RESEARCH PAPER

Controls on groundwater chemical quality in Semnan aquifer, central Iran

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Abstract
Considering the significance of groundwater for human activities, it is imperative to primarily focus on assessing both the quality and quantity of the water resources. Various hydrochemical processes such as dissolution and precipitation of minerals perpetually change groundwater quality. Identifying the dominant factors that impact groundwater chemistry is crucial for comprehensive management of these vital resources. This study was aimed to assess groundwater quality to identify factors affecting hydrochemistry of the groundwater in Semnan aquifer (central Iran) using chemical and statistical techniques. In this regard, 36 samples were collected from proper locations and analyzed for major ions and physicochemical parameters. The main factors affecting groundwater quality was inferred by applying composite diagrams and simultaneous integration of statistical (Principal Component Analysis) and hydro-chemical methods. This study reveals that chemical quality of the groundwater resources in Semnan aquifer are primarily influenced by geological formations due to dissolution of evaporate minerals. The results indicate the minor impact of the ion exchange and precipitation of calcite due to common ion effect, as compared with the significant role of dissolution of evaporates.

Keywords: Hydro-Chemical Approach, Statistical Technique, Hydrogeochemistry, PCA, Semnan

Introduction

With the continuous growth and development of human societies, along with increasing sanitation measures in recent decades, qualitative studies of water resources have gained heightened significance. Consequently, numerous studies are conducted worldwide each year in the field of water resources quality. The chemical composition of water is influenced by several factors, with the most noteworthy being evaporation, mixing, ion exchange, mineral dissolution, oxidation, reclamation and sedimentation of secondary minerals (Appelo & Postma, 2004). However, at times, additional factors come into play, often resulting from human intervention in nature or human-related influences in general, leading to alterations in water quality. Many developing countries grapple with issues related to water resource pollution due to the influx of industrial wastewater. These nations bear substantial costs to mitigate these pollutants. Recognizing and pinpointing the factors that impact changes in water quality can play a pivotal role in addressing a multitude of management challenges, including providing viable solutions to enhance or sustain aquifer quality. Numerous studies have been undertaken both in Iran and across the globe to

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investigate water quality. The chemical composition of underground water in an aquifer can be influenced by geological formations, the composition of recharge water, and the hydrochemical processes governing the porous layers (Andre et al., 2005). Consequently, the hydrochemical processes within an aquifer play a pivotal role in dictating water chemistry. Diverse methods are employed to process and interpret measured data in order to reach desired conclusions. Graphs or maps are often employed to determine chemical change trends. Additionally, bivariate diagrams aid in identifying water chemistry origins, while statistical techniques like factor analysis simplify complex relationships among diverse parameters (Liu et al., 2011). Schurch & Vuataz (2000) highlighted those chemical reactions between water and rock that significantly influence hydro-chemical parameters. Barzegar et al., (2017) explored hydro-geochemical processes impacting the Marand aquifer and concluded that factors like dissolution and weathering of various rocks, reverse ion exchange, and agricultural activities were the primary factors affecting water quality. Khaska et al., (2013) employed geochemical and isotopic methods to investigate the source of salinity in a coastal aquifer developed in Cretaceous limestone on the Mediterranean Sea's western coast (southern France). Gopinath et al., (2018) conducted an in-depth study on groundwater hydrochemical and salinity properties in the Navaratnam range, India. Their findings indicated that saltwater intrusion, ion exchange, and anthropogenic factors significantly affect the water chemistry in the region. The study also identified salinity sources from salt ponds and agricultural activities. Researchers worldwide employ diverse techniques to comprehend and differentiate the processes changing the water quality. Among those, various hydrochemical methods including bivariate or multivariate ionic ratios and diagrams, isotopic approaches, and statistical analyses are dominantly used. Generally, determination of main factors which affect the groundwater quality is essential in term of water resources management and planning.

Semnan aquifer which is extensively used for various purposes including agriculture, industrial uses and drinking water supply (Ekramipour et al., 2023) is one of the main groundwater resources in arid regions of central Iran. Identifying the dominant factors that impact groundwater chemistry is crucial for comprehensive management of these vital resources. So, this study was aimed to assess groundwater quality to identify factors controlling hydrochemistry of the groundwater in Semnan aquifer using chemical and statistical techniques.

Methodology

The article proposes methods for classifying hydro-chemical parameters to grouping water samples with similar properties and differentiating main factors affecting groundwater chemistry. The methodology involves several steps that briefly showed in Fig. 1. It consists:
Step 1: Sampling and preparing data
Step 2: Applying hydrochemical and statistical methods to classify chemical data
Step 3: Interpretation of the results to identify controls on groundwater chemistry

