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Research papers

Seasonal recharge of spring and stream waters in a karst catchment revealed by isotopic and hydrochemical analyses

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ABSTRACT

Quantifying and understanding recharge behavior of aquifers in complex hydrogeological systems is challenging, which limits our ability to manage water resources in karstic areas. In this study, we analyzed the seasonal recharge sources and processes of a stream, an intermittent spring, and a perennial spring in a small dolomitic catchment. Weekly monitoring of stable isotopes and chemical characteristics and daily hydrological data of these waters was performed in 2017 and 2018. There were broad seasonal variations in rainfall isotopes, with more negative values observed in the wet season and more positive values observed in the dry season, while narrow ranges were observed in spring and stream waters. Such values plotting on a LMWL represented a homogeneous mixing of rainfall without the effective evaporation effect. Hydrograph separation showed that the mean proportion of old water was approximately 94% for the springs and stream, which indicated a mixing mechanism in recharge processes. The mean residence time was approximately 23 weeks for spring 1, 201 weeks for spring 2, and 43 weeks for stream. The significant difference between springs was attributed to the combined effects of relatively higher proportions of rocky outcrops, thinner soil–epikarst, and better karstic development in the aquifer of spring 1, which enhanced the sensitivity to rainfall. The stream was recharged by waters from hillslopes, which mixed extensively in the depression, accompanied by soil–epikarst interaction. However, only approximately 1.5% of total stream flow was recharged by springs annually, and most of the stream was recharged by water through underground paths, based on the discharge analyses. Moreover, stream was recharged by subsurface flows, which were considerably affected by soil, leading to the fluctuating stream discharge characteristics during the wet season. The results suggest that greater attention should be paid to the roles of near-surface soil–epikarst architecture in hydrological processes.

1. Introduction

Karstic regions comprise approximately 7–12% of the Earth's continental surface (Chen et al., 2017; Hartmann et al., 2017). Statistically, approximately 15–25% of the world's population relies on karst freshwater resources (Stevanovic, 2018). However, surface water is relatively scarce, and groundwater extraction is challenging in these regions because of their unique hydrogeological structure (De Giglio et al., 2018; White, 2002; Yu et al., 2015). Moreover, the permeable formations of karst systems contribute to the mosaic distribution of surface waters, which frequently exchange with groundwater (Bailly-Comte et al., 2009; Barberá and Andreo, 2015), rendering it difficult to establish the interactions among various water types. A better understanding of the hydrological processes of karst aquifers is therefore critical for groundwater development and for the sustainable management of karst water resources.

Most of the water derived from rainfall reaches groundwater systems through conduit–fissure networks, rather than hillslope surface runoff (McDonnell, 2003; Peng and Wang, 2012). Thus, more studies focusing on the recharge processes of subsurface runoff are needed. However, such studies are challenging because of the geological complexity of karstic systems, uneven distribution of groundwater, frequent interactions between surface and groundwaters, and intense hydrological variability (Chu et al., 2017; Musgrove et al., 2010). Several classical methods, such as cave surveys, water equilibrium analyses, and discharge hydrographs and models, have been used to explore hydrological processes in karst aquifers (Bakalowicz, 2005; Chang et al., 2015). However, these methods cannot be extended to an entire

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aquifer, which limits our understanding of karstic systems by masking water sources and flow paths (Moore et al., 2009). Ambient tracers, such as deuterium (D) and ^{18}O, and hydrochemical characteristics (e.g., total organic carbon (TOC), NO_3^-, Ca^{2+}, Mg^{2+}, and HCO_3^-), are affected by unique processes in different types of water (Brenot et al., 2015; Klaus and McDonnell, 2013; Wang et al., 2018), such that they may be used for hydrograph separation and water transit times (Li et al., 2017a; Liu et al., 2017; Mosquera et al., 2016; Paces and Wurster, 2014; Sprenger et al., 2019; Tweed et al., 2015). Some hydrochemical tracers (e.g., TOC and NO_3^-) have been used to reflect the effects of soil layers (Wexler et al., 2011), while others (e.g., Ca^{2+}, Mg^{2+}, and HCO_3^-) have provided evidence of water–rock interactions (Bicalho et al., 2012), such that they were used to trace the flow paths. Therefore, the employment of ambient tracers has provided effective information about runoff mechanisms and the functions of aquifers and catchments (Iván and Mádl-Szőnyi, 2017; Mudarra et al., 2019; Pavlovskiy and Selle, 2015).

