapid soluble Triassic or carbonate/lime salt [56, 57]. This dissolution process was supported by the Langelier saturation indices (LSI). The calculated index showed that over 80% of samples have a positive value of LSI for both periods of sampling. Thus, the groundwater aquifer was supersaturated by mineral carbonates (e.g., calcite, dolomite, and aragonite) [58]. The NO₃⁻ showed a very weak negative correlation with other components, which indicated that it might be coming from external sources, i.e., from nitrogenous fertilizers in the study area [59]. All the parameters were not correlated with water depth because the entire samples were collected from the same upper shallow aquifer. The deep aquifers started from over 150 m below the surface of the study area. Matrix Table 3 explores the information of evaluating the hydrogeochemistry of the study areas.

PCA was performed using a varimax rotation, which brings the measurements onto a common scale, and the main components were extracted based on eigenvalues greater than or equal to 1 with the PCs being sorted in a diminishing order of variance, such that the axis of the greatest variance becomes the first principal component (PC1) and the axis of the second greatest variance becomes the PC2 [60, 61]. To ensure that the factors do not correlate with each other and the parameters do not correlate significantly with more than one factor, varimax rotation was used. Varimax rotation produces orthogonal factor rotation, such that the resultant factors are uncorrelated and simply
understandable [62, 63]. Usually, parameters with high commonalities are the parameters that contribute significantly to the factors [64]. An intercomponent correlation was used to determine the 40 samples with each having 14 variables for both the PRM and POM sampling periods of the original data structure (Table 4). The biplot of robust PCA shows characteristics of the components and helps to understand the relative importance of variables in components (Figure 6). The results showed a total variance of 74.50% and 74.49% in the PRM and POM seasons, respectively, with eigenvalue > 1 extracted, as determined by five PCs of R-mode. About 60% of the total variance in both seasons is displayed in the first three loadings (Table 4). The positive and negative values in PCA clarified that the water samples were affected or unaffected by the presence of extracted loads on an exact constituent. The parameters EC, TDS, Ca^{2+}, SO_{4}^{2-}, and HCO_{3}^{-} showed a strong association (bold type) with PC1 in the PRM, but 4 components viz. Ca^{2+}, TH, EC, and HCO_{3}^{-} showed the same loading as PC1 in the POM period of the original sampling. The high concentration of HCO_{3}^{-} in the groundwater, the high concentration of NO_{3}^{-} was related to the dissolved CO_{2}, which originated from decay of soil organics and plant root respiration [70]. The connotation of these two parameters reflected the impact of chemical fertilizers on groundwater contamination and can be called the agriculture pollution factor [71]. The following reactions can explain the process, where an increase in nitrate (NO_{3}^{-}) and bicarbonate (HCO_{3}^{-}) concentrations occurs in the aqueous media:

1. \[ \text{NH}_4^+ + O_2 \rightarrow \text{NO}_3^{-} + H_2O \] (nitrogenous fertilizers) + O_2 (oxic condition)
2. \[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \] (leached and root respiration)
3. \[ \text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3^{-} + \text{H}_3\text{O}^+ \]

Hierarchical cluster analysis was performed for 40 groundwater samples with 14 hydrochemical parameters to identify the group of sampling sites (clusters) exhibiting similar water chemistries. In agglomerative schedule cluster analysis, the most similar variables are sited in one cluster and linked to a closely associated cluster(s) and, further, clusters with less relative connection, all of which are linked to form one big cluster [27]. The hydrogeochemical parameters of samples in both seasons showed five (5) and seven (7) smallest single clusters in the PRM and POM period.
respectively, and two (2) main cluster groups (cluster I and cluster II) in both periods based on a dendrogram using Ward’s method (Figures 7(a) and 7(b)).

