

Statistical Analysis of the Hydrogeochemical Evolution of Groundwater in Alluvial Aquifer of Arak Mighan Playa, Markazi Province, Iran

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ABSTRACT

This paper presents results of hydro-chemical processes controlling groundwater chemical composition, using an integrated application of hierarchical cluster analysis and factor analysis of a major ion data set of groundwater from Mighan playa aquifer. Cluster analysis classified samples into four clusters(A, B, C and D) according to their dominant chemical composition: cluster A (dominant composition: Ca-HCO₃; mean TDS: 267 mg/l), cluster B (dominant composition: Ca-Mg-SO4-Cl; mean TDS: 1029 mg/l), cluster C (dominant composition: Na-Mg-SO₄; mean TDS 667 mg/l) and cluster D (dominant composition Na-Mg-SO₄-Cl; mean TDS 2998 mg/l), which were described by the first factor of factor analysis. Results of the factor analysis suggested that the spatial variation of groundwater quality is influenced by processes of carbonate minerals dissolution and mixing of saline water (Mighan playa). The calculated playawater fractions (f_{plava}) of the groundwater shows that cluster D water is almost four times more saline than cluster B water and twice and a half more saline than cluster C water, where the difference between salinities can be explained by proximity of cluster D water to the playa. In the present study, 23.8 % of the playawater samples were found to contain chloride concentrations above 250 mg/l suggesting that playawater intrusion has reached alarming levels yet. The saline/brackish groundwater is the result of the processes of evaporation (for samples close to the Mighan playa) and dissolution of SO_4 and Cl evaporative salts (such as thenardite, gypsum and halite).

Keywords

Diffraction; Groundwater; Playawater; Hydrochemistry; Cluster Analysis; Factor Analysis

1. Introduction

In Arak city, some of the aquifers are not of adequate potable quality due to natural factors. In the Mighan Playa aquifer, occurrence of groundwater with high salinity is a major groundwater quality problem particularly in unconsolidated deposits around the Mighan playa where Na, $SO₄$ and Cl concentrations up to 1000, 2000 and 1400 mg/l, respectively, have been reported (Zamani 1999). An understanding of hydrogeochemical processes affecting water quality in this aquifer is essential in order to assess potential effects of changes in environmental pressures and identify necessary abatement actions to sustain usable water supplies. The objective in this study was to examine the

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relationship between groundwater chemistry and geology around the Mighan playa in order to better understand the dominant hydro-geochemical processes controlling spatial variations in chemical composition of the groundwater. Hydro-geochemical processes governing water quality were determined through an integrated application of two well-proven multivariate statistical methods; hierarchical cluster analysis and factor analysis.

2. Studied area

The Mighan playa (fig. 1) is located in the Arak region, central part of Markazi province. The pre-Neogene basement in the lake ranges in age from Mesozoic to Pliocene and comprises metamorphic (slate, metamorphic sandstone and crystalline limestone) in the southern west part of the playa, carbonate in eastern. Paleogene assemblages consist of clastic and tuff deposits and volcanic rocks in the northern part of the playa.

Fig. 1 Location and geologic framework map of the study area, showing sample locations and clusters obtained from Hierarchical Cluster Analysis

The Neogene sedimentary sequences around the Mighan playa are shale, marl and volcanic conglo-merate. Mighan playa with 1700 m above sea level has an area about 5500 $km²$ and is a closed basin. The mean annual temperature is 14° C. The mean annual precipitation (350 mm) is far less than the mean annual evaporation (1450 mm). The playa has no outlet but is fed by fresh water from the whole margins. The playa water chemistry is dominated with ions Na, Mg, Cl, SO4, and also contains smaller amounts of Ca, K and $HCO₃$ (Zamani 1999).

The aquifer of Mighan playa is developed into the medium to fine phases of the Pleistocene sediments, which occupy a broad graben between mountains of Arak and Ashtian. The bedrock of these formations is composed of crystalline limestone of the zone of low metamorphism rocks. The study area is situated in the alluvial plain and the aquifer is directly fed by stream water coming from different reliefs surrounding the depression intermountainous of Mighan playa. The plain hosts a large number of water–wells with depths varying from 70 to 150 m. Most of these wells supply water for drinking and agriculture needs.

