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RESEARCH PAPER

Hydro-geochemistry of the Asadabad plain, West of Iran: Application of statistical methods

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Abstract
Groundwater is basically known to be an essential source for drinking and agricultural uses. Therefore, the study of water resources is of great significance to manage its quality and control related pollutions. There are various ways to survey the quality of groundwater among which the statistical methods like cluster analysis and principal component analysis (PCA) are widely used. In this paper, a new method is introduced to determine aquifer hydrochemistry in the areas with similar quality characterization. After analyzing water samples in the laboratory, as the first step, the factor analysis was performed to determine the main factors controlling hydrochemistry. For example, the weathering of the carbonic rocks was determined as the primary factor to be used in the suggested statistical method in Asadabad study area. Then, the parameters were changed by rating them in new classes from 1 to 3. Finally, all samples with the new quantitative rates are plotted on a four-dimensional graph to differentiate hydrochemical zones. All samples in each hydro-chemical area were compared based on ionic ratios to ensure reliability of the results. The results showed that the new statistical method has the capability for zoning samples with comparable hydrochemistry features. These findings will help in the efficient use of water sources for various human activities, saving money and time.

Keywords: Hydro-Geochemistry, Factor Analysis, Statistics, Asadabad.

Introduction

Todays, the importance of water quality keeps rising if humans want to have healthier lives. Therefore, knowing and managing groundwater resources is the key to the future (Boateng et al., 2016). Surface and groundwater are highly important to be protected as they are crucial for drinking and agriculture uses. Groundwater resources are generally threatened and polluted by many sources and causes mostly classified as natural and anthropogenic factors (Elumalai et al., 2017; Ren et al., 2021). These pollution sources are assessed by different methods such as statistical and hydrochemistry methods that focus mainly on the various components that can affect quality of the groundwater samples. These methods can be combined with geological and hydrogeological characters to calculate representative evaluation indicators, for example to estimate vulnerability of groundwater aquifers accurately. Many researchers provided applied methods to survey the aquifer vulnerability (Mendie et al., 2005; McMurry et al., 2004). The DRASTIC method has been completely adopted as a vulnerability mapping model, which is one of the methods used to map vulnerable areas to pollution (Aller et al., 1985).

There are numerous indices based on chemical and physical properties of water samples that help to determine its suitability for various uses (Elumalai et al., 2017; Wildemeersch et al.,

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2010; Amiri et al., 2021). The most important method is classification of water quality using Water Quality Index (WQI) which was developed by Horton (1965). In addition, there are some studies based on the statistical methods that describe and find similarities between parameters in water samples, among which the most important ones are factor analysis (FA) and discriminant analysis (DA) (Sun et al., 2014; Aydin et al., 2021). Interpolation techniques also precisely aid in predicting the amount of concentration in areas where it has not been sampled (Machiwal et al., 2015). Many methods may be used in combination with statistical approaches to reach meaningful interpretation of water quality (Mamun et al., 2021). Elumalai et al. (2017) used statistical methods and kriging interpolation to mapping groundwater contamination in a coastal area. To sum up, many methods are available for surveying groundwater characteristics, and the results vary according to the type of data available. Eventually, any method can be applied by decision-makers in different areas as a tool to evaluate groundwater quality.

In this study the quality of groundwater in the Asadabad aquifer, Hamadan province, was evaluated. The main aim is to find an approach to determine hydrochemical factors that change the water properties in order to develop a groundwater quality managing strategy. In this regard, factor analysis was firstly employed to determine the main factors affecting groundwater quality and then the aquifer was divided into areas with similar chemical properties using a new proposed graphical method.

Area of study

The Asadabad plain with 965 km^2 area is located in the west of the Hamadan province (Fig. 1) between latitude 34°35' N and latitude 48°16' W. The average elevation of Asadabad plain is about 1600 m above sea level. The most important river is the Shahab River which is flowing in the center of the plain. Geological formations generally range from metamorphic dolomite and limestone in the north to pegmatite, granodiorite, and schist in the west of the study area.

