Investigation of Drainage Structures In The Karst Aquifer System Through Turbidity Anomaly, Hydro Geochemical And Stable Isotope Analyzes (Kiyan Springs, Western Iran)

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Abstract

Karst aquifers typically have desirable physicochemical properties and can provide an important source of groundwater for drinking. Kiyan karst springs, located in the geological region of the Zagros (western Iran), consist of two springs (Keder and Zolal) situated 3 meters apart. The water of Zolal spring is always clear, with no turbidity during rainfall or earthquake phenomena, but Keder spring, which also provides drinking water to a city of 10,000 inhabitants (Kiyan city), has very high turbidity in these conditions, and this disrupts the drinking water supply for about 1 month per year in the study area. The interpretation of discharge time series diagrams, precipitation, and turbidity in different rainfall and earthquake conditions, composite diagrams, and stable isotope concentrations shows this study area to be a well-developed karst environment with a highly eroded tectonic zone and large karst conduits along with turbulent water flow. In general, the difference in the behavior of the two springs is related to different paths of water movement through the drainage area. The two springs share the same source of recharge from rainfall and the same initial underground drainage path from the largest sinkhole in the region; although the path of water movement is divided into two branches, with Zolal spring water entering a narrower fault channel. In the Zolal spring pathway, a siphon-shaped reservoir is formed where muddy rainwater settles, so that the water from this spring is clear but has higher concentrations of all ions analyzed here than Keder spring water.

Introduction

Humans have always been dependent on water, but currently climate change, excess withdrawal and contamination are threats to groundwater such as karst aquifers (Amilet et al. 2020). Karst aquifers provide the water supply for hundreds of millions of people, accounting for 25% of the world's drinking water, and 35% of the drinking water in Iran (Ford and Williams 2007). Thanks to their favorable physicochemical characteristics, karst aquifers can accumulate large quantities of groundwater, much of which is used as drinking water in Iran and more country (Vasić et al, 2020; Kiyani, 2021). However, drinking water is frequently contaminated by turbidity in karst springs (Massei et al. 2006). Lacroix et al. (2000) noted that during recharge periods, particles infiltrate aquifers either diffusely through the soil (autogenic recharge) or concentrated in swallow holes (allogenic recharge). Turbidity can be classified as primary or secondary, and as allochthonous or autochthonous. Primary turbidity is observed during or after a rainfall event, together with increased discharge. A secondary turbidity peak can be observed many days later during the period of decreasing discharge without rainfall (Lacroix et al. 2000). Amraoui et al (2003) indicated secondary turbidity peak arrived many days later after decreasing discharge and without rainfall and they originate from infiltration of sediments into sinkholes (allochthonous turbidity). In the other hand turbidity may be either allochthonous or result from remobilization of sediments inside the aquifer (autochthonous), including mineral particles (Amraoui et al. 2003). Turbidity is useful indicator of contaminations in karst springs (White et al, 2018). The relationship between discharge, turbidity and contamination is ambiguous in karst spring: turbidity involves a complex of particle types from different direct and indirect sources (Schippers et al. 2016; White et al. 2018).

Understanding hydrological systems can be challenging in the field of groundwater management, due to the lack of hydrological information (Clark 2015). Owen (2016) recommended hydro geochemical approaches and isotopic properties of groundwater as aquifer quality indicators. The use of stable isotopes as natural tracers contributes to the effective management of karst waters. In addition, some researchers have proposed the use of simple indicators such as dissolved oxygen, discharge, turbidity, and electrical conductivity to identify periods of contamination in karst springs (Pronk et al. 2006). Monitoring water level, spring discharge and water quality (turbidity and spring hydrochemistry) are thus key factors in karst research (Bakalowicz 2005).

Climate change is one of the critical factors that causes spring discharge attenuation (He et al. 2019). Statistical relationships between turbidity and geological features in karst springs are highly site-specific and need to be locally calibrated for each karst basin (White et al. 2018). Water level of the spring acts as a natural piezometer, and also provides information about the overall dynamics of the system. Physicochemical evolution can indicate the behavior of karst springs, although sinkhole dynamics do not reflect the observed hydraulic variations (Massei et al. 2006); In the other hand system behaves linearly with respect to mass transport from the surface (sinkhole) to the spring, with hydraulic standpoint extremely non-linear.

All studies to date conclude that turbidity responses can be highly variable even within the same system, depending on which processes are involved. The process of exogenous turbidity generation depends on composition of rocks and amount of sinkholes in the drainage basin.

Surface water may contain organic particles such as fecal bacteria, organic matter, or chemical compounds such as nitrates and other phytosanitary products (Savary et al. 2021). Also Lateral flow on the subsurface to preferential recharge areas such as sinkholes result in concentrated infiltration that bypasses the soil (Pronk et al, 2006), and contaminants (soil...) can move unimpeded from recharge areas (sinkholes) to the water-supply extraction area (White et al, 2018). Hydrological compartments interact through network of fractures and faults and it is connections between the surface and deep levels of karst aquifer too (Bicalho, 2016). Karst aquifers are prone to high pollution due to fast water transfer channel structures. In this kind of aquifer, untreated pollutants flow through sinkholes and submerged rivers, rapidly enter karst aquifers, and subsequently appear downstream in karst springs. It should be noted that the complex karst structures and different movement paths within the karst make it difficult to interpret the water quality of karst aquifers and springs (Field 2021). Some heavy metal such as arsenic, ... have above concentration in Karst spring; Simsek et al (2008) stated that elevated arsenic concentrations were related to local geologic