Springs are important discharge points and the majority of groundwater is eventually supplied through an extensive network of groundwater conduits or matrices in karstic aquifers (Li et al., 2017b). Therefore, the characteristics of spring water can reflect groundwater recharge and the variability in groundwater storage throughout hillslopes. Several previous studies have shown that rapid flow through subsurface fractures and conduits exerts spatial control over the spring recharge process (Hartmann et al., 2017; Rosenberry and LaBaugh, 2008). For example, Yang et al. (2019b) reported that although conduits and fracture zones accounted for 2–22% of the cross-sectional area of the aquifer, they contributed between 75 and 96% of the total groundwater flow at Silver Springs in Florida, USA. Other studies have shown similar results, such as those of Liu et al. (2011) in Southwest China and Geyer et al. (2008) in the Mediterranean. However, these studies were dependent upon the scale of rainfall events. Recently, Bicalho et al. (2017) found that multiple hydrological components were recharging spring waters, which interacted through a network of fractures and faults and contributed 92.6% of the groundwater flow at Lez Spring in France during a two-year observation period. Adji et al. (2016) suggested that matrix flow predominantly controlled spring recharge during the dry season, while the proportion of diffuse flow decreased drastically during the wet season, despite a predominance of flow through conduits and fractures, in the Petoyan Spring of Indonesia. Similar results were also reported by Zhang and Li (2019), who found mixed effects in the groundwater recharge of springs in Southwest China. These differences might be attributable to varying geological backgrounds and climatic conditions. Filippini et al. (2018) noticed that even adjacent karstic springs, which appear to drain the same mountain, can exhibit different behaviors. Mudarra and Andreo (2011) suggested that the degree of aquifer karstification controlled the differences observed in hydrogeological function for three springs with similar geological and climatic contexts. As recharge processes are influenced by multiple factors, such as soil distribution, lithology, epikarst, vegetation, and precipitation (Küry et al., 2017; Luo et al., 2018), a more detailed consideration of the factors that affect seasonal spring recharge, accounting for the heterogeneity of karstic media, is warranted. Additionally, adequate investigations are needed to inform the sustainable management and protection of groundwater karst areas.

In general, spring water flows out at a footslope which contributes to stream waters through a depression unit. Hydrological, hydrochemistry and stable isotopes data from such observation sites (springs and streams) enable us to analyze hydrological behaviors of different hydrological units or media (Parise et al., 2018). Bailly-Comte et al. (2008, 2009) reported that the hydrodynamic behavior of the hydrological system reveals the dynamics of storage and of the release and contribution of surface waters which was outlined by applying auto- and cross-correlation analyses for regional rainfall, fluvial discharge, spring flow, and water level data from caves and boreholes. Herman et al. (2009) reported that specific karstic water resources in Pennsylvania, USA exhibit widely varying inertia, with lag times that overlap with those of groundwater and surface water. However, they did not identify the origin or seasonal variability of the water. The comparison of isotopic and chemical compositions between spring and stream waters should reflect the hydrological interactions between slopes and depressions. Hu et al. (2015) compared the mean residence times between spring and stream waters and found that a poorly developed conduit system and deep soil layer in a depression would buffer the recharge process of the stream from rainfall and spring water. However, with limited isotopic data, Hu et al. (2015) have only speculated on the possible functions of soil layers in depressions, while largely ignoring the role of the epikarst layer. Although the soil layer in depressions is deeper than that on slopes, its composition mainly consists of clay, which results in a lower drainage efficiency (Yang et al., 2016). Therefore, it is inconsistent with the general understanding of karstic systems (i.e., that they are highly permeable). Fu et al. (2016) showed that the volume of water drained by conduits was 25.43%, despite their poor development (effective porosity: 0.07%). However, they described the relationships among different water sources and the function of epikarst without quantifying the recharge processes.

