

Article

Hydro-Geochemical Assessment of Groundwater Quality in Aseer Region, Saudi Arabia

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Received: 30 October 2018; Accepted: 6 December 2018; Published: 13 December 2018



Abstract: Saudi Arabia is an arid country with very limited water resources. The absence of surface water bodies along with erratic rainfall renders groundwater as the most reliable source of potable water in arid and semi-arid regions globally. Groundwater quality is determined by aquifer characteristics regional geology and it is extensively influenced by both natural and anthropogenic activities. In the recent past, several methodologies have been adopted to analyze the quality of groundwater and associated hydro-geochemical process i.e., multivariate statistical analysis, geochemical modelling, stable isotopes, a redox indicator, structural equation modelling. In the current study, statistical methods combined with geochemical modelling and conventional plots have been used to investigate groundwater and related geochemical processes in the Aseer region of Saudi Arabia. A total of 62 groundwater samples has been collected and analyzed in laboratory for major cations and anions. Groundwater in the study region is mostly alkaline with electrical conductivity ranging from 285–3796 $\mu\text{S}/\text{cm}$. The hydro-geochemical characteristics of groundwater are highly influenced by extreme evaporation. Climatic conditions combined with low rainfall and high temperature have resulted in a highly alkaline aquifer environment. Principal component analysis (PCA) yielded principal components explaining 79.9% of the variance in the dataset. PCA indicates ion exchange, soil mineralization, dissolution of carbonates and halite are the major processes governing the groundwater geochemistry. Groundwater in this region is oversaturated with calcite and dolomite while undersaturated with gypsum and halite which suggests dissolution of gypsum and halite as major process resulting into high chloride in groundwater. The study concludes that the combined approach of a multivariate statistical technique, conventional plots and geochemical modelling is effective in determining the factors controlling the groundwater quality.

Keywords: hydro-geochemical; multivariate statistics; groundwater; Aseer region

1. Introduction

The absence of surface water bodies renders groundwater as most reliable source of potable water in arid and semi-arid regions globally [1]. High evaporation and low precipitation ensure fewer surface water bodies resulting in a higher dependency on groundwater. In Saudi Arabia, owing to rainfall variability and scarce surface waterbodies, demand for the desalination of seawater and to some extent

dependency on groundwater resource in Aseer province has increased tremendously in past few years. The groundwater in Saudi Arabia is found in eight large sedimentary basins. The groundwater reserves have been estimated at $1919 \times 10^9 \text{ m}^3$ of which $160 \times 10^9 \text{ m}^3$ is stored in deeper aquifers [2]. In general, groundwater is considered as safe from microbial contamination, but the presence of inorganic contaminants from the underlying rocks alleviates the problem. Groundwater is a significant hidden resource in context of quality and quantity. However, once contaminated it is not easy to restore the aquifer and this escalates the pollution impact [3–5].

The quality of groundwater is determined by the regional geology and aquifer characteristics and it is extensively influenced by both natural and anthropogenic activities. Hydro-geochemical processes i.e., precipitation, dissolution, recharge, discharge, oxidation-reduction, ion exchange, water mixing residence time etc. greatly influence the composition of groundwater [6]. When groundwater flows in an aquifer system it interacts with the aquifer minerals along with intermixing of water, chemical characteristics at the recharge zone, interaction between rock-water, climatic conditions, topography, flow direction, geological formations which governs the groundwater quality [7–9]. Also, anthropogenic activities such as over exploitation, sewage/fertilizers leaching, spillages etc influence groundwater quality. The chemical characteristics of groundwater are significant as they determine the suitability for domestic, industrial or agricultural use [5,10].

In the recent past, several methodologies have been adopted to analyze the quality of groundwater and associated hydrogeochemical process i.e., multivariate statistical analysis [3,9,11,12], geochemical modeling [13–16], stable isotopes [17,18], redox indicator, structural equation modeling [19]. These methods have been employed to analyze the geochemical evolution and hydro-chemical processes governing chemical composition of groundwater in their respective regions. The current study evaluates the groundwater and related geo-chemical processes using conventional graphical methods and statistical analysis in the Aseer region of Saudi Arabia.

2. Material and Methods

2.1. Study Area

The Aseer region of the Kingdom of Saudi Arabia lies between the latitude of $17.367079^\circ \text{ N}$ to $21.033532^\circ \text{ N}$ and longitude of $41.302589^\circ \text{ E}$ to $44.520914^\circ \text{ E}$ (WGS_1984) with area 84231 sq. km (Figure 1). The primary aquifers include quaternary alluvium, quartz sandstone and conglomerates while secondary aquifers include mainly limestone with lateral diagenetic alterations with increased original porosity along with karstification. Most of the aquifers consist of sedimentary rocks excluding Harrart and Wadi (filled with Shields).

Unconfined quaternary alluvial aquifers are important source of groundwater particularly where fed by runoff from the mountains of the Aseer. These shallow aquifers with poor to good quality have average annual recharge of $1196 \times 10^6 \text{ m}^3$ [20]. The good quality of groundwater in Wadi-ad-Dawasir is due to 100 m thick alluvial fill. The majority of average annual rainfall (355 mm) occurs between March–June and October, while the temperature in the study area varies from 19.3° C to 29.7° C .

