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Article

Hydro-Geochemical Applications and Multivariate Analysis to Assess the Water–Rock Interaction in Arid Environments

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Abstract: Thirty groundwater samples were taken from Assiut’s northern outskirts. The physico-chemical properties of these samples were investigated. For the evaluation of water–rock interaction, the saturation index (SI), chloro-alkaline indices (CAI1 and CAI2), Gibbs ratios for cations and anions (GC and GA), principal component analysis (PCA), and hierarchical cluster analysis (HCA) were used. (1) With the exception of five samples that were supersaturated, the rest of the groundwater samples were under-saturated with carbonate mineral dissolution (calcite, dolomite, and aragonite) and evaporite mineral dissolution (anhydrite, gypsum, halite, and sylvite). (2) The presence of ion exchange between alkali elements ($\text{Na}^+ + \text{K}^+$) and earth alkaline elements ($\text{Ca}^{2+} + \text{Mg}^{2+}$) is explained by the positive values of the chloro-alkaline indices. (3) In four groundwater samples, negative chloro-alkaline indices suggest reverse ion exchange and an increasing alkali element content. (4) The Gibbs diagram demonstrates that, with the exception of four samples that reflect saline groundwater, the majority of the groundwater samples are freshwater recharging from the fresh surface water in the research area. (5) Groundwater types include Ca-HCO_3 (11%), Mg-HCO_3 (48%), Na-HCO_3 (23%), Mg-Cl (13%), and Na-Cl (3%). (6) The alkali, earth alkaline elements, and sulphate are the key controls on groundwater salinity, according to PCA and HCA. (7) The somewhat saline groundwater in the research area’s western desert margins should not be used since it poses a health danger to people.

Keywords: groundwater; interaction; saturation index; Gibbs diagram; principal component analysis; Assiut Governorate



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1. Introduction

Water shortages in hyper-arid regions such as southern Egypt are a serious concern for hydrologists, who should evaluate and protect every accessible water source. Water scarcity in these hyper-arid areas might affect a number of activities (including the economy and human life); as a consequence, different actions are needed to avert the expected disasters and conflicts that may develop as a result of insufficient water supplies [1]. Groundwater is the second source of water used in agriculture, industry, and domestic applications [2]. Groundwater flow models are used to analyze groundwater flow behavior and recharge in vast aquifers [3], but these techniques might be challenging to implement due to a lack of datasets and the time and resources required to obtain them. For quantification of the groundwater storage changes on a regional scale, the gravity datasets from the Gravity Recovery and Climate Experiment mission, combined with other relevant information, have been extensively used in several study areas (e.g., [4–13]). Additionally, regional and global gravity and magnetic data are used to investigate heat flow in different regions [14,15].

Hydro-chemically, the groundwater is influenced by precipitation, geological structure, rock type, residence time, and geochemical activity along groundwater flow paths. In this sense, it is vital and necessary to study the mechanisms that alter groundwater and its chemistry via rock interactions. The term “water–rock interaction” refers to how groundwater interacts with the host rocks in a unique way that changes its chemical composition and properties [16]. The primary interaction between groundwater and ambient rock formation results in minerals with unique hydrochemical compositions and stability dynamic features [17]. Interaction mechanisms result in the creation of numerous dissolved element components in the aquifer, which can influence the groundwater quality, particularly in arid zones [18,19]. Furthermore, precipitation absorbed through the soil and sediments can dissolve carbonate minerals, such as calcite, aragonite, dolomite, and other minerals, in the flow path [20–22].

The chemical interaction between water and rock is one of the most intriguing and intricate phenomena in water geochemistry. The composition of surface water and groundwater is determined by how water reacts to rocks and minerals. The chemical reactions of water–rock interaction at high temperatures are associated with hydrothermal features, hydrothermal mineral deposits, and geothermal fields. The surface outcrops of rocks from deeper levels of the crust, such as lower crustal and mantle exposures, typically reveal features produced by supercritical aqueous fluid interaction at extremely high temperatures. Many researchers have investigated the water–rock interaction [17–19,22–26].

The purpose of this research is to examine how the groundwater chemistry is affected by the lithologic nature and structural geology. The aforementioned aim is crucial for long-term groundwater development in hyper-arid environments. As a consequence, researchers identified the geology and geochemistry of water-bearing strata along the flow path to the analyzed aquifers. The location was chosen as an example from the hyper-arid zone to carry out this scientific approach. To interpret the hydrochemical data based on factor scores, statistical measures such as the saturation index (SI), principal component analysis (PCA), and hierarchical cluster analysis (HCA) were used [27,28]. The SI can be used to assess the flow of groundwater in aquifer systems [29]. PCA and HCA are also used to assess the aquifer’s geochemical mineralization and groundwater contamination [22,30,31]. PCA and HCA can also be used to describe how agricultural and mining operations affect groundwater [32].

2. Material and Methods

2.1. Location

The research area is located in the northern section of the Assuit region, near the Nile Valley. It spans the latitudes of 27°10′ and 27°40′ N, and the longitudes of 30°40′ and 31°20′ E. It is geomorphologically divided into lowland and highland, with the Eocene plateau to the west and the Nile River to the east. The older alluvial plain (agricultural land) and the younger alluvial plain are represented by the morphological units (the reclaimed land; Figures 1 and 2; [33]). According to [34], the geologic succession is represented by rock units ordered from bottom to top as Eocene rocks (Mokkatom group), Pliocene deposits, and Quaternary sediments. In the researched area, groundwater is the second source of water for drinking water, domestic purposes, and irrigation. According to [35], the groundwater aquifer is made up of coarse and sandy clay with cobbles, gravels, and calcareous rock fragments from the middle Pleistocene (Prenile) (Figure 3). The aquifers are primarily replenished from surface water and precipitation, and groundwater moves westward [23,36].