For Chinese karst, Yuan (1994) described the dual spatial structure of "upstairs is soil, downstairs is water". Rain, spring, and stream waters serve as the sole sources of domestic water for 1.7 million inhabitants of southwest China (Jiang et al., 2014; Li et al., 2016). Cockpit karst is the dominant landscape in this area and is characterized by similar dimensions of enclosed depressions surrounded by steep hillslopes, markedly differing from other karstic areas. Many researchers have worked in this area, obtaining important information on the functions of aquifers and predicting water resources by applying numerous karst-specific methodologies (e.g., Chang et al., 2015; Fu et al., 2016; Hu et al., 2015). However, the relationships among rain, spring, and stream waters, such as how rainwater recharges springs and streams and how spring waters recharge streams, remain uncertain. These gaps in the knowledge necessitate more detailed studies in relatively closed catchments with typical underground flow basins. In this study, our aim is to advance our understanding of the hydrogeological dynamics of karstic landscapes by combining hydrochemical and isotopic analyses and quantifying recharge. Therefore, herein, we

(1) characterized the seasonal variations of discharge and multiple tracers (e.g., D, ^{18}O, TOC, NO_3^-, Ca^{2+}, Mg^{2+}, and HCO_3^-) for rain, spring, and stream waters in a small-scale, dolomitic catchment in Southwest China. This allowed us to reveal the recharge sources of springs and streams and discuss the effects of karstic hydrogeology on their recharge processes.
(2) compared the springs and streams to define the relationships among them and to discuss the correlation of hydrological components and their storage functions for water resources.

Our findings establish foundational data and methods for future assessments of water supplies and modeling studies in karstic landscapes.

2. Materials and methods

2.1. Study area

The study catchment (24°43′58.9″–24°44′48.8″N, 108°18′56.9″–108°19′58.4″E; 272–647 m) is a typical cockpit karst catchment that spans 1.14 km^2; it is located in Huanjiang County in the northwest of Guangxi Province, China (Fig. 1). A subtropical mountainous monsoon climate dominates, with a mean annual air temperature of 18.5°C and mean annual rainfall of 1461 mm (from 2006 to 2018). In general, the wet season lasts from late April until the end of September and provides > 60% of the total annual rainfall (Yang et al., 2019a). This catchment experienced severe deforestation from

