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Sources of Nitrate and Bromide Contaminants in Groundwater of the Alluvial Aquifer of Arak, Iran

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ABSTRACT

The present study investigated $NO3^-$ and Br^- contamination in groundwater of Arak aquifer, Markazi province, Iran. Correlation and factor analyzes were used to detect interrelations and sources of $NO3^-$ and Br^- ion concentration and other physicochemical variables. No correlation was observed between $NO3^-$ and others contents, but a positive correlation was identified between Br^- and other major variables such as EC, TDS, Cl^- and $SO4^{2-}$ in the groundwater. The results showed that groundwater samples of two areas of Arak aquifer were severely contaminated by $NO3^-$ (up to 50 mg/L) and Br^- (up to 0.5mg/L), which exceeded the WHO and EU provisional guideline values. Nitrate showed an anthropogenic source that originated from sewage water from domestic and industrial activities. Bromide originated from palaeo-salty water of Mighan Lake with a geogenic source.

Keywords

Arak aquifer; Factor analysis; Mighan Lake; Nitrate and bromide; Salty water

1. Introduction

Sewage water is considered as a significant source of NO_3^- and Br^- into the groundwater. Groundwater NO_3^- contamination is a threat to human health (Bryan and Loscalzo, 2011; Johnson et al., 2010). Nitrate has been listed as one of the most common groundwater contaminants by the WHO (2011). High nitrate levels in water can result in 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; Gu et al., 2013; Baily et al., 2012; Pastén-Zapata et al., 2014). 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).

Bromide is one of the halogen elements found in trace amounts in all ground water. 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

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1*Corresponding Author email: drghadimi@yahoo.com 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). In dilute natural waters, the main control on the geochemistry of Br^- is likely to be the source of salinity. The hydrogeochemistry of Br^- is very similar to that of Cl^-. 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 was to assess the influence of the natural and anthropogenic activities on the groundwater quality of the Arak aquifer using hydrochemical methods and factor analysis on 36 samples. In order to interpret the complex groundwater hydrochemistry of Arak aquifer, the origin and interconnection of these water types were first explained in relation to the shallow groundwater and mixing with palaeo-saltwater and human intervention. Then, factor analysis was used to identify the major natural and anthropogenic processes occurring in the entire plain by extracting several factors.

2. 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 the eastern part. Paleogene assemblages consist of the 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. The Mighan Lake, which is located 1700 m above the sea level, has an area of about 5500 km^2 and is a closed basin. The mean annual temperature and precipitation are 14^o C and 350 mm, respectively. This lake is fed by fresh water from the whole margins. The lake water chemistry is dominated with Na^+, Mg^{2+} , Cl^- , $SO4^{2-}$ ions and also contains smaller amounts of Ca^{2+} , K^+ and HCO_3^- ions (Zamani, 1999). Bedrock of these formations is composed of the crystalline limestone with low metamorphism rocks. The study area is situated in the alluvial plain and the aquifer is directly fed by the 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.

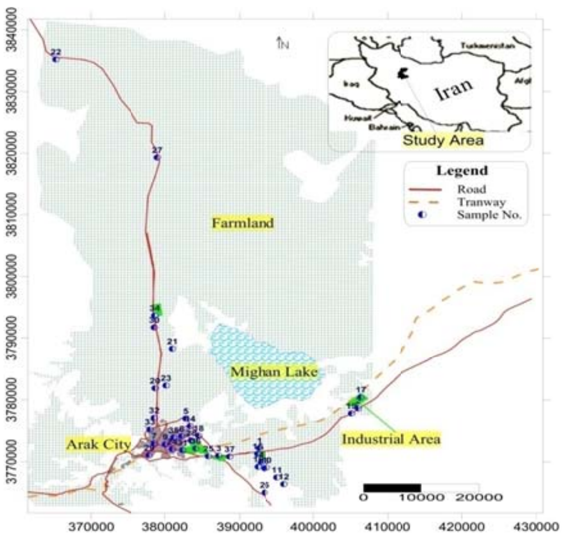

Fig.1. Location of the study area and sampling sites in the Arak city.

3. Materials and Methods

3.1. Sample collection and chemical analysis

Alluvial groundwater samples were collected from 36 wells in September, 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 $HCO3^-$ concentrations. Samples for the laboratory analysis were immediately filtered through 0.45 μm cellulose membrane filters. Samples were acidified to pH by adding several drops of ultra-pure nitric acid for the analysis of cations and were kept at 4 °C in an ice box before the 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 solids (TDS) value was calculated by adding the mass of analyzed ions plus Si^{4+}. Quality control of the analytical data was done by routinely analyzing blanks, duplicates, and standards and by checking ion balances. The ion balance errors for the analyzes 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 the analysis. Because some of the variables were not symmetrically distributed, normality of each variable was examined based on the skewness and and if a variable does not have normality, variables were transformed (Reimann and Filzmoser, 2000). In the present data set, none of the variables passed this normality distribution (except pH, Si^{4+} and NO_3^-) (Table1). Therefore, Logratio transformations were conducted for the skewed variables to achieve the 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 classes of Logratio transformations with good theoretical properties. In addition to data transformation, all the 15 variables were standardized as follows (Eq.1):