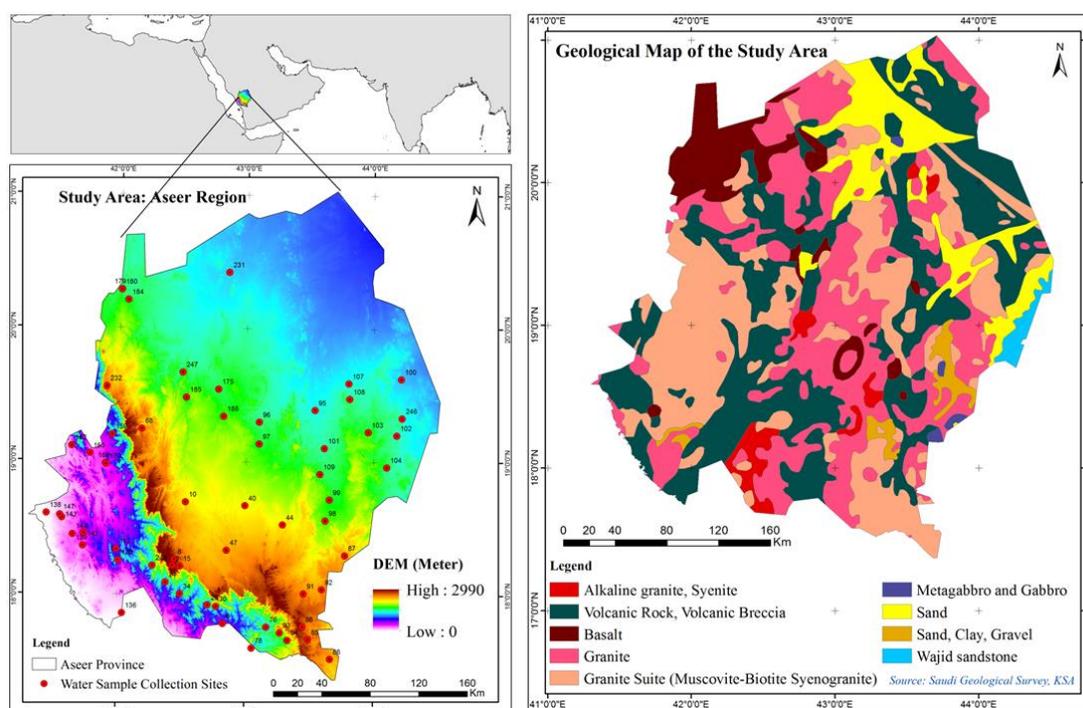


Figure 1. Study area map with sampling location of groundwater.

2.2. Sampling and Analysis

Sixty-two groundwater samples were collected during November 2017 to January 2018 and tested onsite for pH, electrical conductivity (EC) and total dissolved solid (TDS) using portable pH, EC electrode (Oakton) and TDS meter (HANNA). The samples were acidified using nitric acid (50%) pH < 2 for cation analysis, while samples collected for anion analysis were not acidified. The samples were stored in an ice box, carried to the laboratory and kept at 4 °C for further chemical analysis. The samples were analyzed for the major cations (Mg^{2+} , Ca^{2+} , Na^+ , K^+) along with iron (Fe) using an atomic absorption spectrometer (Thermo Fisher Scientific M series), and the major anions (F^- , Cl^- , SO_4^{2-} , NO_3^-) were analyzed using an ion chromatograph (Dionex). Bicarbonate (HCO_3^-), total alkalinity and hardness of the samples was determined by titrimetric method as described in APHA 1995 [21]. After the analysis of all the groundwater quality parameters normalized charged balance index (NCBI) was calculated using the following formula [22,23]:

$$NCBI = (\Sigma T_z^- - \Sigma T_z^+) / (\Sigma T_z^- + \Sigma T_z^+)$$

where, ΣT_z^+ = total sum of cations (in epm) and ΣT_z^- = total sum of anions (in epm). The values of NCBI ranged between +0.15 to −0.15.

2.3. Statistical Analysis

Correlation analysis of the groundwater quality parameters was studied to understand the degree of relationship/association between the water quality parameters. The correlation value (r) varies from +1 to −1. Variables with r value > 0.7 are considered strongly correlated while values between 0.5–0.7 are considered moderately correlated.

The multivariate technique, principal component analysis (PCA), is employed for large dataset to reduce volume of redundant information [5,9]. PCA has been performed using the XL-stat extension of Microsoft Excel. Bartlett's sphericity test of normalized data has been carried out which shows χ^2 (cal) = 1190.4 is greater than the χ^2 (crit) = 202.5 (at degree of freedom 171, significant level 0.05 and p value < 0.0001); these values indicate successful data dimension reduction performed by PCA.

During the PCA analysis all the variables has been scaled using the mean value 0 and variance of 1 and the eigen values > 1 has been used for the interpretation of the dataset [24].

2.4. Geochemical Modeling

Inverse geochemical modelling along with thermodynamic program Phreeqc was employed to estimate saturation index and aqueous mineral phases [25]. The inverse geochemical modelling consisted of the following assumptions: (1) analysis of two groundwater from the initial and final water-wells should represent groundwater that flows along the same path; (2) hydrochemistry should not be affected significantly by diffusion and dispersion; (3) the groundwater system is steady in terms of chemical composition; and (4) the inverse calculation is based on the mineral phases present in the aquifer [8,9,25]. The validation of the inverse modeling results depends upon input data accuracy, degree of understanding of local geochemical processes, groundwater system conceptualization and basic hydrochemical concepts. Changes in saturation state are useful for distinguishing the different stages of hydro-chemical evolution and the identification of important geochemical reactions controlling the groundwater chemistry [25–27]. Geochemical modeling of the groundwater samples was carried out using Phreeqc version 3. It operates according to the mass balance method, which determines the change in the chemical properties of the mineral species present in the groundwater [26]. Saturation indices (SI) of groundwater were calculated using the equation below:

$$SI = \text{Log} \frac{IAP}{K_{t_{sp}(T)}}$$

where, IAP is ion activity product and $K_{t_{sp}}(T)$ is equilibrium solubility product of the mineral. Negative values of SI suggest groundwater is undersaturated while the positive values suggest oversaturation of groundwater with respective minerals.

