

## Determination of karst aquifer characteristics using physicochemical parameters (A case study from west of Iran)

Haji Karimi\*<sup>1</sup>, Ezzatollah Raeisi<sup>2</sup>, Abolfazl Rezaei<sup>3,4</sup>

<sup>1</sup> Agriculture Faculty, Ilam University, Ilam, 69315-516, Iran

<sup>2</sup> Department of Earth Science, Faculty of Science, Shiraz University, 71454, Shiraz, Iran

<sup>3</sup> Faculty of Earth Sciences, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran

<sup>4</sup> Center for Research in Climate Change and Global Warming (CRCC), Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran.

\*Corresponding author, e-mail: h.karimi@ilam.ac.ir

(received: 21/03/2018 ; accepted: 25/06/2018)

### Abstract

The karstic Rijab Spring with an average discharge of 3290 l/s is located in the Alvand River basin in the northwest of the Zagros, Iran, which drains Asmari formation. To investigate groundwater flow in the catchment area of the Spring, the physicochemical parameters include major cations and anions, discharge, EC, pH, and temperature were studied from September 2000-2002. The results indicate that the karst aquifer has a diffuse-conduit flow system since the diffuse condition supplies mostly base flow whereas the conduit system, providing quick flow, activates mostly during snowmelt period at late-winter and early-spring. The spring hydrograph shows two recession coefficients in both 2000-01 and 2001-02 water years. In both years, the steep recession coefficient ( $\alpha_1=0.0225$  on average) which occurs in the wet season is related to the conduit flow system whereas the gentle recession coefficient ( $\alpha_2=0.00685$  on average) corresponds with the dry period and related to the diffuse flow. Moreover, the temporal variations of EC, major ions concentrations and saturation indices of the calcite and dolomite also suggest diffuse-conduit flow system. Furthermore, investigation of both the hydrograph and chemographs of the Rijab Spring indicates that about half of the spring catchment area is distributed out of surface catchment boundary.

**Keywords:** Karst, Diffuse-Conduit Flow System, Physicochemical Parameters, Alvand Basin, Rijab Spring.

### Introduction

Temporal variations of physiochemical parameters of karstic springs often use to determine aquifer characteristics. White and Schmidt (1966) and White (1969) classified flow system in karst aquifers into two different categories of diffuse and conduit based on hydrogeological and geomorphological conditions. Shuster and White (1971) concluded that the type of flow (diffuse or conduit) can be determined using chemograph. Jacobson and Lamgmuir (1974) categorized flow systems into conduit, diffuse-conduit, diffuse, and Gatesburg diffuse in accord to recharge sources, electrical conductivity (EC), and coefficient of variation of discharge. In addition, the other criteria including the type of recharge, coefficient of variation of EC, temperature and temporal variations of different parameters are used to find flow system in karst terrains (Jacobson & Langmuir 1974; Ede, 1972; Cowell & Ford 1983; Birk *et al.*, 2004; Zhou *et al.*, 2008; Moore *et al.*, 2009; Mohamadi & Shoja 2014; Nassery *et al.*, 2014; Adji & Bahtiar 2016). Temporal variations of physicochemical parameters of karstic springs were inspected by various researchers to determine

groundwater flow system (i.e., diffuse or conduit) in karstic aquifers (e.g., Ashton, 1966; White, 1988; Williams, 1983; Sauter, 1992; Ryan & Meiman 1996; Raeisi & Karami 1996; Desmarais & Rojstaczer 2002).

In a diffuse flow system, recharge is generally occurred through a dispersed network of numerous small joints and fractures with width opening of smaller than one centimeter where allows groundwater to move in a laminar manner. One of the main peculiarities of these aquifers is a small variation of physiochemical parameters of spring's water. Natural discharge from such a system is usually through a large number of smaller springs and seeps. In contrast, in a conduit flow system, the aquifer is fed through either large open fractures (ranges from one centimetre up to more than one meter) or dolines. In such systems, quick recharge into karstic aquifer after intense precipitation events causes the turbulent behaviour of karstic springs. Note that in this case, karstic aquifer drains mostly through a single large karstic spring. In most cases, a combination of diffuse-conduit flow system often occurs in natural karstic systems and not a purely diffuse or conduit.

The karstic Rijab Spring, located in the southwest of Kermanshah, Iran, drains groundwater produced by the Rijab Anticline (RA). The spring water is used for drinking and irrigation purposes. There is no any production well and/or piezometer in the RA. Since there is a rough topography, expensive road construction and a deep water table in the karstic RA, drilling piezometer is very expensive. In such conditions characterizing the karst system using wells and piezometers is not possible.

Several studies were conducted in the Alvand Basin which the Rijab Spring is located inside the basin. Hydrogeological characteristics of the Alvand Basin karst aquifers was studied by Karimi *et al.* (2005). Karst development of the basin using spring recession coefficients was evaluated by Bagheri Seyed Shokri *et al.* (2015). The hydrodynamic behaviour of the Gilan karst spring which is situated in the Alvand Basin was considered by Karimi *et al.* (2003) and Bagheri Seyed Shokri *et al.* (2013).

The main goal of this study is to determine catchment area, karst development and flow system of the Rijab Spring, using its temporal variations of physicochemical parameters from September 2000 to September 2002 in combination with geological settings.

### Hydrogeological setting

The study area is located 150 km southwest of Kermanshah, west of Iran (Fig.1). The annual average precipitation is about 530 mm which falls mostly in the form of snow over mid-autumn to mid-spring (i.e., November to June). The topography of the study area is dominated by the folded mountain structure of the Zagros thrust zone, High Zagros (Sahabi *et al.*, 1998). Geological formations in the study area in increasing order of age are the recent alluvium, Tertiary Aghajari marl and sandstone, Tertiary Gachsaran gypsum and marl, Tertiary Asmari dolomitic limestone and dolomite, Cretaceous Pabdeh-Gurpi marl and shale with interbedded thin marly limestone, and Cretaceous Ilam limestone (Fig.1). Stratigraphic and structural characteristics of the Zagros sedimentary sequence were described in detail by Falcon (1974) and Stocklin & Setudehnia (1977).

The RA, with a length of 80 km and a width of 10 km, follows a general northwest-southeast direction of the Zagros Mountain Ranges. The highest elevation is about 2420 m a.s.l., while the least elevation is about 1100 m a.s.l. in the southwest of the anticline. Due to an existence of several cross faults and the Kerend-Rijab thrust, the RA has no distinct anticlinal structure.

