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Sources of nitrate and bromide contaminants of groundwater in alluvial aquifer of Arak, Iran

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Abstract

The present study investigated NO_3^- and Br^- contamination in groundwater of Arak aquifer of Markazi province. Correlation and factor analysis were used to detect interrelation and sources of concentration of NO_3^- and Br^- ions and others physicochemical variables. No correlation was observed between NO_3^- and others contents, but positive correlation was identified between Br^- with other major variables such as EC, TDS, Cl^- and SO_4^{2-} in the groundwater. The resulted data indicated that groundwater samples of two areas of Arak aquifer were severely contaminated with NO_3^- (up to 50 mg/L) and Br^- (up to 0.5mg/L),which were exceeded the WHO and EU provisional guideline values. Nitrate was shown anthropogenic source and originated from sewage water from domestic and industrial activities. Bromide was originated from palaeo-salt water of Mighan Lake and has geogenic source.

Keywords: Arak aquifer, Factor analysis, Mighan Lake, Nitrate and bromide, Salt water.

1- Introduction

Sewage water represents a significant source of NO3- and Br- into the groundwater. Groundwater NO3- contamination is a threat to human health (Bryan and Loscalzo, 2011; Johnson *et al*., 2010; Jurec and Jazbec, 2016). Nitrate has been listed as one of the most common groundwater contaminants by WHO (2011). High nitrate levels in water can result blue baby syndrome. Ingestion of water with elevated nitrate levels can also cause spontaneous abortions and non- Hodgkin's lymphoma (Nolan and Hitt, 2006; Nolan, 2001) and an MCL of 50 mg/L has been set by EU (1998). Nitrate contamination of aquifers has been an important issue in hydrogeology and hydrochemistry over the last two decades. Nitrate in groundwater originates largely from diffuse (non-point) sources in relation to diverse agricultural and domestic practices, as well as from point sources such as sewage effluents (Canter, 1997; Fogg *et al*., 1998; Pastén-Zapata *et al*., 2014; Ma *et al*., 2016). In particular, aquifers in urban area are highly vulnerable to nitrate contamination, due to the widespread application of sewage waters (Panno *et al*., 2006; Jin *et al*., 2012; Brandao *et al*., 2014; Ghadimi and Ghomi, 2013; Ghadimi, 2015; Rebolledo *et al*., 2016).

Bromide is one of the halogen elements found in trace amounts in all groundwater. Bromide occurs as the free Br^- ion in most natural waters and it only forms significant complex ions under hypersaline conditions. Bromide is corrosive to human tissue in a liquid state and its vapors irritate eyes and throat. Bromide vapors are very toxic with inhalation (Carpenter, 1978). Inorganic Br^- is found in nature, they occur naturally and humans have added too much through the years. Through food and drinking water humans absorb high doses of inorganic Br^-. These Br^- can damage the nervous system and the thyroid gland. The geochemistry of Br^-

is similar to that of Cl^- but distinctive difference makes it a valuable tracer in groundwater studies (Shouakar-Stash *et al*., 2007; Heeb *et al*., 2014; Bero *et al*., 2016). In dilute natural waters, the main control on the geochemistry of Br^- is likely to be the source of salinity. Bromide has a molar Br^-/ Cl^- ratio of 1.57× 10^{-3}. In marine aerosol however the ratio is generally slightly higher than sea water due to some enrichment near the sea surface. The general geochemistry of Br^- in groundwater has been covered by Rittenhouse (1967), Carpenter (1978), Edmunds (1996), Davis *et al* (1998) and others. Characteristics of Br^- as reported by these authors include the following: (1) Almost all Br^- from natural sources found in groundwater is in the form of the simple negative monovalent ion, Br^-. (2) Inorganic compounds of both Cl^- and Br^- are highly soluble. However, because those of Br^- are most soluble, evaporation to partial dryness will leave residual brine rich in Br^- after Cl^- solids start to precipitate. (3) Bromide, like Cl^-, is normally conservative in a groundwater system; however, some of the Br^- will adsorb on organic solids (Gerritse and George, 1988; Reeve, 2002; Brindha and Elango, 2013) and on mineral surfaces in water having a low pH (Seaman *et al*., 1996). (4) Human activity has introduced a large number of compounds of Br^- into aquifers (Andreae *et al*., 1996).

The objective of this work is to assess the influence of natural and anthropogenic activities on the groundwater quality of the Arak aquifer using hydrochemical methods and factor analysis methods based on 36 samples. Firstly, in order to interpret the complex groundwater hydrochemistry of Arak aquifer, the origin and interconnection of these water types are explained in relation to shallow groundwater and mixing with palaeo-saltwater and human intervention. Secondly, factor analysis is used to identify the major natural and anthropogenic processes occurring in the entire plain by extracting several factors.

2- Description of the study area

The Mighan lake is located in the Arak region, central part of Markazi province (Fig.1).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 part of the lake and carbonate in eastern part. Paleogene assemblages consist of clastic and tuff deposits and volcanic rocks in the northern part of the lake. The Neogene sedimentary sequences around the Mighan Lake are shale, marl and volcanic conglomerate.

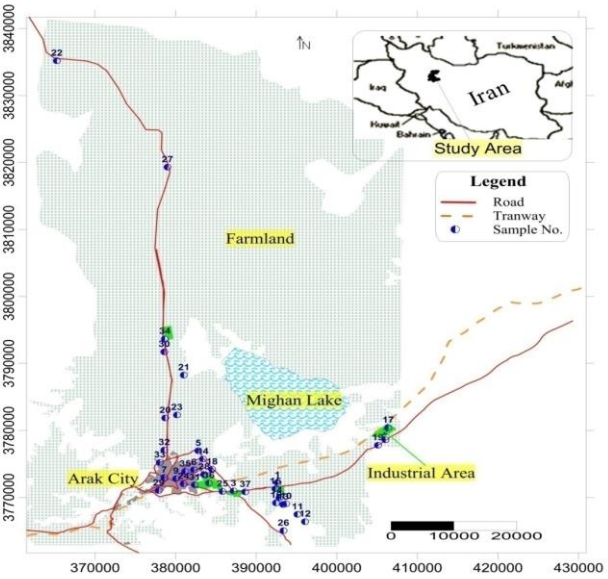

Figure 1) Maps showing the locations of study area and sampling sites in the Arak city

Mighan Lake with 1700 m above sea level has an area about 5500 km^2 and is a closed basin. The mean annual temperature and precipitation are 14^o C and 350 mm. This lake is fed by fresh water from the whole margins. The lake water chemistry is dominated with ions Na^+, Mg^{2+}, Cl^-, $SO4^{2-}$, and also contains smaller amounts of Ca^{2+}, K^+ and HCO_3^- (Zamani, 1999). Bedrock of these formations is composed of crystalline limestone with 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 inter-mountainous of Mighan Lake. 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 chemical analysis

Alluvial groundwater samples were collected from 36 wells in September of 2012 (Fig. 1).Water samples were collected using suction pumps after purging at least three well volumes. Unstable parameters such as temperature, pH and electrical conductivity (EC) were measured in the field using a specially designed flow-through chamber to minimize the contact with air. Alkalinity was also measured using the acid neutralizing titration technique in the field and then converted to the equivalent HCO_3^- concentrations. Samples for laboratory analysis were immediately filtered through 0.45 μm cellulose membrane filters. Samples for the analysis of cations were acidified to pH by adding several drops of ultra-pure nitric acid. The samples were kept at 4 °C in an ice box before analysis within a few days after sampling. Major cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}), and dissolved silica were analyzed using ICP-AES, while anions (Cl^-, SO_4^{2-}, Br^-, B^-, F^- and NO_3^-) were analyzed using Ion Chromatography at the Water Organization of Markazi province. The total dissolved solid (TDS) of the water was calculated by adding the mass of analyzed ions plus Si^{4+}. Quality control of analytical data was undertaken by routinely analyzing blanks, duplicates, and standards and by checking ion balances. The ion balance errors for the analyses were generally within ±5%.