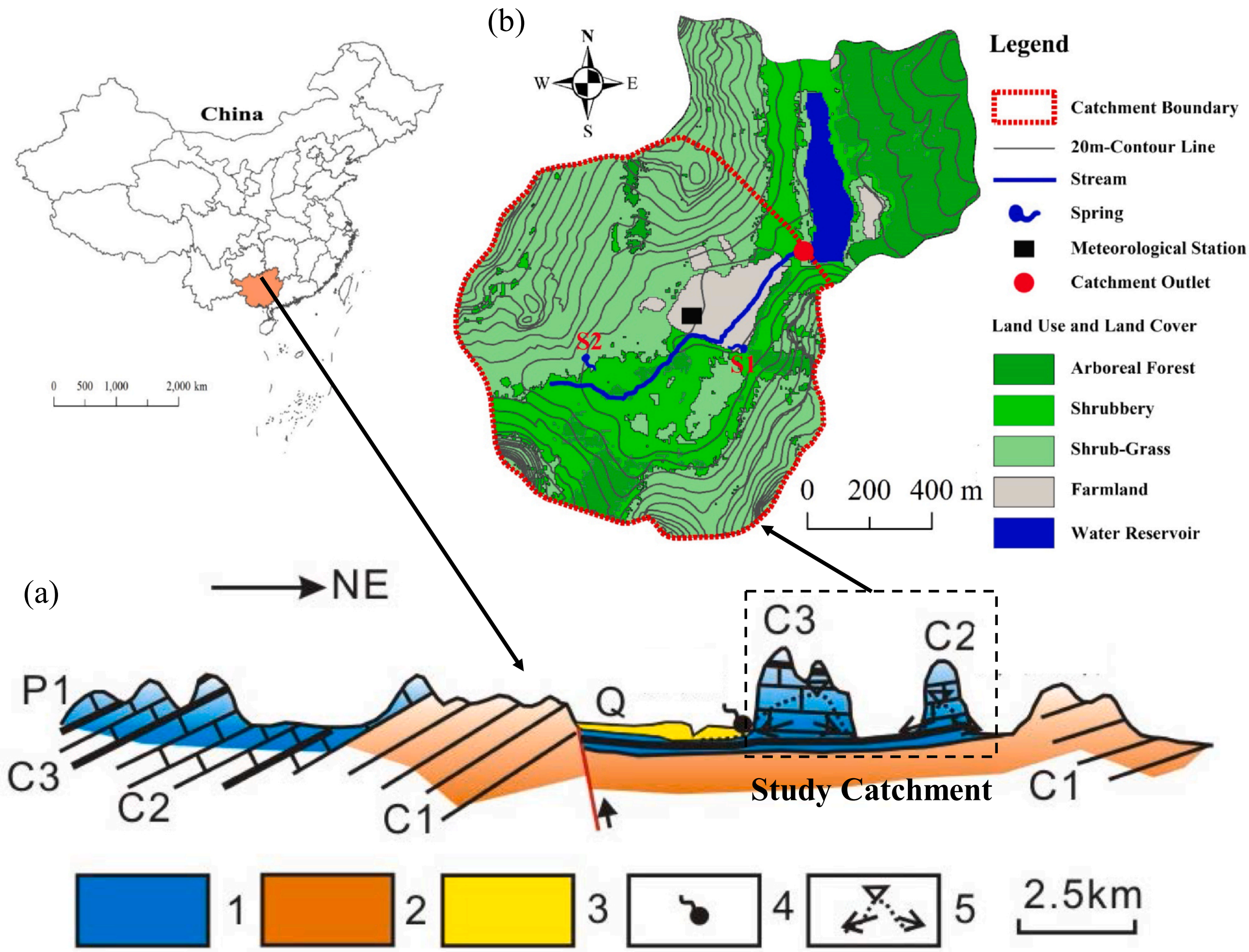

Fig. 1. Overview of the study area. (a) Geohydrological background surrounding the study catchment. Numbers 1–5 refer to the karst aquifer, sandstone aquifer (relatively impermeable layer), porous quaternary aquifer, spring, and groundwater flow paths, respectively; P1, Early Permian; Q, Quaternary; C1, C2, and C3, Early, Middle, and Late Carboniferous. (b) Hydrogeological and land use\land cover map of catchment with sampled springs.

1958 until the mid-1980 s and has undergone natural restoration for over 30 years. Depression has been partly rezoned as cultivated land since 2004. At present, shrubbery and shrub–grass dominate most areas, while secondary forests are only found on continuous rocky outcrops in the eastern hills and at the footslope (Nie et al., 2011).

The lithology is mainly comprised of Middle–Late Carboniferous dolomite underlain by an Early Carboniferous sandstone aquifer, which is a relatively impermeable layer (Fig. 1a). Approximately 28% of the total catchment area is a flat depression surrounded by mountains, for which ~ 60% of the slopes have a gradient > 25° except for an outlet in the northeast. Superficial deposits (0–50 cm) are loose and rocky, with high hydraulic conductivity along hillslopes; however, the soil depth was 20–160 cm in the depression, except for an area of continuous rocky outcrops (0.11 km^2) in the south. Isolated rocky outcrops without superficial deposits are also widespread in the catchment area.