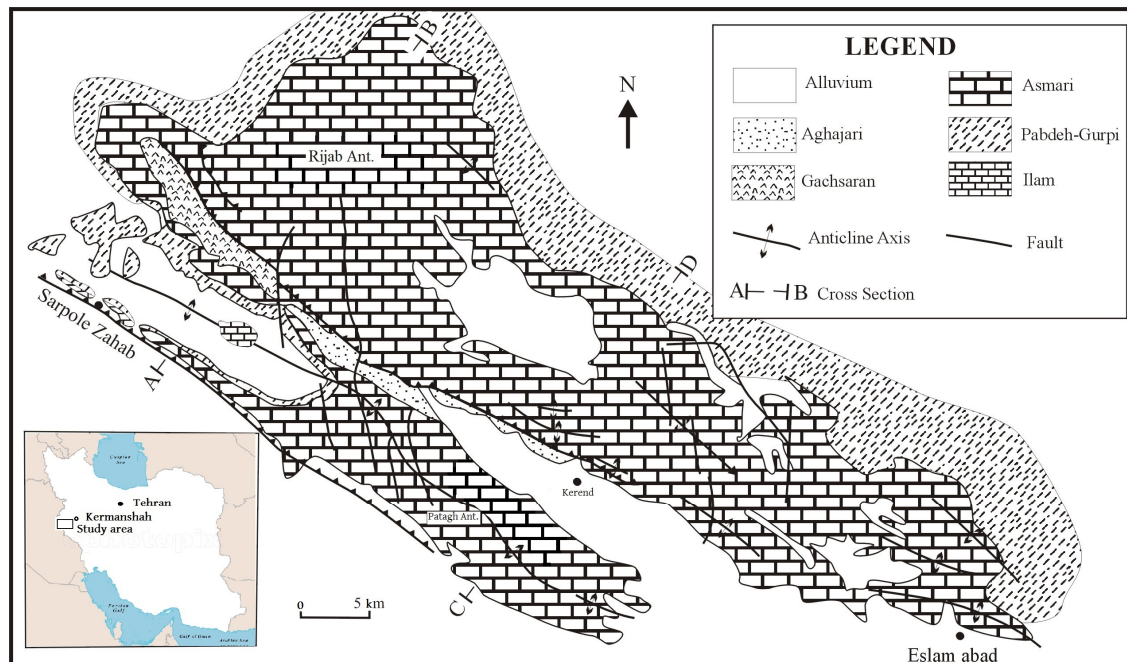


Figure 1. Geological map of the study area

The Kerend-Rijab thrust fault with more than 40 km length acted in the southwestern flank of the RA and thrust the Asmari Formation over the Aghajari Formation. The Asmari Formation encompasses the main aquifer of the RA, which is underlined by the very-low permeable Pabdeh-Gurpi Formation. Karst water produced by the RA discharges mostly through the springs of Rijab, Babayadegar, Kerend, and Eslamabad (Nos. 1, 2, 3, and 4, respectively, on Fig.2) in southern flank and the springs of Barreh-shah and Tootshami (Nos. 5 and 6, respectively, on Fig. 2) from the northern flank of the anticline which the summary of their physicochemical parameters are listed in Table 1. Note that the Rijab Spring is the largest-volume discharge spring in the area. The maximum,

minimum and mean annual discharge values of the Rijab Spring were measured to be 11338, 1015 and 3291 l/s, respectively, during the study period from September 2000 to September 2002.

**Method of study**

To investigate groundwater flow system of the Rijab Spring, we analysed the physicochemical parameters in conjunction with the geological and topographical conditions of the area. EC, water temperature, pH, major ions (calcium, magnesium, sodium, potassium, bicarbonate, sulphate and chloride) and discharge of the Rijab Spring were measured every two weeks during the period from September 2000 to September 2002.

Table 1. Characteristics of the springs drain the Rijab Anticline (RA).

Row	Spring	No. on Fig.1	Elevation (m)	Mean Q (lit/s)	Mean EC (µS/cm)	Formation
1	Rijab	1	1120	3291	370	Asmari
2	Babayadegar	2	1430	12	370	Asmari
3	Kerend	3	1670	23	367	Asmari
4	Eslamabad	4	1340	170	419	Asmari
5	Tootshami	5	1620	270	374	Asmari
6	Barreshah	6	1650	1200	377	Asmari

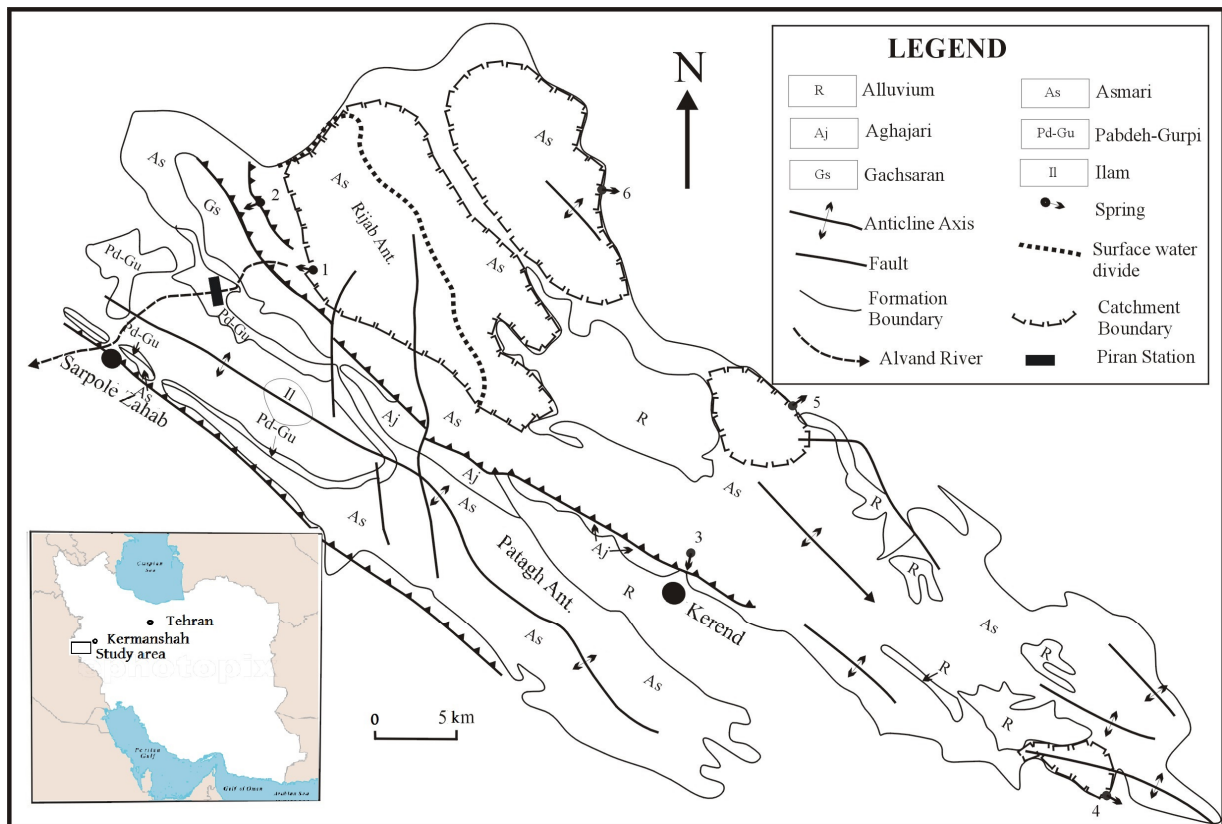


Figure 2. Hydrogeological map of the Rijab anticline (RA) and the catchment area of the Rijab Spring (No 1)

