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RESEARCH PAPER

# Hydrochemistry and Stable Isotopes Characteristics of Groundwater in an Urban Aquifer, Southwest of Iran

**Hassan Daneshian [1],*, Nasrollah Kalantari [1], Farshad Alijani [2]**

[1] Faculty of Earth Sciences, Shahid Chamran University of Ahvaz, Golestan Blvd., Ahvaz, Iran
[2] Faculty of Earth Science, Shahid Beheshti University, Evin, Velenjak, Tehran, Iran

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## Abstract

The effect of different recharge sources on the chemical evolution of an urban aquifer, Behbahan plain, southwest of Iran, has been studied using hydrogeochemistry and stable isotopes ($^{18}O$ and $^{2}H$). Groundwater samples were collected from 40 water wells in June 2017 and April 2018 as the dry and wet periods, respectively. The water samples were analyzed for the determination of major ions, nitrate, fluoride, and bromide for both periods and stable isotopes concentrations only for the dry period. The main hydrochemical characteristics of groundwater sources in the Behbahan plain were determined as natural groundwater recharge (R) and discharge (D) areas, Marun (M) and Bonehbasht (B) irrigation and drainage networks, contact with gypsum bedrock (G) of the Gachsaran formation, and waste water of Behbahan City (T). The hydrochemical maps of electrical conductivity, chloride, ionic ratios, stable isotopes, and nitrate concentrations was investigated to determine anomalous groundwater zones associated with urban sources of groundwater pollution. Characteristic bivariate composition diagrams and cluster analysis (CA) method were employed to identify the hydrochemical processes and to evaluate the recharge sources. Two major water types Ca–SO4 and Ca (Na)–SO4(Cl) were present in the Behbahan groundwater plain. The high concentrations of $SO_4^{2-}$, $Ca^{2+}$, and $Mg^{2+}$ were reflected in moderate to high total dissolved solids (TDS) (about 3000 mg/l). The dominant hydrogeochemaical processes in the aquifer were the dissolution of gypsum and somewhat halite, dedolomitization, scant normal and reverse cation exchange, and mixing. The main sources of the nitrate pollution of groundwater were leaching of organic manure applied to cultivated areas as well as wastewater of Behbahan City. The minimum and maximum concentrations of nitrate in groundwater of the Behbahan plain were 5 to 105 mg/Land 5 to 150 mg/L in dry and wet periods, respectively. About one–third of groundwater samples in the Behbahan plain had $NO^{3-}$ concentrations above the drinking water standard (45 mg/L). Five distinct recharge sources were recognized for the Behbahan aquifers based on the characteristics of $^{2}H$ and $^{18}O$ isotopes. The hydrochemical characteristics and stable isotope indicators of the groundwater recharge sources are disturbed as a result of the mixing process.

**Keywords:** Hydrochemistry; Stable isotopes; Groundwater; Nitrate; Iran.

## Introduction

Groundwater is the source of drinking water for many people around the world, especially in urban areas. This has become the most concerning issue for most countries in the Middle East. In addition to being vital for drinking, agriculture, and industries, it can contribute to socio-environmental problems. The population of Iran has rapidly doubled in the past 40 years and as a result, the use of water for different purposes has increased enormously in this country. Agriculture uses the major portion of available freshwater where about 60% of this water is

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* Corresponding author e-mail: h.d6643@yahoo.com

wasted due to inefficient agriculture methods and leaky irrigation systems. In addition to this, pesticides and fertilizers are also leached into the aquifers.

Groundwater can become contaminated naturally or because of numerous types of anthropogenic activities. Urban, industrial, and agricultural activities can degrade groundwater quality in different ways. Immethodical use of fertilizers, irrigation activities, and infiltration of urban waste water can lead to elevated nitrate levels in the subsoils which can leach into the aquifer, causing degradation of groundwater quality, especially in the urban aquifers. The sustainability of safe groundwater resources is the most important challenge in the urban areas, as exacerbated by the increasing water shortage in arid climates. The exploitation of groundwater is related to understanding groundwater sources, groundwater quality, and anthropogenic activities.

The effect of human activities on groundwater chemistry is probably greatest in vulnerable hydrogeologic settings, such as karstic aquifers or shallow parts of sand and gravel aquifers. The occurrence of high nitrate concentrations in groundwater in response to the interaction of agricultural activities, wastewater, and septic effluent infiltration in urban areas has been reported in many previous studies (Showers et al., 2008; Xue et al., 2009; Burow et al., 2010; Zhang et al., 2018).

Over the past few decades, many investigations have dealt with application of hydrochemical methods (Monjerezi et al., 2011; Nandinamandalam 2012; Xiao et al., 2015; Yidana et al., 2017), environmental tracers (Li et al., 2011; West et al., 2014; Petelet-Giraud et al., 2016; Joshi et al., 2018), multivariate statistical techniques (Kshetrimayum, 2015; Kshetrimayum & Laxmi, 2017; Bodrud-Doza et al., 2018; Khanoranga, 2018) and so forth to identify the origins and sources of groundwater. Groundwater chemical and isotopic composition offer unique information to determine the sources, residence time, mixing, mineralogy, and hydrogeochemical processes. The hydrochemical and isotopic composition of groundwater characterizes the interaction between the water and lithology, and reflects the history of groundwater migration in the aquifer (Barbieria et al., 2005; Zhu et al., 2007; Yangui et al., 2011; Morán-Ramírezet et al., 2016). However, when it comes to urban aquifers, a great deal of ambiguity arises in the interpretation of hydrogeochemistry in urban aquifers due to the simultaneous effects of geogenic and anthropogenic factors or mixing (Fukada et al., 2004; Choi et al., 2005; Bottrell et al., 2008; Hosono et al., 2010; Salcedo Sánchez et al., 2017). The anomalous hydrochemistry is complex, especially with respect to groundwater flow. The hydrochemical studies in an urban aquifer should be done with regards to the amounts and duration of infiltration and rising of groundwater level. However, evaluating the impact of recharge on groundwater resources in an urban environment is different from assessing the effect on natural systems for three reasons (Tam & Nga, 2018): (1) recharge sources being radically different; (2) lack of detailed information on the sewerage system and water distribution system as well as the position, duration and volume of water leaked from these systems; and (3) reduction of recharge and decline of groundwater level due to urbanization. They are inter-related as mentioned above, which cannot be independently quantified by a single simulation. Multivariate statistics are useful tools to conclude other findings and obtain significant information from complex hydrochemical datasets in aquifers.

This study attempts to identify the recharge sources of the Behbahan aquifer as well as main hydrogeochemical processes controlling groundwater quality to distinguish the effects of water-rock interactions, infiltration, and mixing. Despite the reported pollution of the Behbahan alluvial aquifer, detailed studies of the hydrogeochemistry and groundwater contamination have not been conducted yet. In the Behbahan plain, the southern part of the plain functions as an urban aquifer, where nitrate contaminations of groundwater (more than 45 mg/L NO3) have also been reported over the last decades. Irrigation water is mainly supplied from the Marun and Boneh Basht irrigation as well as drainage networks across 80 km$^2$ of the plain. The main objective of this study is to describe hydrochemical and stable isotopes characteristics of the groundwater in Behbahan alluvial aquifer using graphical and multivariate statistical methods to identify various recharge sources of contamination, with emphasis on nitrate pollution of the aquifer.

## Materials and Methods

### *Study Area, Geology, and Hydrogeology*

The study area is a 430 km$^2$ alluvium at 330 m a.s.l., located in the southwest of Iran, approximately 200 km northeast of Ahvaz and 1100 km southwest of Tehran (Fig. 1). The study area is located between the 30°30′ and 30°40′ and the 50°08′ and 50°23′ geographic latitude and longitude, respectively.

The main river running through the Behbahan plain is the Marun River. The study area includes the Behbahan City plus the Marun and Bonehbasht irrigation and drainage networks. In the surrounding environs, the primary land use is agriculture in the networks with crops such as corn and wheat grown by the farmers. In the study area, Behbahan City is the main population center, with over 130,000 inhabitants.

The average annual rainfall is 370 mm, with the major part of the precipitation format the late of autumn and early spring thunderstorms. The main annual temperature is 30$^o$C, with a July high of 50$^o$C and a February low of 5$^o$C. The average annual transpiration from the free surface of the water is 2900 mm. The climate across the Behbahan requires farmers to supplement precipitation with irrigation to sustain their crops. Overall, 70% all irrigations uses surface water of the Marun and Boneh Basht rivers, about 150 MCM (million cubic meters) in the year on the southern part of the plain. The remaining cultivation areas are supplied by groundwater as 30 MCM per year.

The commonly used N and P fertilizers include urea, ammonium sulfate, and super phosphate. The N fertilizers are applied to the vast grain-fields on early February, with an application rate of 100 Kg/ha. The Marun River flows in the middle of the plain with an average discharge of 80 m$^3$/s which is considered as the northern boundary of the study area. The drinking water for Behbahan City, 10 MCM per year, is supplied from Kheirabad River, 10 km east of the plain.

