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Stable isotopes (δD, $\delta^{18}O$ and $\delta^{13}C_{DIC}$) characteristics of karstic groundwater in Qori Meydan plain, NE of Iran

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Abstract

Due to the scarcity of surface water in many regions around the world and the rapid increase in the population, there has been sharp increase in the potable water demand. Groundwater is becoming an important source of drinking water supply. In this study, for the first time, the isotopic composition ($\delta^{18}O$ or δD) of precipitation and the karstic water resources and also the carbon isotope composition ($\delta^{13}C_{DIC}$) of springs in Qori Meydan Plain (QMP - northeastern of Iran) were investigated. In QMP with semi-arid climate, springs have a key role in meeting water needs. Stable isotopic composition ($\delta^{13}C_{DIC}$, $\delta^{18}O$ & δD) of water resources were employed to trace their origin(s). The $\delta^{18}O$ composition of these water bodies range from –9.6‰ to −7.5 ‰VSMOW with corresponding variation in δD varies from −69.0‰ to – 53.6 ‰ VSMOW. The water samples were plotted close to Global Meteoric Water Line (GMWL) which means that local precipitation is the main factor in recharging the water resources. Samples more exposed to sunlight (Qorte spring and Atrak river) have least d-excess values. DOC values in water resources predominantly originate from plants and green algae. The $\delta^{13}C_{DIC}$ ratios of water samples vary from −10.0 ‰ to -4.1 ‰VPDB, which points that the main source of DIC in groundwater is limestone beds.

Introduction

Stable isotope compositions of karst spring waters provide critical information regarding sources of groundwater recharge, timing of recharge, water-rock interaction along flow paths, and mixing of distinct groundwater bodies. Ionic and isotopic concentrations can be easily changed or fractionated in aquifers through processes such as plant activity (O'Leary, 1988), isotopic exchange with surrounding materials, mineral or gas dissolution (Lesniak and Sakai, 1989), or redox reactions such as denitrification (Bottcher et al., 1990), sulfate reduction (Machel et al., 1995) and sulfide oxidation (Fry et al., 1988) along the flow path. Water isotopic composition ($\delta^{18}O$ or δD) behaves conservatively in low-temperature aquifer environments (Kendall et al., 1995). Carbon isotopes are used to assess the origin of dissolved inorganic carbon (DIC), which is the main species in waters draining carbonate watersheds. Concentrations of DIC and its stable carbon isotope ratios ($\delta^{13}C_{DIC}$) are governed by processes occurring in the soil–aquifer system, and these vary seasonally. Changes in $\delta^{13}C_{DIC}$ result from the fractionation accompanying transformation of carbon or from mixing of carbon from different sources. The major sources of carbon to aquifer DIC loads are dissolution of carbonate minerals, soil CO_2 derived from root respiration and from microbial decomposition of organic matter. As a result, researchers have often used stable isotope composition of water as tracers for determining the water provenance (Cartwright et al., 2000; Larsen et al., 2001).

In Qori Meydan plain (QMP), located in about 70 km west of Bojnord city - northeastern Iran, with limited water resources, groundwater is the most important source for domestic and agricultural purposes. The main objective of the present study is to better delineate origin(s) of karstic groundwater in the QMP within the framework of its complex geology using geochemistry and stable isotopes. This may provide a theoretical basis to the decision makers for developing suitable water resource utilization strategies and policies for northeast Iran in this area.

Setting and geology

QMP with 600 km^2 area placed between latitudes 37°44' 04" to 37°36' 37" and longitude 56°44' 09" to 56°27' 00" in Man-e-Samalqan study area at North Khorasan province. This area has the annual precipitation rate of 290 mm/year and located in semi-arid area. In the southern part of the QMP, villages are facing a problem with the lack of safe drinking water. Dashtak karstic spring, located near the village of Dashtak Olyawith and is discharging groundwater with long-term average of 270 liters per second flow, is the only and the most important water resource in QMP.