3.Materials and methods 3.1. Sample collection and analysis

Fifty five wells currently in use were selected based on the preliminary field survey carried out to understand the overall distribution of the various types of wells in the studied area (fig. 1). Selected wells are used for domestic and agricultural purposes and uniformly distributed over the area of concern. Groundwater samplings were performed during dry months in 2011. Samples were collected after pumping by

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using acid-washed polypropylene containers. Each sample was immediately filtered on site through 0.45 µm filters on acetate cellulose. Filtrate for metal analyses were transferred into 100 cm³ polyethylene bottles and immediately acidified to pH<2 by adding nitric acid. Samples for anions analyses were collected into 250 cm^3 polyethylene bottles without preservation. PH and electrical conductivity (EC) were immediately measured in the field after sampling, using a multi-parameter WTW and total dissolved solids (TDS) calculated by TDS=6.6EC equation. Subsequently, the samples were analyzed in the laboratory for their chemical constituents such as calcium, magnesium, sodium, potassium, chloride, bicarbonate and sulfate. This was achieved using standard methods as suggested by the American Public Health Association $(APHA 1989)$. Ca, Mg, HCO₃ and Cl were analyzed by volumetric titrations. Concentrations of Na and K were measured using a flam photometer and that of sulfate by using turbid metric method. The accuracy of the chemical analysis was verified by calculating ion-balance errors where the errors were generally within 10 %.

3.2. Multivariate statistical analysis 3.2.1. Hierarchical cluster analysis

Hierarchical cluster analysis (HCA) was used to determine if the samples could be grouped into statistically distinct hydrochemical groups. A number of studies used this technique to successfully classify water samples (Lambrakis et al. 2004; Monjrezi et al. 2011). Comparisons based on multiple parameters from different samples were made and the samples were grouped according to their similarity to each other. In the present study cluster analysis was

used to classify the samples into distinct hydrochemical groups. The Ward's linkage method (Ward 1963) was used in this analysis. A classification scheme using Euclidean distance for similarity measurement, together with Ward's method for linkage, produces the most distinctive groups where each member within the group is more similar to its fellow members than to any member outside the group. All 12 hydrochemical variables measured (Consisting of EC, TDS, PH, Ca, Mg, Na, K, Cl, SO₄, HCO₃, TH and SAR) were utilized in this analysis. For statistical analysis, all the variables were standardized to their standard scores. Hydrochemical results of samples were statistically analyzed by using STATISTICA software.

3.2.2. Discriminant analysis

To understand the principal role of the variables discriminating groups obtained by cluster analysis, a discriminate analysis was applied to hydrochemical data of the study area. The qualitative–dependent variable consists of the classified groups of samples that resulted from cluster analysis. Our aim was to verify if these groups were divided correctly by cluster analysis, so we used discriminant analysis (Varol et al. 2012).

3.2.3. Factor analysis

Factor analysis are the most common multivariate statistical methods used in environmental studies (Lamarckism et al. 2004; Liu et al. 2003; Love et al. 2004). Factor analysis, widely used to reduce data and to a smaller number of independent factors (factor components) for analyzing relationship between observed variables (Matalas and Reiher 1967; Subbarao et al. 1995), starts with the correlation matrix describing the dispersion of the original

variables and extracting the eigenvalues and eigenvectors (Kim et al. 1987). An eigenvectors is a list of coefficients multiplying the original correlated variables to obtain new uncorrelated (orthogonal) factor analyses, which are weighted linear combinations of the original variables. Factor analysis can reduce the number of correlated variables to a smaller set of orthogonal factors, making it easier to interpret a given multidimensional system by displaying the correlations among the original variables. Factor analysis and derivative methods have been widely applied to various environmental media, such as sediments (Tahri et al. 2005; Wenchuan et al. 2001), soil (Tahri et al. 2005; Zheng et al. 2008) and water (Reyment et al. 1993), to identify pollution sources.