Concerning regional geology, the Behbahan region is located in the Folded Zagros zone. Geological formations from Oligo-Miocene to recent age have outcrops in Behbahan area (Fig. 1). Thick limestones of the Asmari formation are overlaid by gypsum and marl beds of Gachsaran formation, sandstone, and marl of the Mishan and Aghajari formations, conglomerate of the Bakhtiari formation, and alluvial sediments, respectively. Although Gachsaran formation has some outcrops in the margin of the plain (Fig. 2), there are residuals of this formation, including gypsum, halite, and marl in the alluvium that deteriorate the groundwater quality, considerably. Quaternary sediments include pebble, gravel, sand, and some silt composed of alluvial fans in the border of Behbahan plain. Fine sediments such as silt, clay, and fine sand are deposited beneath the plain locally. The thickness of the Behbahan unconfined aquifer ranges from 40 m in the marginal areas to over 150 m in the middle parts.

The Behbahan unconfined aquifer is composed of gravel and silty sand deposits with hydraulic conductivity ranging from 1 to 7 m/day. This lithological unit overlies fine sediments (silt and clay) with very low hydraulic conductivity in the east of the plain. The main surface recharges to the Behbahan alluvial aquifer include infiltration of rainfall, irrigation water, as well as the Marun and Boneh Basht irrigation and drainage networks. The Khaviz karst aquifer, in the north east of the Behbahan plain, is the main source for subsurface recharge of the aquifer, though the underground recharge from the Bakhtiari and Gachsaran formations also occurs, with high and low quality of groundwater, respectively.

Depth to the water table ranges from 3 m in the Behbahan City to higher than 32 m in the northwest of the plain. The iso-potential map (Fig. 2) provides a good description of the alluvial aquifer. According to the iso-potential map of the aquifer, it can be seen that the ground water elevations range from 335 m in the recharge areas in the southeast of the plain to lower than 290 m in the discharge area in the west. The highest groundwater elevations exists in the north of the plain. The groundwater head distribution for the Behbahan aquifer shows recharge zones, on the eastern and northern sides of the plain through the Bakhtiari and Asmari formations, respectively. The groundwater flow lines are oriented towards the discharge area in the west of the plain.

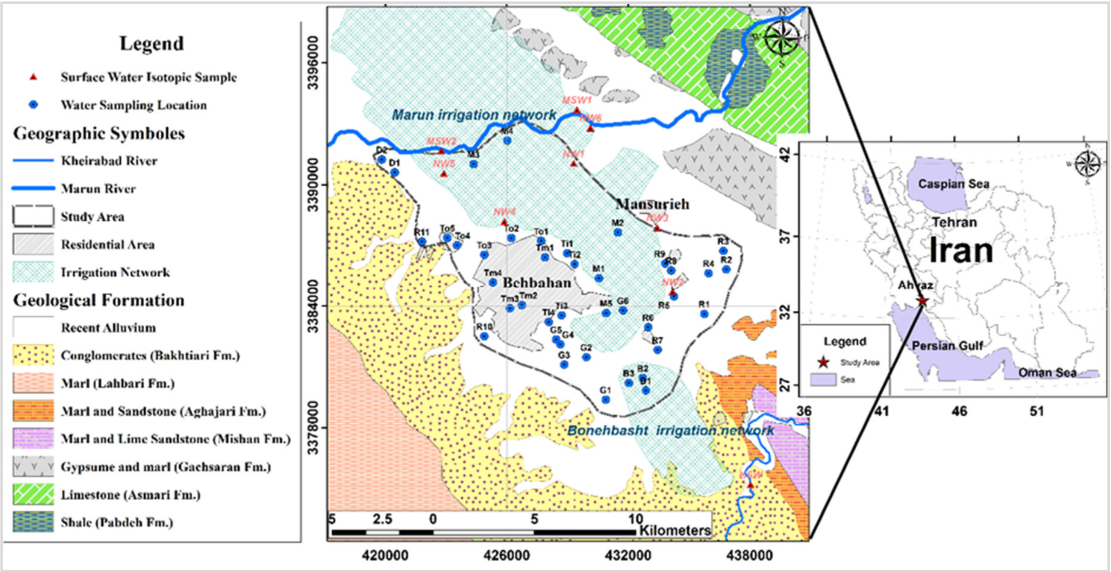


**Figure 1.** Location map of the Behbahan plain in the southwest of Iran

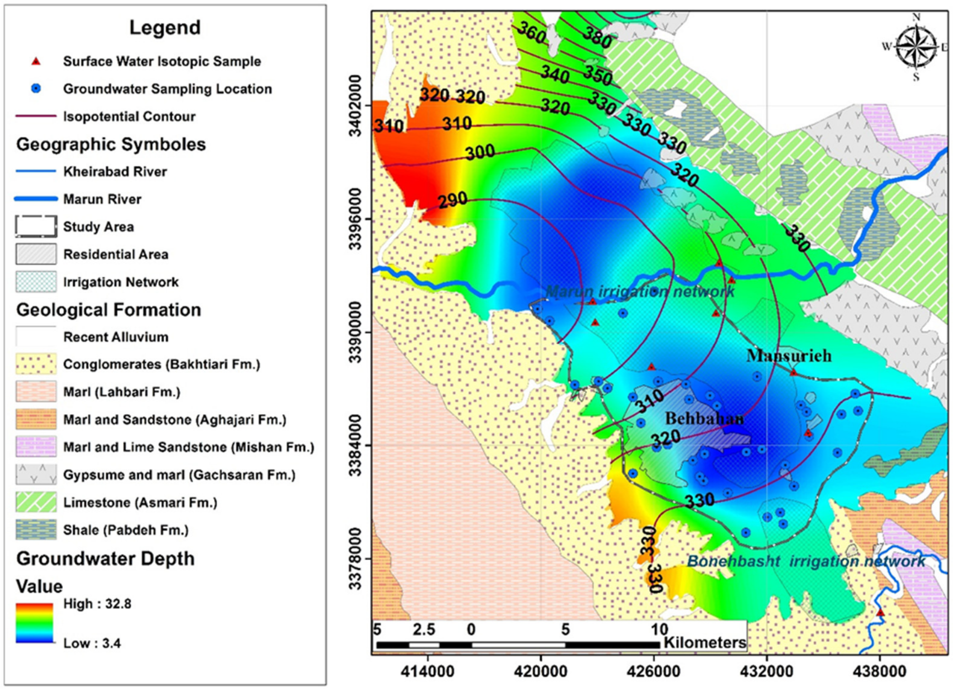


**Figure 2.** Location of groundwater samples on hydrogeological map of the Behbahan Plain

Although the main recharge sources of the aquifer are infiltration from the irrigation networks and wastewater of Behbahan City, the directions of flow lines are not affected significantly.

The groundwater has been exploited from the Behbahan aquifer to supply agricultural activities. Surface water infiltration of the Behbahan aquifer from the irrigation water (150 MCM annually) and the presence of fine layers in the uppermost part of the aquifer caused rising groundwater levels in the west of plain, despite the occurrence of drought since 2008, causing serious problems for the Behbahan City.

## Data Collection

The groundwater sampling (number of water samples, periods of sampling, types of water sources, depth of sampling, and selection of representative samples) is dependent on the aim and type of the study, spatial changes in groundwater quality, extent and type of the aquifer, and economical considerations. Groundwater samples were collected from 40 water wells in the Behbahan plain in both wet and dry periods, June 2017 and April 2018 in according to dry (minimum level of water table) and wet periods (maximum level of water table), respectively. The depth of the selected water wells for sampling ranges from 40 to 80 m for avoiding of local variability in groundwater quality at shallow depth of the aquifer due to infiltration from the different sources. They are named with respect to their probable origins as (1) natural groundwater recharge (R) and (2) discharge (D) areas, (3) the Marun (M) and (4) Bonehbasht (B) irrigation and drainage networks, (5) in contact with gypsum bedrock (G) of the Gachsaran formation, and (6) waste water of Behbahan City (T).

The sampled wells were distributed throughout the southern part of the Behbahan plain (Fig. 2) because of diversity in recharge sources of the aquifer. The sampling water wells have been selected to reflect the process of qualitative changes due to different recharge resources, taking into account the groundwater flow directions and the focus of human and agricultural activities on the plain. Forty water wells were selected for sampling in the Behbahan aquifer (well depth between 40 to 80 meters). Average representative area of a water sample is 3.45 km$^2$, considering the extent of the study area in the southern half of the Behbahan plain (138 km$^2$), which may allow a detailed analysis of the groundwater system. This coverage of groundwater sampling locations is unique in hydrogeochemical studies and can therefore be assured that all possible anomalies and recharge sources be identified in the groundwater system. Sampling procedures consisted of well purging, sample collection, and sample preservation (when required). The water samples were analyzed for determining major ions, nitrate, fluoride, and bromide for both periods and stable isotopes concentrations only for the dry period, because of financial limitations.