formations which are likely to contain oxidized sulfite minerals in clay stones. In Ireland (McGrory et al, 2016) a national-scale research assessment of groundwater identified isolated clusters of elevated arsenic and indicated that lithology was a major controlling factor on arsenic in groundwater too. Nasrabadi and Bidabadi (2013) mentioned existence of volcanic activities within the upper Miocene and Pleistocene in study area (western Iran) may be addressed as the main geopogenic source of arsenic pollution. Significant differences between different aquifer lithology, indicating that sandstone, shale and Limestone; and locally important fractured bedrock aquifers presenting high risk of arsenic too (McGrory et al, 2016). Karst aquifers are highly susceptible to the transfer of pollutants, especially turbidity, and the presence of highly turbid water is one of the characteristics of karst aquifers. The origin of the turbidity process in karst can be explained by characterizing the physical mechanisms. In karstic aquifers with porous environments and unsaturated zone systems, water has the opportunity to be filtered before entering the aquifer environment; hence in this aquifer type, turbidity phenomena rarely occur. When the karst system is developed, turbidity that enters the aquifer can come from two completely different sources. One is exogenous turbidity, which originates externally and enters the karst aquifer from runoff outside the basin. The other source is endogenous turbidity resulting from sedimentary deposits within the aquifer itself. To determine whether the source of turbidity is rainfall or not, it is necessary to carefully examine the relationship between rainfall and turbidity (Savary et al. 2021). During the increased flow rate instability in the chaotic regime that was represented by suspended matter, which was evacuated independent of the discharge rate and the sediment is evacuated towards the outlet in waves of turbidity; which must be control before drinking by karstic water treatment stations (Bouchaouet al, 2002).

The aim of the present study is to improve our knowledge of the hydro geological system of Kiyan karst springs by using hydro geochemical information and stable isotopes, and by identifying the reasons for turbidity anomalies that appear with sudden increases in discharge. For this purpose, physicochemical data (electrical conductivity, total dissolved solids, pH, dissolved oxygen, turbidity, and water temperature), main ions, some heavy metal and stable isotopes of oxygen 18 and deuterium were analyzed. This study is the first report, to our knowledge, that provides hydro geochemical and stable isotope data for the karst springs in the study region. The discharge data were obtained for two springs: Zolal and Keder. By plotting the recession curve of the springs, calculating the dynamic storage volume of the reservoirs, determining the alpha coefficient, and finally examining isotopic and chemical results, the hydrogeology of these two karst springs and their underground drainage systems were characterized in detail, and possible reasons for the turbidity of Keder spring were identified. Any way this study yielded important results for understanding the karst water system in the study area and can be used for comparing with similar situation in every karst study.

The Study Area

The Kiyan springs are located in the Gamasiyab Basin within the Zagros Zone (Garin Mountains) in western Iran (Fig. 1) and comprise Keder and Zolal springs. The distance between these two karst springs ranges from 1 to 5 m (mean 3 m). The springs have been supplying irrigation and drinking water to the area of Kiyan city for approximately 5700 years (since 3700 years BCE) (Gerishman et al. 1939).

The discharges of Keder and Zolal springs increased abruptly on 5 May 2019, in the absence of stresses such as earthquake or storm events. During this period of increased discharge, the turbidity of Keder spring increased, whereas Zolal spring water remained clear. Zolal spring water is always clear during and after earthquake events and prolonged rainfall, but Keder spring is characterized by heavy turbidity during and after these phenomena. The water discharged from Keder spring (60 L/s) supplies drinking water for 10,000 people in Kiyan city. The different behaviors of the two springs pose an interesting phenomenon for scientific research, and we hope that discovering the reasons for the transient turbidity of Keder spring will help to find a solution for this problem in the future.

2.1. Geological and hydro geological setting

Iran is divided into five major geological zones: Zagros, Sanandaj-Sirjan, East and Southeast, Central Iran, and Alborz. Western Iran is comprised of major mountain chain, the Zagros Fold and Thrust Belts. Zagros zone is separated from the Central zone by the narrower Sanandaj-Sirjan metamorphic zone. Geomorphologic investigations have found clear differences between the extent and intensity of karst surface landform development and have being abundant karst spring especially in Zagros zone. (Karimi Vardanjani et al, 2017). The study area located in Zagros zone. The research area covers approximately 9800 hectares, and is characterized by two karstic springs. These Kiyan springs discharge from orbitoline-containing limestone dating from the Cretaceous and located between the K¹¹m and K^{1v}1 contact unit as a thrust fault. The K^{1v}1 unit (pyroclastic rocks) is mixed with crystalline limestones and fragments of volcanic rocks as TRjvm unit (Fig. 1). TRjvm unit consist of interbedded metavolcanics (lava flows and tuffs) and thin bedded, well foliated marbles with thin, upward increasing slate layers. This area is composed mainly of Mesozoic carbonate with layers of light gray, well-bedded limestones interbedded with marly, orbitoline-bearing limestones, and subordinate volcanic rock from the Cretaceous. Erosion and dissolution along the axis of the syncline led to the formation of the semi-arid Kiyan Spring Valley (Fig. 2), according to research by Ashjari and Raeisi (2006). Geomorphology of this area consists of a plane (about 80 km²) with many sinkholes; The Kiyan springs lie at the junction of a northeast-trending thrust fault (Figs. 1 and 3) and a northwest-trending cross strike fault. Also Zolal and Keder springs are according to major (active) and minor (nonnatives) faults respectively; this spring's located in path of faults and tectonic fractures (Fig. 1)

