**ORIGINAL PAPER**

# Hydrochemical assessment of groundwater using statistical methods and ionic ratios in Aliguodarz, Lorestan, west of Iran

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## ABSTRACT

Hydrochemistry of groundwater is considered as an appropriate guide to recognize the occurred reactions in aquifers and water sources. In the present study, composite diagrams, saturation indices (SI), and statistic parameters were used as a tool to interpret groundwater chemistry ($SI_{Calcite}$ 0.16 to 1.19; $SI_{Dolomite}$ 0.10 to 1.0, $SI_{Gypsum}$ -2.35 to -1.74; $SI_{Halite}$ -8.86 to -7.5; $SI_{Aragonite}$ 0.02 to 1.04; $SI_{Anhydrite}$ -2.57 to -1.96 ). According to composite diagrams, factors like dissolution, weathering of silicates and carbonate formations were determined as the most effective ones on chemical compounds of the groundwater in the area. Moreover, calculation of the saturation indices for the samples revealed that ions like calcite, dolomite, and aragonite were in the super-saturated mood while inertia, gypsum, and halite were in the under-saturated mood. The total density of soluble ions (TDI) versus the density of anions showed that as the TDI density increased the density of bicarbonate, calcium, and magnesium linearly. However, potassium remained unchanged. Statistic parameters in the Pearson correlation proved that the electrical conductivity (EC) and total dissolved solids (TDS) had the highest correlation. Moreover, there was a high correlation between the EC, TDS, and total hardness with $HCO_3$. The first, second and third components with more than 70% variability justified statistic population in the principal component analysis method, revealing that the first factor was determined as the most effective factor on the groundwater of the region. This factor included a set of dissolution, sedimentation and ionic exchange.

**Keywords:** Hydrochemistry, Saturation Indices, Ionic Ratios, TDI, Principal Component Analysis

## Introduction

Groundwater is one of the most important sources of human freshwater supply. Since groundwater sources have lower pollution and higher storage capacity than surface water sources, they are considered as the most important sources of water.[1-3] Due to the invisibility of these water sources, most people do not have sufficient knowledge about their importance and also about the harmful effect of environment pollution.[4-7] As a matter of fact, the chemistry of groundwater is highly dependent on the petrology of the aquifer, in which the water is flowing.[8] Moreover, a chemical compound of groundwater would change by different factors like mineralogy of field,

aquifer, air, topography, etc.[9] There are a lot of studies focusing on the quality and chemistry of groundwater, in which the effective processes in the origin of dissolution, weathering of silicates and carbonate formations have been identified.[10-13] The present study aimed to investigate the main processes controlling the groundwater hydrochemistry in Aliguodarz, Lorestan. The groundwater in the study area is affected with the increase of anions and cations, and its degradation causes some problems for drinking and farming purposes. The study area, as an agricultural zone in Lorestan Province, west of Iran, is of great importance. In the present study, the sources of groundwater salinity and water chemistry were identified using geochemical methods. The chemical quality of groundwater is related to the lithology of the area. In addition, the study focused on the hydrochemical assessment of groundwater sources in the study region using saturation indices, ionic ratio, and statistical analyses.

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## Materials and Methods

The chemical quality of groundwater in this study included salt remains, electrical conductivity, acidity, bicarbonate, chlorine, sulfate, all anions, calcium, magnesium, sodium, potassium, all cations, and total hardness (TH). By analyzing the qualitative data of the groundwater, their degree of accuracy was determined by calculating the error of ionic charge balance or reaction error using the following formula, if the value is more than 5%, the data has an accuracy problem.

$$E = \frac{\sum Cations - \sum Anions}{\sum Cations - \sum Anions} \times 100 \qquad (1)$$

PHREEQC Interactive softwar[14] and saturation index were applied to study the reaction between water and rock in the region and its relationship with ground and geology. The saturation index (SI) of a mineral is a logarithmic quantity, which shows the dissolution of a mineral in the water. It is calculated by the following formula.