2.2. Sampling and Laboratory Methods

From the research region, 30 groundwater samples were taken. The samples were placed in pre-rinsed polypropylene bottles and carefully sealed. Standard techniques were used to filter the samples and analyze their chemical components [38].

The pH-meter was used to measure the temperature, electric conductivity (EC), total dissolved salts (TDSs), and hydrogen ion concentration (pH) while the Flame-Photometer was utilized to assess the sodium and potassium concentrations. Titration was used to determine the amounts of calcium, magnesium, carbonate, bicarbonate, sulphate, and chloride. The ionic balances identified the analytical precision of the ion's measurements, which was less than 5%.

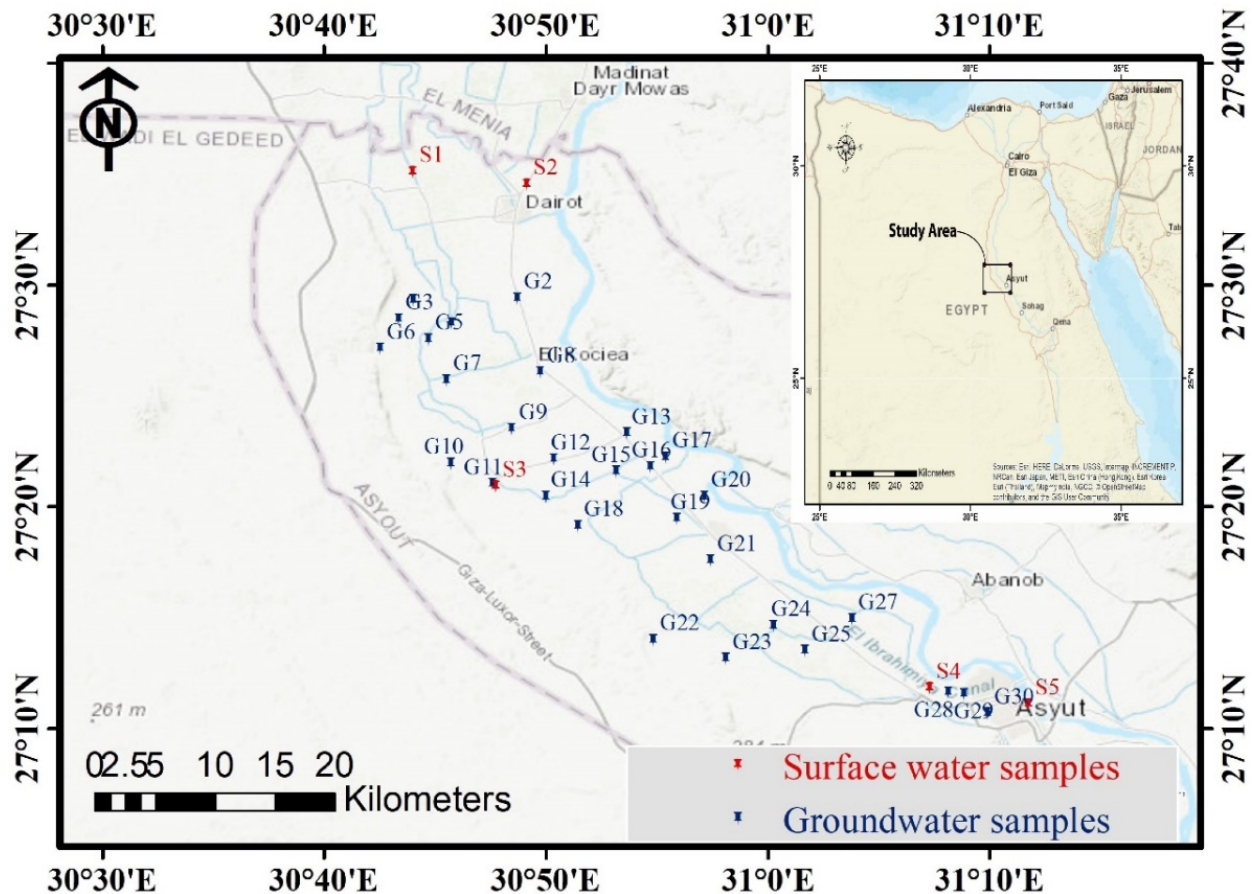


Figure 1. Location map of the study area.

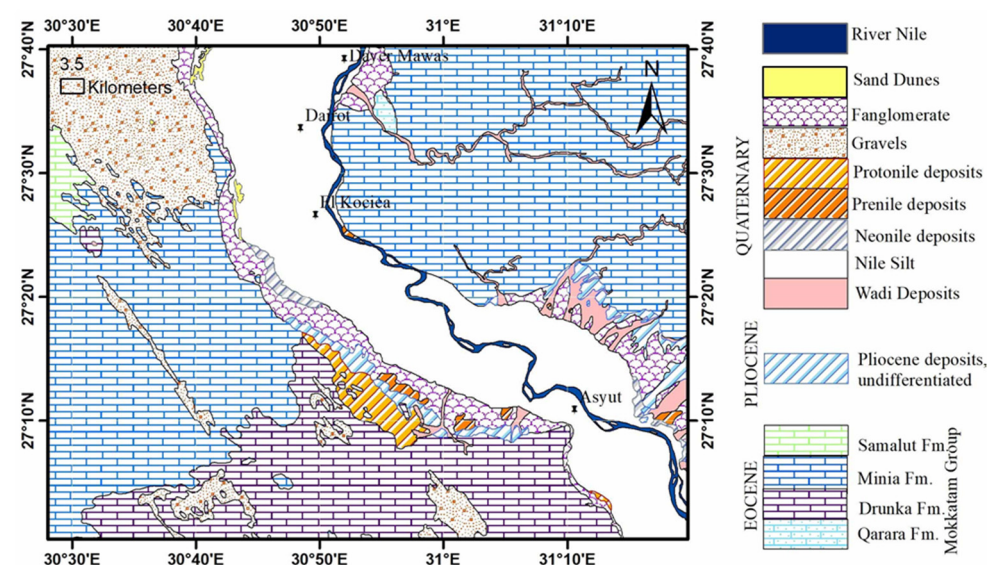


Figure 2. Geologic map of the study area (after [37]).