2.5. Geospatial Database

The spatial analysis tool of ArcGIS 10.3 was used to analyze the spatial variation of groundwater quality parameters in the study area. The inverse distance weighted (IDW) algorithm was used to interpolate the point data [11] in order to generate the surface map. The IDW method has been successfully used to a power (e.g., linear, squared and cubed) to model different geometries (e.g., line, area, volume). Weights are computed by taking the inverse of the distance from an observation's location to the location of the point being estimated [28].

3. Results and Discussion

3.1. Distribution of Major Ions

Chemical characteristics of groundwater in mainly dependent on the interaction of rock and water along with geochemical process occurring into the aquifer system. The basic statistics of the analyzed groundwater quality parameters along with their World Health Organization (WHO) limits are presented in Table 1 [29]. The pH of water samples varied from 5.6 to 9.2 and only 4 out of 62 groundwater samples have pH values < 7 which suggest high interaction between soil and water resulting into high alkalinity of the aquifers.

Table 1. Descriptive statistics with World Health Organization (WHO) guidelines of groundwater quality parameters (ND; Not Defined).

Parameter	Minimum	Maximum	Mean	Standard Deviation	WHO 2009
pH	5.6	9.2	7.7	1.2	6.5–8
EC	285	3796	1221.5	713.6	1500
TDS	155	2619	713.9	478.7	1000
Alkalinity	56	1899	223.8	229.8	-
TH	104	1658	387.3	252.7	-
Na ⁺ (mg/L)	3.5	72.8	29.0	15.9	200
K ⁺ (mg/L)	BDL	9.6	3.3	2.4	30
Ca ²⁺ (mg/L)	48.8	540	246.9	94.8	200
Mg ²⁺ (mg/L)	2.9	214	36.4	36.6	150
Fe (mg/L)	BDL	1.1	0.1	0.1	0.3
F (mg/L)	BDL	0.86	0.23	0.35	1.5
NH ₄ (mg/L)	BDL	0.1	0.0	0	-
NO ₃ ⁻ (mg/L)	BDL	155	31.4	41.9	50
Cl ⁻ (mg/L)	12	825	173.8	146.7	250
SO ₄ ²⁻ (mg/L)	29	557	145.7	111.6	250
HCO ₃ ⁻ (mg/L)	136	864	401.5	129.9	300

The total alkalinity of groundwater varied between 56 to 1899 mg/L. Wide variation in the EC and TDS is observed and EC varied from 285 to 3796 $\mu\text{S}/\text{cm}$. The high aridity of the Aseer region due to low precipitation and high evaporation contributes to high salt concentration in groundwater [9]. According to the classification by Davist and Dewiest 1967 [30], only 6 samples out of 62 (10%) has EC < 500 $\mu\text{S}/\text{cm}$ and it can be considered similar to freshwater while 44 out of 62 (%) is under marginal water type with EC 500–1500 $\mu\text{S}/\text{cm}$ and rest 12 has EC > 1500 $\mu\text{S}/\text{cm}$ which is unfit for drinking [29,30]. Based on the mean concentration of the major cations, Ca²⁺ is found as the most dominant cation ranging from 48.8 to 540 mg/L with an average of 246.9 mg/L followed by Mg²⁺, Na⁺ and K⁺ (Figure 2).