$$SI = Log\ IAP/K \qquad (2)$$

In which IAP represents the ionic power, made by the ionic activity, and K represents the fixed balance, made by the dissolution of the mineral. The balanced moods less than zero show the under-saturated mood of the mineral in the water. In fact, the saturation index can be a useful device to perceive the interactions between groundwater sources and host stone.[15-17]

## Results and Discussion

By calculating the error of the ionic balance (Eq.1), it was demonstrated that the value of the error was less than the standard, 5%, which proved the accuracy of the data. Moreover, the saturation index of the mineral (Table 1) showed that all the samples of groundwater in the region were supersaturated from aragonite, calcite, and dolomite leading to sedimentation. However, according to the ground and geology of the region, this was highly expected. Moreover, groundwater in the region was not saturated with inertia, gypsum, and halite whose dominant process was dissolution. Halite of the region

groundwater had a considerable negative saturation index. The saturation indices from geochemical modeling of the groundwater sources proved that there was a suitable chemical environment not only for the dissolution of halite and gypsum but also for calcite and dolomite sedimentation. Furthermore, since gypsum had more dissolution than calcite, Ca increased the supersaturating of the groundwater from calcite. The minimum and maximum values of the calcite saturation indices were 0.16 (a water sample from Asmahour well) and 1.19 (a water sample from Sharif Abad), respectively. Moreover, the minimum and maximum values of the dolomite saturation indices were 0.10 (a water sample from Asmahour well) and 1 (a water sample from Sharif Abad Qanat), respectively. The minimum values of the inertia and gypsum saturation indices were -2.57 and -2.35, respectively, which were related to the water samples from Gaykan Well. Generally, the lowest value of the saturation index was -8.86 for halite, which was related to the water sample from Zazam Qanat. In the study area, there was the dissolution of halite, gypsum, and inertia, simultaneously with the sedimentation of calcite and dolomite. Therefore, it was inferred that dissolution of carbonate minerals was not carried out anymore by the groundwater in a vast area of aquifers. The maps of co-indexed saturation of calcite, dolomite, aragonite, anhydrite, halite, and gypsum are presented in Figs. 1, 2, and 3. The lowest value of the saturation index, about zero, was for calcite, dolomite, and aragonite, which was near Beranabad, Zazam Village, and Asmahour Station. This value indicated less sedimentation in the region. Moreover, the highest value of the saturation index for calcite and aragonite was seen in northern and northeast of the region. The highest value of the dolomite saturation index was in the northwest and southeast of the region, proving that these regions faced the highest sedimentation. Furthermore, the highest value of the gypsum saturation index was seen in the northeast of the plain near Sharifabad Station, while the lowest index value was seen near Gandomineh, Gaykan, Fighan and Beranabad

City. The halite saturation index had the highest and lowest amount of dissolution near Zazam and Shahryar villages. Sharifabad and Sanj villages had the highest and lowest amount of dissolution, respectively, indicating that the groundwater in these villages was gradually going to be saturated. Moreover, the lowest value of the inertia saturation index was seen near Sahrif Abad while the highest was seen near Moshale, Fighan, Chamansoltan, and Shahryar. Different composite diagrams were made to recognize the geochemical processes, which affected the quality of groundwater sources in the study area. Figure 4 shows a two-variable diagram, TDI versus the density of calcium, magnesium, sodium, potassium, bicarbonate, chloride, and sulfate. The diagrams

revealed that: 1. the increase of the TDI did not affect potassium density and there was a slight change, proving that the dissolution of the rocks containing potassium occurred partially; 2. as the TDI increased, the density of bicarbonate, calcium, and magnesium increased linearly, revealing the dissolution of calcite, dolomite, aragonite, and carbonate minerals in aquifers; 3. there was no obvious relationship between the TDI and chloride, sulfate, and sodium. Three composite diagrams were prepared using the functions among chemical formations from the process of ionic exchange in order to determine the processes of ionic exchange and reverse ionic exchange in the groundwater of the area.

