Hydrochemical characteristics and aquifer properties present a better understanding of the mitigation of groundwater pollution, which has become one of the leading environmental concerns and threats to the sustainable ecosystem. Seventy-seven groundwater samples were collected from Sargodha District (Pakistan) and characterized for their physical and chemical properties. The analytical data were processed for the evaluation of the processes that control the groundwater chemistry using various drinking and agricultural indices with statistical and hydrochemical modeling. The predominant hydrochemical type was found to be Ca-HCO$_3$ type, followed by Na-HCO$_3$ and Mg-Ca-Cl types. The present study showed that the main factors controlling the groundwater chemistry were the prevalent rock dominance alongside the weathering of silicates, solubilization of carbonates, and cation exchange processes. Entropy water quality index (EWQI) revealed that 6.51% represented "poor water," while 7.79% were considered "extremely poor" for drinking purposes. However, USSL classification, Wilcox diagram, and other agricultural indices (RCS, SAR, %Na, MH, PI, and PS) showed that the majority of the samples were classified as suitable for irrigation purpose. However, 16% of the samples for %Na and 24% of the samples for MH were not suitable for agricultural purposes. Overall, the groundwater quality was affected by the anthropogenic stress in the study area.

1. Introduction

The quality of life, stability of the ecosystem, and socioeconomic development are critically dependent on the provision of safe water resources [1]. The total volume of fresh groundwater ($3.0 \times 10^6$ km$^3$) is only a small fraction (0.199%) of the overall volume of water on earth but it is under severe threats due to overconsumption and deteriorating quality [2]. The blaming factors for the depleting freshwater resources are both anthropogenic and geogenic [3]. Abrupt climatic changes, temperature, soil moisture, disruptions in rainfall patterns, rapid population growth, intense urbanization, groundwater overexploitation, and overpumping [4–6] are the key factors posing the negative effects on available freshwater resources. Moreover, the groundwater is more vulnerable to pollution through multiple pathways [7] which may cause critical health damages [8]. Therefore, the deteriorating quality of groundwater must be controlled for sustainable environment and preservation of the ecosystem [9]. The improper use of fertilizers, pesticides, mining activities, and industrial effluents [10] has a direct impact on groundwater quality. Besides anthropogenic activities, some natural processes are also associated with serious damages, including waterlogging/salinization and seawater intrusion [11]. Effective measures for groundwater preservation and management should be implemented by considering all adverse factors.

Every country prioritizes the provision of safe water supplies to its nation, but water-related risks pose hindrances to the stable supplies [12]. Pakistan is one of the thirty-six
countries with “extremely high” baseline water stress levels. About 80% of the available water is vulnerable to scarcity for domestic, agricultural, and industrial needs [13]. With deteriorating water quality [1], Pakistan is also facing water resource deficiency. Shortage of the storage capacity [14], drop in per capita water availability (82.73%), and abruptly elevating growth rate (2.5%) [15] are the key stress factors under the current scenario. Generally, rainfall recharge, groundwater recharge, and irrigation system recharge contribute to the overall potential of groundwater [16]. In recent decades, the vulnerability of Pakistan groundwater has been exacerbated by multiple factors. Entrapped heavily mineralized groundwater has been reported containing 400-20,000 ppm of TDS [17]. The higher concentrations of arsenic and chromium have been reported in the groundwater of Lahore, Muzaffargarh, and Maili [18, 19]. Similarly, excessive fluoride concentration has been reported in Rahim Yar Khan [20]. Various hydrogeochemical methods have been applied to evaluate the suitability of groundwater for drinking and agricultural purposes in different parts of the world; these methods suggested diverse approaches to cope up with the deteriorating water quality [21, 22].

The agricultural and domestic needs are mostly met by groundwater, which is getting vulnerable by the aforementioned factors. Strict measures to protect and preserve the groundwater resources must therefore be launched. The present study was conducted in Sargodha District, Pakistan, with the major aim to determine the drinking and irrigation reliability of the groundwater samples collected from the confined aquifer. Previous works in the study area include preliminary and simplistic estimation of the condition of groundwater without characterizing the specific factors that influence the quality of the water. However, the main objective of the current study was to assess the quality of water by analyzing different physicochemical parameters and their interrelationships by statistical techniques and graphical analysis. Such integrated approaches help to determine the unknown factors affecting the hydrochemistry of the groundwater and yield more meaningful results for the efficient management of the water resources. The finding from this study would provide valuable knowledge on the study area’s groundwater quality, and it may assist in the implementation of a sound management method in other regions.

2. Description of the Study Area

Sargodha District is the part of Punjab which is the most populated province of Pakistan [18]. Sargodha covers a surface of 5,854 km² (Figure 1) from latitudes 31°34’ to 32°36’ N and length 72°10’ to 73°18’ E. With a population of 659,862, Sargodha is Pakistan’s 12th largest city. River Chenab bounds it on the east, district Jhang on the south, and district Khushab on the west [19]. The region has a hot semi-arid climate (BSH), hot and sprinkling summers and dry cool winters with a minimal level of precipitation. The annual average temperature and precipitation were recorded at
23.8°C and 410 mm, respectively, in the study area [23]. The main crops of the area are wheat, gram, barley, rice, sugarcane, and cotton.

