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Geochemical Evaluation of Drinking Water in Arak City, Iran

Feridon Ghadimi[1*] and Mohammad Ghomi[1]

1. Arak University of Technology, Department of Mining Engineering, Arak, Iran.

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Abstract

This paper presents results of an assessment of dominant hydro-geochemical processes controlling groundwater chemical composition, using an integrated application of cluster analysis and factor analysis. The area is located in south of saline playa and in Arak city. Cluster analysis classified samples into two main clusters according to their dominant chemical composition: cluster A (dominant composition: Ca, Cl and SO_4) and cluster B (dominant composition: Ca–HCO_3). These clusters were in turn described by factor analysis. Results of factor analysis and geochemical interpretation suggest that spatial variation of groundwater quality in the area is influenced by different processes: Analyses revealed three major sources of variation in groundwater composition: carbonate and silicate mineral weathering, saltwater intrusion and anthropogenic contamination. Factor 1 shows processes of dissolution of Cl and SO_4 evaporative salts (for samples close to Arak playa). Factor 2 exhibits strong positive correlation in Zn and Cu and shows anthropogenic or industrial sources. Factor 3 exhibits HCO_3 and NO_3 and is resulted from weathering of carbonate and silicate minerals by percolating water and disposal of domestic wastes.

Keywords: *Arak, Cluster Analysis, Factor Analysis, Groundwater, Hydrochemistry.*

1. Introduction

Chemical composition of groundwater is controlled by many factors which include composition of precipitation, mineralogy of watersheds and aquifers, geochemical processes within aquifer [19, 1]. These processes occurring within groundwater and reactions with aquifer minerals have a profound effect on water quality and are responsible for variations in groundwater composition [7].

Hence quality of water along its underground movement is therefore dependent not only on chemical and physical properties of surrounding rocks but also varies as a result of human activity [7]. Variation in groundwater chemistry is mainly a function of the interaction between groundwater and mineral composition of aquifer materials through which it moves [16, 24]. Hydrochemical processes, including dissolution, precipitation, weathering together with residence time occurring along flow path, control variation in chemical composition of groundwater [18, 21].

In this study hydrochemical information from groundwater system are integrated and used to determine main factors and mechanisms controlling chemistry of drinking groundwater in area.

Main issues that will be addressed by this study include: (1) validity of statistical clustering techniques in classifying the samples into hydrochemical facies on a regional scale and (2) development of hydrochemical properties for the region.

2. Material and methods

2.1 Area Descriptions

Study area is located in center of Iran and characterized by a semi-arid climate and an average precipitation and temperature is 280 mm/year and 18°C respectively [26]. Most of its inhabitants are concentrated Arak city with more than 400000 inhabitants working mainly in industrial plants. Aquifer of Arak is developed into medium to fine sediments of Pleistocene age, which occupy a broad graben between mountains Arak and Ashtian (Fig.1). Bedrock of these formations is composed of crystalline limestone. Study area is situated in alluvial plain and aquifer is directly fed by stream water coming from different reliefs surrounding the depression inter-mountainous of Mighan playa. Study area includes two alluvial plain called Arak plain and Aman-abad plain. Most of these wells supply water for drinking. The direction of groundwater flow around Arak plain is from southwest to northeast and toward saline Mighan playa (Fig. 1).

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*Corresponding author.
E-mail address (es): drghadimi@yahoo.com

