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Geochemical and multi-isotopes ($\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$, ^{3}H and $\delta^{37}Cl$) evidences to karst development and flow directions in transboundary aquifer, Northeast of Iran

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ABSTRACT

The first systematic research of the geo-hydrogeological and hydrogeochemical characteristics and isotopic signatures was carried out in the transboundary karstic aquifer in northeast of Iran, in order to investigate the groundwater origin, flow directions and karst development. The karstic springs of the area are characterized by discharge rate of 50–500 L/s, EC values of 370–1050 μS/cm and the Ca–Mg–HCO_3 water type. Stable isotope values of the precipitations resulted in a LMWL ($\delta^2H = 7.2 \times \delta^{18}O + 8.6$, $R^2 = 0.96$, $n = 96$) with a lower slope and a lower intercept than the global meteoric water line (GMWL) due to isotope kinetic fractionation effects during precipitation. The $\delta^{18}O$ precipitation gradient is −0.32‰ per 100 m of altitude. Isotopes data reveals that recent Mediterranean meteoric water (rain and/or snow) is the main origin of groundwater in the study area. The depleted isotope composition of some of the springs can be attributed to their higher catchment area and more recharge by snow. Groundwater budget analysis reveals that a large amount of water migrates toward the neighboring country. Fold and fault zones can be important variables on groundwater local and regional flows in the karstic aquifer. In terms of karst development, the Sarani spring in transboundary karstic aquifer with lower $\delta^{18}O$, $\delta^{37}Cl$ and EC values and higher $\delta^{13}C_{DIC}$ has conduit flow regime and more karst development in its catchment area. In comparison, the isotopic values as well as physic-chemical characteristics of the springs confirm larger residence times (>30 years) and lower karst development in the other karstic springs. Consequently, the geo-hydrogeological and tectonic settings as well as isotopic approaches enhances knowledge in both groundwater flow direction and karst development and, ultimately, to better evaluate and manage water resources in the study area, and also in other transboundary karstic regions.

1. Introduction

Most potable and irrigation waters of the inhabitants are supplied by springs that emerge from karstic formations. Karst aquifers represent extremely heterogeneous porous rocks and have complex characteristics which make them different from other aquifers (Bakalowicz, 1977; Freeze and Cherry, 1979; Todd and Mays, 2005). Understanding groundwater flow direction, karstic spring recharge processes and its sources and karst development are essential for sustainable karstic resource management (Fetter, 1999; Ford and Williams, 2007; Bonacci and Andric, 2015). Fold and fault zones can be important determinants of groundwater flow in karstic aquifer (Apaydin, 2010; De La Torre and Andreo, 2020).

The geological setting, groundwater budget and geochemical characteristics of the spring waters are widely employed in karstic environments to investigate their hydrogeological conditions (Dincer, 1985; Kohfahl et al., 2008; Bouchaou et al., 2009; Schwarz et al., 2009; Einsiedl et al., 2009; Jeelani et al., 2010; Marques et al., 2010; 2013; Dhakal et al., 2014; Guo et al., 2015; Verbovsek and Kanduc, 2016; Bagheri et al., 2017a,b; Bai et al., 2020). Lately, the stable (^2H, ^{18}O and ^{13}C) and radioactive (^3H) isotopes of water have provided a better tracer to evaluate groundwater flow path, karst development and its origin to

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management of the karstic resources (Bagheri et al., 2014; Bonacci and Andric, 2015; Guo et al., 2015; Mustafa et al., 2015; Asmael et al., 2015; Ayadi et al., 2018; Jin et al., 2018; Joshi et al., 2018; Jia et al., 2020; Liu et al., 2020; Razum et al., 2020; Gao et al., 2020; Chen et al., 2019). Recently, chlorine stable isotopes (δ^{37}Cl) in groundwater are used to distinguish several origins. Apart from dissolved halite from evaporates, it can originate from sources such as rainwater (Wassenaar and Kohler, 2004; Kohler and Wassenaar, 2009), and water-rock interaction with chloride bearing minerals such as apatite (Eggenkamp and Schuiling, 1995). Our knowledge on the behavior and application of δ^{37}Cl data in karstic aquifer is still in its infancy.

The main transboundary karstic aquifers in the northeast of Iran are discharged by a few karstic springs with different discharge rates (50–500 L/s). These transboundary karstic aquifers are located near Turkmenistan border and they are considered as the principal sources of groundwater for drinking and agricultural purposes in the northeast of Iran. The recharge areas of these springs are in different locations due to their elevation, discharge rate, catchment area, karstification degree and intense development of epikarst. Some of the karstic springs are at the base flow of artificial reservoirs (at the Shirindareh and Barzo dams) which are used for drinking water and agricultural purposes. This area is characterized by a complex and heterogeneous geological structure including consecutive folds and faults. Thus, the understanding of the hydrodynamic system of this karstic region is particularly difficult.

The main aims of this study are (1) determining the local meteoric water line (LMWL) of the atmospheric precipitation which represents important baseline information for numerous karst hydrogeology and climatological investigations, ranging from global to local scales, (2) investigating chemo-isotopic characteristics of the karstic springs, (3) evaluating the groundwater origin the water residence time, (4) determining the recharge elevation and (5) evaluating groundwater flow path and karst development in the transboundary karstic aquifers of the area. To achieve these objectives, comprehensive geochemical characteristics and multi-isotope tracers (δ^{18}O, δ^{2}H, ^{3}H, δ^{13}C and δ^{37}Cl) of the water resources are applied. This is the first systematic research on the hydrogeological and hydrogeochemical characteristics, including isotopic signatures, especially δ^{37}Cl, at an appropriate scale in this important transboundary karstic aquifers and Iran. Our results show the potential to apply this type of research in other karstic sites.

2. Geological and hydrogeological settings

The region studied for this research is situated in Northern Khorasan province, northeast of Iran. This province has an international boundary with Turkmenistan in the north and national boundaries with Golestan, Semnan and Khorasan Razavi provinces from the west to the east (Fig. 1). The elevation in the region varies from 1100 to 2900 m.a.s.l. and it is dominated by carbonate and shale formations. It also includes quaternary and alluvium sediments especially in the flat areas. The study area is situated in the center of the Kope-Dagh structural-sedimentary zone. This zone is located east of the Caspian Sea and includes north eastern Iran, southern Turkmenistan and northern Afghanistan. The Kope-Dagh zone is characterized by a repetition of long anticlinal and synclinal folds. The stratigraphic and structural settings of the Kope-Dagh sedimentary sequence were described in detail by Afshar-Harb (1979). The main exposed geologic formations in descending order of age are the Shurijeh Sandstone with shale and gypsum Formation (Jurassic-Cretaceous), the Tirgan limestone Formation (Lower Cretaceous), the Sarcheshmeh Formation (Upper Cretaceous), the Sanganeh Formation (Lower Cretaceous), the Atamir Formation (Upper Cretaceous) and quaternary alluvium (Fig. 1).