3-2. Data transformation and standardization

A total of 15 physicochemical variables (EC, pH, TDS, HCO_3^-, NO_3^-, Cl^-, F^-, SO_4^{2-}, Br^-, B^-, Si^{4+}, Na^+, K^+, Ca^{2+} and Mg^{2+}) from 36 groundwater samples were used in our analysis. Because, some of these variables are not symmetrically distributed, we examined normality of each variable based on skewness and, if a variable does not have normality, we transformed variables (Reimann and Filzmoser, 2000). In our data set, none of the variables passed this normality distribution (except pH, Si^{4+} and NO_3^-) (Table 1). Therefore, logratio-transformations were conducted for the skewed variables to achieve normality and transformation. Various possibilities for data transformation of compositional data have been introduced in the literature; the most widely used is logratio transformations (Aitchison, 1986). The isometric logratio (ilr) transformation considers log transformations of the ratios formed by the compositional parts. Isometric logratio (ilr) transformations (Egozcue *et al*., 2003; Carranza, 2011) are useful class of logratio transformations with good theoretical properties. In addition to data transformation, all the 15 variables were standardized as follows (*Eq.1*):

$$\text{Ilr (x)} = \sqrt{1}/2Ln(\frac{xi}{xj}) \qquad \textit{Eq.1}$$

where ilr (x_i) is the normalized and standardized value for x_i (=ith variable for jth sample); x_j is the mean of variables. Through the standardization procedure by isometric logratio the influence of different units of measurement is eliminated. Thus, each variable obtains equal weight in the statistical analyses.

3-3. Multivariate statistical analysis using factor analysis

Factor analysis is a mathematical procedure that uses an orthogonal transformation to convert a set of observations of possibly correlated variables into a set of linearly uncorrelated variables called factors. The number of factors is less than or equal to the number of original variables. As a multivariate analysis method, factor analysis can provide a powerful tool for analyzing the complex high dimensional hydrochemical data sets of groundwater (Jolliffe, 2002). It has been successfully applied to clarify the contributions of hydrogeological and hydrogeochemical processes to groundwater quality and identify the influence of ecological pollution on the environment (Kim *et al*., 2005; Panda *et al*., 2006), to distinguish natural and anthropogenic sources affecting groundwater quality in aquifers (Jiang *et al*., 2009; Zhao *et al*., 2010) and to assess the impact of anthropogenic activities on groundwater quality in a lowland plain (Güler *et al*., 2012). We performed factor analysis to evaluate the correlations among multivariate variables. The factor analysis has developed in geochemical and environmental studies to quantify the correlations among complex variables (Gooverts, 1998). The Statistica software was used to analyze the high dimensional groundwater quality data of the samples. Factor analysis was chosen and used to identify the contributions of different natural and anthropogenic factors that influence the groundwater hydrochemistry of the study area. The chosen variables for factor analysis are EC, pH, TDS, HCO_3^-, NO_3^-, Cl^-, F^-, SO_4^{2-}, Br^-, B^-, Si^{4+}, Na^+, K^+, Ca^{2+} and Mg^{2+}. The detailed factor analysis, advantage and application of factor analysis have been described in many previous studies (Helena *et al*., 2000; Jiang *et al*., 2009; Güler *et al*., 2012). In order to investigate the effects of heterogeneous geochemical processes and anthropogenic activities of the Arak aquifer, the spatial distributions of factor scores (FS) were interpolated using symbolic method. Values outside the [0, 1] range are inappropriate. Thus, factor analysis is inappropriate for studies wherein the response variable is binary (present or absent) because the predicted response must be in the interval [0, 1]. In order to constrain the values of the predicted response variable within the unit interval [0, 1], Cox and Snell (1989) recommended to use a logistic model. Hence, to calculate the logistic function has been used to fuzzy FSs (FFS) of each sample per indicator factor, thus (*Eq.2*):

$$FFS= e^{Fs}/1+e^{Fs} \qquad \textit{Eq.2}$$

where Fs is the factor score of each sample obtained in a factor analysis. The FFS is, therefore, a fuzzy weight of each sample for each indicator factor. In this way, the weights of different classes of evidential maps are calculated based on the FSs of samples per indicator factor obtained in the factor analysis.

4- Results and discussion

4-1. Hydrochemical study

The Table 1 summarizes the descriptive statistics of 15 physicochemical variables for a total of 36 groundwater samples within the WHO (2011) guidelines for drinking water. The ilr transformation (Eq. 1) in Filzmoser *et al* (2009a) was used to open the raw data. The histograms for the raw data and ilr transformed Br^- and SO_4^{2-} data are shown in Figure 2. They suggest that the raw datasets have right-skewed distributions, and logratio transformed datasets are symmetrically distributed. The logratio transformation can reduce the effects of outliers to some extent and make the data more symmetrically distributed than those of the raw data. The mean and median concentrations of the major ions in the Arak aquifers are within the WHO (2011) guidelines for drinking water. The maximum NO_3^- and Br^- concentrations of 166 mg/L and 1.6 mg/L respectively are, however higher than their respective WHO (2011) and EU (1998) standards of 50 mg/L and 0.01 mg/L. Nitrate and Br^-concentrations in alluvial groundwater ranged widely from 14 to 166 mg/L and 0.20 to 1.6 mg/L, respectively with a very high mean value (72mg/L and 0.58 mg/L; Table 1), indicating a significant NO_3^- and Br^- contamination in the study area. Seventy-two percent (Fig. 3) and all of the samples (Fig. 4) showed NO_3^- and Br^- concentrations exceeding WHO (2011) and EU (1998) standard, respectively. These are isolated cases resulting from contamination from surface point sources such as domestic sewage. The mean and median EC values of

1615 µS/cm and 1196 µS/cm, which correspond to total dissolved solid concentrations of 789 mg/L and 586 mg/L respectively and are below the WHO (2011) guideline value of 1000 mg/L. Maximum concentrations of some of the major ions such as Na^+ and Cl^- are higher than the WHO (2011) recommended values for taste purposes. However, the low mean and median values of the concentrations of these ions imply that most of the locations sampled have concentrations lower than the recommended maximum values for domestic usage.

Table1) Descriptive statistics for 15 physicochemical variables for alluvial groundwater in the Arak area.

	Mean	Geometric- Mean	Median	Min.	Max.	Skewness	Skewness logratio
EC	1615	1340.	1196	528	5070	1.84	0.79
pH	7.36	7.35	7.35	6.70	7.90	-0.02	-0.13
TDS	789	658	586	263	2500	1.84	0.74
Ca^{2+}	103.	86	88	21	317	1.66	-0.07
Mg^{2+}	66	51	47	10	402	3.78	0.82
Na^+	237	153	142	23.	1005	1.87	0.34
K^+	0.46	0.13	0.07	0.07	3.70	2.71	1.58
HCO_3^-	428.	315	277	128	2782	3.66	1.79
Cl^-	260	175.	171	7.09	840	1.35	-0.81
SO_4^{2-}	276	199	183	50	1475	2.83	0.85
F^-	0.57	0.52	0.53	0.19	1.08	0.39	-0.26
Si^{4+}	8.43	8.05	8.47	3.87	14	0.30	-0.59
Br^-	0.58	0.53	0.50	0.20	1.60	1.68	-0.06
B^-	0.46	0.239	0.26	0.07	3.230	3.16	0.63
NO_3^-	72	61	64	14	166	0.49	-0.65

The pH is neutrality but it is well within the acceptable range. The aquifer of the Arak formation, which is mostly sedimentary aquifer, therefore produce groundwater of acceptable quality for most uses. High Br^- in groundwater in the area has two major sources: rock-water interactions and salt lake water intrusion. In the Arak aquifer, salinity is very high and might be associated with the combined effects of salt water intrusion and rock-water interactions in the area. Mean and median NO_3^- concentrations in the Arak aquifer are higher than the WHO (2011) values. There are, however, isolated cases of extremely high values, which result predominantly from contamination from domestic sewage and agricultural chemicals in the area. The hydrochemical processes in the study area also can be illustrated by the relationships between TDS and some constituents (e.g., NO_3^- and Br^-), likely in relation to the inputs of saline waters (Fig. 5). Fig. 5 shows that TDS negatively correlated with NO_3^- concentration. In contrast, the relationship between TDS and Br^- is positive correlated. Positive relationships TDS and Br^- values reveals that hydrochemistry of alluvial groundwater in the study area is controlled by saline water processes.