The pH, temperature, and EC were measured in the field using a portable instrument model HACH. One sample was placed in 250 ml polyethylene bottle (for analyses of major ions, $NO^{3-}$, $Br^-$, and $F^-$). Samples were acidified to pH <4 with concentrated $HNO^{3-}$ for cation analysis. Water samples were filtered with 0.45 micron filter in the field to separate the suspended sediment, and kept at approximately 5 $^oC$ during transport and storage. Hydrochemical analyses were performed at Khuzestan Water and Power Authority (KWPA) Laboratory, in Ahvaz, Iran.

Concentrations of $Ca^{2+}$, $Mg^{2+}$, $HCO3^-$, and $Cl^-$ were analyzed by volumetric titrations, while the concentration of sulfate was measured by turbidimetric method. Also, those of $Na^+$ and $K^+$ were determined using a flame photometer. The analytical errors were determined to be lower than 5 % based on cation–anion concentrations balance for all samples. The $\delta D$ and $\delta^{18}O$ were measured versus the internationally accepted standard V–SMOW with a precision of ±1‰ and ±0.2‰ using a Finnigan MAT–253 isotope–ratio mass spectrometer at Kumamoto University Environmental Hydrology Laboratory, Japan. The results of hydrochemical (Tables 1 and 2) and isotopic analyses (Table 3) of groundwater samples in the Behbahan plain were obtained in June 2017 and April 2018 as the dry and wet periods of the study, respectively.

**Table 1.** Statistical parameters of hydrochemical analysis of groundwater samples in the Behbahan plain in June 2017 as dry season (EC as µS/cm, ion concentrations as mg/l)

| Parameter | T | EC | pH | Ca | Mg | Na | K | $HCO_3$ | Cl | $SO_4$ | $NO_3$ | F | Br |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Max.** | 29.5 | 6610 | 8.0 | 728 | 290 | 641 | 37 | 397 | 728 | 2473 | 102.9 | 2.18 | 1.07 |
| **Min.** | 22.5 | 1537 | 6.6 | 176 | 13 | 37 | 2 | 145 | 55 | 306 | 6.2 | 0.33 | 0.10 |
| **Avg.** | 26.6 | 3608 | 7.1 | 459 | 122 | 251 | 10 | 268 | 365 | 1397 | 42.2 | 1.19 | 0.49 |
| **S.D.** | 1.5 | 1179 | 0.3 | 132 | 71 | 137 | 6 | 53 | 184 | 544 | 24.3 | 0.44 | 0.24 |
| **C.V. %** | 5.7 | 32.7 | 4.7 | 28.7 | 58.1 | 54.5 | 66.3 | 19.7 | 50.4 | 38.9 | 57.6 | 36.5 | 48.6 |

* Max: Maximum, Min: Minimum, Avg.: Average, S.D.: Standard Deviation, C.V.%: Coefficient of Variation as percent.

**Table 2.** Statistical parameters of hydrochemical analysis of groundwater samples in the Behbahan plain in April 2018 as the wet season (EC as µS/cm, ion concentrations as mg/l)

| Parameter | T | EC | pH | Ca | Mg | Na | K | $HCO_3$ | Cl | $SO_4$ | $NO_3$ | F | Br |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Max.** | 28.0 | 6190 | 7.7 | 754 | 329 | 616 | 34 | 370 | 880 | 3116 | 154.0 | 2.11 | 1.12 |
| **Min.** | 21.9 | 1682 | 6.6 | 239 | 51 | 33 | 4 | 145 | 53 | 616 | 4.7 | 0.34 | 0.15 |
| **Avg.** | 25.0 | 3604 | 7.0 | 480 | 136 | 272 | 10 | 250 | 381 | 1551 | 44.1 | 1.19 | 0.49 |
| **S.D.** | 1.3 | 1175 | 0.2 | 133 | 68 | 158 | 6 | 53 | 217 | 584 | 28.8 | 0.42 | 0.25 |
| **C.V. %** | 5.4 | 32.6 | 3.5 | 27.6 | 49.8 | 58.3 | 62.8 | 21.0 | 57.1 | 37.6 | 65.3 | 35.7 | 51.1 |

* Max: Maximum, Min: Minimum, Avg.: Average, S.D.: Standard Deviation, C.V.%: Coefficient of Variation as percent.

**Table 3.** Results of isotopic analysis of groundwater samples in the Behbahan plain in June 2017 as the dry season (δ1 8O and δD as per mil)

| **Groundwater samples** | | | **Surface water samples** | | | |
|---|---|---|---|---|---|---|
| ID* | δD | δ18O | ID* | Sources Type | δD | δ18O |
| G5 | -16.6778 | -5.27756 | NW1 | Irrigation canal | -16.3583 | -4.75662 |
| M3 | -16.4277 | -4.72627 | NW2 | Irrigation canal | -16.7279 | -4.92677 |
| M1 | -16.086 | -5.00572 | NW3 | Irrigation canal | -17.5211 | -5.08986 |
| R8 | -15.7979 | -4.83677 | NW4 | Irrigation canal | -16.6871 | -4.9494 |
| R9 | -15.0407 | -4.62966 | NW5 | Irrigation canal | -17.2713 | -5.01299 |
| M2 | -15.02 | -4.46529 | NW6 | Irrigation canal | -17.1613 | -4.90911 |
| M4 | -14.9922 | -4.37107 | MSW1 | Marun River | -13.3451 | -3.42566 |
| Ti1 | -14.8968 | -4.69056 | MSW2 | Marun River | -11.9198 | -3.78198 |
| G2 | -13.9622 | -4.16842 | KSW | Kheirabad River | -10.0434 | -3.23763 |
| R6 | -13.551 | -4.19237 | | | | |
| R5 | -13.1463 | -4.29742 | | | | |
| B2 | -11.1232 | -3.13245 | | | | |
| B1 | -10.5833 | -3.18504 | | | | |
| G1 | -8.97699 | -3.09843 | | | | |
| G4 | -8.53953 | -2.78984 | | | | |
| To5 | -7.53122 | -2.91767 | | | | |
| R11 | -7.04284 | -3.04435 | | | | |
| R10 | -6.99746 | -3.26637 | | | | |
| G3 | -6.10926 | -3.16782 | | | | |
| R3 | -6.07147 | -2.8356 | | | | |
| Tm3 | -5.56837 | -2.29381 | | | | |
| R4 | -5.42482 | -2.80717 | | | | |
| R2 | -5.14419 | -2.52883 | | | | |

## Methodology

After describing the hydrochemical data and determining the types and facies of water samples using Piper diagrams, the spatial variations of electrical conductivity (EC), concentrations of $Cl^-$, $SO_4^{2+}$, fluoride$^-$, $Br^-$, and $NO_3^-$, ionic ratios ($Na^+/Cl^-$, $SO_4^{2+}/Cl^-$, $Ca^{2+}/Mg^{2+}$, and $Br^-/Cl^-$), and stable isotopes, were investigated to determine anomalous groundwater zones with regards to the urban sources of groundwater pollution.

A variety of composition diagrams of major ions and nitrate data were interpreted for assessing hydrogeochemical processes and understanding the hydrochemical characteristics of the origins of groundwater. The diagrams of total dissolved ions (TDI as meq/L) versus major ions and bivariate cation and anion relations were applied for detecting the dominant hydrogeochemical processes in the aquifer.

The proposed methodology combined isotope and hydrochemical data in order to explain processes occurring in groundwater system using restricted datasets. The syncretic analysis based on bivariate diagrams (δ18O versus δD with respect EC and ion concentrations and EC versus stable isotopes) was applied to distinguish the sources of groundwater in the study area.

To evaluate the analytical data, multivariate statistical techniques, i.e. item analysis and cluster analysis (CA), were used in this study by MINITAB (version 18.0) software. Cluster analysis was applied to identify groups or clusters of similar water wells based on similarities and dissimilarities in hydrochemical and isotopic specifications. Hierarchical clustering is the most popular approach, which provides intuitive similarity relationships between every sample and the entire dataset, and can be illustrated by a dendrogram (McKenna, 2003). The input hydrochemical data including major ion, $NO_3^-$, $F^-$, and $Br^-$ concentrations, EC values, and stable isotopes data were chosen for cluster analysis. After standardization, the hydrochemical and isotopic data were clustered using the Ward's linkage method with squared Euclidean distances as the similarity measurement between two samples.