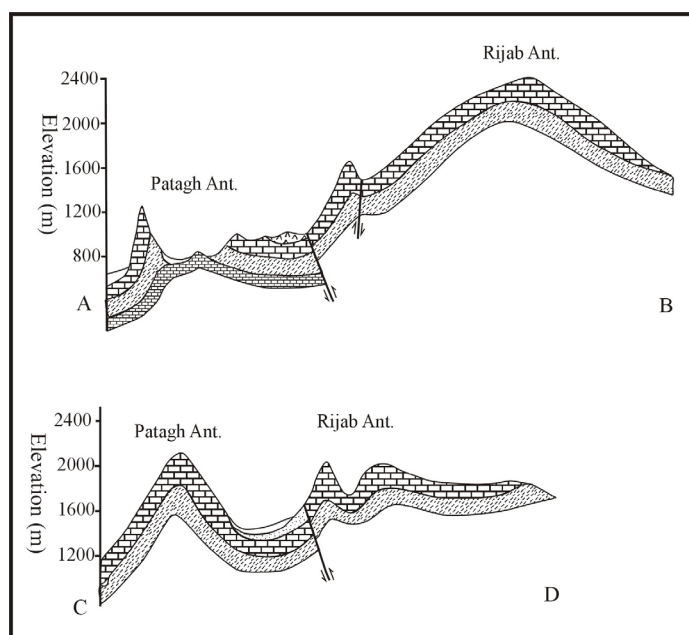


Figure 3. Geological cross sections of the study area (location of the cross sections are shown in Fig. 1).

Note that to improve the accuracy of the investigation we measured the above parameters once every two days during the wet season.

Temperature, EC, pH and discharge of the spring water were determined in the field during sampling. Calcium and magnesium were determined by titration with EDTA and Murexide and Eriochrom Black-T as indicators. Flame photometry methods were used to determine the concentrations of sodium and potassium. Chloride and sulphate were determined by the standard Mohr and turbidity methods, respectively. Bicarbonate was determined by titration with HCl and Methyl orange as indicator.

Carbon dioxide partial pressure ( $P_{CO_2}$ ), calcium saturation index ( $SI_c$ ), dolomite saturation index ( $SI_d$ ) and gypsum saturation index ( $SI_g$ ) were calculated using the WATEQF model (Plummer *et al.*, 1978). The accuracy of the analysis was estimated from the electro neutrality (E.N.) condition:

$$E.N. (\%) = \frac{|\text{sum cations} - \text{sum anions}|}{(\text{sum cations} + \text{sum anions})} \times 100 \quad (1)$$

where concentrations of the cations and anions are expressed by meq/l. The error values were less than 5% for all the water samples.

### Catchment area of the Rijab Spring

Exact determination of the catchment boundary is one of the most complex and difficult problems to

deal with in karst hydrogeology (Bonacci & Zivaljevic 1993; Connair & Murray 2002). Area of the watershed of the Rijab Spring was calculated by a simple balance equation during the 2000-2002 water years.

$$A = V / (PI) \quad (2)$$

where  $A$  is the catchment area ( $m^2$ ),  $V$  represents the annual volume of water discharged from the Rijab Spring ( $m^3$ ),  $P$  is annual precipitation occurred over the catchment area (m) and  $I$  denotes the groundwater recharge coefficient. The study area received 552 and 480 mm precipitation during the 2000-01 and 2001-02 water years, respectively. The groundwater recharge coefficient in this area is expected to be in the range of 0.5 to 0.7 based on catchment and climate characteristics of the studied region and also experiences on other karst sites of the Zagros Mountains, Iran (Rahnamaie, 1994; Pezeshkpour, 1991; Rezaei *et al.*, 2017). Area of the spring catchment ranges from 221 to 309  $km^2$ , considering the uncertainty in groundwater recharge coefficient. The underground catchment area of the Rijab Spring is distributed beyond the surface catchment area. For example, as can be seen in Fig. (2), about 122  $km^2$  of the minimum area of the spring catchment (i.e., when the infiltration coefficient is considered to be equal to 0.7) which covers southern flank of the RA, falls within the surface catchment area of the spring

whereas the rest, with the area of about 99 km<sup>2</sup> located in the northern flank of the anticline, is distributed outside the surface catchment area. Such situation in which the karst groundwater boundary is different from the surface catchment boundary also was reported by other researchers from other karst terrains (Currens, 2002; Chen *et al.*, 2004; Rezaei *et al.*, 2013; Eris & Wittenberg 2015; Rezaei *et al.*, 2017). The detailed procedure of determining the catchment area boundary of the spring is described by Karimi (2003). However, the following evidence is justified to determine the catchment area boundary of the Rijab Spring:

(1) All parts of the determined catchment area is located at the higher elevation than the Rijab Spring,

(2) There is no any sign of hydrogeological and tectonic barriers to disconnect hydrogeological relationships between the determined area and the spring location; thus groundwater produced over different parts of the area can move easily towards the spring (Fig. 3).

(3) Groundwater budget of the adjacent anticlines which was calculated by Karimi, (2003) indicates that most of the water produced by them is discharged through their own spring(s).

(4) The calculations also show that total discharge from the northern part of the RA by the Barreh-Shah and Tootshami springs is smaller than that produced in the northern flank. The Barreh-Shah and Tootshami springs (No. 5 and 6 in Fig. 2) with total volume discharges of 37.8 and 8.5 million cubic meter (MCM), respectively, can drain only groundwater produced by a limestone with an area of 120 km<sup>2</sup> (98 and 22 km<sup>2</sup> respectively) whereas the total area of the limestone crops out in the northern flank of the RA is 220 km<sup>2</sup>.

(5) Small values of EC and sulphate concentration, low temperature and light isotope ratio of the Rijab Spring [ $\delta^{18}\text{O}$  (‰)=-7.01 and  $\delta^2\text{H}$  (‰)=-35.9] reasonably consistent with lithological (carbonates) and topographical (high elevation) situations of the catchment area. Most of the karstic springs with a good water quality (i.e., low EC) in the Zagros region emerge from the Asmari Formation (carbonate). The evaporative Gachsaran Formation, which causes degradation of the water quality in the Zagros Mountains (Karimi *et al.*, 2005; Raeisi *et al.*, 2013; Rezaei *et al.*, 2017) does not crop out within the determined catchment area. The high elevation of the area causes a low temperature and a light isotope ratio of rainfall and groundwater.

Therefore, the fact is that water quality of the karstic spring can reasonably reveal characteristics of the karstic aquifer (Zhou *et al.*, 2008).