The largest sinkhole in the study area, locally named the Gachal sinkhole and located in the northwest of the Kiyan watershed, has an area of about 800 hectares and is situated in the K¹¹m limestone unit with a depth of more than 200 m according to field observations (Fig. 2). The sinkhole is at an altitude of 2815 m above sea level, and the springs are situated 1715 m above sea level, so the difference in altitude between the potential recharge (sinkhole) and discharge sites (springs) is 1100 m over a distance of 6 km from the doline to the springs. According to synoptic meteorological data for Nahavand city (Meteorological Organization of Iran), the average annual rainfall in the Kiyan catchment area is 500 mm.

Figure 4 shows the turbidity of the Keder spring after the 2017 earthquake and 2018 rainfall. As can be seen, the Keder and Zolal springs are about 3 m apart (i.e., in close proximity to each other). The turbidity caused by precipitation and earthquakes is completely different in terms of color, origin, appearance, type, and amount of sediments (Fig. 4).

2.2. Condition of the alluvial aquifer adjacent to Kiyan Karst area

A karst aquifer can affect an adjacent alluvial aquifer and vice versa if there is a hydraulic connection between them through a fracture or fault. However, if these two sources are not connected, karst and alluvial aquifers can differ in their properties.

Groundwater levels in the observation wells nearest to Kiyan karst springs are presented in Table 1. Average groundwater level in the study area is 13.8 m. The exploitation well in the alluvial aquifer nearest to the karst area is more than 5 km away, and the Kiyan springs are located 250 m higher than the alluvial aquifer. The increasing trend in water level in observation (pizometric) wells from March 2019 (Table 1) illustrates the recharge of alluvial aquifers from the karst area.

Table 1
Groundwater level (m) of pizometric wells nearest to Kiyan karst springs in water-year 2018–2019

Well name	UTM (x)	UTM (y)	Sept 2018	Oct 2018	Nov 2018	Dec 2018	Jan 2019	Feb 2019	Mar 2019	Apr 2019	May 2019	June 2019	July 2019	Aug 2019
Hoseinabad	249497	3784016	10	10.78	9.23	8.16	7	13.54	15.16	16.6	16.12	17.1	16.29	17.1
Miyanabe	244650	3785080	10.4	13.96	13.43	11.52	9.54	14.24	15.46	16	16.8	17.6	17.22	17.7

Material And Methods

Recognizing whether the recharge path drains exclusively via a canalized system and through karstic layers or not requires the preparation of a hydrograph and a recession curve. Analysis of the hydrographs was used to determine the amount of karstification and to trace water passage paths in the two springs. In carbonate areas, the characteristics of karst springs can be determined by investigating changes in discharge, water quality, and temperature. Among the techniques to study karst springs are calculating their dynamic storage volume, investigating the drying time, calculating the recession curve and recession coefficient, and investigating quantitative and qualitative changes in the concentration of isotopes and other chemicals in spring water. The Maillet experimental formula can be used to calculate the alpha coefficient (discharge reduction coefficient) (Maillet 1905). In this formula, the discharge coefficient is expressed as the tangent of the angle between the recession line and the horizontal axis.

$$a = \frac{\log \frac{Q_0}{Q_t}}{0.4343(t)} \quad (1)$$

Dynamic storage volume, a factor dependent on specific geological conditions and feedback from the karst development in a given area, can be obtained with the following equations:

$$v = \frac{(Q_0 * 86400)}{a} \quad (2)$$

$$t_0 = \frac{t * \log e}{\log \frac{Q_0}{Q_t}} \quad (3)$$

Where Q_0 is the primary discharge calculated from the recession curve, Q_t is the secondary discharge in the recession curve at a point located at distance t , v is the dynamic storage, t_0 is the spring drainage time assuming a discharge of Q_0 , and t is the time between primary and secondary discharge.

To evaluate the water quality of springs in this study, electrical conductivity, temperature, total dissolved solids (TDS), and pH were measured with a multimeter device (model HQ40d, Hach) and turbidity was measured with a turbidity meter (model 2100N, Hach). Discharge was measured with a volumetric and flowmetric method at the site. Nitrate, nitrite, chloride, fluoride, and sulfate concentrations were measured with a DR-5000 device

(Hach) according to standard methods, and carbonate and bicarbonate concentrations were determined with a titration method (with 0.02 N hydrochloric acid, pH approximately 4.5) One day after sample collection, these analyses were done at the water laboratory of Nahavand city (Iran). Concentrations of sodium, potassium, calcium, barium, arsenic, manganese, cobalt, nickel, copper, zinc and ferric were also measured by inductively coupled plasma mass spectrometry (ICP-OES, SPECTRO, Kleve, Germany) at the University of Tehran (Iran).

Before the analysis of stable isotopes, samples with high turbidity were diluted at a rate of 1 mL/cm with 0.45 µm paper filter, then stable isotopes $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were analyzed by laser spectrophotometry (Liquid Water Isotope Analyzer LWIA-24d) at a precision of $\pm 2\%$ in the laboratory of the Atomic Energy Organization of Iran. Isotopic data were corrected according to the Vienna Standard Mean Ocean Water (VSMOW).