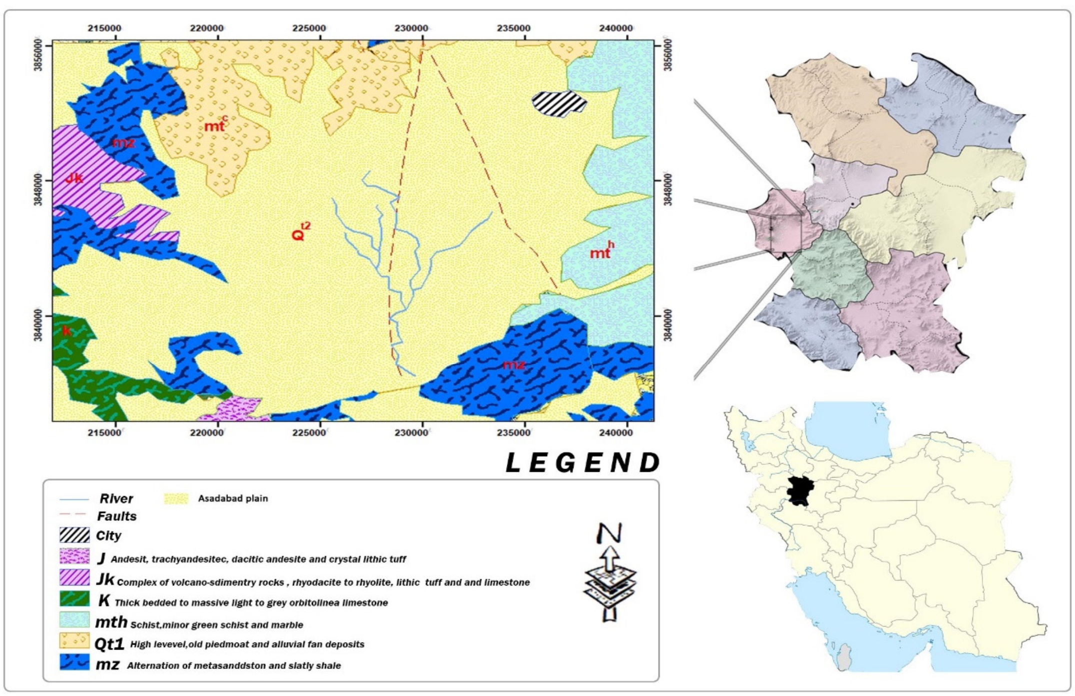

Figure 1. Geological map of the study area

Materials and methods

In this paper, a new method was proposed to classify the aquifer hydrochemical parameters in order to grouping water samples with similar hydro-chemical properties spatially located in a close region. The methodology is consisting of the following steps:

Sample collection and analysis

A total of 32 groundwater samples were collected from Asadabad aquifer with a proper spatial distribution in June 2021 (Fig. 2 and 3). The samples were quickly transferred to the laboratory of Hamedan Regional Water Authority, where the electrical conductivity (EC), pH and major ions (Calcium, Magnesium, Sodium, Potassium, Chloride, Sulfate, and Bicarbonate) were measured by standard instruments and methods. Total dissolved solids (TDS) were also calculated by the formula of (Lloyd and Heathcote, 1985) (Table.1).

Factor Analysis Method

Statistical techniques such as principal component analysis (PCA), discriminant analysis (DA), clustering analysis (CA), and factor analysis (FA) are mainly used to recognize the relationships between variables.

Table 1. The concentration of major ions and TDS in groundwater samples from Asadabad aquifer