The karstic aquifer contains of a sequence of anticlines which occupies an area of about 6800 km^2 and which is about 92 km long and 74 km wide. These anticlines follow the general E-W trend of the Kope-Dagh range. In terms of the structural setting, the study area is significantly affected by folding and faulting structures which provide a

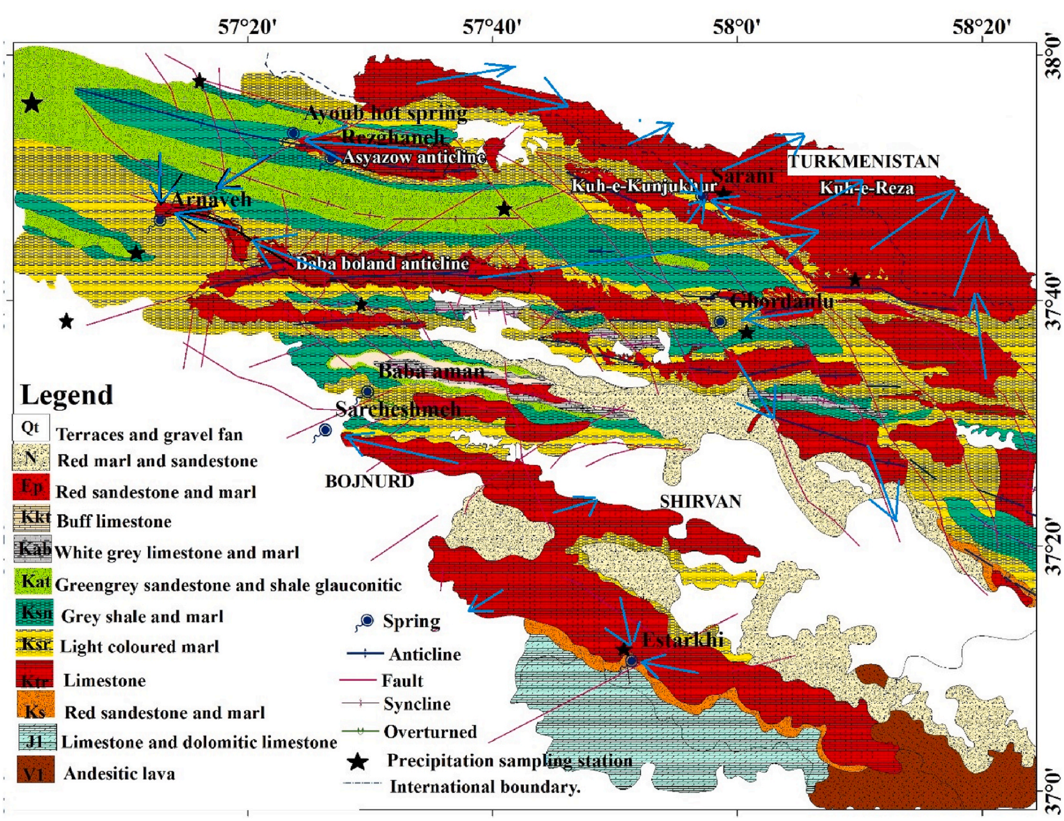

Fig. 1. Geological map, spring locations and probable groundwater flow directions (blue arrow) in the study area.

fracture system that leads to more infiltration and the development karstic channels. The main aquifer is made in the Cretaceous limestone unit of the Tirgan Formation in the area. The Karstic aquifer discharges through several springs, the most important of which are Arnaveh, Rezghaneh, Sarani, Ghordanlu, Estarkhi and Ayoub. These springs are located in different anticlines. The Arnaveh and Rezghaneh springs, as the two main karstic springs with discharge rates of about 550 and 200 L/s respectively, form the main inflow to the Shirindareh Dam reservoir. The other springs have discharge rates which are lower than 80 L/s. The warm spring Ayoub is located to the west of Rezghaneh spring. Travertine around this spring is evidence of a long discharge history at Ayoub thermal spring. This indicates that the water of Ayoub thermal spring has previously moved upward through faults where the surface temperature and pressure conditions led to oversaturation of the water with respect to carbonate minerals ($CaCO_3$) which in turn caused travertine precipitation.

The mean annual temperature in the region varies from 9 °C in the north to 14 °C in the south of the province. July and January are the warmest and coldest months with mean temperatures of 22 °C and −2 °C, respectively. The precipitation pattern depends on the physiographic condition and varies from snow in the mountains in the north to rainfall in the south. The mean annual precipitation varies from 230 to 370 mm of which 74% is received in the period from December to April. The winter season airflow is wet and cold; while the summer season is thermal and dry. Mean annual evaporation in this basin is about 300 mm.

3. Sampling and analytical methods

Monthly groundwater samples were collected from the 6 main karstic springs during one hydrological cycle from July 2016 to June 2017. Also, in order to investigate the isotopic characteristics of the precipitation and to determine the LMWL of the area, a few uniformly distributed rainfall stations around the study area were selected according to their elevation and precipitation and evaporation amount. Totally, 54 rainwater and 42 snow samples were collected on event basis during consecutive rainy days for one year (July 2016 to June 2017), and rains are analyzed based on the volume-weighted monthly average samples. All bottles were cleaned with triple distilled water to avoid contamination and were rinsed with sample water before filling. The field parameters electrical conductivity (using a portable HANA Multirange EC Meter-HI8733), pH (using portable AZ pH Meter-8601), temperature the discharge flow of the springs was measured in situ. The concentrations of the major ions (Na^+, Ca^{2+}, K^+, Mg^{2+}, HCO_3, Cl^-, SO_4^{2-}) were measured at the geochemistry laboratory by Ion Chromatography (IC) and alkalinity was measured by titration in Shahrood University. The ion balance error of the samples was computed by the following equation (1): (concentration in meq/l)

$$IB = \frac{\sum cations - \sum anions}{\sum cations + \sum anions} \times 100 \tag{1}$$

The ion balance of samples was better than 5%. 30 ml of the groundwater samples were stored in dark bottles to be analyzed for ^{18}O and ^{2}H in the isotope Laboratory of Utrecht University, the Netherlands. Hydrogen and oxygen isotope were conducted by off-axis integrated cavity output laser spectroscopy (OA-ICOS, Los Gatos Research, Mountain View CA, United States of America) against carefully calibrated inhouse standards and controls; selected samples were analyzed in replicates on different OA-ICOS instruments. All results are reported in ‰ relative to the VSMOW-SLAP scale standard with a precision of ±0.6‰ (2σ) and ±0.1‰ (2σ) for δ^2H and $\delta^{18}O$, respectively.

The chlorine stable isotope ($\delta^{37}Cl$) values of 10 water samples were measured in the Institute de Physique du Globe de Paris, France, using the procedure described by Eggenkamp (1994) and Godon et al. (2004). The stable isotope composition of chlorine ($\delta^{37}Cl$) is expressed as the parts per thousand or permil difference from the reference. SMOC is the name of the reference used, in this case Standard Mean Ocean Chloride (Kaufmann et al., 1984).

$$\delta^{37}Cl = \left(\left(\frac{^{37}Cl}{^{35}Cl}\right)_{sample} \Big/ \left(\frac{^{37}Cl}{^{35}Cl}\right)_{SMOC} - 1\right) \times 1000 \tag{2}$$

This procedure is based on the precipitation of silver chloride the amount of sample depends on chloride concentration in samples. For each measurement 1 mmol Cl^- is necessary. To produce a fixed ionic strength and fixed pH, 4 ml of a 1M KNO_3 solution is added to the chloride solution. Then 2 ml of a Na_2HPO_4 - citric acid solution is added to buffer the pH at 2.2 to avoid precipitation of Ag_2O. After heating the mixture about 80 °C, 1 ml of $AgNO_3$ (0.2 N) is added and silver chloride starts precipitating. This suspension is filtered over a Whatman GF/F glass fiber filter. The filters with silver chloride are covered with aluminum foil and dried overnight at 80 °C. Then, AgCl is reacted with CH_3I in evacuated Pyrex tubes for 48 h at 80 °C. In the sealed tube silver chloride reacts with iodomethane (CH_3I) to form AgI and CH_3Cl. CH_3Cl and CH_3I are separated by gas chromatography. The isotope composition of CH_3Cl is measured on a Thermo Fisher Delta V isotope ratio mass spectrometer. With this method the standard deviation of a series of measurements (including sample preparation) is normally 0.05‰ or better.