$$\mathrm{Ilr}\,(\mathrm{x}) = \sqrt{1}/2Ln\left(\frac{xi}{xj}\right) \qquad (1)$$

where *ilr* (x_i) is the normalized and standardized value for x_i (=i*th* variable for j*th* sample) and x_j is the mean of variables. Through the standardization procedure by the isometric Logratio, the influence of different units of measurement was eliminated. Thus, each variable obtained 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. This transformation is defined in such a way that the first factor accounts for as much of the variability in the data as possible, and each succeeding factor in turn has the highest variance possible under the constraint that it be orthogonal to (i.e., uncorrelated with) the preceding factors (Jolliffe, 2002). As a multivariate analysis method, factor analysis can provide a powerful tool for analyzing the complex high dimensional hydrochemical data sets of groundwater. 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). Factor analysis was performed to evaluate the correlations among the multivariate variables. The factor analysis was develop-ed 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 were 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. In factor analysis, the response variable was continuous and unbounded, i. e. the predicted response variable can take any value. However, 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 [0, 1] interval. 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, the logistic function has been used to fuzzy FSs (FFS) of each sample per indicator factor, thus (Eq. 2):

$$FFS= e^{Fs}/1+e^{Fs} \qquad (2)$$

where F_s is the factor score of each sample obtained in the 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 F_Ss of samples per indicator factor obtained in the factor analysis.

4. Results and discussion

4.1. Hydrochemical study

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 Fig. 2. They suggested 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 were 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, were however higher than their respective WHO (2011) and EU (1998) standards of 50 mg/L and 0.01 mg/L, respectively. 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) standards, 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, respectively correspond to total dissolved solid concentrations of 789 mg/L and 586 mg/L, respectively which were below the WHO (1984) guideline value of 1000 mg/L. Maximum concentrations of some of the major ions such as Na^+ and Cl^- were 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. The pH was neutrality but it was well within the acceptable range. The aquifer of the Arak formation, which is mostly a sedimentary aquifer, therefore produced a 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 were higher than the WHO (2011) values. There were, 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 was negatively correlated with NO_3^- concentration. In contrast, the relationship between TDS and Br^- was positively correlated. Positive relationships between TDS and Br^- values reveals that the hydrochemistry of alluvial groundwater in the study area was controlled by saline water processes.

Table 1. Descriptive statistics for 15 physicochemical variables for alluvial groundwater in the Arak area

	Mean	Geometric-Mean	Median	Minimum	Maximum	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