2.1. Geological and Hydrogeological Setting. The southwest slope of the land is approximately 0.3 to 0.4 meters per kilometer. The adjacent flooding plains in the center of the plain rise by terraces or bars to 50 feet. Explorative drilling showed that the 1500-meter thick quaternary alluvium with the scattered bedrock hills (Kharana Hills) had overlaid Precambrian basement rocks and breaks the low relief of the plain and terraces [21]. Meander-belt deposits, stream-belt deposits, and flood-plain deposits (Figure 1) cover the area. The soils consist of the alluvial substance carried by the river Indus and its tributaries. There are heterogeneous alluvial deposits, and the vertical and horizontal continuity of individual strata is limited. The soil is mostly reddish-brown to grayish-brown, medium-textured with a high portion of very fine sand, and small amounts of clay and gravel [22]. The alluvial complex is composed mainly of fine to medium sand, silt, and clay. Silty or clayey sand is found to embed pebbles of siltstone and mudstone. Despite their heterogeneity, the alluvial deposits form a unified highly transmissive nonartesian aquifer [24]. The uppermost 300-feet strata are compacted but highly productive. The water table in the area extends from 2 to 7 m with an average depth of 3.5 m. The contour map of the water level (Figure 1) is obtained by the calculation of the individual hydraulic heads, which determines the direction of flow of the groundwater, which is mostly southwest. The hydraulic head in the study area varies from 129 m to 171 m (with average of 150 m) [22].

3. Material and Methods

3.1. Sample Collection and Analysis. Groundwater samples (n = 77) were collected in 1.5 L capacity polystyrene bottles from various tube wells, dug wells, boreholes, and hand pumps located in the study area from the nonartesian aquifer. The detailed analyses were carried out employing standard methods in the water quality labs of the Pakistan Water Resources Research Council (PCRWR) [25]. The sampling of groundwater was carried out using 0.45 μm membranes through the filtration process. After filtration, groundwater samples were put in two simulated polyethylene bottles. A multiparameter analyzer (Hanna HI9829) was used to measure the values of EC, TDS, and pH at the field. A UV–Visible spectrophotometer was used for the analysis of sulfate. Bicarbonates were titrated against sulfuric acid as a titrant in 100 mL of water using a volumetric process. In order to analyze the main cations, an atomic emission spectrometer was used. Other ions were estimated by volumetric methods. Cations and anions were computed through standard ionic concentration procedures. The analytical methods used in the present study are summarized in the supplementary material (Table S1). The credibility of every sample was validated by computing the charge balance error (CBE) as shown in equation (1) (where all ionic concentrations refer to meq/L). The samples having CBE < ±5% were chosen for further analyses [26].

\[
CBE = \left[ \frac{\Sigma \text{Cations} - \Sigma \text{Anions}}{\Sigma \text{Cations} + \Sigma \text{Anions}} \right] \times 100. \tag{1}
\]

3.2. Water Quality Assessment

3.2.1. Entropy Water Quality Index (EWQI). Water quality index (WQI) is a basic and effective method for determining the drinking water suitability, which has been commonly used worldwide [27]. The traditional WQI approach suffers from some serious limitations and could not provide meaningful information on the quality of groundwater (inconclusive weight for every chemical parameter). The results therefore cannot be representative of the quality of groundwater. In the present work, an advanced WQI method was used to measure the overall quality of groundwater using entropy weight (entropy water quality index (EWQI)) [28]. EWQI was determined using the following relationship [29]:

\[
\text{EWQI} = \sum_{j=0}^{n} w_j q_j, \tag{2}
\]

where \( n \) corresponds to the number of chosen parameters for calculating the EWQI, \( w_j \) indicates the \( j \)th parameter entropy weight, and \( q_j \) indicates the \( j \)th parameter quality rating scale. Equation (3) was used to calculate the entropy weight \( (w_j) \) for each parameter.

\[
w_j = \frac{1 - e_j}{\sum_{j=1}^{n} (1 - e_j)}. \tag{3}
\]

The information entropy \( (e_j) \) is expressed by following relationship:

\[
e_j = -\left( \left( \frac{1}{\ln m} \right) \right). \tag{4}
\]

where \( m \) indicates the overall sample number and \( P_{ij} \) is the index value ratio for the \( j \) index for sample \( i \) and is calculated by using equation (5):

\[
\frac{y_{ij}}{\sum_{i=1}^{m} y_{ij}}, \tag{5}
\]

where \( y_{ij} \) is the standardized value of the \( j \)th parameter for the \( i \)th sample. The construction function of normalization for efficiency type is calculated by using following equation:

\[
y_{ij} = \frac{C_{ij} - C_{j}^{\min}}{C_{j}^{\max} - C_{j}^{\min}}, \tag{6}
\]

where \( C_{ij} \) represent the observed value of the \( j \)th parameter of \( i \)th sample, \( C_{j}^{\min} \) and \( C_{j}^{\max} \) represent the minimum and maximum values of the \( j \)th parameter, respectively.
The second step in the EWQI estimation is the calculation of a quality rating scale \( q_j \) for each parameter. The \( q_j \) value is calculated by using the following relationship:

\[
q_j = \frac{C_j}{S_j} \times 100, \quad (7)
\]

while \( C_j \) is the measured concentration (mg/L) of each parameter and \( S_j \) is the desirable limit (mg/L) for an individual parameter according to WHO standards.