The main geological formation in the study area mostly consist of limestone, marl, shale and sandstone (Fig. 1). According to existence water resources (Dashtak, Qorte and Taqdanloo springs; Behkade Qanat and Soqa well), Tirgan formation has significant role in groundwater storage in QMP. In the terms of topography and structural geology QMP located in a syncline and embedded with high mountains of Tirgan formation in south and north.

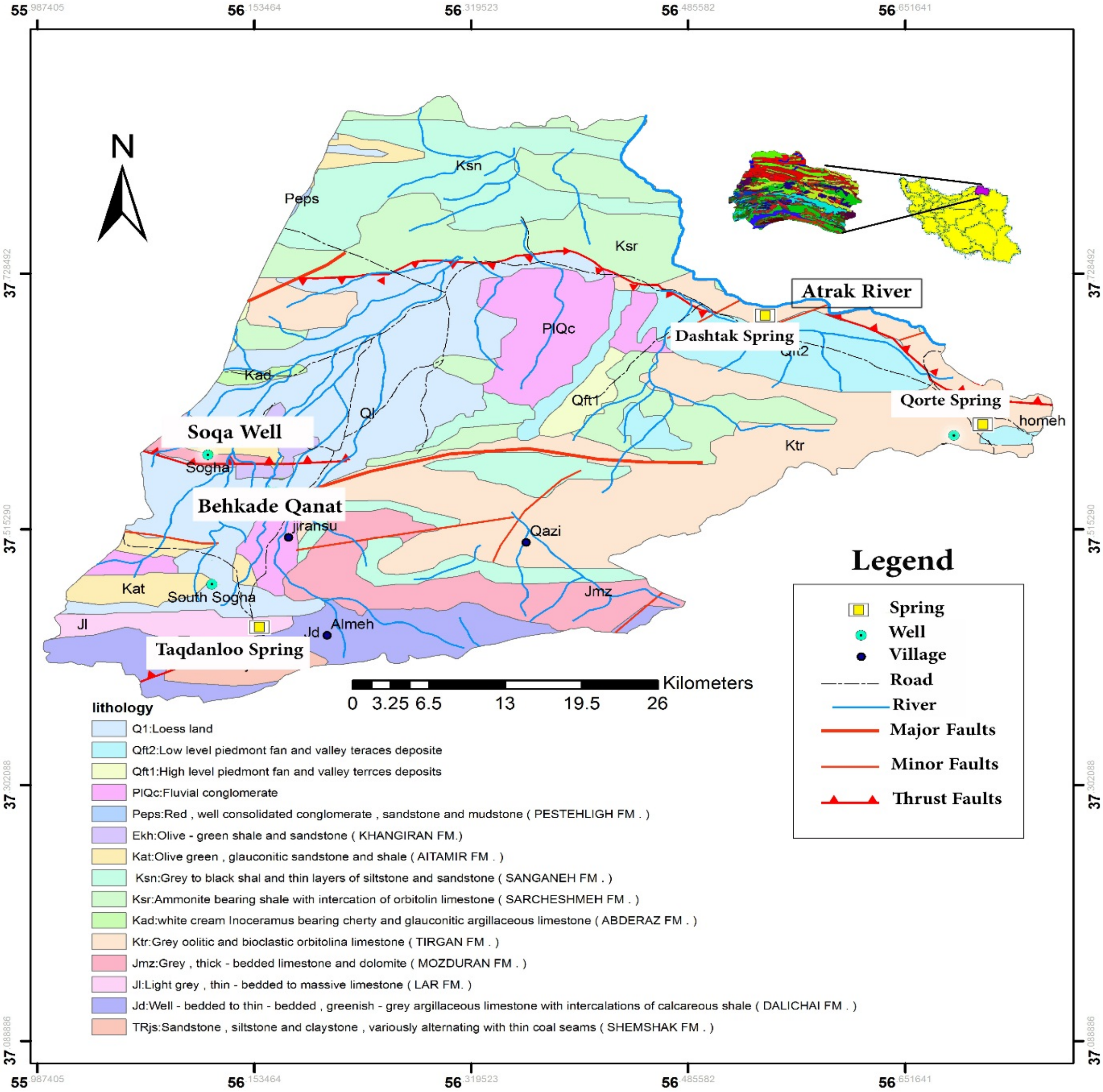

Fig. 1. Geological map of study area (QMP) and sampling locations.