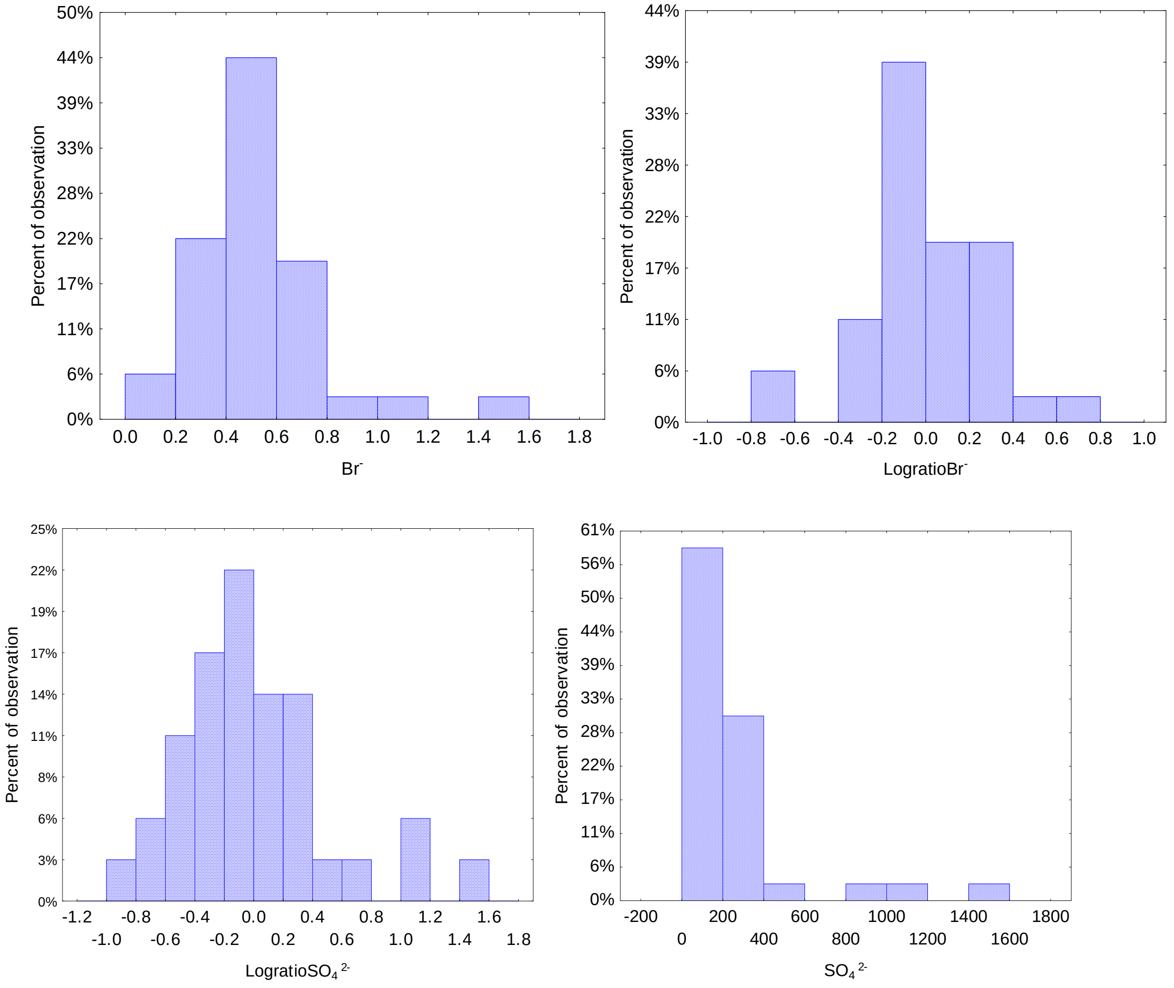

Fig.2. Raw Br^- and SO_4^{2-} data and Logratio-transformed Br^- and SO_4^{2-}data

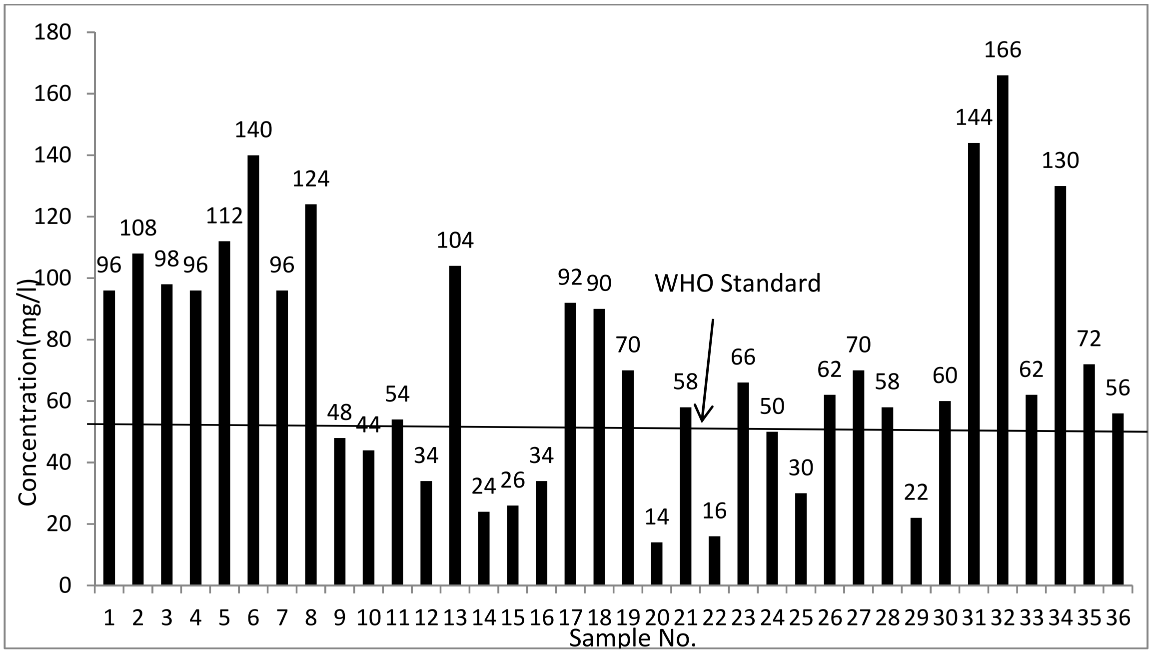

Fig. 3. NO_3^- concentration in 36 boreholes for alluvial groundwater in the Arak area (for sample no. refer to Fig.1)