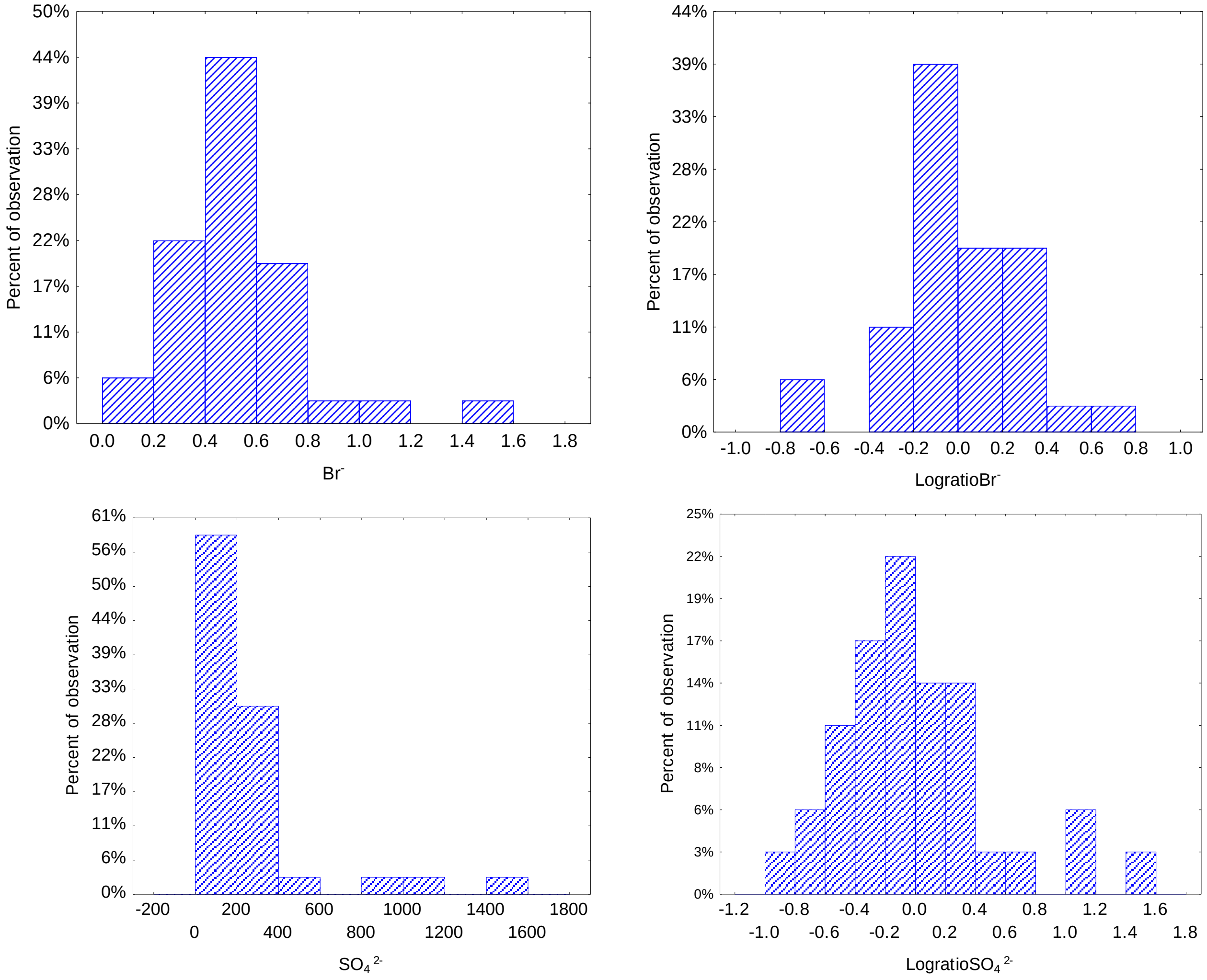

Figure 2) Histograms for the raw Br$^-$ and SO$_4$$^{2-}$ data and logratio -transformed Br$^-$ and SO$_4$$^{2-}$ data.

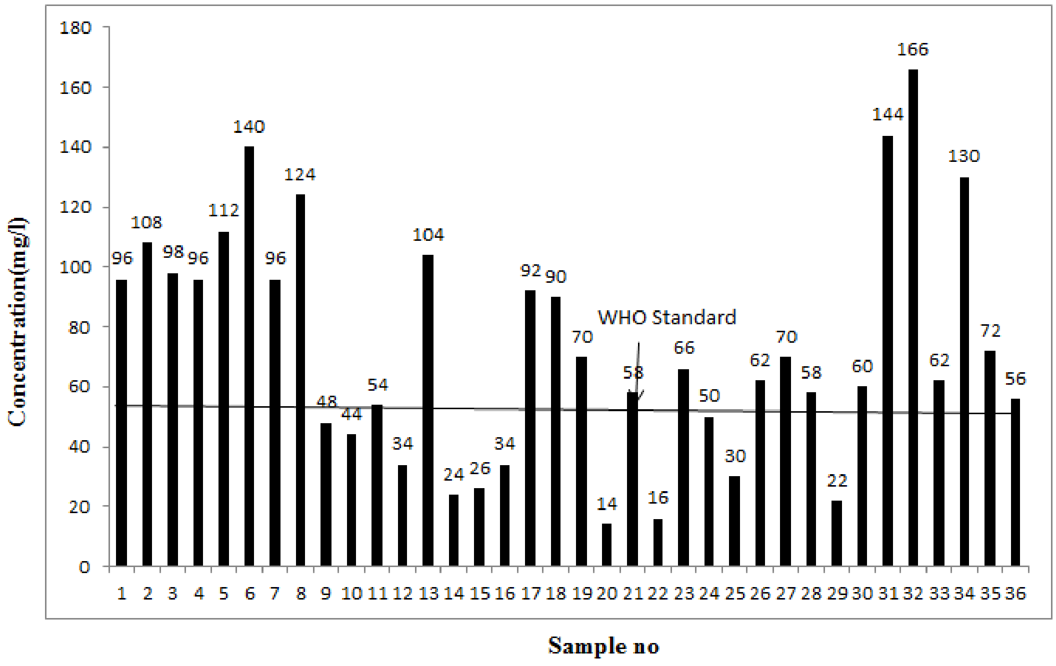

Figure 3) Histogram of NO$_3$$^-$ concentration in 36 boreholes for alluvial groundwater in the Arak area (for sample no. refer to Fig.1).

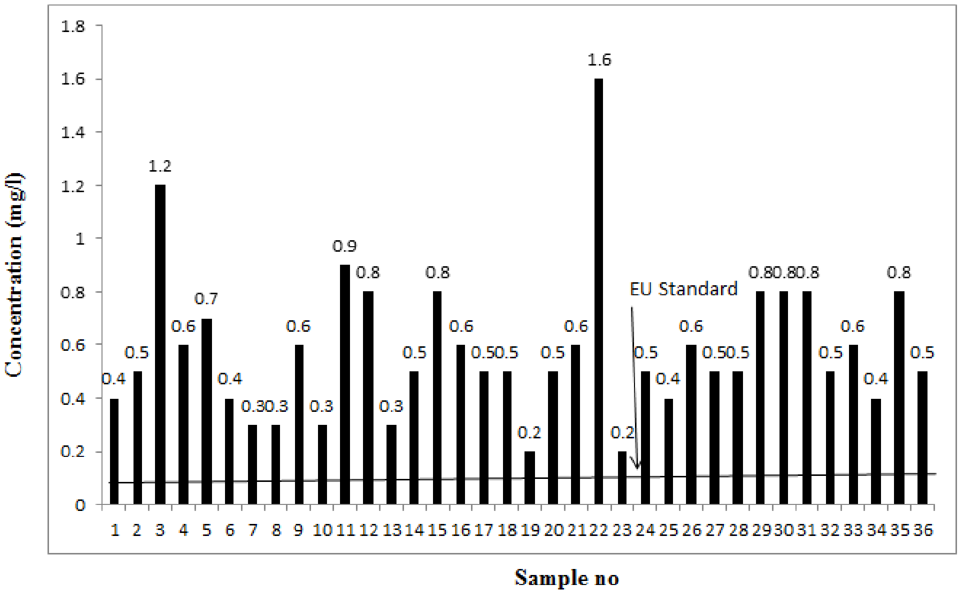

Figure 4) Histogram of Br^- concentration in 36 boreholes for alluvial groundwater in the Arak area (for sample no. refer to Fig. 1).