Carbon isotope analysis was carried out at the Stable Isotope Laboratory of Utrecht University, the Netherlands. 200 μg of water sample were injected to vials and capped and flushed with helium gas. Several drops of phosphoric acid were added to every vial. The reaction with the carbonate at 72 °C produced carbon dioxide, which was measured by mass spectrometer. This analysis was run three times with different international standards for normalization purposes. Isotope data reported in the delta (δ) notation as per mil (‰) deviation relative to the Vienna Standard Pee Dee Belemnite (V-PDB) with analytical precision better than ± 0.05‰.

Tritium (^3H) samples are analyzed following NEN-EN-ISO 9698, determination of tritium activity was done by the concentration-liquid scintillation counting method in the water laboratory, Het water laboratorium in Amsterdam. Following this procedure, samples are distilled with sodium carbonate and sodium thiosulphate to eliminate color and salts to get a pure water sample. A part of this sample is being mixed with scintillation liquid in a counting bottle and put in a Quantulus 1220 scintillation counter. The measuring sequence contains a procedure blank (very low tritium amount, “dead water”), calibration standard, control standard and samples. The whole sequence is being counted 5 times for each sample for 2 h. The calculated detection limit is 1.26 Bq/l (1Bq/l = 8.47 TU) and the reporting limit is 2 Bq/l.

The meteorological data for this research was obtained from sampling stations and recorded during sampling period.

4. Results and discussion

In this research, by analyzing the chemical composition and isotopic data ($\delta^{18}O$ and δD, $\delta^{13}C$, $\delta^{37}Cl$ and ^3H), the general hydrochemistry and dominant geochemical processes which affect the spring's hydrochemistry are discussed. Later the local meteoric water line (LMWL), water origin, recharge mechanism, residence time and flow directions and also karst development are determined based on geological and hydrogeological investigations and hydrochemical and isotopic techniques as well.

4.1. General hydrochemistry characteristic

Table 1 gives the average values of the physico-chemical and isotopic compositions of the karstic springs in the study area. The measured temperatures of the springs vary from 14 (in Sarani spring) to 43 °C (in Ayoub thermal spring) and they have variable discharge rates between 11 and 500 L/s (in Arnaveh). The lowest and highest discharge rates in

Table 1
The average value of general physico-chemical parameters and isotopic compositions of the springs in the area (ion concentrations in meq/l).

	Arnaveh	Sarani	Rezghaneh	Ayoub	Ghordanlu	Estarkhi
EC (μS/cm)	830	370	670	1050	400	670
T (°C)	21	15	19	40	17	19
pH	7.9	8	8	7.5	7.8	7.8
Discharge (L/s)	500	35	250	11	13	180
Ca^{2+}	2.8	2.1	2.5	4	1.8	4.5
Mg^{2+}	3.3	2	3.3	3	2.3	2.5
SO_4^{2-}	2.5	0.6	1.8	5.5	0.7	1.6
HCO_3^-	4.6	3.5	4.7	4.2	3.3	5
Na^+	2.8	0.25	1.8	3.7	0.3	1.2
Cl^-	1.2	0.3	1.3	1.5	0.5	1
K^+	0.06	0.01	0.03	0.08	0.01	0.04
$\delta^{18}O$ (‰)	−10.22	−11.53	−11.28	−11.01	−11.19	−10.26
δD (‰)	−66.92	−73.2	−72.59	−72.88	−70.22	−61.54
$\delta^{13}C$ (‰)	−3.72	3.02	−2.9	−1.93	−5.2	−1.86
$\delta^{37}Cl$ (‰)	0.19	−0.04	0.17	0.2	–	0.06

the springs were measured in the Ayoub and Arnaveh springs, respectively. The pH values of the springs vary from 7 to 8.2 (Table 1). The EC values of the springs range from 370 to 1050 μS/cm.

For evaluation of the chemical characteristics of the spring water samples, a piper diagram is plotted (Fig. 2). According to this diagram, Ca^{2+}, Mg^{2+} and HCO_3^- are the most abundant ions in all springs and is attributed to the dissolution of carbonate rocks from the Tirgan Formation, indicating comparable initial water origins. Ca–Mg–HCO_3, Ca–HCO_3 and Mg–HCO_3 are the main water types of the karstic springs in the study area which resulted from congruent dissolution of carbonate hosted lithology. The water type of Ayoub thermal spring is Ca–Mg–SO_4 which is due to its long circulation and dissolution of carbonate and evaporite rocks (Jeelani et al., 2011). HCO_3 contributes to 60–80% of the anions, and SO_4 and Cl to less than 30% of the anions. Ca^{2+} and Mg^{2+} contribute from about 70 to more than 90% of the cations, while Na^+ is less than 30% of the total cations. Arnaveh and Rezghaneh samples show a mixed cation-HCO_3 water type that suggests the dissolution of clay minerals.

The saturation index is useful for determining the existence of some common minerals in the groundwater system (Deutsch, 1997) and to determine the spring's origin. Fig. 3 shows the $SI_{calcite}$ and SI_{gypsum} versus $SI_{dolomite}$ and $SI_{anhydrite}$ for the all groundwater samples. All groundwaters in the study area were under-saturated with anhydrite and gypsum indicating that these minerals are prone to dissolution. The Ayoub thermal spring is more saturated in comparison to other the springs followed by Arnaveh, Rezghaneh, Sarani and Ghourdanlu. This can be attributed to groundwater flow paths through different formations. Almost all water samples are supersaturated with respect to calcite and dolomite. However, the depth of groundwater with CO_2 circulation through karstic formations such as the Tirgan limestone is responsible for the calcite and dolomite saturation index for the Arnaveh, Rezghaneh and Ayoub thermal spring. The hydrochemistry results show that the dissolution of interlayers of evaporite rocks in Sarcheshmeh, Sanganeh and Aitamir at the top of the Tirgan karstic formation is the main cause of the higher concentrations of sulfate and chloride in the Ayoub thermal spring.

4.2. General environmental isotope characteristics

The $\delta^{18}O$ and δ^2H contents of precipitation and springs are powerful

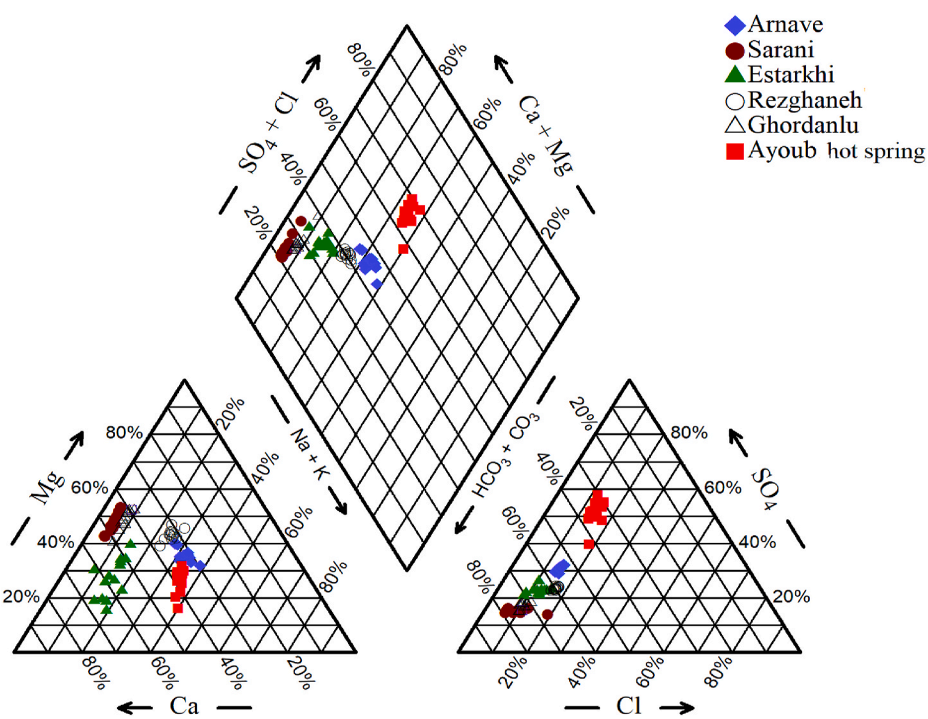

Fig. 2. Piper diagram of the karstic springs.