WQI is an effective technique for the demarcation of groundwater quality and its appropriateness for drinking. This approach is aimed at providing a framework for the presentation of a cumulatively generated numerical expression that describes a given water quality that is commonly used around the world because of the ability to convey knowledge regarding water quality entirely. Several scholars around the world performed studies in different areas, such as the quality evaluation of groundwater [30–33]. However, the weight of a parameter is typically provided by specialists based on their specific knowledge during the WQI estimation process. These are very arbitrary, with a lot of important and beneficial water quality details missing. The EWQI has been regarded as the most unbiased index for the measurement of drinking quality across all widely used indices. The present study provides an outline of groundwater quality evaluation in the Sargodha District with entropy weights for drinking purposes.

### 3.2.2. Agricultural Water Quality Assessment

The assessment of water quality for irrigation purposes was evaluated by considering United States Salinity Laboratory (USSL) diagram, Wilcox diagram, sodium absorption ratio (SAR), residual sodium carbonate (RSC), percentage sodium (%Na), permeability index (PI), magnesium hazard (MH), and potential salinity (PS). The significance/methodology for calculation of these indices is briefly described below:

**Sodium Hazard** may result in the reduction of the soil permeability and osmotic activity, and therefore, it can inhibit the water from reaching branches and leaves. Sodium absorption ratio (SAR) was quantified by following relation [34]:

\[
\text{Sodium Absorption Ratio} = \text{SAR} = \frac{\text{Na}^+}{\sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+})/2}}. \quad (8)
\]

The adequacy of groundwater for irrigation can also be measured using residual sodium carbonate (RSC) using the following relationship [35]:

\[
\text{Residual Sodium Carbonate} = \text{RSC} = \left(\text{CO}_3^{2-} + \text{HCO}_3^-\right) - \left(\text{Ca}^{2+} + \text{Mg}^{2+}\right). \quad (9)
\]

RSC measured the association between the sum of carbonates/bicarbonates and the sum of calcium/magnesium. Generally, if adsorption of sodium in the soil can be increased at higher RSC values, this may lead to the infertility of soil [36]. Elevated levels of Na are commonly associated with saline soil formation, which in return causes less productivity and severe environmental impacts on the irrigation. Crop germination/yields are adversely affected by saline conditions [37]. Percentage sodium was calculated by the following relationship:

\[
\text{Percentage sodium} = \%\text{Na} = \left[\frac{\text{Na}^+ + \text{K}^+}{\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+} + \text{Mg}^{2+}}\right] \times 100. \quad (10)
\]

Prolonged use of highly saline irrigation water can adversely affect the permeability of soil [38]. Doneen [39] proposed the permeability index (PI) which may be used to assess the influence of the ionic contents on soil’s permeability. PI was calculated by following relationship:

\[
\text{Permeability Index} = \Pi = \left[\frac{\text{Na}^+ + \sqrt{\text{HCO}_3^-}}{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+}\right] \times 100. \quad (11)
\]

Magnesium hazard was proposed by Szabolcs [40], and it can be calculated by following relationship:

\[
\text{Magnesium Hazard} = MH = \left[\frac{\text{Mg}^{2+}}{\text{Ca}^{2+} + \text{Mg}^{2+}}\right] \times 100. \quad (12)
\]

It is another agricultural index which can evaluate the extent of damage caused by magnesium in irrigation water with respect to the soil structure. The soil’s infiltration capacity is reduced by the higher content of Mg in groundwater, which may lead to the higher adsorption of water between magnesium and clay particles [41].

Potential salinity is an important index which depends upon the chloride and sulfate concentrations. Doneen proposed that the precipitation of low soluble salts in soils hinders the infiltration capacity, which consequently affected the productive yields [39]. Potential salinity can be calculated by the following relationship:

\[
\text{Potential Salinity} = \text{PS} = \text{Cl}^- + \sqrt{\text{SO}_4^{2-}}. \quad (13)
\]

Concentrations of all parameters are shown as meq/L in the above relationships.