Study area description

The Semnan alluvial plain aquifer spans approximately 543 km² and is situated within the latitude range of 53° 00' N to 53° 40' N and the longitude range of 35° 22' W to 35° 39' W (Fig. 2). The average elevation of the plain is about 1300 meters above mean sea level, with mean temperature and precipitation values of 13°C and 126 mm, respectively. This unconfined aquifer is being served for various purposes, including agriculture, industry, and drinking water supply. Groundwater generally flows from north to the south of the aquifer, with its primary underground recharge from east and north and discharge mainly from southern parts. The water table is influenced by multiple factors including recharge and pumping wells.
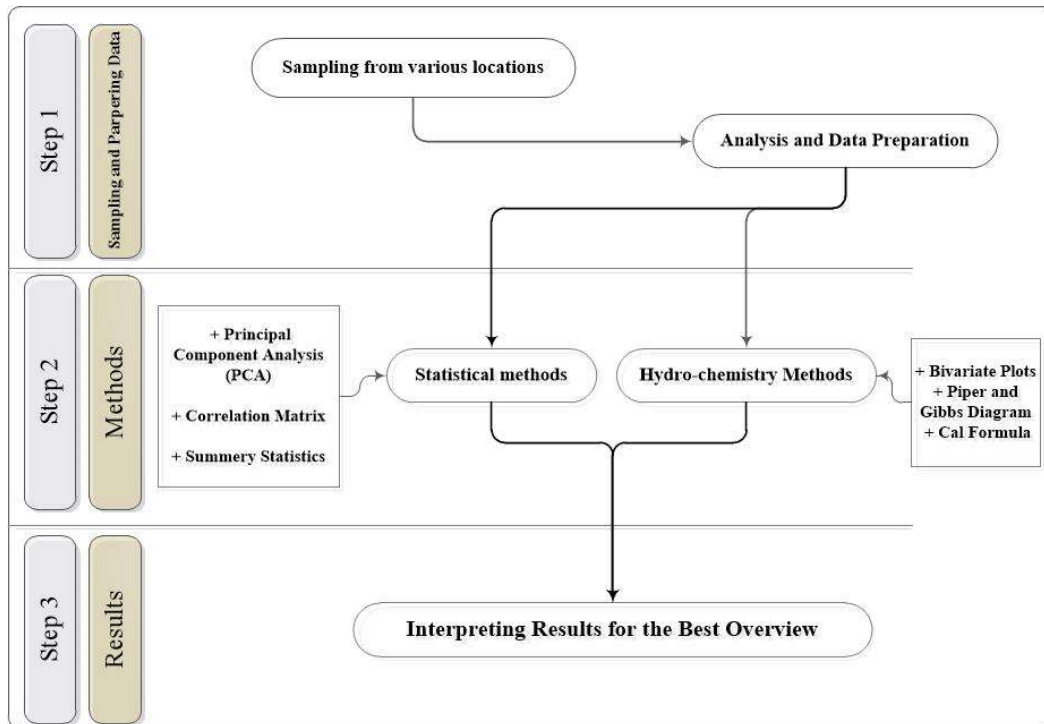
Figure 1. Research flowchart representing the steps to identify controls on groundwater chemistry in Semnan aquifer
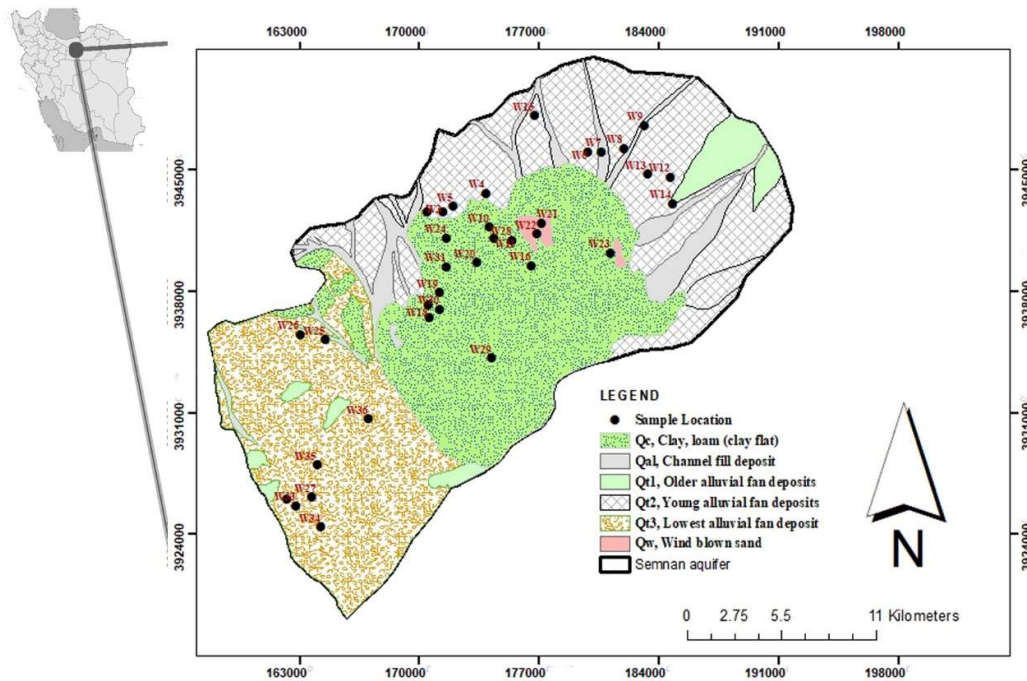
Figure 2. Geological map of the study area showing groundwater sampling locations

Sampling Data

In June 2021, a total of 36 groundwater samples were collected from the Semnan aquifer, ensuring evenly spatial distribution throughout the area (Fig. 2). These samples were promptly

transferred to the Water and Environment laboratory in Shahrood University of Technology. Standard techniques and tools were employed to measure chemical parameters including electrical conductivity (EC), pH and major ions (Calcium, Magnesium, Sodium, Potassium, Chloride, Sulfate, and Bicarbonate). The results of chemical analysis of the water samples are presented in Table 1.