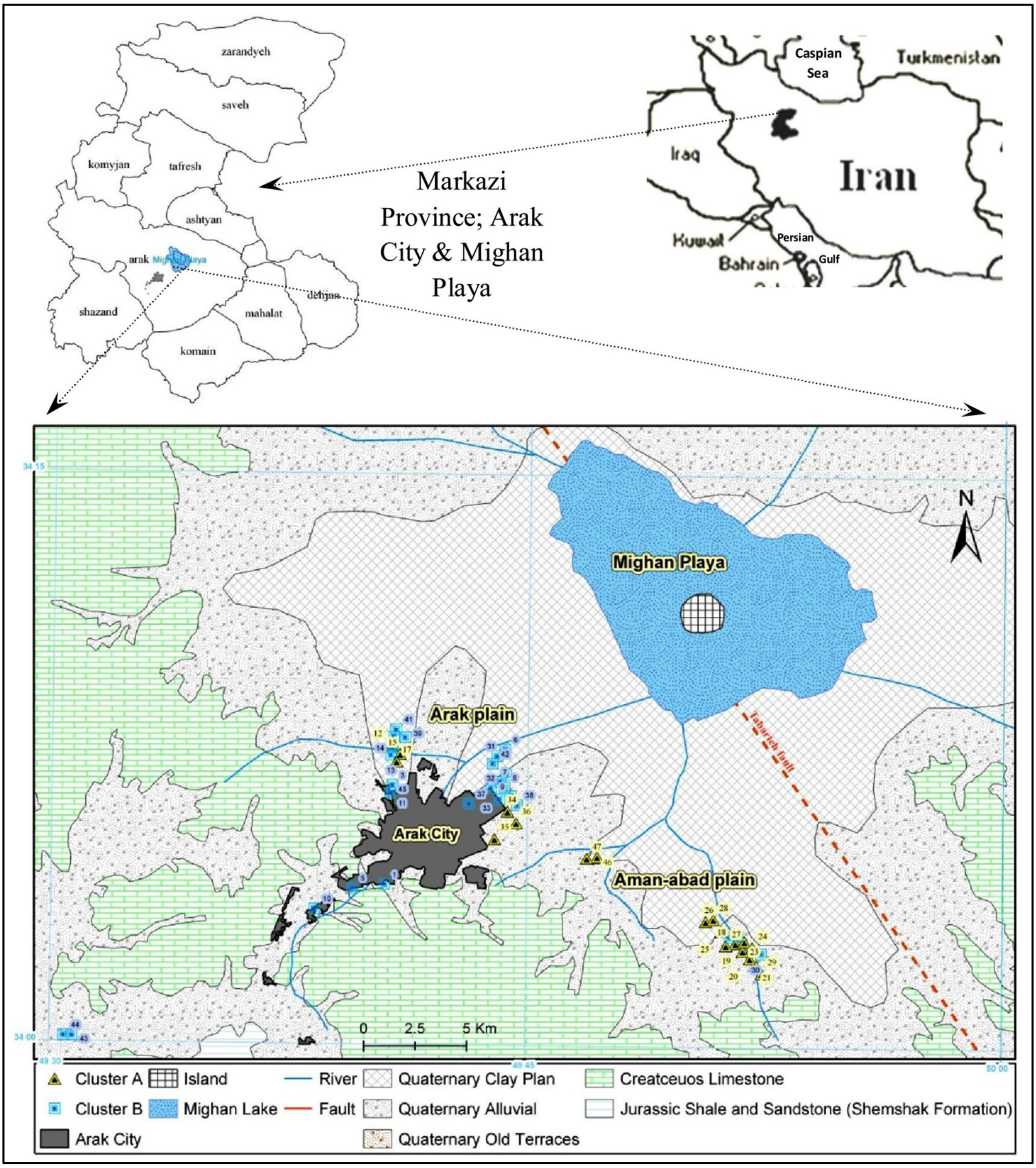


Fig.1. Map of the study area showing two plains and samples location

2.2. Sampling and Analyses

Total of 47 samples were taken for this study in 2012. Samples were collected in 250 ml sterilized polythene bottles. For all samples collected, parameters such as electrical conductivity (EC), and pH values were measured in field. On-site testing was necessary for these parameters since they are likely to change during transport and storage. These variables were measured using a WTW Universal Conductivity Meter Multi Line P4 set and probes. The pH-meter was calibrated against a standard solution of 3mol KCl each morning and also during fieldwork if unusual readings were made. Water samples were analyzed at Wastewater and Water Organization of Markazi Province. Parameters analyzed include major ions of

Calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), chloride (Cl), sulfate (SO_4) and minor ions such as fluoride (F), nitrate (NO_3), and phosphate (PO_4) in milligram per liter using ion chromatograph (I.C). Bicarbonate ion concentration in water was determined by titration. Heavy metals were determined by Graphite Furnace Atomic Absorption Spectrophotometer (Perkin–Elmer Analyst 700) using multi element Perkin–Elmer standard solutions. Accuracy of chemical analysis was verified by calculating ion-balance errors where errors were generally within 10%.

2.3. Statistical Analyses

Univariate statistical analysis has been generally to treat hydrochemical data in environmental samples. Simplicity of univariate statistical analysis is obvious [2]. Multivariate analysis such as factor analysis is used to explain correlation amongst a large number of variables in terms of a small number of underlying factors without losing much information [8, 15]. Use of multivariate analysis is to achieve great efficiency of data compression from original data, and to gain some information useful in interpretation of environmental geochemical origin. This method can also help to simplify and organize large data sets to provide meaningful insight and can help to indicate natural associations between samples and/or variables [23] thus highlight information not available at first glance. This multivariate treatment of environmental data is widely successfully used to interpret relationships among variables so that environmental system could be managed [13].

In this work, hydrochemical measurements were subjected to quantitative statistical analyses in order to draw a valid conclusion regarding nature and significance of hydrochemical elements distribution in Arak city. Main statistical software in use was “Statistica version 8”. Applied statistical analyses include basic statistics, correlation analyses, normal plots, cluster analysis and factor analysis.

3. Results and Discussion

3.1. Hydrochemistry of groundwater

Table 1 presents statistical summary of all parameters analyzed for this study. Mean concentrations of major ions in Arak aquifers are within Iran Standard guidelines [20] for drinking water. Maximum Cl, NO_3 and SO_4 concentrations are 1435 mg/l, 102 mg/l and 300 mg/l respectively and are however, higher than their respective Iran Standard guidelines of 200 mg/l, 45 mg/l and 250 mg/l. These are resulted from contamination of sources such as domestic sewage and agricultural activities. In Arak area, salinity is different and might be associated with combined effects of saltwater intrusion and rock-water interactions. Mean and median EC values of 955 µS/cm and 859 µS/cm, which correspond to total dissolved solid concentrations of 680 mg/l and 618 mg/l, respectively and are below Iran Standard guideline value of 1000 mg/l. Maximum concentrations of some of the major ions such as Na and Cl are higher than Iran Standard. However, low mean and median values of concentrations of these ions imply that most of locations sampled have concentrations lower than recommended maximum values for domestic usage. The pH is neutral but it is within acceptable range. In study area, ionic concentrations follow a similar trend. Except for Na and EC, whose maximum values of 361 mg/l and 4570 µS/cm (equivalent to TDS of 3199 mg/l) are slightly higher than Iran Standard guidelines recommended values. All other major parameters have concentrations lower than standard guideline limits. Aquifers of alluvial Arak, which are mostly sedimentary aquifers, therefore produce groundwater of acceptable quality for most uses. In Arak aquifers, concentrations of Pb, Zn and Cu are higher than recommended Iran Standard guidelines. Value of Pb, Zn and Cu ranges from 2 to 9 mg/l, 4 to 50 mg/l and 4 to 50 mg/l in groundwater and recommended Iran Standard ranges 0.05mg/l, 5 mg/l and 0.05 mg/l, respectively.

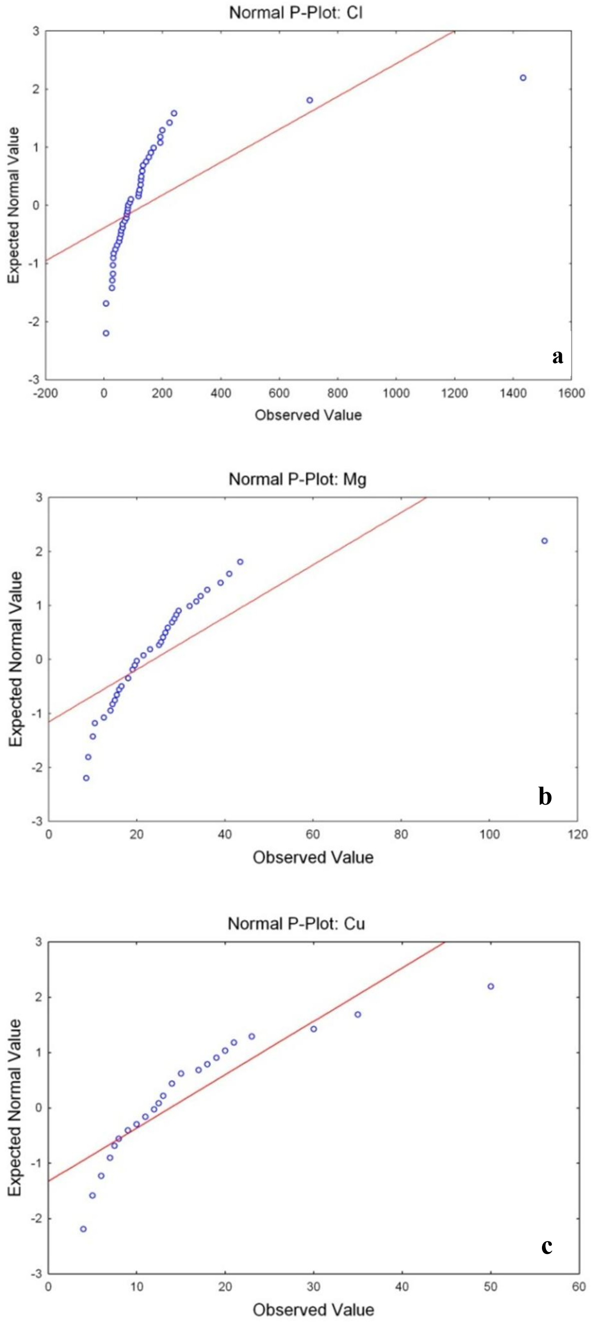
Table1. Statistical characteristics of hydrochemical variables in Arak aquifer