Figure 8 displays the spatial distribution of the two distinct groundwater clusters in the study area of both periods. The first cluster starts near the two riverbanks of the Ganges and Gorai River, and the maximum sampling sites of cluster I were situated on both riversides. On the other hand, the sampling sites of cluster II were situated far from the riverbank of both rivers. The groundwater flows east-north to the west-south direction in the study area. The upper basin area is mainly the recharge zone, and the down basin area is the discharge zone. The maximum sampling sites of clusters I and II were sited in recharge and discharge zones, respectively. Irrigation water returns equally dispersed in both clusters’ farmlands. Due to geogenic and/or anthropogenic causes, samples no. 19, 22, 23, and 28 of cluster I in the PRM and POM periods, respectively, and sample no. 5

### Table 4: Principal component (5 components extracted) loadings of the analyzed parameters in the study areas (sorted by size).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Premonsoon (PRM)</th>
<th>Postmonsoon (POM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PC1</td>
<td>PC2</td>
</tr>
<tr>
<td>(1) EC</td>
<td>0.938</td>
<td>0.042</td>
</tr>
<tr>
<td>(2) TDS</td>
<td>0.937</td>
<td>-0.047</td>
</tr>
<tr>
<td>(3) Ca²⁺</td>
<td>0.865</td>
<td>0.110</td>
</tr>
<tr>
<td>(4) SO₄²⁻</td>
<td>0.828</td>
<td>-0.141</td>
</tr>
<tr>
<td>(5) HCO₃⁻</td>
<td>0.812</td>
<td>0.271</td>
</tr>
<tr>
<td>(6) TH</td>
<td>0.692</td>
<td>0.367</td>
</tr>
<tr>
<td>(7) K⁺</td>
<td>0.627</td>
<td>-0.303</td>
</tr>
<tr>
<td>(8) Mg²⁺</td>
<td>0.580</td>
<td>0.309</td>
</tr>
<tr>
<td>(9) Na⁺</td>
<td>0.431</td>
<td>-0.672</td>
</tr>
<tr>
<td>(10) pH</td>
<td>-0.224</td>
<td>0.624</td>
</tr>
<tr>
<td>(11) Depth</td>
<td>-0.091</td>
<td>-0.314</td>
</tr>
<tr>
<td>(12) Cl⁻</td>
<td>0.405</td>
<td>0.292</td>
</tr>
<tr>
<td>(13) PO₄³⁻</td>
<td>0.130</td>
<td>0.220</td>
</tr>
<tr>
<td>(14) NO₃⁻</td>
<td>0.362</td>
<td>-0.263</td>
</tr>
</tbody>
</table>

Note: bold numbers indicate strong loading (over 0.75).

**Figure 6**: Biplot (axis PC1 and PC2) of robust principal component analysis for (a) premonsoon (PRM) and (b) postmonsoon (POM) sampling periods.
of cluster II in the POM were detached from their cluster. So, except for the spatial cause, other factors were connected to the cluster deviation process.

\[
\text{Bicarbonate index (BCI)} = \frac{[Ca^{2+}] + [Mg^{2+}] + [HCO_3^-]}{[Na^+] + [K^+] + [Cl^-]}.
\]  

The bicarbonate index (BCI) measured (Equation (2)) the comparable ratio to bicarbonate of earth metals and chloride of base metals. The higher BCI value indicated the dominance of Ca-Mg-HCO_3 over sodic ions that lead to the priority of carbonate rock-water interaction rather than silicate or other rock weathering and seawater intrusion. It showed that the BCI values of the sampling stations included in cluster I were higher than those in cluster II in both periods (Table 5 and Figure 8). In PRM season, the BCI values were very scattered in both clusters. In the dry period, the river flow could not impact the mineralogy of water samples. But after the heavy rain, i.e., the POM season, the BCI values were very scattered in both clusters. In the dry period, the river flow could not impact the mineralogy of water samples. But after the heavy rain, i.e., the POM season, the BCI values were higher than those in cluster II in both periods than in cluster II. The effect of river flows on the mineral/weathering course and the mineralization of water in the aquifer basement are assumed. These assumptions are clarified through the next discussions.