Samples of spring water were collected twice a year and also on different days during the sudden turbidity episode, by judgmental sampling (Table 7). In the judgmental method (Zhang, 2007), sensitive areas (e.g. drinking water) are sampled. Because Keder spring water is used for drinking and turbidity is a major issue in this spring, turbidity was analyzed during the 2017 earthquake, precipitation in 2018, the phenomenon of a sudden increase in turbidity in 2019, and during precipitation in 2020. Sampling was performed twice in the 2018–2019 water years in the dry season (mid-October 2018) and the wet season (mid-April 2019) to measure physicochemical properties, stable isotopes, and turbidity anomalies.

Table 7
Turbidity of Keder spring after earthquake, precipitation and turbidity phenomenon

* Earthquake (autumn 2017)		*Rainfall (spring 2018)		Rainfall (winter 2020)			Phenomenon (spring 2019)			
Date (November)	Turbidity (NTU)	Date (May)	Precipitation (mm)	Turbidity (NTU)	Date (February)	Precipitation (mm)	Turbidity (NTU)	Date (May)	Precipitation (mm)	Turbidity (NTU)
12	296	5	0	NA	22	0	NA	1	0	1.78
13	18	6	0	NA	24	33	NA	5	0	293
15	2.7	7	9.2	70	25	88	189	6	0	37.6
*We acknowledge missing an opportunity to sample the spring after the 2017 earthquake and 2018 rainfall for chemical and isotopic analyses.		9	40	552	26	0	61	7	0	15.9
		11	12	12	27	0	18.7	8	0	7.46
		13	5	8	28	0	7.8	9	0	6.46
		17	0	2.8	29	0	4.9	11	0	4.89
		NA (Not available)						14	0	2.96
								18	0	1.89

Because both discharge and turbidity increased abruptly on 5 May 2019, a series of samples collected on this date were analyzed to measure the physical and chemical properties and stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$). A total of 73 samples Kiyansprings water were tested, as shown in Table 2. The calculated parameters and analyzed data from both Zolal and Keder karst springs are presented in Tables 3, 4 and 5.

Table 2
Sample amount and type of analysis

Spring name	Sample amount	Analysis type	Date/Season/occasion
Keder	28 Sample	Turbidity	Earthquake 2017, Wet & dry season 2018–2019, phenomena 2019 and storms 2018 & 2020
	17 Sample	Physicochemical	Wet & dry season 2018–2019, phenomena 2019 and storm 2020
	10 Sample	stable isotopic	Wet & dry season 2018–2019 and phenomena 2019
Zolal	9 Sample	Turbidity	Wet & dry season 2018–2019, phenomena 2019 and storm 2020
	9 Sample	Physicochemical	Wet & dry season 2018–2019, phenomena 2019 and storm 2020
	2 Sample	Stable isotopes	Wet season 2018–2019 and phenomena 2019

Table 3
Physicochemical and stable isotope data for Kiyan springs

Parameter / Ion	Kederspring			Zolal spring		
	October 2018	April 2019	5 May 2019	October 2018	April 2019	5 May 2019
Discharge $\pm 10\%$	1314	2804	3642	87	130	243
Turbidity (NTU)	0.72	1.78	293	0.43	0.86	1.23
C) $\pm 0.1^\circ$ Temperate (	14.5	14.4	14.2	15.1	18.3	14.9
pH ± 0.1	8.13	8.2	7.8	8.41	7.63	9.76
EC ($\mu\text{c}/\text{cm}$) ± 1	249	200.1	244	NA	243	225
TDS (mg/L)	138.2	124.9	134.1	NA	133.7	134.2
DO	9.1	6.32	3.15	7.8	6.96	8.38
Cl	8.5	9	1.3	NA	14.18	3
F	0.5	0	NA	NA	NA	0.03
SO ₄	0	0	3.517	NA	0.29	1.91
Co ₃	0	0	0	0	0	0
HCO ₃	140	116	NA	NA	128.14	56
Ca	34	16.657	18.186	NA	32.06	12.67
Mg	8.4	2.685	3.272	NA	10.93	3.988
Na	8.28	1.577	1.784	NA	7.59	2.164
K	0.39	0.0433	0.0792	NA	0.39	0.0545
Total hardness	119.5	120	58.885	NA	125.1	48.06
Alkalinity	140	60	78	NA	128.14	56
Fe ($\mu\text{g}/\text{l}$)	39.5	11.676	434.823	20.8	NA	62.651
As	19.1	8.334	11.272	NA	NA	24.068
Co	< 0.043	< 0.043	0.305	NA	NA	< 0.043
Cu	24.8	0.457	4.65	NA	NA	< 0.306
Zn	181.6	2.116	22.609	NA	NA	4.129
Ni	2.7	< 0.286	5.455	NA	NA	< 0.286
Mn	1.7	0.355	29.345	NA	NA	6.637
Ba ($\mu\text{g}/\text{L}$)	13.7	5.338	12.404	NA	NA	8.06
$\delta^{18}\text{O}(\text{‰ vs. SMOW})$	-7.06 ± 0.24	-6.54 ± 0.21	7.14 ± 0.13	-7.16 ± 0.23	NA	-7.09 ± 0.33
$\delta^2\text{H}(\text{‰ vs. SMOW})$	-41.62 ± 0.62	-43.12 ± 0.94	-32.99 ± 0.85	-42.19 ± 0.75	NA	-39 ± 0.82

