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Evaluation of Groundwater Quality and Suitability for Irrigation Purposes and Human Consumption in Saudi Arabia

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Abstract: Studying groundwater quality is crucial for ensuring its safety because it is widely used for drinking and for domestic, agricultural, and industrial purposes. Owing to the lack of surface water in the Tabuk area of Saudi Arabia, here groundwater wells are one of the primary sources of water for drinking, agriculture, and industry. Groundwater quality is determined by the aquifer characteristics of the regional geology, and it is extensively influenced by both natural and anthropogenic activities. To understand the geochemical evolution and assess the suitability of groundwater for irrigation, major ion geochemistry was utilized to characterize the chemical composition of groundwater in the Tabuk area, which is considered a semiarid plateau region. Depending on its mineral composition, irrigation water's quality reflects how it affects plants and soil. In total, 80 groundwater samples have been collected and analyzed in laboratory for major cations and anions. Temperature, alkalinity (ALK), pH, total dissolved solids (TDS), electric conductivity (EC), total hardness (TH), oxidation reduction potential (ORP), and cation and anion concentrations were measured. Water chemistry classification was carried out by using a Piper diagram and a Gibbs diagram. In the current study, statistical methods, combined with geochemical modeling and conventional plots, have been used to investigate groundwater and related geochemical processes in the Tabuk area of Saudi Arabia. Applications and calculations of hydrogeochemical parameters, specifically SAR, RSC, PI, CR, MH, Na%, KR, and HI, showed that 92.5% of the collected groundwater well samples are suitable for drinking and irrigation purposes after treatment processes.

Keywords: groundwater; irrigation; crops; anions; cations; hydrochemical parameter; Saudi Arabia

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1. Introduction

The Kingdom of Saudi Arabia (KSA) is a barren desert that occupies the majority of the Arabian Peninsula and has sizable Red Sea and Persian Gulf coastlines. Saudi Arabia is like most of the arid region countries, with low rainfall (1.3–6.2 inches) and no permanent water river. About 50% of its drinking water comes from desalination, 40% from the mining of nonrenewable groundwater, and only 10% from surface water in the mountainous southwest of the country. This low amount of rainfall is the primary source of recharge for the groundwater system. Globally speaking, groundwater is a crucial natural resource for present and future generations, and it is predominant. Groundwater is the sole source of water in hyperarid, arid, and even semiarid regions. In the Tabuk area, groundwater supplies are the primary source of water for drinking, agriculture, and industry [1].

Groundwater resources in KSA comprise about 75% of the primary freshwater resources in the entire nation [2]. The remaining 25% is provided by desalination. The quality and the quantity of groundwater resources in KSA are very vulnerable to anthropogenic and natural influences such as population increases, overuse, and pollution. These activities

have a substantial impact on groundwater storage capacity and have considerable potential to change how the KSA's freshwater resources are used in the future [3]. Moreover, according to the World Health Organization (WHO), about 80% of all diseases in human beings are caused by water. The lack of hydrogeochemical studies in such areas contributes to limiting the knowledge and evaluation of the chemical state of groundwater [4,5]. However, because of water contamination, not all water accessible in the previously listed locations may be safe for human consumption or human activities such as fish farming, crop irrigation, or other agricultural activities.

The Tabuk area is one of the most suitable locations for agricultural development, where groundwater is available mostly from the confined part of the Saq aquifer, through many small diameter wells. Most of the area is cultivated by Tabuk Agricultural Development Company (TADCO), which drilled about 260 wells at an average depth of 750 m. Many of the wells are connected to circular sprinkler pivots, while others have two or three circular pivots for irrigation, which indicates that a large amount of water is extracted. All these wells penetrate and extract the water from the Saq aquifer [1–3].

At the Tabuk area, the water pumped from wells can be considered the major discharge from the Saq aquifer, where many drilled wells are used mainly to irrigate large areas of cultivated lands. All wells in the study area penetrate the Saq aquifer, and many are used as the center for pivot irrigation around the well site. There are no historical records of the total water quantity extracted from the existing wells in the study area. However, the total daily volume of water extracted from the wells was estimated to be 336,960 m^3/day [2,3].

The groundwater quality deteriorates because of either anthropogenic sources or natural/geogenic sources [6]. The facies type of groundwater is determined mainly using the major ion chemistry. Therefore, theoretically, geochemical processes occurring in the groundwater subsurface are the basic and major factors controlling groundwater quality indicators, particularly major hydrochemical ions [7].

Assessing the chemistry of groundwater helps understand the groundwater evolution, characterize the dominant geochemical interactions, and identify the anthropogenic effects. In addition, the climate, the rocks' weathering, and the percolation through and in contact with the lithologic soils enhance the dissolution and accumulation of ions in the aqueous environment, which is exacerbated during the long dry seasons, which have become more frequent in hyperarid regions as a result of climatic change [8].

Zhou et al. [7] studied the water quality of Xinle City, which is located in the upper reaches of the Daqing River Basin in northern China. The problem in this study area was that the groundwater is influenced by intense and extensive industrial and agricultural activities and sodium and nitrate pollution. The study revealed that the groundwater of the study area is of a suitable quality for both drinking and irrigation. On the other hand, the high concentrations of nitrates were classed as having an anthropogenic source. Li et al. [8] conducted a hydrogeochemical study in the Dongsheng Coalfield, Ordos Basin, China, by using trilinear diagrams, principal component analysis, and correlation analysis, and they concluded that the shallow groundwater that was affected by the chemical weathering of rock-forming minerals was generally suitable for agricultural use and human consumption.

The interactions between water chemistry, hydrology, sedimentology, and mineralogy physically manifest in modifying the landscape, karst lineaments, permeability and porosity distribution, and the establishment and operation of local and regional flow systems. The processes controlling the resultant groundwater chemical character have also been highlighted. Potential impacts on groundwater quality include recharge sources, geological structures, hydrological contexts, the mineralogy of the watersheds and aquifers, and water–rock interactions, including mineral dissolution, ion exchange, redox, and anthropogenic activities [9].

Aquifer characteristics and the strata overflow have an impact on the hydrochemistry of groundwater. The sorts of minerals that comprise the aquifer, how long groundwater is in contact with the minerals, and the groundwater's chemical composition are the factors that control which minerals dissolve in the groundwater. The chemical composition of

groundwater and its temporal variations are controlled by processes such as evaporation, oxidation/reduction, ion exchange, mineral weathering, the precipitation of secondary minerals, and the mixing of water [10,11].

Groundwater quality depends mainly on the type of dissolved salts present in the groundwater supply. There are some basic criteria for assessing groundwater quality for drinking and irrigation purposes. For example, measures of electrical conductivity are used to address the salinity hazard; estimates of the relative proportion of Na^+ to Ca^{2+} and Mg^{2+} ions, which is referred to as the sodium-adsorption ratio (SAR), are used to address the sodium hazard; and estimates of the residual sodium carbonates (RSC) that take into account the HCO_3^- and CO_3^{2-} anions and Ca^{2+} and Mg^{2+} cations in irrigation water are used to address the alkalinity (ALK) hazard [12–14].

This work aims to study the hydrochemistry of groundwater in the Tabuk area to determine its availability for drinking, irrigation purposes, and human consumption. Our understanding of the hydrogeochemical processes that lead to the formation of ions in groundwater as well as the variables that affect the quality of the local groundwater will be improved as a result of this study.

2. Materials and Methods

2.1. Geological Setting

In the Tabuk Formation, there are sandstones, siltstones, and shale deposits that are ap-proximately 1050 m thick. A low relief surface is formed by the erosion of individual sandstone units, creating slopes, mesas, and dissected plateaus 50 to 200 m high. It has both been defined as conformable and para-conformable because of its poorly exposed undivided contacts with the Cambrian and Ordovician Ram and Umm Sahm Sandstones. The Ram and Umm Sahm Sandstones, equivalent in part to the Saq Sandstone, are 600 m thick and have a flat surface interrupted by widely spaced bosses and stacks (Figure 1).