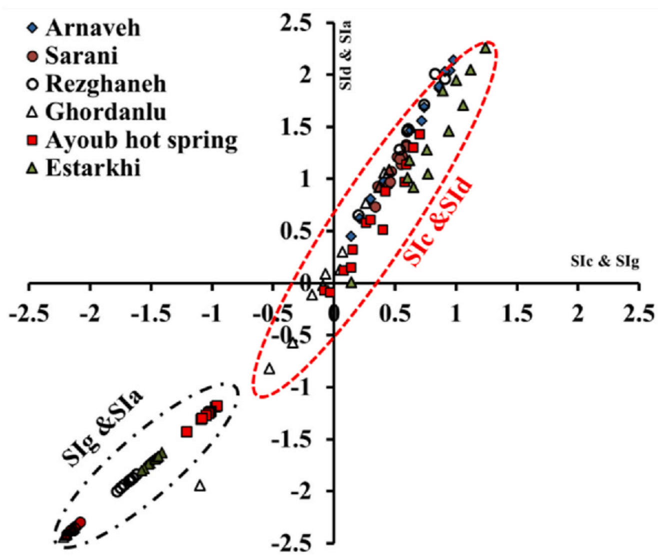

Fig. 3. Saturation index (SI) of different minerals in the water samples of the study area SI_{gypsum} and $SI_{calcite}$ are shown on the X axis and $SI_{dolomite}$ and $SI_{anhydrite}$ are shown on the Y axis.

tools to determine the origin of groundwater and the geochemical evolution in karstic systems (Clark and Fritz, 1997; Bagheri et al., 2014).

- Isotopic content of the precipitation

In order to determine the LMWL and consequently the origin of the water, the isotope values of monthly rainfall and snow samples in the study area are also measured. The precipitation samples were taken from 9 stations near the springs at an elevation range from 637 to 2110 m above sea level. The study area experiences clear seasonality with four distinct seasons: spring (March–May), summer (June–August), autumn (September–November), and winter (December–February). The $\delta^{18}O$ and δ^2H of precipitation (rainwater and fresh snow) shows spatial and temporal variations. The amount-weighed annual precipitation $\delta^{18}O$ values vary between +1.08‰ and −11.4‰ with a mean of −5.6‰, while δ^2H ranges from +18.8‰ to −73.2‰ with a mean of −32.2‰ over the entire sampling period, which are within both Iranian and global ranges. The deuterium-excess values range from 21.6 to −11 with a mean value of 11‰. The samples are depleted in their stable isotope composition during the winter and also at higher elevations. The lowest values are observed in February and the highest in July (Fig. 4). The correlation between $\delta^{18}O$ and δD values of all the stations is defined as the local meteoric water line (LMWL): $\delta^2H = 7.2 \times \delta^{18}O + 8.6$, $R^2 = 0.96$ (Fig. 5). The lower slope and intercept of the local LMWL as compared to the Global Meteoric Water Line (GMWL: $\delta D = 8 \times \delta^{18}O + 10$) (Craig, 1961), indicates that local precipitation has experienced the sub-cloud raindrop evaporation. It leads to the enrichment of heavy isotopes in precipitation under arid and semi-arid climate conditions of the area (Craig, 1961; Price et al., 2008). The air temperature can be seen as the main controlling factor that impacts the stable isotope composition of precipitation in the study area (Fig. 4). The precipitation data suggest a trend of increasing isotope values with increasing air temperature and decreasing rainfall (Fig. 4). Lower isotope values are observed for snow events, particularly in December and March. The large rainfall events displayed overall the steepest slope, and highest intercept and d-excess values which are nearly similar to the snowfall samples, indicating re-evaporation effects on the low rainfall amounts (Bagheri et al., 2019). Precipitation during the summer season (Jun–August) with higher isotope values and lower d-excess values mainly originate from polar and Caspian Sea air moisture; while, moisture contributing to high d-excess and low isotope precipitation during January is mainly transported by Mediterranean air moisture (Bagheri et al., 2019; Juhlke et al., 2019). As in arid and semi-arid climates, re-evaporation of raindrops during precipitation results in enrichment of $\delta^{18}O$ of the precipitation (Clark and Fritz, 1997).

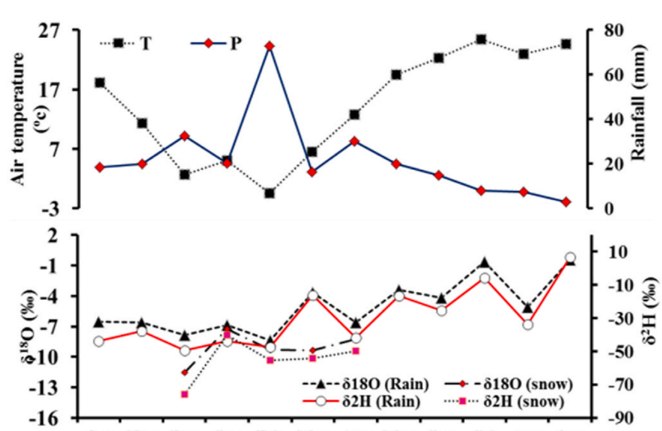

Fig. 4. Temporal variation of weighted average $\delta^{18}O$ and δ^2H of the precipitation samples and its relationship with air temperature and rainfall amount.

The data for ^{18}O and ^2H isotopes in 6 of the karstic springs (Arnaveh, Rezghaneh, Ghourdanlu, Sarani, Estarkhi, Ayoub hot spring) are shown in Fig. 5 along with the Global Meteoric Water Line (GMWL) (Craig, 1961), Local Meteoric Water Line (LMWL) and Mediterranean meteoric water line ($\delta^2H = 8 \times \delta^{18}O + 22$) (Gat and Carmi, 1970). The $\delta^{18}O$ and δD values of the springs vary from −10.2 to −11.8‰ and −61.5 to −73‰, respectively. Almost, all the samples in the study area plot near and around the LMWL with a small shift, as expected in this area, indicating present meteoric water as the main origin of the groundwaters. The spring water samples that are situated between the rain and snow samples, indicate that mixing of rain and snow can be the main source of this water sample (Fig. 5). The Sarani, Rezghaneh, Ghordanlu and Ayoub springs are depleted in $\delta^{18}O$ and δ^2H relative to the Arnaveh samples, indicating that the catchment area of these springs is situated at higher elevations. Overall, all spring water samples plot between the GMWL and the Mediterranean Meteoric Water Line (MMWL) and this reflects that the origin of the recharge in this region is mainly from Mediterranean vapor masses. The distribution of karstic water samples near the LMWL may imply high hydraulic connectively in the karst and rapid infiltration of precipitation before considerable evaporation. The groundwater samples can be classified into three main groups based on their $\delta^{18}O$ and δD values (Fig. 5). The first group, including the Estarkhi samples, are clustered above the GMWL and near the MMWL (Fig. 5), indicating that this water mainly originated from the Mediterranean vapor masses. The second group (Arnaveh spring) falls around the LMWL reflecting local precipitation origin with little evaporation effect. The isotope compositions of Arnaveh are higher than the other springs in the region. During infiltration of rain waters through the thick epikarst zone as well as the argillaceous carbonates with lower permeability, the isotope values of pore waters are little enriched due to the evaporation process especially in the Arnaveh catchment area. The other springs, Sarani, Rezghaneh, Ghordanlu and Ayoub with lower isotope values are classified in group 3. The Ayoub spring in group 3 showed a slight departure may due to little evaporation.