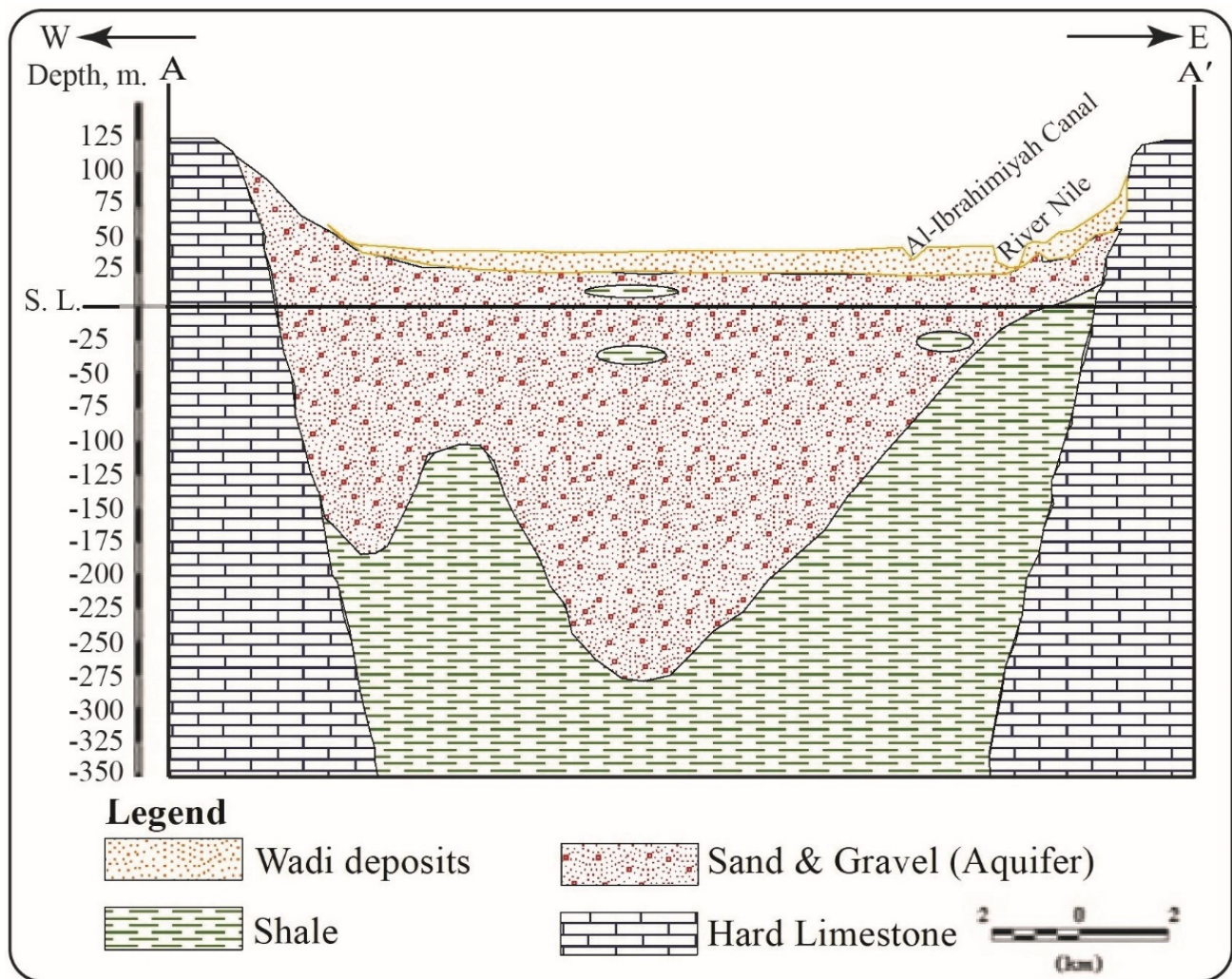


Figure 3. Geoelectrical cross section A–A' of the study area (after [35]).

2.3. Saturation Index (SI)

The SI investigates the chemical equilibrium of processes involving aqueous species and minerals [23,24,39]. The Phreeqc Interactive version 3.4 was used to calculate the saturation indices for the groundwater samples. The SI system is defined by the equation:

$$SI = \log_{10} \frac{IAP}{K_{\text{mineral}}}$$

where IAP signifies the ion activity product and K_{mineral} denotes the mineral's solubility constant. When SI equals 0, the dissolved mineral in the water sample is entirely saturated. Positive SI values indicate that the sample is super-saturated, and the mineral will tend to precipitate; negative SI values indicate that the sample is under-saturated, and the mineral will dissolve [40].

2.4. Chloro-Alkaline Indices (CAIs)

CAIs describe ion exchange processes that occur when one ion is replaced by another ion at the solid material surface of a soil or rock, such as a clay mineral, and organic matter or metal oxyhydroxide [20,23,41,42]. The concentration of ions and the transit of contaminants in groundwater are controlled by ion exchange and sorption processes [20].

The following equation is used to determine CAI, where the concentrations are represented in equivalent per mill (epm):

$$CAI_1 = [Cl^- - (Na^+ + K^+)]/Cl^-$$

and:

$$CAI_2 = [Cl^- - (Na^+ + K^+)]/(SO_4^{2-} + HCO_3^- + CO_3^{2-})$$

The obtained positive results indicate that groundwater alkalis ($Na^+ + K^+$) interchange with alkaline earth ions ($Ca^{2+} + Mg^{2+}$) in the host rocks. As a result, the concentrations of Ca^{2+} and Mg^{2+} in the groundwater are rising [43]. Negative values, on the other hand, show that reverse exchange occurs and the alkali ions ($Na^+ + K^+$) in the solution exceed the limit [43]. Furthermore, negative values refer to rainwater recharge, which seeps into the sediments and replenishes the groundwater table [44].