Methods

Sampling was performed during wet season in 2015. Samples for $\delta^{18}O$ and δD analyses were collected in 30ml HDPE bottles. For $\delta^{13}C_{DIC}$ and DOC analyses, samples were collected in 40 ml glass vial bottles, filled with no headspace and sealed with caps. All samples were filtered through 0.5µm filters and were keep cold until they were sent to the laboratory. All measurements were performed in the G.G. Hatch stable isotope laboratory of university of Ottawa. The stable isotope ratios are expressed in δ‰, i.e. as the difference in parts per mil of the isotopic ratios $^{13}C/^{12}C$, $^{18}O/^{16}O$ and $^{2}H/^{1}H$ from those of the reference materials VPDB (carbon isotopes) and VSMOW (oxygen and hydrogen isotopes).

Results and Discussion

The isotope values ($\delta^{18}O$, δD and $\delta^{13}C_{DIC}$) of precipitations and karstic water samples were tabulated in Table 1.

Table.1. DIC and DOC concentrations and isotope ($\delta^{18}O$, δD and $\delta^{13}C_{DIC}$) values in water resources and Bojnord synoptic station.

Parameter	Dashtak Spring	Qorte Spring	Taqdanloo Spring	Atrak River	Behkade Qanat	Soqa Well	Bojnord Synoptic Station			
							Jan	Feb	Mar	Apr
$\delta^{18}O$ (‰VSMOW)	-9.3	-7.8	-8.5	-7.5	-7.6	-9.6	-7.5	-9.1	-4.4	-1.8
δD (‰VSMOW)	-64.2	-58.0	-59.6	-54.9	-53.6	-69.0	-42.9	-56.6	-27.2	-5.6
d-excess (‰)	10.2	4.4	8.4	5.1	7.2	7.8	-	-	-	-
DIC (mg/l)	270.5	318.9	299.7	367.3	261.1	323.6	-	-	-	-
DOC (mg/l)	0.23	0.54	0.74	0.77	-	-	-	-	-	-
$\delta^{13}C_{DIC}$ (‰VPDB)	-4.1	-10.0	-8.9	-7.7	-7.8	-6.8	-	-	-	-

Hydrogen and oxygen isotopes can, to some extent, trace the circulation of water through the atmosphere and are, therefore, widely applied in studies of the origin of water (Chandrajith et al., 2013; Chatterjee et al., 2016). Locating the developed Bojnord Meteoric Water Line (BMWL, expressed as $\delta D = 7.5\delta^{18}O + 8.9$) on the left hand side of the Global Meteoric Water Line (GMWL - $\delta D = 8\delta^{18}O + 10$; Craig, 1961), as illustrated in Fig. 2, indicate less humidity of the study area. The slope of BMWL is about 7.5, which is a bit less than that of GWML, this means that evaporation is more intense in the study area rather than global average. The $\delta^{18}O$ and δD values of karstic spring waters vary from -9.6‰ to -7.5‰, and from -69.0‰ to -53.6‰, respectively. These fairly stable values of isotopic composition are indicative of a similar hydrogeological genesis for the karst spring waters. The Dashtak and Taqdanloo springs samples were plotted almost along the global meteoric water line. This means that all water samples derived from meteoric water which is typical for arid environment (Clark and Fritz, 1997) with minimal isotope exchange with reservoir rock (Oyuntsetseg et al., 2014). Qorte spring and Behkade qanat samples plot far from this line. This may be due to evaporation because in both sites the water flowed and stored in a pool. In addition, Atrak river plots far from the GMWL and shows more $\delta^{18}O$ enrichment because of evaporation process occurred. In general, plotting of all samples below the BMWL shows that evaporation process occurred before the recharge process.