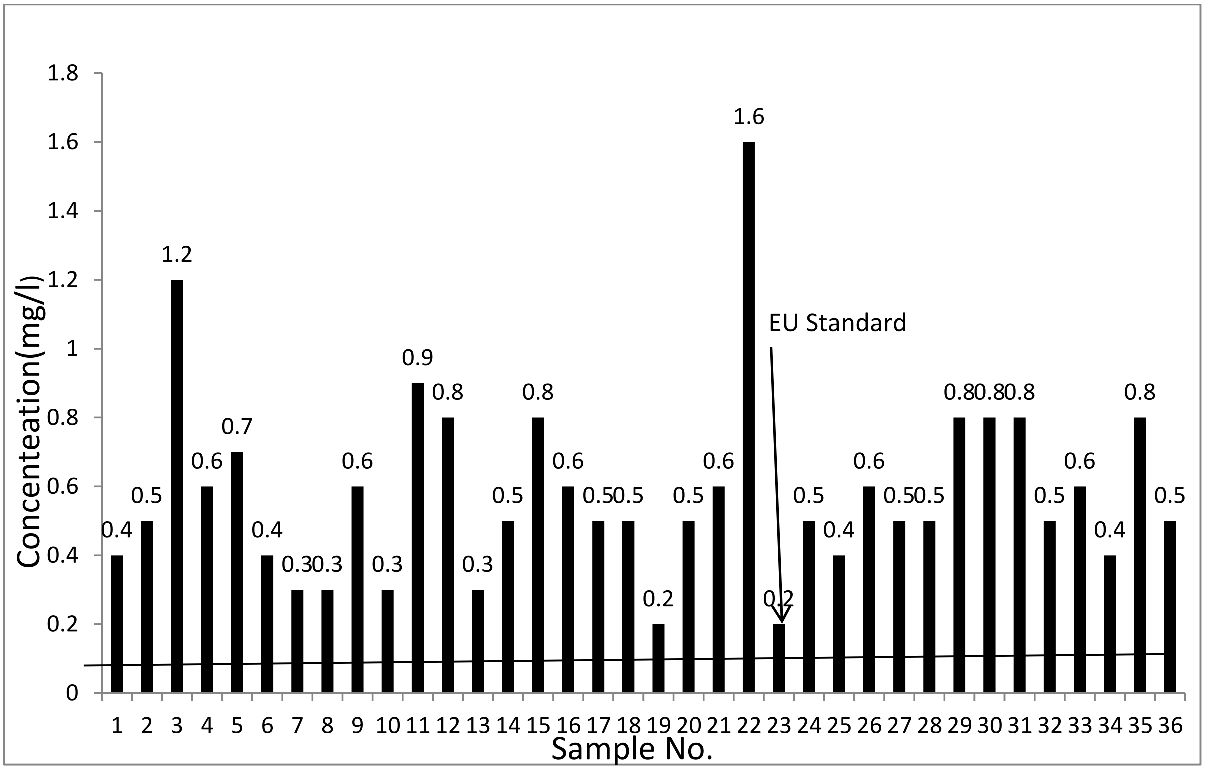

Fig. 4. Br^- concentration in 36 boreholes for alluvial groundwater in the Arak area (for sample no. refer to Fig.1)