Major Iond (meq/l)							TDS (mg/L)
Sample	**Ca**	**Mg**	**Na**	**Cl**	**HC0$_3$**	**SO$_4$**	
101	2.7	1.7	0.48	0.5	4	0.3	314.88
102	2.5	1.3	0.38	0.7	3.1	0.3	278.4
103	2.7	1.5	0.47	0.6	3.8	0.2	302.08
104	1.9	1.4	0.66	0.4	3.3	0.21	244.48
105	2.5	1.5	0.67	0.7	3.6	0.32	283.52
106	2.3	1.4	0.46	0.5	3.3	0.32	262.4
107	2.8	1.4	0.55	0.4	4.2	0.12	269.44
108	2.6	1.9	0.96	0.6	4.3	0.5	318.72
109	3.2	2.8	0.93	0.9	5.6	0.4	462.15
110	2.6	1.6	0.94	0.6	4.3	0.15	319.36
111	3.2	2.2	0.75	0.8	5	0.32	435.84
112	3.9	1.8	0.59	0.7	4.9	0.68	385.28
113	2.3	2.1	0.56	0.5	4.2	0.22	319.36
115	2.7	2.5	0.99	0.6	5.3	0.26	396.8
116	2.5	2.3	0.39	0.7	4.2	0.24	332.8
122	3.3	1.4	0.83	0.8	4.4	0.3	326.4
123	3.9	3	4.16	2.6	5.1	3.3	741
124	2.3	2.2	1.42	0.5	5	0.32	361.6
125	3.8	2	1.57	0.9	5.2	1.23	512.85
126	2.6	2.1	1.1	0.7	4.7	0.32	345.6
127	2.3	1.5	0.48	0.5	3.4	0.34	277.12
128	2.9	2.1	0.89	0.7	4.6	0.5	405.12
236	2.5	1	0.37	0.3	3.4	0.12	211.2
237	1.9	1.1	0.29	0.4	2.6	0.24	225.28
238	3.7	2	0.6	0.7	5	0.5	390.4
239	2.7	1.8	0.76	0.5	4.5	0.24	342.4
240	2.5	1.5	0.48	0.4	3.8	0.21	281.6
242	2.5	1	0.39	0.2	3.5	0.12	213.76
243	3.5	2.9	0.86	1	5.8	0.35	468
244	2.7	1.1	0.52	0.3	3.8	0.15	261.76
245	3.9	2.7	3	2.3	5.4	1.85	640.25
246	2.3	1.9	1.5	0.5	4.8	0.32	336.64

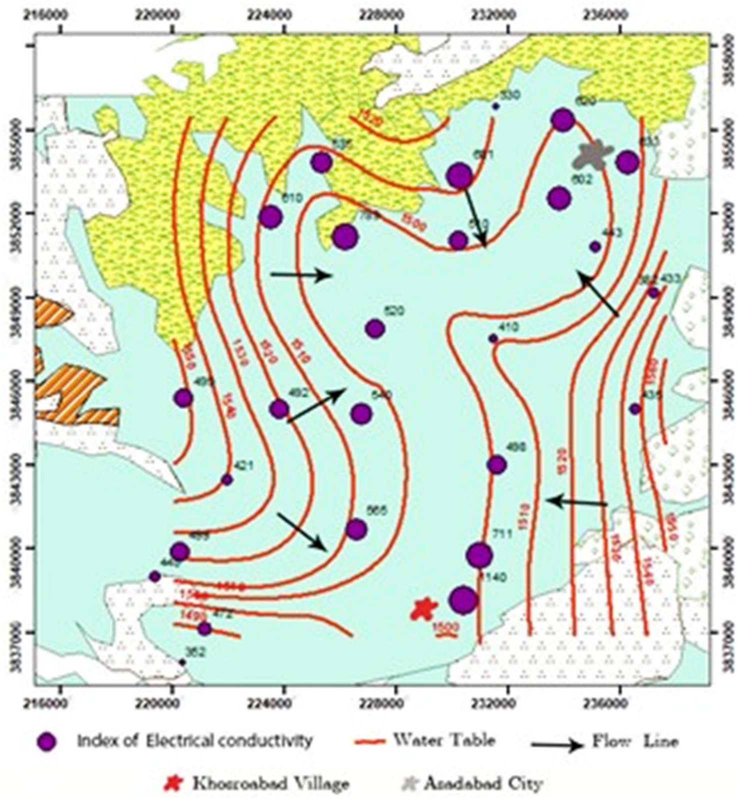

Figure 2. Distribution of water table level, flow direction and location of water samples in Asadabad plain