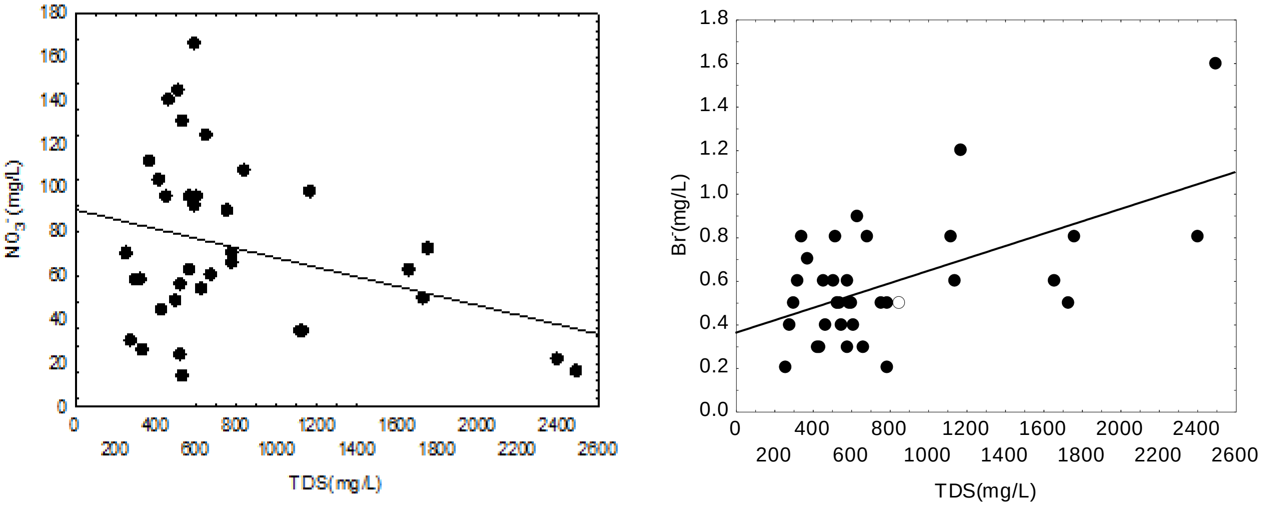

Figure 5) Plots showing the relationships between TDS with NO_3^- and Br^-.

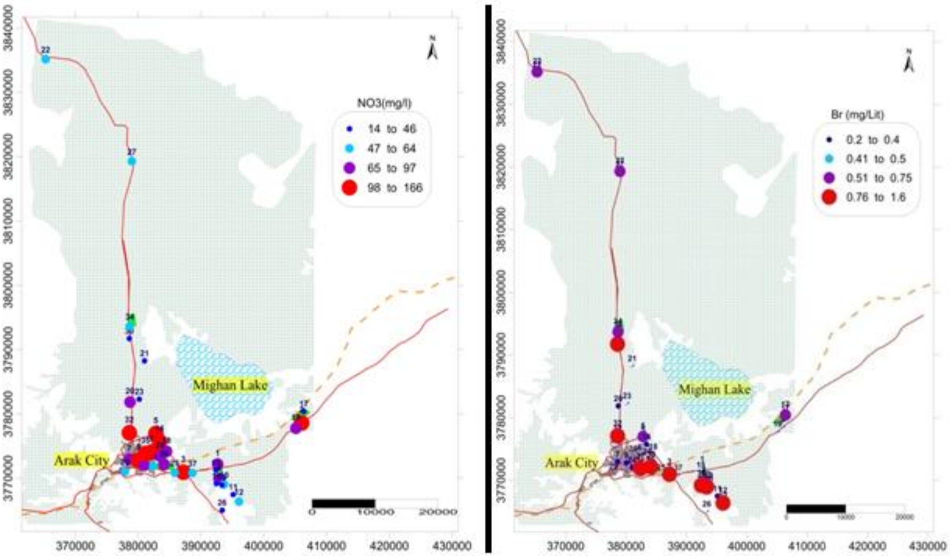

Figure 6. Maps showing the distributions of NO_3^- and Br^- variables in groundwater of Arak aquifer. The values in the scale bar of each map correspond to the minimum, 25th percentile, 50th percentile, 75th percentile, and maximum data.

The spatial variations of NO_3^- and Br^- variables for groundwater are illustrated in Figure 6. Nitrate value as indicator of anthropogenic source increase near the Arak city. Nitrate concentrations show an opposite spatial pattern with $Br^-$and decrease significantly down to a minimum level of 50 mg/L to the Mighan Lake. The spatial distribution of Br^- concentration is opposite to nitrate and shows a large increase (up to 0.6 mg/L) toward the Mighan Lake. We suggest that Br^-changes is related to the characteristic hydrogeologic condition near Mighan lakes, where the hydraulic gradient is lowered and thus the groundwater movement is retarded due to the dominance of silty alluvium. It is also noticeable that the concentrations of SO_4^{2-} and Cl^- tend to increase toward down-gradient (i.e., toward the Mighan Lake) and decrease in Arak city (Fig. 7). Similarly, very high concentrations of Br^- (to a maximum level of 1.6 mg/L) are observed toward the Mighan Lake. Here, we should note that those variables such as SO_4^{2-} and Cl^- can originate from saline water of Mighan Lake. Thus, it is evident that the alluvial aquifer in the study area is extensively affected by saline water, especially in down-gradient area of Mighan Lake.

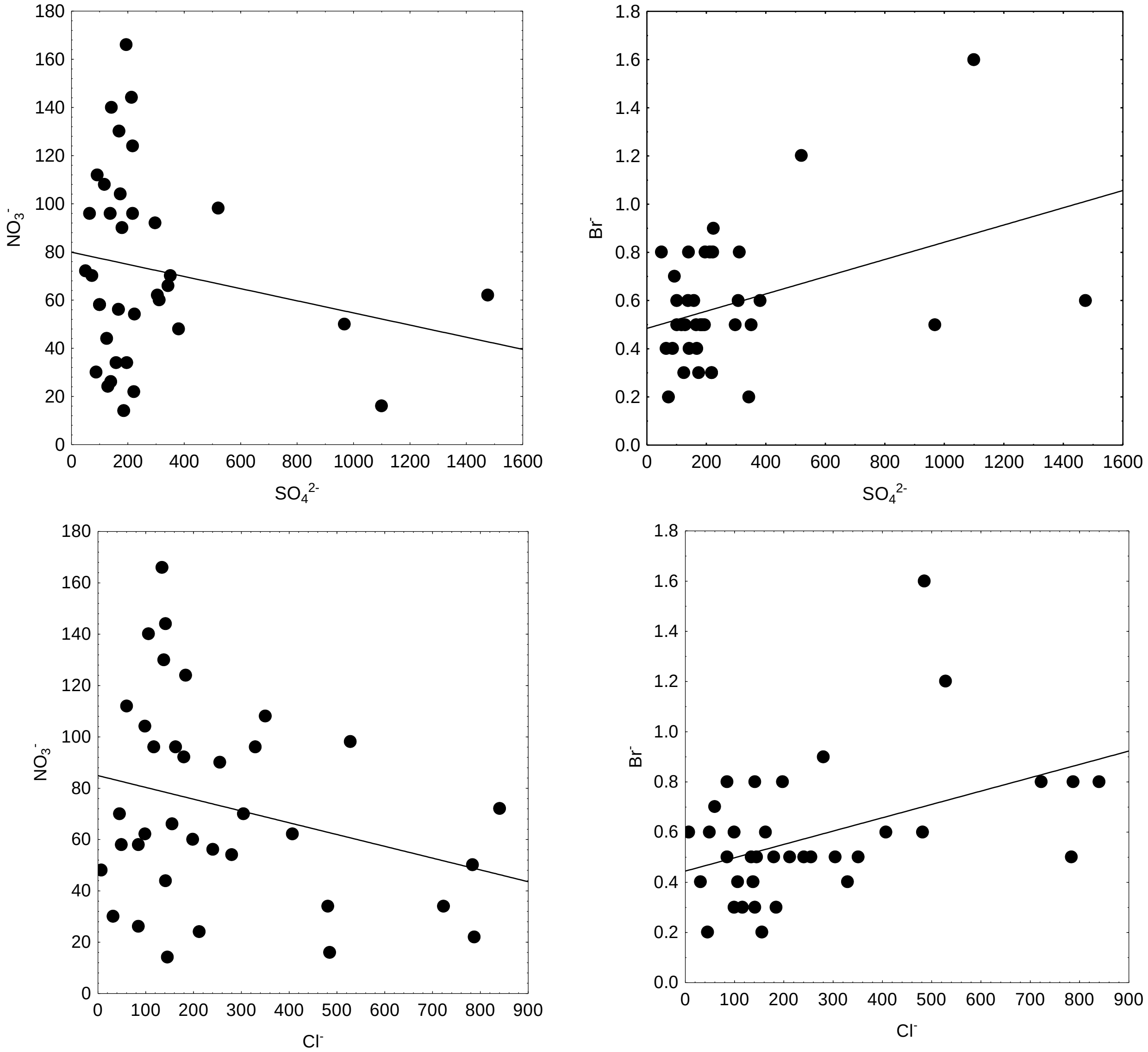

Figure 7) Plots showing the relationships between SO_4^{2-} and Cl^- with NO_3^- and Br^-