4. Results and discussion

4.1. Groundwater chemistry

All major elements were determined for 55 samples and its statistical parameters (i.e., mean, minimum, maximum and standard deviation) are presented in table 1. This table shows that groundwater was mildly alkaline (pH: 6.91-8.46) and similar to rainwater pH based on WHO (1984). Electrical conductivity (EC) of this groundwater varied from 274-9400 µS/cm. This showed that the EC increased significantly towards the Mighan playa due to the impact of playawater incursion, because its values were 3170 µS/cm and 9400 µS/cm (in table 1). By examining EC (Mondal et al. 2008), the groundwater was classified into (1) fresh $\left($ <1500 μ S/cm), (2) brackish (1500-3000 μ S/cm), and (3) saline (>3000 µS/cm). Based on this classification pattern, the percentages of groundwater

samples in each group show that 29 % of groundwater samples had fresh quality and saline water was 14.5 % in the study area. The rest of groundwater was brackish (56.5 % of samples).

Total dissolved solids (TDS) also showed a wide variation from 129-5850 mg/l. High values of EC and TDS were recorded in saline water and in wells close to the Mighan playa. According to the salinity classification by Rabinove et al. (1958), groundwater were classified into non-saline/ freshwater (TDS $\langle 1,000 \rangle$ mg/l), slightly saline (TDS= 1000-3000 mg/l), moderately saline (TDS= 3000- 10,000 mg/l) and very saline (TDS> 10,000 mg/l). They were 58 %, 22 % and 20 % of the sampled groundwater, respectively. This may indicate the possibility of a high rate of intrusion of saline water.

Chemical analysis of water samples indicated that the most dominant ions were sodium (Na), calcium (Ca), magnesium (Mg), sulfate (SO_4) , chloride (CI) and bicarbonate $(HCO₃)$. The order of abundance of major cations was Na> Ca> Mg> K and 51 % of samples exceeded the desirable limit of Ca for drinking water (75 mg/l), but only 24 % of them exceed that of Na (200 mg/l) and 25 % of them exceed that of Mg (50 mg/l). The abundance of major anions was SO_4 > Cl > $HCO₃$ and almost 22 % of the samples exceeded the desirable limit of $SO₄$ (500) mg/l), but the Cl concentrations were 22 % above the health guidelines (250 mg/l).

As regards groundwater irrigation suitability, the Wilcox (Wilcox 1948) diagram was used to rate the samples. In the Wilcox diagram, the EC is related to Na percent (meq/l). The EC in irrigation water can be classified into low $(C1)$, medium $(C2)$, high (C3) and very high (C4) salinity zones. The zones (C1-C4) have the value of EC less than 250, 250-750, 750-2250 µS/cm and more than 2250 µS/cm, respectively. The sodium hazard is expressed in terms of classification of irri-gation water, as low (S1: <10), medium (S2: 10-18), high (S3: 18-26) and very high $(S4: >26)$. In this study, the majority of the samples fall in the good to moderate field (fig. 2).

Fig. 2. A plot of SAR against EC (water samples are according to their clusters).

Fig.3. Dendrogram of groundwater samples, showing the division into four clusters