(6) Another issue confirms the hypothesis is that a large amount of the discharge of the Rijab Spring comes from outside the surface catchment area is the flow coefficient (FC) which can be defined as follows:

$$FC = Q_{Total} / Q_{Rain} \quad (3)$$

where  $Q_{Total}$  is the total discharge volume of sub-basin and  $Q_{Rain}$  represents the total volume of rainfall (MCM) falls in the sub-basin. If there are no losses from rainfall (ideal condition) then the value of  $FC$  is 1. But in fact, phenomena like evapotranspiration and surface runoff loss some amount of precipitation; therefore, the value of  $FC$  is always less than 1. Here, the flow coefficient was calculated to be 1.38 for the Piran station (Fig.2), in the adjacent downstream the Rijab Spring, implying that some amount of discharging water from the Rijab Spring comes from adjacent areas.

Based on the above mentions, the catchment area of the Rijab Spring was determined. As can be seen in Fig. 2, some area of the catchment area is distributed outside the surface catchment area. Exact determination of the catchment boundary of the Rijab needs more detailed studies such as tracing test.

### Hydrograph and recession coefficient of the Rijab Spring

The Rijab Spring hydrograph and daily rainfall from 2000 to 2002 are presented in Fig. 4. The spring has a karstic behaviour since it's hydrograph after receiving the percolated rainfall increases with a steep slope up to the peak and then at beginning of the dry period get to start coming down slowly. Although it is a karstic spring, but discharge does not increase suddenly after starting main precipitation in November (Fig. 4) due to (1) the elevation difference between the spring and the surrounding highlands is large (i.e., thick unsaturated zone) and (2) the precipitation in the RA occurs mostly in the form of snow during autumn and winter and snow melting does not occur until the late winter; therefore, recharge rate is not significant during the autumn and early-winter. At the end of winter and early-spring, discharge of the spring increases when precipitation falls mostly in the form of rain as well as the snowpack getting start to melting by air temperature increasing. By

the end of rainy season and snowmelt (i.e., at the beginning of the dry period), the spring discharge reduces to the base flow discharge in two to three months. There are no significant variations in the spring discharge during the dry period of both the 2000-01 and 2001-02 water years.

The base flow and quick flow of the spring was separated using the local minimum method presented by Ward and Robinson (2000) as outlined in Fig. (4a). The base flow is obtained to be 62.2% and 62.3% in the 2000-01 and 2001-02 water years, respectively (Table 2). The relatively high volume of quick flow (about 38%) implies that the karstification is well-developed. It seems that the flow type in the Rijab aquifer is diffuse-conduit where the large volume of groundwater stores in the rock matrix and small joints and fractures (i.e., diffuse flow system) quickly drains to the spring by larger fractures and karst features (i.e., conduit flow system) during a period from late-winter to early-spring.

The  $Q_{\max}/Q_{\min}$  ratio is about 11.2 which implies that karstification is well-developed in the catchment area and the existence of karst features like grikes, karrens, shafts and small shelter caves in the area confirms this claim.

To investigate the karst development in the area we tried to explore recession curve of the Rijab Spring (Fig 5). The recession coefficients for the 2000-01 and 2001-02 water years were calculated by a curve-fitting algorithm presented by Vasileva & Komatina (1997). Two following recession coefficients can be seen in recession curve of the Rijab Spring: a steep recession ( $\alpha_1=0.02$ ) occurring after the rain period and during snowmelt and a gentle one ( $\alpha_2=0.006$  for 2000-01 and  $\alpha_2=0.0075$  for 2001-02) for the dry period. Various coefficients of the recession curve in a karstic spring can result from (1) change in micro-regime of the karstic system, particularly change in caves and joints

systems which control the discharge; (2) sharp change in area of the catchment of the spring and (3) heterogeneity in the karst aquifer which leads to various conductivity values (Petras, 1986; Bonacci, 1993; Amit *et al.*, 2002). In the cases that there are three different recession coefficients (i.e., steep, intermediate and gentle), the steep one represents the role of large karstic conduits with high hydraulic conductivity like caves (Ford & Williams 2007). The absence a hydrograph with three different recession coefficient for the Rijab Spring may suggest that the large conduits which can control the conduit flow system is not developed in the area. Nevertheless, a hydrograph with two different recession coefficients for the spring reasonably reveals that the karstification is well-developed. Note that the large volume of the quick flow in the wet season also confirms this hypothesis. It seems that the  $\alpha_1$  recession coefficient of the Rijab Spring is related to the contribution of snowmelt or dominating conduit flow with greater conductivity while the  $\alpha_2$  recession coefficient indicates that the discharging water comes from smaller joints and fractures having smaller conductivity (Sauter, 1992, Amit *et al.*, 2002; Mohamadi & Shoja 2014). The notable point is that since the contribution of the quick flow in the spring is large, we can suggest the conduit flow has a very important role not only in transporting but also in storing water in the catchment area of the Rijab Spring.

The mode of entry (recharge) to the Rijab aquifer can be called autogenic (Williams, 1983; Ford & Williams 1989), which implies that recharge is diffuse through joints, fractures and shafts over the entire catchment, and not as recharge via stream sinks or dolines. No sign of dolines or large caves is observed in the catchment area of the Rijab Spring. Grikes, karrens, shafts and small shelter caves are main karst features developed in the catchment.

Table 2. The values of base and quick flow for the Rijab Spring.

Year	Period	Volume (MCM)		Percent of volume (%)	
		Base	Quick	Base	Quick
2000-2001	Dry period	26.82	4.54	85.5	14.5
	Wet period	19.44	23.54	45.2	54.8
	Total year	46.26	28.08	62.2	37.8
2001-2002	Dry period	53.8	18.1	74.8	25.2
	Wet period	24.4	29.21	45.5	54.5
	Total year	78.18	47.31	62.3	37.7
2000-2002	Total period	124.4	75.39	62.25	37.75