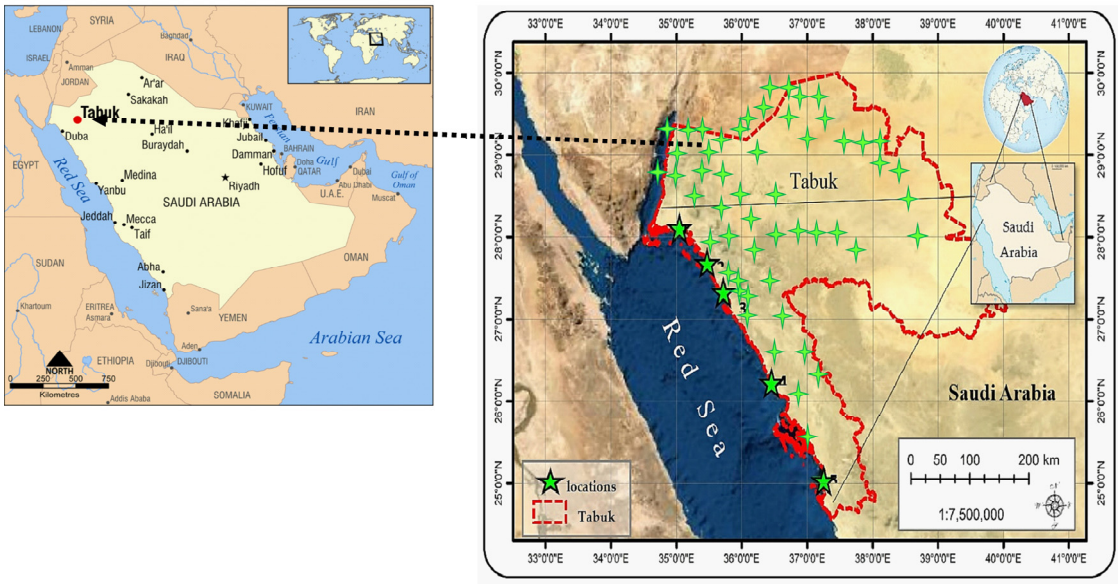


Figure 1. Location map of the study area and sample's locations: the Tabuk area [15].

2.2. Sample Collection

In total, 80 groundwater samples with a size of 2 L each were collected for this study. The wells with depths of 30–140 m that tap into the cracked basement, Saq, and Tabuk aquifer systems were sampled (Figure 1). From June to December, samples were obtained according to the regulations of KSA's Ministry of Environment, Water, and Resources. Prior to sampling, each well was left running for 10 to 15 min to ensure the flow of groundwater from the wells. Each well had 2 L of groundwater sampled from it and was stored in

plastic containers after adding 5 mL of HNO_3 to store the collected groundwater with a pH of 2. A fraction of each sample, about 100–150 mL, was kept in a separate polyethylene bottle without acidification—for pH, CO_3^{2-}, and HCO_3^- determinations. A small field instrument (Hanna, George Washington Hwy Smithfield, Washington, DC, USA) was used to quickly measure the pH values and total dissolved solids (TDS) in the water samples at the site. The Solar M-5 Atomic Absorption Spectrometer (Thermo Elemental, London, UK) was used to perform flame atomic absorption spectrophotometry for the analysis of Na^+ and K^+. A standard solution with known concentrations was used to calibrate the instrument. The statistical error was within ±8%. The wet analyses were completed utilizing standard techniques. Ca^{2+} and Mg^{2+} were analyzed by using the titrimetric method no. 2340C-EDTA, whereas CO_3^{2-} and HCO_3^- were analyzed by using the titrimetric method no. 2320B. Analyses of Cl^- and SO_4^{2-} were performed by using the argentometric method no. 4500B and the turbidimetric method no. 4500E, respectively. The analyses were performed in duplicate, and the standard deviation was within ±10%. The determination of the total hardness in groundwater was conducted by complexometric titration with sodium salt of ethylene-di-amine-tetraethanoic acid (EDTA). ORP as determined by measuring the potential of a chemically inert (platinum) electrode, which was immersed in the solution. The sensing electrode potential was read relative to the reference electrode of the pH probe, and the value was presented in millivolts (mV).

2.3. Groundwater Quality Characterization

Groundwater is widely used for irrigation in the Tabuk area. Depending on its mineral composition, irrigation water's quality reflects how it affects plants and soil. Agricultural soils and plants are directly affected by the irrigation water's chemical composition, which can lead to lower productivity [15,16]. The source, regional geological variances, and climatic conditions all affect the irrigation water's chemical content. For instance, groundwater with a high salt content can seriously harm plants by changing their metabolism and stifling their ability to absorb water. The sodium-adsorption ratio (SAR), residual sodium carbonate (RSC), sodium percentage (Na%), permeability index (PI), magnesium hazard (MH), Kelly's ratio (KR), magnesium ratio (MR), and corrosivity ratio (CR) tests were used to evaluate the quality of the irrigation water. These criteria are all essential for determining the quality of groundwater for irrigation purposes [17].

2.3.1. Sodium-Adsorption Ratio

The concentration of the primary alkaline and earth alkaline cations present in the water is used to calculate the SAR value, where cations concentrations are measured in units of meq/L. A high salt concentration in irrigation water may raise the sodium content of the soil, which may thus alter the soil's permeability and lead to infiltration issues. It is possible for soil to become dispersed, making it difficult to plow. SAR was calculated by using Equation (1), from Keesari et al., 2016 [18]:

$$\mathrm{SAR} = \frac{\mathrm{Na}^+}{\sqrt{\frac{\mathrm{Ca}^{2+}+\mathrm{Mg}^{2+}}{2}}} \quad (1)$$

2.3.2. Residual Sodium Carbonate (RSC)

All the anions and cations are expressed in meq/L. Another indicator of the suitability of water for irrigation purposes is the RSC ratio. If groundwater has a larger percentage of HCO_3^- and CO_3^{2-}, these ions may tend to precipitate with Ca^{2+} and Mg^{2+} ions, and the resulting excess of $NaHCO_3$ and $CaCO_3$ may be dangerous for the structure of soil. Residual sodium carbonate can be calculated by using Equation (2) [19]:

$$\mathrm{RSC} = \left(\mathrm{HCO}_3^- + \mathrm{CO}_3^{2-}\right) - \left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right) \quad (2)$$

2.3.3. Sodium Percentage (Na%)

Because excessive sodium concentrations in water and soil slow plant growth by reducing soil permeability, the measurement of Na% is essential for the management of water for irrigation purposes. It is calculated by using Equation (3) [20]:

$$\text{Na\%} = \frac{\text{Na}^+ + \text{K}^+}{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+} \times 100 \quad (3)$$

2.3.4. Permeability Index (PI)

The use of mineral-rich water for an extended period of time reduces soil permeability, which indirectly affects crop output. The formula used to calculate the PI in accordance with the normative requirements was given by Falowo et al., 2017 [21]:

$$\text{PI} = \frac{\text{Na}^+ + \sqrt{\text{HCO}_3^-}}{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+} \times 100 \quad (4)$$

2.3.5. Magnesium Hazard (MH)

Ca^{2+} and Mg^{2+} are typically present in balance. The equilibrium can occasionally be thrown off by a high Mg^{2+} concentration, and an excess of Mg might stunt plant growth by making the water more alkaline. The MH concentration is measured according to the formula given by Abdulhussein, 2018 [22]:

$$\text{MH} = \frac{\text{Mg}^{2+} \times 100}{\text{Ca}^{2+} + \text{Mg}^{2+}} \quad (5)$$

2.3.6. Kelly's Ratio (KR)

A Kelly's ratio (KR) of more than 1.0 indicates excessive sodium in water and can be calculated as follows [23]:

$$\text{KR} = \frac{\text{Na}^{2+}}{\text{Ca}^{2+} + \text{Mg}^{2+}} \quad (6)$$

2.3.7. Corrosivity Ratio (CR)

The CR is the susceptibility of groundwater to corrosion. It is expressed as a ratio of alkaline earths to saline salts in groundwater. The CR is calculated by using Equation (7) [22]:

$$\text{CR} = \frac{\frac{\text{Cl}^-}{35.5} + 2\left(\frac{\text{SO}_4^{2-}}{96}\right)}{2\left(\frac{\text{HCO}_3^- + \text{CO}_3^{2-}}{100}\right)} \times 100 \quad (7)$$

3. Results and Discussion

3.1. Hydrochemical Characterization

A vast number of dissolved substances may be present in groundwater at high concentrations. It is necessary to investigate the presence of different elements in this water and characterize how these constituents relate to utilization in order to ensure that the groundwater is suitable for diverse uses, including drinking and domestic and industrial uses. Many factors can have an effect on the composition of groundwater, including the porosity and permeability of the host rock or soil [24], the amount and kind of organic matter present in the aquifer, and others. The chemistry of natural water and, in turn, the chemistry of groundwater are both influenced by the water's contact with air, the geography of the land, and the local climate. Groundwater properties are also significantly influenced by the geological setting, subsoil hydrological variables, and anthropogenic disturbances. In determining the type, quality, and nature of the water, the physical characteristics of the

groundwater are thought to be the most important factors [25]. Table 1 lists the results of the groundwater physical parameters of the study area.

Table 1. Physical parameters measured in the collected groundwater samples from the Tabuk area.