2.5. Gibbs Diagram (GD)

The GD depicts groundwater evolution processes and the effects of surrounding sediments on groundwater chemistry [23,45,46]. Aside from the water–rock interaction and atmospheric precipitation, evaporation is an important mechanism that regulates water chemistry [45,47]. The following equations were used to compute the Gibbs ratio for cations and anions (GC and GA):

$$GC = Na^+ / (Na^+ + Ca^{2+})$$

$$GA = Cl^- / (Cl^- + HCO_3^-)$$

The concentration is expressed in epm in this case. By plotting both the GC and GA values against TDS, a Gibbs diagram can be generated. The ion concentrations and physicochemical properties are shown in Table 1.

Table 1. The ion concentrations and physicochemical values in the studied groundwater samples.

Ion-Indices	Concentrations (ppm)			Concentrations (epm)		
	Min	Max	Aver	Min	Max	Aver
pH	6.4	7.0	6.7	-	-	-
TDS	156	1069	552	-	-	-
T (°C)	23	33	26	-	-	-
Ca^{2+}	30	240	89	1.5	12	4.4
Mg^{2+}	21	170	63	1.7	14	5
Na^+	23	575	139	1	25	6
K^+	5	23	11	0.14	0.6	0.3
CO_3^{2-}	0	0	0	0	0	0
HCO_3^-	189	915	439	3.1	15	7
Cl^-	50	886	186	1.4	25	5
SO_4^{2-}	7	912	171	0.15	19	3.6
SI	−7.6	4.2	−2.6	-	-	-
CAI_1	-	-	-	−2.7	24	3.1
CAI_2	-	-	-	1.05	24	4.2
GC	-	-	-	0.13	0.88	0.50
GA	-	-	-	0.16	0.86	0.34

2.6. Statistical Analysis

Principal component analysis (PCA) is a method for determining the dynamics of all variables in a system under study. Its goal is to minimize the multivariate dataset's dimensionality by extracting information in the form of a minimal number of main components while representing typical environmental factors. As a result, by eliminating information omission, the key principal components may be retrieved, comprising all of the essential data. The equations were reported in detail by [48].

Hierarchical cluster analysis (HCA) is a clustering method that explores the placement of data in groups and within groups in a hierarchical fashion. HCA outcomes are frequently presented in the form of a dendrogram, which is a tree-like representation of the structure of samples and their interactions. There are two primary approaches to solving the grouping problem in HCA: agglomerative and divisive [49]. A single sample is initially considered a cluster in the agglomerative technique, and subsequently pairs of clusters are merged. The divisive algorithm begins with a single cluster containing all samples and then separates them recursively.

PCA and HCA statistical analysis were used to describe the quality of pumped water and determine the extent to which it may be influenced by environmental parameters and the interaction between soil and water. PCA and HCA were both performed with the [50].

3. Results and Discussion

The interaction between groundwater and host rocks is determined by dissolution and precipitation, which are influenced by a variety of factors, including solution composition and the degree of saturation of the aqueous solution with respect to the various mineral phases [24].

3.1. Saturation Index

Because the groundwater system is affected by diverse solutes resulting from the interaction with the surrounding sediments, SI aids in the realization of reactive minerals in the groundwater system [39,40]. SI values indicated that the bulk of groundwater samples are undersaturated in these minerals (Figure 4), except five samples: No. G7, G19, G21, G25, and G26. Sample No. G7 is supersaturated with anhydrite, aragonite, calcite, dolomite, gypsum, halite, and sylvite minerals. Sample No. G19 is supersaturated with aragonite, calcite, and dolomite while samples No. G21 and G25 are supersaturated with dolomite only. Moreover, sample No. G26 is supersaturated with dolomite and aragonite. This supported by [51], who proved the presence of carbonate minerals in Assuit soils, which leached to the groundwater, using XRD, XRF, and SEM techniques.

The SI values for the five surface water samples, on the other hand, are undersaturated with the previously mentioned minerals (Figure 4). This indicates that the groundwater in the study area is primarily recharged by surface water [23]. The evaporite and carbonate minerals are dissolutions based on the SI results, except in the supersaturated samples. These minerals are prone to precipitation [23,39,40]. The very strong correlation between TDS and Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , and SO_4^{2-} , where $r = 0.940, 0.935, 0.939, 0.962$, and 0.848 , respectively, supports the presence of carbonate and evaporite minerals in the groundwater (Table 2). This proved that the motioned ions (Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , and SO_4^{2-}), which were indicated on both carbonate and evaporite minerals, are the main control in TDS.

Table 2. Correlation matrix of the groundwater hydrochemical variables.

	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	Cl^-	SO_4^{2-}	pH	TDS
Ca^{2+}	1								
Mg^{2+}	0.778	1							
Na^+	0.910	0.914	1						
K^+	0.374	0.446	0.429	1					
HCO_3^-	−0.63	−0.044	0.005	0.467	1				

Table 2. Cont.

	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ [−]	Cl [−]	SO ₄ ^{2−}	pH	TDS
Cl [−]	0.965	0.965	0.955	0.365	−0.146	1			
SO ₄ ^{2−}	0.884	0.885	0.943	0.393	−0.061	0.872	1		
pH	0.002	−0.005	0.080	0.069	0.240	0.054	−0.070	1	
TDS	0.940	0.935	0.939	0.442	−0.001	0.962	0.848	0.095	1

Bold numbers indicate the variable is significant if its value is more than 0.5.