### 4. Results and Discussion

#### 4.1. Physicochemical Characteristics

The statistical summary related to the distribution of physicochemical parameters is presented in Table 1. The groundwater showed mostly neutral to slightly alkaline pH, which ranged from 6.94 to 8.22 with a mean value of 7.6. The pH of groundwater in the present study thus remained within the range of national (Pakistan Environmental Protection Agency) and international standards (WHO & USEPA). The measured levels of electrical conductivity (EC) and total dissolved solids (TDS) in the present study showed moderate to high trends ranging from 220 to 1901 μS/cm (average...
Table 1: Statistical summary of the physicochemical parameters (units of all parameters are mg/L, except pH and electrical conductivity (EC) μS/cm) (n = 77).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>pH</th>
<th>EC</th>
<th>TDS</th>
<th>TH</th>
<th>HCO₃⁻</th>
<th>Cl⁻</th>
<th>F</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>Fe</th>
<th>Reference</th>
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<tr>
<td>Minimum</td>
<td>6.94</td>
<td>220</td>
<td>141</td>
<td>11</td>
<td>95</td>
<td>7</td>
<td>0.01</td>
<td>0.19</td>
<td>9</td>
<td>20</td>
<td>2.43</td>
<td>6</td>
<td>0.9</td>
<td>0.01</td>
<td>Present study</td>
</tr>
<tr>
<td>Maximum</td>
<td>8.22</td>
<td>1901</td>
<td>1206</td>
<td>760</td>
<td>575</td>
<td>330</td>
<td>2.88</td>
<td>14</td>
<td>442</td>
<td>180</td>
<td>75.3</td>
<td>255</td>
<td>142</td>
<td>2.88</td>
<td></td>
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<tr>
<td>Mean</td>
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<td>596</td>
<td>265</td>
<td>287</td>
<td>82.5</td>
<td>0.48</td>
<td>1.60</td>
<td>114</td>
<td>61.86</td>
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<td>9.64</td>
<td>0.332</td>
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<tr>
<td>Median</td>
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<td>870</td>
<td>556</td>
<td>265</td>
<td>285</td>
<td>67</td>
<td>0.34</td>
<td>0.60</td>
<td>101</td>
<td>56</td>
<td>24.3</td>
<td>96</td>
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<tr>
<td>Standard Deviation</td>
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<td>486</td>
<td>308</td>
<td>131</td>
<td>119</td>
<td>74.8</td>
<td>0.504</td>
<td>2.57</td>
<td>92.5</td>
<td>33.71</td>
<td>16.7</td>
<td>70.2</td>
<td>20.5</td>
<td>0.568</td>
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</tr>
<tr>
<td>WHO limits</td>
<td>6.5-8.5</td>
<td>1000</td>
<td>600</td>
<td>300</td>
<td>250</td>
<td>250</td>
<td>1.50</td>
<td>10</td>
<td>250</td>
<td>200</td>
<td>150</td>
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<td>NSBL (%)</td>
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<td>38</td>
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<td>—</td>
<td>500</td>
<td>250</td>
<td>250</td>
<td>1.50</td>
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<td>50</td>
<td>189</td>
<td>182</td>
<td>3.22</td>
<td>0.08</td>
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<td>10</td>
<td>50</td>
<td>189</td>
<td>182</td>
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<td>—</td>
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<td>8.64</td>
<td>56.6</td>
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<td>292</td>
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<td>456</td>
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<td>— [52]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Northeastern Mexico</td>
<td>7.47</td>
<td>1176</td>
<td>—</td>
<td>369</td>
<td>56.5</td>
<td>—</td>
<td>—</td>
<td>240</td>
<td>187</td>
<td>20.9</td>
<td>50.6</td>
<td>0.84</td>
<td>— [58]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

939.1 μS/cm) and 41 to 1206 mg/L (average 596.2 mg/L), respectively. Nonetheless, about 41% of the samples for EC and 13% of the samples for TDS were found to exceed the WHO guideline limit [42]. Total hardness (TH) of the groundwater ranged from 11 to 760 mg/L with an average value of 265.3 mg/L; more than 38% of the samples were found to exceed the WHO guidelines. Significantly random variations of the abovementioned parameters were mainly attributed to the interaction of rock water under the influence of excessive anthropogenic activities, which lead to the solubilization of the minerals and salts [41].

The general abundance of the major cations in the groundwater was found in the order of Na > Ca > Mg > K > Fe as shown in Table 1. Measured concentrations of Na and K vary from 6 to 255 mg/L and 0.9 to 142 mg/L with average levels of 99.7 mg/L and 9.6 mg/L, respectively. It was noted that nearly 10% of the samples for Na and 16% of the samples for K exceeded the WHO guideline value. Extensive interaction and contact between groundwater and surrounding rocks under anthropogenic influence may lead to the elevated contents of Na and K [43]. Among rest of the elements, Ca and Mg ranged from 20 to 180 mg/L and 2.43 to 75.3 mg/L, with mean concentrations of 61.9 mg/L and 7.1 mg/L, respectively. Relatively higher levels of Ca and Mg may be ascribed to the dissolution of the carbonates in the rocks under extensive environmental stress. The concentration of Fe in the current study varied from 0.01 mg/L to 2.88 mg/L with the mean contents of 0.300 mg/L; in this case, about 23% of the water samples exceeded the WHO standard limits.

The dominance of anions in the groundwater was found in the order of HCO₃⁻ > SO₄²⁻ > Cl⁻ > NO₃⁻ > F⁻. The concentration of HCO₃⁻ in the present study ranged from 95 to 575 mg/L with an average level of 287.5 mg/L and approximately 57% of the samples were found to exceed the WHO guidelines. The measured concentration of Cl⁻ and SO₄²⁻ varied from 7 to 330 mg/L and 9 to 442 mg/L, respectively. About 6% of the samples for Cl⁻ and 4% of the samples for SO₄²⁻ were found to exceed the WHO guidelines. Elevated concentrations of these ions may be credited to the solubilization of halite, gypsum, and sulfate-bearing minerals under varying anthropogenic influences. The measured levels of nitrate-N ranged from 0.19 to 14 mg/L with an average level of 1.60 mg/L; in this case, majority of the groundwater
samples fall within the safe limits. Wastewater irrigation and prolonged use of the fertilizers were the primary causes of moderately higher concentrations of nitrate-N in the groundwater of the study area [44]. The estimated concentration of F⁻ in the groundwater ranged from 0.01 mg/L to 2.88 mg/L (average level of 0.50 mg/L), and most of the samples were found within the WHO permissible limits.

Elevated concentration of fluoride can be associated with serious toxicological and geoenvironmental issues; long-term consumption may cause dental decay and skeletal fluorosis [45].

Average levels of various parameters in groundwater samples from Sargodha were also compared with the mean levels reported from other regions around the world as shown in Table 1. Present levels of pH, EC, TDS, and TH were found to be almost comparable to those reported from Toba Tek Singh Pakistan [46]; Balochistan, Pakistan [47]; Uttar Pradesh, India [48]; and Thrace, Turkey [49]. However, the present values were comparatively lower than the reported levels from Heze, China [50], Northwest of Saudi Arabia [51], and Florina Basin, Greece [52]. However, the present mean values of these parameters were found to be considerably higher than the others reported studies in Table 1.