There are two epikarstic springs and a stream in the catchment. The springs are at the bases of hillslopes; spring 1 is an intermittent spring that flows during the wet season and spring 2 is a perennial spring. The perennial stream originates from the southwest corner of the catchment and flows into a water reservoir in the northeast (Fig. 1b). Spring 2 can freely flow into the depression; however, spring 1 flows into a stream with an excavated channel, which is linked through cultivated lands via planning controls. Based on the contour lines and groundwater flow paths, the study catchment is closed to both surface and groundwater, and water in the aquifer is only drained by the stream (Fu et al., 2016). Therefore, stream discharge processes may reflect the overall characteristics of the aquifer, including the soil layer, epikarst layer, and the underlying massive, compact dolomite (Fu et al., 2016).

2.2. Water sampling and data measurement

The discharge of the springs and stream were obtained using Manta 2 (Eureka, USA) at daily intervals from January 2017 to December 2018, and water samples for hydrochemistry/stable isotope analyses were collected weekly. Three samples were collected per site. The first sample was collected in a 2-mL high-density polyethylene (HDPE) bottle, which was sealed for isotopic measurements and stored at 4 °C. The second sample, which was used for ions (Ca^{2+}, Mg^{2+}, and NO_3^-) and TOC measurements, was collected in a 100-mL HDPE bottle that was sealed after being mixed with 2 mL of 85% H_3PO_4 and stored at –20 °C. The third sample was used for HCO_3^- and CO_3^{2-} measurements and was collected in a 100-mL HDPE bottle, which was taken directly to the laboratory for measurement.

Cations (Ca^{2+}, Mg^{2+}) were measured via ion chromatography (MP-AES42100, Agilent Technologies, USA), while NO_3^- concentrations were analyzed with a flow injection analyzer (AA3, Seal Analytical, UK). Total organic carbon was determined with a TOC-VWP analyzer (Shimazdu Corp., Japan). Anions (HCO_3^- and CO_3^{2-}) were measured using a titrimetric analytical method with hydrochloric acid. Stable isotopic compositions of hydrogen and oxygen (i.e., D and ^{18}O) were analyzed with a liquid–water isotope laser spectrometer (DLT-100, Los Gatos Research, Inc., USA) and are reported using the standard delta