Variables	Temperature °C	pH –	TDS mg/L	EC µS/cm	TH mg/L	ORP mV	ALK mg/L
N	80	80	80	80	80	80	80
Mean	15	–	2483.4	4264.0	1018.1	368.06	213.3
Median	34.3	7.43	2179.5	3615.5	920.5	365.5	200
Variance	28.3	0.14	2,640,206.8	9,373,688	573,743.3	4826.3	5160.2
Std. deviation	0.21	0.38	1624.9	3061.6	757.5	69.5	71.83
Minimum	25	6.5	411	626	185	183	85
Maximum	41	8.1	11,167	21,733	6146	542	475
Range	2.1	1.7	10,756	21,107	5961	359	390
Skewness	0.22	−1.78	8.03	9.86	0.15	1.66	4.19
Kurtosis	0.45	0.27	17	23.18	48.83	0.76	4.47
Shapiro–Wilk	0.11	0.036	0.00	0.00	0.00	0.078	0.200
Kolmogorov–Smirnov	0.1	0.200	0.00	0.00	0.00	0.200	0.00
Desirable limit [26]	12	6.5	500	500	200	300	20
Permissible limit [26]	25	8.5	1500	1500	500	500	200

Groundwater can be classified into seven temperature ranges, from extremely cold springs (with temperatures close to 0 °C) to extremely hot springs (with temperatures over 100 °C). The WHO, 2017 [26], has estimated that the acceptable range for groundwater temperature is from 12 to 25 °C. The collected groundwater samples' temperatures in the current study ranged from 25 to 41 °C, with an average of 32 °C (Table 1). When groundwater samples from the fields were being collected, the temperature was directly measured.

The pH values of the groundwater well samples from the study area were within the permissible limits, specifically 6.5–8.5, according to WHO, 2017 [26], indicating slightly acidic to basic in nature. In determining the suitability of groundwater for domestic and industrial purposes, water hardness is an important factor; the total hardness is related to the total quantities of Ca and Mg in the groundwater. The total hardness values in the collected groundwater well samples ranged from 185 to 6164 mg/L, with an average of about 1018 mg/L (Table 1). According to Saywer and McCarty, 1967 [27], the collected groundwater samples were classified as very hard water.

TDS values in the collected groundwater well samples ranged from 411 to 11,167, with an average of 2483 mg/L (Table 1). It is clear that some of the collected groundwater samples were under the permissible limit of 2000 mg/L, while others were over the limit. The groundwater samples with TDS values higher than 1000 mg/L were considered to be fresh water [28]. The total charge of the dissolved cations is not balanced with that of the dissolved anions. This means that there may be other dissolved ions or solutes imposing influences on water quality. Organic and inorganic carbon, nitrogen, phosphorus, and microbiological pathogens are indispensable indicators to evaluate water quality and water-use safety. The groundwater collected from the Tabuk area's wells are not directly suitable for irrigation purposes and reclamation from the desert; rather, it needs treatment before using it.

EC is a tool for measuring the salinity of water [28]. Values of EC ranged from 626 to 21,733 µS/cm, with an average of 4264 µS/cm (Table 1). Because the permissible limit of electron conductivity is 1500 µS/cm [26], this indicates that some of the collected groundwater samples should be classified as brines with an extremely high concentration [29].

An important technique for evaluating the quality of groundwater is the oxidation reduction potential (ORP). When an object lacking electrons, referred to as an oxidizing agent, searches for electrons from other substances, oxidation takes place. On the other hand, reducing agents are substances that have additional electrons to donate. On the basis of ORP values, compounds are categorized as either oxidizing agents or reducing

agents, and ORP is measured in millivolts (mV). An oxidizing agent is present when the ORP value is high; a reducing agent is indicated by a low value. With low ORP values and high readings, water pollution levels typically rise. Groundwater with high concentrations of oxidizing (chlorine) and reducing (sulfite ions) chemicals can be evaluated by using ORP levels. It is crucial to take into consideration additional factors, such as how biological matter degrades in the groundwater system. For instance, a low ORP measurement, between 100 and 400 mV, may indicate the fermentation-related release of biological phosphorus or acid. The permissible limit of ORP according to WHO, 2017 [26], is 300–500 mV. The values of ORP ranged from 183 to 542 mV, with an average 368 mV (Table 1).

The concentrations of sodium (Na^+) in the collected groundwater wells ranged between 36 and 1527 mg/L, with an average of 413 mg/L (Table 2). These values were within the permissible limit in some collected samples and exceeded it in others. The permissible limit according to WHO, 2017 [26], is 200 mg/L. Sodium is more abundant in igneous rocks. In resituates and hydrolytes, the amount of sodium is relatively lower, but in carbonate rocks, very small amounts are present. Nearly all sodium compounds are readily soluble, and in general, when it is leached from rocks, it tends to remain in the solution.

Table 2. Basic descriptive statistics for concentrations of cations and anions in the collected groundwater samples.

	Cations				**Anions**					
Variables	**Na^+ mg/L**	**K^+ mg/L**	**Ca^{2+} mg/L**	**Mg^{2+} mg/L**	**Cl^- mg/L**	**SO_4^{2-} mg/L**	**HCO_3^- mg/L**	**CO_3^{2-} mg/L**	**NO_3^{2-} mg/L**	**F^- mg/L**
N	80	80	80	80	80	80	80	80	80	80
Mean	413.1	3.7	269.2	82.5	793.9	597.9	341.3	279.7	38.3	1.05
Median	297	3	213.8	58	526	489	308	252.5	39.7	1
Variance	134,302	7.42	75,799.4	6525.7	733,109.8	258,167.4	14,638.4	9826.7	843.2	0.96
Std. deviation	366.5	2.7	275.3	80.8	856.2	508.1	121	99.1	29.04	0.98
Minimum	36	0.34	59.3	4	47.2	40.7	110	90	0.3	0
Maximum	1527	10.6	2452.3	338	6331	2106	600	492	120	4
Range	1491	10.3	2393	334	6283.8	2065.3	490	402	119.7	4
Skewness	6.02	3.07	24.1	7.94	14.44	6.29	1.646	1.65	2.45	2.7
Kurtosis	3.96	−0.184	95.84	7.71	40.57	5.38	−1.011	−1.09	0.065	0.05
Shapiro–Wilk	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.014	0.056	0.00
Kolmogorov–Smirnov	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.001	0.001	0.078
Desirable limit [26]	200	10	75	50	250	200	200	200	25	1
Permissible limit [26]	600	12	200	100	500	250	600	600	45	1.5

Almost all the collected groundwater samples were above the permissible limit of calcium: 75 mg/L [26]. The concentrations of calcium were between 59 and 2452 mg/L, with an average of 269 mg/L (Table 2). Owing to the widespread occurrence and solubility of calcium, it is present in many surface bodies of water and many sites of groundwater. Magnesium is the other major cause of hardness in groundwater, along with calcium. It is widely present in many common minerals, such as dolomite and magnetite. The permissible limit of Mg^{2+} is 50 mg/L [26]. Further, the concentration of Mg^{2+} in the collected groundwater samples ranged from 3.7 to 338 mg/L, with an average of 82 mg/L (Table 2).

The concentrations of HCO_3^-, CO_3^{2-}, and Cl^- in the collected groundwater samples respectively ranged from 110 to 600, with an of average 341 mg/L; from 90 to 492, with an average of 280 mg/L; and from 47 to 6331, with an average of 794 mg/L (Table 2). The permissible limits of HCO_{3-}, CO_3^{2-} and Cl^- were 500, 500, and 250 mg/L, respectively [26,30]. The high concentration values of HCO_3^- and Cl^- can be attributed to the dissolution of minerals in water such as silicate and sedimentary rocks, carbonate precipitates, and the dissolution of atmospheric CO_2 in the groundwater [30]. The NO_3^{2-} concentration in the collected groundwater samples ranged from 0.3 to 120 mg/L, with an average of 38 mg/L (Table 2). According to WHO, 2017 [26], the permissible limit of NO_3^{2-} is 45 mg/L (Table 2). Anthropogenic sources cause the pollution of NO_3^{2-} [31].

Sulfate (SO_4^{2-}) is one of the major anions occurring in groundwater. Sulfur occurs in water largely in oxidizing form (S^{6+}), or under some reducing conditions, it may be present as sulfide (S^{2-}). The concentration of SO_4^{2-} in the collected groundwater samples ranged from 41 to 2106 mg/L, with an average of 598 mg/L (Table 2). The permissible limit of SO_4^{2-} according to WHO, 2017 [26], is 250 mg/L (Table 2). The concentration of fluorine (F^-) in the collected groundwater samples ranged from 0 to 4 mg/L, with an average 1 mg/L. According to WHO, 2017 [26], the permissible limit of F^- is 1.5 mg/L (Table 2). Fluoride is a vital component of the human body, and the fluoride content of potable water should not reach 1.5 mg/L. F^- is primarily attributed to the oxidation of minerals and the weathering of granite and igneous rocks. Potential causes include agricultural inputs, the burning of coal in brick kilns, industrial emissions, and atmospheric deposition [26]. The formation of higher F^- values in groundwater is influenced by water–rock interactions and dry weather conditions. In acidic circumstances, clay minerals have adsorbed F^-, which is then desorbed in an alkaline pH [29,30].