Table1. Saturated Index of minerals of groundwater in the study area

| Location | SI Halite | SI Gypsum | SI Dolomite | SI Calcite | SI Aragonite | SI Anhydrite |
|---|---|---|---|---|---|---|
| Sanj | -7.5 | -2.14 | 0.58 | 0.42 | 0.28 | -2.36 |
| Gaykan | -7.91 | -2.35 | 0.53 | 0.84 | 0.70 | -2.57 |
| Chahasmahour | -7.89 | -2.18 | 0.10 | 0.16 | 0.02 | -2.40 |
| Chamansoltan | -8.17 | -2.08 | 0.59 | 0.38 | 0.24 | -2.30 |
| Beranabad | -8.07 | -2.28 | 0.23 | 0.25 | 0.10 | -2.50 |
| Zazam | -8.86 | -2.23 | 0.27 | 0.27 | 0.13 | -2.45 |
| Shahriar | -8.60 | -2.15 | 0.75 | 0.52 | 0.38 | -2.37 |
| Sharifabad | -7.58 | -1.74 | 1 | 1.19 | 1.04 | -1.96 |
| Moushleh | -7.91 | -1.99 | 0.89 | 1.12 | 0.98 | -2.21 |
| Jouz | -8.17 | -2.15 | 0.92 | 1.06 | 0.92 | -2.37 |
| Gandomineh | -7.96 | -2.28 | 0.69 | 0.96 | 0.82 | -2.50 |
| Fighan | -7.95 | -2.34 | 0.87 | 0.97 | 0.75 | -2.27 |
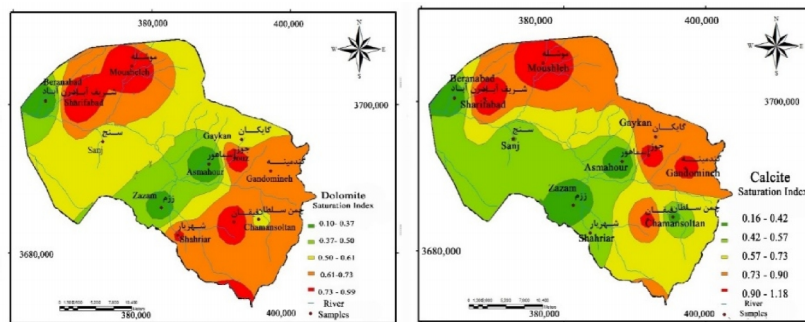


Fig. 1. The saturation Index map of Dolomite and Calcite of the study area
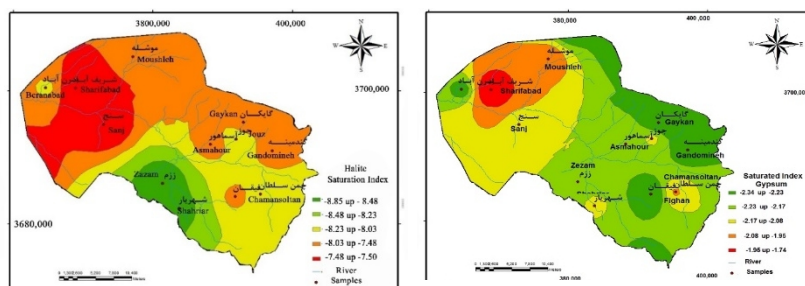