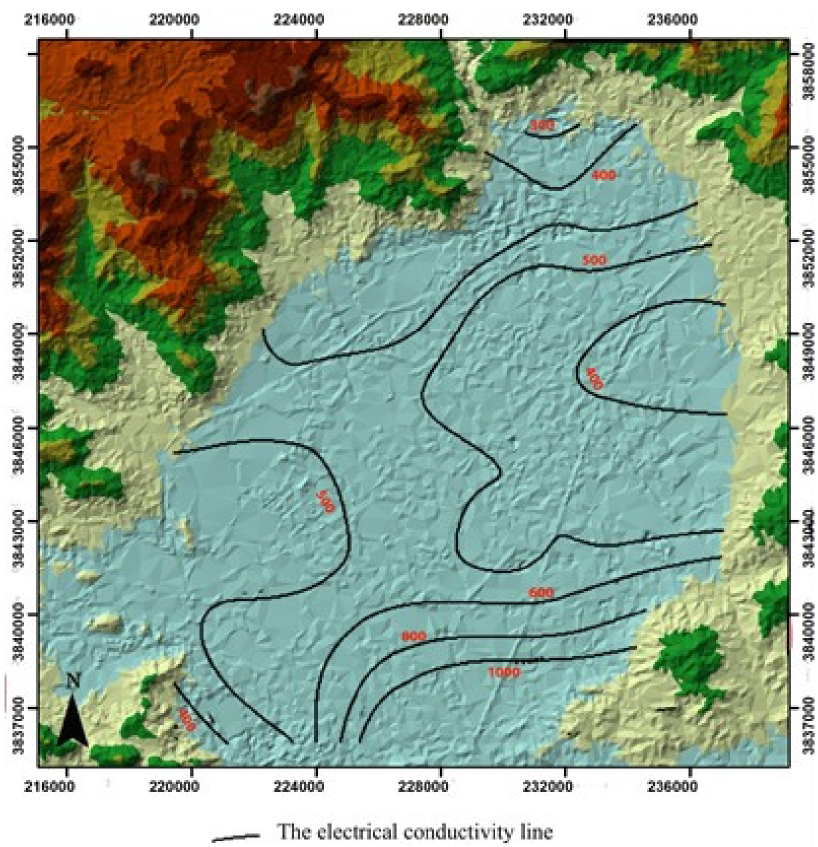

Figure 3. Iso-Ec map of the Asadabad aquifer

PCA and FA is thought to be one of the important methods that make a functional grouping (Kumar al., 2017; Tlili-Zrelli et al., 2013). FA can identify the variations of the hydrochemistry of groundwater and classify specific areas which were created by natural and human activity (Soltan et al., 2017). When FA was carried out on major ions, there may be one or more factors with a higher eigenvalue. The component which has a higher value of Varimax rotation is responsible for the most changes in all the samples. In this research, FA was applied to hydrochemical data to infer major components responsible for the quality of the groundwater samples.

Proposed method

A new method was developed to classify hydro-chemical features of aquifer areas based on the results of FA. The method can be used for dividing aquifer areas into more detailed areas with similar quality to obtain essential perspective of the study aquifer.

This method firstly uses the result of FA, the main factor that controls the hydro-chemical feature of aquifer. The steps carried out in the proposed methodology are summarized as following:

Selection of main factors affecting groundwater quality derived from statistical method of factor analysis

Converting the system parameters by rating the quantitative parameters from 1 to 3

Displaying the data on a graph of 4-dimensions that includes main factors affecting groundwater quality to creating groups with specific hydrochemistry features

Drawing and interpolating the result on the aquifer map and validating results with hydro-chemical scatter plots

Results and Discussion

Investigating spatial variations of physico-chemical parameters

The physico-chemical parameters of groundwater are used to identify variations in the quality and quantity of groundwater (Mohamed, 2005). The results of the chemical analysis on samples from Asadabad aquifer are presented in Table 1.

Based on the results, pH values range between 7.3 and 8.1 with a mean value of 7.6. The mean value of electrical conductivity (EC) is 536 µS/cm, which is indicative of low concentration of dissolved ions in groundwater resources. In accordance with groundwater flow direction from the surrounding heights (recharge area) to the center and south of the plain (discharge area), EC values gradually increases from the recharge area to the discharge points (Fig. 3). Generally, groundwater types are changing from Ca-HCO_3 to Na-HCO_3 along the flow path from recharge zone to the discharge area of the aquifer.