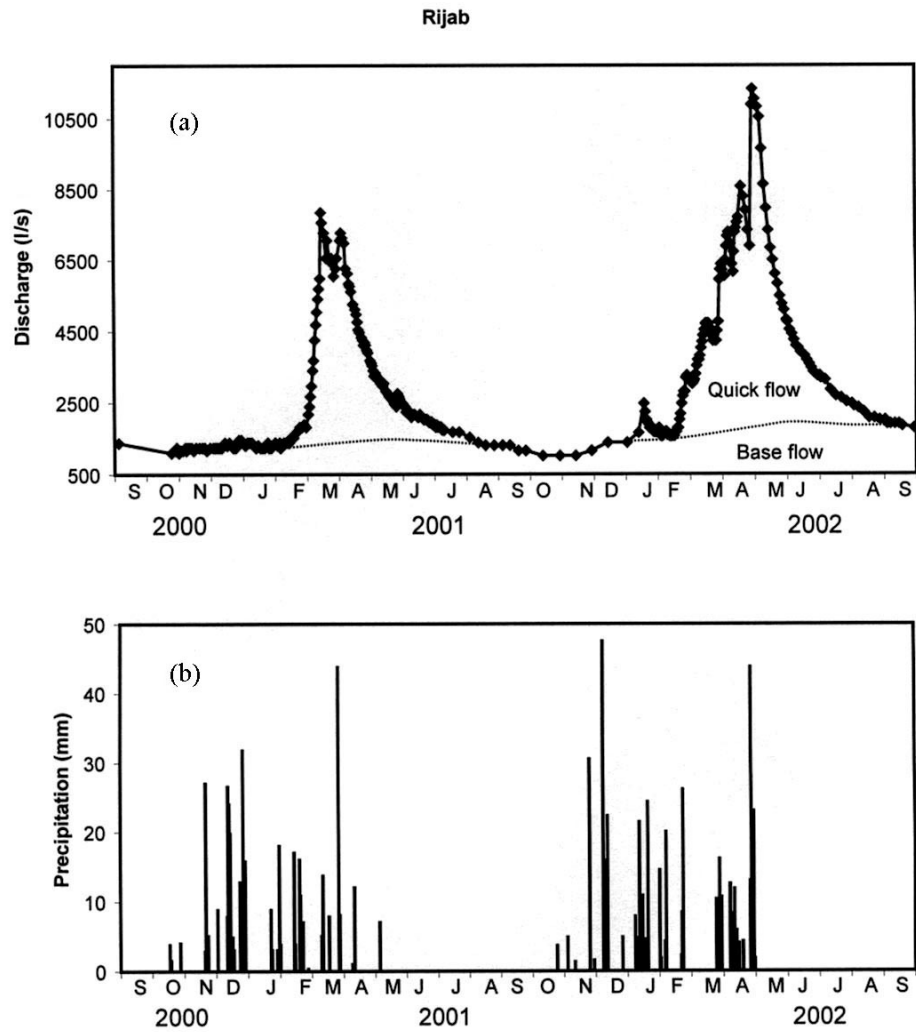


Figure 4. (a) Hydrograph of the Rijab Spring and (b) precipitation the Piran station during a period from September 2000 to September 2002.

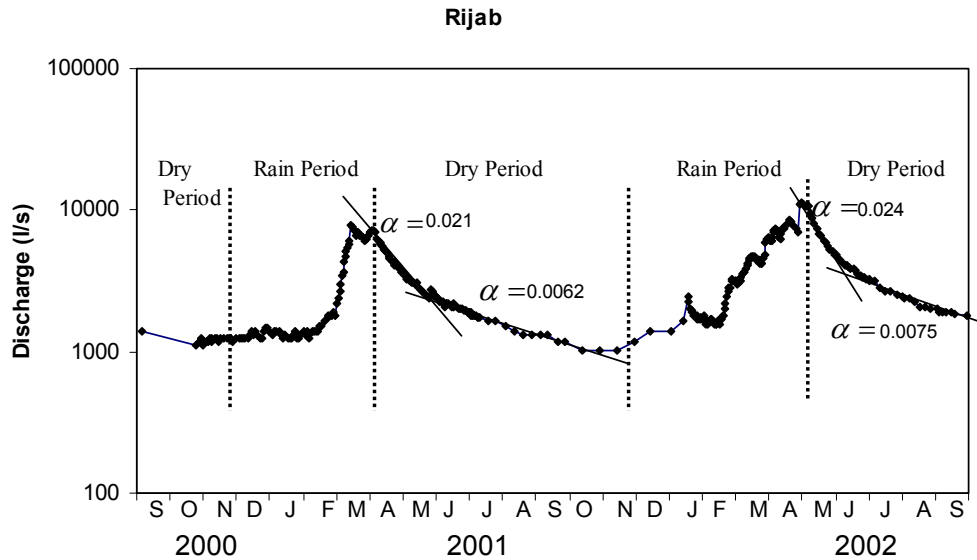


Figure 5. Recession curve of the Rijab Spring for the 2000-01 and 2001-02 water years

### Hydrochemistry of the Rijab Spring

Average, minimum, maximum, standard deviation (S.D.) and coefficient of variations (C.V.) of physicochemical parameters of the Rijab Spring during the 2000-2002 period are presented in Table 3. Over the study period (2000-02), average, minimum and maximum values of discharge and EC of the spring were measured to be 3291, 1015 and 11338 l/s and 370, 337 and 393  $\mu\text{S/cm}$ , respectively. The hydrochemistry analysis results indicate that the ions of bicarbonate (44.9%), calcium (31.5%) and magnesium (16.3%) are the major constituents of the spring water. Both sulphate and chloride compose less than 6% of the total ions in the spring water, demonstrating the absence of gypsum bearing Gachsaran Formation in the catchment area. It seems that the Asmari carbonate formation mostly produces the spring water since the type of the spring water is calcium-magnesium bicarbonate and the Ca/Mg ratio is equal to 2.

Table 3. The summary of physicochemical parameters of the Rijab Spring water (concentrations in meq/l).

Parameter	Average	Min.	Max.	S.D.	C.V.
T (°C)	13.71	12.6	15	0.613	4.47
EC ( $\mu\text{S/cm}$ )	370.4	337	393	13.62	3.68
PH	7.742	6.41	9.09	0.652	8.43
Q (l/s)	3291	1015	11338	2195	66.7
HCO <sub>3</sub>	4.015	3.55	4.3	0.203	5.05
Cl	0.359	0.25	0.7	0.086	23.9
SO <sub>4</sub>	0.194	0.015	0.48	0.09	46.2
Na	0.093	0.04	0.17	0.032	34.2
K	0.019	0	0.16	0.026	135
Ca	2.816	2.3	3.3	0.184	6.52
Mg	1.463	1	2	0.225	15.4
TDS	343.8	309	385	18.69	5.44
LogpCO <sub>2</sub>	-2.528	-3.9	-1.1	0.588	-23.3
SI <sub>c</sub>	0.346	-1.1	1.46	0.558	161
SI <sub>d</sub>	0.368	-2.6	2.73	1.128	307
SI <sub>g</sub>	-2.731	-3.8	-2.2	0.315	-11.5
Ca/Mg	1.985	1.438	3	0.331	16.7
T.Hard. (ppm)	212.2	191.6	241.3	13.57	6.4

It seems that flow system of the Rijab Spring is a combination of both diffuse and conduit since (1) the coefficient of variations for the hardness is 6.4 (Table 1) suggesting that flow system is a combination of both diffuse and conduit according

to Shuster & White (1971); (2) the standard deviation of temperature values of the spring water is 0.61 implying diffuse flow system based on Cowell and Ford's method (1983) and (3) using Jacobson & Langmuir's (1974) criteria, flow system is diffuse-conduit to conduit-diffuse. Therefore, we can categorize flow system of the catchment area of the Rijab Spring as a diffuse-conduit with a well-developed karstification (Nassery *et al.* (2014), in which diffuse system acts mostly as a reservoir whereas conduit system moves mostly the water stored in the diffuse system to the spring.