Table 4
Physicochemical and stable isotopic data of Keder spring on 5 May 2019 phenomena

Day (May)	Discharge (l/s)	Turbidity (NTU)	Temperature (°C)	TDS (mg/l)	EC c/cm) μ (	pH	DO (mg/l)	$\delta^{18}\text{O}$ (‰ vs. SMOW)	$\delta^2\text{H}$ (‰ vs. SMOW)
1	2804	1.78	13	124.9	200.1	7.74	7.96	-6.54 ± 0.21	-43.12 ± 0.94
5	3642	293	14.2	134.1	244	7.8	7.88	-7.14 ± 0.13	-32.99 ± 0.85
6	3051	37.6	15.4	126.8	225	6.36	7.53	-7.02 ± 0.27	-33.98 ± 0.74
7	2998	15.9	12.6	127.8	202.7	6.91	7.9	-6.44 ± 0.43	-43.3 ± 0.74
8	2984	7.46	12.3	127.1	200.3	9.36	8.75	-6.24 ± 0.17	-44.49 ± 0.84
9	2957	6.46	12.5	128.2	202.8	9.99	8.58	-6.92 ± 0.32	-36.64 ± 0.88
11	2860	4.89	12.5	126.6	200.3	9.46	7.58	-6.78 ± 0.13	-38 ± 0.82
14	2635	2.96	14.1	130.7	225	8.3	8.18	-6.59 ± 0.3	-39.91 ± 0.64
18	2498	1.89	13.2	128.1	206.4	9.57	7.98	-6.4 ± 0.09	-42.43 ± 0.81

Table 5
Physicochemical data of Keder & Zolal springs on rainfall 25 February 2020

Day (February)	Discharge (l/s)		Turbidity (NTU)		Temperature (°C)		TDS (mg/l)		EC (μ c/cm)		pH		DO (mg/l)	
	Keder	Zolal	Keder	Zolal	Keder	Zolal	Keder	Zolal	Keder	Zolal	Keder	Zolal	Keder	Zolal
22	4426	276	1.9	0.9	12	13	138	134.2	206	222	7.8	8.5	8.5	8.6
25	5166	NA	189	NA	12.5	NA	118.1	NA	167	NA	6.53	NA	9.74	NA
26	5863	366	61	1.33	12.1	13.7	118.4	138.5	186	225	7.78	7.66	8.94	8.59
27	5587	349	18.7	3.24	13.6	15.5	121.5	133.4	197.5	227	8.72	8.83	8.89	9
28	5216	327	7.8	1.71	12.4	14	126.3	134.4	199.3	220	8.68	7.53	9.6	9.2
29	4438	278	4.9	1.3	12.7	13.6	128.1	145.2	203.7	219.5	9.08	8.65	9.24	9.19
* Not available (NA), due to distorted rode by water flow														

Results And Discussion

The discharge data for Zolal and Keder springs were extracted, and by plotting the recession curve for each spring, the dynamic storage volume of their reservoirs was determined, and the alpha coefficient was calculated. In addition, examining the isotopic chemical characteristics and heavy metal of the springs allowed us to analyze karst development in this study area and identify the likely reasons for the turbidity of Keder spring, as discussed below.

4.1. Water quantity of springs

The special conditions of the drainage regime which result from factors such as precipitation regime, lithology, the arrangement of rock layers, and their thickness, texture, and porosity, affect the hydrographic characteristics and recession curve of springs in karst areas compared to other areas. In non-karst or less developed karst areas, springs typically show a downward curve with a uniform linear trend and low alpha content in the recession curve. However, in areas with high karst development, springs either have a linear trend with high alpha content or yield three different linear slopes with different recession coefficients, normally with recession coefficient α_1 being less than α_2 and more than α_3 (Ford, 2007). The alpha coefficient, which indicates the discharge coefficient or the ability to discharge groundwater, expresses the hydro geological characteristics of the area that result from parameters such as porosity and the aquifer transmissivity coefficient. In this framework, the larger the alpha coefficient is, the higher the slope of the recession curve, and the greater the flow discharge, thus indicating the speed of flow discharge from rainfall and the degree of porosity and karstification of the basin. However, in the inverse case, non-karstification or low karstification of the basin is observed. In Fig. 5 the recession curves for Zolal and Keder spring discharges are plotted semilogarithmically against time. The data are from discharges of both springs in 2018 September to 2019 September. Recession curve data are also presented in Table 6.

Table 6
Coordinates, discharge and dynamic volume reservoir

Attribute	Kiyan springs	
	Keder	Zolal
Latitude (X)	243709	243715
Longitude (Y)	3781363	3781366
Altitude (Z)	1715	1716
Discharge mean (l/s)	1800	120
Recession coefficient	0.04	0.04
Type of current	conduit	conduit
Dynamic volume reservoir (million m ³)	49	3.1
T ₀	158	158

The recession coefficient curves show a completely linear trend for both springs. According to Fig. 5 and Table 6, the recession coefficient (0.04) and drying coefficient (158 days) are equal for both springs, but the dynamic volume of the Keder aquifer (49 million m³) is larger than the volume of the Zolal aquifer (3 million m³); On the other hand dynamic reservoir volume in Keder spring is 16 more times bigger than Zolal spring. According to Malík and Vojtková, (2012), this alpha value, despite the observation of a linear regime in the recession diagram, represents a karstic area with highly tectonic and permeable areas and conduit flows. This is also evident from the hydrographs of the two karst springs as shown in Fig. 6. Aquifer permeability is so high that rainfall in the region leads to a sudden rise in discharge from the springs. For example, average monthly discharge from Zolal spring is 120 L/s and average flow from Keder spring is 1800 L/s, but during periods of heavy rainfall, discharge reached 243 L/s in Zolal spring and 3642 L/s in Keder spring. The long-term hydrograph of Keder spring confirms this increase. As shown in Fig. 6, during the period from 2011 to 2019, increased discharge was associated with an increase in rainfall. Geomorphologic features such as the nearby large sinkhole and high discharge suggest, along with the discharge characteristics, that the Kiyan Karst system is well developed and can be said to be similar to the Dinaric Karst system (Stevanović, 2019).