4-2. Correlation between variables

Table 2 shows the correlation matrix of the 15 variables. Positive and relatively strong correlations can be observed between these pairs: SO_4^{2-} and Na^+ (0.54), SO_4^{2-} and Mg^{2+} (0.45), SO_4^{2-} and Br^- (0.31), Cl^- and Na^+ (0.70) and Cl^- and Br^- (0.35). Most of these ions have known mineral sources such as mirablite, glauberite in and around nearby Mighan lake (Ghadimi and Ghomi, 2012), so these associations can be explained by palaeo-saltwater intrusion (Ghadimi and Ghomi, 2012). The strong positive correlation between HCO_3^- and Mg^{2+} (0.57), HCO_3^- and K^+ (0.55), HCO_3^- and Na^+ (0.46) indicates that they are likely derived from the dissolution of carbonate (Jiang *et al.*, 2009) as well as by cation exchange in the aquifer. In general, the mineral contents found in groundwater samples often come from the dissolution of mineral materials predominant in the sediments (Ghadimi and Ghomi, 2012).

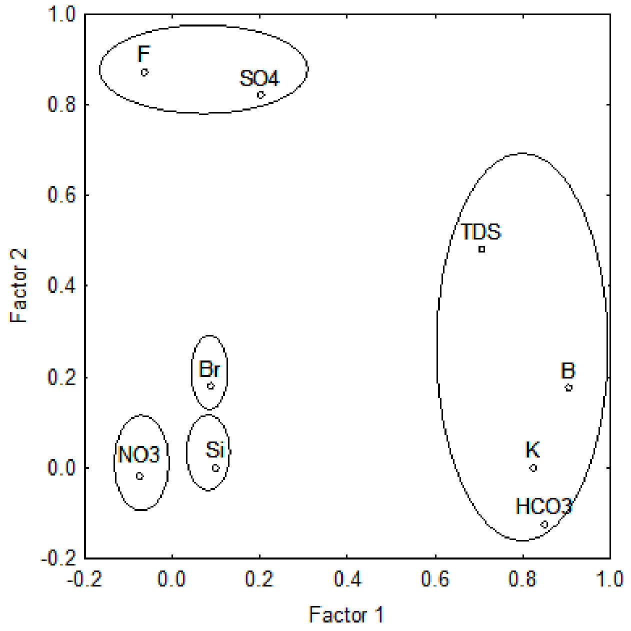

Figure 8) Relationships between different factors were illustrated in loading plots

Those that have no known mineral sources such as NO_3^- could be attributed to some non-natural processes, such as sewage effluents and industrial wastes (Jiang *et al.*, 2009; McMahon and Bohlke, 2006; Rekha *et al.*, 2011; Güler *et al.*, 2012). Both the palaeo-salt water intrusion and the dissolution of carbonate contribute to the strong positive correlation of TDS with each other, however, the correlation between SO_4^{2-}, Br^-, Cl^-, Na^+ and Mg^{2+} suggest that palaeo-salt water intrusion plays a more important role. In addition, the occurrence of cation exchange in the discharge zone induces the increased of correlation between Cl^-, Ca^{2+} and Mg^{2+} and the decreased correlation between HCO_3^- and Ca^{2+} (-0.08). The weak negative correlation between HCO_3^- and Ca^{2+} also suggests that the dissolution of carbonate minerals is limited due to the limitation and heterogeneous distribution of carbonate rock in and/or around the study area. Moreover, the strong positive correlation of TDS, Cl^- and Na^+ with each other (with r values ranking from 0.79 to 0.86) suggests that both palaeo-salt water intrusion and mineral precipitation/evaporate mineral deposits are important factors in contributing to groundwater chemistry of the Arak aquifer. The pH shows a weak correlation with NO_3^- (0.23), which can be explained by the strong acidity of the NO_3^- ion. This behavior can be partially attributed to pollution, i.e. domestic and/or industrial waste waters. Fluorine and B^-shows a positive and moderate correlation with some of the chemical variables examined, indicating that the sources of them are either from pollution or from the carbonate area (Ozsvath, 2006; Kern *et al.*, 2008; Ghadimi and Ghomi, 2012).

4-3. Factors controlling the groundwater chemistry

The chemical composition of groundwater reflects the geologic source and contaminants from anthropogenic sources. Factor analysis technique can highlight those groups of samples or outliers that are controlled by such factors from the more pervasive natural background (Thyne *et al.*, 2004). In this study, logratio data matrix was used in the factor analysis as described by Guler *et al* (2002) to give each variable equal weight in the multivariate statistical analysis. Statistical software was used to perform the factor analysis. Rotation of factor analysis was carried out using the $vari_{max}$ method, where both Kaiser criterion was used to determine the number of factors. In this study, by applying the factor analysis, 15 variables were combined to produce five significant factors explaining 81.80% of the variance of the original data set (Table 3 and Fig. 8).

Table 2) Correlation matrix of the 15 physical–chemical variables of groundwater samples

	EC	pH	TDS	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	Cl^-	SO_4^{2-}	F^-	Si^{4+}	Br^-	B^-	NO_3^-
EC	1														
pH	-0.33	1													
TDS	0.99	-0.32	1												
Ca^{2+}	0.44	-0.09	0.47	1											
Mg^{2+}	0.70	-0.26	0.70	0.12	1										
Na^{+}	0.86	-0.19	0.86	0.29	0.49	1									
K^{+}	0.49	-0.36	0.53	0.23	0.25	0.44	1								
HCO_3^-	0.59	-0.43	0.58	-0.08	0.57	0.46	0.55	1							
Cl^-	0.79	-0.36	0.79	0.47	0.49	0.70	0.44	0.33	1						
SO_4^{2-}	0.58	-0.03	0.57	0.35	0.45	0.54	0.15	0.10	0.26	1					
F^-	0.28	0.08	0.29	0.41	-0.03	0.39	-0.01	-0.11	0.18	0.49	1				
Si^{4+}	0.23	0.12	0.18	-0.27	0.38	0.19	-0.06	0.35	0.01	0.25	-0.11	1			
Br^-	0.48	-0.39	0.47	0.19	0.38	0.38	0.15	0.20	0.35	0.31	0.05	0.24	1.		
B^-	0.70	-0.25	0.70	0.09	0.54	0.60	0.58	0.76	0.51	0.36	0.03	0.20	0.04	1	
NO_3^-	-0.22	0.23	-0.20	0.26	-0.07	-0.33	-0.11	-0.15	-0.10	-0.14	-0.09	0.01	-0.24	-0.04	1

Most of the variance in the original data set is contained in the factor 1 (42.04%), which is associated with the variables EC, TDS, K^+, HCO_3^- and B^- (Table 3). Factor1 contains both classical hydrochemical variables, such as Mg^{2+}, Na^+ and Cl^- originating from the natural weathering processes of sedimentary/evaporitic rocks (e.g., dolomite and halite) found in the recharge areas(Ghadimi and Ghomi, 2012). Factor 2 explains 13.53% of the variance and is mainly related to elements Na^+, SO_4^{2-} and F^-. Factor 2 includes classical hydrochemical variables that indicate salinization processes. It is also worth to mention that in Arak aquifer the highest values of Na^+ and SO_4^{2-} generally occur in the low gradient areas intruded by the salt water.