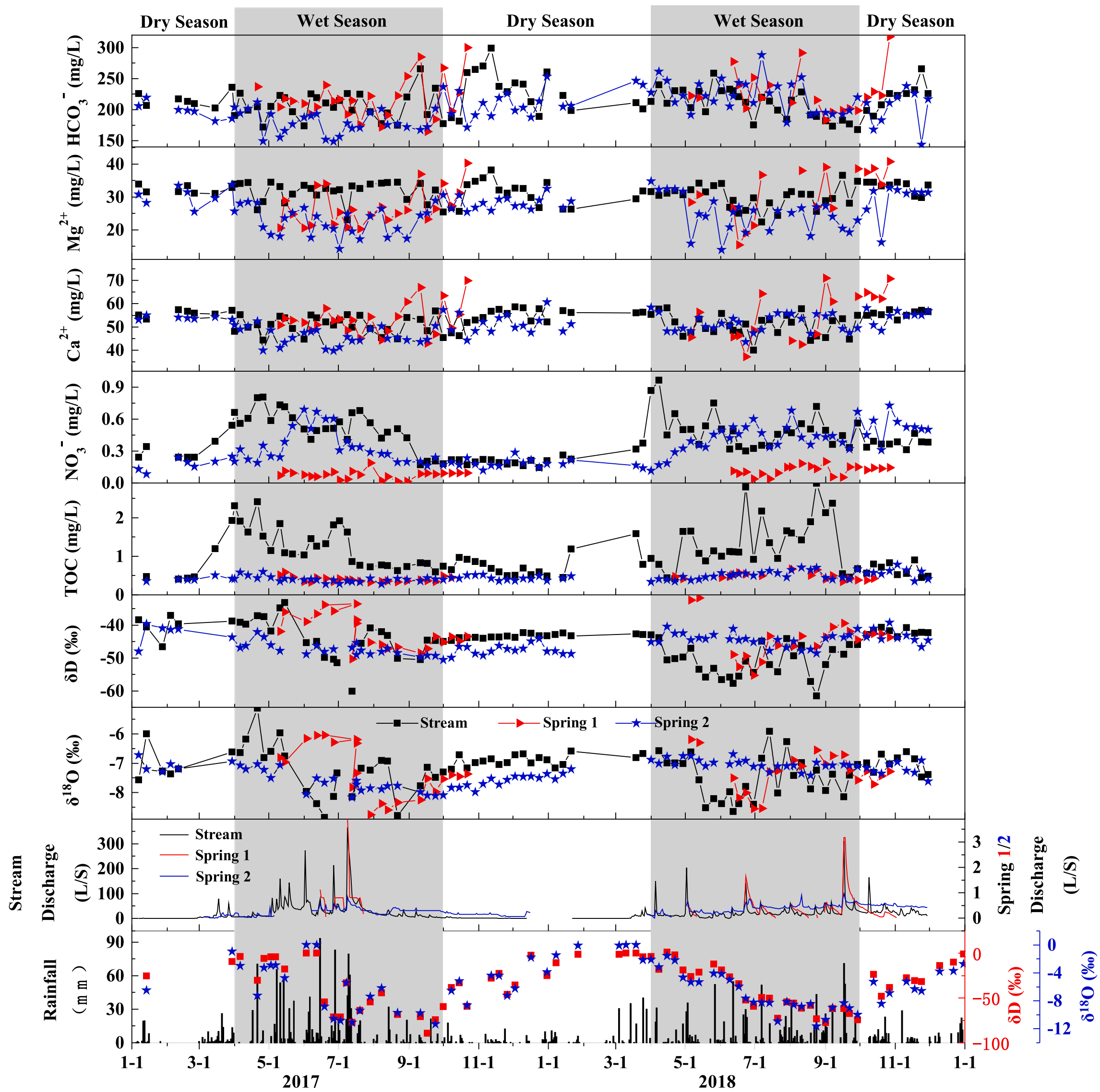

Fig. 2. Temporal evolution of discharge, isotopes and chemical components of springs and stream water during 2017 and 2018.

notation relative to the V-SMOW standard of 0‰.

We measured precipitation with a HOBO rain gauge (BHW-PRO-CD) and pendant event logger (UA-003–64, Onset Computer Corp., USA) at meteorological stations in the catchment at a 0.2-mm resolution (Fig. 1b). Precipitation samples were immediately collected from passive collectors located at each station after a precipitation event. One (mixed) rainwater sample was collected during each precipitation event. Sample preservation and analytical methods were similar for springs and stream.

2.3. Methodology

Although some studies have reported that multiple components (rain, soil, epikarst, and ground waters) have been separated by a multi-end member equation with multi-tracers (Lee and Krothe, 2001a, 2001b), the spatial heterogeneity of interactions among multiple water sources present challenges for collecting a representative sample which could identify different sources. Thus, in our study, we assumed a simple mixture of two end-members (new water and old water) to quantify the mixing proportions of rainwater recharging the springs and stream for assessing the storage and transit function of the aquifer. We used the weighted mean of the rainfall samples within a week as new water (C_{new}) and the isotope of stream samples of the week before as the old water (C_{old}). Their contributions were calculated using the following equations:

$$X_{new} \times C_{new} + X_{old} \times C_{old} = C_{event} \quad (1)$$

$$X_{new} + X_{old} = 1 \quad (2)$$

where X_{new} and X_{old} are the proportions of water discharge by new water and old water.