Variables	Mean	Median	Minimum	Maximum	Skewness
pH	7.5	7.54	7.21	7.71	-0.52
EC	955	859	316	4570	4.01
TDS	680	618	221	3199	3.21
SiO_2	17	17	10	23	-0.38
F	0.22	0.21	0.10	0.79	3.55
Cl	135	83	6.50	1435	4.95
SO_4	95	95	7	300	2.83
HCO_3	195	169	90	616	3.05
PO_4	0.14	0.14	0.02	0.23	-0.24
Ca	96	87	44	408	4.11
Mg	23	20	8.50	112	3.96
Na	76	54	9.50	361	2.85
K	0.84	0.79	0.30	1.9	1.30
Fe	0.02	0.02	0.01	0.02	0.07
Mn	0.01	0.01	0.01	0.10	5.87
Pb	6.52	7	2	9	-0.48
Zn	15	14	4	50	1.60
Cu	13	12	4	50	2.09
NO_3	34. 20	25	12	102	1.14

3.2. Statistical results

3.2.1. Normal plots

In order to obtain a better understanding of the distribution normality, normal plots were produced for all hydrochemical variables (Fig.2). Observed values were plotted on x-axis, and values expected for a normal distribution were plotted on y-axis. Samples with a normal distribution collected along a diagonal straight line. In Fig. 2, deviations from normality were observed for most of the hydrochemical variables. It is clearly shown that most of figures showed a concave feature, with both the low values and high values. A few of variables showed a slightly normal feature, e.g. SiO_2, PO_4, Fe and Pb. These variables are shown by low skewness, but other hydrochemical data have high skewness (Table 1) and without normal distribution.



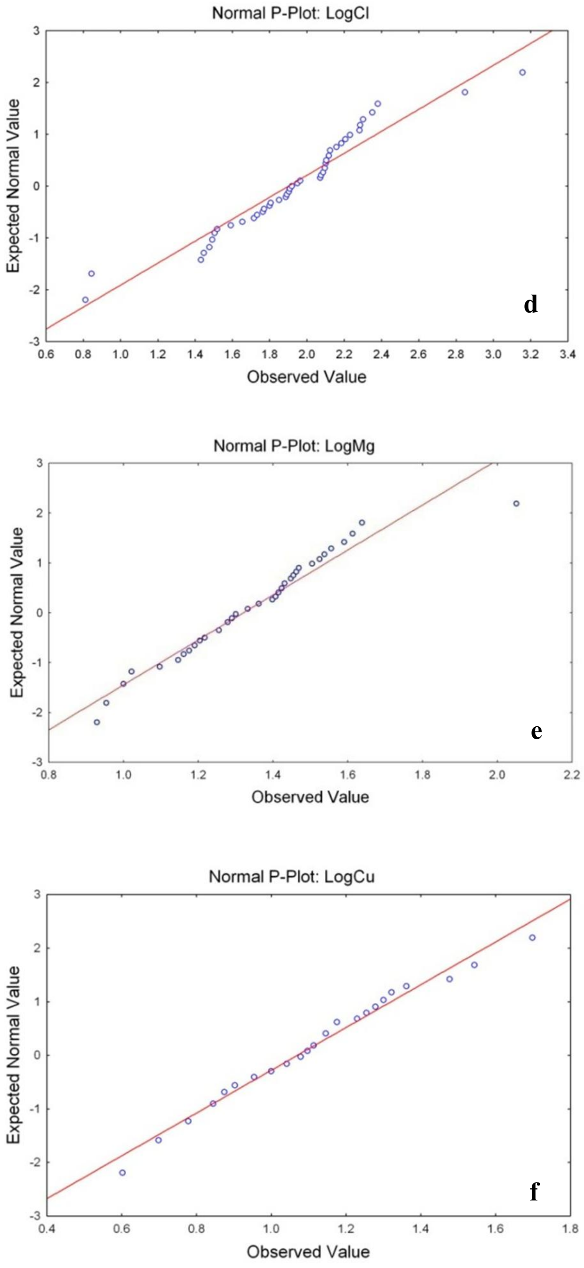


Fig. 2. Plots of some of hydrochemical variables before (a, b, c) and after normalization (d, e, f)

They have strong effect on overall feature of data sets, and may cause biased results for statistical analyses, which are sensitive to outliers, such as calculation of mean and variance, as well as Pearson correlation analysis.

3.2.2. Cluster analysis

Hydrochemical data were classified by cluster analysis and results were presented as a dendrogram (Fig. 3). Two groups are selected based on visual examination of dendrogram. Each cluster represented a hydrochemical group with means for each parameter shown in Table 3. Choice of number of clusters is subjective. Choosing optimal number of groups depends on researcher since there is no test to determine optimum number of groups in dataset [12, 16]. This is a universal problem in all statistical clustering schemes, sometimes called cluster validity problem. This is why we use the criteria of spatial coherence and geochemical validity as established by inverse modeling to support the clusters chosen from cluster analysis [22, 24]. In cluster A, samples have mean values of Cl, SO_4, Na of 251 mg/l, 142mg/l and 126 mg/l but in cluster B, concentrations of above parameters are 57mg/l, 63 mg/l and 42 mg/l, respectively (Table 3). Electrical conductivity (EC) in cluster A is 1290 µS/cm but in cluster B 704 µS/cm. Groundwater in cluster A is more saline than cluster B. Value of HCO_3 in cluster B (mean value of 226 mg/l) is more than cluster A (mean value of 150 mg/l). Cluster B is composed of 28 wells and concerns 60% of water samples. This type of water is relatively fresh with a mean value of EC relatively 704 µS/cm.

Table 2. Comparative of hydrochemical variables before and after normalization.