The anion sequences based on relative proportions were in the following order: $Cl^- > SO_4^{2-} > HCO_3^- > CO_3^{2-} > NO_3^{2-} > F^-$ (Figure 2a). The cation sequences in the collected groundwater samples were in the following order: $Ca^{2+} > Na^+ > Mg^{2+} > K^+$ (Figure 2b). Importantly, the samples of groundwater were increasing in the silicate weathering area (Figure 2c,d). The higher concentration of Na^+ in the collected groundwater is attributed to the weathering of silicate rocks. The higher concentrations of Ca^{2+} and of Mg^{2+} over K^+ in the collected groundwater may be attributed to their mineralogical presence in the soil. Relationships of HCO_3^-/Na^+ versus Ca^{2+}/Na^+ and Mg^{2+}/Na^+ versus Ca^{2+}/Na^+ indicated evaporite mineral dissolution, carbonate, and silicate weathering (Figure 2e,f).

The ratio of Ca^{2+}/Mg^{2+} is usually used as indicator for seawater contamination if the ratios are less than unity [31]. When Ca^{2+}/Mg^{2+} ratios equal to unity or near unity, this indicates meteoric water mixing in the groundwater bodies. The ratios of Ca^{2+}/Mg^{2+} in the collected groundwater samples were higher than unity, which indicated anhydrate dissolution, meteoric water mixing, or dolomite and calcite dissolution, followed by silicate mineral dissolution (Figure 2). The excess of Ca^{2+} and Mg^{2+} in the collected groundwater samples indicated the occurrence of silicate weathering over carbonate weathering (Figure 2). In the study area, the sodium was released into the groundwater by halite and silicate minerals. If the mole ratio of Na/Cl is < 1, then halite dissolution may have occurred, or a mole ratio of Na/Cl > 1 may indicate silicate dissolution (Figure 2). Igneous rock is composed of mostly silicate minerals, as 95% of the Earth's crust is composed of silicate minerals and the mantle. Silicon and oxygen are the primary components of silicate. The known minerals of silicon include quartz, mica, feldspar, pyroxene, olivine, amphibole, and clay. In comparison, the common minerals include quartz, tridymite, coesite, cristobalite, keatite, and lechatelierite [32].

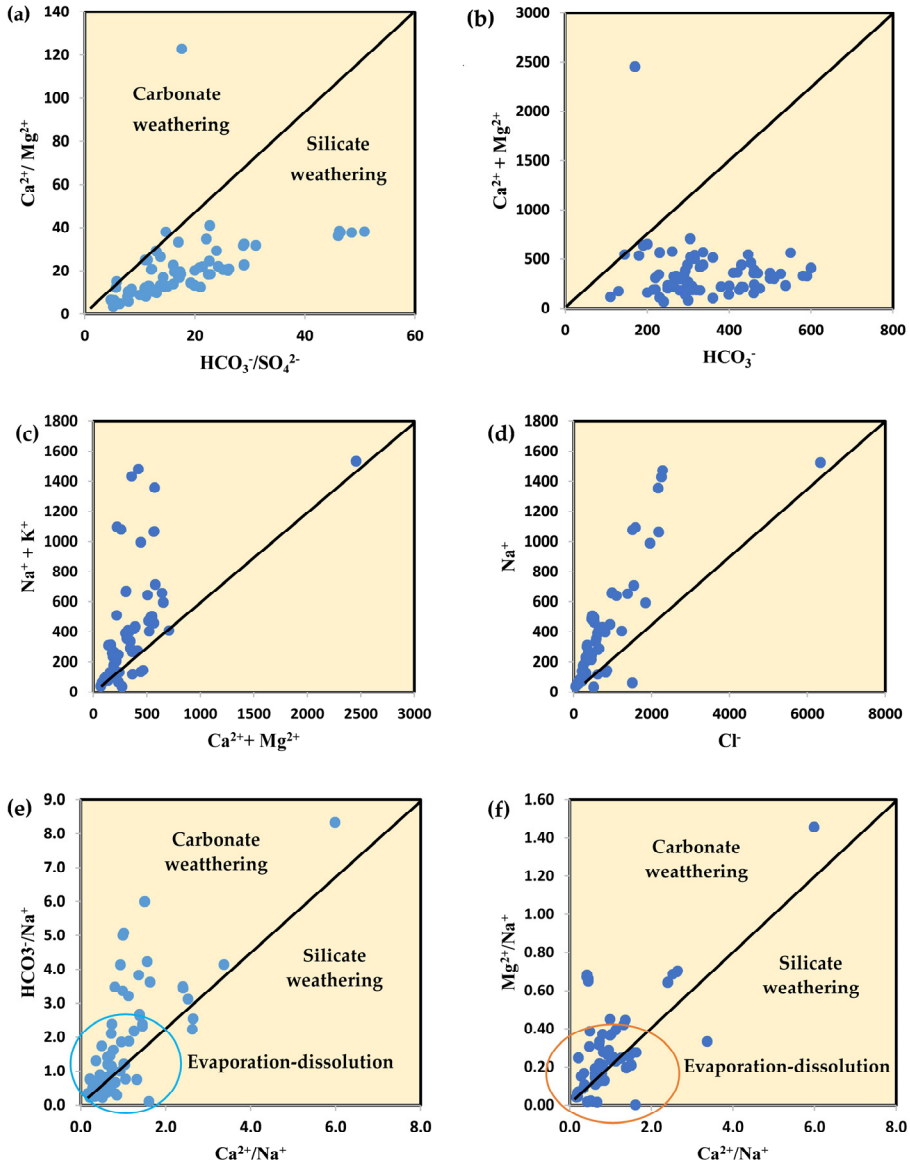


Figure 2. (**a**) Scatter plot between Ca^{2+} + Mg^{2+} vs. HCO_3^- + SO_4^{2-}, (**b**) scatter plot between Ca^{2+} + Mg^{2+} vs. HCO_3^-, (**c**) scatter plot between Na^+ + K^+ vs. Ca^{2+} + Mg^{2+}, (**d**) scatter plot between Na^+ vs. Cl^-, (**e**) scatter plot between HCO_3^-/Na^+ vs. Ca^{2+}/Na^+, and (**f**) scatter plot between HCO_3^v/Na^+ vs. Ca^{2+}/Na^+.

3.2. Characterization of Groundwater Chemistry

Groundwater is often categorized according to the Piper Hill diagram [33]. In such a diagram, the hydrogeochemical features of water can be inferred by defining the predominant cations and anions that affect the local hydrochemistry. Two triangles are shown in these plots (see Figure 3), one for charting cations and the other for calculating anions. The regions of the cation and anion fields are merged to represent a single point in a diamond-shaped field, from which inference is derived on the basis of the hydrogeochemical faces concept. In contrast to other alternative plotting techniques, these trilinear diagrams are effective in highlighting chemical correlations among groundwater samples in more-precise terms. The notion of distinct zones of hydrogeochemical faces with cation and anion concentration categories helps to categorize the composition of water into different groups [34]. A Piper trilinear graphical representation of the collected groundwater samples' chemical data is identified with blue dots and shown in Figure 3.

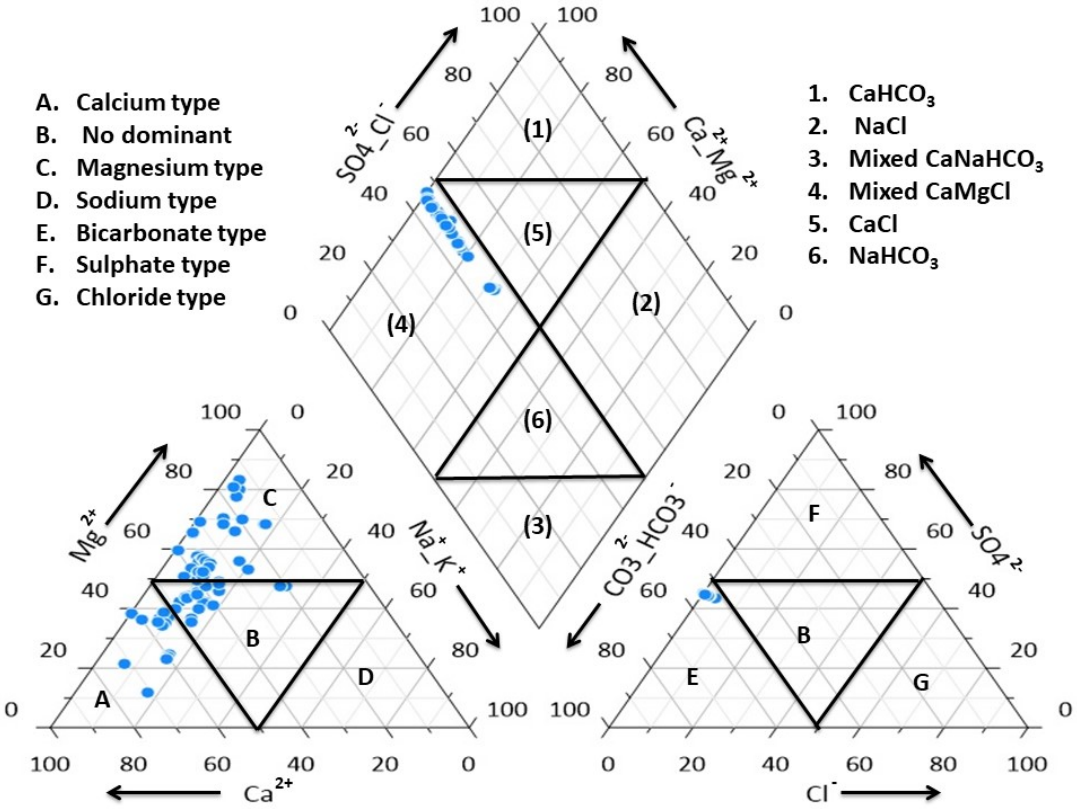


Figure 3. Piper trilinear diagram of the collected groundwater samples from Tabuk area.