Mean levels of the anions estimated in the present study were relatively less than the reported levels from Balochistan, Pakistan and Heze, China, while almost comparable levels were reported from Thrace, Turkey. However, average concentrations of anions found in the present study were greater than most of the reported levels given in Table 1. The mean levels of major elements (Ca, Mg, Na, K, and Fe) showed higher mean concentrations in Sargodha compared with most of the reported levels in Table 1. However, the reported levels from Peshawar, Pakistan [53]; Heze, China; and Northwest of Saudi Arabia were found to be higher than the present mean levels. Nevertheless, the present levels showed almost comparable levels to those of Balochistan, Pakistan and Jalandhar, India [54].

4.2. Correlation Analysis. Pearson correlation is an important tool to express the association among different parameters in the groundwater. Table 2 shows the correlation coefficient matrix for various variables which revealed that Na was strongly correlated with Cl⁻ (r = 0.762) and SO₄²⁻ (r = 0.732), suggesting their derivation from mirabilite (Glauber's salt) and halite in the groundwater. Similarly, moderately strong correlation of HCO₃⁻ with Ca (r = 0.545) and Mg (r = 0.437) depicted the solubilization of carbonate-bearing rocks such as calcite and dolomite under anthropogenic influences. Very strong correlations were found between TDS and major ions including Na (r = 0.896), SO₄²⁻, Cl⁻ (r = 0.830), Mg (r = 0.725), HCO₃⁻ (r = 0.713), and Ca (r = 0.632). Similarly, EC also exhibited strong relationships with TDS (r = 0.986), Na (r = 0.900), Cl⁻ (r = 0.845), NO₃⁻ (r = 0.815), TH (r = 0.770), Mg (r = 0.709), HCO₃⁻ (r = 0.691), and Ca (r = 0.599). These relationships reflected the major contributions of these ions towards total ionic strength of groundwater and indicated considerable effects/contributions by human activities towards total pollution stress.

4.3. Hydrogeochemical Process. The interrelationship between Na and Cl is shown in Figure S1 (supplementary material). The molar ratio of Na⁺/Cl⁻ approaching to 1 suggested halite dissolution as a sole source for Na in the groundwater [55]. However, in the present study, majority of the samples deviated from the equilibrium line; therefore, the increase of Na in groundwater may be caused by other sources, such as silicate weathering and albite contribution under anthropogenic stress; extensive human activities in the area are other contributing factors elevated Na levels in the aquifer. Undersaturation of the groundwater with respect to the halite also supports this argument.

The existing levels of Ca, Mg, and HCO₃ in the groundwater are mainly dependent on the weathering of silicates, solubilization of the carbonates, and/or ion-exchange processes in the aquifer [56]. Relatively higher abundance of HCO₃ among the anions pointed out the prominence of weathering and solubilization [57]. Its influence can be further illustrated by the molar ratio of Na and total cations (TZ⁺) as shown in Figure S1 (supplementary material), where most of the samples fall near Na = 0.5 TZ⁺, which indicated the increment of Na in groundwater by silicate weathering and carbonate solubilization. These processes can be enhanced under anthropogenic influence particularly by the excessive use of the fertilizers, pesticides, and to some extent acid rain.

The scatter plot between Ca+Mg and HCO₃⁻+SO₄²⁻ (Figure S1) suggested that most of the samples fall along with the equilibrium-line (1:1), which indicated their major derivation by the solubilization of carbonates and sulfates. Generally, a close association with the equilibrium line is the indication of the dissolution of calcite, dolomite, and gypsum as the main sources of these ions [58]. In addition, a significant number of the groundwater samples fall around the equilibrium line in Ca + Mg versus HCO₃⁻ plot (Figure S1), which indicated considerable contribution of Ca by the solubilization of carbonates, which also increases under the varying anthropogenic stress. In addition, groundwater oversaturation of calcite and dolomite shows that groundwater can no longer be dissolved (Figure S2).

In order to elaborate the influence of silicate weathering, carbonate solubilization and evaporite dissolution, the Na-normalized Ca versus HCO₃⁻ plot (as shown in Figure 2(a)) and the Na-normalized Ca versus Mg plot (as shown in Figure 2(b)) were considered. Figure 2(a) illustrated that most of the groundwater samples fall within the silicate weathering zone and a few towards carbonate dissolution zone but none of them appeared near evaporite dissolution zone. Likewise, Figure 2(b) supported the derivation of Mg from silicate weathering as well as carbonate dissolution but negligible to the evaporite dissolution. Excessive silicate weathering also indicated considerable anthropogenic impact in the study area because under natural conditions silicate weathering is very slow and show only minor contribution. The evolution of groundwater geochemical developments can be significantly interpreted by cation exchange processes [59]. Schoeller [60] proposed the two chloroalkaline indices (CAI-1 and CAI-2) to explain the cation exchange processes occurring in the groundwater systems.
Following equations shows the relationship for calculating CAI-1 and CAI-2, where concentrations are expressed in meq/L.

\[
\text{CAI-1} = \frac{\text{Cl}^-}{(\text{Na}^+ + \text{K}^+)}
\]

\[
\text{CAI-2} = \frac{\text{Na}^+ + \text{K}^+}{(\text{Ca}^{2+} + \text{Mg}^{2+})}
\]

If both indices give positive values, then direct ion exchange occurs, while negative values show reverse ion exchange. Values of the two chloroalkaline indices are plotted in Figure 3(a). Majority of samples fall in the lower left corner undergoing the reverse ion exchange, which causes the Na increment and Ca decrement in the groundwater system. Few samples lie in the upper right corner signifying the direct ion exchange process in the groundwater. Such mixed contributions again specified anthropogenic impact.