## Results and Discussion

### *General Hydrochemistry*

The results of chemical analyses of water samples in dry and wet periods were used for hydrogeochemical investigations of the Behbahan alluvial aquifer. The solute chemistry of major ions in the two periods is demonstrated in Piper diagrams (Fig. 3). The groundwater samples in Piper diagrams show cluster and line patterns in cationic and anionic triangles, respectively. There are two major water types Ca-$SO_4$ and Ca (Na)-$SO_4$(Cl). The high concentrations of $SO_4^{2-}$, $Ca^{2+}$, and $Mg^{2+}$ are reflected in moderate to high TDS (about 3000 mg/l). In the dry period, the samples are more outspread than in wet periods because of no mixing due to recharge from precipitation or irrigation.

According to the hydrochemical data in the Behbahan aquifer (Fig. 4), the groundwater has a $Ca^{2+}$concentration ranging from 11.2 to 37.7 meq/L and from 8.80 to 36.4meq/L with the mean concentrations of 23.3 and 24.2 meq/L in wet and dry periods, respectively. The mean concentrations of $SO_4^{2-}$ranges from 12.84 to 64.91 meq/L and from 6.37 to 51.53 meq/L in wet and dry periods, respectively, with the mean concentrations 32.0 and 29.8 meq/L, where dissolution of gypsum is the most probable source of $SO_4^{2-}$. On the other hand, differences in $Ca^{2+}$and $SO_4^{2-}$concentrations are to some extent involved in dedolomitization possibly causing elevated $Mg^{2+}$concentrations with the mean concentrations of 10.9 and 10.3 meq/L in wet and dry periods, respectively. In addition, the mean concentrations of $Cl^-$ have been 10.8 and10.4 meq/L while those of $Na^+$ have 11.8 and 11 meq/L in wet and dry periods, respectively. The strong correlation between $Cl^-$ and $Na^+$ in the Behbahan aquifer suggests that there is no evidence of cation exchange. In the study area, the mean concentrations of $HCO_3^-$ have been 4.1 and 4.4 meq/L in wet and dry periods, respectively, indicating that the carbonate dissolution is a minor hydrochemical process in the aquifer. Nevertheless, this could be a result of saturation with respect to calcite and dolomite of the formation groundwater in the entrance of the alluvial aquifer as the recharge areas.

The occurrence of high-fluoride groundwater has been reported in a few regions in Iran (Battaleb-Looie et al., 2013; Akhavan et al., 2016; BaghalAsghari et al., 2017; Dehbandi et al., 2018; Dehghani et al., 2018; Enalou et al., 2018; Karimi et al., 2018; Neisi et al., 2018; Pazand et al., 2018; Radfard et al., 2018a; Shakerkhatibi et al., 2018) as well as in other countries (Li et al., 2017; Raj & Shaji, 2017; Colombani et al., 2018; Emenike et al., 2018; Gupta & Misra, 2018; Wu et al., 2018) because of its considerable effects on human health. Long-term exposure to high-fluorine water can seriously affect the health of the body, leading to chronic fluorosis (Wang et al., 2001). As an essential trace element in the human body, the concentration of F in drinking water should not exceed 0.7 to 2.1 mg/L in the wet and dry time periods, respectively, (Biglari et al., 2016) depending on the concentration and daily ingested dose.

According to the standard of drinking water, the optimum concentration of fluoride in drinking water is 0.7 mg/L during warm months, while it is 2.1 mg/L in the cold months. The average fluoride concentration of groundwater samples in the Behbahan aquifer ranged from 0.33 to 2.18 mg/L with a mean concentration of 1.19 mg/L in the dry period (Table 1).

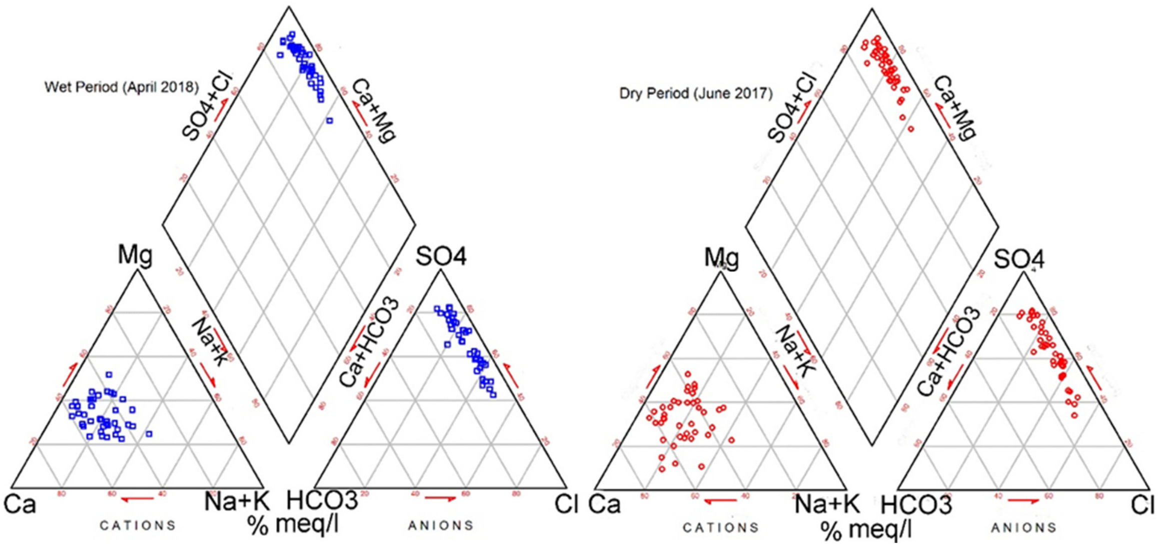


**Figure 3.** Piper diagram of groundwater samples in Behbahan plain (left: June 2017, right: April 2018)

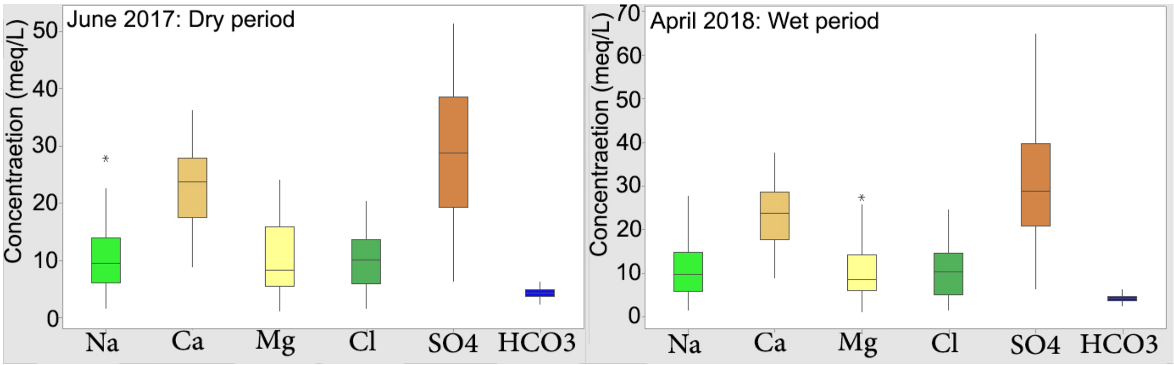


**Figure 4.** Boxplot of ground water samples in Behbahan plain (left: June 2017, right: April 2018)

$Br^-$ is commonly found in nature along with $Na^+$ and $Cl^-$, owing to the different physical and chemical properties, although in smaller quantities. The natural source of bromide is usually geothermal, seawater, and dissolution of rocks (Bero et al., 2016; Nair et al., 2016; Hildenbrand et al., 2017). In residential areas, due to treatment of water for drinking by disinfection processes, $Br^-$ gets converted into bromate which is a potential carcinogen. In addition, agricultural fertilizers contribute to a significant amount of $Br^-$ in groundwater as well. The concentrations of $Br^-$ in groundwater samples in the study area ranged from 0.1 to 1.07 mg/L (Table 1).

$NO_3^-$ is the major contaminant of groundwater resources in urban areas in Iran (Jalali, 2005; Nassery et al., 2009; Kazemi, 2011; Rahmati & Melesse, 2016; Asadi et al., 2017; Bay et al., 2018; Jalali et al., 2018; Radfard et al., 2018b). In recent decades, the average levels of $NO_3^-$ have increased in groundwater resources due to the urban, industrial, and agricultural sewage. The data reveal that the groundwater has a concentration of $NO_3^-$ ranging from 4 to 154 mg/L and from 6 to 103 mg/L with the mean concentrations of 41.2 and 41.9 mg/L in wet and dry periods, respectively. Among 40 samples of groundwater in the Behbahan plain, 15 and 13 samples in wet and dry period, respectively, had the concentration above World Health Organization's (WHO) permissible limit for $NO_3^-$ in drinking water which has been set at 45 mg/L. In the study area, 27 samples were polluted samples whose $NO_3^-$ concentration was above 25 mg/L; in comparison, only 1 sample could be regarded as unpolluted with a $NO_3^-$ concentration less than 10 mg/L.