Statistical	SO_4	Cl	HCO ₃	K	Na	Mg	Ca	pH	TDS	TH	SAR	EC
parameter												
Cluster A $(N_0, 16)$												
Mean	68.97	38.62	80.38	1.82	34.28	18.42	42.06	7.93	267	181	1.081	516
Minimum	9.60	9.23	63	0.79	9.43	9.48	25.60	7.48	129	103	0.40	274
Maximum	140	88.39	96.30	1.97	64.40	25.08	57.40	8.25	355	247	2	673
Standard deviation	38.30	20.58	9.05	0.34	16.77	4.62	10.15	0.22	74.61	39.81	0.48	131
Cluster B $(N_0, 11)$												
Mean	399	202	135	3.19	192	55.40	109	7.62	1029	503	3.78	1843
Minimum	99.84	98.33	71	2.37	110	24	55	7.12	475	239	2.54	887
Maximum	811	384	179	4.34	257	110	180	8.46	1680	910	5.37	2720
Standard deviation	194	78	36.22	0.61	51.92	26.11	35.30	0.35	353	191	0.78	562
Cluster C $(No. 20)$												
Mean	229	143	106	2.54	116	37	82.92	7.72	667	361	2.67	1229
Minimum	90.240	56.09	71	1.97	57	24	55	7.16	395	239	1.58	748
Maximum	495	299	136	3.16	181	63	132	8.46	1069	538	3.43	1844
Standard deviation	105.18	71.26	15.95	0.39	29.88	10.70	21.91	0.32	167	90	0.55	289
Cluster $D(N_0, 8)$												
Mean	1224	752	158	6.51	508	168	313.	7.31	2998	1485	5.73	5181
Minimum	643	355	87.60	4.74	334	75.84	148	6.91	1710	760	3.50	3170
Maximum	2300	1475	256	10.66	1066	292	465	7.67	5850	2382	9.50	9400
Standard deviation	487	348	58	1.79	238	59	110	0.29	1223	477	1.94	1829

Table 1. Statistical summary of hydrochemical parameters of groundwater in Mighan playa

Spatial variation of selected water quality parameters shows that elevated concentrations are associated with samples in the south part of the district, which may give concern for both domestic and irrigation purposes (samples in cluster A and cluster C; fig. 1).

4.2. Multivariate statistical analyses

4.2.1 Hierarchical cluster analysis

The groundwater samples were classified by HCA into four main clusters (A, B, C and D) according to their dominant chemical composition (fig. 3). Samples in cluster A have a cationic composition that is dominated by Ca, with abundance orders Ca >Na>Mg>>K(mg/l) and anionic composition dominated by bicarbonates $(HCO₃)$ $SO₄ > Cl$) (fig. 4). Thus their chemical composition is characterized by Ca-HCO₃ and $Ca-HCO₃-Cl$ (fig. 5). Water samples have low salinity (TDS=267 mg/l), whilst samples in cluster B and C have intermediate salinities between cluster A

and D (mean TDS=1029 mg/l; mean TDS=667 mg/l). B and C clusters are characterized by relatively high salinity. Samples in B and C are also characterized by cationic composition dominated by Na (Na > Ca > Mg > \geq K), but their anionic composition is dominated by sulfate $(SO₄)$ C = HCO₃). Cluster D is characterized by high salinity (mean TDS=2998 mg/l). Cationic and anionic composition in cluster D is similar to B and C clusters. Thus their chemical composition in B, C and D clusters is characterized by Ca-Cl and mixed cation-Cl types (Ca-Na-Cl).

To understand the principal role of the variables discriminating the four groups obtained by cluster analysis, discriminant analysis was applied to hydrochemical data of the study area. The qualitative– dependent variable consists of classified groups of samples that resulted from cluster analysis. Our aim was to verify if these groups were divided correctly by cluster analysis (Geoffrey et al. 2003).The discriminant analysis was 100 % successful, as all samples

classified to the correct cluster, thus indicating the feasibility of cluster analysis (fig. 6).

The individual hydrochemical para in groundwater can be affected by a number of factors, such as (1) geological compositions of the soils or rocks, (2) mineral contents of water. Pearson correlation coefficient between hydro-chemical parameters measured in groundwater was calculated and is summarized in the form of correlation matrix in table 2. asibility of clu
le individual l
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s, such as (1) para-meters eters measured
ted and is summar
matrix in table 2.

The terms strong, moderate, and weak for correlations refer to absolute coefficient

icating values of >0.75, 0.75-0.50 and 0.50-0.36,
respectively. Alpha level for testing
meters correlations significance was maintained at respectively. Alpha level for testing P<0.05 for samples. We observe strong and positive correlations of clusters as follows: >0.75 0.75, 0.75-0.50 0.50 and 0.50 0.50-0.36,

- -Cluster A: SO₄ with Na, Mg, TDS, EC; Cl Cluster A: SO_4 with Na, Mg, TDS, EC; Cl
with Na, Mg, TDS, EC and Ca with TDS (table 2). 0.05 for samples. We observe
sitive correlations of clusters as
luster A: SO_4 with Na, Mg, TI
with Na, Mg, TDS, EC and Ca
(table 2).
luster B: SO_4 with Na, Mg, TI
with Na, Mg, TDS, EC and Ca
- -Cluster B: SO₄ with Na, Mg, TDS, EC; Cl with Na, Mg, TDS, EC and Ca with TDS and EC; K with Mg, Ca, TDS and EC (table 2).