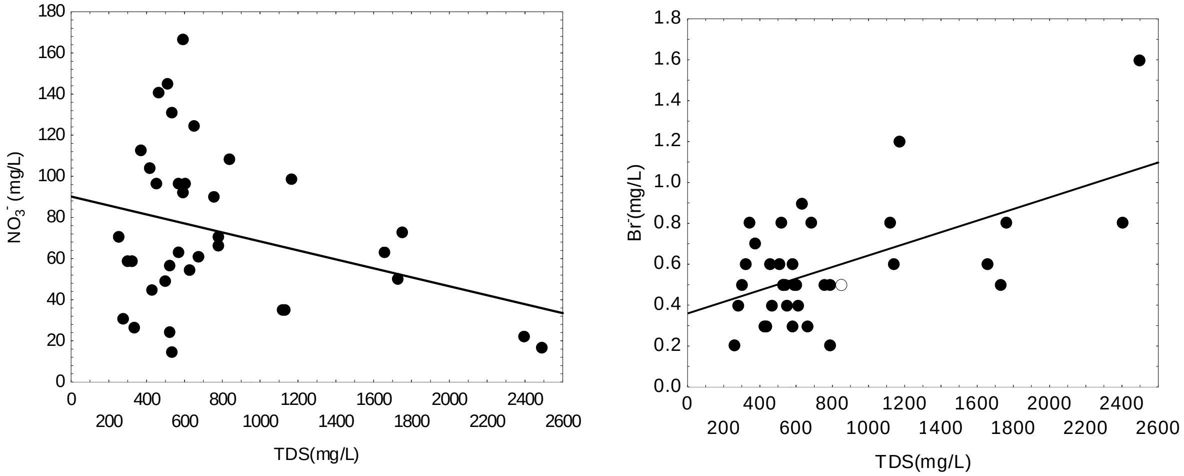

Fig. 5. Relationship between TDS with NO_3^- and Br^-

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

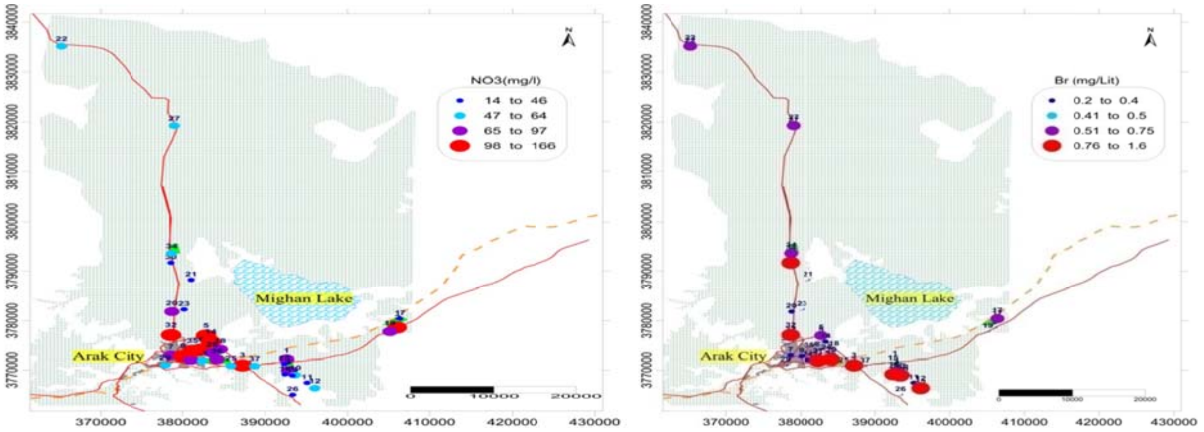

Fig. 6. Distribution of NO_3^- and Br^- variables in groundwater of the Arak aquifer. The values in the scale bar of each map correspond to the minimum, 25th percentile, 50th percentile, 75th percentile, and maximum data