Variables	**Skewness (before normalization)**	**Variables**	**Skewness (after normalization)**
pH	-0.52	pH	-0.52
EC	4.01	Log EC	0.77
TDS	3.21	Log TDS	0.67
SiO_2	-0.38	SiO_2	-0.38
F	3.56	Log F	0.80
Cl	4.95	Log Cl	-0.21
SO_4	2.83	Log SO_4	-1.41
HCO_3	3.05	Log HCO_3	1.04
PO_4	-0.24	PO_4	-0.24
Ca	4.11	Log Ca	1.06
Mg	3.96	Log Mg	0.60
Na	2.86	Log Na	-0.05
K	1.30	Log K	-0.01
Fe	0.07	Fe	0.06
Mn	5	Log Mn	1.18
Pb	-0.48	Pb	-0.44
Zn	1.60	Log Zn	0.07
Cu	2.09	Log Cu	0.36
NO_3	1.14	NO_3	0.36

Piper diagram plots major ions as percentages in two base triangles. Total cations and total anions are set equal to 100% and data points in two triangles are projected onto an adjacent grid. Ion concentration distribution is displayed on Piper-diagram (Fig. 4), where trilinear diagrams illustrate relative concentrations of cations and anions in each sample. In case of cations, clusters show Na-K (cluster A) and Ca (cluster B) dominance. In case of anions, cluster A and cluster B show Cl and HCO_3 respectively. Sulfate content is relatively low. Durow diagram also exhibits difference of two cluster A and cluster B (Fig. 5). Table 4 shows water type in cluster A and cluster B. Water types of Ca-Na-Mg-Cl-HCO_3-SO_4 and Na-Ca-Cl-HCO_3-SO_4 are dominant in cluster A but in cluster B, water type is mainly Ca-Mg- Na- HCO_3 -Cl- SO_4 and Ca-Mg- HCO_3.It is clear, sources of water type are different in two clusters. Based on Shoeller diagram, dominant anions are Cl and SO_4 in cluster A but HCO_3 is dominants in cluster B and Ca cation is dominant in two clusters (Fig. 6).

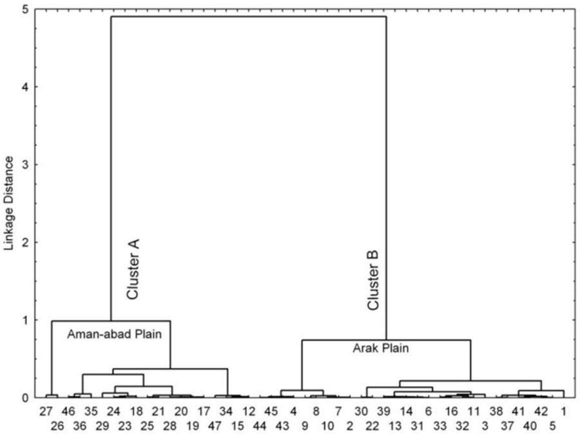


Fig.3. Dendrogram of hierarchical cluster analysis.

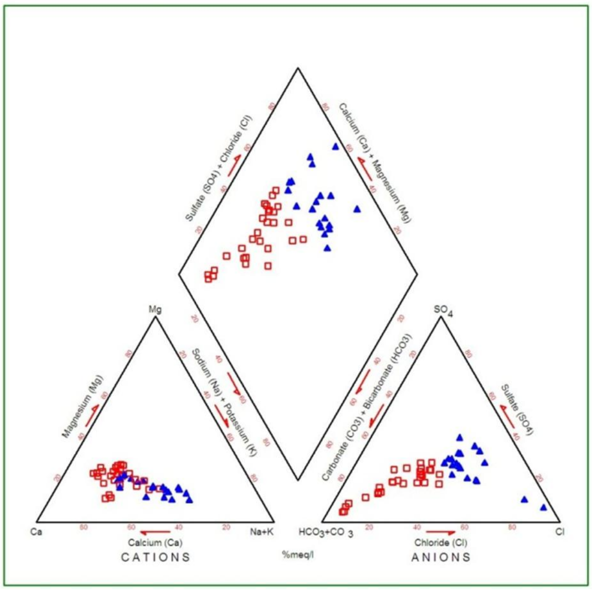


Fig.4. Piper diagram for cluster (three angular) and cluster B (square)

Table 3. Statistical summary of hydrochemical parameters in cluster A (19 samples) and in cluster B (28 samples)

	Cluster A				Cluster A			
	Mean	Median	Minimum	Maximum	Mean	Median	Minimum	Maximum
pH	7.4	7.5	7.2	7.7	7.5	7.6	7.3	7.7
Ec	1290	1103	364	4570	704	664	316	1264
TDS	899	772	254	3199	526	508	221	884
SiO_2	18	19	10	23	16	16	11	21
F	0.21	0.21	0.11	0.43	0.22	0.20	0.10	0.79
Cl	251	153	89	1435	57	56	6.50	126
SO_4	142	134	65	300	63	66	7.	126
HCO_3	150	149	90	201	226	210	143	616
PO_4	0.14	0.14	0.12	0.23	0.14	0.14	0.02	0.23
Ca	115	104	54	408	84	82	44	144
Mg	28	23	12	112	20	19	8.50	43
Na	126	105	37	361	42	41	9.50	91
K	0.98	0.92	0.50	1.90	0.74	0.74	0.30	1.40
Fe	0.02	0.02	0.01	0.02	0.02	0.01	0.01	0.02
Mn	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.10
Pb	7	7	5.50	9	6	6	2.	9
Zn	15	14	6	28	16	13	4	50
Cu	12	12	5	23	15	13	4	50
NO_3	26	16	12	63	40	31	12	102