Table 1. Results of the chemical analysis of the groundwater samples from Semnan aquifer

Sample	EC (μS/cm)	pH	Cl (epm)	SO4 (epm)	Na (epm)	K (epm)	Ca (epm)	Mg (epm)	HCO3 (epm)
W1	2210	7.39	10.23	8.31	6.39	0.08	6.90	6.64	3.50
W3	766	7.69	1.61	1.67	2.65	0.04	3.15	2.05	4.50
W4	1896	7.28	8.20	7.13	7.43	0.12	6.00	5.41	3.20
W5	1934	7.28	10.20	5.00	7.57	0.09	5.10	5.41	3.30
W6	2840	7.25	16.50	10.67	13.74	0.10	4.40	8.03	2.50
W7	3310	7.46	6.87	27.16	15.13	0.15	8.60	9.51	2.10
W8	3110	7.46	8.11	11.33	10.87	0.12	7.40	7.70	3.60
W9	2110	7.40	3.13	12.40	9.26	0.31	6.55	5.16	3.10
W10	2580	7.14	11.40	1.06	9.70	0.11	5.25	5.82	5.80
W11	2120	7.18	15.40	15.12	16.96	0.12	6.90	8.36	4.70
W12	3810	7.39	15.78	22.50	17.39	0.19	9.50	9.43	2.50
W13	5280	7.24	41.70	15.13	32.61	0.15	14.70	17.70	1.90
W14	3630	7.23	15.21	14.75	15.13	0.10	6.80	6.89	2.50
W15	4000	7.20	17.60	24.69	20.65	0.13	14.75	8.61	1.80
W16	5590	7.35	24.85	19.25	12.00	0.15	13.50	19.18	4.60
W17	6660	7.08	68.00	5.04	16.09	0.19	20.45	26.23	2.00
W18	1821	7.32	13.40	0.88	7.30	0.12	5.10	5.66	2.90
W19	2590	7.11	23.20	0.69	11.22	0.10	6.45	8.36	2.70
W20	4350	7.07	31.50	24.08	33.04	0.20	10.75	12.30	4.60
W21	1620	7.39	4.20	1.27	1.74	0.08	3.90	4.18	3.40
W22	1411	7.41	7.90	0.83	3.78	0.08	3.30	3.85	3.80
W23	2120	7.32	13.40	1.38	9.52	0.11	3.75	5.41	1.70
W24	2300	7.09	13.20	12.91	14.74	0.11	7.05	7.50	4.50
W25	6440	7.18	47.20	4.67	21.91	0.27	23.45	7.46	2.40
W26	4720	7.20	5.75	50.45	19.04	0.23	22.80	10.82	2.60
W27	4080	7.12	18.30	49.24	34.78	0.19	22.25	7.38	1.60
W28	1592	7.39	3.69	1.27	3.35	0.03	2.70	3.69	3.40
W29	5000	7.06	37.80	12.25	19.57	0.15	13.80	14.75	4.80
W30	2960	7.13	20.20	2.08	10.43	0.10	8.90	7.87	3.80
W31	2260	7.25	17.20	0.72	9.21	0.09	7.20	7.03	3.60
W32	3610	7.55	1.71	39.74	12.09	0.15	19.80	7.54	0.20
W33	3520	7.50	16.50	13.50	11.48	0.10	18.25	6.72	1.40
W34	3920	7.58	10.99	35.92	17.17	0.13	23.50	6.97	1.30
W35	3400	7.52	8.34	33.25	17.83	0.16	18.92	5.25	1.50
W36	10300	7.50	53.30	11.92	0.96	0.42	48.13	19.84	1.20

Hydro-chemistry approach

Bivariate plots are mainly used to investigate the impact of geological settings and human activities on groundwater. The samples are plotted on bivariate diagrams to determine the origin and mixing process of the groundwater (Mazore, 2004). Additionally, mass balance method is used to determine the origin of cations and anions employing ionic ratios for the geochemical investigation of groundwater resources (Hounslow, 2018).

According to Schoellor (1977), ion exchange is one of the key factors that control groundwater chemistry. The chloro-alkaline index (CAI) is widely used to assess the ion exchange reactions between groundwater and its host rock.

$$CAI = \frac{Cl - Na + K}{Cl}$$

The Piper diagram is utilized to ascertain the hydrochemical facies of groundwater and to determine the geochemical characteristics and evolutionary sequence along the flow path. It allows for the simultaneous representation of multiple water samples. In addition, the factors influencing water chemistry are examined using the Gibbs diagram to comprehend the mechanisms governing evolutionary processes, based on parameters such as TDS and the Na/Na+ca ratio (Wu & Gibson, 1996). In this work, AqQA and Excel software were used to create needed diagrams and plots.

Statistical approach

Statistical methods are approaches that can illuminate the complexity of data. The outcomes of these methods provide an overview and reveal the central tendency and distribution of the data (e.g., Mean, Variance, mode, etc.). Principal component analysis (PCA) is used to identify dominant patterns within the matrix of a complementary source set (Wold et al., 1987). It is widely utilized due to the simplicity of its algebra and its straightforward nature (Sanchez et al., 2001). In other words, PCA as a mathematical technique identifies existing patterns in the data and simplifies its complexity without demanding complex assumptions (Mondal et al., 2010). This process involves rotating the axis defined by PCA (Shrestha & Kazama, 2007; Elumalai et al., 2017).