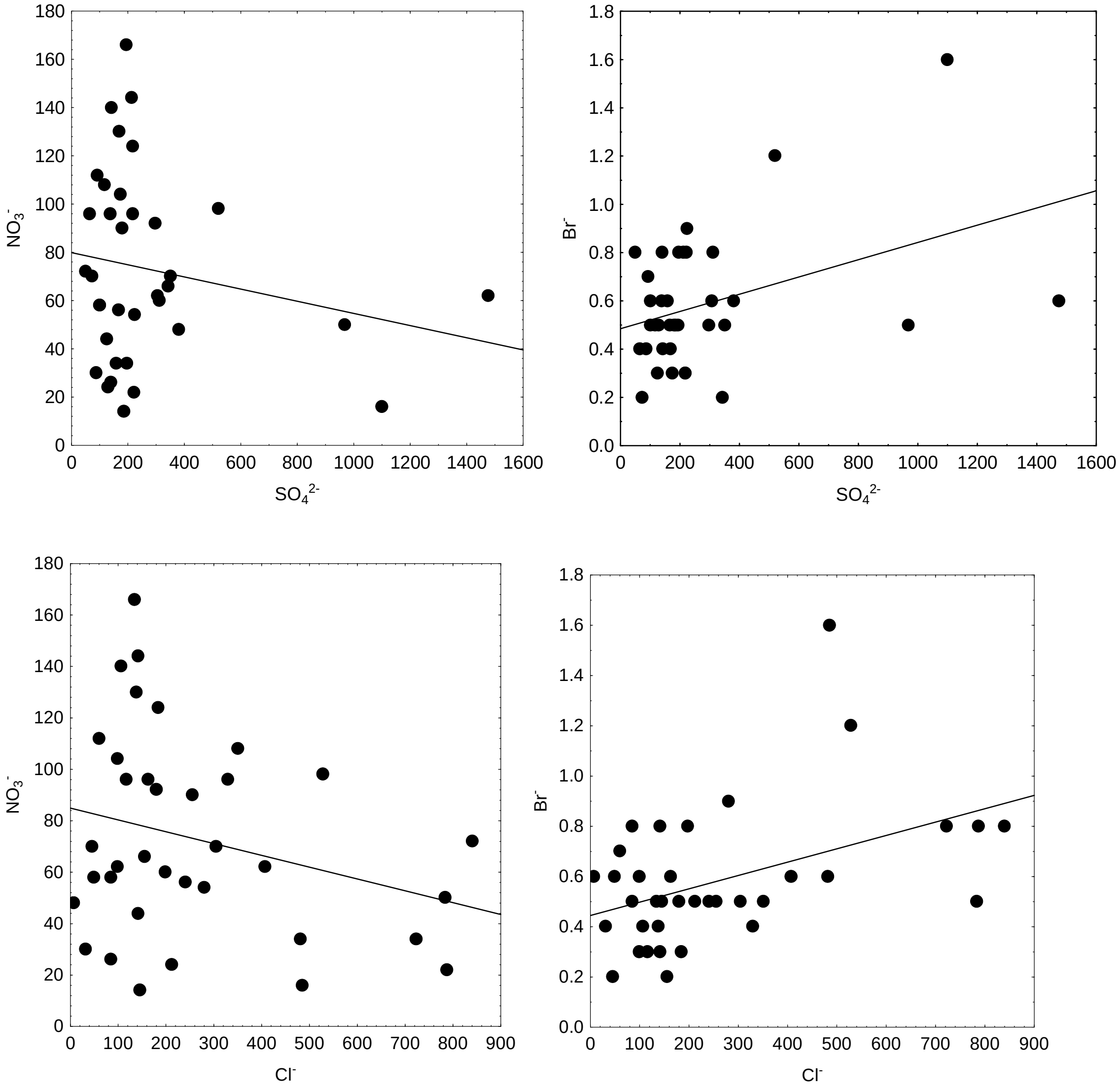

Fig.7. Relationship between SO_4^{2-} and Cl^- with NO_3^- and Br^-

4.2. Correlation between the 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 the Mighan Lake (Ghadimi and Ghomi, 2012). Therefore, 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) indicated that they are likely derived from the dissolution of carbonate (Jiang et al., 2009) as well as the 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). 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 values. However, the correlation between SO_4^{2-}, Br^-, Cl^-, Na^+ and Mg^{2+} suggested that palaeo-salt water intrusion plays a more important role. In addition, the occurrence of cation exchange in the discharge zone induced an increased correlation between Cl^-, Ca^{2+} and Mg^{2+} and a decreased correlation between HCO_3^- and Ca^{2+} (-0.08). The weak negative correlation between HCO_3^- and Ca^{2+} also suggested 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 r values ranging from 0.79 to 0.86) suggested that both palaeo-salt water intrusion and mineral precipitation/evaporation of mineral deposits are important factors contributing to the groundwater chemistry of the Arak aquifer. The pH showed 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 the 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 they either originate from the pollution or from the carbonate area (Ozsvath, 2006; Kern et al., 2008; Ghadimi and Ghomi, 2012).

Table 2. Correlation matrix of the 15 physical–chemical variables of the 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

4.3. Factors controlling the groundwater chemistry

The chemical composition of groundwater reflects the geologic source and contaminants from the 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 an 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 Varimax method, where both Kaiser criteria were used to determine the number of factors. In this study, 15 variables were combined by applying the factor analysis to produce five significant factors explaining 81.80% of the variance of the original data set (Table 3 and Fig. 8).

Table 3. 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

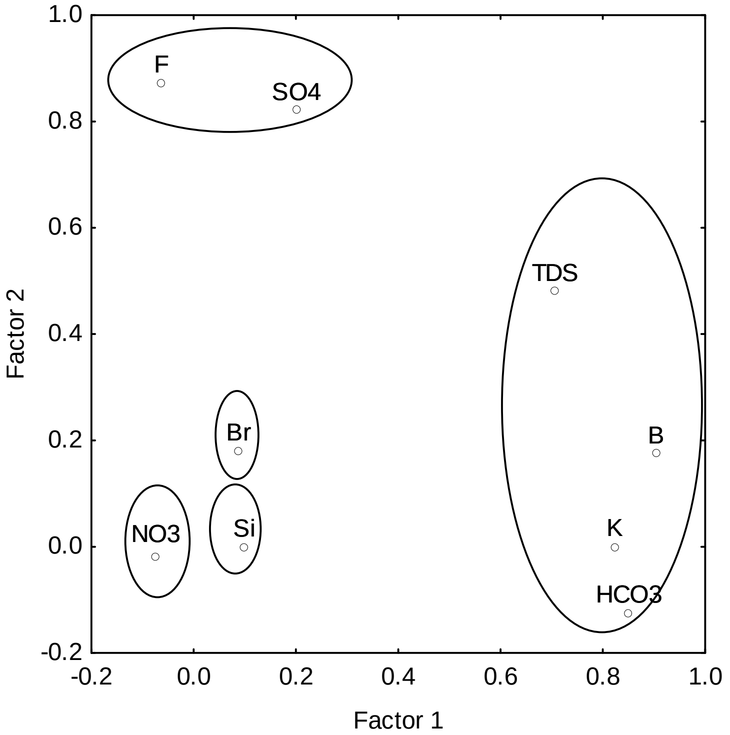

Fig.8. Relationships between different factors illustrated in loading plots

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). Factor 1 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 Na^+, SO_4^{2-} and F^- elements. Factor 2 includes classical hydrochemical variables that indicate salinization processes. It is also worth mentioning that in the Arak aquifer, the highest values of Na^+ and SO_4^{2-} generally occur in the low gradient areas intruded by the salty water. In addition, 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, salty water 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 the 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 the Mighan Lake and where saline water activities of the Lake are widespread. Several factors control the general distribution of Cl^-/Br^- ratios in the ground water. The most important factor is probably the distance from the recharge area to the nearest source of particulate Cl^-, which most commonly is around the saline lakes (Tweed et al., 2011). Based on Fig. 9, approximately 83% of the samples were located above the marine line. Therefore, these groundwater samples are originated from saline waters. The only saline water in the study area is the Mighan Lake (Fig. 1). It is obvious that Br^- ions in the groundwater have a non-anthropogenic source (natural source). Finally, the fifth factor has the most negative strong contribution to NO_3^- that explains 7.21% of the total variance (Table 3). Nitrate and Br^- have an opposite relationship in the Arak aquifer (Fig. 10). Therefore, NO_3^- has another source and has originated during the anthropogenic activities. Most of the ground-water wells that are located in the urban area of Arak have NO_3^- problem. Approximately, every family has at least one disposal waste water in the house and there are many industrial ones in the urban area that intrude sewage water to the groundwater (Ghadimi and Ghomi, 2012).