Magnesium and calcium, which can be found in the groundwater resources generally come from carbonate minerals such as calcite and dolomite. The average concentration of Mg and Ca in groundwater samples are 1.8 and 2.7 epm, respectively. It indicates the major effects from dissolution of carbonate formations on groundwater quality in the study area.

The main sources of Cl in groundwater samples are the solubility of Cl-bearing evaporation deposits. The anthropogenic activities are also other sources that increase the Cl content of the groundwater resources (Hinkelmann at el., 2015). The mean concentration of Cl is not so high, indicating minor effects of the chloride sources on the quality of the Asadabad aquifer.

The amount of bicarbonate and its correlation with Mg and Ca (Table 2) indicates that the major source of HCO_3 in the aquifer is the dissolution of carbonate minerals.

Table 2. Correlation Matrix between chemical parameters in Asadabad plian aquifer

	SO_4	Cl^{2-}	HCO_3	NO_3	pH	TDs	K	Na^{2+}	Mg^{2+}	Ca^{2+}
SO_4	1									
Cl^{2-}	**0.94**	1								
HCO_3	0.36	0.43	1							
NO_3	0.23	0.22	-0.08	1						
pH	0.25	0.27	-0.19	0.13	1					
TDs	**0.85**	**0.88**	0.74	0.10	0.06	1				
K	**0.75**	**0.82**	0.62	0.10	0.04	**0.839**	1			
Na^{2+}	**0.93**	**0.91**	0.49	0.20	0.26	**0.869**	0.74	1		
Mg^{2+}	0.54	0.63	**0.82**	0.07	-0.03	**0.831**	0.74	0.64	1	
Ca^{2+}	0.59	0.61	0.71	-0.04	-0.08	0.655	0.65	0.50	0.48	1

From the result given by Spearman's correlations coefficient matrix between main ions, EC and pH (Table 2), the highest correlations are observed between EC, HCO_3, Mg, and Ca. The results confirm the dissolution of carbonate minerals as the main factor influencing the groundwater quality in Asadabad aquifer.

Factor Analysis

The factor analysis decreases the data value and finds the variation between parameters to access the main factors (Boateng at el., 2016). From the factor analysis, two main factors that influence the aquifer's water quality were found that accounted for 83 percent of the total variance. Factor 1 shows highest positive loadings on TDS, Ca, Mg, HCO_3, and K, which can be attributed to the weathering of carbonate rocks. In addition, factor 2 that explains 24.5 percent of the total variance is mainly contributed by SO_4, Cl, and Na. This factor may be indicative of the dissolution of evaporative rocks (Table 3).

Proposed method

After doing FA the main factor including four parameters of Mg^{+2}, Ca^{+2}, HCO_3, and TDS was selected and the system parameters were changed by rating the qualitative parameters in new classes from 1 to 3 as represented in Table 4.

To evaluate possible hydro-chemical areas having special features, new rated parameters (factor 1 of the FA method) was plotted on a 4-dimensional system (Fig 4) that shows the aquifer consists of four areas that are displayed in Fig 5.

Based on Table 5, and Figures 4 and 5, there are low concentrations of EC in areas 2 and 3, which indicate that these areas lie in the recharge zones of the aquifer. The concentrations of Na and SO_4 ions are low in these areas. According to the proposed method, area 1 is located in the transition zone where the level of concentration of its ions is between areas 3 and 4, so that the amount of the EC gradually increases, reaching at 800 µS/cm. Area 4 (discharge zone) is located in the south of the Asadabad aquifer where it has the lowest level of the water table and is the end of the groundwater flow path. Therefore, the high values of ions concentration and EC are observed.

Composition plots (Ca + Mg/HCO3, Ca+Mg/ SO4+HCO3, and Na+Cl/EC) are shown in Figure 6. Each plot consists of the samples scattered in four areas that are completely corresponding to the zones obtained by the proposed method. All the samples from area 3 have the lowest levels of dissolved ions which locate in the recharge zones of the aquifer. The samples from area 4 with the highest ions concentrations are found in the discharge zone located at the south of the plain. From arae1 to area 4, the concentration of dissolved ions increased along flow path from the recharge zone to the discharge zone.