Table 4. Water type in cluster A and cluster B

Cluster A		**Cluster B**			
Sample No.	**Water type**	**Sample No.**	**Water type**	**Sample No.**	**Water type**
12	Ca-Na-Mg-Cl-HCO_3-SO_4	1	Ca-Mg- Na- HCO_3 -Cl- SO_4	37	Ca-Mg- Na- HCO_3 -Cl- SO_4
15	Ca-Na-Mg-Cl-HCO_3-SO_4	2	Ca-Mg- Na- HCO_3	38	Ca-Mg- Na- HCO_3 - SO_4
17	Na-Ca-Cl-HCO_3-SO_4	3	Ca-Na-Mg- HCO_3- Cl	39	Ca- Na-Mg- HCO_3 -Cl
18	Na-Ca-Cl-HCO_3	4	Ca-Mg- HCO_3	40	Ca- Na-Mg- HCO_3 -Cl
19	Na-Ca-Cl-HCO_3-SO_4	5	Ca-Mg- Na- HCO_3	41	Ca- Na-Mg- HCO_3
20	Na-Ca-Cl-HCO_3-SO_4	6	Ca-Mg- Na- HCO_3 -Cl- SO_4	42	Ca- Na- HCO_3
21	Na-Ca-Cl- SO_4.HCO_3	7	Ca- Na- HCO_3	43	Ca-Mg- HCO_3
23	Ca-Na- Cl-HCO_3-SO_4	8	Ca- Na- HCO_3	44	Ca-Mg- HCO_3
24	Ca-Na -Cl-HCO_3	9	Ca- Na- HCO_3	45	Ca-Mg- HCO_3
25	Na-Ca-Cl- SO_4.HCO_3	10	Ca-Mg - HCO_3		
26	Na-Ca-Cl	11	Ca-Mg- Na- HCO_3 -Cl- SO_4		
27	Ca-Na-Mg-Cl	13	Ca- Na-Mg - HCO_3 -Cl		
28	Na-Ca-Cl-HCO_3-SO_4	14	Ca- Na Mg - HCO_3 -Cl- SO_4		
29	Na-Ca-Cl -SO_4	16	Ca-Mg- Na- HCO_3 -Cl- SO_4		
34	Ca-Na-Mg-Cl- SO_4.HCO_3	22	Ca-Mg- Na- HCO_3 -Cl- SO_4		
35	Ca-Na- SO_4-Cl- HCO_3	30	Ca-Mg- Na- HCO_3 -Cl- SO_4		
36	Ca-Na-Mg-Cl -SO_4	31	Ca- Na-Mg- HCO_3 -Cl- SO_4		
46	Ca-Na -Cl- SO_4	32	Ca- Na-Mg- HCO_3 -Cl		
47	Ca-Na-Mg-Cl-HCO_3-SO_4	33	Ca-Mg- Na- HCO_3 -Cl- SO_4		

Table 5. Correlation coefficient for cluster A (marked values are significant at p <0.05)

Variables	pH	Log EC	Log TDS	SiO_2	Log F	Log Cl	Log SO_4	Log HCO_3	PO_4	Log Ca	Log Mg	Log Na	Log K	Fe	Log Mn	Pb	Log Zn	Log Cu	Log NO_3
pH	1.00																		
Log EC	-0.06	1.00																	
Log TDS	-0.06	1.00	1.00																
SiO_2	-0.43	0.19	0.22	1.00															
Log F	-0.16	-0.03	-0.03	0.05	1.00														
Log Cl	0.05	0.84	0.84	0.25	-0.32	1.00													
Log SO_4	0.52	0.36	0.39	0.15	0.18	0.32	1.00												
Log HCO_3	-0.06	0.01	0.02	-0.15	0.47	-0.43	0.16	1.00											
PO_4	-0.21	-0.06	-0.05	0.17	-0.05	-0.10	-0.15	-0.01	1.00										
Log Ca	0.36	0.72	0.72	0.10	-0.31	0.81	0.52	-0.27	-0.15	1.00									
Log Mg	0.28	0.78	0.77	0.07	-0.26	0.80	0.50	-0.22	-0.26	0.92	1.00								
Log Na	-0.15	0.83	0.84	0.40	-0.05	0.86	0.36	-0.17	0.01	0.51	0.54	1.00							
Log K	-0.29	0.64	0.66	0.42	-0.02	0.63	0.20	-0.14	0.16	0.44	0.30	0.69	1.00						
Fe	-0.01	-0.11	-0.09	0.55	0.26	0.00	0.03	-0.07	0.09	-0.18	-0.21	0.15	-0.05	1.00					
Log Mn	-0.11	-0.50	-0.49	0.35	0.05	-0.37	-0.48	-0.25	0.21	-0.45	-0.55	-0.28	-0.19	0.66	1.00				
Pb	-0.20	0.22	0.23	0.38	0.20	0.08	-0.18	0.15	0.17	-0.01	-0.13	0.21	0.50	0.37	0.42	1.00			
Log Zn	0.31	0.33	0.31	0.03	-0.49	0.52	0.36	-0.36	-0.19	0.39	0.41	0.40	0.16	0.03	-0.35	-0.25	1.00		
Log Cu	0.41	0.29	0.28	0.06	-0.32	0.36	0.53	-0.04	-0.24	0.41	0.42	0.26	0.05	-0.07	-0.48	-0.25	0.85	1.00	
Log NO_3	0.62	-0.21	-0.22	-0.36	-0.08	-0.28	0.22	0.21	-0.28	0.26	0.22	-0.54	-0.49	-0.31	-0.10	-0.24	-0.19	0.13	1.00

Table 6. Correlation coefficient for cluster B (marked values are significant at p <0.05)

Variables	pH	Log EC	Log TDS	SiO_2	Log F	Log Cl	Log SO_4	Log HCO_3	PO_4	Log Ca	Log Mg	Log Na	Log K	Fe	Log Mn	Pb	Log Zn	Log Cu	Log NO_3
pH	1.00																		
Log EC	-0.12	1.00																	
Log TDS	-0.21	0.85	1.00																
SiO_2	-0.32	0.40	0.52	1.00															
Log F	-0.10	0.19	-0.01	0.38	1.00														
Log Cl	-0.16	0.87	0.88	0.54	0.18	1.00													
Log SO_4	-0.25	0.82	0.91	0.60	0.17	0.95	1.00												
Log HCO_3	-0.12	0.50	0.49	0.31	0.05	0.19	0.31	1.00											
PO_4	-0.16	-0.09	0.16	-0.02	-0.32	-0.04	0.09	0.06	1.00										
Log Ca	-0.10	0.91	0.84	0.44	0.01	0.78	0.75	0.65	-0.03	1.00									
Log Mg	0.21	0.76	0.82	0.42	0.05	0.70	0.73	0.51	0.13	0.78	1.00								
Log Na	-0.36	0.81	0.84	0.64	0.27	0.91	0.89	0.17	0.04	0.63	0.55	1.00							
Log K	-0.22	0.66	0.59	0.59	0.15	0.45	0.53	0.64	-0.15	0.62	0.50	0.49	1.00						
Fe	0.38	-0.17	-0.04	-0.40	-0.45	-0.14	-0.15	-0.09	0.23	-0.15	0.09	-0.20	-0.19	1.00					
Log Mn	0.21	0.18	-0.02	0.10	0.02	0.01	-0.04	0.09	-0.11	0.08	0.12	0.04	0.15	0.50	1.00				
Pb	0.16	0.38	0.17	0.12	0.22	0.17	0.08	0.19	-0.33	0.25	0.16	0.18	0.33	-0.05	0.31	1.00			
Log Zn	0.12	0.03	-0.08	0.08	-0.03	-0.09	-0.10	0.17	0.30	0.01	-0.05	-0.04	0.02	0.25	0.33	0.26	1.00		
Log Cu	0.14	0.08	-0.07	0.15	0.08	-0.09	-0.09	0.28	0.17	0.11	-0.02	-0.08	0.12	0.14	0.38	0.33	0.91	1.00	
Log NO_3	-0.15	0.77	0.65	0.34	-0.01	0.57	0.51	0.64	0.04	0.88	0.56	0.46	0.51	-0.24	-0.06	0.13	0.09	0.18	1.00