In addition to that, high values of Na^+ and SO_4^{2-} are mainly confined to the area where evaporite dissolution (mainly glauberite) is the main process affecting the groundwater chemistry. Additionally, saltwater trapped in the sediments or lake-spray probably contributes to salinization of the groundwater in the area (Ghadimi and Ghomi, 2012). The silica contributes most strongly to the third factor that explains 10.20% of the total variance (with a positive loading) (Table 3). The chemical variables with strong correlations with factor 3(Si^{4+}) are associated with groundwater chemistry mainly governed by silicate weathering (Ghadimi and Ghomi, 2012). The fourth factor is concerned solely with Br^- and represents 8.81% of the total variance (Table 3). Figure 6 displays the distribution of the factor 4 scores in the study area, where the highest scores are generally observed around Mighan Lake and where saline water activities of lake are widespread. Several factors control the general distribution of Cl^-/Br^- ratios in ground water. The most important is probably the distance from the recharge area to the nearest source of particulate Cl^-, which most commonly is the around the saline lakes (Tweed *et al*., 2011).

Table3. Factor loadings (varimax rotated) for groundwater samples of the Arak aquifer (n = 36)

	F1	F2	F3	F4	F5
EC	**0.68**	0.52	0.20	0.41	-0.03
pH	-0.38	0.21	0.23	-0.06	-0.18
TDS	**0.70**	0.53	0.16	0.40	-0.04
Ca^{2+}	0.12	0.54	-0.34	0.30	-0.58
Mg^{2+}	0.52	0.17	0.53	0.36	-0.11
Na^{+}	0.59	**0.61**	0.12	0.23	0.17
K^{+}	**0.78**	0.01	-0.24	0.11	0.01
HCO_3^-	**0.83**	-0.14	0.30	0.11	0.14
Cl^-	0.58	0.36	-0.09	0.46	-0.17
$SO_4{}^{2-}$	0.16	**0.75**	0.32	0.11	0.01
F^-	-0.05	**0.83**	-0.18	-0.10	0.06
Si^{4+}	0.07	0.01	**0.89**	0.02	0.04
Br^-	0.01	0.18	0.25	**0.85**	0.09
B^-	**0.90**	0.15	0.18	-0.08	-0.01
NO_3^-	-0.08	-0.17	0.05	-0.21	**-0.89**
Eigenvalue	6.30	2.02	1.53	1.32	1.08
% Total - variance	42.04	13.53	10.20	8.81	7.21
Cumulative - %	42.04	55.57	65.77	74.59	81.80

* Significant loadings are in bold

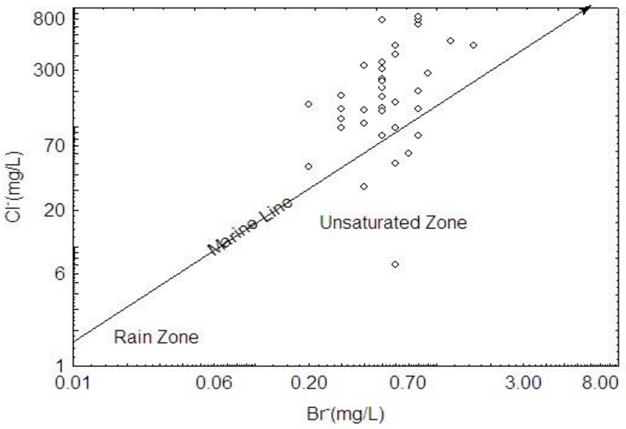

Figure 9) It shows Cl^-/Br^- relationship in Arak groundwater relative to Cl^-/Br^- in sea water, in rain and unsaturated zone (Edmunds, 1996).

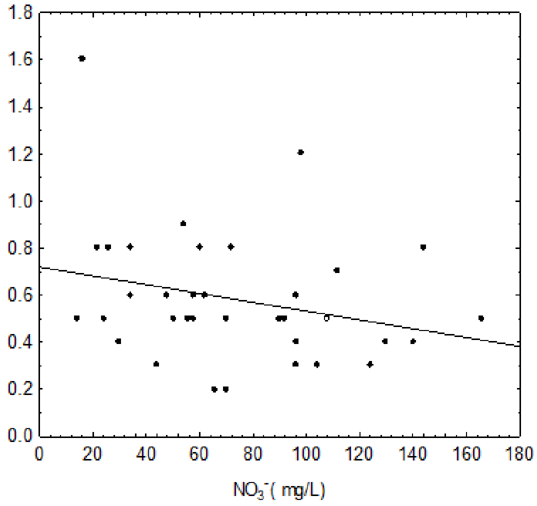

Figure 10) Plot showing the relationships between NO3$^-$ and Br$^-$ variables

Based on Figure 9, approximately 83% of samples are located in above marine line. Therefore, these groundwater samples are originated from saline waters. The only saline water in the study area is Mighan Lake (Fig. 1). It is obvious, Br^- ions in ground water have non-anthropogenic source (natural source). Finally, the fifth factor contributes most negative strongly to NO_3^- that explains 7.21% of the total variance (Table 3). Nitrate and Br^- have opposite relationship in Arak aquifer (Fig. 10). Therefore, NO_3^- has another source and it originated during anthropogenic activities. Most of groundwater wells that are located in urban area of Arak have problem for NO_3^-. Approximately, each people has at least one disposal waste water in their house and there are many industrial in the urban area that intrude sewage water to the groundwater (Ghadimi and Ghomi, 2012).

Factor scores (FS) can be related to intensity of the chemical process described by each factors, where extreme negative scores (<-1.0) reflect areas essentially unaffected by the process and positive scores (>+1.0) reflect areas most affected (Dalton and Upchurch, 1978). Near-zero scores approximate areas affected to an average degree by the chemical process of that particular factor. Therefore, varimax factor scores of groundwater samples (n = 36) were separately interpolated for factor 4 and factor 5.

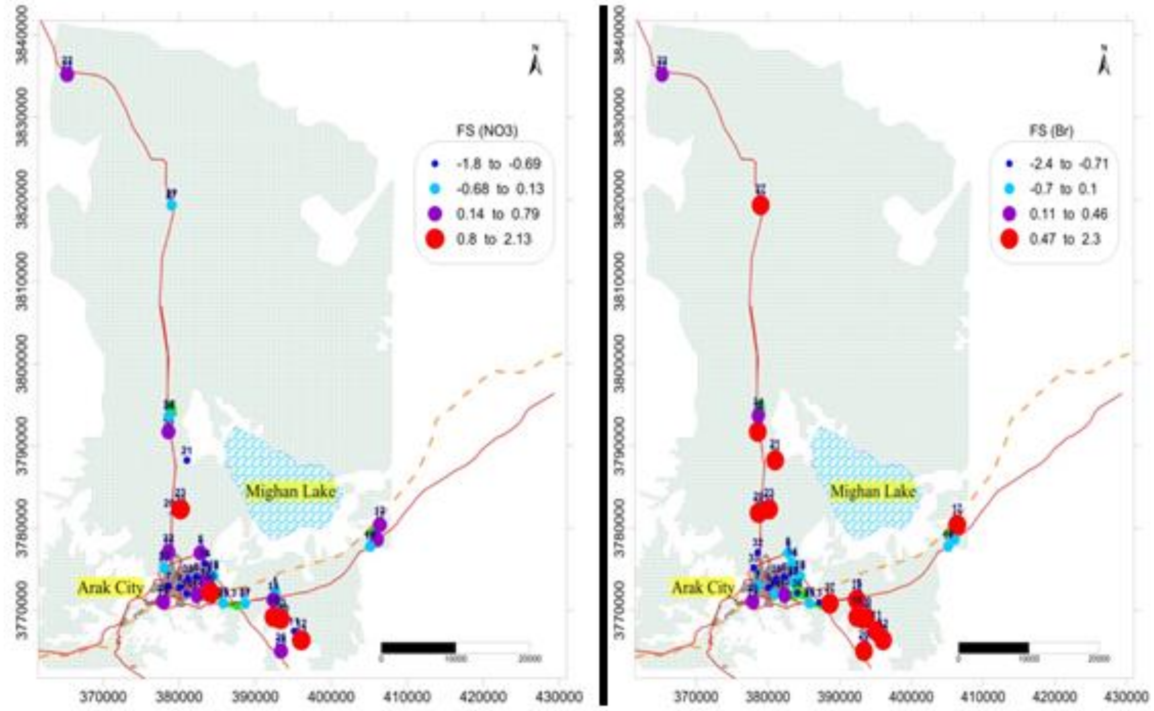

Figure 11) Maps showing the spatial distribution of two factor scores (FS) (NO_3^- and Br^-) obtained by factor analysis of the groundwater samples in Arak aquifer. The values in the scale bar of each map correspond to the minimum, 25th percentile, 50th percentile, 75th percentile, and maximum data.