The lithological formation can be a source of groundwater contamination. Several rock formations contain minerals such as Ca, Mg, Fe, Mn, and As, as well as some radioactive elements. The study observed a lithologic impact on the ionic concentration of samples. The upper Ganges basin (study area) is divided into two platforms viz. young Gangetic alluvial, Ga (Holocene), and deltaic flood plain alluvial deposit, Da (early Pleistocene). Ga consists of marsh clay, tidal mud, and deltaic silt, and Da consists of unconsolidated and partly consolidated sand, silt, and clay with some gravel [72]. The clay layer thickness of the platforms is significantly different approximately between 15 and 40 m, and it showed that this thickness of the Ga platform is higher than that of the Da platform [73]. The cluster analysis represented through the next discussions.

Figure 7: Hierarchical cluster analysis (HCA) showing associations between samples from different parts of the hydrologic system (x-axis: subgroups of samples with the number of samples in parentheses; definitions are in Table 3).
increases with the clay thickness \((m)\) of the sublayers in the sampling well increase (Table 5). So, the lithological formations are one of the most key impact factors controlling the groundwater chemistry. It seemed that the dissolved organic carbon and oxygen rich in clays and the subclay layer of aquifers cause the extra reductive dissolution of minerals and liberated excess ionic components into the water phase [74, 75].

Due to heavy rainfall in the monsoon, the heavy mineralization during weathering of minerals happened that contributed to more ionic components into the water phase. Instead, a huge recharge occurred through the coarse sandy soil/sediment formation of the Da platform in the monsoon period. For this reason, the higher water movement and lower residence time make lower contents of soluble water constituents. While in summer, except irrigation returned flow, there is no recharging that has occurred through rainfall or river water. In this period, the dissolution of minerals through weathering becomes in a lowering position. Moreover, a relatively higher level of \(Na^+, K^+, \text{ and Cl}^-\) in samples was obtained in the premonsoon due to excess evaporation in summer (see Table 2).

3.4. Geochemical Evaluation: Source Rock Weathering. The weathering processes of rock-water interaction are partially influenced by evaporation, carbonate dissolution, silicate weathering, evaporate dissolution, etc. [15, 76]. The feature of weathering processes illustrated in the bivariate plots of \(Ca^{2+}/Na^+\) vs. \(HCO_3^-/Na^+\) indicated a complete carbonate mineral dissolution during the PRM and POM seasons (Figure 10(a)). Another bivariate plot of \(Mg^{2+}/Na^+\) vs.
Figure 9: Bivariate plots of sample no. vs. bicarbonate index (BCI) value of each cluster.

Figure 10: Bivariate plot (a) Ca/Na vs. HCO₃/Na, and (b) Ca/Na vs. Mg/Na to classify the mineral weathering of groundwater in the study area. The boxes characterize the ranges of estimated compositions of the three main source end members (evaporate dissolution, silicate weathering, and carbonate dissolution) without any mixing.
Ca\(^{2+}/Na^+\) (Figure 10(b)) demonstrates higher magnitudes of Ca\(^{2+}/Na^+\) and Mg\(^{2+}/Na^+\) ratios for groundwater (PRM: 4.0, 2.33; POM: 5.8, 2.4, respectively). The observed higher molar ratio of groundwater ascribed the influence of carbonate dissolution rather than silicate weathering [77]. So, carbonate dissolution was a major process controlling the salt contents in groundwater for both seasons.