Table 3. Principal components loadings and explained variance for the two components with Varimax normalized rotation

Parameter	Factor 1	Factor 2
SO_4^{2-}	0.436	**0.883**
Cl^-	0.51	**0.828**
HCO_3	**0.983**	-0.076
Na^+	0.547	**0.766**
Mg^{2+}	**0.863**	0.214
Ca^{2+}	**0.728**	0.285
TDS	**0.806**	0.573
pH	-0.176	0.387
% Total variance	55.807	24.532
Cumulative (%)	55.807	80.339

Table 4. Rating the parameters in new classes (reclassification)

Ca^{2+}	0<= x <=1.45 = "**1**" and 1.46<= x <= 2.91="**2**" and 2.92<= x <=4.36 = "**3**"
Mg^{2+}	0<= x <=1.75= "**1**"and 1.76<= x <= 3:6 = "**2**" and 3.7<= x <=8.3 = "**3**"
HCO_3	0<= x <=1.9="**1**" and 2<= x <=3.9="**2**" and 4<= x <=8="**3**"
TDs	0<= x <=200 = "**1**" and 201<= x <= 400="**2**" and 401<= x <= 800="**3**"

X is the amount of the parameter.

Table 5. Mean value of some hydrochemical parameters in different areas of the aquifer

Areas	**Mean (Na+Cl/Ec)**	**Mean (Ca+Mg/HCO₃)**	**Mean (EC)**	**Mean (Ca)** meql	**Mean (Mg)** Meql/l	**Mean (HCO_3)** meql/l
Area1	0.9	3.8	600	3	2	4.7
Area2	0.5	3	400	2	1.5	3
Area3	0.3	2.4	300	2.5	1	4
Area4	0.4	1.5	1100	4	3	5

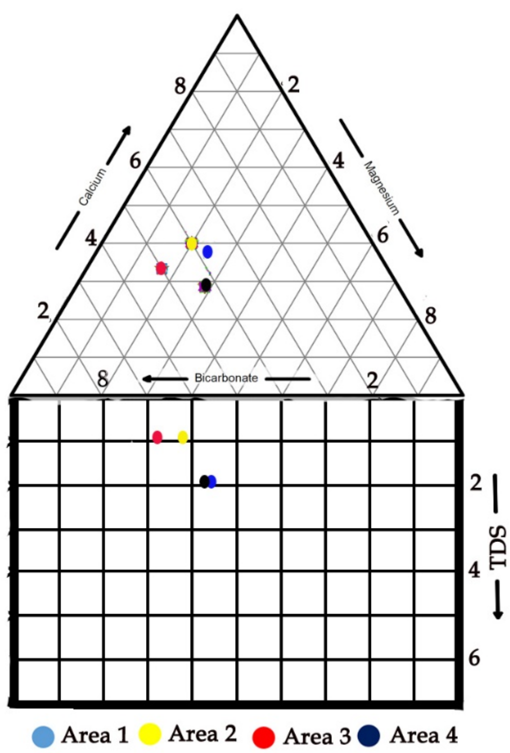

Figure 4. Results of the proposed method on 4-D graph

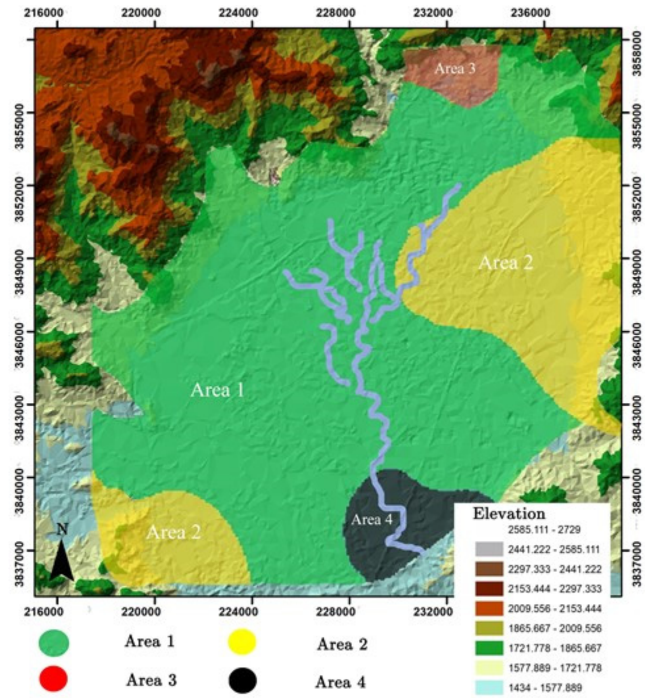

Figure 5. Zoning Asadabad aquifer based on groundwater quality derived from the new proposed method