Cation exchange can be further illustrated by the bivariate diagram between \((\text{Na}^+ + \text{K}^+)\) and \(\frac{(\text{Ca}^{2+} + \text{Mg}^{2+})}{(\text{HCO}_3^- + \text{SO}_4^{2-})}\) (Figure 3(b)). The increment of Na in the groundwater system excluding halite dissolution in expressed by \((\text{Na}^+ + \text{K}^+ - \text{Cl}^-)\), while the increment or decrement of Ca and Mg excluding the carbonates (calcite and dolomite) and sulfates (gypsum) dissolution is expressed by \(\frac{(\text{Ca}^{2+} + \text{Mg}^{2+})}{(\text{HCO}_3^- + \text{SO}_4^{2-})}\) [46]. In the present study, a linear trend between \((\text{Na}^+ + \text{K}^+)\) and \(\frac{(\text{Ca}^{2+} + \text{Mg}^{2+})}{(\text{HCO}_3^- + \text{SO}_4^{2-})}\) was witnessed with a slope value -0.944, which almost approached to -1, thereby indicating the ion exchange between Na and Ca/Mg.

4.4. Formation Mechanism of Groundwater Chemistry. Evaporation, crystallization, rock weathering, and precipitation are the key factors which can significantly affect the formation of groundwater chemistry [61]. Gibbs diagram [62] helps to determine the most influential factors and visualizes the association between aquifer lithological framework and groundwater chemistry [63]. The two subplots (Figures 4(a)

<table>
<thead>
<tr>
<th>pH</th>
<th>EC</th>
<th>TDS</th>
<th>TH</th>
<th>HCO$_3^-$</th>
<th>Cl$^-$</th>
<th>F</th>
<th>SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>Fe</th>
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<td>pH</td>
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<tr>
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<tr>
<td>TDS</td>
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</tr>
<tr>
<td>TH</td>
<td>-0.277</td>
<td>0.770</td>
<td>0.801</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>HCO$_3^-$</td>
<td>-0.094</td>
<td>0.691</td>
<td>0.713</td>
<td>0.593</td>
<td>1</td>
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<td></td>
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</tr>
<tr>
<td>Cl$^-$</td>
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<td>0.845</td>
<td>0.830</td>
<td>0.642</td>
<td>0.326</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>F</td>
<td>0.332</td>
<td>0.241</td>
<td>0.241</td>
<td>0.005</td>
<td>0.306</td>
<td>0.024</td>
<td>1</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>0.029</td>
<td>0.375</td>
<td>0.381</td>
<td>0.445</td>
<td>0.236</td>
<td>0.243</td>
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</tr>
<tr>
<td>NO$_3^-$</td>
<td>-0.114</td>
<td>0.815</td>
<td>0.841</td>
<td>0.741</td>
<td>0.417</td>
<td>0.641</td>
<td>0.221</td>
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</tr>
<tr>
<td>Ca</td>
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<td>0.599</td>
<td>0.632</td>
<td>0.870</td>
<td>0.545</td>
<td>0.479</td>
<td>-0.169</td>
<td>0.326</td>
<td>0.524</td>
<td>1</td>
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<tr>
<td>Mg</td>
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<td>0.709</td>
<td>0.725</td>
<td>0.803</td>
<td>0.437</td>
<td>0.619</td>
<td>0.199</td>
<td>0.439</td>
<td>0.749</td>
<td>0.417</td>
<td>1</td>
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<td></td>
</tr>
<tr>
<td>Na</td>
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<td>0.900</td>
<td>0.896</td>
<td>0.498</td>
<td>0.645</td>
<td>0.762</td>
<td>0.303</td>
<td>0.174</td>
<td>0.732</td>
<td>0.310</td>
<td>0.544</td>
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<tr>
<td>K</td>
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<td>0.242</td>
<td>0.225</td>
<td>0.095</td>
<td>0.298</td>
<td>0.102</td>
<td>0.448</td>
<td>0.152</td>
<td>0.050</td>
<td>0.165</td>
<td>-0.028</td>
<td>0.088</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td>-0.146</td>
<td>0.262</td>
<td>0.289</td>
<td>0.396</td>
<td>0.352</td>
<td>0.170</td>
<td>-0.006</td>
<td>0.128</td>
<td>0.223</td>
<td>0.264</td>
<td>0.422</td>
<td>0.177</td>
<td>-0.033</td>
</tr>
</tbody>
</table>

**Figure 2:** Plots of (a) Na-normalized Ca versus Mg and (b) Na-normalized Ca versus HCO$_3^-$.
and 4(b)) represent the association of TDS with weight ratio of Cl$^-$ versus (Cl$^-$ + HCO$_3^-$) and weight ratio of (Na + K) versus (Na + K + Ca), respectively. Rock/evaporation/precipitation dominances are the controlling factors that influence the groundwater chemistry as proposed by Khan [64]. As shown in Figure 4, all groundwater samples included in the present study fall into the rock dominance zone, thus signifying that rock weathering mainly controls the major ion chemistry in the study area and it helped to increase the soluble salts and minerals into the groundwater; these processes can be accelerated under the anthropogenic influence [36].