Fig.4. Average composition (mg/l) of the four groundwater clusters.

Fig.5. Piper diagram for groundwater samples from the study area labeled according to their groundwater clusters

Fig.6. Discrinant analysis for verifying clusters in clustering samples

Table 2. Matrix correlation for hydrochemical parameters i groundwater for clusters A, B, C and D

Cluster A	SO ₄	CI	HCO ₃	$\mathbf K$	$\mathbf{N}\mathbf{a}$	Mg	Ca	pH	TDS	EC
SO ₄	$\mathbf{1}$									
\mathbf{C}	0.57	$\,1$								
HCO ₃	0.11	.39	$\mathbf{1}$							
K	0.46	0.47	0.43	$\mathbf{1}$						
Na	$0.81\,$	0.81	0.25	0.46	$\mathbf{1}$					
Mg	0.80	0.77	0.34	0.62	0.75	$\mathbf{1}$				
Ca	0.57	0.59	0.63	0.45	0.40	0.58	$\mathbf{1}$			
pH	-0.50	-0.14	0.04	-0.30	-0.26	-0.33	-0.36	$\mathbf{1}$		
TDS	0.84	0.87	0.50	0.59	0.87	0.88	0.76	-0.34	$\mathbf{1}$	
EC	0.86	0.87	0.46	0.58	0.89	0.89	0.74	-0.35	0.99	1
Cluster B	$\mathbf{1}$									
SO_4 Cl	0.52	$\mathbf{1}$								
HCO ₃	-0.12	-0.02	$\mathbf{1}$							
K	0.72	0.68	-0.19	$\mathbf{1}$						
Na	0.83	0.42	0.29	0.44	$\mathbf{1}$					
Mg	0.78	0.84	-0.01	0.82	0.57	$\mathbf{1}$				
Ca	0.80	0.85	0.01	0.77	0.64	0.87	$\mathbf{1}$			
pH	-0.04	-0.35	-0.56	-0.13	-0.21	-0.33	-0.25	$\mathbf{1}$		
TDS	0.88	0.81	0.09	0.77	0.79	0.93	0.94	-0.30	$\mathbf{1}$	
EC	0.90	0.78	0.13	0.75	0.84	0.90	0.93	-0.32	0.99	1
Cluster C										
SO ₄	$\mathbf{1}$									
$_{\rm Cl}$	-0.05	$\mathbf{1}$								
HCO ₃	0.03	-0.28	$\mathbf{1}$							
K	0.47	0.41	-0.40	$\mathbf{1}$						
Na	0.74	0.46	-0.10	0.58	$\mathbf{1}$					
Mg	0.61	0.54	0.10	0.53	0.69	1.				
Ca	0.53	0.58	0.06	0.38	0.53	0.65	1			
pН	-0.30	-0.26	-0.45	-0.06	-0.28	-0.50	-0.56	1.		
TDS	0.76	0.55	0.03	0.54	0.88	0.88	0.79	-0.53	$\mathbf{1}$	
EC	0.73	0.60	0.03	0.56	0.86	0.88	0.84	-0.53	0.99	1
Cluster D										
SO_4	$\mathbf{1}$ 0.83									
CI HCO ₃	-0.30	$\mathbf{1}$ -0.62								
K	0.22	0.20	$\mathbf{1}$ -0.32							
Na	0.95	0.74	-0.06	$\mathbf{1}$ 0.12						
Mg	0.95	0.88	-0.45	0.16	$\mathbf{1}$ 0.86	$\mathbf{1}$				
Ca	0.57	-0.79	0.90	0.26	0.41	0.66	$\mathbf{1}$			
pH	0.45	0.51	-0.20	-0.19	0.37	0.66	0.38	$\mathbf{1}$		
TDS	0.96	0.93	-0.37	0.17	0.92	0.94	0.71	0.50	$\mathbf{1}$	
EC	0.97	0.93	-0.40	0.20	0.92	0.95	0.71	0.50	0.99	1

-Cluster C: SO4 with TDS; Na, Mg and Ca with TDS, EC (table 2).