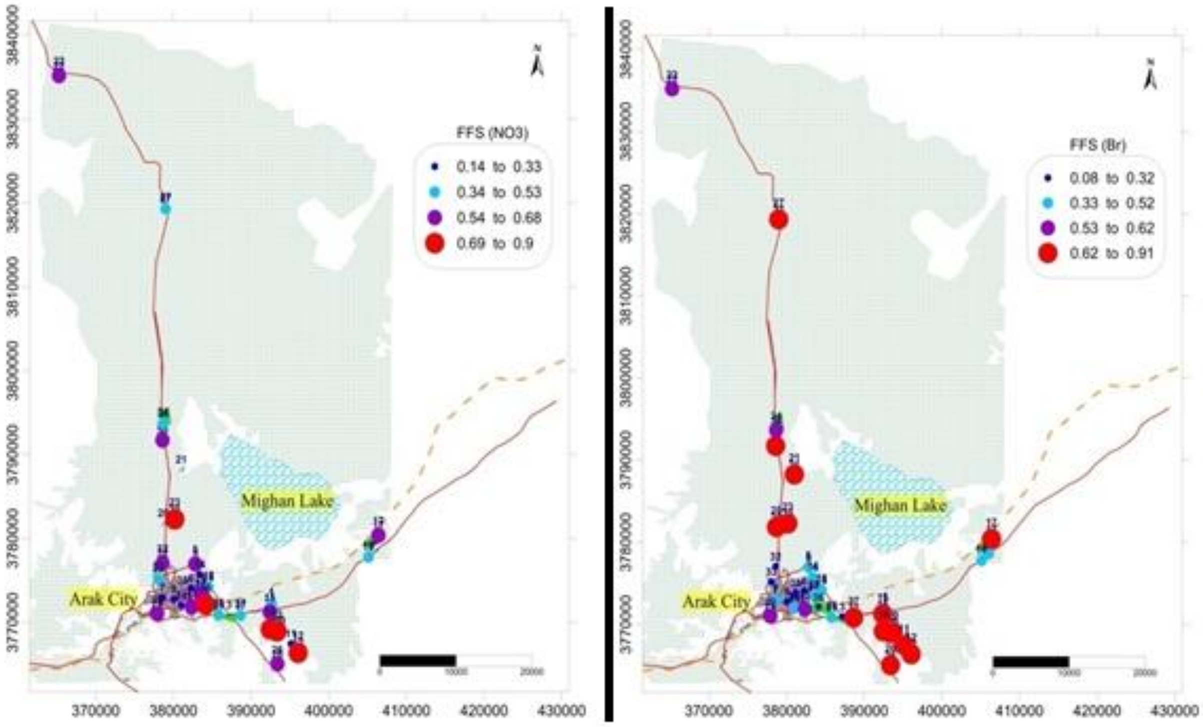

Figure 12) Map of fuzzy factor scores (FFS) of NO_3^- and Br^- in the Arak aquifer. The values in the scale bar of each map correspond to the minimum, 25th percentile, 50th percentile, 75th percentile, and maximum data.

Figure 11 shows the spatial distribution of the factor scores for two factors. For NO_3^- in Fig. 11, where high scores (i.e., values from 0.14 to 2.13) are generally observed at the central parts of the study area, where anthropogenic activities are high. But, for Br^- high scores (i.e., values from 0.11 to 2.3) are identified at the peripheral parts of the Mighan lake, where natural effects are significant. Tweed *et al* (2011) showed the contents of Br^- is high in Eyre lake, but it decrease in groundwater of peripheral lake. In addition to palaeo-salt water for the source of Br^- in the study area, it is possible to be atmospheric origin. The Br^- concentrations in the atmosphere may be due to flux of Br^- from salt lake to the atmosphere. In arid environments, if the residence time is sufficient, there can be Br flux directly from the salt lakes to the atmosphere, surface and groundwater (Risacher *et al.*, 2006; Wood and Sanford, 2007). The fuzzy factor scores (FFS) approach is a more powerful tool than ordinary factor score for fuzzification of $NO_3^-$and Br^- data to generate an evidential map (Fig. 12). Distribution of $NO_3^-$and Br^-in fuzzy factor score is similar to the factor score map.

5- Conclusions

Correlation and factor analysis has proven a useful tool in providing insights to the problem of $NO_3^-$and Br^- contamination of alluvial groundwater in Arak aquifer. These tools have improved the understanding of the role of sewage water and intrinsic factors such as aquifer lithology and salt water in Mighan Lake, on the $NO_3^-$and Br^- contamination degree. At the study area, high $NO_3^-$and Br^- concentrations are seen to occur preferably in the urban areas and low lowland of Mighan Lake. According to the factor scores and fuzzy factor scores, the highest concentrations of Br^-, EC, TDS, Cl^- and SO_4^{2-} in the groundwater occur near the Mighan Lake, but most of NO_3^- ion occurs in urban area of Arak. The main source of NO_3^- released into groundwater is believed to be reduced conditions by human activities. The introduction of NO_3^- from domestic and industrial products, such as sewage water, is considered a potentially source.

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References

Aitchison, J. 1986. The statistical analysis of compositional data. London, UK: Chapman and Hall; p. 416.

Andreae, M. O., Atlas, E., Harris, G. W., Helas, G., De Kock, A., Koppmann, R., Maenhaut, W., Manr, S., Pollock, W. H., Rudolph, J., Scharffe, D., Schebeske, G., Welling, M. 1996. Methyl halide emissions from savanna fires in southern Africa. Journal of Geophysical Research: 101, 23603–23613.

Bero, N. J., Ruark, M. D., Lowery, B. 2016. Bromide and chloride tracer application to determine sufficiency of plot size and well depth placement to capture preferential flow and solute leaching, Geoderma: 262, 94–100.

Brandao, G. C., Matos, G. D., Raimundo, N., Sergio, P. L. C. Ferreira., L. C. 2014. Development of a simple method for the determination of nitrite and nitrate in groundwater by high-resolution continuum source electrothermal molecular absorption spectrometry. Analytica Chimica Acta: 806, 101–106.

Brindha, K., Elango, L. 2013. Causes for Variation in Bromide Concentration in Groundwater of a Granitic aquifer, International Journal of Research in Chemistry and Environment: 3, 163–171.

Bryan, N. S., Loscalzo, J. 2011. Nitrite and Nitrate in Human Health and Disease. Humana Press, New York. 250 p.

Canter, L.W. 1997. Nitrates in Groundwater. Lewis Publisher, Florida. 320 p.

Carpenter, A. B. 1978. Origin and chemical evolution of brines in sedimentary basins. Oklahoma Geological Survey Circular 79.

Carranza, E. J. M. 2011. Analysis and mapping of geochemical anomalies using logratio transformed stream sediment data with censored values. Journal of Geochemical Exploration: 110, 167–185.

Cox, D. R., Snell, E. J. 1989. Analysis of Binary Data, 2nd ed. Chapman and Hall, London.

Dalton, M. Gand Upchurch, S. B. 1978. Interpretation of hydrochemical facies by factor analysis. Ground Water: 16, 228–233.

Davis, S. N., Whittemore, D. O., Fabryka-Martin, J. 1998. Uses of chloride/bromide ratios in studies of potable water. Ground Water: 36, 338–350.

Edmunds, W. M. 1996. Bromine geochemistry of British groundwaters. Mineralogical Magazine: 60, 275–284.

Egozcue, J. J., Pawlowsky-Glahn, V., Mateu-Figueras, G., Barceló-Vidal, C. 2003. Isometric logratio transformations for compositional data analysis. Mathematical Geology: 35, 279–300.

E.U.1998. Council, Council directive 98/83 about water quality intended for human consumption, Official paper of the European Communities: L330, 32–54.

Filzmoser, P., Hron, K., Reimann, C. 2009. Principal components analysis for compositional data with outliers. Environmetrics: 20, 621–632.

Fogg, G. E., Rolston, D. E., Decker, D. L., Louie, D. T., Grismer, M. E. 1998. Spatial variation in nitrogen isotope values beneath nitrate contamination source. Ground Water: 36, 418–426.