4.3. Groundwater flow direction

The karstic aquifer in the study area contains a sequence of anticlines which occupies an area of about 6800 km^2 and which is about 92 km long and 74 km wide. These anticlines follow the general E-W trend of the Kope-Dagh range. In terms of the structural setting, the study area is significantly affected by folding and faulting structures which provide a fracture system that leads to infiltration and the development karstic

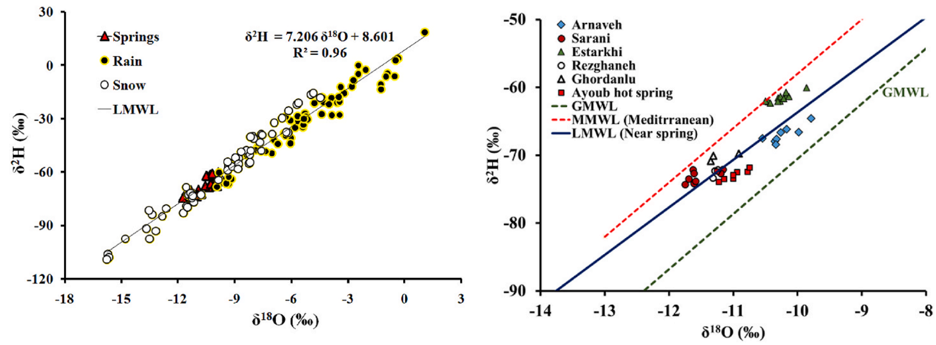

Fig. 5. The isotopic composition of springs compared to the precipitation samples (Rain and Snow) and LMWL, GMWL and MMWL.

- δ^{18}O and δD contents of the karstic springs

channels. In tectonically complex areas such as the study area, an adequate comprehension of the geological framework is crucial for successfully addressing hydrogeological dillemas. By combining conventional methods, e.g. geological mapping and the estimation of groundwater budget components, one can easily deduce reliable information about the hydrogeological setting of karst aquifers in tectonically complex areas.

The main aquifers in the area are made in the Cretaceous limestone unit of the Tirgan Formation. The Karstic aquifers discharge through several springs. The recharge elevation, groundwater budget and tectonic setting are the main effective parameters to determine the flow path in the area.

- Recharge elevation of the karstic springs

The highest recharge elevation is in the Sarani catchment area with most snow precipitation during the year. The rain and snow samples were collected at an average elevation in the study area. Locally sourced springs generally have an isotopic signature similar to the local precipitation for that region and elevation. Springs with a very different isotope composition than local meteoric inputs likely have non-local recharge, representing a more regional source. The combination of location-specific precipitation data with stable isotope data of the groundwater provides an effective method for flow path determination in springs (Springer et al., 2017). Arnaveh and Rezghaneh springs show an isotope composition that is almost similar to the LMWL with a little departure. The infiltrated water probably traveled through steep and/or short flow paths and resulted in locally sourced springs which show isotope values that are in agreement with the higher elevation of the karstification system. The elevation of the springs and their isotope values are used to interpret the elevation of the source of the recharge of the springs. It was assumed that a spring with isotopic ratios that are comparable to the meteoric input for its elevation range has a local flow path. The difference in the δ^{18}O value between the spring water value, and the δ^{18}O value predicted for the regional precipitation elevation line were calculated for the springs and are within ±2‰ δ^{18}O, indicating that they are all locally sourced springs and within the range of seasonable variability of δ^{18}O in precipitation.

In the study area, the δ^{2}H and δ^{18}O isotope composition of the precipitation shows a reverse relationship with altitude which is known as the altitude effect (Dansgaard, 1964). This isotopic gradient is used to estimate the mean elevation of the recharge areas of aquifers. It is based on the weighed mean annual isotopic composition of precipitation versus elevation. The δ^{18}O precipitation gradient is −0.32‰ per 100 m of altitude (Fig. 6). The mean recharge elevation zone of the springs in the research area ranges from 2200 to 2700 m.a.s.l (Fig. 6). The average estimated recharge elevation of Arnaveh spring is higher than the highest top in its mountains. The Arnaveh spring which is characterized by higher discharge value has enriched isotope compositions as compared to the other springs, indicating that the spring mainly recharges from a lower altitude or from snow pack melting water. On the other hand, the depleted stable isotope signature of springs such as Rezghaneh, Ghordanlu, Estarkhi and Sarani which are located at a higher elevation than Arnaveh might be a result of the elevation effect, snowmelt percolation and/or a more developed karst system in their catchment area.

The recharge percentage in study area varies from 45% to 50%. The catchment areas of the Arnavah, Rezeganeh, Sarani, Estarkhi and Ghordanlu Springs are 160, 70, 5.6, 5 and 5.4 Km^2, respectively. Arnaveh karst spring is discharge from Baba Boland anticline. The annual discharge volume of the spring is estimated about 15.8 Mm^3 (average flow rate of 500 L/s). The volume of recharge to the whole Baba Boland anticline is about 49.2 Mm^3. This is also the case with the Sarani karstic spring. The annual discharge volume of the spring is 1.1

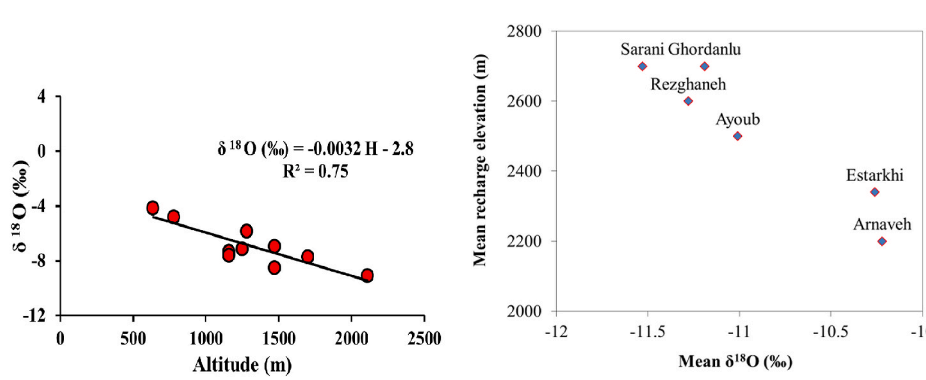

Fig. 6. Weighed mean annual δ^{18}O values of precipitation versus elevation (left) and recharge elevation of the springs (right).

- Groundwater budget and Tectonic setting

Mm^3 and the recharge volume is about 7 Mm^3. Totally, the sum of annual discharge volume of the total springs is about 25 mm^3, which is far less than the annual recharge volume to the karstic formations of the study area (about 120 mm^3). Due to the large difference between the annual discharge and the obtained recharge volume to the whole study area, the anticlines in the study area have the potential not only to supply water to the springs, but also have a larger excess groundwater storage volume that can migrate far from the recharge areas.

Fold and fault zones can be important determinants on groundwater flow in karstic aquifer. Faults are known to influence groundwater flow fields, spring discharge, and water-table elevations (Apaydin, 2010; De La Torre and Andreo, 2020). Faulting is often accompanied by a parallel set of joints which makes the whole formation permeable and much more significant hydrogeologically. Folding can affect groundwater flow as well as faulting.