-Custer D: SO4 with Cl, Na, Mg, TDS, EC; Na with Mg and Ca with $HCO₃$ (table 2).

Sulfate, chloride, sodium and magnesium are dominant ions of playawater in all clusters, while calcium is generally the major ion of freshwater (Hem 1989). Thus, high levels of Na, SO_4 and Cl ions in groundwater may indicate a significant effect of playawater mixing, while considerable amounts of Ca mainly reflect the contribution of water-rock interaction (Park et al. 2005).

4.2.3. Factor analysis (FA)

The chemical composition of groundwater reflects the chemical composition of the geologic units found in the drainage basin and provides valuable information about the contributions of source formation and other sources such as intrusion of playawater (Belkhirl et al. 2010). In this study, factor analysis was used to identify most important variables in separating the classes, in effective extracting of the factors that control the chemical variability in groundwater samples. Rotation of FA was carried out using varimax normalized method, where both Kaiser Criterion and Cattell scree plot were used to determine the number of factors for the clusters.

In cluster A, most of the variance in the original data set is contained in F1 (64.34 %), which is associated with $HCO₃$, Ca, TDS and EC variables (with loading> 0.7) (table 3), while $HCO₃$ in other clusters (B, C and D) (table 3) is in F2 and their variances are 16.46, 16.96, and 14.89 percentages, respectively. These variables, mainly $HCO₃$ and Ca originating from the natural weathering processes of sedimentary rocks (e.g., limestone/dolomite) were found in the

recharge area. A map showing the spatial distribution of cluster A is presented in fig. 1, where high $HCO₃$ and Ca values are generally observed at the western parts of the study area, where cluster A groundwater prevails. Therefore, F1 in cluster A and F2 in other factors (or as it is called water-rock interaction factor) can be accepted as the main controlling factor of cluster A groundwater chemistry. Most of the samples in cluster A can be regarded as recharge area groundwater due to dominance of $Ca- HCO₃$ water type.

Cluster B and C groundwater are transitional in character, chemically as well as geographically, between cluster A and Cluster D groundwater. Based on X Ray Diffraction (XRD) analysis, dissolved constituents in cluster A water come primarily from dissolution reactions of calcite, that form the limestone rocks (Belkhiri et al. 2011) (fig. 7a, 7b). Minerals were identified by X-ray diffraction (XRD) technique in limestone and dolomitic limestone of source rocks and are quartz $(SiO₂)$, calcite $(CaCO₃)$, dolomite $(CaMg (CO₃)₂)$ and illith $((K,H₃O) (Al,Mg,$ Fe)₂ (Si,Al)₄O₁₀ [(OH)₂, (H₂O)]) (Zamani, 1999).

F1 in D, C and B clusters explains 67.01 %, 58.04 % and 66.13 % of the variance and is mainly related to variables Na, Mg, SO₄ and Cl (loading >0.7). These factors include classical hydrochemical variables that indicate Salinization processes. It is also worth mentioning that in cluster D, the highest values of Na, Mg, SO4 and Cl generally occur in the playa areas intruded by the playawater (fig. 1).