Fig. 6 shows temporal variations of physicochemical parameters of the Rijab Spring water during the study period. The discharge values are approximately constant during the first six months (September 2000 to February 2001) since rainfall starts in October 2000. This may probably be due to (1) thick unsaturated zone and (2) precipitation occurrence predominantly in the form of snow as discussed in section 5. The discharge increases significantly afterward 20 days from rainfall occurred in the mid-February 2001 and finally reaches its peak in March 2001. This may probably be due to the higher temperature of this rainfall occurrence which causes melting of piled up snow resulted in the previous precipitation occurrences over the catchment area. Furthermore, air temperature shows an increase during this period. The notable point is that the spring hydrograph shows another peak in April 2001 (the beginning of spring season) and then continuously reduces to reach base flow. Most probability, the second peak in April 2002 is referring to the very important rain event on March 2001 (Fig. 4). The recession limb of the hydrograph has two different slopes. The first one with a very high rate indicates both the contribution of snowmelt water and dominance of conduit flow while the second one has a lower rate of recession, indicating the most important role of smaller fractures on flow (i.e. diffuse flow). Generally, behaviour of the spring in the 2001-02 water year is similar to that of the 2000-01 water year except due to different patterns of precipitation, the rising limb of the hydrograph of 2001-02 (1) has more fluctuations; (2) starts sooner than that of 2000-01 and (3) also has a larger peak of discharge. Noticeably, the recession limb of the hydrograph for both the 2000-01 and 2001-02 water years has a similar behavior (Fig. 4).

As mentioned above, since most of precipitation



over the RA is in the form of snow, early precipitation events in any water year do not significantly contribute to the spring discharge. Consequently, it seems that discharging water from the spring at the beginning of the wet season comes from precipitation events occurred in the previous

year which has a longer residence time and larger EC values (Desmarais & Rojester, 2002; Sauter, 1992; Ford & Williams 2007). Therefore, EC of the spring has an increasing trend at the beginning of the wet period of the 2000-01 water year (Fig. 6).

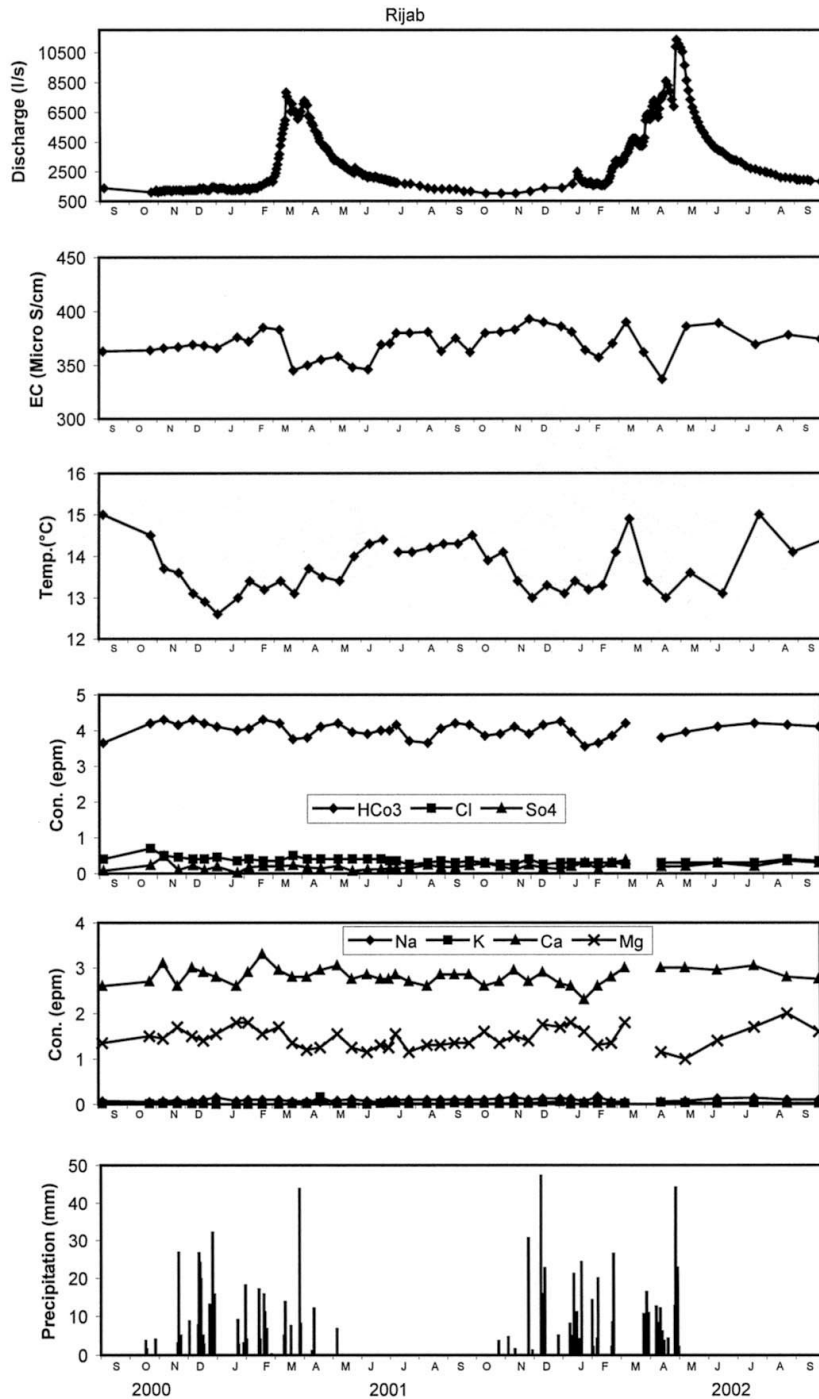


Figure 6. Time series of physicochemical parameters of the Rijab Spring water along with daily precipitation in the Piran station precipitation.