The structural complexity of the anticlines in the study area, despite the folds and faults with northeast-southwest, northwest-southeast trends, makes regional flow water possible. Also, tensile joints that are located in large dimensions in the axis of the anticlines can play an essential role in the development and direction of karst water flows. Due to Iran's proximity to Turkmenistan and also the much higher altitude of Iran compared to neighboring country, there is a large potential for water migration toward the neighboring country through the main faults in the region. Determining the groundwater flow direction of karstic springs is one of the most complex, extremely sensitive and difficult problems to deal with in karst hydrology, hydrogeology and geology due to the unknown morphology of underground karst features. Consequently, the effects of tectonic structures are important to determine the flow direction and groundwater management. However, the probable local and regional groundwater flows in the study area are presented in Figs. 1 and 7.

4.4. Karst development inquiry

Different hydrogeological, hydrochemical and isotopic methods were used to determine the types of flow regime and evaluating karst development in the study area.

4.4.1. Hydrogeology and hydrochemical methods

The time series of discharge, temperature, electrical conductivity and ions concentration have little variation indicating diffuse flow system (Bagheri, 2018). Also, the analysis of recession curves in Arnaveh, Razghaneh, Estarkhi and Ghordanlu springs show that the groundwater is mainly drained from the fractures and small joints, indicating the diffuse flow regime in the area. In comparison, in Sarani spring, the greater slope of the recession curve indicates the drainage of groundwater mainly from medium fractures, indicating higher degree of karst development and diffuse-conduit flow regime in its catchment area (Bagheri, 2018). The most changes in discharge are observed in Sarani, which is due to the very high slope of the basin, the small catchment area, the bare limestone and the larger share of snow in annual rainfall. In Arnaveh and Razghaneh springs, whose catchment area is mainly covered with soil, changes in discharge rates as well as karst development are low.

From the perspective of karst morphology in the region, the most important evidences of karst development in the Sarani catchment area near the international transboudary are Karrens, sinkhole, dry valley, small karstic cave and closed depression. The presence of some of these important karst complications can be a strong reason for the development of karst in this area.

4.4.2. Isotopic methods

In this method, to determine the type of flow regime, stable and unstable isotopes of the karst springs in the region have been used.

- Temporal isotope variations of the groundwaters

The δ^2H and $\delta^{18}O$ of the water samples show little monthly fluctuations. The groundwater isotope behavior of springs are closely aligned with isotopic variations of the precipitation. In Fig. 8, histograms of the average monthly rainfall versus the monthly isotopic values are also shown. The temporal isotope variations of the karstic springs in the area can be classified mainly into two different groups based on the monthly isotopic values during the period from 2017 to 2018 (Fig. 8). The Sarani springs and to a lesser extent Arnaveh spring fluctuate seasonally with higher values in the summer and lower values in the winter (Fig. 8), which is similar to the weighted average $\delta^{18}O$ and δ^2H of the precipitation. It's indicating diffuse-conduit groundwater flow regime in a medium karstified system in their catchment area, especially in Sarani area. The lower EC and isotopic value of the Sarani further confirm the higher karstified system in that area compared to the other springs (Fig. 8). It can be seen that the groundwater and precipitation isotope

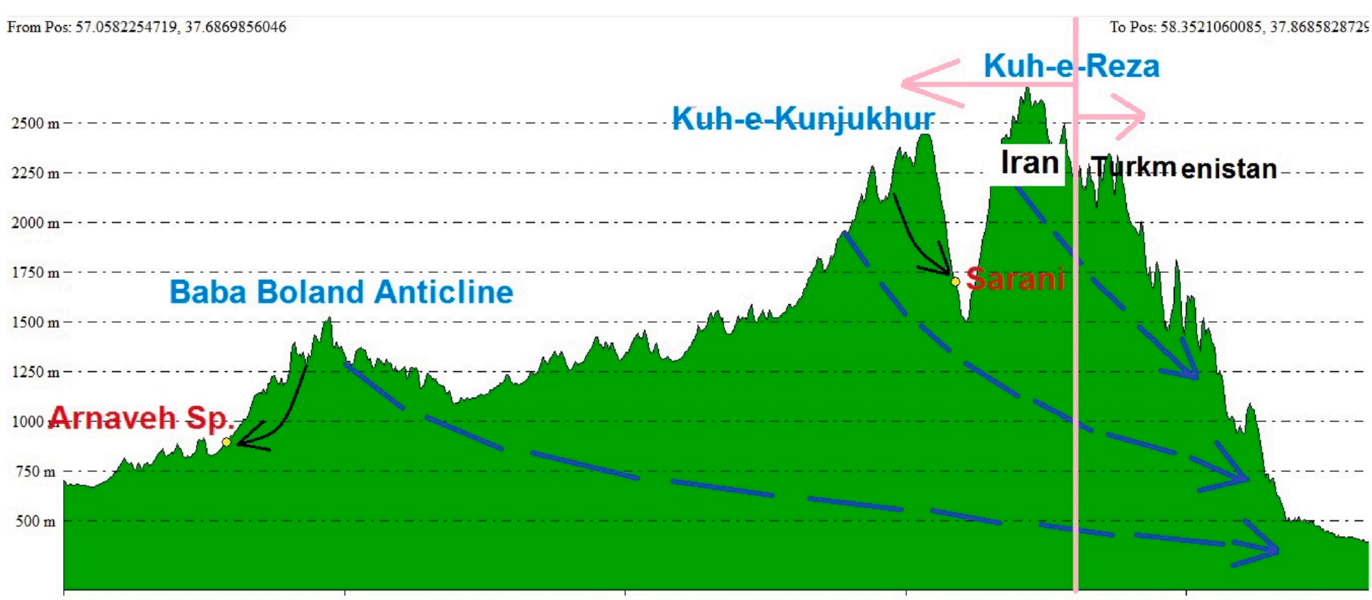

Fig. 7. Hydrogeological cross section from Arnaveh to Sarani Springs and probable local (black arrows) and regional flow (dash blue arrows) direction.

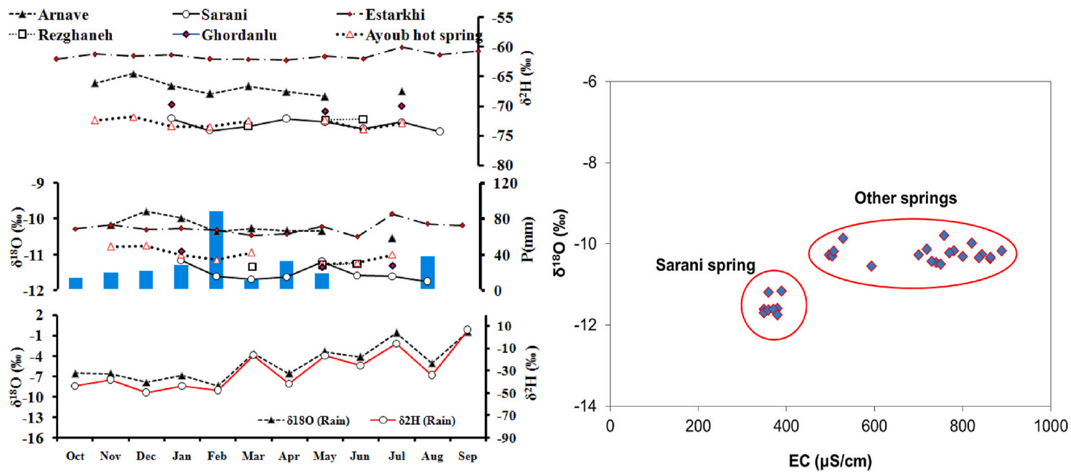

Fig. 8. Temporal variation of $\delta^{18}O$ and $\delta^{2}H$ of springs compared to the weighted average $\delta^{18}O$ and $\delta^{2}H$ of local rain and amount of the average rainfall (histogram) (left) and $\delta^{18}O$-EC relation for the springs (right).