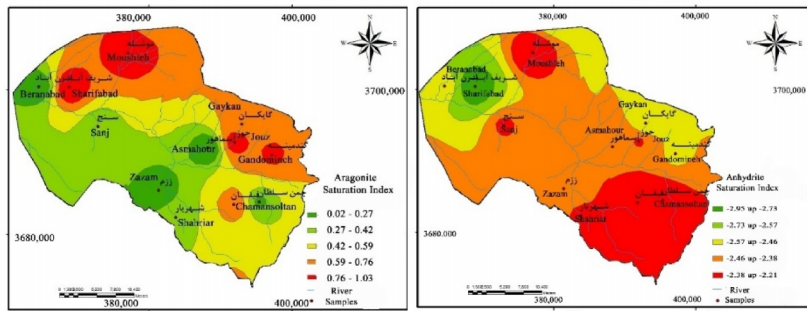Fig. 2. The saturation Index map of Gypsum and Halite of the study area

Fig. 3. The saturation Index map of Aragonite and Anhydrite of the study area
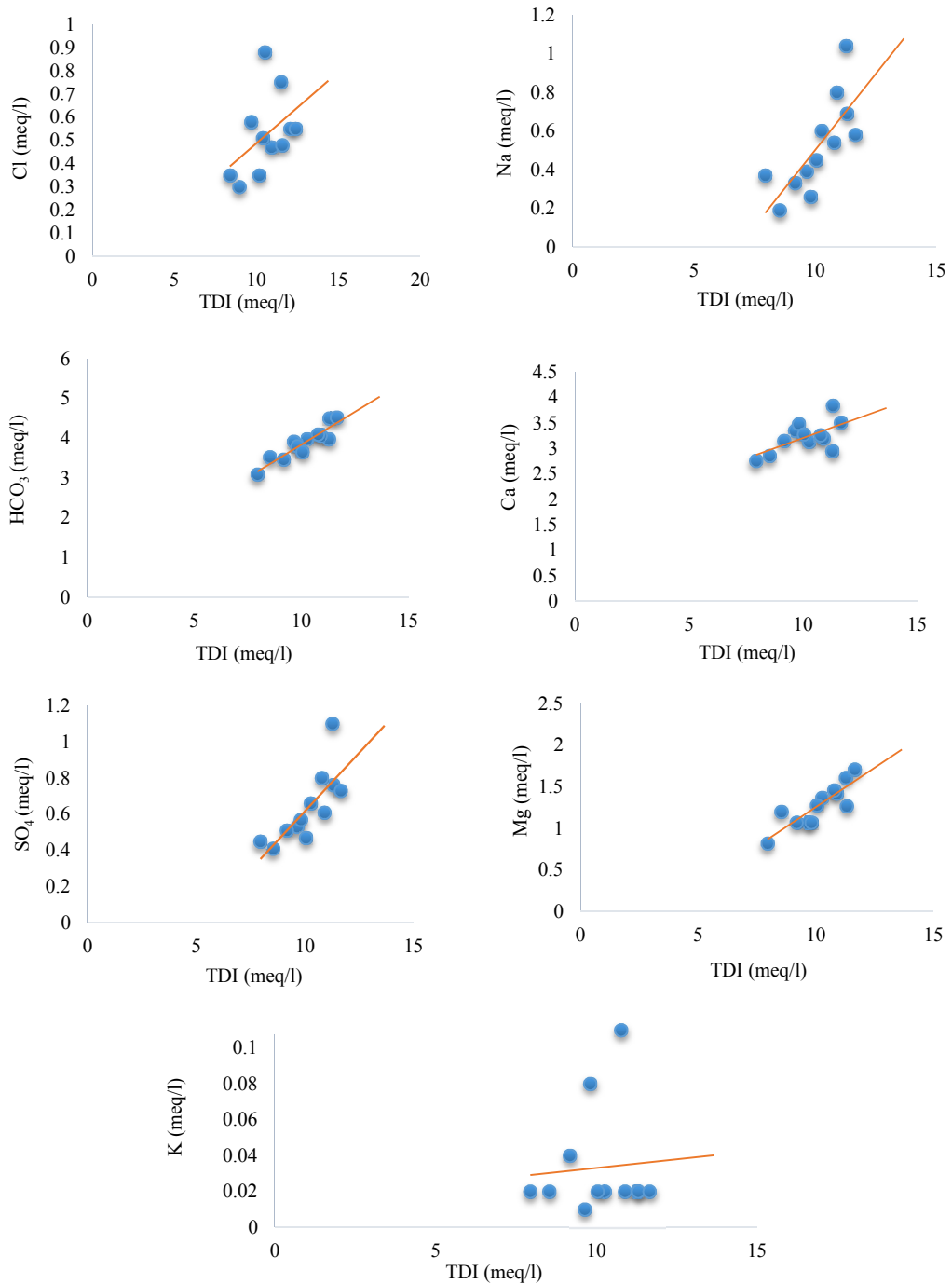