4.5. Hydrochemical Facies Classification. The interaction of chemical processes with lithological framework and flow dynamics are generally described by hydrochemical facies [65]. The Piper plot [66] is commonly used for the hydrochemical representation of the samples with their different hydrochemical regimes. In the present study, the majority
of groundwater samples belonged to Ca-HCO₃ type (42%) and Ca-Na-HCO₃ type (37%), followed by, Na-Cl type (15%) and Ca-Mg-Cl mixed type (5%) as shown in Figure 5. Consequently, it can be credited to recharge water, mineral solubilization, evaporation of shallow groundwater, and mixing of wastewater with Ca-HCO₃ water [67]. Majority of the samples fall in zone D (Na and K type) and zone B (mixed type) concerning cations, while few samples fall in zone A (Ca type), which showed the dominance of silicate weathering and ion exchange. As far as anions were concerned, majority of the samples fall in zone E (HCO₃⁻ type), followed by zone B (mixed type), depicting the prominence of carbonate weathering, while the dissolution of evaporite and gypsum is less influential in this study. The water type in the study area is thus significantly affected by excessive anthropogenic activities which resulted in dissolution of carbonate rocks.

![Piper plot](image)

**Figure 5: Piper plot for groundwater facies classification.**

<table>
<thead>
<tr>
<th>Water type</th>
<th>Excellent</th>
<th>Good</th>
<th>Moderate</th>
<th>Poor</th>
<th>Extremely poor</th>
</tr>
</thead>
<tbody>
<tr>
<td>EWQI range</td>
<td>&lt;50</td>
<td>50-100</td>
<td>100-150</td>
<td>150-200</td>
<td>&gt;200</td>
</tr>
<tr>
<td>No. of samples</td>
<td>24</td>
<td>28</td>
<td>14</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>%age of samples</td>
<td>31.6</td>
<td>36.3</td>
<td>18.2</td>
<td>6.51</td>
<td>7.79</td>
</tr>
<tr>
<td>%age of area</td>
<td>43</td>
<td>27</td>
<td>14</td>
<td>7</td>
<td>9</td>
</tr>
</tbody>
</table>

**Table 3: Classification of the groundwater samples according to EWQI.**

4.6. Suitability of Groundwater for Drinking Purpose. The classification of groundwater samples as per their EWQI ratings is illustrated in Table 3. In the present study, EWQI values varied from 14.03 to 344.3 among which 24 samples (31.6%) represented “excellent water,” 28 samples (36.3%) showed “good water,” 14 samples (18.2%) indicated “moderate water,” 5 samples (6.51%) represented “poor water,” while only 6 samples (7.79%) were considered “extremely poor.” Also, 7% and 9% of the total area lies under the poor and extremely poor water quality zone, respectively. The spatial distribution map of EWQI which demonstrates the suitability of water in the study area is shown in Figure 6, which revealed significant pollution and poor/very poor water quality in the northeast region of the study area along with some areas in southwest region. Consequently, the EWQI suggested that the impacted study areas required immediate
attention and remedial measures to address this issue before it may escalate to a major environmental hazard.

4.7. Suitability of Groundwater for Agricultural Purpose. Groundwater can be classified into four categories based on their SAR values; excellent (SAR < 10), good (10 < SAR ≤ 18), doubtful (18 < SAR ≤ 26), and unsuitable (SAR > 26). In the present study, the estimated SAR values ranged from 0.23 to 6.81 (average 2.61) as shown in Table 4. Consequently, the groundwater was categorized as excellent for agricultural purpose based on the SAR value. The USSL diagram may provide better insight by plotting SAR values against EC, and the results are shown in Figure 7(a), which revealed that 63 samples (81.2%) fall in $C_1S_1$, $C_2S_1$, and $C_3S_1$ categories which are considered suitable for irrigation purposes and portrayed little harm of Na exchange while only 14 samples (18.8%) fall in $C_2S_2$ and $C_3S_2$ categories, which cannot be recommended for irrigation due to their higher salinity [68]. Similarly, RSC values greater than 2.5 reflected unsuitability of the water for irrigation. In the present study, seventy-two samples (93.51%) were found suitable for agricultural practices as shown in Table 4.

Generally, %Na value less than 60 is assumed suitable for the irrigation. In the present study, its value ranged from 9.83 to 73.91 with an average value of 41.83; consequently, majority of the samples (84.42%) were found suitable for irrigation purposes. Wilcox diagram (Figure 7(b)) also showed that 63 samples (81.2%) fall in excellent to permissible zone, while only 14 samples lied in the permissible to the doubtful zone with respect to irrigation. Likewise, permeability index value greater than 25 is generally considered safe and suitable for the irrigation purpose. All groundwater samples in the current study were found to be suitable for irrigation with

<table>
<thead>
<tr>
<th>Indices</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Permissible limit</th>
<th>Unsuitable samples</th>
<th>Suitable samples (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAR</td>
<td>0.23</td>
<td>6.81</td>
<td>2.61</td>
<td>1.73</td>
<td>≤18</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>RSC</td>
<td>-11.18</td>
<td>3.85</td>
<td>-0.64</td>
<td>2.14</td>
<td>≤2.5</td>
<td>5</td>
<td>93.51</td>
</tr>
<tr>
<td>%Na</td>
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<td>73.91</td>
<td>41.83</td>
<td>16.17</td>
<td>≤60</td>
<td>12</td>
<td>84.42</td>
</tr>
<tr>
<td>PI</td>
<td>34.51</td>
<td>101.87</td>
<td>67.54</td>
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<td>&gt;25</td>
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<td>100</td>
</tr>
<tr>
<td>MH</td>
<td>4.73</td>
<td>73.33</td>
<td>41.73</td>
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<td>≤50</td>
<td>18</td>
<td>76.62</td>
</tr>
<tr>
<td>PS</td>
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<td>11.62</td>
<td>3.77</td>
<td>2.60</td>
<td>≤10</td>
<td>2</td>
<td>97.40</td>
</tr>
</tbody>
</table>

Figure 6: Entropy water quality index map.
respect to PI as it ranged from 34.51 to 101.87 as shown in Table 4.