- $\delta^{13}C$ content

values vary seasonally in accordance with atmospheric temperature (T) and is the inverse of atmospheric humidity (RH) and precipitation amount (P). The Estarkhi water samples show a different behavior, as it reveals almost constant isotope values most of the time.

The isotope values of Estarkhi spring are more enriched than of Sarani spring, indicating the lower recharge elevation. Its constant isotope deviation may be due to a diffuse groundwater flow regime in a lesser karstified system in its catchment area and also rain water as its main origin. The isotope composition of Arnaveh and Sarani water reflects a small variation range and more negative values than in rain water samples, indicating that winter precipitation with snow fall dominates and more isotopically depleted rainwater is the main source of recharge water to its groundwaters. The snowpack with higher isotope values due to evaporation and distillation processes and the precipitation of enriched rainfall in the spring and summer seasons are the main reasons for enhanced isotope values in the springs in this area.

The $\delta^{13}C$ of DIC was used to determine the origin of HCO_3 in the groundwater and karst development of the study area. The stable carbon isotope values change widely in different carbon origins, so it can help in identifying origin and evolution of carbon in groundwater (Clark and Fritz 1997). The $\delta^{13}C$ of DIC in the karstic springs are affected mainly by soil CO_2 that ranges from −26‰ to −10‰ and dissolution of carbonate bedrock that ranges between 0‰ and 2‰ (Cerling, 1984; Fritz et al., 1989; Can and Clark, 1999).

The $\delta^{13}C_{DIC}$ values of the karstic springs in our study area vary from −8.9‰ to +3‰ (Fig. 9). According to common pH values for the karstic springs (≈7), it can be concluded that HCO_3 is the main source of DIC. Organic matter degradation (soil CO_2) can be the other source of the $\delta_{13}C_{DIC}$ value of the karstic groundwater (Fig. 9). However, it can be observed that the Sarani karstic is characterized with lower $\delta^{18}O$, higher $\delta^{13}C_{DIC}$ and almost constant variation $\delta^{13}C$ with the time than others (Fig. 10). It indicates more carbonate dissolution and a low soil CO_2 contribution and as a result more karst development in this area. In other springs in the region, the $\delta^{13}C$ values tend to be more negative during rain season (Fig. 9). The more depleted $\delta_{13}C_{DIC}$ values (−8.9‰) and higher EC value of the other springs are related to the presence of thick soils cover (thick epikarst and greater soil CO_2 contribution) in the recharge areas (Fig. 10). These indicate lower karst development in the catchment area of these springs and more diffuse flow regime than the Sarani spring.

Tritium (^{3}H) is one of the radioactive isotopes used to estimate the groundwater age. A recent recharge of such an aquifer may be marked by tritium contents greater than 1 TU, whereas water with tritium contents less than 1 TU is considered as water that recharged before nuclear testing (Mazor, 1991). The presence of detectable activities of tritium in groundwater highlights modern infiltration of rainwater in aquifers (Clark and Fritz, 1997). Tritium activities were measured two rainwater and three spring water samples to establish residence time of karstic groundwater. Tritium contents in the study area range from less than 0.1 to 2.5 TU in the springs and 9.3 to 10.6 TU in the rain waters. Based on a qualitative interpretation of ^{3}H, two distinctive recharge events are recognized in the area. The presence of immeasurable tritium concentrations (<0.1 TU) of a sample reflects a low recharge of aquifers in the study area. The karstic groundwaters were mainly recharged by

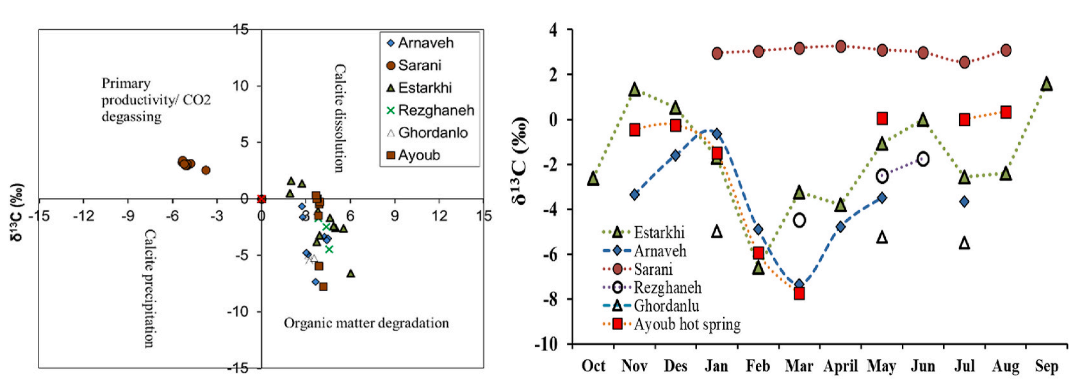

Fig. 9. Seasonal variations in $\delta^{13}C_{DIC}$ values for spring waters in the northeast of Iran.

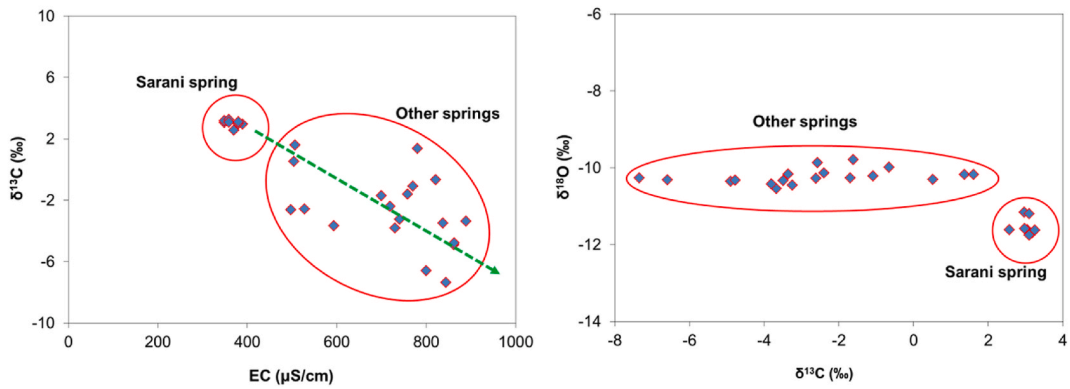

Fig. 10. The δ^{13}C vs. EC and δ^{18}O values of the springs in the northeast of Iran.

- Groundwater age

recent precipitation, while the thermal groundwater with tritium contents <0.1 TU were dominantly recharged by precipitation priors to 1952. Groundwater age (t) based on ^{3}H decay was calculated using the following equation (Clark and Fritz, 1997):

$t = -17.93 \times \ln (a_t{}^{3}H/a_o{}^{3}H)$

where $a_o{}^{3}H$ and $a_t{}^{3}H$ are tritium contents in rainwater and the sample respectively. Based on the measured 10 TU in rain water samples in the area, the age of karstic groundwaters in the study area are calculated to be about 30–40 years in the fresh and cold karstic spring waters and more than 60 year in the thermal groundwater. A groundwater age of 30–40 years at Arnaveh and Rezghaneh karstic springs indicates that the groundwater flow rate in the catchments area of these springs is low at about 700–1000 m/year, which depends on the extent of their catchments. In terms of karst development, karst is not well developed in this area, and the dominant flow regime is diffuse flow, except in Sarani spring which is diffuse-conduit flow regime. Therefore, it can be concluded that percolated rain water and snow melt flows in about 30 years through the joints and fractures and it drains from the springs.