Moreover, PCA entails grouping data by identifying connections between samples based on similarities in chemical and physical contributions (Mencio et al., 2014). It is appropriate for exploring clusters with similar characteristics. For a more comprehensive understanding of PCA methodology, further details can be provided regarding the specific number of components extracted, the rotation method employed, and how criteria such as eigenvalues or the percentage of variance explained were utilized to determine the significance of principal components. This additional information ensures a thorough and transparent depiction of the analytical approach used.

Results and Discussion

Based on the result of the chemical analysis of water samples the mean values of EC and pH are 3424 µS/cm and 7.3 respectively. Chloride (Cl), sulphate (SO4) and sodium (Na) with average values of 17.7, 14.2 and 13.5 epm, respectively, have the highest concentrations.

The Iso-potential and electrical conductivity maps of the Semnan aquifer are provided in Figure 3 and 4. Generally, a noticeable trend is observed in the water table, showing a consistent decline from the north region of the Semnan aquifer towards the south. However, a different pattern in electrical conductivity (EC) map is considered.
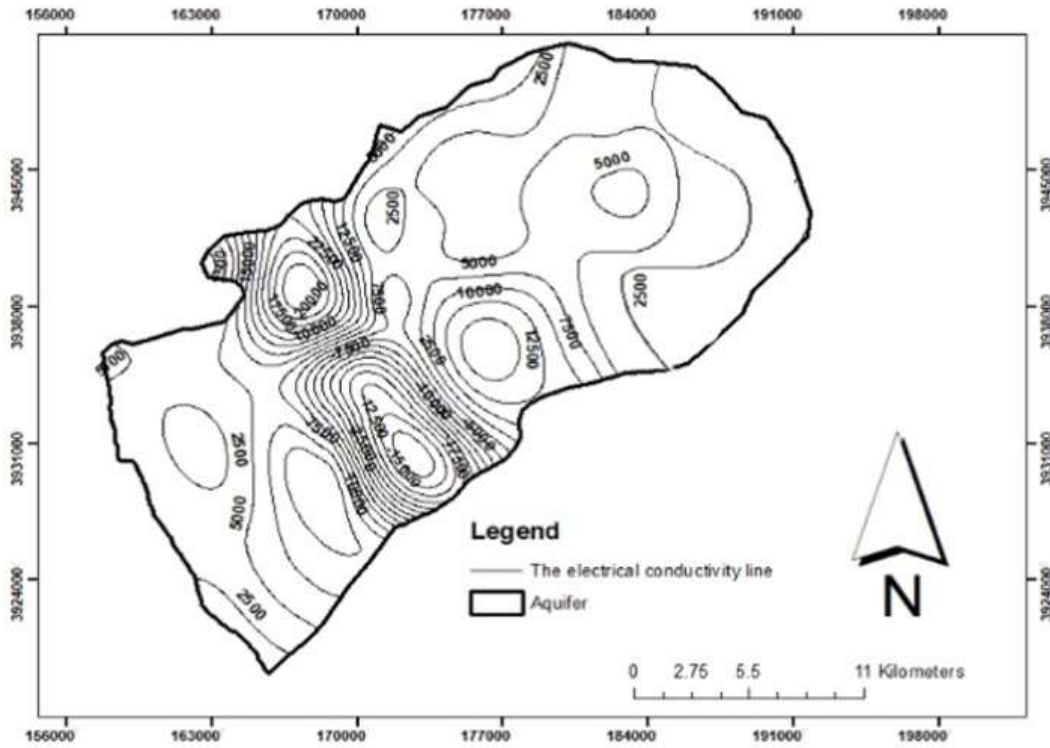
Figure 3. The electrical conductivity (µS/cm) map of the Semnan aquifer
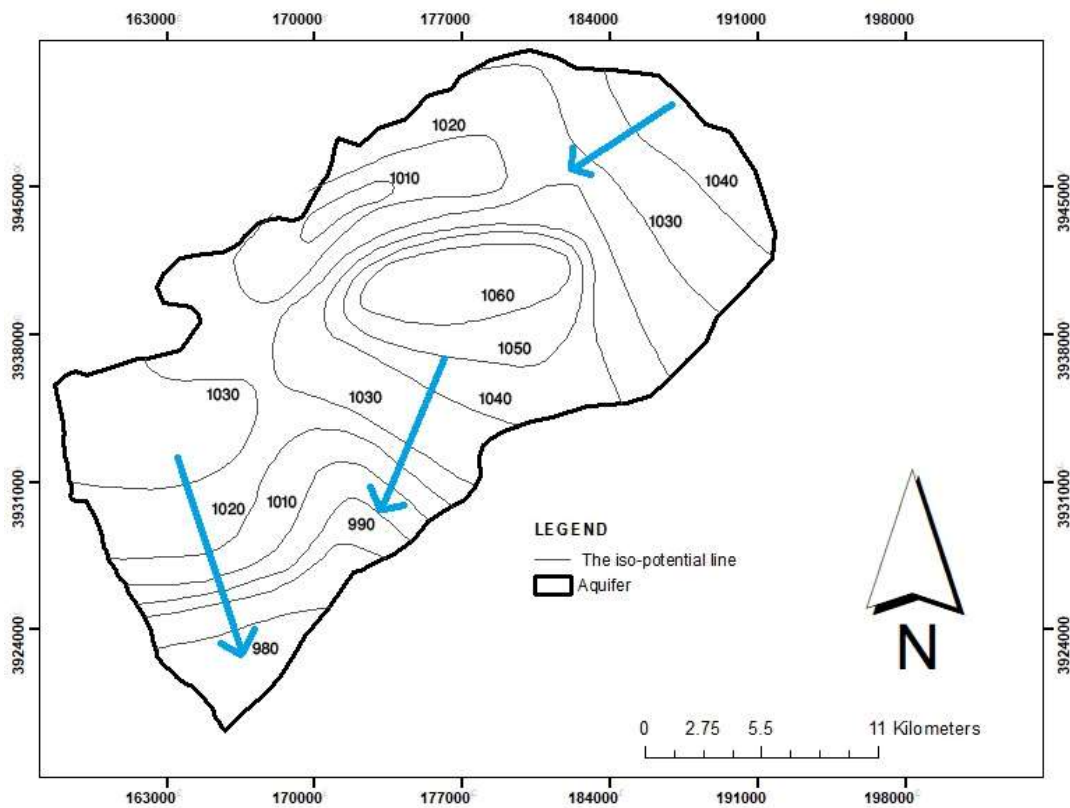