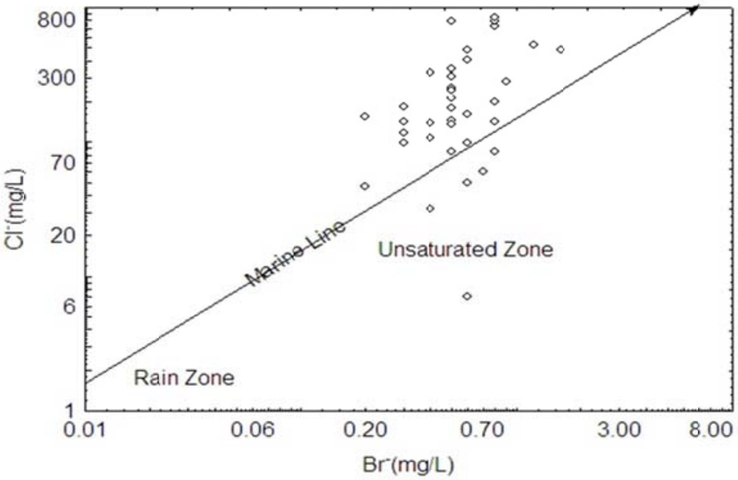

Fig. 9. Cl^-/Br^- relationship in the Arak groundwater relative to Cl^-/Br^- in the sea water, in rainy and unsaturated zone (Edmunds, 1996).

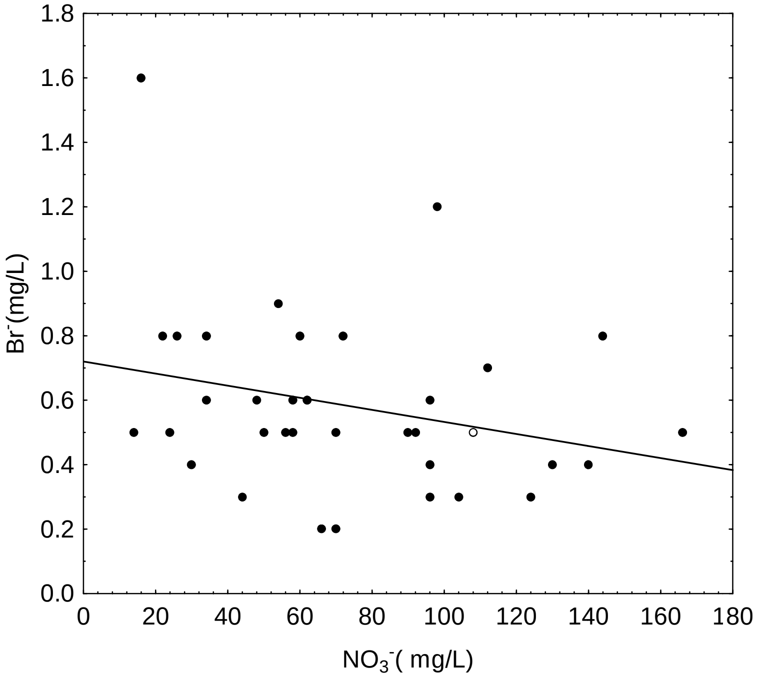

Fig.10. Relationship between NO_3^- and Br^-

Factor scores (FS) can be related to the intensity of the chemical process described by each factor, 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 shows the spatial distribution of the factor scores for two factors. For NO_3^- in Fig. 11, high scores (i.e., values from 0.14 to 2.13) were generally observed at the central parts of the study area, where anthropogenic activities are high. However, high scores of Br^- (i.e., values from 0.11 to 2.3) were identified at the peripheral parts of the Mighan Lake, where natural effects are significant. Tweed et al. (2011) showed that the content of Br^- was high in Eyre Lake, but it decreased in groundwater of the peripheral lake. In addition to palaeo-salt water as the source of Br^- in the study area, it may have an atmospheric origin. The Br^- concentrations in the atmosphere may be due to flux of Br^- from the salt lakes 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 in comparison to the ordinary factor score for the fuzzification of NO_3^- and Br^- data to generate an evidential map (Fig. 12). Distribution of NO_3^- and Br^- in the fuzzy factor score is similar to the factor score map.