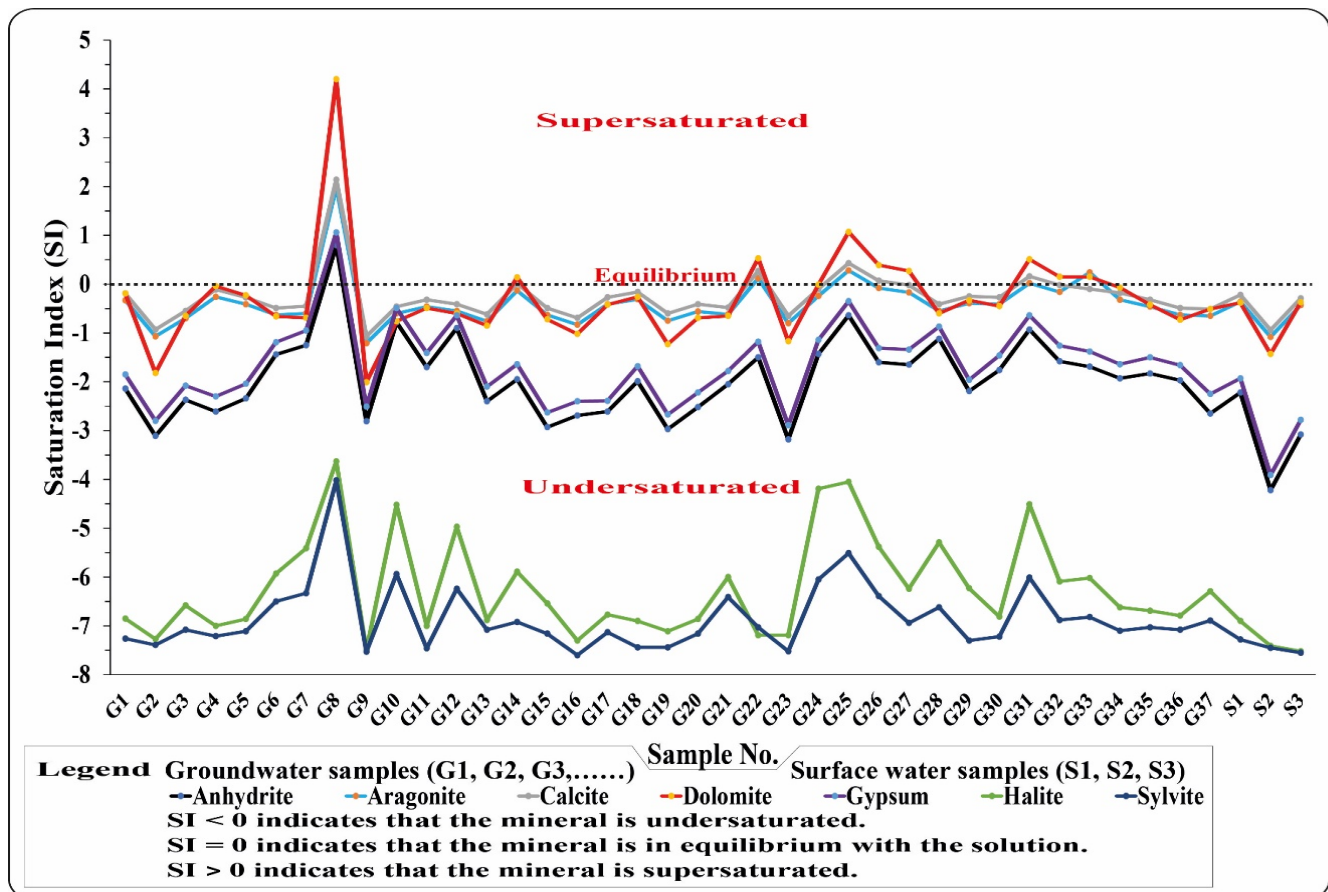


Figure 4. Saturation indices for the studied water.

3.2. Chloro-Alkaline Indices

The CAIs indicate the ion exchange between groundwater and solid constituents in ambient sediments [20,23,39,41]. Except for four samples that have negative CAI values, all of the groundwater samples had positive CAI values (Figure 5). This shows that alkali ions (Na⁺ + K⁺) in groundwater interact with earth alkaline elements (Ca²⁺ + Mg²⁺) in ambient sediments at the solid surface material [23,39,43].

As a result, the concentrations of calcium and magnesium in groundwater are raised, indicating the dominance of carbonate mineral dissolution [23,39,43]. The samples with negative CAI values, on the other hand, showed reverse replacement. As a result, the sodium and potassium concentrations in the groundwater are too high (Figure 5; [23,39,43]). The negative numbers showed that the percolated rainwater is recharging the groundwater [44]. The substantial positive correlation coefficients ($r = 0.910\text{--}0.914$) between Ca²⁺ and Mg²⁺ with Na⁺ demonstrate these replacements (Table 2).