The earth metal ions Ca\(^{2+}\) and Mg\(^{2+}\) may come to the groundwater from dolomite or other rocks like magnesite, calcite, aragonite, and gypsum. The study observed that these ions are not strongly correlated and associated with any component number in the component analysis (Tables 2 and 3). So, they are not driven into groundwater from the same rock source. As stated by Woocay and Walton [16], if the molar ratio of Ca\(^{2+}/Mg\(^{2+}\) in the groundwater sample is equal to one (1) it indicated both cations originated from the same source (dolomite rocks), while a greater ratio than 1 (one) may represent a more dominant calcite contribution from the rocks [78]. This molar ratio of Ca\(^{2+}\) and Mg\(^{2+}\) in the samples ranges from 0.94 to 4.08 with an average of 1.95 in the PRM period, whereas 1.16 to 3.98 with an average of 2.53 in the POM period. The datasets showed that both cations originated from separate sources, i.e., Ca\(^{2+}\) from calcite and Mg\(^{2+}\) from dolomite in 80% of the samples. The same source (dolomite) was found in 20% of the samples in the POM season. But these cations were driven 100% of the samples into groundwater from separate sources in the POM season. The spatial pattern in the ratio of Ca\(^{2+}\) and Mg\(^{2+}\) showed the variation from the southwest to northeastern parts of the study area. The ratio was the highest towards the lower flood plain to the upper flood plain zone (cluster I), due to the increase in Ca\(^{2+}\) concentration through the weathering of carbonate rocks in the discharge area.

There was not enough cation exchange occurred in groundwater of the study area that could be clarified by the plot of \([\text{Na} + K]-\text{Cl} vs. [(\text{Ca} + \text{Mg}) - (\text{HCO}_3^- + \text{SO}_4^{2-})]\) (Figure 11(a)). If the effective cation exchange within Na\(^+\) and (Ca\(^{2+}\) + Mg\(^{2+}\)) was active in an aquifer, the slope would be the negative value (i.e., \(m = -1\) in \(y = mx + c\)). In the scattered plot, the weak negative slope \((m = -0.408)\) of the plot was found only in the POM sampling period. Thus, this fact indicated a minor cation exchange occurred in the POM season [15, 35]. But in the PRM season, the slope showed a slightly positive value \((m = +0.1088)\), indicating no cation exchange occurred in that season. So, earth metal concentrations are mostly depending on mineral dissolution or weathering processes.

The Cl\(^-)/HCO_3^-\) ratio shows the influence of salinization may be due to the seawater mixing with groundwater. This ratio is ranged from 0.05 to 0.24. Figure 11(b) shows that the linear line has significantly correlated between Cl\(^-)/HCO_3^-\) and Cl\(^-\). All groundwater samples exhibited Cl\(^-)/HCO_3^-\) ratio lower than 0.5, which means the groundwater was unaffected by seawater [16, 79]. Especially in the dry season, the saltwater of the Bay of Bengal blowup to the Southern zone is just behind the 100 km distance [80, 81]. So, the aquifers of the study area are safe from saltwater intrusion.

3.5. Saturation Index (SI) and Mineral Solubility. The water-rock interaction controls the geochemistry of the groundwa-
ter. The equilibrium calculation of mineral-water reaction can predict the thermodynamic control on the composition of groundwater [82]. The saturation index (SI) was applied to predict the reactive minerals in the subsurface layers. The index value illustrated whether water would tend to dissolve or precipitate a particular mineral. The SI is calculated by comparing the chemical activities of the dissolved ions of the mineral (ion activity product (IAP)) with their solubility product \((K_{sp})\) at a certain temperature Equations (3) and (4) with the help of the PHREEQC-3v program [83].

\[
A_iB_j(\text{mineral}) := [A]^a \times [B]^b, \tag{3}
\]

\[
SI = \log \frac{[A]_{\text{actual}}^a \times [B]_{\text{actual}}^b}{[A]_{\text{eq}}^a \times [B]_{\text{eq}}^b} = \log \left(\frac{\text{IAP}}{K_{sp}}\right). \tag{4}
\]

A positive SI value indicates the supersaturation with minerals and a tendency for the mineral to precipitate from the groundwater, and negative SI indicates the tendency of the minerals to dissolve in groundwater. The SI values within a range of -0.5 to +0.5 for a given mineral can be interpreted as representing apparent equilibrium mixing in groundwater, which designates the tendency of minerals neither to dissolve nor precipitate in groundwater [84]. The saturation index values of some minerals are shown in Table 6.