## Spatial variations of hydrochemistry

The chemical composition of groundwater is a result of many hydrogeochemical factors including the composition of initial water that infiltrates to the aquifer and its reactions with minerals in the rock matrix, hydraulic properties of the aquifer (residence time), evapotranspiration, mixing with infiltration of waste water resulting from residential, industrial, and agricultural activities, and so forth. The major ion analyses of groundwater seek to produce basic, yet valuable, information concerning the water composition. Hydrochemical maps are usually compiled to display the regional distribution of water composition and quality with respect to recharge sources as well as the water-rock interactions. Hydrochemical mapping has been used by many researchers for the representation of spatial variability of ion concentrations in the aquifer (Ghesquière et al., 2015; Maurya et al., 2018; Romero-Sierra et al., 2018; Zereg et al., 2018). The hydrochemical maps of both sampling period in the Behbahan plain were prepared and investigated preliminarily with respect to each sampling period to capture the hydrochemical processes. According to these maps, it is observed that the data of the wet period are slightly indeterminate possibly due to mixing with infiltration of precipitation. Hence, the hydrochemical maps of the Behbahan plain in the dry period (June 2017) have been presented as EC, chloride, $SO_4^{2-}$, $F^-$, $Br^-$, and $NO_3^-$ concentrations (Fig. 5), ionic ratios ($Na^+/Cl^-$, $SO_4^{2-}/Cl^-$, $Ca^{2+}/Mg^{2+}$, and $Br^-/Cl^-$) (Fig. 6), and stable isotopes (Fig. 7) to determine anomalous groundwater zones in association with various recharge sources of the aquifer.

The TDS concentrations, which could be expressed by EC, is one of the most important factors originating from the progress of hydrochemical processes and infiltration of irrigation and sewage of urban areas, especially in arid and semi-arid regions. In the Behbahan plain, the EC map (Fig. 5a) shows increasing EC from the upstream to the middle parts of the plain, homogenously, while in the central area near the Behbahan City, the EC tends to decrease. The infiltration of wastewater of Behbahan city could be potentially characterized by low salinity. On the other hand, the increase in EC is remarkable in the downstream area, which is probably related to the evapotranspiration in the fine sediments of shallow groundwater depths in the northwestern part of the plain. Further, the imperceptible rise of the EC in the Marun irrigation network area is likely due to significant groundwater recharges with lower TDS than the background groundwater.

The $Cl^-$ concentrations range between 1.44 meq/L in the recharge areas and 20.41 meq/L in the discharge area (Fig. 5b). The observed pattern of $Cl^-$ values in the Behbahan aquifer may arise from the factors including dissolution of evaporate minerals and the recharge from miscellaneous sources. The $Cl^-$ concentrations of the Behbahan alluvial aquifer are strongly affected by the residuals of evaporite minerals of the Gachsaran formation in the plain. The maximum chloride concentration was observed in the separated points in the middle and the northwest of the Behbahan plain. In these areas, groundwater samples are probably in contact with halite beds of the Gachsaran formation.

$SO_4^{2-}$ appears to be the most dominant anion in the aquifer (Fig. 5 c) with the data suggesting that in much of the area, $SO_4^{2-}$and $Cl^-$ concentrations are higher than the Iranian recommended maximum permissible concentration for drinking purposes. The high concentrations of $SO_4^{2-}$ in groundwater of the plain are essentially due to the dissolution of weathered minerals such as gypsum and anhydrite in the alluvium and recharge from gypsum karst aquifer of the Gachsaran formation in the north and east of the plain as well as the bedrock lithology. Initially, through the dissolution process in the aquifer, the concentrations of $Ca^{2+}$ and $SO_4^{2-}$ have been elevated in the aquifer; however, eventually the concentration of $Ca^{2+}$ would be compensated by $Mg^{2+}$, given the dedolomitization in the study area. The Gachsaran formation (the upstream eastern and northern boundaries of the plain) constitutes a potential sulfate source, making it the predominant ion in the aquifer. The $SO_4^{2-}$ map shows a spatial decline in the central parts of the plain in response to the infiltration of municipal wastewater with low sulfate concentrations. In the Marun and Bonehbasht irrigation and drainage network areas, the concentration of $SO_4^{2-}$ is lower than expected. This implies that a groundwater recharge (due to irrigation) causes $SO_4^{2-}$ depletion. Nevertheless, the gypsum dissolution proceeds continuously in the aquifer.

Among the two sampling periods, the maximum concentrations of $NO_3^-$ in the groundwater occurred in April 2018. Oxidation of $NH_4^+$ resulting from rapid leaching of organic fertilizers applied on the irrigation networks lands and wastewater of Behbahan City caused elevated $NO_3^-$ in the groundwater. According to the iso-$NO_3^-$ map of the alluvial aquifer in June 2017 (Fig. 5d), it is observed that the $NO_3^-$ concentration in the middle parts in neighborhood areas of Behbahan City is higher than the maximum permissible concentration for drinking water, 45 mg/L. In Behbahan City, many aspects of the relationship between the details of ground water flow and geochemical processes that influence the N discharged from shallow aquifers have not been resolved yet. In particular, it has been suggested that geochemical reactions, such as denitrification, may have the capacity to substantially reduce N loads in the alluvial aquifer. Denitrification is a process by which bacteria obtain energy through the chemical reduction of $NO_3^-$ and the oxidation of organic matter or other reduced compounds in the absence of oxygen. If proceeded completely, denitrification transforms dissolved $NO_3^-$ to N gas. Denitrification and decrease in $NO_3^-$ concentrations of groundwater in the urban areas result from the occurrence of reducing conditions in the aquifer.

There is a high degree of variability of $Br^-$ concentrations in the aquifer (Fig. 5f). This may indicate a wide range of geogenic and anthropogenic sources which vary in the study area. The $F^-$ concentration map (Fig. 5e) represents a relatively similar trend of spatial variability with $Br^-$, although it is comparable with EC map. The possible sources of variation in the concentrations of the $F^-$ are in accordance with $SO_4^{2+}$ in the aquifer.

The representative ionic ratios for the study are shown in Fig. 6. The values of $SO_4^{2+}/Cl^-$ (Fig. 6a) have been mainly greater than 1 given the dominant dissolution of gypsum in the area. The representative ionic ratios for the study are shown in Fig. 6. The values of $SO_4^{2+}/Cl^-$ (Fig. 6a) have been mainly greater than 1 given the dominant dissolution of gypsum in the area.