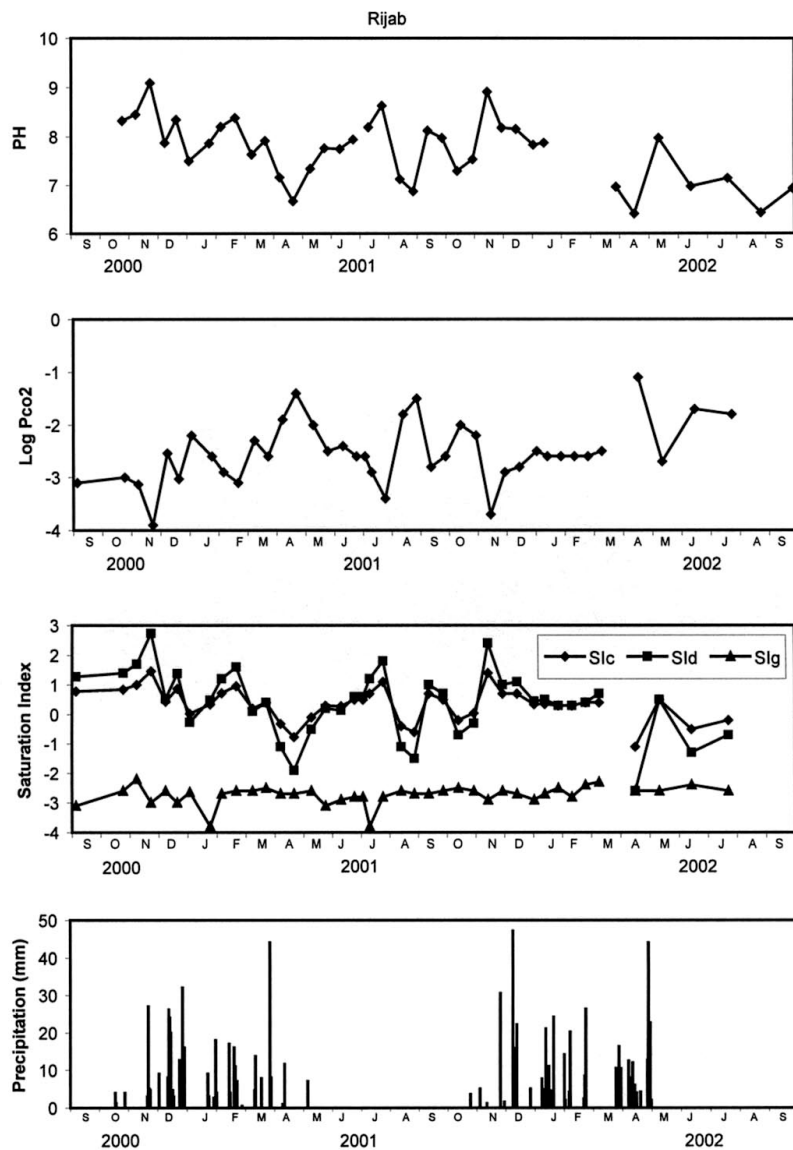


Figure 6. To be Continued.

After that by more increasing of the discharge rate, EC reduces due to dilution by fresh water with short residence times which comes from fresh rainfall. Interestingly, variations of bicarbonate and calcium ions, major ions of the karstic Rijab Spring water, are reasonably consistent with that of EC values. Nevertheless, there is no good consistency between magnesium and bicarbonate concentrations. In addition, as can be expected in karstic carbonate terrains, there is a good agreement between pH values and saturation indices of calcite and dolomite minerals (Fig. 6), signifying further solubility of carbonate in acidic water. As can be seen in Fig. 6, the most acidic water has a greater

saturation index for both calcite and dolomite minerals. Saturation indices of calcite and dolomite minerals are close to zero and have negative values during high discharge and snow melt, denoting more contribution of water with shorter residence time to the spring water which expected to come from snow melt passing through conduit system. The gypsum saturation index is very low, demonstrating the absence of Gachsaran Formation within the catchment area of the spring.

Temperature variations of the spring are more consistent with air temperature since the maximum values are observed during summer while the smallest values of spring temperature are measured

in winter. For example, the temperature of the spring water decreases progressively from summer to winter in the 2000-01 water year since the smallest value is observed in December 2000 and January 2001 (Fig. 6). This may be due to the fact that the spring water emerges from an area with a long length (about 100 m) which allows karst groundwater to mostly influence by the local air temperature.

### Conclusions

Physicochemical parameters of discharge, electrical conductivity, pH, temperature, major ions of the Rijab Spring water were investigated during a period from September 2000 to September 2002 to determine catchment area boundary of the spring and to study the karstification development in the area. The results indicate that the spring not only drains the groundwater of its own surface catchment but also about the half amount of discharging volume at the springs come from groundwater produced by the northern part although the northern part is not located in the surface catchment area of the Rijab Spring.

It is calculated that about 62 percent of discharging water from the Rijab Spring is quick flow. The diffuse system supplies motley base flow of the spring while the conduit system provides the quick flow and activates mostly during the late-winter and early-spring when precipitation is mostly in the form of rain as well as snowpack is melting. Flow system in the catchment area of the Rijab Spring is, therefore, a diffuse-conduit with a well-developed karstification. The  $\alpha_1$  recession coefficient for both the 2000-01 and 2001-02 water years corresponds with conduit system and the  $\alpha_2$

recession coefficient denotes diffuse behavior. Moreover, temporal variations of electrical conductivity, concentrations of the major ions, and saturation indices of calcite and dolomite minerals confirm the diffuse-conduit flow system.

Results also indicated that the spring does not respond to early precipitation events occurred during autumn quickly since (1) most of the precipitation over the Rijab Anticline falls in the form of snow and (2) unsaturated zone of the karstic aquifer is thick. It seems that discharging water from the spring at the beginning of the wet season comes from precipitation occurred in a previous water year, which has been longer in contact with matrix rocks; thus has a greater EC. Furthermore, when the discharge of the spring increased, EC of the spring water reduced. This may be due to dilution of the spring water by fresh water resulted from fresh rainfall. By increasing the contribution of the fresh percolated water to the spring water, the saturation indices of calcite and dolomite minerals are smaller (i.e., close to zero) whereas they are negative at high discharge rates. Moreover, it seems that the Gachsaran Formation does not exist within the catchment area of the spring since the gypsum saturation index is very low and we have not observed any sign of its crops out in the catchment area.

Variations of the temperature of the spring water are more consistent with air temperature variations whereas the maximum values are observed during summer and the minimum values of spring temperature are measured in winter. Most probably, this is due to that the Rijab Spring emerges along a long distance which allows the water temperature to re-equilibrate with the local air temperature.

### References

- Adji, T.N., Bahtiar, I.Y., 2016. Rainfall–discharge relationship and karst flow components analysis for karst aquifer characterization in Petoyan Spring, Java, Indonesia. *Environ Earth Sci.*, 75: 735-742.
- Amit, H., Lyakhovskiy, V., Katz, A., Starinsky, A., Burg, A., 2002. Interpretation of spring recession curves. *Ground Water*, 40 (5): 543-551.
- Ashton, K., 1966. The analysis of flow data from karst drainage systems, *Trans. Cave Research Group, G.B.*, 7: 161-203.
- Bagheri Seyed Shokri, S., Yamani, M., Jafar Beyglo, M., Karimi, H., Moghimi, E., 2013. Hydrodynamic characteristics evaluation of the karst aquifers using time series analysis (Case study: Gilan and Khorin karst aquifers in Kermanshah Province). *Journal of quantitative geomorphological researches*, 2 (3): 1-16 (In Persian).
- Bagheri Seyed Shokri, S., Yamani, M., Jafar Beyglo, M., Karimi, H., Moghimi, E., 2015. Investigation of development and hydrodynamic characteristics of karst systems using analysis of hydrograph recession curve, case study: karstic aquifers of Alvand basin. *Physical geography research quarterly*, 47 (3): 333-346. (In Persian)
- Birk, S., Liedl, R., Sauter, M., 2004. Identification of localised recharge and conduit flow by combined analysis of hydraulic and physico-chemical spring responses (Urenbrunnen, SW-Germany). *Journal of Hydrology*, 286: 179-193.
- Bonacci, O., Zivaljevic, R., 1993. Hydrological explanation of the flow in karst: example of the Crnojevic spring. *Journal of Hydrology*, 146: 405-419.
- Chen, J.S., Li, L., Wang, J.Y., Barry, D.A., Sheng, X.F., Gu, W.Z., Zhao, X., Chen, L., 2004. Groundwater maintains