Given that the age of groundwater in the Baba Boland anticline is estimated to be about 30 years, so this outflow water is related to earlier times, probably recharged by snow, depleted in stable isotope values. Therefore due to the recent droughts regime, the discharge rate of the karstic springs, especially Arnaveh is expected to diminish by times. Given the importance of these springs in supplying drinking water to the region, management plans for these karstic springs should be considered in future critical times.

- δ^{37}Cl stable isotope

δ^{37}Cl content in groundwater can have several origins. Except for dissolved halite from evaporites it can originate from sources such as rainwater (Kohler and Wassenaar, 2009; Wassenaar and Kohler, 2004), and from water-rock interaction with chloride bearing minerals such as apatite (Eggenkamp and Schuiling, 1995). The main factors responsible for δ^{37}Cl values in groundwater are water-rock interactions and mixing of waters with different δ^{37}Cl compositions (Shmulovich et al., 1999). The chlorine stable isotope composition of the spring water in this study vary from −0.04 to 0.31‰ (Fig. 11). Rainwater has very little δ^{37}Cl isotopic content near zero. The Arnaveh, Rezghaneh and Ayoub springs are characterized by higher δ^{37}Cl values than others in the study area. The Sarani spring in the aquifers has the lowest δ^{37}Cl isotopic and Cl content that is within the range of the recharge (rain) water (Fig. 12). Both δ^{37}Cl and chloride concentration increase through groundwater flow paths from the recharge to the discharge area (Fig. 12). The springs with longer residence times have the highest chlorine isotope ratio. The water source of Ayoub which is more than 60 years old has the highest

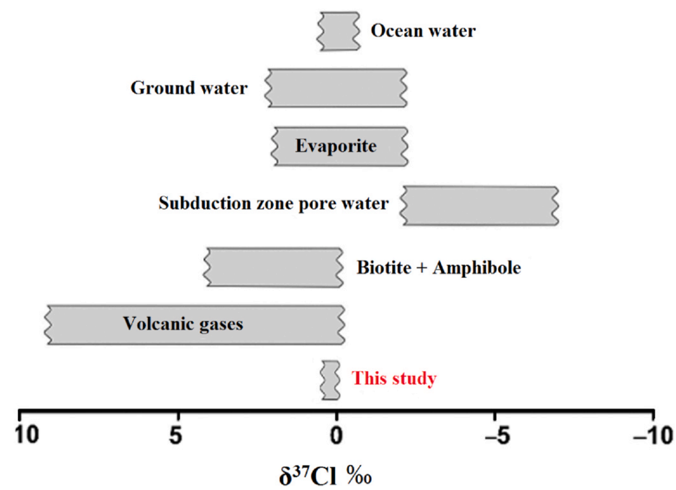

Fig. 11. δ^{37}Cl values of the water samples in comparison to the other resources.

chlorine isotope ratio.

Overall, the water resources in the area can be classified into three distinct groups. The first group contains only the Ayoub thermal spring which has the highest age and isotope value and which is different from the δ^{37}Cl content of the rain water sample. The second group, Arnaveh and Rezghaneh springs, have high δ^{37}Cl values and longer residence time than the fresh-cold karstic springs. This is most probably due to water-rock interaction during the time and mixing of waters with different δ^{37}Cl compositions. The third group, including the Sarani and Estarkhi springs, has the lowest δ^{37}Cl that is near the δ^{37}Cl of the rainwater sample. They have the highest recharge elevation and are mainly recharged by snow melt water. The karst formation in the catchment area of theses springs, especially Sarani spring, is more developed than others. So, the rainwater flows through the conduit systems and consequently it shows lower water-rock interaction and lower δ^{37}Cl values and more δ^{13}C that are comparable to rain water (Fig. 12). Most probably, snow-melt water has the lowest δ^{37}Cl, even lower than rainwater.

Consequently, based on the recharge elevations, groundwater budget and tectonic setting analysis, the local and regional flows control the hydrogeological settings of the area. A large amount of water migrates toward the neighboring country. Fold and fault zones can be important variables on groundwater flows in the karstic aquifer. In terms of karst development, around the Sarani region in transboundary karstic aquifer, the karst is more developed and conduit flow is the dominant flow regime in this area in comparison to the other regions.

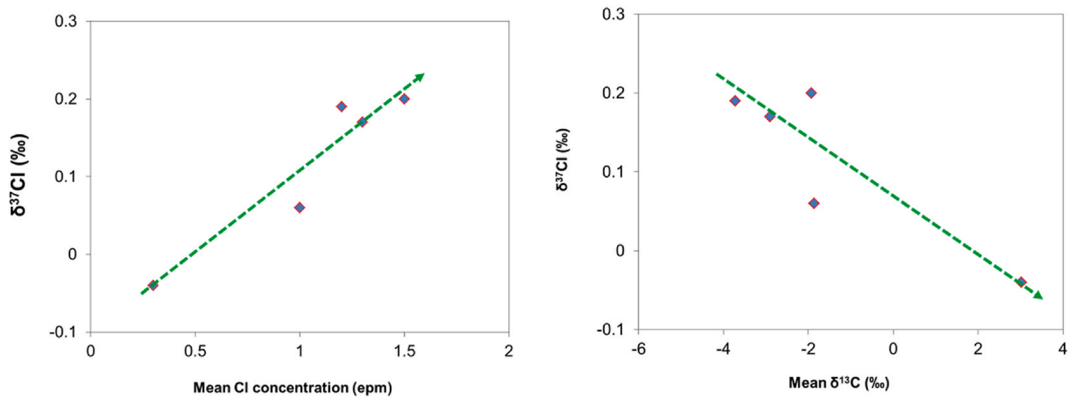

Fig. 12. δ^{37}Cl vs. δ^{13}C and Cl ion concentration of the water samples.

5. Conclusion

The groundwater origin, flow direction, residence time and karst development of some springs in a transboundary karstic region in northeast Iran were studied by hydrogeological, chemo-isotopic (δ^{18}O, δ^{2}H, δ^{13}C, ^{3}H and δ^{37}Cl) and tectonic characterization. The origin of the recharge in this region is mainly from Mediterranean vapor masses. The $\delta^{13}C_{DIC}$ values of the karstic springs in the study area vary from −8.9‰ to +3‰ and more positive values in Sarani indicates more carbonate dissolution and low soil CO_2 contribution and more depleted $\delta_{13}C_{DIC}$ values (−8.9‰) in the other springs are related to the presence of thick soils cover. The mean recharged elevation zone of the area ranges from 2200 to 2700 m.a.s.l. The different isotopes techniques confirm more karst development and conduit flow regime in Sarani region and not well karst developed and dominate diffuse flow regime in the other regions.

Based on the recharge elevations, groundwater budget and tectonic setting analysis, the local and regional flows control the hydrogeological settings of the area. A large amount of water migrates toward the neighboring country. Fold and fault zones can be important variables on groundwater flows in the karstic aquifer. In terms of karst development, around the Sarani region in transboundary karstic aquifer, the karst is more developed and conduit flow is the dominant flow regime in this area in comparison to the other regions.

Due to the recent droughts regime, the discharge rate of the karstic springs, especially Arnaveh is expected to diminish by times. Given the importance of these springs in supplying drinking water to the region, management plans for these karstic springs should be considered in future critical times.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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