It was observed from the dataset that there are around 90%, 20%, and 10% of the total groundwater samples \((n = 40)\) in the PRM season; the SI value for calcite, dolomite, and aragonite was found to be more than 0, respectively. These findings indicate that groundwater is oversaturation for those minerals, and therefore, they are precipitated [84]. So, the result indicated that most of the samples are supersaturated concerning calcite mineral \((\text{CaCO}_3)\) and lead to higher concentrations of Ca\(^{2+}\) and HCO\(_3^-\) in groundwater samples in both sampling periods in the study area. It was observed that the SI value of all minerals is somewhat higher in the POM relative to the PRM sampling season. For this reason, the concentration of Ca\(^{2+}\), Mg\(^{2+}\), and HCO\(_3^-\) in POM was found higher than that in the PRM season. The elevated SI value for calcite directed the possibility for a further increase in Ca\(^{2+}\), Mg\(^{2+}\), and HCO\(_3^-\) concentration in the waters of the study area due to additional dissolution of this type of mineral. Moreover, the partial pressure of carbon dioxide \((p\text{CO}_2)\) has a vital role in the rock weathering process. Equilibrium with atmospheric p\text{CO}_2 creates oversaturation concerning calcite and dolomite. But dolomite has slower precipitation kinetics than calcite [83]. The dissolution of carbonate minerals in the aquifers can be presented by the following chemical reactions:

\[
\text{CO}_2(\text{leached}) + \text{H}_2\text{O}(\text{saturation zone}) = \text{H}_2\text{CO}_3 \tag{5}
\]

\[
\text{CaCO}_3(\text{mainly calcite}) + \text{H}_2\text{CO}_3 \rightarrow \text{Ca}^2+ (\text{aq}) + \text{HCO}_3^- (\text{aq}) \tag{6}
\]
CaMg(CO$_3$)$_2$ (dolomite) + H$_2$CO$_3$ $\rightarrow$ Ca$^2+$ + H$_2$O + CO$_3$$_2^-$ (degas) (7)

H$_2$CO$_3$: $\rightleftharpoons$ H$_2$O + CO$_3$$_2^-$ (degas) (8)

In the above reactions, CO$_2$ is consumed and increased the concentration of Ca$^{2+}$, Mg$^{2+}$, and HCO$_3^-$ through H$_2$CO$_3$ formation. As the pCO$_2$ decreased, the HCO$_3^-$ concentration increased with the pH. The groundwater samples with calcite mineral saturated suggested that these carbonate minerals were the main components in the host rock. The concentrations of HCO$_3^-$ are caused by the CO$_2$ present in the soil zone formed by the weathering of rock materials due to alternate wet and dry conditions. Besides, the average temperature of the study area is 29°C which is sufficiently high to reduce the pCO$_2$. The origins of CO$_2$ in groundwater are (a) leached atmospheric CO$_2$, (b) weathering of carbonate minerals, and (c) microbial oxidation of organic carbon in oxic conditions and CO$_2$ from plant respiration [85]. The log$_{10}$($p$CO$_2$) of 40 groundwater samples in the study area was measured by the PHREEQC-3v program, and the average values of both sampling periods are shown in Table 6. The log$_{10}$($p$CO$_2$) values in groundwater range from -2.461 to -0.880 with an average of -1.953 ($\pm$0.261) in premonsoon (PRM) and -3.512 to -1.259 with an average of -2.272 ($\pm$0.446) in postmonsoon (POM) season which is higher than the atmospheric partial pressure of CO$_2$ ($p$CO$_2$ = $10^{-3.414}$ or log$_{10}$($p$CO$_2$) = -3.414, or 385 ppm) at equilibrium condition [86]. It indicated that above (b) and (c) sources of CO$_2$ (soil CO$_2$) in groundwater are predominant in the study area, which controls the total geochemical process. Since the dissolved CO$_2$ gas pressure of the water is higher than that of the atmosphere, the waters are supersaturated concerning carbonate minerals. Besides, the soils of the study area are sandy, clay-sandy, and gravel type that make very coarse topsoil. During the infiltration of rainwater, the atmospheric CO$_2$ enters the soil, producing H$_2$CO$_3$ that increases the dissolution of carbonate rocks.