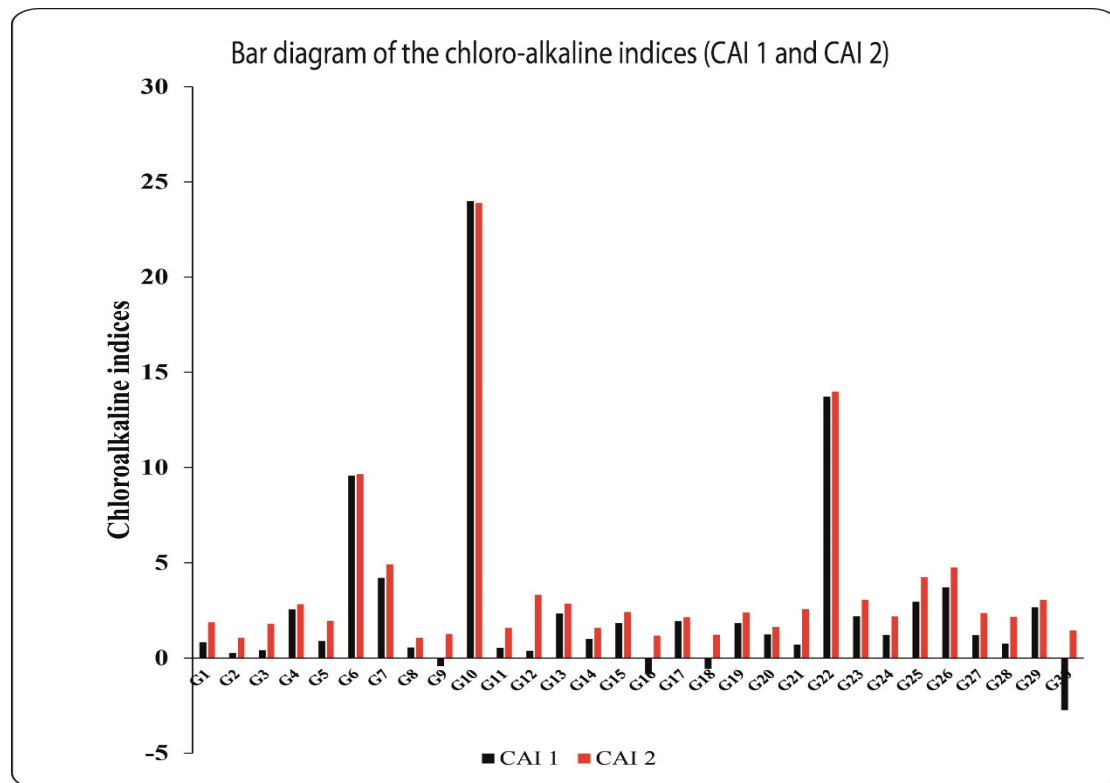


Figure 5. Chloro-alkaline indices (CAI₁ and CAI₂) for the groundwater samples.

3.3. Gibbs Diagram

In addition to the water–rock interaction (rock dominance) and precipitation, the GD considers evaporation as a significant mechanism that can alter groundwater chemistry [45–47]. According to GD in this study, the majority of groundwater samples were located in the rock-weathering dominance field (Figure 6). This suggests that the water–rock interaction is the most important natural factor determining the groundwater chemistry. The term “rock-weathering dominance” refers to the recharging of fresh groundwater from fresh surface water. Furthermore, it suggests that the majority of carbonate minerals are dissolved in groundwater [46,47]. It is also obvious that evaporation processes influenced the groundwater, implying that a considerable ion exchange occurred between groundwater and solid constituents in ambient sediments ([46]; Figure 6).

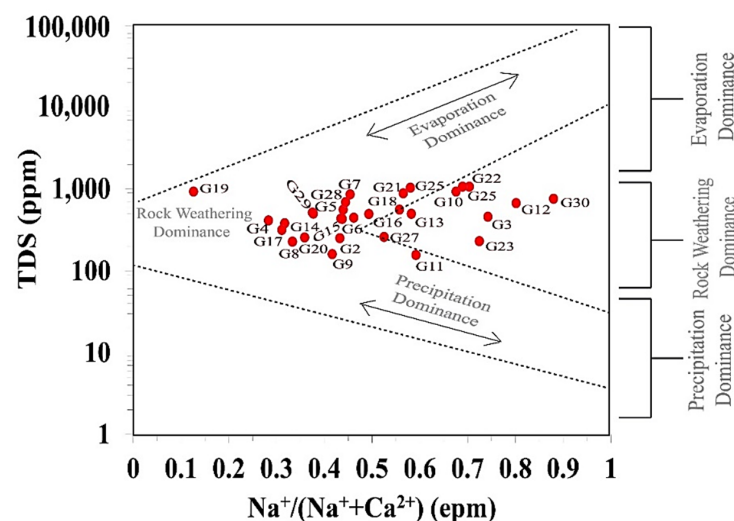


Figure 6. Cont.

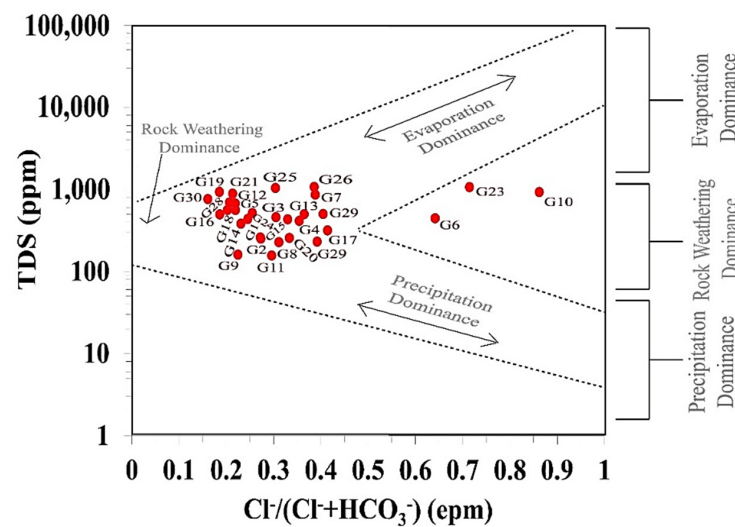


Figure 6. Gibbs diagram for the groundwater samples.

The evaporation dominance, on the other hand, indicated that saline groundwater may be the consequence of groundwater mixing with saline surface water, older deep water, and/or evaporites dissolved along the groundwater flow channel [23,46,47].

3.4. Water Type

Figure 7 shows the water types, with Ca-HCO_3 (13%), Mg-HCO_3 (48%), and NaHCO_3 (23%), indicating the higher solubility of carbonate minerals, particularly calcite, in groundwater samples [20,45,47]. Mg-Cl (13%) and Na-Cl (3%), respectively, are present in the other samples of groundwater, owing to the evaporite minerals' high solubility [20,45,47]. Surface water samples, on the other hand, revealed Mg-HCO_3 (67%), Na-HCO_3 (28%), and Na-Cl (5%), indicating that the groundwater is mostly replenishing from the surface water. The bicarbonate ions are prevalent in the groundwater samples, according to the water type data.