3.2.3. Correlation analysis

Correlation analysis has been carried out, as a bivariated statistics in order to determine mutual relationships and strength of association between pairs of variables through calculation of linear Pearson correlation coefficient. Results for Pearson correlation coefficients between all studied variables for cluster A and cluster B are shown in Tables 5 and 6, respectively. Correlation matrix of cluster A shows high positive correlation between variables EC ,TDS, Cl, Ca, Mg, Na, K(>0.6); pH, SO_4, NO_3(>0.5). High positive correlations have also been found between EC, TDS, Cl, SO_4, HCO_3, Ca, Mg, Na, K (>0.5) in cluster B. This may indicate that difference of two clusters is in SO_4, HCO_3. Cl, Ca, Mg, Na, K.

3.2.4. Factor analysis

In Table 7, each factor is described by correlations, for chemical parameters .In this study, number of factor to keep was based on Kaiser Criterion **[10]**. As a result, three factors were extracted, accounting for 79.36% of total variance (Table 7). First factor explains 35.31% of variance and thus, account for majority of variance in original dataset. Factors 2, 3 explain 23.00% and 21.04% of variance, respectively. First factor is characterized by high positive correlations in EC, TDS and all major ions (Ca, Na, Mg, Cl and SO_4) having the highest correlation and is characteristic of samples in cluster A. Fig. 7 presents individual sample (observations) scores generated by factor analysis. Samples 1 to 19 in Fig. 7 belong to cluster A and most of the samples have positive values scores and F1 is the most important factor in cluster A. Second factor analysis (F2) exhibits strong positive correlation in Zn and Cu (Table 7), which are the most symptomatic for samples in cluster B (Fig. 8). Sources of Cu and Zn could be anthropogenic. Zinc and copper are markers for industrial pollution. Therefore, this source could be seen as an industrial activity. Arak is one industrial city in Iran. Effluents or discharges from industries could have raised concentrations of these elements [26].

Third factor (F3) is characterized by strong positive correlations with HCO_3 and NO_3 and corresponded to cluster B (Fig. 8).Third factor is characterized based on positive score value in Fig.8.It is clear, three factors inferred have different source and groundwater are mixture of three dominant hydrochemical origin. The source of groundwater is natural in F1. Factor1 is rich of anions Cl and SO_4 but, factor 3 has natural and anthropogenic source and is rich in HCO_3 and NO_3. Factor 2 has anthropogenic source and Zn and Cu are dominant in this factor.

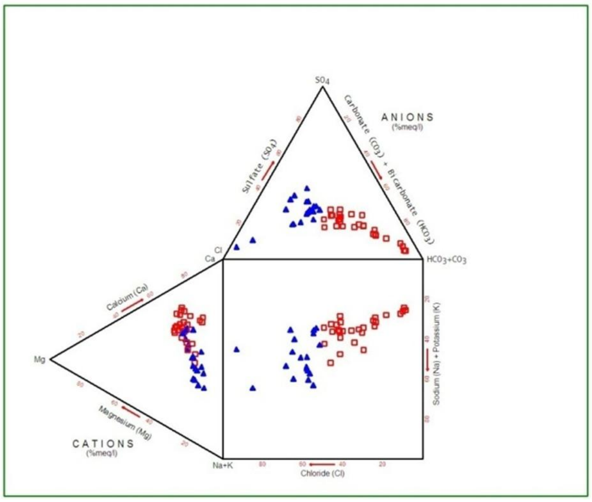


Fig. 5. Durow diagram for cluster A (three angular) and cluster B (square)

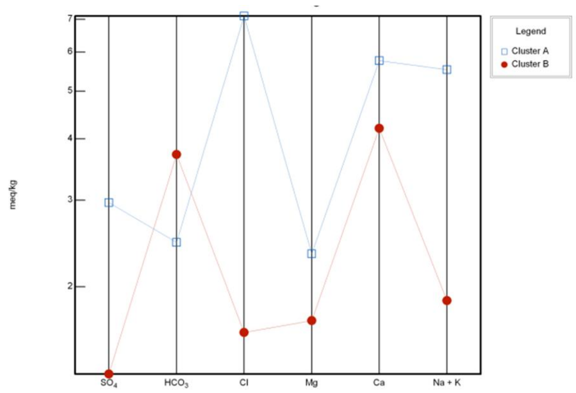


Fig. 6. Schoeller diagram for cluster A and cluster B

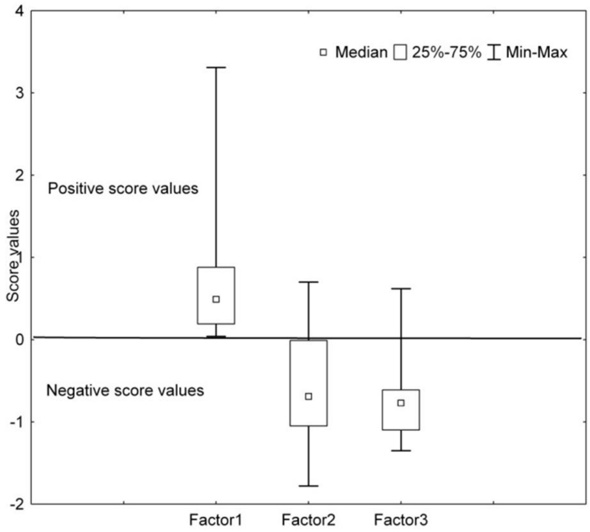


Fig.7. Box-Whisker diagram of factor score for cluster *A*

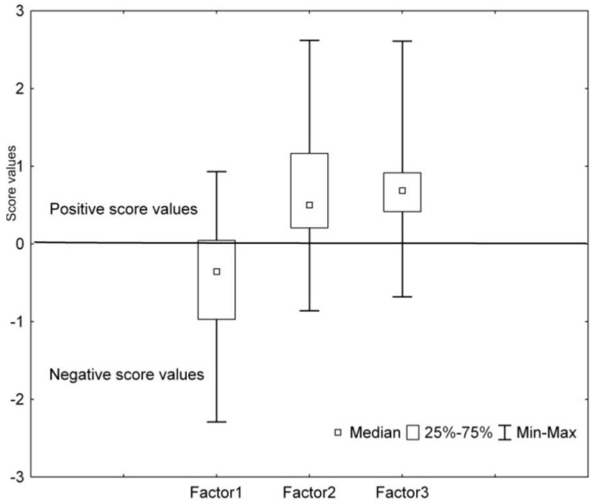


Fig.8. Box-Whisker diagram of factor score for cluster *B*

First component in factor analysis correlates positively with EC, SO_4, Cl, Na and K. This is a mixed component, which represents saltwater intrusion [14].