Regarding the potentiality of rocks saturation in groundwater, the value of log$_{10}$($p$CO$_2$) mutually depends on the concentration of HCO$_3^-$, water pH, the quantity of organic matters, and the equilibrium constant for H$_2$CO$_3$ ($H_2CO_3$ $\rightleftharpoons$ $H^+$ + HCO$_3^-$) [71, 86–88]. But the molar concentration of HCO$_3^-$ is very insignificant to $p$CO$_2$ for groundwater compared to the pH value [85]. For the calculation of log$_{10}$($p$CO$_2$), Macpherson [86] used a modeled equation, alike to PHREEQC-3v, in which the term of log$_{10}$[HCO$_3^-$] is small compared to the pH because concentrations are the order of $10^{-3}$ molar and values of pH mostly range from 6.5 to 8.5, suggesting a minimal effect on the estimated CO$_2$ values. In the PRM season, the maximum groundwater...
samples are slightly acidic (pH < 7) and HCO₃⁻ were found relatively at a lower concentration than the POM season. As expected, the average value of log₁₀(pCO₂) is inversely proportional to that of pH (Figure 12) and directly proportional to that of HCO₃⁻ (Figure 13).

The high pCO₂ in the saturation zone led to producing more H₂CO₃ by adding H₂O, and the association constant of CO₂ is sufficiently high (K_{CO₂} = 10^{-1.5}, at 25°C) [75, 76]. This weak acid has a low dissociation constant (K_{H₂CO₃} = 10^{-6.40}, at 25°C) that indicated a few amounts of
H$_2$CO$_3$ dissociation or degassing of CO$_2$ occurred (Equation (8)). But at higher pH, the rate of forwarding reaction of H$_2$CO$_3$ dissociation becomes high. The excess H$_2$CO$_3$ will react with Ca$^{2+}$ and Mg$^{2+}$ and may precipitate in calcite supersaturation solution. So, log$_{10}$($p$CO$_2$) governs the rate of recrystallization of carbonate minerals. For the above-mentioned reasons (Equations (5)–(8)), at high pH in the postmonsoon (POM) period, the log$_{10}$($p$CO$_2$) value of water samples is getting higher than that in the premonsoon (PRM) season. That is why, the overall HCO$_3^-$ concentration of samples in the POM period was found higher than PRM. In addition, based on hierarchical cluster analysis (Figure 6), sample sites of cluster I are situated in the riverbanks, and those samples carry a higher concentration of HCO$_3^-$ and lower pH value. The $p$CO$_2$ in river water is usually out of equilibrium with the atmosphere. These waters contain a significant portion of CO$_2$, and the rate of reequilibrium with the atmosphere is relatively slow. Especially in POM, large amounts of river water penetrate the groundwater and make it over H$_2$CO$_3$ saturation, and HCO$_3^-$ concentration becomes high with lower pH in the same season.