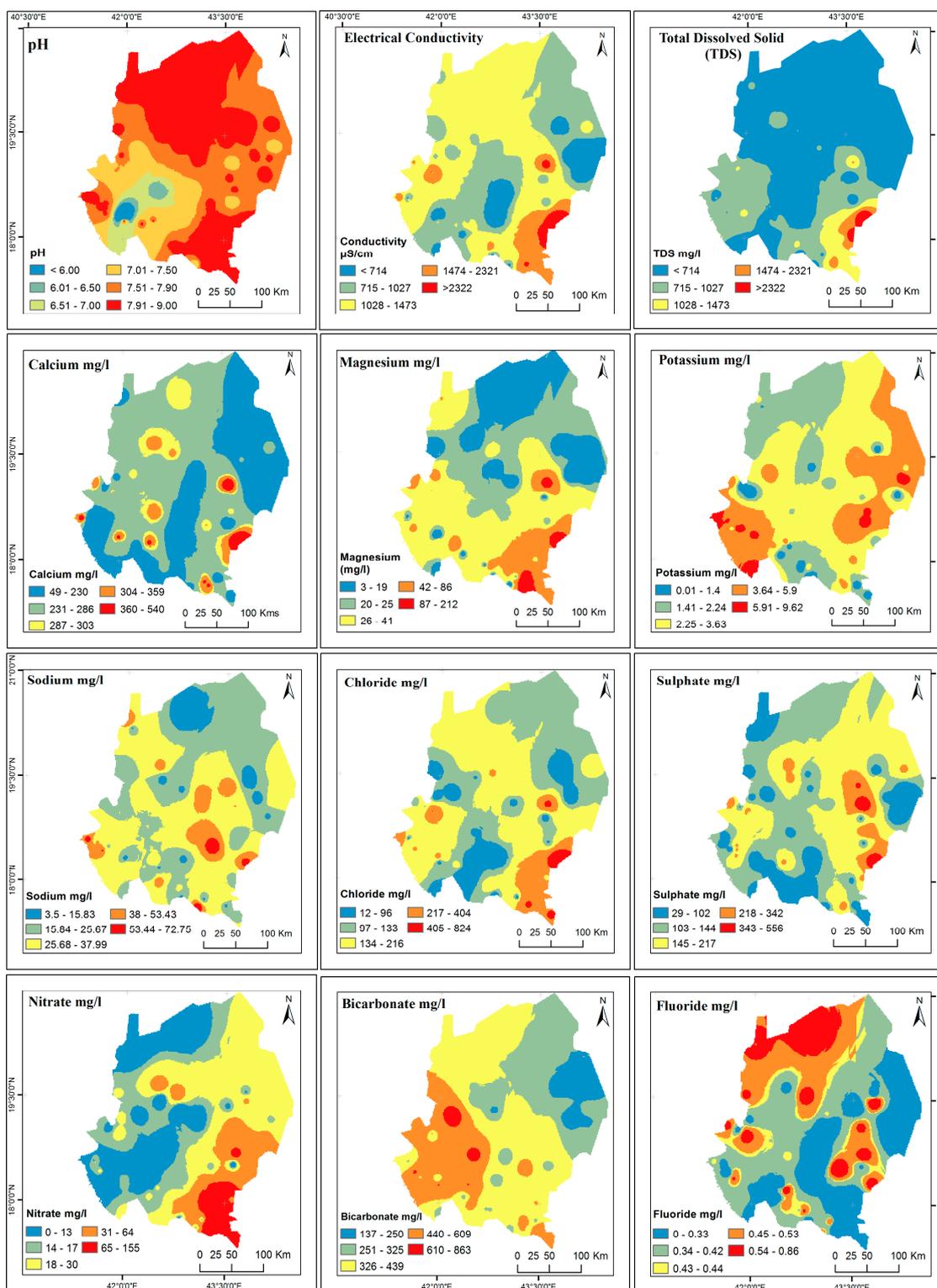


Figure 2. Distribution of major pH, electrical conductivity (EC) and major ions.

The concentration of Mg^{2+} ranged between 2.9 mg/L to 214 mg/L with an average of 36.4 mg/L while Na^+ concentration ranges from 3.5 to 72.8 mg/L with an average of 29 mg/L. The K^+ concentration ranged between BDL (below detection limits)—9.6 mg/L (avg. 3.3 mg/L). The weathering of K-feldspar is mainly responsible for the K^+ concentration in groundwater. HCO_3^- is most dominant among the anions followed by Cl^- , SO_4^{2-} and NO_3^- . The combination of Ca^{2+} ,

Mg²⁺ along with HCO₃⁻ is responsible for hardness of the groundwater. In this study, we found a high concentration of the ions that contribute to the hardness of the groundwater, i.e., 104–1658 mg/L, with an average value of 387.3 mg/L. The concentration of HCO₃⁻ ranged from 136 mg/L to 864 mg/L with an average of 401.5 mg/L. High HCO₃⁻ values indicate the presence of carbonate containing minerals in the study area, as well as the presence of degraded organic matter that can also contribute to the presence of HCO₃⁻ in groundwater [31]. Concentration of Cl⁻ in groundwater varied from 12 mg/L to 825 mg/L with an average of 173.8 mg/L. The high rate of evaporation might be attributable to high Cl⁻ concentration in the groundwater while SO₄²⁻ and NO₃⁻ concentration in groundwater varies from 29 mg/L to 557 mg/L (avg. 145.7mg/L) and BDL to 155 mg/L with an average of 31.4 mg/L respectively. The SO₄²⁻ in the groundwater might be due to the dissolution of gypsum/anhydrite minerals while fertilizers, agricultural/municipal waste and leaching of sewage might contribute NO₃⁻ in groundwater. F⁻ concentration ranges from BDL to 0.86 mg/L which is below the WHO guidelines with an average of 0.35 mg/L (Table 1).

3.2. Association between Water Quality Parameters

Statistical Analysis

The correlation analysis of groundwater quality parameters suggests the hydrological process controls the evolution of groundwater and its chemical properties. The result of the correlation analysis suggests strong association between pH, alkalinity, F⁻ and iron (Fe) (Table 2). EC is strongly associated with Ca²⁺ Mg²⁺, Cl⁻ and SO₄²⁻ indicating high conductivity of groundwater due to the presence of these ions. Ca²⁺ and Mg²⁺ show moderate association between Cl⁻, SO₄²⁻ and Cl⁻, NO₃⁻. A strong association between Fe and F⁻ is observed (R = 0.88), however none of the samples exceeded WHO guidelines either for Fe or F⁻. The high concentration of these ions may be due to the dissolution of evaporitic minerals, since a high proportion of EC favors the dissolution of evaporite minerals and sulphate salts, resulting in an increase in concentration of Mg²⁺ and Ca²⁺ in groundwater [32].