The diamond-shaped field of the Piper diagram can be further classified as (I) Ca^{2+}-Mg^{2+}-Cl^{-}-SO_4^{2-}, (II) Na^{+}-K^{+}-Cl^{-}-SO_4^{2-}, (III) Na^{+}-K^{+}-HCO_3^{-}, and (IV) Ca^{2+}-Mg^{2+}-HCO_3^{-}. The collected groundwater well samples belong to the Ca^{2+}-Mg^{2+}-Cl^{-}-HCO_3^{-} water type. Gibbs, 1970 [35], proposed a diagram in which ratios of dominant anions and cations are plotted against the TDS values to determine groundwater chemistry and relationships between chemical components collected from different aquifers, including rock chemistry, water chemistry, and evaporation rate. A Gibbs diagram is used to assess the functional sources of dissolved chemical constituents, such as precipitation dominance, rock dominance, and evaporation dominance, on the basis of their ratio-I for cations (Na)/(Na + Ca) and ratio-II for anions Cl/(Cl + HCO_3) as a function of TDS. Figure 4 shows a Gibbs diagram plotted with the chemical data of the collected groundwater samples. As a result of the dissolution of rocks, the chemical weathering of rock-forming minerals influences the quality of groundwater.

3.3. Assessment of Groundwater Quality

The quality of the groundwater that has been gathered for irrigation purposes is typically shown by the SAR in a reciprocal manner. The SAR was between 1 to 19 meq/L, with an average of 6 meq/L (Table 3). Salifu et al., 2021 [36], noted that SAR values higher than 10 were deemed undesirable for irrigation purposes. By lowering the amount of soil water available and lowering the ratio of the two primary minerals, calcium and magnesium, high SAR values pose a risk for sodium salinity, which in turn affects crop growth. We determined that 88.7% of the groundwater samples gathered from wells were acceptable for irrigation and that 11.3% of the groundwater samples were not suitable for irrigation (Table 3).

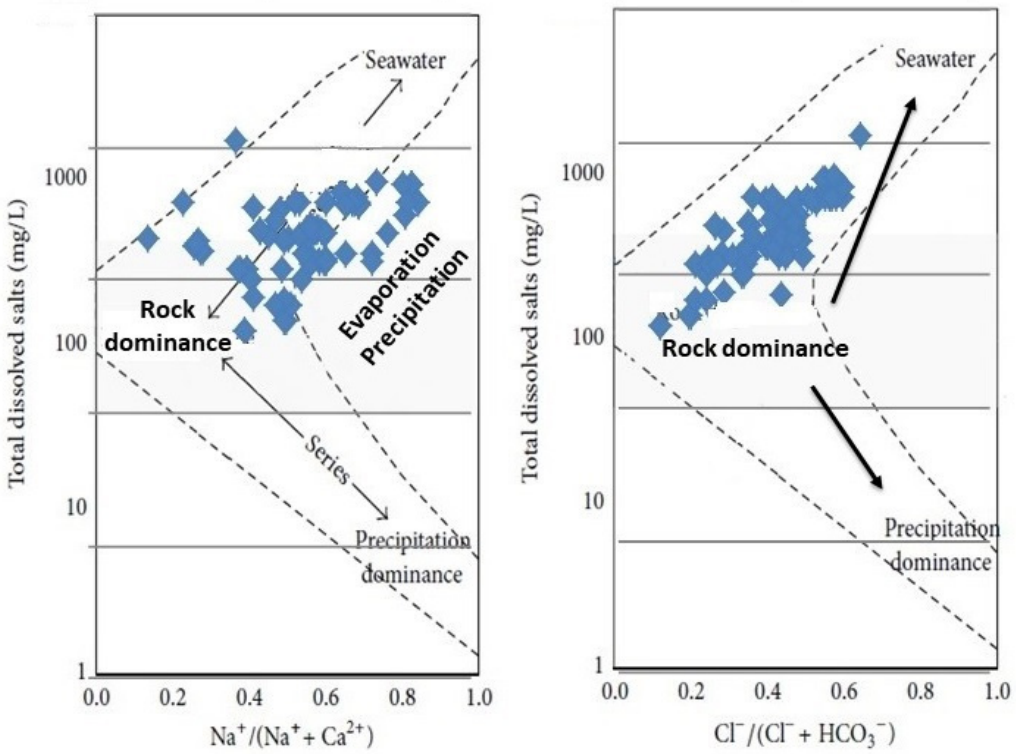


Figure 4. Gibbs variation diagram, TDS vs. $Na/(Na + Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$ for the collected groundwater sample.

Through the use of the carbonate and bicarbonate ratio, RSC is thought to be a useful technique for determining whether groundwater is suitable for irrigation [37]. The extra sodium ion balances out the excess calcium and magnesium by precipitating calcium as CO_2 and leaving behind a negative result for RSC. Additionally, the higher concentration of calcium and magnesium, due to the interaction with HCO_3^- to create calcium bicarbonate and magnesium bicarbonate, is indicated by the positive value of RSC [38,39]. RSC values lower than 1.25 meq/L were classified as good for irrigation purposes; values ranging from 1.25 to 2.5 meq/L were classified as doubtful; and values higher than 2.5 meq/L were classified as unsuitable (Table 3). The values of RSC in the collected groundwater samples ranged from −118 to 5 meq/L, with an average of −10 meq/L. The results showed that 88.7% of the collected groundwater samples were good for irrigation purposes; that 1.3% of the collected groundwater samples were doubtful; and that 10% of the collected groundwater samples were unsuitable for irrigation purposes (Table 3).

PI values higher than 75 meq/L were considered as good for irrigation purposes, values ranging from 25 to 75 meq/L were considered as doubtful, and values lower than 25 meq/L were considered as unsuitable (Table 3). The results ranged from 23 to 83 meq/L, with an average of 52 meq/L. The results showed that 5% of the collected groundwater samples' PI values were higher than 75 meq/L and that 93.7% of the collected groundwater samples' PI values ranged from 25 to 75 meq/L, which could be considered as doubtful for irrigation purposes. In the rest of samples, 1.25% of the collected groundwater was lower than 25 meq/L and could be considered as unsuitable for irrigation purposes (Table 3).

In comparison with calcium, magnesium can have a more detrimental effect on soil. Table 3 shows an average of 24 meq/L, ranging from 0 to 62 meq/L. It is estimated that about 90% of groundwater samples are below 50%, making them suitable for irrigation. About 10% are above 50% and thus unsuitable for irrigation (Table 3).

Table 3. Classification of the collected groundwater samples of the Tabuk area according to some hydrogeochemical parameters.

Parameter	Min	Max	Mean	SD	Median	Suitability for Irrigation [33]	Tabuk Groundwater Suitability
SAR	1	19	6	4	5	- **<10 Excellent** - **10–18Good** - **18–26 Doubtful** - **>26 Unsuitable**	- **88.7% Excellent** - **11.3% Doubtful**
RSC	−118	5	−10	16	−6	- **<1.25 Good** - **1.25–2.5 Doubtful** - **>2.5 Unsuitable**	- **88.7% Good** - **1.3% Doubtful** - **10% Unsuitable**
PI	23	83	52	13	53	- **>75% Good** - **25–75% Doubtful** - **<25% Unsuitable**	- **5% Good** - **93.7% Doubtful** - **1.25% Unsuitable**
CR	0	0.9	0.1	0.1	0.1	- **<1 Suitable** - **>1 Unsuitable**	- **100% Suitable**
MH	0	62	24	14	20	- **<50 Suitable** - **>50 Unsuitable**	- **90% Suitable** - **10% Unsuitable**
Na%	10	79	43	14	41	- **<20 Excellent** - **20–40 Good** - **40–60 Permissible** - **60–80 Doubtful** - **>80 Unsuitable**	- **6.25% Suitable** - **41.25% Good** - **37.5% Permissible** - **15% Doubtful**
KR	0.3	1	0.7	0.2	0.7	- **<1 Suitable** - **>1 Unsuitable**	- **100% Suitable**
HI	0.006	2	0.7	0.5	0.7	- **<1 Suitable** - **>1 Unsuitable**	- **82.5% No health risk** - **17.5% High health risk**

The use of agrochemicals in agricultural practices and lithological sources that result in the solubility of such minerals in water are the most likely causes of the high levels of sodium in the water.