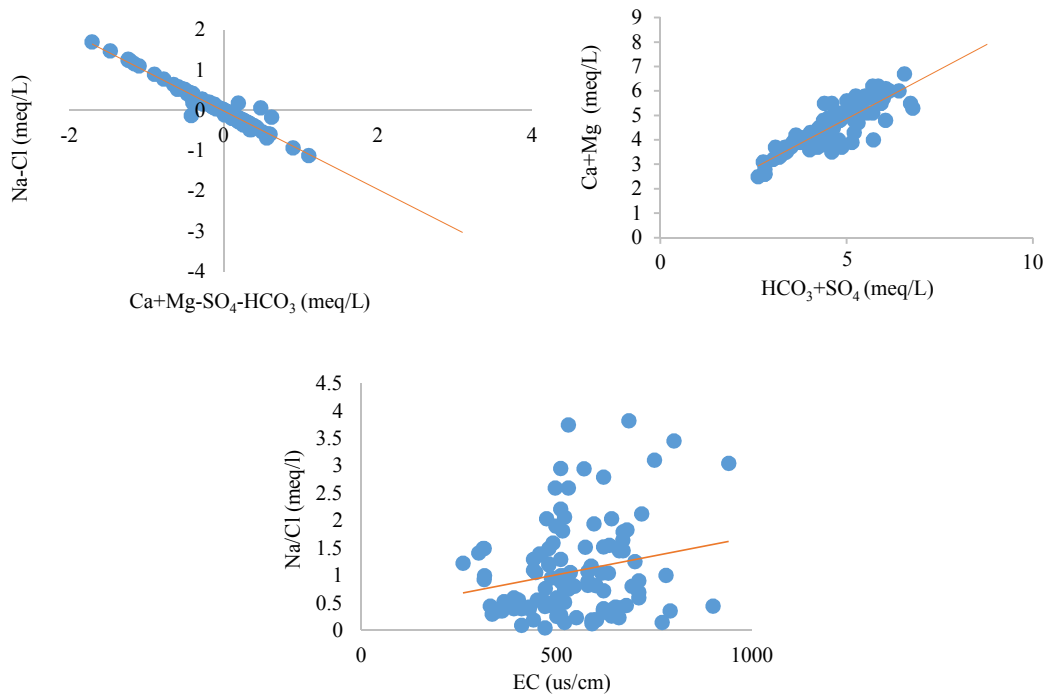Fig. 4. Composite diagrams of ions versus TDI in the study area

Fig. 5. Two-variable diagrams of ions exchange

As shown in Fig. 5, chloride versus the electrical conductivity (EC) was used to study ionic exchange, in which the samples above Na/Cl=1 showed both ionic exchange[18,19] and their dual origin. In this diagram, if most of the samples are above the line, normal ionic exchange (dominant dissolution of calcite and dolomite) is more than reverse ionic exchange (dominant dissolution of gypsum), and vice versa. Moreover, the samples whose electrical conductivity was more than 5000 (μmho/cm) indicated that halite would be their dominant origin. A two-variable diagram, Na/Cl versus EC, is presented in Fig. 5 for the groundwater samples. The total electrical conductivity of the samples was under 5000 (μmho/cm), showing that halite was not their dominant origin. According to Fig. 5, the dominant ionic exchange on the samples was reversed, revealing that gypsum dissolution was dominant. A two-variable diagram, Ca+Mg versus $HCO_3+SO_4$, is presented in Fig. 5. The line 1:1 signed the dissolution processes of calcite, dolomite, and gypsum. The samples above the line 1:1 had reverse ionic exchange (dominant gypsum dissolution) while the samples under the line 1:1 had normal ionic