Table 2. Correlation analysis of groundwater quality parameters (bold depicts moderate to strong correlation).

	pH	EC	TDS	Alk	TH	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Fe	F	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻
pH	1.00														
EC	0.33	1.00													
TDS	0.39	0.94	1.00												
Alk	-0.10	-0.03	0.18	1.00											
TH	0.02	0.80	0.78	0.09	1.00										
Na ⁺	0.01	0.22	0.16	-0.07	0.17	1.00									
K ⁺	-0.02	-0.09	-0.06	0.20	0.00	0.21	1.00								
Ca ²⁺	0.12	0.66	0.65	0.27	0.67	0.19	0.03	1.00							
Mg ²⁺	0.40	0.70	0.71	-0.05	0.52	0.23	-0.03	0.44	1.00						
Fe	0.06	-0.03	0.18	0.84	0.06	-0.16	0.15	0.22	-0.03	1.00					
F	-0.22	0.14	0.04	0.00	0.25	0.00	-0.02	0.42	-0.11	-0.02	1.00				
NO ₃ ⁻	0.56	0.46	0.56	-0.03	0.07	-0.04	-0.09	0.18	0.57	0.01	-0.36	1.00			
Cl ⁻	0.48	0.81	0.83	0.09	0.46	0.30	-0.05	0.58	0.68	0.15	0.02	0.56	1.00		
SO ₄ ²⁻	0.13	0.65	0.54	-0.07	0.60	0.22	0.10	0.68	0.47	-0.12	0.34	0.06	0.48	1.00	
HCO ₃ ⁻	-0.18	0.21	0.20	0.28	0.21	0.20	0.02	0.39	0.23	0.05	0.09	0.07	0.08	0.07	1.00

PCA results indicate five principal components (PCs) with eigenvalues, representing 84.5% of the total variance in the dataset. PC1 explains around 32.3% of the total variance whereas PC2 explains 26.4%, PC3 10.3% PC4 7.9% and PC5 7.37% of the total variance (Table 3). The loading >0.6 has been considered for the interpretation of the data. In PC1, the high loading of EC, TH, Ca²⁺ Mg²⁺, Cl⁻, and SO₄²⁻ has been found which indicates mineralization of rocks and soil [32,33]. A high loading of SO₄²⁻ and Cl⁻ together depicts the dissolution of evaporitic minerals. In PC2, a negative loading of NO₃⁻ and pH while a high positive loading of alkalinity, Fe and F is observed. In PC3, a high loading of NO₃⁻ alone indicates anthropogenic influence on groundwater quality, while in PC4 Na⁺ and K⁺ is positively loaded and in PC5 HCO₃⁻ loading is found to be higher than 0.6 alone but negative and moderately high loading of K (-0.48) is also observed.

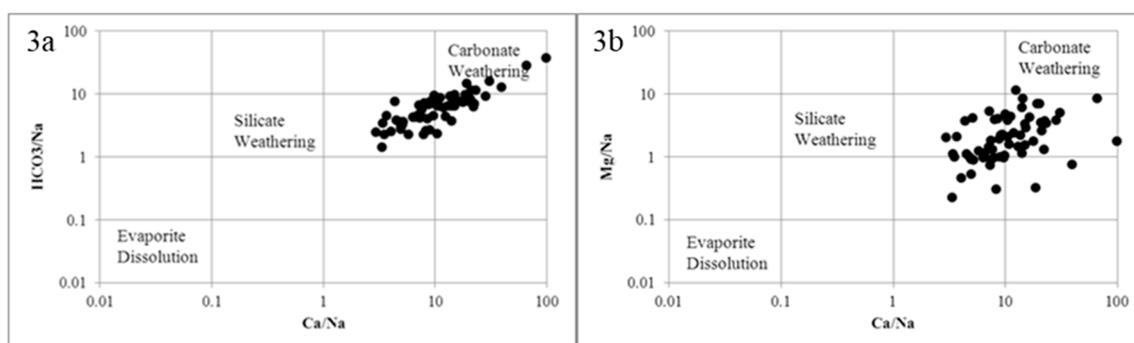
Table 3. Factor loading along with eigenvalue, %variance and cumulative % (Bold depicts significant loading of the variables).

Factor Loading	F1	F2	F3	F4	F5
pH	0.412	−0.827	0.142	0.108	−0.032
EC	0.952	0.027	0.041	−0.109	−0.005
Alk	−0.167	0.956	0.065	0.093	0.118
TH	0.729	0.287	−0.249	−0.338	−0.017
Na	0.358	−0.029	−0.472	0.575	−0.012
K	−0.062	0.239	−0.401	0.545	−0.485
Ca	0.721	0.449	−0.219	−0.197	0.090
Mg	0.807	0.055	0.250	0.183	0.002
Fe	−0.171	0.880	0.234	0.018	−0.069
F	−0.251	0.931	0.150	−0.004	−0.128
NO ₃	0.494	−0.033	0.722	0.322	0.021
Cl	0.806	0.227	0.294	0.141	−0.151
SO ₄	0.725	0.106	−0.341	−0.275	−0.271
HCO ₃	0.274	0.229	−0.267	0.267	0.810
Eigenvalue	4.525	3.702	1.454	1.118	1.033
% variance	32.318	26.444	10.389	7.986	7.376
Cumulative %	32.318	58.763	69.151	77.137	84.513

3.3. Hydro Geochemical Processes

3.3.1. Weathering and Dissolution

A scatter plot between $\text{Ca}^{2+}/\text{Na}^+$ and $\text{HCO}_3^-/\text{Na}^+$ is used to determine the effect of weathering of silicates or carbonate minerals or evaporation dissolution in the groundwater. Figure 3a shows weathering of carbonate minerals is the most dominant process affecting the groundwater quality. In Figure 3b, Na^+ normalized Ca^{2+} vs. Mg^{2+} also refers carbonate dissolution as the major hydrogeochemical process. The ratio of Ca^{2+} and Mg^{2+} is used to understand the effect of dissolution of calcite and dolomite in groundwater. The value of $\text{Ca}^{2+}/\text{Mg}^{2+} > 1$ indicates dissolution of calcite as main source of these ions in the study; the ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$ varies from 1.05 to 57, and indicates the dominance of calcite dissolution as a major process (Figure 4a) [5,9,11,31].