There was a variation in the KR values in the groundwater samples collected in the study area, which ranged from 1.43 to 0.03, and 100% had KR values lower than unity (Table 3), suggesting that the collected groundwater was suitable for irrigation. Na% in the collected groundwater samples ranged from 10 to 79%, with an average of 43% (Table 3). The results showed that 6.25% of the collected groundwater samples were suitable for irrigation purposes, 41.25% of the collected groundwater samples were good for agronomy purposes, 37.5% of the collected groundwater samples were doubtful, and 15% of the collected groundwater samples were unsuitable (Table 3). High levels of salt in soil have detrimental effects on soil aeration, infiltration, and structure [40]. For instance, it has been seen that prolonged agricultural practices in more-alkaline water reduce crop production because of osmotic pressure in the soil-plant system brought on by sodium buildup. The ability of plants to absorb water or nutrients from the soil medium is slowed down by the high osmotic pressure in the soil-plant system [41].

The groundwater samples collected from some wells are used for crop irrigation purposes, so it is important to calculate and study the health risks of the collected groundwater samples. F^- and NO_3^{2-} are among the most dangerous noncarcinogenic substances in many countries [42,43] where most people rely on groundwater for drinking. According to our calculations, the hazard index (HI) is determined by combining the hazard quotients (HQs) for fluoride and nitrate ($HQ_{fluoride}$ + $HQ_{nitrate}$, respectively), and can range from 0.006 to 2 meq/L. From the results, we can conclude that 82.5% of the collected groundwater well samples pose no health risks, as they were less than 1 meq/L (Table 3). Furthermore, 17.5% of the collected groundwater well samples pose high health risks, measuring more

than 1 meq/L. Critical exposure to higher nitrate concentrations by ingesting drinking water can result in methemoglobinemia and also raises the risk of some cancers, including stomach (gastric) and esophageal cancer, and of diabetes and spontaneous abortions [44].

3.4. Statistical Analysis

The data were statistically analyzed using IBM SPSS statistics software. The data were simplified into destructive statistics to produce a summary. The destructive statistics calculated include the mean, median, variance, standard deviation, minimum, maximum, range, skewness, and kurtosis (Tables 1 and 2). For pH, TDS, EC, TH, ORP, and AlK, the standard deviations that are lower than the means indicate a high degree of uniformity. Applying the Shapiro–Wilk and Kolmogorov–Smirnov tests to the obtained results of the collected groundwater samples showed that they are highly significant, with p-values ≤ 0.05, which confirms that all the current results do not follow a normal distribution (Table 1). A positively skewed or right-skewed distribution is a type of distribution in which most values are clustered around the left tail of the distribution and the right tail of the distribution is longer. A negatively skewed distribution is one in which more values are plotted on the right side of the graph and the tail of the distribution is longer on the left. The histogram and the frequency distribution curve were the physical parameters determined for the collected groundwater samples (Figure 5).

EC is strongly associated with Ca^{2+}, Mg^{2+}, Cl^{-}, and $SO_4{}^{2-}$, indicating that the high conductivity of the groundwater is due to the presence of these ions. Ca^{2+} and Mg^{2+} show moderate association between Cl^{-}, $SO_4{}^{2-}$ and Cl^{-}, $NO_3{}^{-}$. The high concentration of these ions may be due to the dissolution of evaporitic minerals in that a high proportion of EC favors the dissolution of evaporite minerals and sulfate salts, resulting in an increase in the concentration of Mg^{2+} and Ca^{2+} in the groundwater [44].

Figure 5 and Table 2 show the frequency distribution of pH, TDS, EC, TH, ORP, and AlK measured in the collected groundwater sample. It is clear that the positive values of the skewness of pH, TDS, EC, TH, ORP, and AlK indicate that their distributions are not perfectly symmetrical but rather deviate to the right as positively skewed.

A percentage frequency diagram is a useful tool that can determine the most influential cation in the collected groundwater samples (Figure 6). The concentrations of potassium (K^{+}) in the groundwater samples ranged from 0.3 to 10.6 mg/L, with an average of 4 mg/L (Table 2 and Figure 6). Several minerals contribute to potassium sources in the groundwater, including silicate minerals, orthoclase microcline, hornblende, muscovite, and biotite; evaporating gypsum and sulfate deposits cause considerable amounts of potassium to be released [44]. The permissible limit, according to WHO, 2017 [26], is equal to 12 mg/L. Accordingly, all collected groundwater samples are lower than the permissible limit for potassium.

For Na^{+}, K^{+}, and Ca^{2+}, the standard deviations that were lower than the means indicated a high degree of uniformity, with the exception of Mg^{2+}, which has a standard deviation value higher that its mean. Thus, the Mg^{2+} result showed a degree of orderliness (Table 2). Figure 6 shows a histogram of the frequency distribution of Na^{+}, K^{+}, Ca^{2+}, and Mg^{2+} measured in the collected groundwater sample, and it is clear that the positive values of skewness and their distribution were not perfectly symmetrical. They are highly significant, with p-values ≤ 0.05 after applying the Shapiro–Wilk and Kolmogorov–Smirnov tests (Table 2). The weathering of K-feldspar is mainly responsible for the K^{+} concentration in the groundwater. $HCO_3{}^{-}$ is most dominant among the anions, followed by Cl^{-}, $SO_4{}^{2-}$, and $NO_3{}^{-}$. The combination of Ca^{2+}, Mg^{2+}, and $HCO_3{}^{-}$ is responsible for the hardness of the groundwater. High $HCO_3{}^{-}$ values indicate the presence of carbonate-containing minerals in the study area and the presence of degraded organic matter that can also contribute to the presence of $HCO_3{}^{-}$ in groundwater.