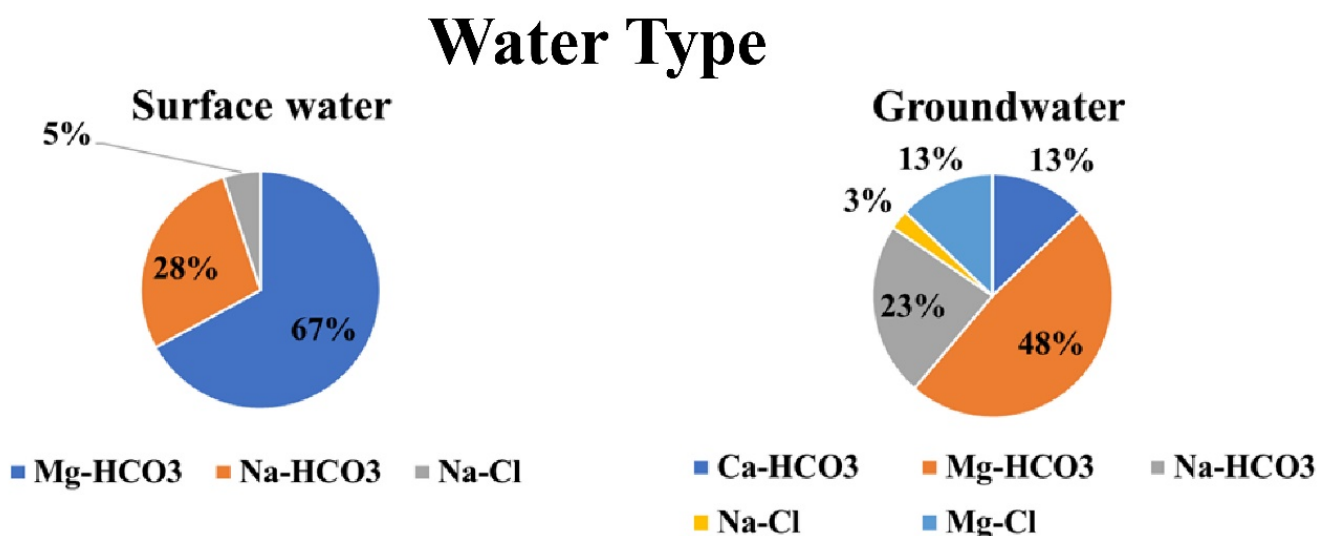


Figure 7. Water types of the studied water samples.

3.5. Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA)

The major goal of using such factor analysis methods is to explain the variance in the data and to discover the essential processes that drive the pumped water's quality. The main components are shown in Table 3 and Figure 8. PC1 contains very substantial positive

loadings for Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , SO_4^{2-} , and TDS, accounting for 64.8 percent of the variance. This implies that the main source of groundwater salinity is the dissolution of carbonate and evaporite minerals. PC2 and PC3 account for 16.7% and 10.4% of the total variation, respectively. PC2 had a lot of HCO_3^- positive loadings, whereas PC3 had a lot of pH-positive loadings. This is due to the fact that in the case of groundwater salinity, both HCO_3^- and pH are ineffective (Table 3 and Figure 8). The HCA analysis confirmed that Ca^{2+} , Mg^{2+} , Na^+ , and Cl^- are the primary components of TDS in pumped water, with these parameters grouped in one group (cluster A) and the HCO_3^- and pH parameters clustered in group B, as indicated by HCA (Figure 9).

Table 3. Variables of the principal component analysis for the studied groundwater.

	PC1	PC2	PC3
Ca^{2+}	0.971	−0.089	0.023
Mg^{2+}	0.977	−0.049	−0.019
Na^+	0.971	0.007	0.054
K^+	0.488	0.641	−0.386
HCO_3^-	−0.013	0.894	−0.206
Cl^-	0.978	−0.124	0.100
SO_4^{2-}	0.929	−0.095	−0.078
pH	0.038	0.514	0.848
TDS	0.969	0.016	0.074
Eigen Value	5.838	1.509	0.936
Variance%	64.867	16.761	10.405
Cumulative%	64.867	81.629	92.034

Bold numbers indicate highly-loaded variables.