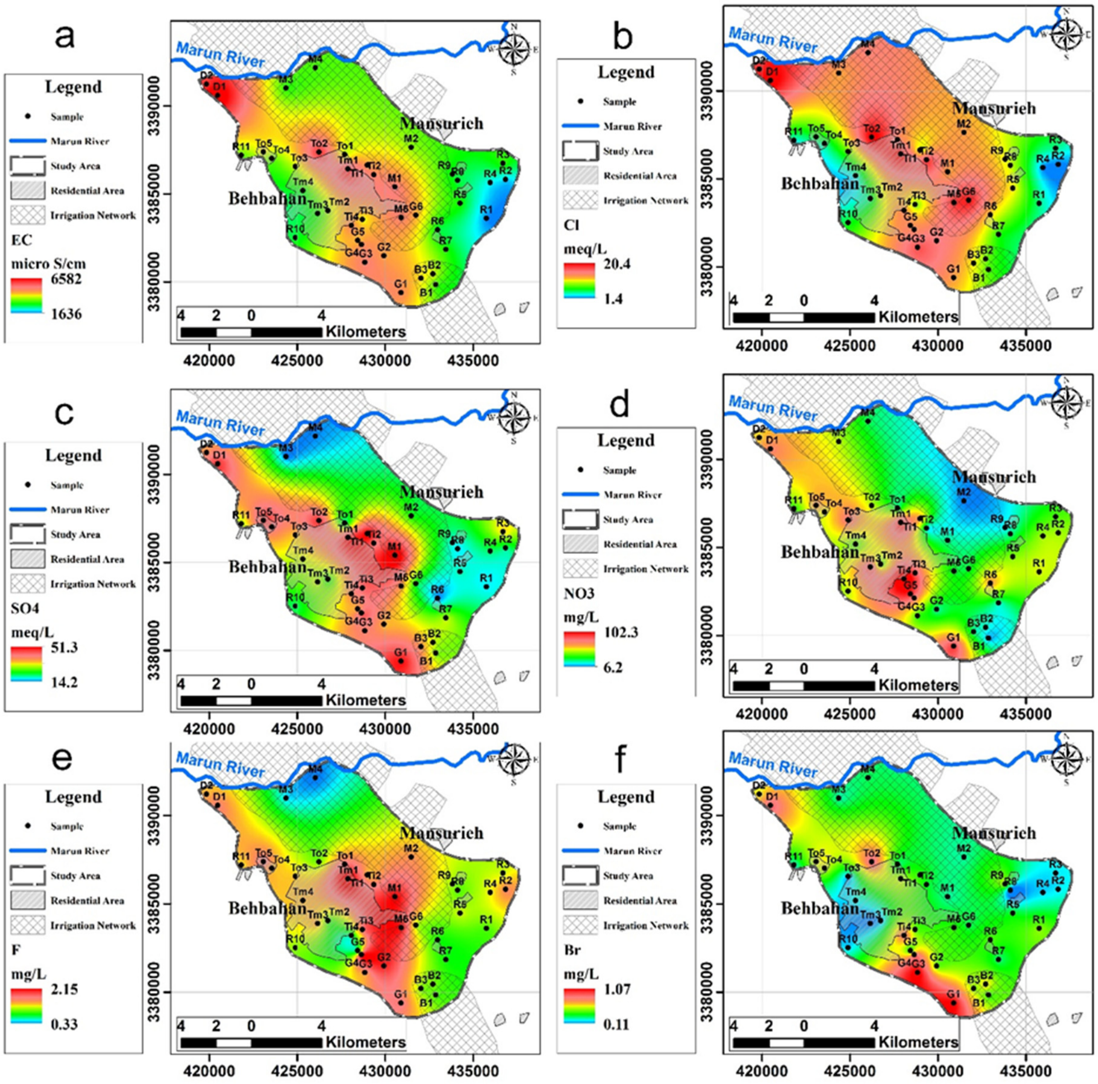


**Figure 5.** The hydrochemical maps of Behbahan aquifer in the dry season (a) EC, (b) $Cl^-$, (c) $SO_4^{2+}$, (d) $NO_3^-$, (e) $F^-$, and (f) $Br^-$ (June, 2017)

The highest ratios in two parts of the aquifer in the recharge areas indicate the gypsum dissolution with slight or no dissolution of halite, exclusively. The inequality of $Na^+$ and $Cl^-$ concentrations, i.e. the $Na^+/Cl^-$ ratio higher than 1.5 (Fig. 6b), could be related to ion exchange processes in northwestern parts of the aquifer. The higher sorption sites for the ions in fine sediments in the aquifer contribute to a relatively higher charge density in the alluvium. The $Ca^{2+}/Mg^{2+}$ ratio higher than 5 (Fig. 6c) as coincidence with gypsum dissolution, especially in the southeast of the Behbahan City, could be associated with the dedolomitization process, leading to the relative high abundance of $Mg^{2+}$ in relation to $Ca^{2+}$ in groundwater. The ratio of $Br^-/ Cl^-$ (Fig. 6d) diminishes from the border of the aquifer to the middle parts as a result of mixing with infiltration of irrigation and municipal wastewater originating from Marun River.

The maps of stable isotopes of the groundwater in the Behbahan aquifer are presented in Fig. 7. Based on these maps, the values of stable isotopes decrease from the borders to the middle parts of the aquifer. This could be caused by mixing with water from the recharge sources through the municipal wastewater and the irrigation networks, both of which are supplied by surface water of Marun River.

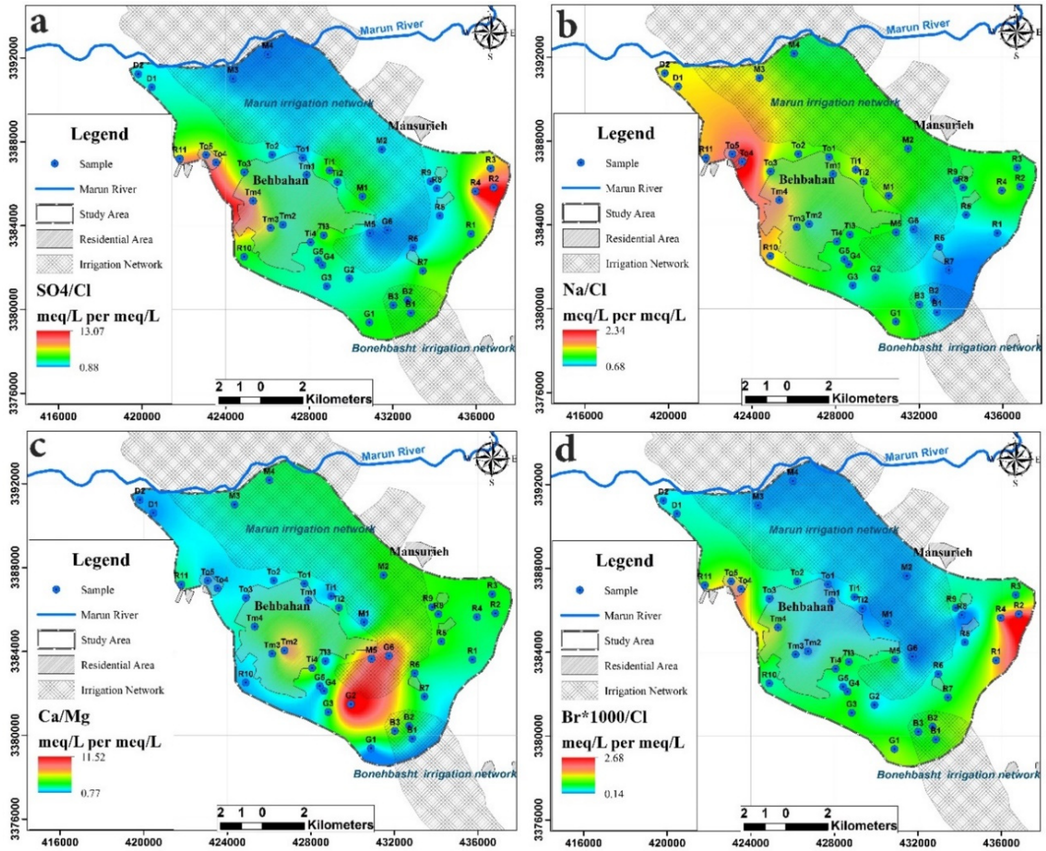


**Figure 6.** The ionic ratio maps of the Behbahan aquifer in the dry season (a) $SO_4^{2+}/Cl^-$, (b) $Na^+/Cl^-$, (c) $Ca^{2+}/Mg^{2+}$, and (d) $Br^-*100/Cl^-$ (June, 2017)

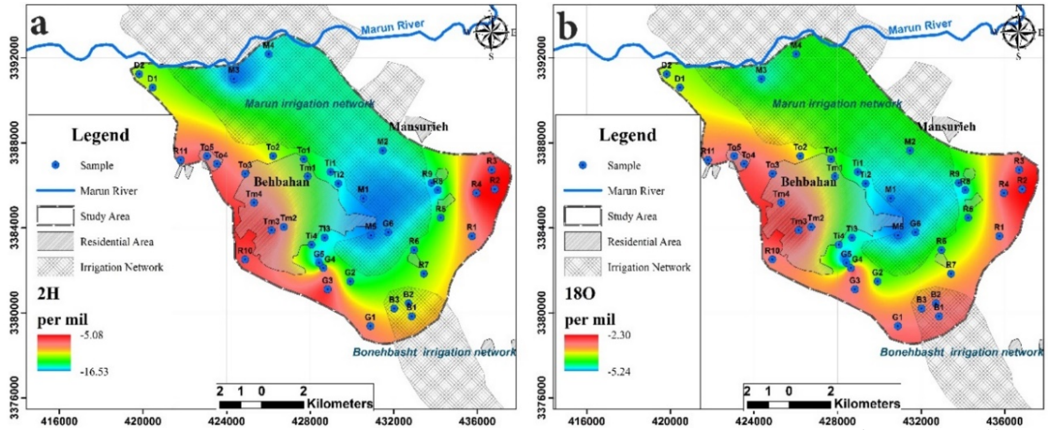


**Figure 7.** The stable isotope maps of the Behbahan aquifer in the dry season (a) $^2H$ and (b) $^{18}O$ (June, 2017)

## Composition diagrams and cluster analysis

To identify the interaction between groundwater and the aquifer minerals, it is essential to verify possible relationships between the ionic ratios and TDI for determining the manner through which the dissolution of minerals (carbonates, gypsum, and halite) evolves depending on the TDI. Groundwater chemistry is an important tool for hydrogeologists for tracing the recharge sources and the migration of water within the aquifer. Although water composition changes through water-rock interactions as a normal hydrochemical evolution, the recharge from urban and agricultural sources could disturb the expectance qualitative scheme. The analyses of groundwater chemistry as bivariate composition diagrams (Ghesquière et al., 2015) provide precious information about the hydrochemical processes and environments through which the water has circulated and mixed.