Figure 4. The iso-potential map of the Semnan aquifer which represents the general flow direction

The iso-potential map illustrates that the recharge area of the Semnan aquifer lies mainly in the north regions. As compared with the EC map, some deviations along the flow path (north to the south) are observed which is mainly due to the effect of other process on groundwater ions and chemistry. Below, these changes in chemical quality of the groundwater in Semnan aquifer are approved by chemical and statistical methods.

Results of the hydro-chemistry methods

It is important to recognize that there is a significant amount of variability and contribution from various factors and processes in overall hydro-geochemistry, such as anthropogenic and geological influences. Many diagrams and graphs are used to interpret groundwater hydro-chemistry. Therefore, for predicting chemical weathering, evaporation, or ion-exchange, bivariate plots of major ions can be utilized.

Bivariate plots (Fig. 5) are employed to illustrate mineral dissolution/precipitation phenomena. Dissolution of carbonate rocks is not dominant as the concentration of HCO3 versus Ca+Mg shows a decreasing trend. It confirms that the precipitation of calcite is likely to be occurred in the aquifer.

Direct relationships between Na-Cl and Ca-SO4 propose dissolution of evaporate minerals like halite and gypsum as the primary source of ions in groundwater. With increasing the concentration of SO4, the amount of Ca dose not increase proportionally, which is probably due to the common ion effect. Increase in Ca by dissolution of gypsum enhances precipitation of calcite that removes Ca and HCO3 from the solution. It causes negative trend in (Ca+Mg)-HCO3 relationship.

The concentration of Na surpasses the concentration of Cl. It proposes the effect of ionic exchange on chemical quality of the groundwater.

The Gibbs diagram is well-known for classifying the hydro-chemistry features of groundwater into three categories: Evaporation, Rock weathering dominance, and Precipitation dominance (Fig. 6). Based on the results the dominance of weathering process is indicated in groundwater samples of the Semnan aquifer.

Fig.7 illustrates the classification of groundwater samples from Semnan aquifer on Piper diagram. It is considered that the samples lie in the middle part of the left triangle with no dominant type of cations. However, Cl and SO4 are dominant anions of groundwater samples which confirm dominance of weathering process (dissolution of gypsum and halite minerals) on groundwater chemistry in Semnan Aquifer. It is further approved by statistical approach at the following section.