The irrigation water is considered suitable if MH value is less than 50. In the present study, fifty-nine groundwater samples (76.62%) of the study area were found suitable for irrigation purpose on MH basis; however, about one-fourth of the samples were found to be unsuitable for irrigation. Generally, potential salinity value of less than ten (10) is considered suitable for the irrigation purpose. In the present study, seventy-five samples (97.40%) were found suitable for agricultural practices based on PS. Overall, SAR and PI showed that all water samples (100%) were suitable for irrigation while PS and RSC indicated that overwhelming majority of the samples (>93%) were suitable for irrigation purpose. However, MH and %Na revealed that considerable number of samples were not suitable for irrigation purpose.

Figure 7: (a) USSL diagram for irrigation water classification. (b) Plot of percentage sodium (%Na) versus EC.

Figure 8: Cluster analysis of the physicochemical parameters in groundwater of the study area.
Nevertheless, the present study revealed that most of the water samples in the study area were highly suitable for irrigation purpose and they can support good agricultural production.

4.8. Multivariate Apportionment. Another important aspect of the present study was the multivariate apportionment of the measured parameters in groundwater samples which was accomplished by cluster analysis. It can provide better understanding related to the multiple relationships and common origin of various physicochemical parameters in the study area. Cluster analysis of the physicochemical parameters was conducted to explore their grouping and communal variations in the groundwater of Sargodha District, Pakistan. It is shown in Figure 8 as a dendrogram, where various parameters were mainly divided into two main clusters; the first cluster consisted of K-F -pH-NO\textsubscript{3} -Fe, while the second cluster was comprised of two subclusters/groups including EC-TDS-Na-Cl-HCO\textsubscript{3} \textsuperscript{2} and TH-Ca-Mg-SO\textsubscript{4} \textsuperscript{2}. The first cluster (K-F -pH-NO\textsubscript{3} -Fe) was mainly derived from the anthropogenic activities in the study area (including excessive use of the fertilizers, pesticides, and wastewater), while the second cluster exhibited contributions from the natural as well as mixed sources. Mutual cluster of EC-TDS-Na-Cl-HCO\textsubscript{3} \textsuperscript{2} showed mixed contributions (from both natural and anthropogenic sources); they were derived from weathering and rock dissolution under the influence of anthropogenic pollution stress; therefore, both natural and anthropogenic contributions were found in this subcluster. However, predominant geogenic contributions were shown by a common cluster of TH-Ca-Mg-SO\textsubscript{4} \textsuperscript{2}, as they were mainly derived from rock weathering under natural conditions. The multivariate study thus exhibited significant contributions of the anthropogenic activities (mainly agricultural practices, fertilizers, pesticides, wastewater, domestic/urban run-offs, and related emissions) in the groundwater of the study area. Consequently, it is high time to address the management and control of these anthropogenic emissions and reduce their effects on the groundwater of the study area.

5. Conclusions

Various statistical and hydrochemical methods were employed to evaluate the quality of groundwater and to gauge the effect of anthropogenic and geogenic factors in district Sargodha, Pakistan. Ionic relationships and hydrochemical facies were computed to identify the major processes controlling the groundwater chemistry. The groundwater was mostly found to be Ca-HCO\textsubscript{3} type, followed by Na-HCO\textsubscript{3} and Ca-Mg-Cl types; it showed an integrated influence of natural factors along with human activities. Gibbs diagram revealed the prominence of rock dominance as a key factor while the correlation analysis indicated that major hydrochemical constituents were derived from silicate and carbonate dissolution under anthropogenic impact. The hydrochemical modeling illustrated major water-rock interactions including the precipitation of calcite/dolomite (oversaturated), solubilization of halite/gypsum (undersaturated), and cation exchange processes. Drinking water suitability assessment by EWQI showed that few samples (7.79%) were unsuitable for drinking, while 6.7% of the samples indicated poor quality; it can be attributed to leaching of ions/pollutants under anthropogenic stress, discharge of effluents, and overexploitation of the groundwater resources. Agricultural suitability of the samples as assessed by USSL classification, Wilcoxon diagram, %Na, SAR, MH, RSC, PS, and PI showed that most of the samples were categorized as suitable for irrigation purpose. However, some samples for %Na and MH (16% and 24%, respectively) were not suitable for agricultural purpose. Multivariate study revealed significant anthropogenic pollution in the groundwater of the study area. Average levels of the physicochemical parameters were also compared with the national/international standards as well as those reported from other regions around the world.

Data Availability

Part of data set can be provided on request.

Conflicts of Interest

The authors declare no conflict of interest.

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Supplementary Materials

Supplementary material file contains additional figures and table. (Supplementary Materials)

References