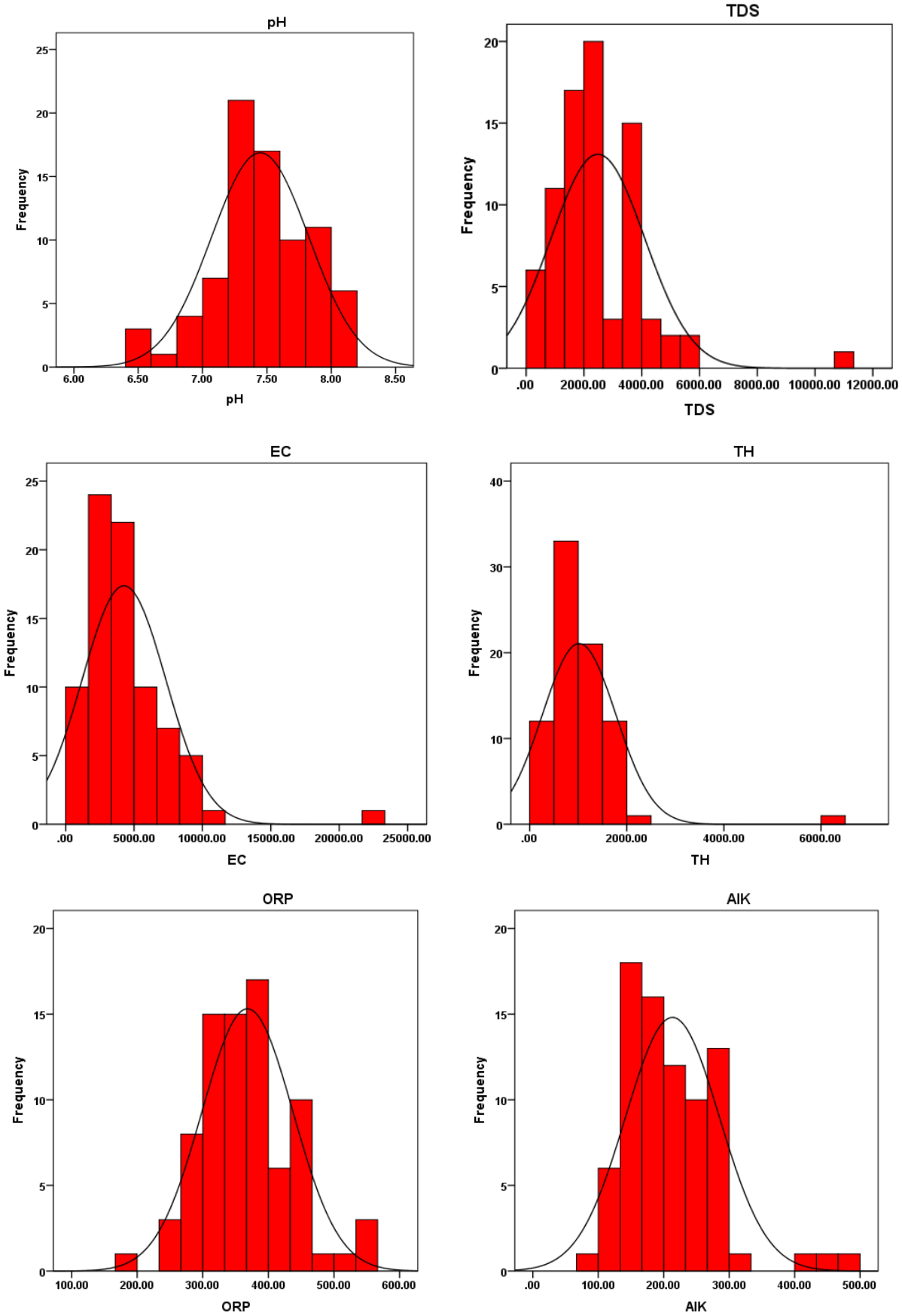


Figure 5. Histogram of the frequency distribution of pH, TDS, EC, TH, ORP, and AlK.

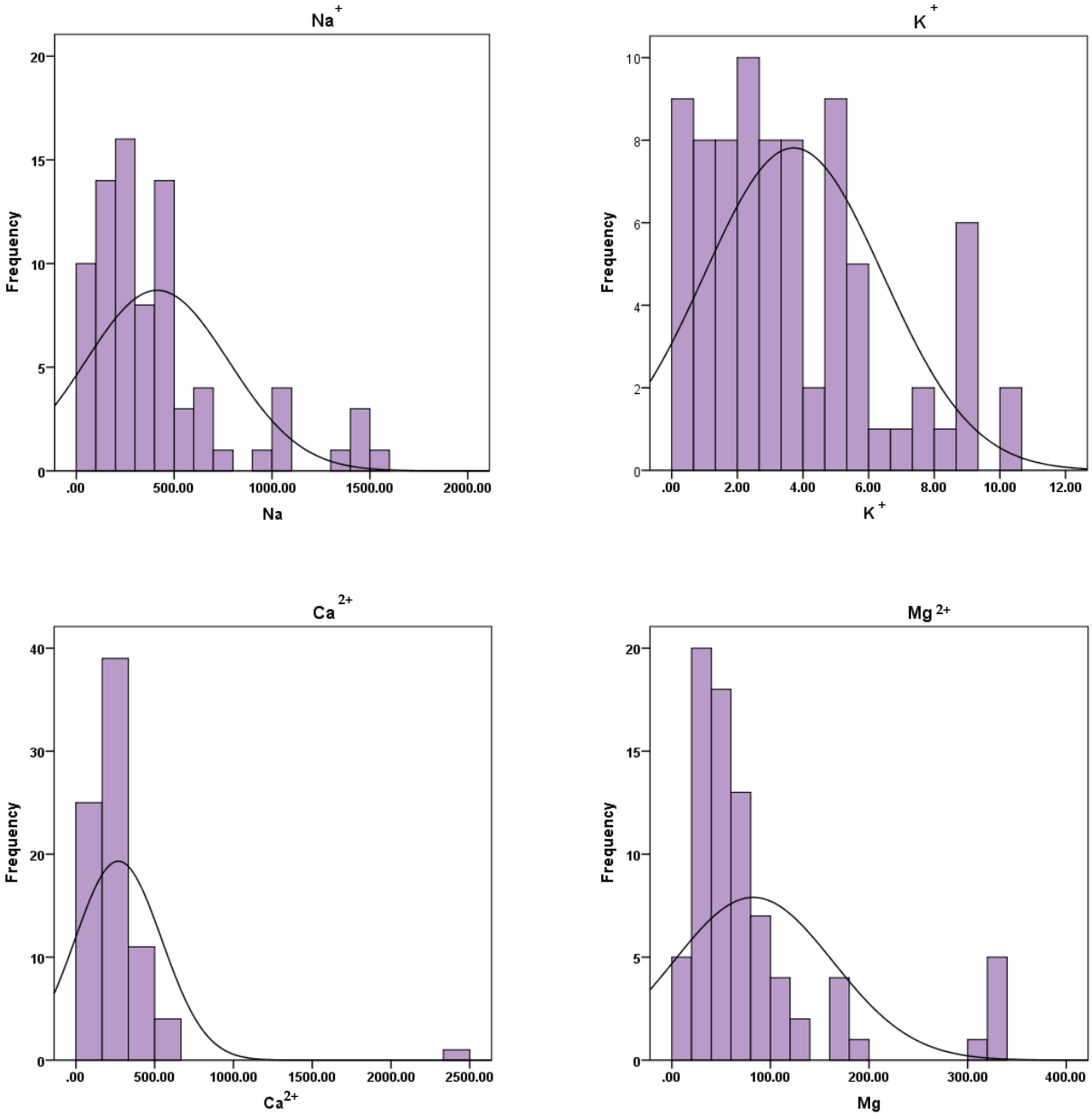


Figure 6. Histogram of the frequency distribution of cations Na^+, K^+, Ca^{2+}, and Mg^{2+} in the collected groundwater sample.

For HCO_3^-, CO_3^{2-}, Cl^-, SO_4^{2-}, NO_3^{2-}, and F^-, the standard deviations that are lower than the means indicate a high degree of uniformity, with the exception of Mg^{2+}, which has a standard deviation value higher that its mean, which means that the Mg^{2+} data show a degree of orderliness (Table 2). Figure 7 shows a histogram of the frequency distribution of HCO_3^-, CO_3^{2-}, Cl^-, SO_4^{2-}, NO_3^{2-}, and F^- measured in the collected groundwater sample, and it is clear that the positive values of skewness and their distribution are not perfectly symmetrical. They are highly significant, with p-values ≤ 0.05 after applying the Shapiro–Wilk and Kolmogorov–Smirnov tests (Table 2).