Both ion exchange and weathering are regular processes that significantly influence the hydro- geochemical features of groundwater (Schooler, 1977).
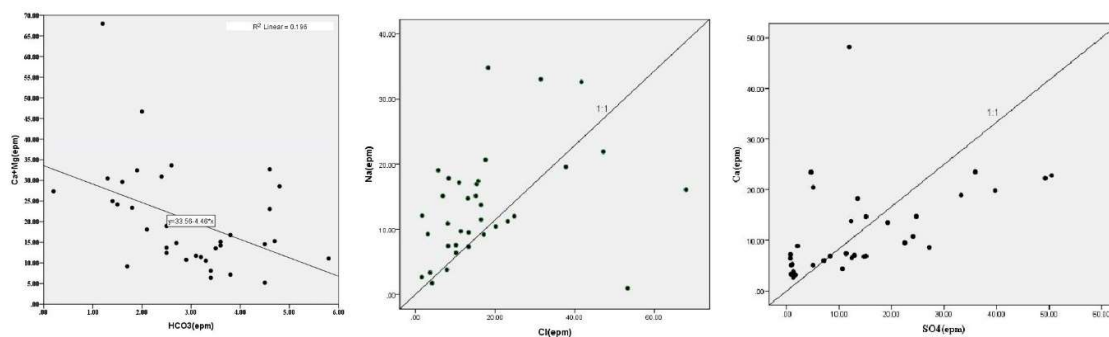
Figure 5. Bivariate plots representing relationships between major ions
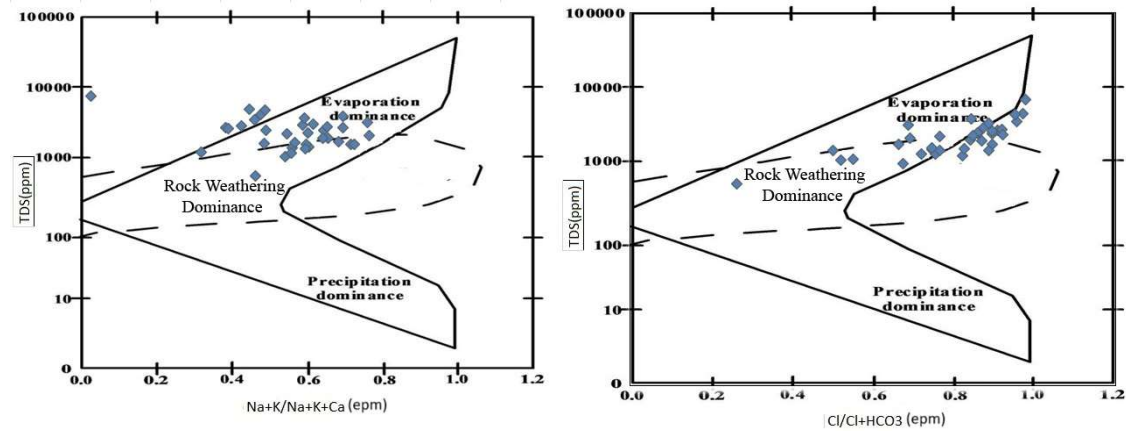
Figure 6. Gibbs diagram (TDS versus (Na/(Na+K+Ca) and TDS versus (Cl/Cl+HCO3))
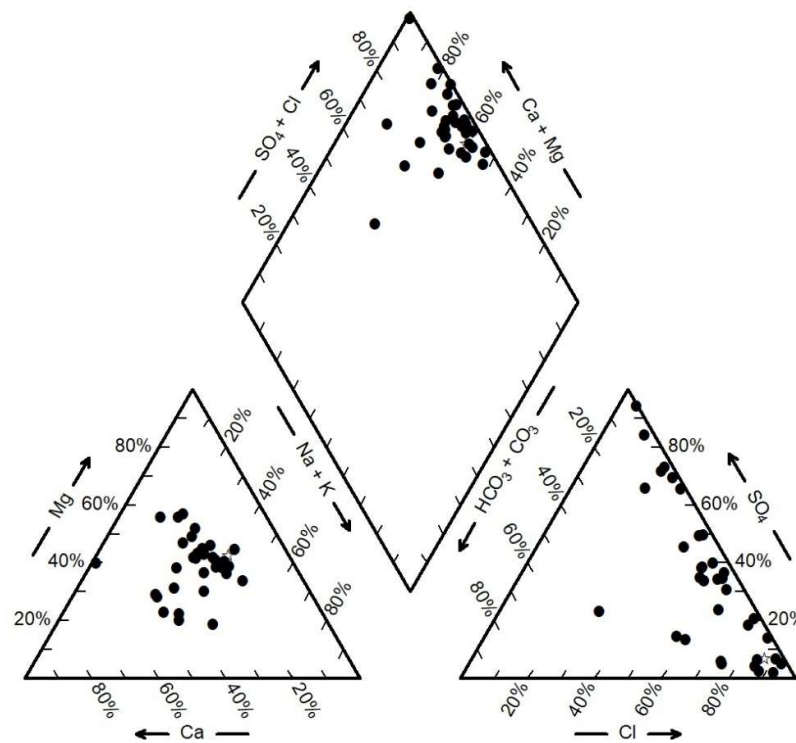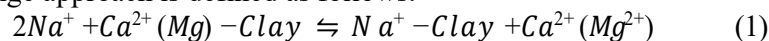

Figure 7. Groundwater samples from Semnan aquifer on Piper diagram

When $Na+K$ dominate the ion composition of groundwater, it becomes evident that cation-anion exchange plays a pivotal role in the hydrochemistry of groundwater (Thakur et al. 2016). The ion exchange approach is defined as follows:

$$2Na^+ + Ca^{2+}(Mg) - Clay \leftrightarrows Na^+ - Clay + Ca^{2+}(Mg^{2+}) \qquad (1)$$

Generally, based on the sample locations on Na-Cl plot (Fig. 5) and excess values of Na, it is evident that ion exchange dominates groundwater chemistry. Additionally, based on Figures 8 to 10, the location of the data samples confirms direct ion exchange, validating previous results. According to CAI calculations, the positive value indicates direct ion exchange, while the negative index suggests reverse ion exchange. Based on the result which is shown on Fig. 11, the most samples form Semnan aquifer show the direct ion exchange.
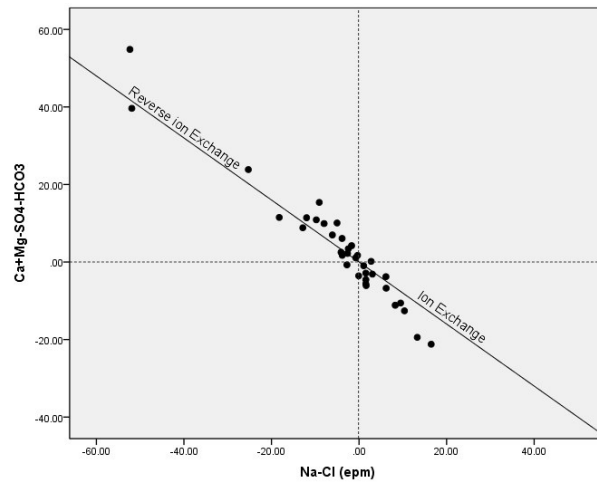
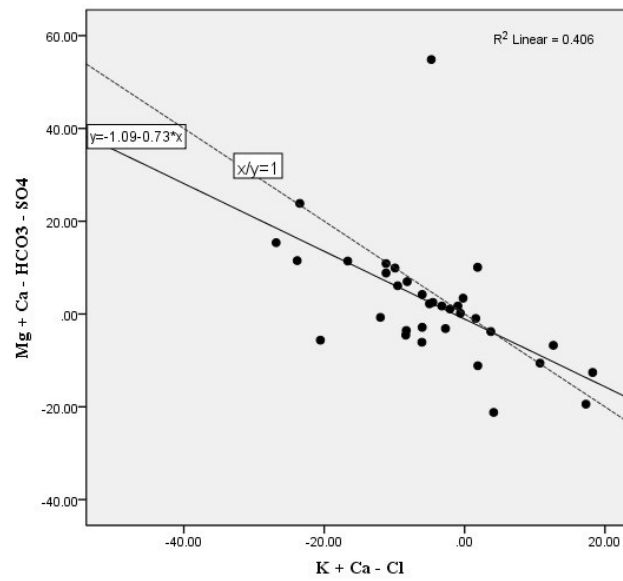**Figure 8.** Bivariate plot of Ca+Mg-SO4-HCO3 versus Na-Cl