exchange (dominant dolomite and calcite dissolution).[20,21] The samples along the line 1:1 showed no dissolution of calcite and dolomite in the aquifer. As Fig. 5 indicates, most of the samples were along the line 1:1, revealing that there was no dissolution of calcite and dolomite in the groundwater of the area. In fact, it proved the accuracy of calcite and dolomite saturation indices, showing the sedimentation process of these two minerals. However, this was expected to occur since the region was geologically made of silicate minerals and carbonate and lime formations. Ionic exchange in groundwater sources can be studied by the diagram Ca+Mg-$SO_4$-$HCO_3$ versus Na-Cl.[22] According to the diagram, the samples near zero and on the horizontal axis had no ionic exchange. However, it should be noted that if the dissolution of calcite, dolomite, and gypsum do not occur in harmony, the samples will be on a horizontal axis.[23] The samples under the line 1 with negative slope showed reverse ionic exchange (dominant gypsum dissolution) and the ones above the line showed normal ionic exchange (dominant calcite and dolomite dissolution). As Fig. 5 shows, most of the samples were on or near the line, indicating no

ionic exchange. In contrast, the samples of Joz in 2005 and 2006 were above the line, expressing normal ionic exchange of the Qanat due to the calcium and bicarbonate increase. The sample of Sharif Abad Qanat in 2012 was under the line and had a reverse ionic exchange. Moreover, the sample of Sharif Abad Qanat in 2005 was on the line and had a normal ionic exchange due to the calcium and magnesium increase. The negative slope near the unit in the diagrams Ca+Mg-$SO_4$ – $HCO_3$ versus Na-Cl showed the pivotal role of the ionic exchange in determining a chemical compound of the groundwater. According to the Gibbs diagram (Fig. 7), the groundwater in the area was severely affected by the reaction of water and rock, dissolution and weathering of carbonate formations. In fact, most of the above mentioned variables were in this area.

### Principal Component Analysis (PCA)

The PCA is one of the statistical methods, which is extensively used in hydrochemical studies.[24-26] The PCA has three levels including making a correlation matrix from all variables, extracting factors, and analyzing results.[27] The results of the Pearson correlation matrix are shown in Table 2. According to this table, the EC and total dissolved solids (TDS) had the highest correlation as there was a direct relationship between them. Moreover, the EC, TDS, and TH had a high correlation with $HCO_3$. As a matter of fact, as bicarbonate increased in water, the amount of the solid solution

increased, leading to the EC and TH increase. The increase of bicarbonate was mainly due to the dissolution and weathering of silicate and sediment and carbonate formations. Moreover, Mg and Ca had a good correlation with the TH since the increase of calcium and magnesium led to the TH increase. Calcium and magnesium increase was mainly due to the dissolution and weathering of dolomite. The analysis of the main components determined 12 main components, as presented in Table 3. As the table shows, the first three components with more than 70% variability justified the statistical population. These factors controlled approximately 46.63 to 80.67% of the water compound in the area. Having the most effect on the water chemistry of the area, the first factor was related to a set of geochemical processes including dissolution, sedimentation, and ionic exchange. This is because most of the cations and anions had high factor load. It should be noted that the dissolution of the region formations, like carbonate and sedimentation formations, played the most important role in this regard. In contrast, nitrate had a negative correlation with this factor. This proved that nitrate did not have natural sources coming to the environment from unnatural and human factors. The second factor included surface water sources, which was due to the dissolution of carbonate and bicarbonate increase. The third factor was the nitrate increase of the groundwater, which was mainly due to the extreme use of fertilizer.