4. Strategy of Water Quality Management

The geochemical processes and lack of management in anthropogenetic activities have a combined effect on the water chemistry in the study area. The geochemical and water quality assessment explored the heavy mineralization through water-rock interaction that occurred in groundwater. The value/concentration of EC, TDS, Ca, and HCO$_3^-$ and total hardness (TH) of groundwater samples crossed the national standard for drinking and irrigation purposes [21]. Other studies of these authors confirmed the higher loading of some trace metals such as Fe, Mn, and Pb in the groundwater of the present study area [88, 89]. Also, these authors evaluated the water quality for drinking and irrigation purposes, and the findings are not fully suitable for these uses. Without any treatment, people in the study area are directly consumed with shallow well raw water. So, special attention should be paid to reducing the heavy hardness and some trace metals in tube wells water and special measures need to be taken to protect children, the most vulnerable population, from trace metal toxicity. The following very simple techniques may be utilized to regulate water quality management:

(i) Mechanical coagulation, low-cost and homemade filtration (using green sand and biosand), and solar disinfection can reduce the water hardness, iron, and microbes. The natural process of oxidation may be used by injecting air into the water to precipitate some harmful metals from the water

(ii) This study suggests that it should use deeper aquifer water that contains a relatively lower amount of Ca, Mg, and HCO$_3^-$ in case of both uses for drinking and irrigation

(iii) A field study confirmed that the hardness and turbidity of single owners’ well water are generally higher than the common user’s well. As much water withdrawal led to higher water movement and mixing heavily in aquifer levels, it results in less water residence time. This could reduce the excess mineralization resulting the less ionic concentration in groundwater. The WHO and other water regulatory authorities have already been emphasized community-based drinking water pumping [90]. So, this study suggests the local government ensure community-based water distributions instead of a single-owner system

5. Conclusion

The study conducted the geochemical analyses using statistical tests, graphical analysis, and computer programs to identify the origin of solutes and evaluate the geochemistry of groundwater. All most neutral pH (PRM: 7.02, POM: 7.83) and higher EC (PRM: 669.6, POM: 956.8), TDS (PRM: 413.2, POM: 601.5 mg/L), and total hardness (PRM: 362.2, POM: 4.4.7 mg/L) of groundwater samples were the main geochemical characteristics in the study area. The result showed that the value of Ca, HCO$_3^-$, and TH crossed the national and international acceptable levels for drinking and irrigation purposes. The study exposed that the order of abundance of cations in samples is Ca$^{2+}$>Mg$^{2+}$>Na$^+$>K$^+$ and of anions is HCO$_3^->Cl^->SO_4^{2-}>NO_3^->PO_4^{3-}$. The correlation coefficient values of water variables indicate the associations among various parameters that find the different natural geochemical processes. The principal component analysis (PCA) revealed that the chemical properties of the groundwater were caused by rock-water interactions, mixing, or external influences. The analysis confirmed a few anthropogenic pollutions (fertilizer depositions) of groundwater with NO$_3^-$ and PO$_4^{3-}$. Hierarchical cluster analysis showed that two distinct groundwater zones were observed to be more affected by neighboring river flow, irrigation return flow, and freshwater intrusion from the rivers. It was found that the samples of cluster I carry more bicarbonate of earth metals with high EC than cluster II’s samples. Diagram methods indicated that the analyzed samples were mainly Ca-HCO$_3^-$ type, and rock-weathering was found to be the dominant natural process in the analyzed samples. The mass balance and saturation index (SI) values indicated that 80% and 20% of groundwater were supersaturated with the calcite and dolomite, respectively, in the PRM season. Besides, nearly 100% of samples were supersaturated concerning only the calcite in the POM period. In the study area, the water CO$_2$ mostly controlled the water pH, and later, both water pH and excess aquifer CO$_2$ controlled the water-rock equilibrium reactions. Thus, the chemical features of groundwater in the study area were largely dependent on the water-rocks interaction, carbonate-based mineral dissolution, and local lithological conditions and mostly on neighboring river morphology. The study findings may be used for better management of the water resources on a regional scale and may put on another area with similar topography.
Data Availability

The data that support the findings of this study are included in the article.

Conflicts of Interest

The authors declare that they have no conflict of interest.

Authors’ Contributions

Islam MS participated in the design and performance of the experiments and writing the primary manuscript draft and revised draft preparation. Mostafa MG analyzed the data, drafted the revision, and finalized the manuscript for submission.

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