Figure 9. Bivariate plot of Mg+Ca-HCO3-SO4 versus K+Ca-Cl
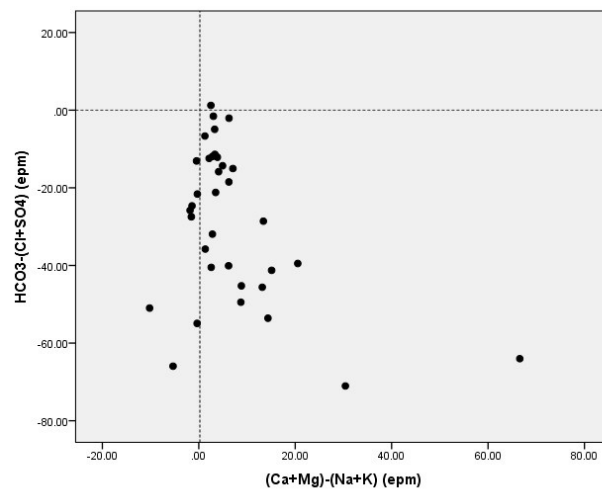

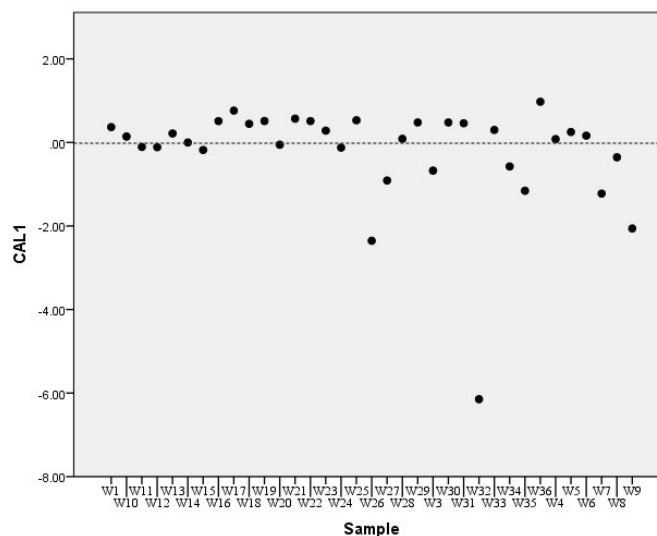**Figure 10.** Bivariate plot of HCO3-(Cl+SO4) versus (Ca+Mg)-(Na+K)

Figure 11. The values of CAl in samples from Semnan aquifer

Results of the statistical methods

Table 2 presents the summary of statistics on chemical parameters including mean, standard deviation, minimum, maximum and coefficient if variation. With the exception of pH, potassium (K) and bicarbonate (HCO3), the other parameters exhibit higher standard deviations indicating a notable degree of variation among the samples, emphasizing their dissimilarity. Furthermore, some parameters (EC, SO_4, Cl and Ca) exhibit significant deviations from their means, particularly in their maximum values, while the others (like HCO_3) do not display such pronounced differences. In conclusion, Table 2 highlights the considerable variation in parameter ranges among the samples. Additionally, it underscores the potential of certain parameters, namely SO_4, Ca^+, and Cl to effectively influence the hydrochemistry of the water.

Table 3 shows the degree of correlation between hydro-chemistry parameters between +1 and -1, indicating strong direct or inverse relationships, respectively. High correlations are observed between EC and Na, Ca and Mg with correlation coefficients of 0.75, 0.737 and 0.857, respectively. Na-Cl, Na-SO4, Ca-SO4 and Mg-Cl pairs also show high degree of correlation.

In order to classify chemical parameters, PCA was performed. Table 4 presents a summary of the variance explained by the principal components. It provides insights into initial eigenvalues, extraction sums of squared loads, and rotation sums of squared loads. Clearly, the initial eigenvalues for each principal component signify the total variance accounted for by each component, as defined by eigenvalues (Choi et al., 2020). Notably, components 1 and 2 collectively explain 76% of the total variance, with component 1 having the highest eigenvalue of 4.58. The number of principal components corresponds to the number of eigenvalues (Fig. 12). Components with eigenvalues exceeding 1 capture the majority of the total variance (Choi et al., 2020).