4.2. Quality of the springs

To further characterize the Kiyan karst area, water quality of the two springs was studied. In areas where water infiltration and flow in the aquifer occur via canals and conduits, the extent of contact between water and the different layers and constituents is less than in areas with lower permeability and a diffuse flow regime. As a result, the amount of solutes will be lower and they will show lower electrical conductivity.

In this study area, high turbidity is one of the problems of Keder karst spring. Water turbidity increases in spring because of processes such as heavy rainfall and earthquakes.

However, on 5 May 2019 turbidity increased in the absence of earthquakes or heavy rain. Turbidity in Keder spring takes more than 1 week to completely disappear. It should be noted that Zolal spring, despite being located only 3 m from Keder spring, remains clear and transparent all year round. To determine the causes of this difference in behavior, information is needed about the structure of the karst. In the following sections, the structure and characteristics of karst in the study area are reported and discussed in connection with water quality in the two springs.

4.2.1. Water turbidity

Turbidity is a property of water that is related to other properties, and different indicators can be used to determine the source of turbidity. Because turbidity is one of the main problems of Keder karst springs in this study area, and because Keder spring water is also a source of drinking water in the region, the turbidity of Keder springs was analyzed after the 2017 earthquake, 2018 rainfall, 2019 phenomenon, and 2020 rainfall. The results of turbidity analyses are presented in Table 7, and changes in turbidity with time are shown in Fig. 6, which illustrates the difference between turbidity due to precipitation and due to the earthquake. The latter increased turbidity during a period of reduced discharge, and the turbidity peak can be attributed to the movement of sediments in the walls of karst conduit networks (autochthonous). However, precipitation also increased turbidity during periods of increased discharge, and the origin of these turbidity peaks is related to unfiltered sediments in dissolved holes (allochthonous). This phenomenon lasted more than 1 week in Keder spring until the water became clear again, whereas Zolal spring had no visible turbidity, and turbidity analyses of water from this spring confirmed the absence of sources of cloudiness (Table 7). The first turbidity peak associated with the 2017 earthquake was 296 NTU, the second peak during the 2018 rainfall reached a maximum of 552 NTU, after which turbidity decreased gradually to 2.8 NTU (Table 7). Earthquake caused rising turbidity, it occurred during a period of decreasing flow rates, and turbidity peak can be explained by remobilization of sediment walls inside conduit network (autochthonous turbidity).

In May 2019 peak turbidity was 293 NTU, and after the 2020 rainfall, maximum turbidity was 189 NTU. To illustrate the effect of rainfall on Keder spring water, daily rainfall in 2018 and 2019 is plotted with turbidity in Fig. 6. In 2018, rain immediately caused turbidity in the spring, and in April 2019, precipitation was in the form of snow, and turbidity due to snowmelt was delayed by about 1 month, occurring in May 2019. This finding reflects the developed karst system in the Keder spring, which transmits precipitation directly to the spring outlet through channel flows. Turbidity indicates the presence of rapid groundwater flow with a relatively short transfer in the karst groundwater aquifer (Perez et al. 2013). Discharge and turbidity are correlated, thus the rapid flow of water immediately after rainfall leads to turbidity. Accordingly, spring discharge is considered an indicator of pollution (turbidity) (Amraoui et al. 2003).

The differences between the two springs in turbidity and discharge indicate the presence of a different flow path for Zolal spring. Considering the recession curves for each spring, the high discharge of Keder spring, the tectonic characteristics of the region, and the location of the springs in fault zones, the development of karstification in the region can be assumed to be very high. As a result, Keder spring, where high turbidity occurs, is likely to transmit rainfall via highly fractured routes and large karst canals immediately after rainfall, with little or no infiltration. Part of the turbidity of Keder spring can also be attributed to the movement of wall sediments within the karst conduit networks (autochthonous). The occurrence of turbidity after the earthquake supports this mechanism. The degree of karstification and the presence of faults and fractures along with instability of the fault walls in the tectonic fold zones in the groundwater flow path have a significant effect on water quality in Keder spring. In contrast, Zolal spring has a siphon-shaped reservoir where water accumulates. After precipitation, the new influx of rainwater or snowmelt has an opportunity to settle, as turbid rainwater replaces the existing reservoir water which flows to the spring. For this reason, the water in this spring, unlike the water in Keder spring, remains transparent when it rains.

The next sections compare other parameters of water quality between the two springs. Our results support the suggestion that Zolal spring water reaches the discharge site from a siphon-shaped reservoir. It should be noted, however, that accurate dye tracer tests are needed to accurately diagnose the factors that influence discharge characteristics in each spring.