**Figure 3.** (a) Na Normalized HCO_3^- vs. Ca^{2+} . (b) Na Normalized Mg^{2+} vs. Ca^{2+} plot.

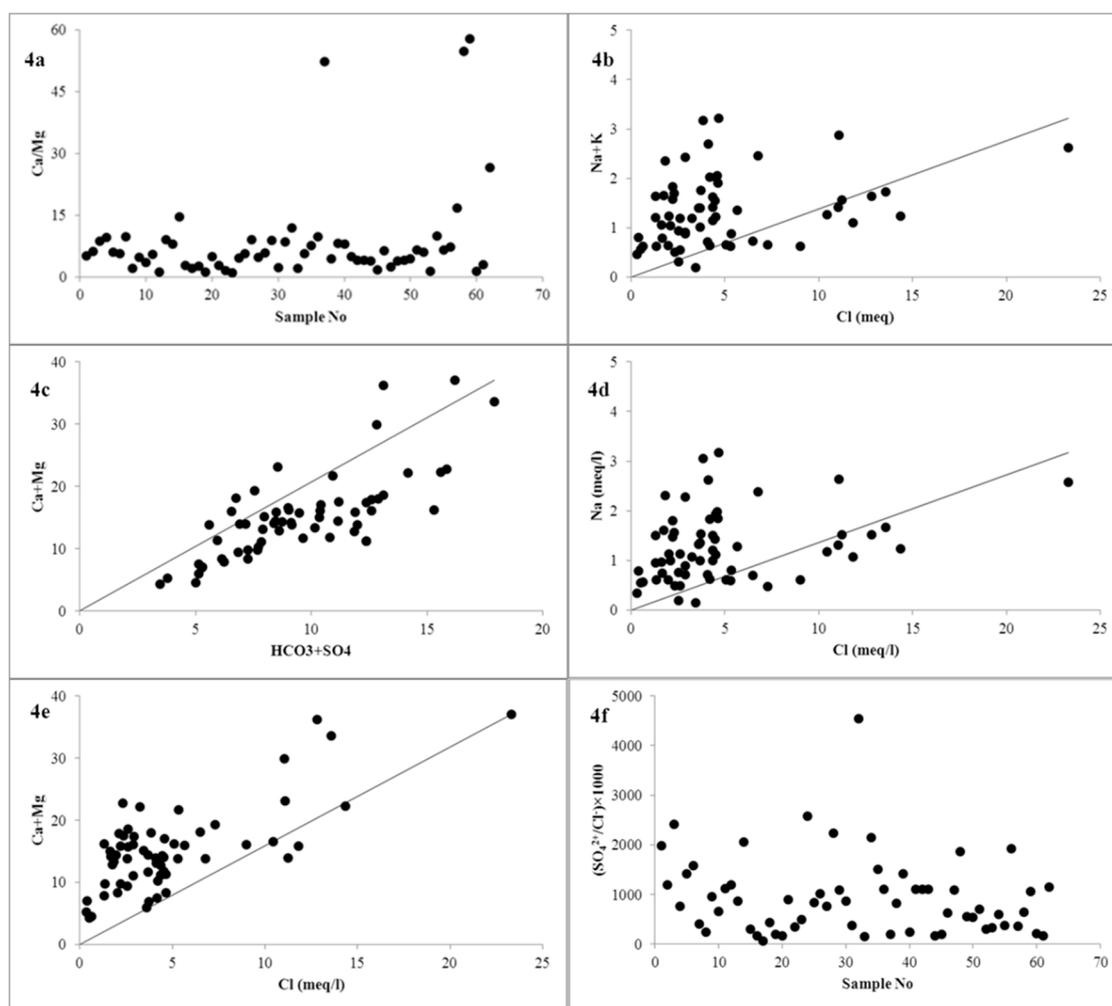


Figure 4. (a) Scatter plots of $\text{Ca}^{2+}/\text{Mg}^{2+}$ versus sample no; (b) Scatter Plots of $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus $\text{HCO}_3^- + \text{SO}_4^{2-}$, (c) Na^+/Cl^- vs. EC plot; (d) scatter plot between $\text{Na}^+ + \text{K}^+$ vs. Cl^- ; (e) scatter plot between Na^+ and Cl^- ; (f) scatter plot of $(\text{SO}_4/\text{Cl}) \times 1000$ vs. sample no.

A $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. $\text{HCO}_3^- + \text{SO}_4^{2-}$ plot has been used to analyze ion exchange process. Samples with approximately 1:1 ratio indicate dissolution of calcite, dolomite, or gypsum (Figure 4b) while if there is exchange of ions it will shift the points away from the equiline i.e., towards the right and reverse ion-exchange will shift it towards the left. In Figure 4c i.e., $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. Cl^- plot, points are mostly on the right of the equiline indicating ion-exchange and weathering of carbonate minerals as the major process controlling the groundwater quality [34].