Table 2. Pierson correlation of groundwater analysis of the study area

|        | $SO_4$ | Cl | $HCO_3$ | K | Na | Mg | Ca | pH | TDS | TH | EC | $NO_3$ |
|--------|------|------|-------|------|------|------|------|------|------|------|------|------|
| $SO_4$ | 1 | | | | | | | | | | | |
| Cl | -0.21 | 1 | | | | | | | | | | |
| $HCO_3$ | 0.04 | 0.48 | 1 | | | | | | | | | |
| K | 0.10 | -0.11 | -012 | 1 | | | | | | | | |
| Na | 0.70 | 0.27 | 0.36 | -0.18 | 1 | | | | | | | |
| Mg | 0.65 | 0.17 | 0.68 | -0.05 | 0.61 | 1 | | | | | | |
| Ca | -0.09 | 0.41 | 0.74 | 0.03 | -0.11 | 0.38 | 1 | | | | | |
| pH | -0.24 | -0.04 | -0.35 | -0.45 | -0.36 | -0.36 | -0.36 | 1 | | | | |
| TDS | -0.04 | 0.76 | 0.82 | 0.24 | 0.43 | 0.50 | 0.57 | 0.82 | 1 | | | |
| TH | 0.32 | 0.35 | 0.86 | -0.05 | 0.29 | 0.82 | 0.83 | -0.43 | 0.64 | 1 | | |
| EC | -0.04 | 0.76 | 0.83 | -0.24 | 0.42 | 0.50 | 0.51 | 0.07 | 1 | 0.65 | 1 | |
| $NO_3$ | -0.49 | -0.20 | -0,45 | -0.18 | -0.37 | -0.71 | -0.35 | 0.30 | -0.40 | -0.64 | -0.40 | 1 |

Table 3. Percentage of total parameters in the study area

| Parameters | Special value | | |
|---|---|---|---|
| | Total | % Variance | % Cumulative |
| 1 | 5.59 | 46.53 | 49.63 |
| 2 | 66.76 | 20.13 | 2.41 |
| 3 | 80.67 | 13.90 | 1.66 |
| 4 | 88.66 | 7.98 | 0.95 |
| 5 | 93.24 | 4.58 | 0.55 |
| 6 | 96.60 | 3.35 | 0.40 |
| 7 | 98.67 | 2.07 | 0.24 |
| 8 | 99.51 | 0.83 | 0.10 |
| 9 | 99.99 | 0.48 | 0.05 |
| 10 | 100 | 0 | 0 |
| 11 | 100 | 3.93 | 4.72 |
| 12 | 100 | -2.31 | -2.73 |

## Cluster Analysis

In this method, the data were classified based on their internal distance. As a result, the data with less distance were grouped together. This method mainly aimed to make the categories with great diversity of their intra-group differentiation, as compared to their subgroup differentiation and distribution.[28-30] According to this diagram (Fig. 6), these elements were in six clusters. The first cluster was related to the TDS, EC and Cl, in which the TDS and EC had the highest correlation. In fact, as the total amount of soluble solids in water increased, the EC increased. The second cluster was $HCO_3$, Ca, and TH. However, this cluster was expected since the region formations were mostly made of lime minerals and carbonate formations whose dissolution caused to increase the bicarbonate and calcium. This led to the TH increase and thus the second cluster was possible. The third cluster was Mg, originating from the dissolution of dolomite lime formations.
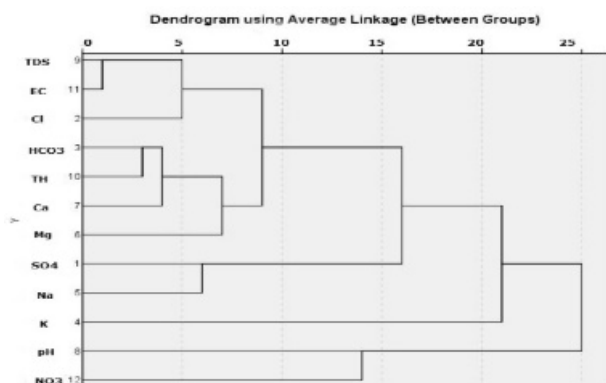