Evaporite dissolution, mainly thenardite and gypsum minerals (fig. 8 displays XRD diagram of these minerals in sediments of mud flat around the cluster D) is the main process affecting on the groundwater chemistry (fig. 1) displays the distribution of

Fig.7. XRD diagram of source rocks (7a) Cretaceous dolomitic limestone (7b) Cretaceous limestone. Ca: calcite; Q: quartz: IL: illite; DO: dolomite

Table 3. Factor loadings for groundwater samples of cluster A, cluster B, cluster C and cluster D

	Cluster A		Cluster B			Cluster C		Cluster D		
	${\bf F1}$	F ₂	F1	F ₂	F1	F ₂	F3	F1	F2	F3
SO_4	0.35	0.87	0.90	-0.08	0.96	0.09	-0.16	0.97	0.18	-0.04
CI	0.50	0.59	0.82	0.11	0.14	-0.18	0.95	0.76	0.61	0.05
HCO ₃	0.89	-0.23	-0.07	0.92	-0.02	0.90	-0.15	-0.09	-0.94	0.11
K	0.58	0.35	0.85	-0.16	0.63	-0.48	0.27	0.16	0.27	-0.84
Na	0.50	0.72	0.73	0.30	0.86	-0.08	0.27	0.99	-0.04	-0.02
Mg	0.60	0.68	0.94	0.09	0.73	0.17	0.49	0.89	0.37	0.14
Ca	0.76	0.29	0.94	0.07	0.56	0.25	0.61	0.45	0.84	-0.01
pH	0.08	-0.69	-0.20	-0.82	-0.30	-0.71	-0.42	0.44	0.30	0.66
TDS	0.75	0.64	0.97	0.16	0.85	0.15	0.47	0.94	0.31	0.03
EС	0.72	0.67	0.96	0.21	0.83	0.14	0.52	0.94	0.33	0.02
Eigenvalue	6.43	1.26	6.61	1.64	5.80	1.69	1.13	5.80	1.69	1.13
Variance %	64.34	12.6	66.13	16.46	58.04	16.96	11.30	67.01	14.89	10.75
CumulativeVariance %	64.34	76.94	66.13	82.59	58.04	75	86.30	67.01	81.90	92.65

the cluster D and transition clusters such as cluster C and cluster B in the study area, where the highest concentration of above variables are generally observed at the northern and eastern parts of the study area.

The increase in salt content of groundwater samples could be accounted by playawater intrusion mechanism (Mondal et al. 2010).

Additionally, playawater trapped in the sediments or playa-spray probably contributes to salinization of the groundwater in the area. In cluster D area, thenardite $(Na₂SO₄)$, gypsum $(CaSO₄.2 H₂O)$ and halite (NaCl) minerals occur in the mud flat sediments that is the area of active playawater intrusion (fig. 8).

Fig.8. XRD diagram of sediment of mud flat around cluster D area .Ca: calcite; Q: quartz: IL: illite; Th: thenardite; H: halite; Ch: chlorite; Gy: gypsum.

As cluster C and cluster B groundwater are transitional in character and move toward part of the Mighan playa, concentrations of major ions increase, producing cluster D type water. These samples have a different geochemistry from cluster A and cluster D groundwater exemplified by increase TDS. The increase in TDS is due to the relatively large increase in Ca, Mg, Na, SO_4 and Cl concentrations suggesting that dissolution is the major control (Fisher and Mulican 1997; McLean and Jankowski 2000).

To evaluate the salinization by playawater intrusion, the playawater fraction (f_{playa}) of each groundwater sample was estimated (using Equ. 1) based on chloride (Cl), since it is considered to be a conservative tracer (Appelo and Postma 1994):

$$
f_{playa} = \frac{(m_{cl})_{Sample} - (m_{cl})_{free}}{(m_{cl})_{player} - (m_{cl})_{free}} \tag{1}
$$

For this calculation, representative Cl concentration of the freshwater end-member $(Cl_(fresh))$ was taken as the average value of the cluster A groundwater samples from the recharge area. On the other hand, representtative Cl concentration of the playawater endmember $(Cl_{(playa)})$ was taken as the average value of the samples from lake of playa (30000 mg/l) (Zamani 1999).