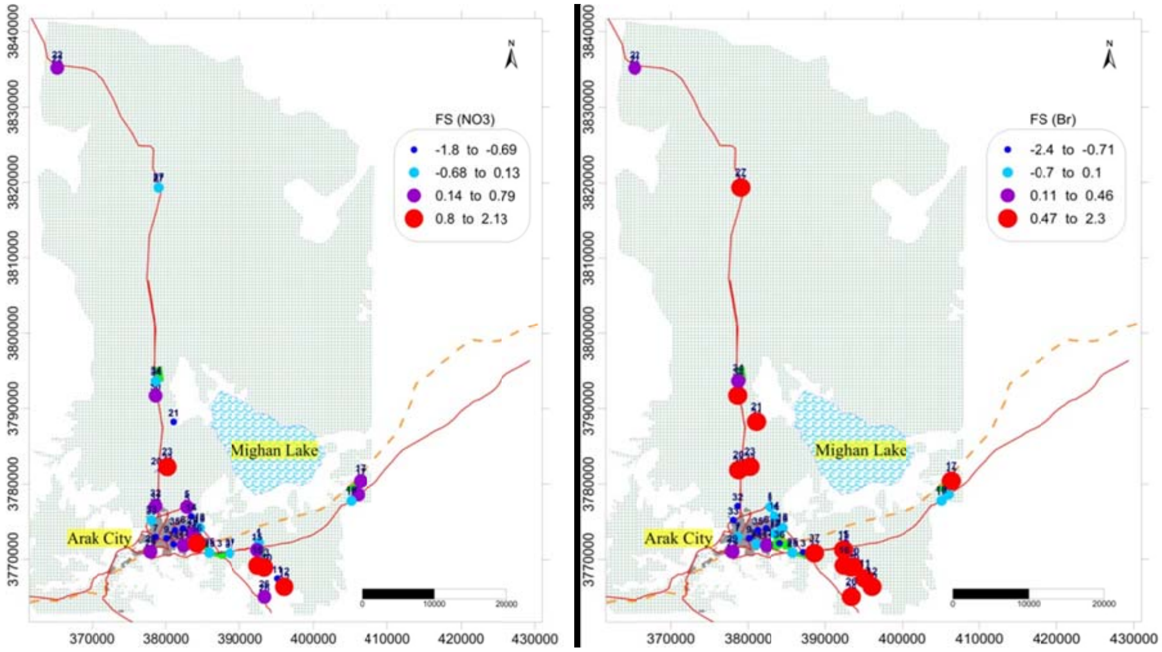

Fig.11. Spatial distribution of the NO_3^- and Br^- factor scores (FS) obtained by the factor analysis of the groundwater samples in Arak aquifer. The values in the scale bar correspond to the minimum, 25th percentile, 50th percentile, 75th percentile, and maximum data

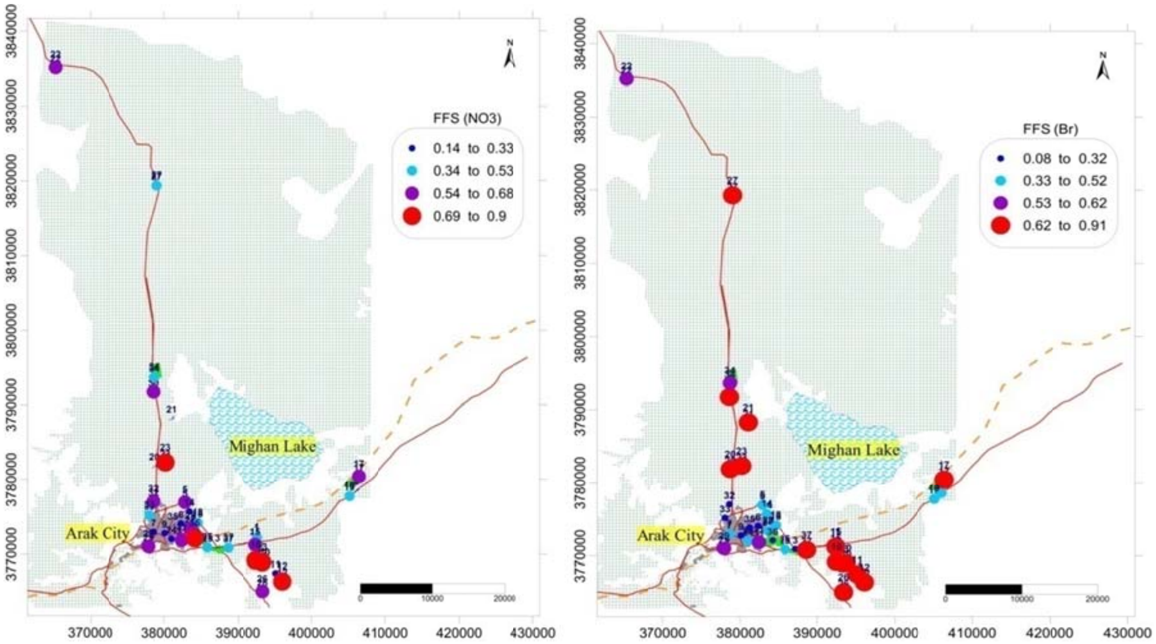

Fig.12. Fuzzy factor scores (FFS) of NO_3^- and Br^- in the Arak aquifer. The values in the scale bar correspond to the minimum, 25th percentile, 50th percentile, 75th percentile, and maximum data

5. Conclusions

Correlation and factor analysis have been proven a useful tools in providing insight to the problem of NO_3^- and Br^- contamination in the alluvial groundwater of the Arak aquifer. These tools have improved our understanding of the role of sewage water and intrinsic factors such as aquifer lithology and salty water in the Mighan Lake on the NO_3^- and Br^- contamination degree. In the study area, high NO_3^- and Br^- concentrations were seen to occur preferably in the urban areas and lowland of the 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 the NO_3^- ion occurs in the urban area of Arak. The main source of NO_3^- that is released into the 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 as a potential source.

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