4.2.2. Karst status in the study area based on physical, chemical and isotopic analyses

4.2.2.1. Gibbs diagrams

To identify the mechanisms that influence water chemistry, a Gibbs diagram (Gibbs 1970) was drawn for water samples (Fig. 9). Gibbs divides the mechanisms that control water chemistry and its evolution into three categories: rock weathering, evaporation, and atmospheric precipitation.

To evaluate the origin of water-soluble chemicals, Gibbs prepared two graphs for the ratio of $\text{Na} / (\text{Na} + \text{Ca})$ and $\text{Cl} / (\text{Cl} + \text{HCO}_3)$ to TDS. In samples with high $\text{Na} / (\text{Na} + \text{Ca})$ and $\text{Cl} / (\text{Cl} + \text{HCO}_3)$ ratios with TDS less than 100 mg/L, precipitation has the greatest effect on water chemistry. Low ratios of $\text{Na} / (\text{Na} + \text{Ca})$ and $\text{Cl} / (\text{Cl} + \text{HCO}_3)$ with TDS between 100 and 1000 mg/L indicate the effect of rock weathering processes. If both ratios are elevated, evaporation is the main factor controlling water chemistry. According to these diagrams, the main factor controlling water composition in both springs is the weathering process of carbonated rocks.

4.2.2.2. Composite diagrams

Composite diagrams are a useful tool for understanding the different sources of groundwater, and have been used to identify geochemical processes affecting groundwater quality (Mazor 2004). The pattern of points is usually single-cluster, two-cluster, triangular, linear, or scattered, each with its own description according to the two factors (x, y). In the line diagram, if the line fits the points at an angle to the x-axis, this indicates the mixing of two types of water, and if the line fits parallel to the x-axis, the diagram indicates no mixing. The x-axis can be the concentration of total soluble ions or TDS. If the fitted line slopes and intersects the TDS axis, ion content in the water entering the aquifer is less than in the aquifer water. If the fitted line intersects the y-axis, the amount of this ion in the water that mixes with the aquifer is greater than in the aquifer. If the fitted line passes through the origin, ion content is the same in both waters, and if the points accumulate in one area of the plot, this reflects a common source of recharge for all samples (Mazor 2004).

Figure 10 plots TDS versus the concentration of calcium, magnesium, sulfate, and bicarbonate ions in Keder and Zolal spring samples. The data for these springs is from samples obtained in October 2018, May 2019, and April 2019 for Keder spring and in October 2018 and May 2019 for Zolal spring. In these diagrams, the water composition of both springs shows the same source, and in all four cases the shape of the plots shows a single cluster (Mazor, 2004). In view of the similar reaction of both hydrographs to spring rainfall, it can be deduced that rainfall provides a direct source of water in both springs. Based on these diagrams, which indicate the same source of recharge for both springs, and because of the proximity of the two springs and the similar behavior of their hydrographs, these two springs likely share the same path of movement in the initial part of their pathways. In the course of the path of water, a small part enters a joint with a narrower duct. In the path of this narrow joint, a siphon tank structure has formed, and as a result the water discharged by this spring is clear. Most likely, the same source of water entry for both springs is the Gachal sinkhole, i.e. the largest sinkhole in the region.

4.2.2.3. Isotopic analysis

Values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in Keder spring range between -6.24‰ to -7.14‰ and -32.99 to -44.49‰ respectively. Concentration of $\delta^2\text{H}$ changed in Keder spring with increase turbidity too, from -32.99‰ reaches to -44.49 and -38‰ after three and six days respectively (Table 4). In the present study the isotopic composition of precipitation in the region was not determined directly, so for local atmospheric isotope composition in the study area, the results of research in western Iran (Zagros region) were used based on the approximate overlap of precipitation sampling time with precipitation in the study area (Mohammadzadeh and Amiri2020). The global line equation was also calculated based on $\delta^{18}\text{O}$ concentration in Keder and Zolal springs with the following equation:

$$\text{Overall atmospheric isotope line equation: } \delta^2\text{H} = 8 * \delta^{18}\text{O} + 10 \text{R}^2 = 0.96$$

Figure 11shows the distribution of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ in samples from Keder and Zolal springs.The location of the values for samples from both springs in October 2018 and May 2019 in the area between the global atmospheric line and the local atmospheric water line indicates that the source of recharge is rainwater. The depth of groundwater rotation is very low, especially in Keder spring. This is consistent with Mazor’sconclusion that the line for isotopic composition of karst springs tends to parallel the line for local atmospheric composition (Mazor 2004).

4.2.2.4. Comparison of water composition in the two springs in April 2019

Data from April 2019 were used to compare the hydrogeochemical status of the two springs in more detail. In water from both springs the predominant mineraliscalcium bicarbonate. Turbidity at this time point was 1.78NTUin Keder spring and 0.86NTUinZolal spring (Table 3). The difference in turbidity between the two springs is due to the different intensities of turbulent flow passing through the joints, and to differences in the structure and pathway of karst passage conduits.

The water temperature of Keder spring (turbid)was 14°C while the temperature at Zolal spring (no turbidity) was 18°C. The higher temperature of Zolal spring water can be attributed to outflow from a greater depth than Keder spring. Temperaturerange of Zolal spring is stable approximately (15.1 and 14.9°C in dry and wet season), but it is variable in Keder spring (18.1 and 13°C in dry and wet season).Therefore, Keder spring recharged from snow sinkholes and it have few temperate in wet season, but Zolal spring has a stable temperature due to deep groundwater circulation (Fig. 13).Ion concentrations (mg/L) in the two springs are compared below.