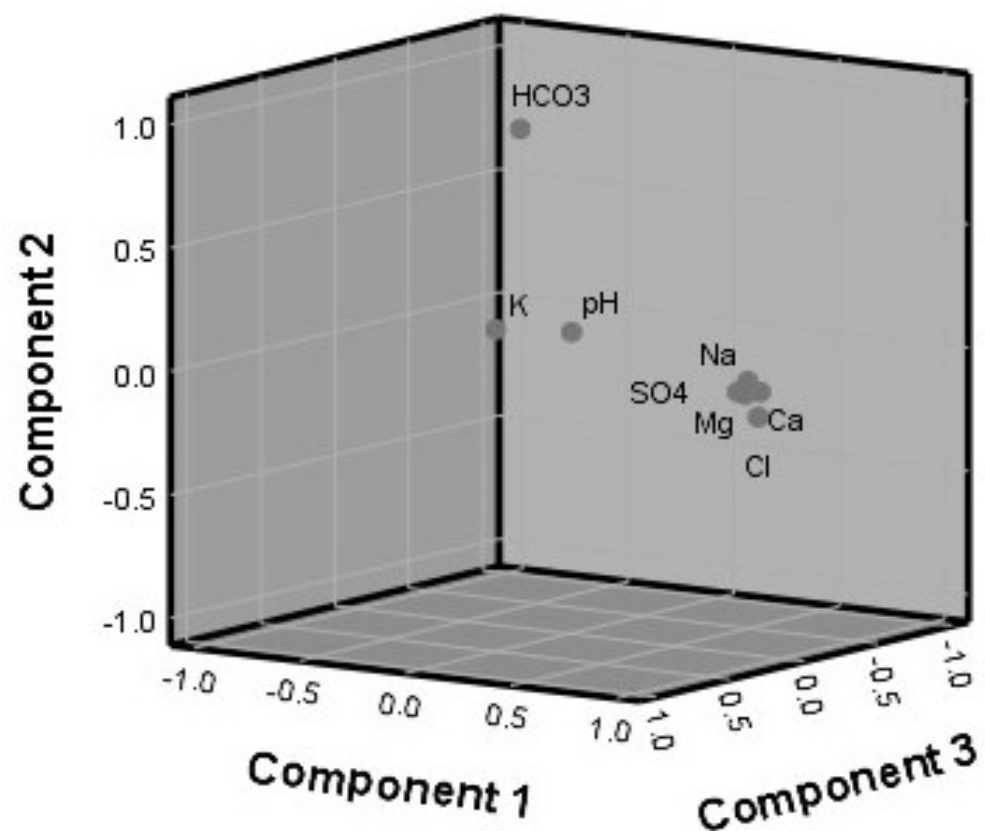


Figure 8. Component plot in the rotated space (PCA).

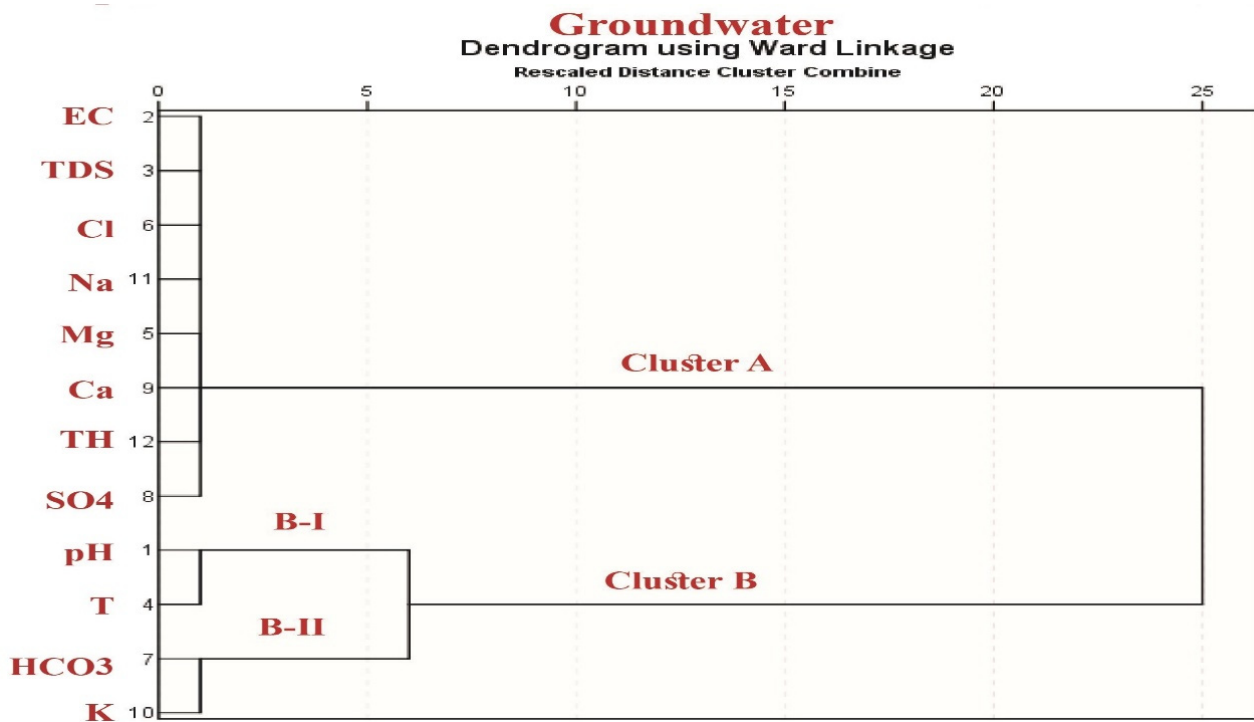


Figure 9. HCA showing the main clusters in the studied groundwater.

4. Conclusions

Many activities, such as dissolution, interaction with rocks, and evaporation during flow paths, have a significant impact on groundwater chemistry. Carbonate minerals (calcite, dolomite, and aragonite) and evaporite minerals were undersaturated in the majority of groundwater samples, according to saturation indices (anhydrite, gypsum, halite, and sylvite). The positive chloro-alkaline indices imply that the alkali ions (Na^+ , k^+) in groundwater are exchanged with earth alkaline ions (Ca^{2+} + Mg^{2+}) in ambient sediments of solid surface materials. As a result, the earth's alkaline ions increase, and the dominant carbonate mineral dissolution in the groundwater is noticed. The chloro-alkaline indices of minor groundwater samples were negative, indicating reverse exchange and an increase in alkali ions; thus, evaporite mineral dissolution is dominant in the groundwater. The majority of the samples were plotted in the rock dominance field and are fresh groundwater recharging from fresh surface water, as shown by the Gibbs diagram. The minor samples were saline groundwater, implying that the groundwater has been mixed with saline surface water, older deep water, and/or evaporites that were dissolved along the flow path. Carbonate and evaporite mineral dissolution were dominant in the groundwater samples. The findings showed that the groundwater is mostly recharged from surface water sources with Mg-HCO_3 (67%), Na-HCO_3 (28%), and Na-Cl (5%) water types, and the presence of bicarbonate ions in the groundwater. The alkali, earth alkaline elements, and sulphate ions are the key regulating variables affecting groundwater salinity. Groundwater in the western half of the research region is slightly saline and should not be used for residential purposes.

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