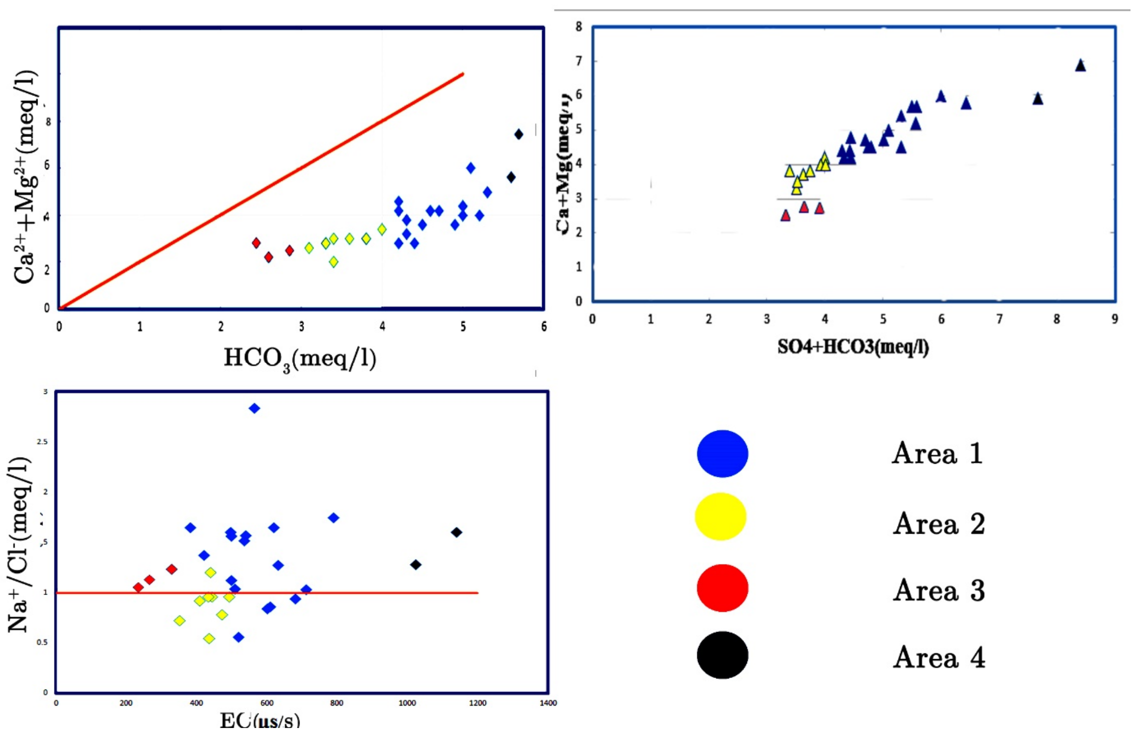

Figure 6. Bivariate plots showing samples from different zones of the Asadabad aquifer

Conclusion

In the Asadabad aquifer, groundwater is the most important source of irrigation and drinking water. Investigation of hydrochemistry is one of the keys to manage this valuable resource.

Results show that the amount of electrical conductivity (EC) increased from the recharge zone to the center and south of the aquifer, having positive correlations with main ions. Factor analysis method shows two factors which explain 80.44% of the total variance. The main factor is attributed to dissolution of carbonate rocks. Based on the method proposed in this manuscript, four areas with special hydrochemistry are discovered which is in coincidence with the recharge, transition and discharge zones of the aquifer. The proposed methodology differentiates the aquifer zones with similar properties in detail, helping to understand main processes affecting the groundwater quality.

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