	Calcium Bicarbonate		Chloride Magnesium		Sodium
Keder	16	60	9	2	1.5
Zolal	32	90	14	10	7.5

The higher concentrations of all ions in Zolal spring support water retention in a reservoir. Accordingly, the results of this analysis are also consistent with the results of other analyses reported above, and support the conclusion that rainwater discharged from Zolal spring remains in a karst reservoir until the next precipitation event, during which the previously stored water is discharged into the spring and is replaced with new rainwater or snowmelt. Thereafter, the turbid water has time to settle and to some extent dissolve ions present in the karst bedrock reservoir. This mechanism would explain whyZolal spring water lacks turbidity and has relatively higher concentrations of ions than the clear water from Keder spring.

AlsoData from May 2019 were used to compare the heavy metal of the two springs in more detail concentration. Ion concentrations (µg/l) in the two springs are compared below.

	Fe	AS	ZN	Ni	Mn	Ba
Keder	434.82	11.27	22.61	5.45	2912	
Zolal	62.65	24.06	4.13	<0.28	6.648.06	

The high concentration of heavy metals in both spring shows that recharge water in the study area pass from volcanic rock and dissolved volcanic composition (Fig. 13).This research approved research of White et al (2018).

This information indicates that the concentration of arsenic in Zolal spring water is higher than inKeder spring; This might be consequence of much deeper groundwater circulation or probably because of zonality in groundwater circulation of Zolal spring around volcanic rocks (It would be related to longer and deeper groundwater flows).But concentration of ferric, copper, zinc, manganese, and nickel in Keder spring water is higher than in Zolal spring is due to dissolving of rocks and lichenin of soil and sediment, because color of around catchment is brown based on fielding observation (this is indicator for exist of ferric).

Conclusion

Karst springs in a given catchment area and aquifer may have different behavioral systems (Jiang and Guo, 2010); however, evaluation of the behavior of two springs in the present study is of interest, because despite their proximity to one another (3 m), they show different behaviors in terms of flow and turbidity.

The observation of a linear regime in the recession diagram, and an alpha value of 0.04 in the recession curve, indicates a karstic area with highly tectonic regions and high permeability and conduit flow.

As a result, permeability of the water flow path of the springs is so high that rainfall in the region leads to a sudden rise in discharge. Of note, the two springs show different behaviors in terms of discharge and turbidity. Maximum flow from Keder spring in May 2019 was about 3642 L/s and the water was markedly turbid, whereas maximum discharge from Zolal spring at the same time was 243 L/s and the water was completely transparent. Turbidity in Keder spring also increases during earthquakes. However, the isotopic concentrations and bivariate plots of the most significant parameters in the samples point to the same source of water for both springs. Also, by examining the composition of water from the two springs on a smaller scale in April 2019, all the evidence indicates that the concentration of mineral ions in Zolal spring water is higher than in Keder spring.

The bivariate plots of the most significant parameters and isotopic data in the samples compared here indicate that the two springs share the same source of recharge from rainfall, and in light of their close proximity and similar hydrographic behavior, these two springs likely also share the same path along part of their initial flow pathway. Part of the water from the main spring passes through a wide channel with turbulent flow, and part of this water enters a sub-joint with a narrower joint and lower flow. Most likely, the same source of water entry in both springs is the largest sinkhole in the region, i.e. the Gachal sinkhole.

The Keder spring transports rainwater from highly-fractured paths and large karstic canals to the discharge point immediately after rain. Part of the turbidity of Keder spring can also be attributed to the movement of wall sediments within the karst duct networks (autochthonous).

The occurrence of turbidity after earthquakes also confirms this. In Zolal spring, a siphon-shaped reservoir in the path of water movement allows rainwater or snowmelt to replace water already present in the reservoir and to settle before it flows to the spring. For this reason, Zolal spring water, unlike Keder spring water, remains transparent when it rains. The results of chemical analyses support this conclusion too.

To further characterize the hydrogeological status of these karst springs as accurately as possible, dye tracer studies should be carried out in the region, and the concentrations of tritium and carbon 14 should be measured to determine the age of the groundwater.

Declarations

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Figures

Figure 1

Position of study area in west of Iran and geological map with faults

Figure 2

Photographs of sinkholes in Kiyan Mountains

Figure 3

Anticline Fault Mountain (above)- southern edge (down right)- northern inverse edge (down mid)- Kiyan Spring (down left)

Figure 4

Zolal (clear) and Keder (turbid) springs after the 2017 earthquake (left) and 2018 storm (right)

Figure 5

Recession curvesfor Zolal and Keder Springs

Figure 6

Hydrographs for Zolal and Keder springs

Log Turbidity (NTU)

Figure 7

The trends of decreasing turbidity associated with the 2017 earthquake, precipitation, and the 2019 turbidity phenomenon

Figure 8
Daily rainfall relative to daily turbidity data

Figure 9
Gibbs diagram for Keder and Zolal springs

Figure 10

Bivariate plots of the most significant parameters of spring samples

Figure 11

Distribution diagram of $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ for Keder and Zolal springs

Figure 12

Multiparametric profiles EC, T, pH, DO, δ18O and δ2H of Keder spring phenomena 2019

Figure 13

Schematic overview of groundwater circulation in Keder and zolal spring