3.3.2. Evaporation

A scatter plot between Na^+/Cl^- vs. EC is effectively used to determine the influence of evaporation on groundwater quality. The Na^+/Cl^- value greater than 1 suggests silicate weathering as a dominant process controlling release of Na^+ in groundwater; while the Na^+/Cl^- ratio is approximately 1, which suggests halite dissolution as a dominant process. The value of Na^+/Cl^- ranges between 0–1.99 which determines the impact of evaporation on groundwater quality (Figure 4d–f). The scatter plot Cl^- vs. $(\text{Na}^+ + \text{K}^+)$ reveals that most samples are above 1:1 line suggesting excess of cations which might be due to the excess of alkali and formation of alkali carbonates or sulfates in the region. The high concentration of Na^+ compared to K^+ may be the result of its resistance to ion exchange, dissolution and chemical weathering. Anthropogenic activities might also contribute high Na^+ in groundwater. The Na^+ and Cl^- plots are used to determine dominant

silicate weathering and ion-exchange in groundwater (Figure 4e,f). The points above the equiline depicts influence of ion-exchange. Majority of the samples above 1:1 line was found to be influenced by ion-exchange while the samples below the equiline indicates evaporation as the influencing process.

3.3.3. Seawater Influences

The $\text{SO}_4^{2+}/\text{Cl}^-$ ratio used as a natural tracer to determine freshwater and seawater mixing [35]. Typically in seawater the value of $(\text{SO}_4^{2+}/\text{Cl}^-) \times 1000$ is found to be 103.4 and, based on the values, the quality of groundwater can be classified into two groups i.e., (a) samples with a $\text{SO}_4^{2+}/\text{Cl}^-$ ratio similar to seawater, and (b) samples with a ratio of $\text{SO}_4^{2+}/\text{Cl}^-$ ratio more than 300, mainly influenced dissolution of evaporites. In the current study, the ratio of $(\text{SO}_4^{2+}/\text{Cl}^-) \times 1000$ ranges from 51 to 4547 and out of 62 sample 48 samples has values >300 indicating the influence of sea water on groundwater (Figure 4f).

4. Geochemical Modeling

4.1. Geochemical Facies

Water type is used as to identify the signature of the soil water interaction and water recharge. The study found Ca^{2+} as the dominant cationic species while in anions HCO_3^- was dominant followed by Cl^- and SO_4^{2-} ; this is also evident from the Piper (1944) trilinear diagram (Figure 5) [36]. The most dominant water types present in this region are Ca- HCO_3 followed by Ca-Cl and Ca- SO_4 . 69% of the samples have Ca- HCO_3 type while the remaining 24% is of Ca-Cl and 4% of the samples are found to be Ca- SO_4 . Dissolution of carbonate minerals containing Ca^{2+} might be the reason behind Ca^{2+} dominance. Exchange of Na^+ , K^+ by Ca^{2+} and Mg^{2+} adsorbed on the surface of clay minerals can cause their higher concentration. The dissolution of gases and minerals, especially CO_2 and CO_3 related compounds in the atmosphere and in the unsaturated area during precipitation and infiltration would give the observed HCO_3^- type water facies [37] while dissolution of halite could contribute to high Cl^- in groundwater.

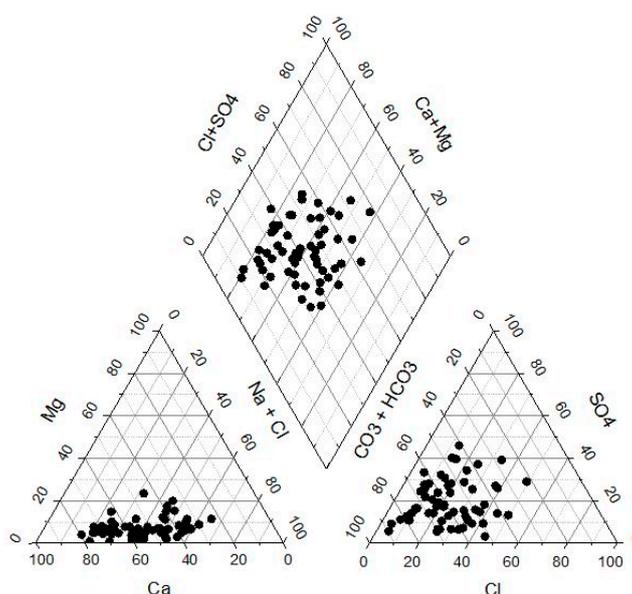


Figure 5. Piper plot.

4.2. Saturation Indices (SI)

SI are important to identify the reactivity of minerals in groundwater. A positive SI value of a mineral shows oversaturation and thus precipitation will occur while a negative SI value shows

undersaturation and thus dissolution of mineral in groundwater. The SI of calcite and dolomite is mostly found >0 except for 4 samples for calcite and 10 for dolomite (Figure 6a,b). Water acts as solvent for calcite and dolomite when it interacts with carbonate minerals. In comparison to dolomite, the dissolution of calcite is a relatively rapid reaction [38,39] and accordingly the system rapidly acquires Ca^{2+} ion. A solution containing Ca^{2+} ions reacts with dolomite, acquires Mg^{2+} and increases Ca^{2+} , CO_3^{2-} and HCO_3^- concentration. The latter process can follow to oversaturation of calcite, which in order to maintain equilibrium, must precipitate. Positive values of SI for these minerals indicates oversaturation, hence precipitation, of these minerals [5]. It also indicates that the groundwater has enough residence time to interact with aquifer minerals and reach up to equilibrium. The groundwater is found to be undersaturated with halite, anhydride and gypsum as the SI values for these minerals are negative (Figure 6c,d), and dissolution of the above minerals is the controlling factor for groundwater quality in the Aseer region. Dissolution of halite and gypsum is probably the reason behind the high concentration of SO_4^{2-} and Cl^- .