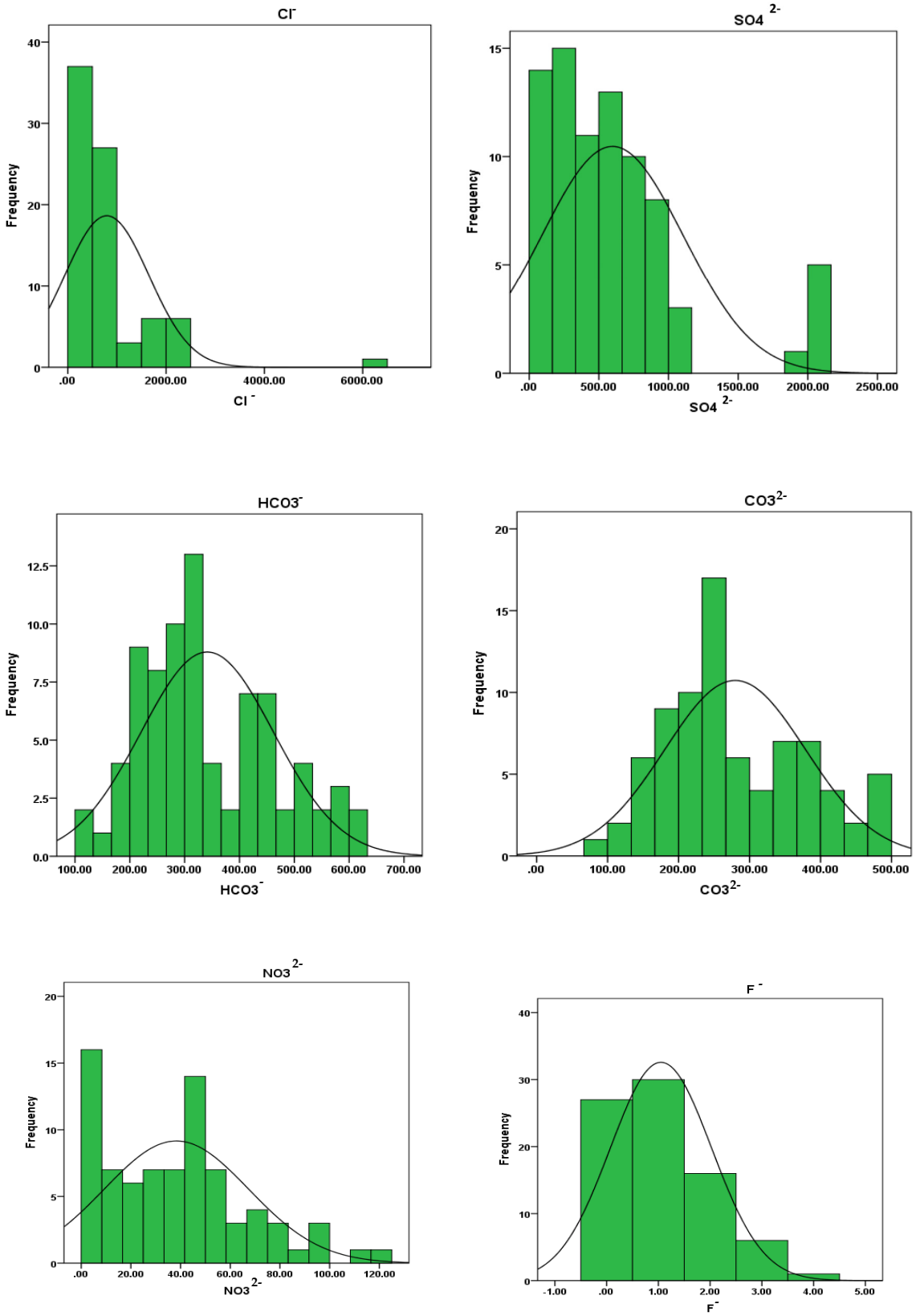


Figure 7. Histogram of the frequency distribution of anions Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, NO_3^{2-}, and F^- in the collected groundwater sample.

Table 4 shows the correlation matrix of the physiochemical parameters of the study area for the collected groundwater samples. According to the Pearson correlation matrix,

it was found that TDS had strong correlation with EC—0.986; TH—0.855; Na^+—0.866; Ca^{2+}—0.771; Cl^-—0.913; K^+—0.417; Mg^{2+}—0.345; and $SO_4{}^{2-}$—0.528. All ionic concentrations increased with the increase in the TDS value. These ions were indicated to be primarily intended for sedimentary rock weathering. The total quantity of components that are dissolved in the groundwater and the TDS values suggest that the dissolution of underground rock in groundwater fluids increased [44]. The bivariate plots between the main ions and TDS may be used to describe the geochemical processes that lead to groundwater mineralization. Na^+ and Cl^- have a positive correlation, which suggests that they have a common origin and indicates that the salinity of groundwater is caused by the mixing of two or more groundwater bodies with various hydrochemical compositions. The high concentration of these ions may be due to the dissolution of evaporitic minerals given that a high proportion of EC favors the dissolution of evaporite minerals and sulfate salts, resulting in an increase in the concentrations of Mg^{2+} and Ca^{2+} in groundwater.

Table 4. Pearson correlation for the variables in the collected groundwater samples.

	ALK	pH	TDS	EC	TH	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	$SO_4{}^{2-}$	$HCO_3{}^-$	$CO_3{}^{2-}$	$NO_3{}^{2-}$	F	ORP
ALK	1															
pH	−0.137	1														
TDS	0.006	0.249 *	1													
EC	−0.041	0.244 *	0.986 **	1												
TH	−0.134	0.103	0.855 **	0.833 **	1											
Na^+	0.072	0.297 **	0.866 **	0.868 **	0.542 **	1										
K^+	−0.195	0.083	0.417 **	0.400 **	0.371 **	0.335 **	1									
Ca^{2+}	−0.141	0.038	0.771 **	0.798 **	0.896 **	0.506 **	0.180	1								
Mg^{2+}	−0.017	0.150	0.345 **	0.239 *	0.419 **	0.190	0.463 **	−0.026	1							
Cl^-	−0.068	0.203	0.913 **	0.956 **	0.779 **	0.816 **	0.280 *	0.861 **	−0.009	1						
$SO_4{}^{2-}$	−0.031	0.194	0.528 **	0.411 **	0.525 **	0.407 **	0.466 **	0.142	0.895 **	0.155	1					
$HCO_3{}^-$	0.361 **	0.000	−0.076	−0.094	−0.121	−0.018	−0.030	−0.117	−0.030	−0.112	0.003	1				
$CO_3{}^{2-}$	0.361 **	−0.001	−0.077	−0.094	−0.121	−0.018	−0.029	−0.118	−0.030	−0.113	0.004	1.000 **	1			
$NO_3{}^{2-}$	0.068	−0.039	0.031	0.086	−0.113	0.214	−0.057	−0.035	−0.178	0.105	−0.188	0.122	0.122	1		
F^-	0.061	0.229 *	0.238 *	0.229 *	0.023	0.280 *	0.011	0.116	−0.194	0.226 *	−0.006	0.068	0.068	0.077	1	
ORP	0.087	−0.220 *	−0.300 **	−0.325 **	−0.294 **	−0.187	−0.109	−0.312 **	−0.018	−0.328 **	−0.048	0.197	0.197	0.220	−0.104	1

Note(s): ** correlation is significant at the 0.01 level (two tailed); * correlation is significant at the 0.05 level (two tailed).

4. Conclusions

The collected groundwater samples have pH values within the permissible limits, 6.5–8.5, indicating that they are slightly acidic to basic in nature. The collected groundwater samples' temperatures in the current study area ranged from 25 to 41 °C, with an average of 32 °C. The collected groundwater samples could be classified as containing very hard water. The groundwater samples with TDS values lower than 1000 mg/L are considered to be fresh water. The total charge of dissolved cations is not balanced with that of dissolved anions. This means that there may be other dissolved ions or solutes affecting water quality. The concentrations of Na^+ in the collected groundwater wells ranged from 36 to 1527 mg/L, with an average of 413 mg/L; the permissible limit is 200 mg/L. The

concentrations of K^+ in the studied groundwater samples ranged from 0.3 to 10.6 mg/L, with an average of 4 mg/L; the permissible limit is 12 mg/L. Almost all the collected groundwater samples were above the permissible limit: 75 mg/L of Ca^{2+}. The values of Ca^{2+} were between 59 and 2452 mg/L, with an average of 269 mg/L. The permissible limit of Mg^{2+} is 50 mg/L, while the concentrations of Mg^{2+} in the collected groundwater samples ranged from 3.7 to 338 mg/L, with an average of 82 mg/L. The concentrations of HCO_3^-, CO_3^{2-}, and Cl^- in the collected groundwater samples ranged from 110 to 600, with an average of 341 mg/L; from 90 to 492, with an average of 280 mg/L; and from 47 to 6331, with an average of 794 mg/L, respectively. The permissible limits of HCO_3^-, CO_3^{2-}, and Cl^- were 500, 500, and 250 mg/L, respectively. The concentration of SO_4^{2-} in the collected groundwater samples ranged from 41 to 2106 mg/L, with an average of 598 mg/L; the permissible limit of SO_4^{2-} is 250 mg/L. The concentration of F^- in the collected groundwater samples ranged from 0 to 4 mg/L, with an average of 1 mg/L; the permissible limit of F^- is 1.5 mg/L. The collected groundwater well samples belong to the Ca^{2+}-Mg^{2+}-Cl^--SO_4^{2-} water type, according to the Piper diagram. The K^+ concentration in groundwater is caused mostly by the weathering of K-feldspar. Among the anions, HCO_3^- is the most prevalent, followed by Cl^-, SO_4^{2-}, and NO_3^-.

The combination of Ca^{2+}, Mg^{2+}, and HCO_3^- is what causes the groundwater to be hard. In this study, we found large concentrations of the ions that are responsible for the groundwater's hardness. High HCO_3^- values show that the research area contains carbonate-containing minerals and degraded organic matter, which can also contribute to the occurrence of HCO_3^- in groundwater. A low ORP measurement, between 100 and 400 mV, may indicate the fermentation-related release of biological phosphorus or acid. According to a Gibbs diagram, it was found that the chemical weathering of rock-forming minerals influenced the groundwater quality by means of the dissolution of rocks.

Applications and calculations of the parameters SAR, RSC, PI, CR, MH, Na%, KR, and HI on the collected groundwater samples showed that 92.5% of the collected groundwater well samples are suitable for drinking and irrigation purposes after treatment processes. According to the designed histograms of the frequency distribution of the physical parameters, cations and anions measured in the collected groundwater sample have positive values of skewness, which indicated that their distributions were not perfectly symmetrical but rather deviated to the right as positively skewed. Destructive statistics were used to summarize data and make it easier to understand. The mean, median, and standard deviation, range, skewness, kurtosis, minimum, and maximum were calculated, and statistical analyses on the obtained data were applied to the physical parameters and to the cation and anion results. A statistical histogram was also designed for the obtained data to study the results, which were positively skewed and negatively skewed. Applying the Shapiro–Wilk and Kolmogorov–Smirnov tests to the obtained results of the collected groundwater samples showed that the results are highly significant, with p-values ≤ 0.05, which confirms that none of the current results follows a normal distribution.

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Conflicts of Interest: The authors declare no conflict of interest.

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