Factor1 therefore, illustrates salinity enrichment from saltwater activities. The positive correlation of Na and Cl with factor 1 suggests saltwater intrusion. Plot of Cl against Na (Fig. 9) shows samples from the Aman-abad plain (cluster A) around the 1:1 line, with some falling on the Cl side. This suggests the effects of saltwater intrusion in these areas. Some of the Arak plain (cluster B) samples also plot on the Na side of the diagram (Fig. 9). These samples account for contribution of silicate mineral weathering.

Strong correlation of HCO_3 suggests that carbonate mineral weathering might be playing a major role in the hydrochemistry. This is true for some of aquifers of Arak sedimentary rocks, which are limestone with some quantities of calcite and dolomite. Yidana et al (2008) indicated that predominant carbonate mineral whose weathering plays an active role in hydrochemistry is dolomite and occurred by carbonic acid from dissolved carbon dioxide in infiltrating rainfall and plant root respiration [25]. Silicate mineral weathering is also occurred by the same mechanism of carbonic acid resulting from plant root respiration and dissolved atmospheric carbon dioxide in infiltrating rainfall. It indicates that in Arak aquifers, freshwater aquifers are dominated by Ca–HCO_3 water types resulting from weathering of carbonate minerals. Predominant anthropogenic activities that have been noted as potential sources of pollution are disposal of domestic wastes, especially among some communities in the Arak plain. Aquifer of Arak plain is particularly vulnerable to these activities since the aquifers have been noted to be shallow. Enhanced nitrate concentrations at some locations in the study area result from the leaching of some nitrate from disposal of domestic wastes.

On a mixing diagram of Na-normalized HCO_3 versus Na-normalized Ca (Fig. 10), a significant number of samples in cluster A plot within the weathering domain and two samples between weathering and evaporate dissolution domain. In cluster B, most of samples demonstrate weathering domain and mixing of silicate weathering and carbonate weathering (Fig. 10). Furthermore, in cluster A, TDS is strongly and significantly correlated to Na and Cl, and moderately correlated to SO4. These ions are also well correlated to each other. In carbonate system, HCO_3 are not correlated with TDS (Table 5). These results verify interpretation of F1 as both silicate weathering and effects of saltwater intrusion [4].Above activities increase ionic components (e.g. Ca and SO_4, and Na and Cl) [17, 6].

Gibb's diagram is widely used to establish relationship of water composition and aquifer lithological characteristics [5]. Three distinct fields such as precipitation dominance, evaporation dominance and (weathering) rock–water interaction dominance areas constitute the segments in Gibb's diagram. Groundwater samples from Aman-abad area (cluster A) fall in both weathering (e rock–water interaction) dominance and evaporation dominance field (Fig. 11a and 11b). This suggested that apart from chemical weathering processes and water percolating under subsurface soils control hydro-geochemical processes in study area [9]. Gibb's diagram (Fig. 11b) for groundwater of Arak area (cluster B) also shows that hydro-geochemical processes in all samples were mainly controlled by weathering [11].

Table 7. Factor loadings from factor analysis

Variables	Factor 1	Factor 2	Factor 3
pH	-0.10	0.19	0.12
Log EC	0.93	0.07	-0.02
Log TDS	0.93	0.01	0.01
SiO_2	0.46	0.06	0.02
Log F	-0.04	-0.08	0.08
Log Cl	0.93	-0.03	-0.23
Log SO_4	0.84	-0.09	-0.03
Log HCO_3	-0.13	0.10	0.89
PO_4	0.01	0.09	0.01
Log Ca	0.87	0.12	0.26
Log Mg	0.85	0.04	0.22
Log Na	0.86	-0.01	-0.30
Log K	0.68	0.06	0.11
Fe	0.07	0.02	-0.28
Log Mn	-0.17	0.05	0.08
Pb	0.33	0.15	-0.07
Log Zn	0.04	0.96	-0.03
Log Cu	0.02	0.95	0.16
Log NO_3	0.16	0.01	0.84
Eigenvalue	6.70	2.47	2.09
% Total - variance	35.31	23.00	21.04
Cumulative - %	35.31	58.32	79.36

Table 8. Correlation matrix of saturation index in all samples

Variables	Calcite	Dolomite	Aragonite	Anhydrite	Gypsum	Halite	TDS
Clcite	1.00						
Dolomite	0.88	1.00					
Argonite	0.95	0.86	1.00				
Anhydrite	0.35	0.29	0.33	1.00			
Gypsum	0.35	0.29	0.33	0.99	1.00		
Halite	0.07	0.03	0.06	0.86	0.86	1.00	
TDS	0.29	0.24	0.29	0.17	0.16	0.04	1.00

Saturation indices (SI) of minerals for two clusters were calculated. Saturation indices express extent of chemical equilibrium between water and mineral phases in the matrix of the aquifers. It could be regarded as a measure of dissolute on and/or precipitation processes relating to the water–rock interaction [3]. Saturation indices of mineral, therefore provides information on whether mineral thermodynamically precipitate or dissolve. If the SI>0, mineral is supersaturated with respect to the system.