One of the most notable composition diagrams in groundwater hydrochemistry is expressed as concentrations of major ions versus TDI. The concentration of ions is presented in miliequivalents per liter of sample (meq/L) for precise understanding of the dominant dissolution process. Based on the composition diagrams of groundwater samples in the Behbahan aquifer (Fig. 8), the hydrogeochemical evolutions of groundwater in the plain involve gypsum and halite dissolution originating from the Gachsaran formation. The concentrations of major ions versus TDI reveals that the salinity is far more involved in the evaporate dissolution than carbonate species is. There are three main hydrogeochemical processes in the aquifer include dissolution of gypsum, halite dissolution, and dedolomitization. Firstly, the strong correlation between $SO_4^{2+}$ as well as $Ca^{2+}$ and TDI is based on the dissolution of gypsum. Secondly, halite dissolution occurs less than gypsum dissolution. Finally, dedolomitization in TDI higher than 100 meq/L has caused elevated $Mg^{2+}$ concentrations, and simultaneously, lowered $Ca^{2+}$ concentrations. The aquifer materials of Behbahan Plain often contain calcite, gypsum, and dolomite as disseminated crystals. When simultaneous equilibrium with calcite and dolomite is combined with the dissolution of gypsum, the process of dedolomitization may take place. The increasing $Ca^{2+}$ concentration due to gypsum dissolution causes calcite to precipitate. The $HCO_3^-$ concentration decreases as calcite precipitates, and this provokes the dissolution of dolomite and an increase of the $Mg^{2+}$ concentration. The net result is that the dissolution of gypsum induces the transformation of dolomite to calcite in the rock and produces waters with increased $Mg^{2+}$ and $SO_4^{2+}$ concentrations and equable decrease of $Ca^{2+}$ concentration in TDI greater than 100 meq/L (Fig. 8 and 11).

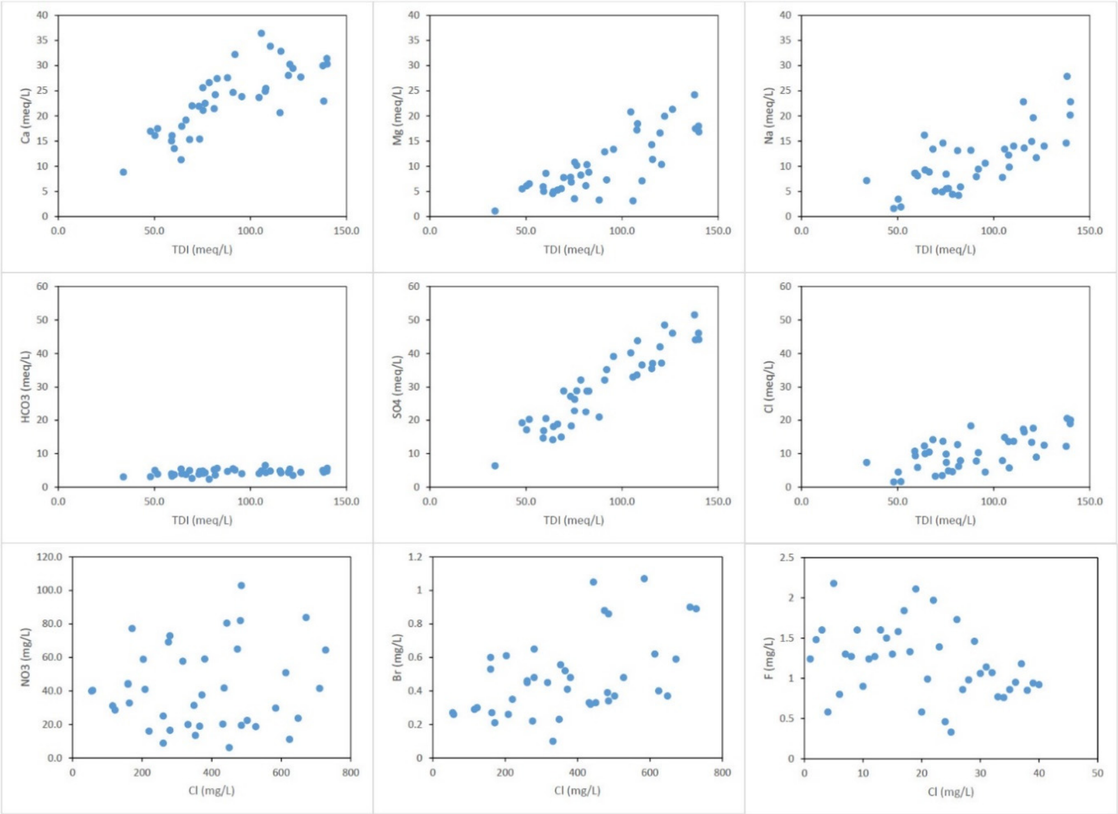


**Figure 8.** The composition bivariate diagrams of Behbahan aquifer in the dry season (June, 2017)

The composition bivariate diagram of $NO_3^-$ versus $Cl^-$, as two indicator conservative ions, bubbled with EC in the dry season presented in Fig. 9. The groundwater in recharge areas (mostly R samples) have low $Cl^-$ and moderate to high $NO_3^-$ concentrations plus moderate EC values, lower than 2000 μS/cm. Although the urban samples (denoted by T) show $Cl^-$ and EC values slightly higher than those of recharge samples, the $NO_3^-$ concentrations have been doubled. The highest EC values are related to groundwater in contact with gypsum bedrock (G samples) in accordance with high values of $NO_3^-$ concentrations, mainly above 60 mg/L. Some of G samples have high EC and $Cl^-$ values with minimum values of $NO_3^-$ concentrations. Groundwaters affected by irrigation water in Marun (M samples) and Bonehbasht (B samples) networks have low $NO_3^-$ values and moderate EC and $Cl^-$ values. However, some deviation from the expected hydrochemical behavior is inevitable possibly due to the mixing process.

Five distinct water groups could be recognized based on the relationship between $^2H$ and $^{18}O$ isotopes (Fig. 10): (1) the waters of the Marun irrigation networks with the minimum values of the stable isotopes accompanied by groundwater samples are probably being recharged from Marun River thought channel network; (2) the surface waters from Marun River show an irrational behavior with higher values of stable isotope contents compared with samples of irrigation networks, which could be explained by incorrect sampling procedure and collecting the samples from the surface of the river; (3) the groundwater samples with highest values of stable isotopes have resulted from enrichment in evaporates; (4) the waters related to the Bonehbasht irrigation network are located in the middle parts of the plot; and (5) the groundwater samples located between the above-mentioned groups show the mixing.

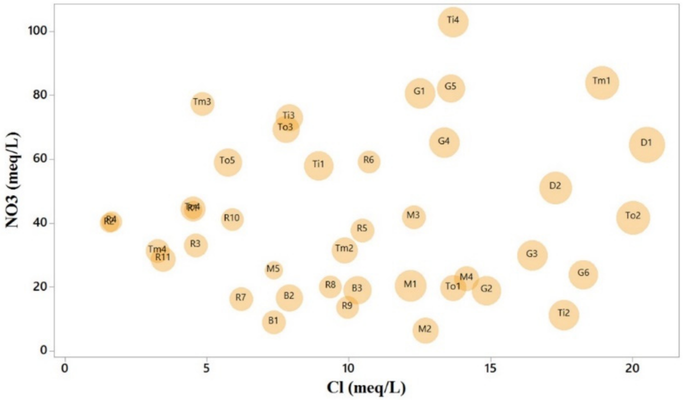


**Figure 9.** The composition bivariate diagram of NO3 versus Cl bubbled with EC of Behbahan aquifer in the dry season (June, 2017)

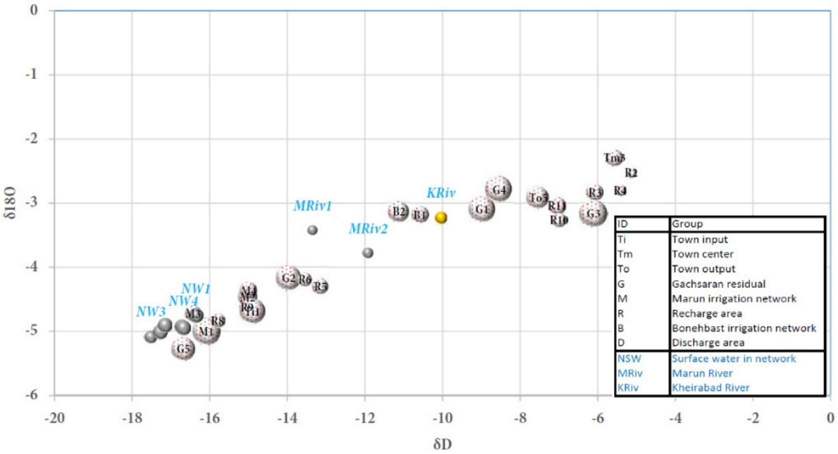


**Figure 10.** The diagram stable isotopes of Behbahan aquifer in the dry season (June, 2017)

A combination of graphs has been used to illustrate all of the hydrochemical and isotopic parameters together in one figure (Fig. 11), so that their interactions with each other can be displayed.