Principal component analysis (PCA) was applied to corroborate the qualitative description from temporal evolution and to interpret the hydrochemical data and their relevant sources and processes (Bicalho et al., 2012; Doctor et al., 2006; Mudarra and Andreo, 2011). The two-dimensional diagrams (NO_3^- and TOC–Mg^{2+}) of these chemical components of the water contribute to the understanding of the characteristics of the groundwater flow. On the one hand, NO_3^- and TOC were derived from soil (important component in the unsaturated zone) and they could assess the transit time of water through the unsaturated zone (Barberá and Andreo, 2015; Batiot et al., 2003). On the other hand, Mg^{2+} concentrations are a better indicator of water residence times than Ca^{2+} in dolomite watersheds because the dissolution rate of Mg^{2+} is lower than that of Ca^{2+} (Barberá and Andreo, 2015; Batiot et al., 2003). Thus, Mg^{2+} was used to assess the residence time and contribution of water from the saturated zone.

With the weekly resolution basic data of deuterium, the sine wave method was used to fit the seasonal variation in isotopes in rainfall, spring, and stream waters, which estimated the transit time of rain water through aquifers using the exponential model (Rusjan et al., 2019). The sine wave model and mean residence time (MRT) equations were defined as follows:

$$\delta D = \delta D_{mean} + A[sin(c \times t - \theta)] \tag{3}$$

$$MRT = c^{-1} \times [(A_s/A_p)^{-2} - 1]^{0.5} \tag{4}$$

where δD and δD_{mean} are the modelled and the mean annual measured δD values, respectively. A_P or A_S are the calculated (fitted) annual amplitudes of precipitation and of stream (spring) water, respectively; c is the radial frequency of annual fluctuations; t is the time in days after the start of the sampling period; and θ is the phase lag.

3. Results

3.1. Precipitation characteristics and variation of springs and stream discharge

The total amount of precipitation in 2017 was 1504 mm, with 81.5% falling during the wet season in 2017, whereas 68.3% of the total rainfall (1440 mm) occurred during the wet season in 2018 (Fig. 2). However, there were significant differences in the annual distribution of rainfall. More heavy rainfall events occurred from March to July in 2017, while there was a relatively even distribution of rainfall from March to October in 2018. During the 2017 wet season, eight storm events occurred that yielded precipitation amounts > 50 mm. However, only four events had exceeded 50 mm in rainfall and were < 55 mm during the 2018 wet season.

The mean discharge of stream flow was 20.8 L/s and significantly greater than spring 1 (0.3 L/s) and spring 2 (0.3 L/s). The hydrographs for the springs and stream discharge exhibit that there were various periods of increased water flow in response to the rainfall events (Fig. 2). There were sharp rises and falls in discharge at monitoring sites and the maximum discharge reached up to 364.9 L/s (stream), 3.2 L/s (spring 1), and 0.9 L/s (spring 2). The global hydrograph (Fig. 2) also indicates that the discharge of spring 1 and stream were more sensitive than spring 2 in which the discharge variation was smaller.

3.2. Isotopic characteristics of rain, spring, and stream waters

The δD and $\delta^{18}O$ values of precipitation samples from 2017 and 2018 showed pronounced seasonal variability (Figs. 2 and 3). Maximum values typically occurred between spring and winter, while minima occurred between summer and autumn. The variations in δD (–93.5 to 4.1‰) and $\delta^{18}O$ (–13 to –0.1‰) were large throughout the two-year study period. Rainfall samples during the wet season were more enriched than those in the dry season, corroborating the findings of Guo et al. (2015). The regression coefficient and intercept of the local meteoric water line (LMWL; $\delta D = 8.1 \times \delta^{18}O + 13.9$; $R^2 = 0.94$) was larger than that of the global meteoric water line (Fig. 3).