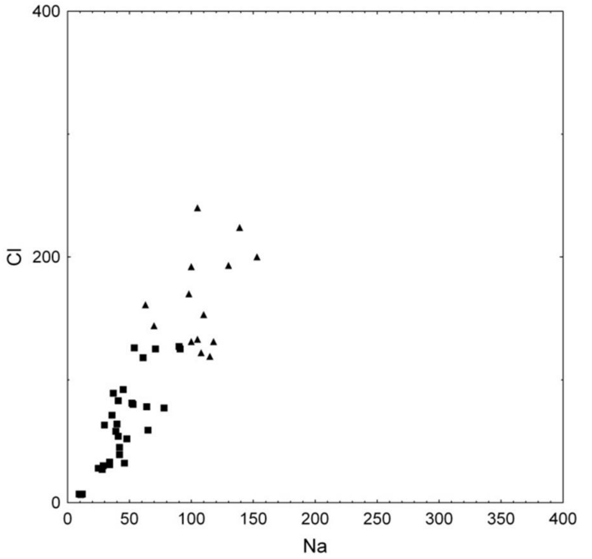


Fig.9. Plot of Cl against Na in cluste A (three angular) and cluster B (square).

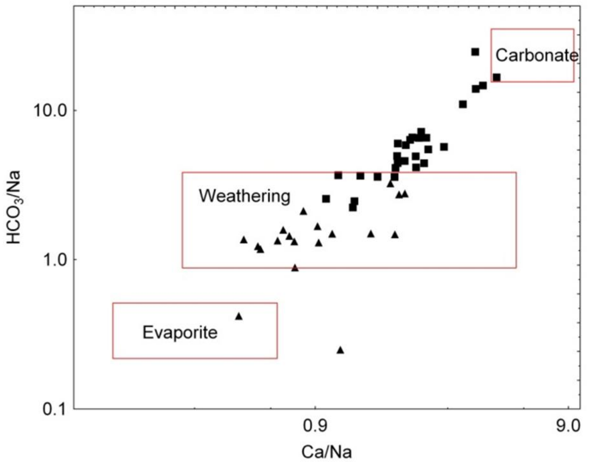


Fig. 10. Bivariate plot of Na-normalised HCO_3 versus Na-normalised Ca show trend of weathering. Rectangular areas demonstrate global average compositions of groundwater with respect to evaporite dissolution (bottom), silicate (middle) weathering, without mixing and carbonate (top) weathering) for samples in cluster A (three angular) and cluster B (square).

This means that precipitation or crystallization is favored. Minerals with SI<0 are under saturated with respect to the solution and are likely to dissolve if present in system. Minerals with SI in close to zero are saturated or are in equilibrium with the solution. Saturation indices have been used in the literature to study the hydrochemistry of groundwater bodies. They provide information on hydrochemical state of water resource in relation to composition of rock mass. Table 8 shows correlation coefficient of SI for various minerals and TDS. All samples are under saturated with respect to anhydrite, gypsum and halite, even for very saline samples (Fig. 12).

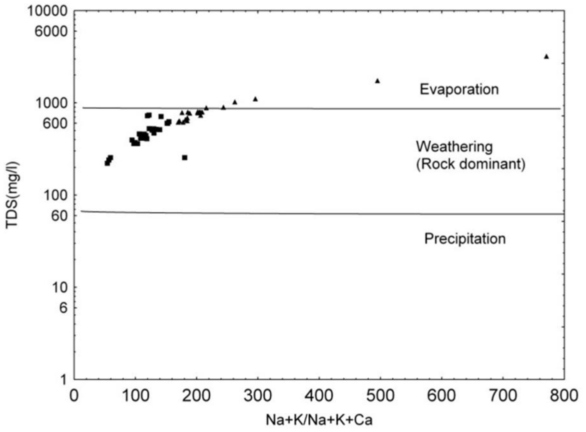


Fig.11a. Gibb's diagram in clusterA (three angular) and cluster B (square).

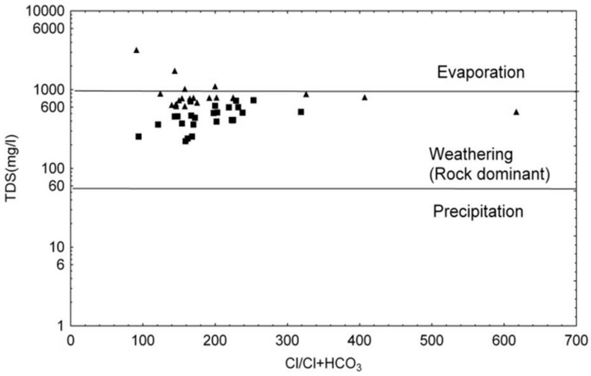


Fig.11b. Gibb's diagram in cluster A (three angular) and cluster B (square).

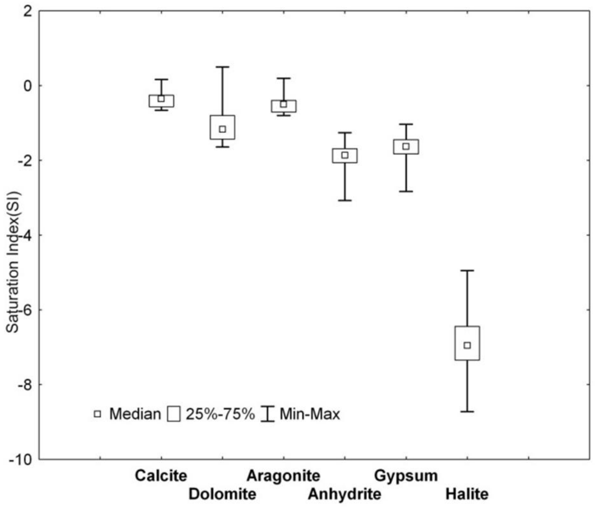


Fig.12. Box-Whisker diagram of saturation index for all samples

Therefore, it may conclude that interaction between groundwater and aquifer matrix is not significant in controlling chemical characteristics of groundwater in study area, i.e. the source of the ions is mostly outside of aquifer matrix.

4. Conclusions

The present study shows that chemical character of groundwater in the studied area of Arak city is extremely variable. Application of cluster analysis resulted into two clusters: cluster A (dominant composition: Ca, Cl and SO_4), cluster B (dominant composition: Ca, HCO_3) which were described by factor analysis F1, F2 and F3, respectively. The results of the factor analysis suggest that spatial variation of groundwater quality in the area is influenced by following processes: In addition to silicate weathering, factor1 exhibits the processes of dissolution of Cl and SO_4 from evaporative salts and followed by mineralized seep from saltwater playa (natural source). Factor2 exhibits importance of Zn and Cu and are markers for industrial pollution (anthropogenic source).Factor3 results mainly from HCO_3 weathering of carbonate and silicate minerals (natural source) and activities producing NO_3 such as disposal of domestic wastes (anthropogenic source). Therefore, drinking groundwater of Arak city has been controlled by the major factors such as carbonate weathering, silicate mineral weathering, saltwater intrusion and anthropogenic effects.

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