Table 5 provides a rotated component matrix of the chemical data. In a general overview, each component consists of multiple variables, specifically hydro-chemistry parameters, some of which exhibit a strong relationship with each other. Notably, there are two components with eigenvalues exceeding 1 (Fig. 12). The first component shows highest loadings on EC, Ca, Na and SO4 and negative loading on HCO3. This component is probably related to the dissolution of gypsum that enhances Ca, SO4 and EC of the groundwater and related common ion effect due to precipitation calcite induced by increase of Ca in groundwater solution. In component 2, there are notable loadings on pH, Cl and Mg as well as the Na. This component is likely related

to dissolution of evaporates (halite and other evaporate minerals) that enhances the major ions in groundwater.

Table 2. Summary of the statistics for groundwater quality parameters in Semnan aquifer

Parameter	Mean	Std. Deviation	Minimum	Maximum	Coefficient of Variation(%)
EC (µS/cm)	3424	1858	766	10300	54
pH	7.30	0.164	7.06	7.69	2.2
Cl (epm)	17.70	15.27	1.61	68.00	86
Ca (epm)	11.70	9.19	2.70	48.13	78
Mg (epm)	8.70	5.12	2.05	26.23	58
Na (epm)	13.51	8.28	0.96	34.78	61
HCO3 (epm)	2.94	1.27	0.20	5.80	43
K (epm)	0.142	0.076	0.03	0.42	53
SO4 (epm)	14.24	13.91	0.69	50.45	97

Table 3. Correlation matrix for water quality parameters in Semnan aquifer

|	EC	pH	Cl	SO4	Na	K	Ca	Mg	HCO3
EC	1								
pH	-0.260	1							
Cl	0.633	-0.604	1						
SO4	0.646	0.058	-0.010	1					
Na	**0.750**	-0.441	**0.641**	**0.658**	1				
K	0.542	-0.161	0.159	0.617	0.561	1			
Ca	0.737	0.063	0.198	**0.867**	0.622	0.497	1		
Mg	**0.857**	-0.382	**0.777**	0.315	0.606	0.403	0.400	1	
HCO3	-0.235	-0.382	0.150	-0.513	-0.231	-0.201	-0.537	0.080	1

Table 4. Total Variance explained by principal components

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total
1	4.545	50.500	50.500	4.545	50.500	50.500	3.708
2	2.285	25.390	75.890	2.285	25.390	75.890	3.123

Table 5. Rotated Component Matrix in PCA

Variable	Component 1	Component 2
Cl	0.079	**0.911**
SO4	**0.936**	0.023
pH	0.176	**-0.788**
EC	**0.708**	0.621
K	0.650	0.266
Na	**0.648**	**0.624**
HCO3	**-0.694**	0.398
Mg	0.362	**0.808**
Ca	**0.916**	0.113
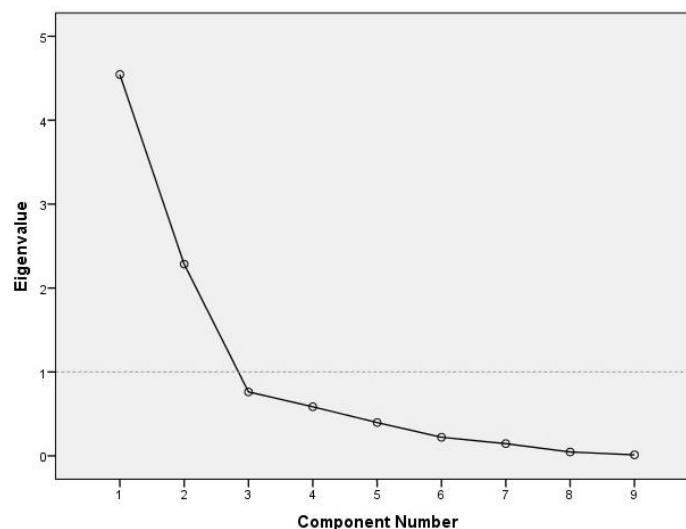
Figure 12. The amount of the Eigenvalue in PCA

Conclusion

Groundwater chemistry is mostly affected by Geogenic and anthropogenic factors. In this study, controls on groundwater in the Semnan aquifer were investigated using hydrochemical and statistical techniques. Bivariate plots show direct relationship of Na-Cl and Ca-SO4 and negative trend in Ca-HCO3 highlighting excess values of Na as compared with deficits in Ca concentrations. These plots as well as the Gibbs and piper diagrams and ion ratios that applied in hydrochemical approach confirmed weathering of the rock minerals (dissolution of evaporates minerals of halite and gypsum), direct ion exchange and precipitation of calcite due to common ion effect (increased Ca by dissolution of gypsum and then precipitation of calcite in super-saturated solution) as the main processes affecting groundwater chemistry in Semnan aquifer. Analysis of data using PCA represents two main components of gypsum dissolution with induced calcite precipitation and halite dissolution. The results further approved the main role of dissolution of evaporates in chemical quality of the groundwater in Semnan aquifer. This study highlights controls of evaporates dissolution, ion exchange and calcite precipitation processes as the main geogenic factors affecting chemical quality of groundwater in Semnan aquifer. Investigating the role anthropogenic factors on pollution of groundwater is highly advised as various probable sources and causes like infiltration of municipal, agricultural and industrial wastewaters are distributed on aquifer plain surface, threatening the quality of the groundwater aquifer.

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