Fig. 6. The cluster diagram of the groundwater samples in the area

The fourth cluster was Na and $SO_4$, the fifth cluster K and the sixth cluster pH and $NO_3$. Being related to nitrate and pH, the sixth cluster showed that nitrate increase depended only on pH and other elements were not effective in this regard.
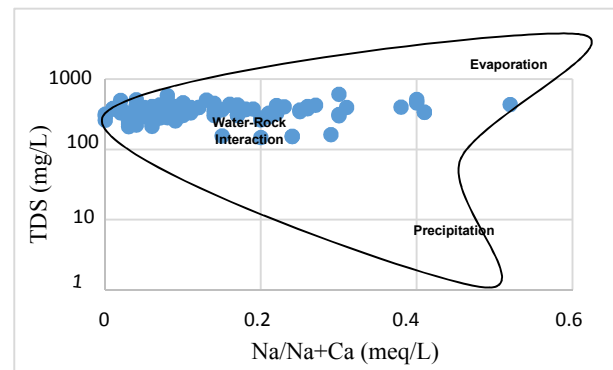


Fig. 7. The Gibbs diagram of the study area

## Conclusion

The chemistry of groundwater is mainly controlled by chemical and hydrologic processes between water and aquifer materials. According to the diagrams, most of the samples revealed non-dissolution of calcite and dolomite in the region groundwater. This event proved the accuracy of the saturation indices of calcite and dolomite, showing their sedimentation. This phenomenon was expected as the region was mainly made of carbonate and lime formations. Based on the diagram $Ca+Mg-SO_4-HCO_3$ versus Na-Cl, most of the samples were on or near the line, indicating that there was no ionic exchange. In contrast, the samples were on the line, due to calcium and bicarbonate increase. The two-variant diagrams, the total TDI versus the density of anions and cations, determined that the density of bicarbonate, calcium, and magnesium increased linearly by increasing the TDI while potassium was fixed. Moreover, there was no specific relationship between the TDI with chlorine, sulfate, and sodium. Furthermore, it was indicated that the increase of calcium and bicarbonate was due to either the dissolution of carbonate and lime formations or the reverse ionic exchange. Due to the dissolution ability of lime and carbonate mineral in the region, water sources were supersaturated to calcite, dolomite, and aragonite while they were undersaturated to inertia, halite, and gypsum. According to the

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Pearson correlation, the EC and TDS had the highest correlation since there was a direct relationship between these two parameters. Moreover, the EC, TDS, and TH had a high correlation with $HCO_3$. Moreover, there was a good correlation between Mg and Ca with the TH on the one hand, and between the pH and Cl with the TDS on the other hand. According to the cluster diagram, the first cluster was related to the TDS, EC and Cl, in which the TDS and EC had the highest correlation. The second cluster was related to $HCO_3$, Ca, and TH, the third cluster to Mg, the forth cluster to $SO_4$ and Na, the fifth cluster to K and the sixth cluster to pH and $NO_3$. Being attributed to the geochemical processes including dissolution, sedimentation and ionic exchange, the factor 1 had the highest effect on the water chemistry. However, nitrate had a negative correlation with this factor. This revealed that nitrate originated from unnatural and human factors. The second factor included a surface water source was mainly due to the dissolution of carbonate formations and bicarbonate increase. The third factor was nitrate increase in the region groundwater made by the fertilizer leaching.

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