Gerritse, R. G., George, R. J. 1988. The role of soil organic matter in the geochemical cycling of chloride and bromide. Journal of Hydrology: 101, 83–95.

Ghadimi, F., Ghomi, M. 2012. Statistical Analysis of the Hydrogeochemical Evolution of Groundwater in Alluvial Aquifer of Arak Mighan Playa, Markazi Province, Iran. Journal of Water Sciences Research: 4, 131–45.

Ghadimi, F., Ghomi, M. 2013. Assessment of the effects of municipal wastewater on the heavy metal pollution of water and sediment in Arak Mighan Lake, Iran. Journal of Tethys, 1, 205–214.

Ghadimi, F. 2015. Prediction of heavy metals contamination in the groundwater of Arak region using artificial neural network and multiple linear regression. Journal of Tethys: 3, 203–215.

Gooverts, P. 1998. Geostatistical tools for characterizing the spatial variability of microbiological and physico-chemical soil properties. Biological Fertility Soils: 27, 315–334.

Güler, C., Kurt, M. A., Alpaslan, M., Akbulut, C. 2012. Assessment of the impact of anthropogenic activities on the groundwater hydrology and chemistry in Tarsus coastal plain (Mersin, SE Turkey) using fuzzy clustering, multivariate statistics and GIS techniques. Journal of Hydrology: 414, 435–451.

Güler, C., Thyne, G. D., McCray, J. E., Turner, A. K. 2002. Evaluation of graphical and multivariate statistical methods for classification of water chemistry data. Hydrogeology 10, 455–474.

Helena, B., Pardo, R., Vega, M., Barrado, E., Fernandez, J. M., Fernandez, L. 2000. Temporal evolution of groundwater composition in an alluvial aquifer (Pisuerga River, Spain) by principal component analysis. Water Research: 34, 807–816.

Jiang, Y. J., Wu, Y. X., Groves, C., Yuan, D. X., Kambesis, P. 2009. Natural and anthropogenic factors affecting the groundwater quality in the Nandong karst underground river system in Yunan, China. Journal Contamination Hydrology: 109, 49–61.

Jin, Z., Pan, Z, Jin, M., Li, F., Wan, Y., Gu, B. 2012. Determination of nitrate contamination sources using isotopic and chemical indicators in an agricultural region in China: Agriculture, Ecosystems and Environment: 155, 78– 86.

Johnson, P. T. J., Townsend, A. R., Cleveland, C. C., Glibert, P. M., Howarth, R. W., McKenzie, V. J., Rejmankova, E., Ward, M. H. 2010. Linking environmental nutrient enrichment and disease emergence in humans and wildlife. Ecological Applications: 20, 16–29.

Jolliffe, I. T. 2002. Principal Component Analysis. Springer Series in Statistics, second ed. Springer, 600 p.

Jurec, J. N., Jazbec, A. 2016. Point source pollution and variability of nitrate concentrations in ater from shallow aquifers, Applied Water Science: DOI 10.1007/s13201-015-0369-9.

Heeb, B., Criquet, J., Saskia, G., Steffens, Z., Urs von Gunten, U. 2014. Oxidative treatment of bromide-containing waters: Formation of bromine and its reactions with inorganic and organic compounds, Water Research, Volume: 48, Pages 15-42.

Kern, M. L., Vieiro, A. P., Machado, G. 2008. The fluoride in the groundwater of Guarani Aquifer System: the origin associated with black shales of Parana Basin. Environmental Geology: 55, 1219–1233.

Kim, J., Kim, R., Lee, J., Cheong, T., Yum, B., Chang, H. 2005. Multivariate statistical analysis to identify the major factors governing groundwater quality in the coastal area of Kimje, South Korea. Hydrology Process: 19, 1261–1276.

Ma, Z., Yang, Y., Lian, X., Jiang, Y., Xi, B., Peng, X., Yan, K. 2016. Identification of nitrate sources in groundwater using a stable isotope and 3DEEM in a landfill in Northeast China. Science of the Total Environment: doi: 10.1016/j.scitotenv.2016.04.117.

McMahon, P. B., Bohlke, J. K. 2006. Regional patterns in the isotopic composition of natural and anthropogenic nitrate in groundwater, high plains, USA. Environmental Science Technology: 40, 2965–2970.

Nolan, B. T. 2001. Relating nitrogen sources and aquifer susceptibility of nitrate in shallow groundwaters of the United States. Ground Water: 39, 290–299.

Nolan, B. T., Hitt, K. J. 2006. Vulnerability of shallow groundwater and drinking water wells to nitrate in the United States. Environmental Science Technology: 40, 7834–7840.

Ozsvath, D. L. 2006. Fluoride concentrations in a crystalline bedrock aquifer Marathon County, Wisconsin. Environvironmental Geology: 50, 132–138.

Panda, S. V., Kelly, W. R., Martinsek, A. T., Hackley, K. C. 2006. Estimating background and threshold nitrate concentrations using probability graphs. Ground Water: 44, 697–709.

Pastén-Zapata, E., Ledesma-Ruiz, R., Harter, T., Ramírez, A. I., Mahlknecht, J. 2014. Assessment of sources and fate of nitrate in shallow groundwater of an agricultural area by using a multi-tracer approach, Science of the Total Environment: 470–471, 855–864.

Rebolledo, B., Gil, A., Flotats, X., Sánchez, J. A. 2016. Assessment of groundwater vulnerability to nitrates from agricultural sources using a GIS-compatible logic multicriteria model. Journal of Environmental Management: 171, 70–80.

Reeve, A. S. 2002. The migration of a sodium bromide tracer in a large Maine peatland. Geological Society of America Abstracts with Programs: 34, 6: 420.

Reimann, C., Filzmoser, P. 2000. Normal and lognormal data distribution in geochemistry: death of a myth. Consequences for the statistical treatment of geochemical and environmental data. Environmental Geology: 39, 1001–1014.

Rekha, P. N., Kanwar, R. S., Nayak, A. K., Hoang, C. K., Pederson, C. H. 2011. Nitrate leaching to shallow groundwater systems from agricultural fields with different management practices. Journal Environmental Monitoring, 13, 2550–2558.

Risacher, F., Fritz, B., Alonso, H. 2006. Non-conservative behavior of bromide in surface waters and brines of Central Andes: a release into the atmosphere. Geochemical Cosmochemical Acta: 70, 2143–2152.

Rittenhouse, G. 1967. Bromine in oil-field waters and its use in determining possibilities of origin of these waters. American Association of Petroleum Geologists Bulletin: 51, 2430–2440.

Seaman, J. C., Bertsch, P. M., Korom,S. F., Miller, W. P. 1996. Physicochemical controls on nonconservative anion migrationin coarse-textured alluvial sediments. Ground Water: 34, 778–783.

Shouakar-Stash, O., Alexeev, S. V., Frape, S. K., Alexeeva, L. P., Drimmie, R. J. 2007. Geochemistry and stable isotopic signatures, including chlorine and bromine isotopes, of the deep groundwaters of the Siberian Platform, Russia. Applied Geochemistry: 22, 589–605.

Thyne, G., Guler, C., Poeter, E. 2004. Sequential analysis of hydrochemical data for watershed characterization. Ground Water: 42, 711–723.

Tweed,S., Leblanc, M., Cartwright, I., Favreau, G., Leduc, C. 2011. Arid zone groundwater recharge and salinization processes; an example from the Lake Eyre Basin, Australia. Journal of Hydrology: 408, 257–275.

WHO. 2011. Guidelines for drinking-water quality. 4th ed. World Health Organization; [accessed at http://www.who.int/water_ sanitation_health/publications/2011/dwq_ guidelines/en/ on 09.11.2011].

Wood, W. W., Sanford, W. E. 2007. Atmospheric bromine flux from the coastal Abu Dhabi sabkhat: a groundwater mass-balance investigation. Geophysics Research Letter: 34, L14405).

Zamani, F. 1999. Sedimentology Arak Mighan Lake. MSc. thesis in Beheshti University of Tehran, Iran.

Zhao, M., Zeng, C., Liu, Z. H., Wang, S. J.2010. Effect of different land use/land cover on karst hydrogeochemistry: a paired catchment study of Chenqi and Dengzhanhe, Puding, Guizhou, SW China. Journal of Hydrology: 388, 121–130.