The deuterium excess (d-excess) is an index defined by $d = \delta D - 8 \times \delta^{18}O$ (Dansgaard, 1964), where δD and $\delta^{18}O$ represents hydrogen and oxygen isotopic composition of water respectively. This parameter tells us how the composition of specific water deviates from the Global Meteoric water composition. In general, the d-excess is correlated well with physical conditions such as air temperature and humidity (Merlivat and Jouzel, 1979). Temperature has a great impact on d-excess values regarding evaporated waters tended to have a lower d-excess. In the study area Qorte Spring and Atrak river more exposed to sunlight and then have least d-excess values among other samples.

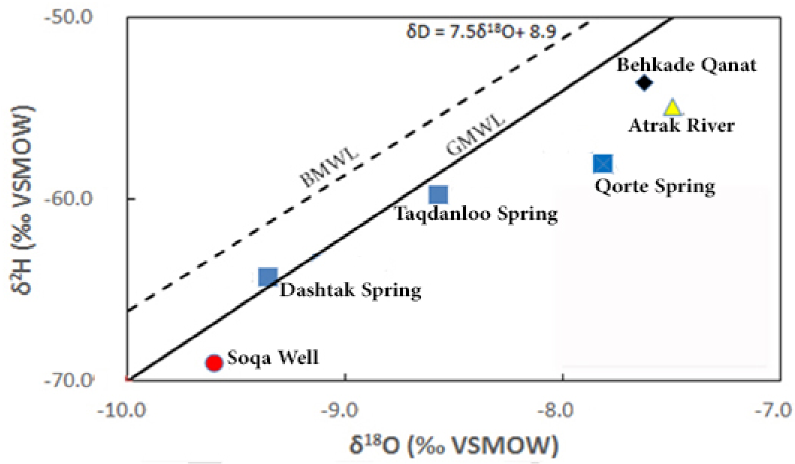

Fig.2. Locations of sampled water resources on $\delta^{18}O$ vs. δD diagram (the solid and dashed lines indicate Global and the Bojnord meteoric water lines (GMWL and BMWL).

DOC values are presented on table.1. DOC values of water resources of study area vary from 0.23mg/l to 0.77mg/l. Atrak river because of agricultural lands and vegetation cover has the highest DOC values (0.77mg/l). Taqdanloo has the second highest value because of its location (Takht Iran forest protected area). Also, DOC in Qorte spring originates from Animal feces and its green algae.

The $\delta^{13}C_{DIC}$ values can determine contributions of organic matter decomposition and carbonate mineral dissolution in springs. $\delta^{13}C_{DIC}$ in spring waters is also controlled by the geological composition of the recharge area (Konduc et al, 2012). The common pH values for groundwater and surface water of the study area (between 6.0 and 7.0) indicate that the bicarbonate (HCO_3^-) is the main form of DIC. The $\delta^{13}C_{DIC}$ values of karst spring waters vary from -10.0‰ to - 4.1‰. which indicate that probably their sources are 1) atmospheric CO_2, 2) limestone beds, 3) C4 crops. The two carbon sources that have the most important role in the $\delta^{13}C_{DIC}$ values of spring waters are: organic matter degradation and carbonate dissolution. As $\delta^{13}C_{DIC}$ values in soils and carbonate rocks are -24.0 ‰ and -2.0‰, respectively, then $\delta^{13}C_{DIC}$ values in karst region depends on mixing of these two distinct sources. Taqdanloo spring located in area with thick vegetation cover (Takht Iran forest protected area), therefore, CO_2 results of decomposition of organic matter has a key role in $\delta^{13}C_{DIC}$ values and shows more depleted $\delta^{13}C_{DIC}$ values (-8.9‰). The same logic is valid for Qorte Spring with existence of a lot of green algae in its pool. On the other hand, in Dashtak spring dissolution of limestone (Tirgan formation) shifted the $\delta^{13}C_{DIC}$ values toward more positive values (- 4.1‰). The $\delta^{13}C_{DIC}$ values of Atrak river mostly affect by vegetation cover and agricultural lands around it.

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