- dune landscape. *Nature*, 432 (7016): 459–460.
- Connair, D.P., Murray, B.S., 2002. Karst groundwater basin delineation, Fort Knox, Kentucky. *Engineering Geology*, 65: 125-131.
- Cowell, D.W. Ford, D.C., 1983. Karst hydrology of the Bruce Peninsula, Ontario, Canada. *Journal of Hydrology*, 61: 163-168.
- Currens, J.C., 2002. Kentucky is karst country! What you should know about sinkholes and springs. Kentucky Geological Survey, Series 12, Information Circular, 4: 29 pp.
- Desmarias, K., Rojstaczer, S., 2002. Inferring source waters from measurements of carbonate spring response to storms. *Journal of Hydrology*, 260 (1-4): 118-134.
- Ede, D.P., 1972. Comments on “Seasonal fluctuations in the chemistry of limestone springs” By: Evan T Shuster and William B. White. *Journal of Hydrology*, 16: 53-55.
- Eris E., Wittenberg H., 2015. Estimation of baseflow and water transfer in karst catchments in Mediterranean Turkey by nonlinear recession analysis. *Journal of Hydrology*, 530: 500-507.
- Falcon, N.L., 1974. An outline of the geology of the Iranian Makran. *Geographical J.*, 140 (2): 284-291.
- Ford, D.C., Williams, P., 2007. *Karst Hydrogeology and Geomorphology*. West Sussex, John Wiley & Sons, 562 pp.
- Jacobson, R.L. Langmuir, D., 1974. Controls on the quality variation of some carbonate springs water. *Journal of Hydrology*, 23: 247-265.
- Karimi, H., 2003. Hydrogeological behavior of the Alvand basin karst aquifers, Kermanshah. Ph.D. Thesis, Shiraz University.
- Karimi, H., Raeisi, E., Zare, M., 2003. Hydrodynamic Behavior of the Gilan Karst Spring, West of the Zagros, Iran. *Cave and Karst Science*, 30 (1): 15-22.
- Karimi, H., Raeisi, E. Bakalowicz, M., 2005. Characterising the main Karst aquifers of the Alvand basin, Northwest of Zagros, Iran, by a hydrogeochemical approach. *Hydrogeology Journal*, 13 (5-6): 787–799.
- Mohammadi Z., Shoja A., 2014. Effect of annual rainfall amount on characteristics of karst spring hydrograph. *Carbonates Evaporites*, 29: 279–289.
- Moore P.J., Martin, J.B., Sreaton E.J., 2009. Geochemical and statistical evidence of recharge, mixing, and controls on spring discharge in an eogenetic karst aquifer. *Journal of Hydrology*, 376: 443-455.
- Nassery, H.R., Aljani, F., Nakhaei, M., 2014. The comparison of hydrodynamic characteristics of karst aquifers: application on two karst formations in Zagros (Asmari and Ilam-Sarvak), southwest Iran. *Arab J Geosci.* 7: 4809–4818.
- Petras, I., 1986. An approach to the mathematical expression of recession curves. *Water S. A.*, 12 (3): 145-150.
- Pezeshkpour, P., 1991. Hydrogeological and hydrochemical evaluation of Kuh-e Gar-Barm-Firooz springs. M.Sc. Thesis, Shiraz University.
- Plummer, L.N., Jones, B.F., Truesdell, A.H., 1978. WATEQF, a Fortran IV version of WATEQ, a computer program for calculating chemical equilibrium in natural waters. *US. Geol. Surv. Water Resources Invest*: 13-76.
- Raeisi, E., Karami, G., 1996. The governing factors of the physical and hydrochemical characteristics of karst springs. *Carbonate and Evaporate*, 11 (2): 162-168.
- Raeisi, E., Zare, M., Aghdam, J., 2013. Hydrogeology of gypsum formations in Iran. *Journal of Cave and Karst Studies*, 75 (1): 68-80.
- Rahnamaie, M., 1994. Evaluation of infiltration and runoff in the karstified carbonatic rocks. M.Sc. Thesis, Shiraz University.
- Rezaei, A., Zare, M., Raeisi, E., Ghanbari, M., 2013. Interaction of a freshwater lake and a karstic spring via a syncline fold: *Groundwater*, 51 (2): 305-312.
- Rezaei, A., Karimi, H., Zhan, H., 2017. The importance of understanding the hydrogeology and geochemistry of Karst terrains for safely sitting dams. *Journal of Cave and Karst Studies*, 79 (1): 48-58.
- Ryan, M. Meiman, J., 1996. An examination of short-term variations in water quality at a karst spring in Kentucky. *Ground Water*, 34 (1): 23-30.
- Sahabi, F., Aghasi, A., Afshar Harb, A., 1998. Geological report of Alvand Basin (Kermanshah Province). West Regional Water Authority, 132 pp. (In Persian)
- Sauter, M., 1992. Quantification and forecasting of regional groundwater flow and transport in a karst aquifer (Gallusquelle, Malm, SW. Germany. Report, Tubinger Geowissenschaftliche Arbeiten (TGA), TGA, C13.
- Shuster, E.T., White, W.B., 1971. Seasonal fluctuations in the chemistry of limestone springs: A possible means for characterizing aquifers. *Journal of Hydrology*, 14: 93-128.
- Stocklin, J., Setudehnia, A., 1977. *Stratigraphic Lexicon of Iran*. Geology Survey of Iran, 376 pp.
- Vasileva, D., Komatina, M., 1997. A contribution to the  $\alpha$  recession coefficient investigation in karst terrains. *Theoretical and Applied Karstology*, 10: 45-54.
- Ward, R.C., Robinson, M., 2000. *Principles of hydrology*. McGraw-Hill Publishing Company, 450 pp.
- Williams, P.W., 1983. The role of the subcutaneous zone in karst hydrology. *Journal of Hydrology*, 61: 45-67.

- White, W.B., 1969. Conceptual models for carbonate aquifers. *Ground Water*, 7 (3): 15-21.
- White, W.B., 1988. *Geomorphology and hydrology of karst terrains*. Oxford university press, 464 pp.
- White, W.B., Schmidt, V.A., 1966. Hydrology of a karst area in east central West Virginia. *Water Resources Research*, 2: 549-560.
- Zhou, W., Beck, B.F., Pettit, A.J., Wang, J., 2008. Application of water quality control charts to spring monitoring in karst terranes. *Environ Geol.*, 53: 1311–1321.