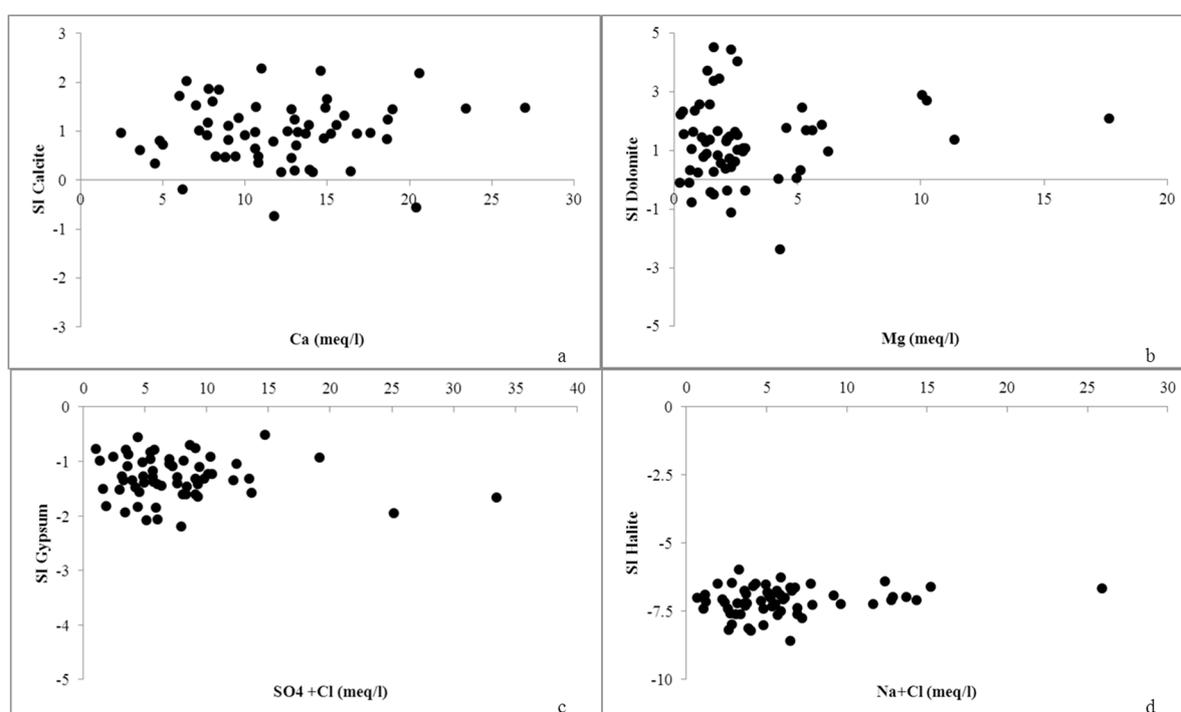


Figure 6. (a) Saturation indices (SI) of calcite vs. Ca. (b) SI of dolomite vs. Mg. (c) SI of gypsum vs. $\text{SO}_4 + \text{Cl}$ (d) SI of halite vs. Na + Cl.

5. Conclusions

This study has been conducted in Asser region of Saudi Arabia. The integrated approach of multivariate statistical methods along with conventional plots and geochemical modelling have been used to identify the major hydrogeochemical processes and groundwater chemistry in the study area. Five principal components (PC1-PC5) were found to explain 79.9% of the dataset when subjected to PCA. The majority of groundwater composition is Ca- HCO_3 followed by Ca-Cl. Groundwater in this region is oversaturated with calcite and dolomite while undersaturated with gypsum and halite, resulting in high concentrations of Ca^{2+} and Cl^- in groundwater. Since the presence and corresponding impact of these chemicals on the overall quality of groundwater is significant, the hydro-geochemical characteristics of groundwater are highly influenced by the climatic condition i.e., extreme evaporation. The climatic condition, coupled with high temperature and less rainfall may result in the highly alkaline conditions. The scatter plots between the ions suggests ion exchange, halite dissolution, carbonate weathering along with seawater mixing are the major process controlling groundwater

quality in the Asser region. High alkalinity along with Cl^- , Ca^{2+} and NO_3^- in groundwater has emerged as a major concern in this study, and hence a sustainable water management plan should be adopted. Immediate action and proper intervention is needed to protect the groundwater quality and further deterioration of groundwater in the study area.

Author Contributions: Conceptualization, J.M. and M.K.A.; Formal analysis, J.M., C.K.S. and A.K.; Funding acquisition, J.M.; Investigation, C.K.S., A.K., R.A.K. and S.I.; Methodology, J.M., C.K.S. and A.K.; Project administration, J.M.; Resources, M.K.A., A.K., R.A.K. and S.I.; Supervision, J.M. and M.K.A.; Visualization, R.A.K.; Writing—original draft, J.M.; Writing—review and editing, J.M., C.K.S. and A.R.

Funding: Funding for this work has been provided by the Deanship of Scientific Research; King Khalid University, Ministry of Education, Kingdom of Saudi Arabia under award numbers R.G.P.1/28/38 (1439).

Acknowledgments: The authors thankfully acknowledge the Deanship of Scientific Research for proving administrative and financial support. The author also acknowledged Engr. Mohammad Ahmed Ibrahim AlFarhan, Ministry of Environment Water and Agriculture, Aseer, Saudi Arabia, for providing the assitant to collect the groundwater sample in the Aseer region.

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

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