The above calculation was carried out by the assumption that chloride is solely originated from playawater intrusion and playa spray. fig. 9 shows the distribution of the playawater fraction $(\%)$ in groundwater samples and the area affected by active

playawater intrusion. The aquifer contains a small portion of playawater in its northern part of Mighan playa. The calculated playawater fractions (f_{playa}) of the groundwater range from 0.19 % to 1.15 % for cluster B water, from 0.05 % to 0.86 % for cluster C and from 1.31 $%$ to 4.81 $%$ for cluster D water. Cluster D water (EC=5181 μ S/cm) is almost four times more saline than cluster B water (EC= $1229 \mu S/cm$) and twice and half more saline than cluster C water(EC= 1843) µS/cm), where the difference in salinities can be explained by proximity of cluster D water to the playa (fig. 10). In the present study, 23.8 % of the playawater samples were found to contain chloride concentrations above 250 mg/l (max. value is 1475 mg/l) suggesting that playawater intrusion has reached alarming

levels yet.

Cl and K elements contribute most strongly to the third factor in cluster C and cluster D that explains 11.30 % and 10.75 % of the total variance (with a positive loading on Cl and negative loadings on K (table 3).

Table 4 displays the distribution of the factor scores in the study area, where the highest third factor scores (i.e., values of Cl from 1.12 to 2.37) are generally observed in the area of cluster C and are enriched relative to Cl concentration (samples 52, 44, 38 and 45). This part of cluster C is a high halite based on XRD diagram (fig. 10). Table 4 that displays the distribution of the third factor scores in cluster D, the highest scores are observed in area of the lowest K concentration (samples 47, 22, 23 and 4).

Fig.9. Map showing the spatial distribution of playawater fractions (ƒplaya) of the groundwater sample.

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Fig.10. XRD diagram of sediment of mud flat around the cluster C area that shows halite. Th: thenardite; H: halite

Table 4. Factor scores, based on groundwater chemistry data for cluster C and cluster D

Well	Cluster C			Well		Cluster C		Well	Cluster D		
No.	F1	F ₂	F ₃	No.	F1	F ₂	F ₃	No.	F1	F2	F3
38	0.01	-2.14	1.14		-0.07	1.33	0.39		-0.01	0.63	-2.21
42	-1.51	-0.95	0.35	2	0.53	0.98	0.07	20	-0.41	0.20	-0.19
35	-1.03	-0.57	-1.67	13	0.65	-0.97	-0.68	47	-0.45	-0.05	
21	-0.19	-0.85	-0.36	14	1.01	2.05	-1.07	22	-0.71	1.43	0.85
12	-0.25	-0.44	-0.65	27	1.50	-1.05	0.32	55	-0.33	0.43	0.27
33	-2.24	0.20	-1.20	30	0.47	0.17	-1.17	4	-0.70	-1.49	-0.30
45	-0.81	0.46	1.12	31	0.64	-0.75	-0.61	51	0.30	-1.41	0.27
44	-0.52	0.85	1.45	37	1.75	-0.42	0.08	23	2.32	0.26	0.32
34	-0.88	0.82	-0.13	43	0.77	0.80	0.06				
52	-0.37	0.32	2.37	53	0.55	0.15	0.20				

5. Conclusion

The present study shows that chemical character of groundwater in the study area of the Mighan playa aquifer is extremely variable, with localized areas of predominantly brackish water. Application of cluster analysis resulted in four clusters: cluster A (dominant composition: Ca-HCO3; mean TDS: 267 mg/l), cluster B (dominant composition: $Ca-Mg-SO₄-Cl$; mean TDS: 1029 mg/l), cluster C (dominant composition: Na-Mg-SO4; mean TDS 667 mg/l) and cluster D (dominant composition Na-Mg-SO4-Cl; mean TDS 2998 mg/l), which were described by the first factor of factor analysis. Results of the factor analysis suggested that the spatial variation

of groundwater quality in the area is influenced by the following processes: low TDS samples in cluster A, result mainly from dissolution of carbonate minerals. High TDS in cluster D, cluster B and cluster C is attributed to mixing of saline water (Mighan playa). Saline/ brackish groundwater in recent clusters results from the processes of evaporation (for samples close to the Mighan playa) and dissolution of SO_4 and Cl evaporative salts (such as thenardite, gypsum and halite).

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