It could be observed that the concentrations of ions, except for $HCO_3^-$, $F^-$, and $Br^-$ have been elevated with EC, while $NO_3^-$ and stable isotopes values have had no obvious relationship with dissolved solids. Among all diagrams in item analysis, the correlations of $Na^+$ with $Cl^-$; F, $Mg^{2+}$, and $SO_4^{2+}$ with $Ca^{2+}$, $SO_4^{2+}$ with $Mg^{2+}$; $Br^-$ with $Cl^-$; HCO3 with stable isotopes; and $F^-$ with $Br^-$ are noticeable.

Cluster analysis was performed using hydrochemical and isotopic parameters illustrated by two dendrograms grouping all 40 groundwater samples of the Behbahan plain into five statistical clusters, according to the main recharge sources (Fig. 12).

Concerning the dendrogram in the dry season, by considering improbability of mixing with precipitation recharge, five clusters with similar hydrogeochemical and isotopic compositions can be distinguished with a high congruence with the initial grouping of samples based on location and most probable sources of water. The largest cluster is related to the underground recharge samples (R) with two samples of B1 and Tm4 revealing similarities with them. The samples of M2 to M4 as well as To1 composed a cluster that could be attributed to Marun irrigation network. A strange cluster in the middle of the dendrogram including a blend of waters B, Tm, Ti, and G may be related to gypsum bedrock. The discharge samples (D) have a greater similarity with Tm1 and To2. Although the municipal clusters are mainly characterized by T samples, samples G1, G4, G5, and M1 are similar to these waters.

## Conclusion

Although it is believed urbanization often results in the deterioration of groundwater quality, in the Behbahan aquifer groundwater freshening could occur with reduction of EC, $SO_4^{2+}$, and $Cl^-$, and enhancement of $NO_3^-$ content.

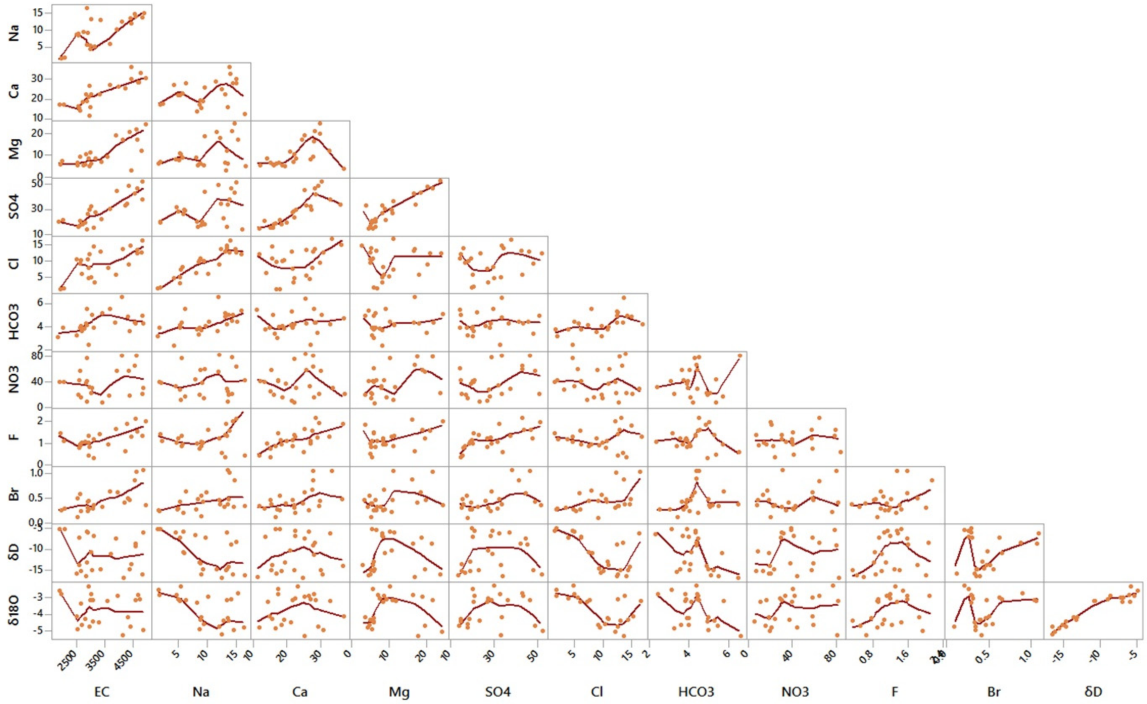
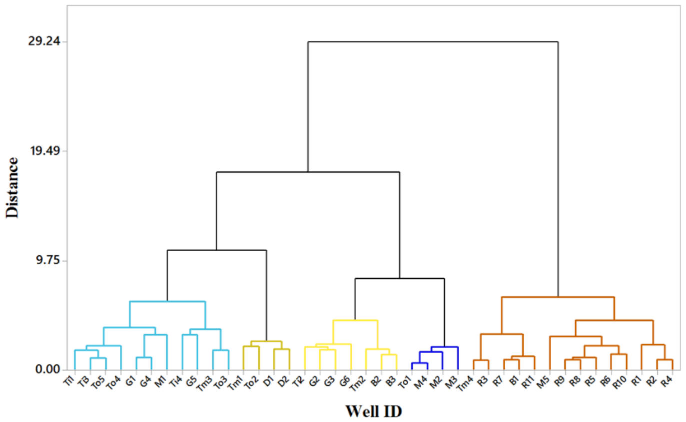


**Figure 11.** The conjugate diagram of hydrochemical and isotopic parameters of Behbahan aquifer in the dry season (June, 2017)

CA of groundwater samples (dry period)



CA of groundwater samples (wet period)

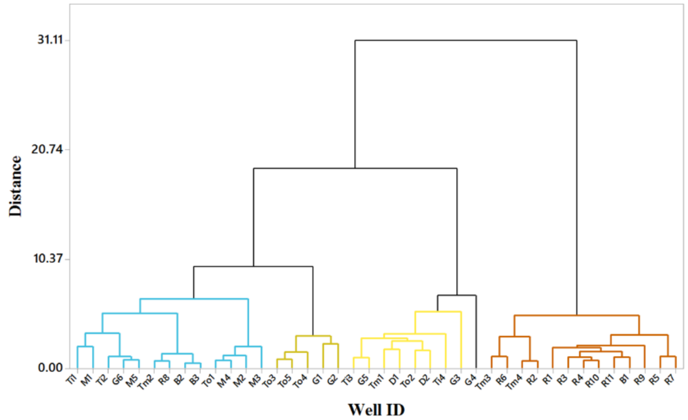


**Figure 12.** Dendrogram based on cluster analysis of hydrochemical and isotopic parameters of Behbahan aquifer in the dry season (June, 2017)

However, the recharge from urban wastewater leads to elevated levels of $NO_3^-$ and probably pathogens in the residential areas.

The hydrochemical evolution revealed that diminished EC and other dominant anion concentrations, as observed on their maps, are strongly influenced by recharge events resulting from urbanization.

The hydrochemical maps and composition diagrams illustrate the hydrochemical evolution in the aquifer, basically controlled by gypsum dissolution and to some extent by halite dissolution, dedolomitization, and abnormal hydrochemical behavior is apparent in the middle parts of the plain due to the recharge from Marun irrigation network and urban areas of Behbahan City. The dissolution of gypsum was presented as the primary process of $SO_4^{2+}$ and $Ca^{2+}$ enrichment with EC values higher than 3000 µS/cm as this evaporate mineral is easily dissolved. The $NO_3^-$ remains the major pollutant in the groundwater of the Behbahan plain, and high concentrations of this ion are due to the agricultural activities and infiltration of the municipal waste water. Generally, the maximum concentrations of $NO_3^-$ in the groundwater of the Behbahan plain, which are presented in the urban areas, are higher than 45 mg/L. The fine textured aquifer materials, thin unsaturated zones, and direct infiltration of highly polluted urban waste water lead to lower $NO_3^-$ concentrations due to denitrification occurrence.

Five distinct recharge sources were recognized for the Behbahan aquifers based on the $^{2}H$ and $^{18}O$ isotope's characteristics including the waters of the Marun irrigation networks with the minimum values of the stable isotopes values, the surface waters from Marun River with higher values of stable isotopes, the groundwater samples with the maximum values of stable isotopes resulting from enrichment in evaporates, the waters related to the Bonehbasht irrigation network, and finally the groundwater samples trending between the above-mentioned groups showing the mixing.

Cluster analysis based on both hydrochemical data identified the sources responsible for water samples and confirmed that in addition to geochemical process, the anthropogenic effect is another major source responsible for groundwater quality deterioration in Behbahan aquifer causing reduced $SO_4^{2+}$ and elevated $NO_3^-$ concentrations.

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