The isotopic compositions of spring and stream waters were relatively stable when compared to those of rainwater (Fig. 3). Variations in the isotopic compositions in spring 1 (δD: –55.3 to –31.7‰; $\delta^{18}O$: −8.8 to –6.1‰), spring 2 (δD: –50.6 to –39.2‰; $\delta^{18}O$: −8.2 to –6.7‰), and stream waters (δD: –61.6 to –33.2‰; $\delta^{18}O$: –8.8 to –5.1‰) were significantly lower than those of rainwater (Fig. 2). The δD and $\delta^{18}O$ values of stream water samples showed pronounced seasonal variability while there was no significant difference between dry and wet season in springs. Fig. 4 exhibits that the mean isotopic values of stream water during the wet season (δD: −47.9‰; $\delta^{18}O$: −7.4‰) were more negative than those in the dry season (δD: −42.3‰; $\delta^{18}O$: −7.1‰). The mean isotopic values of spring 2 water during the wet season (δD: −45.7; $\delta^{18}O$: −7.3‰) were more negative than those in the dry season (δD: −45.5‰; $\delta^{18}O$: −7.4‰), but without significant difference. In addition, there was no significant difference between stream and spring water in dry season while stable isotope (D) of spring 1 was significantly more positive than stream water during wet season.

3.3. Hydrochemical characteristics of spring and stream waters

Solute concentrations (HCO_3^-, Ca^{2+}, and Mg^{2+}) were controlled by water–rock interactions in which no significant differences existed between spring and stream waters for HCO_3^- and Ca^{2+}, while the mean Mg^{2+} value of the stream was significantly higher than the springs (Fig. 4). Such ions were lower during the wet season than in the dry season without being significantly different. However, they were significantly higher during the dry season than that during the wet season at spring 1. At spring 2, only Mg^{2+} exhibited significant difference between seasons.

Chemical indices, such as TOC and NO_3^-, were affected by the soil layer. The TOC in the stream water during the dry season was significantly lower than that during the wet season and was significantly greater than that in the spring waters where there was no obvious seasonal variation. In terms of NO_3^- concentrations, there were significant differences among three sites during the wet season (magnitude of difference in order of: stream > spring 2 > spring 1) while there was no significant difference between the stream and spring 2 and they were significantly higher than spring 1 during the dry season. The seasonal variation trend was similar to TOC except for spring 2 where NO_3^- concentration was significantly higher during dry season than wet season.

4. Interpretation and discussion

4.1. Recharge mechanism in springs

Spring waters were recharged by a relatively constant pool in the karstic study area. Although rainwater, the input water source, displayed significant seasonal variations in isotopic values, those of the springs had a narrow range and undifferentiated values between seasons (Fig. 2 and Fig. 3). The same characteristics were reported by Guo et al. (2015) and were attributed to homogenization via the mixing of meteoric waters in the unsaturated zone. In our study, the isotopic values of spring waters were plotted on the LMWL (Fig. 3), which revealed that rainwater was their only source (Bahir et al., 2018; Bicalho et al., 2017). Thus, the two end member mass balance calculation was used weekly to estimate the proportion of new water (rain water) and old water (pre-event water existing in the reservoir before estimating period) during the whole study period (Jeelani et al., 2013). The results of hydrographic separation inferred from variation characteristics of D isotope indicates that the mean proportions of old water were 93.9% (spring 1) and 94.4% (spring 2); however, the mean proportions of old water were 89.5% (spring 1) and 93.4% (spring 2) during the wet season (Fig. 5). Therefore, old water controlled the recharging of spring water during the whole study period. The same results were reported by Poulain et al. (2018), who found that quick flow accounted for 34% of the recharge of springs, such that springs were mainly recharged by diffuse flow. Hydrograph separation also exhibits that the proportion of new water could be up to 83.3% (spring 1) and 54.8% (spring 2) during several periods of heavy precipitation events. Adji et al. (2016) found that the diffuse flow dominates spring discharge during non-flooding and flooding recession periods and the diffuse proportion decreased drastically due to the conduit flow supply during the rising limb period. Therefore, we suggest that the spring aquifers in this study could provide good storage for the diffuse flow, even though a conduit might be developed.

Although the recharge sources were relatively constant in the two springs, spring 1 displayed more seasonality than spring 2. The more

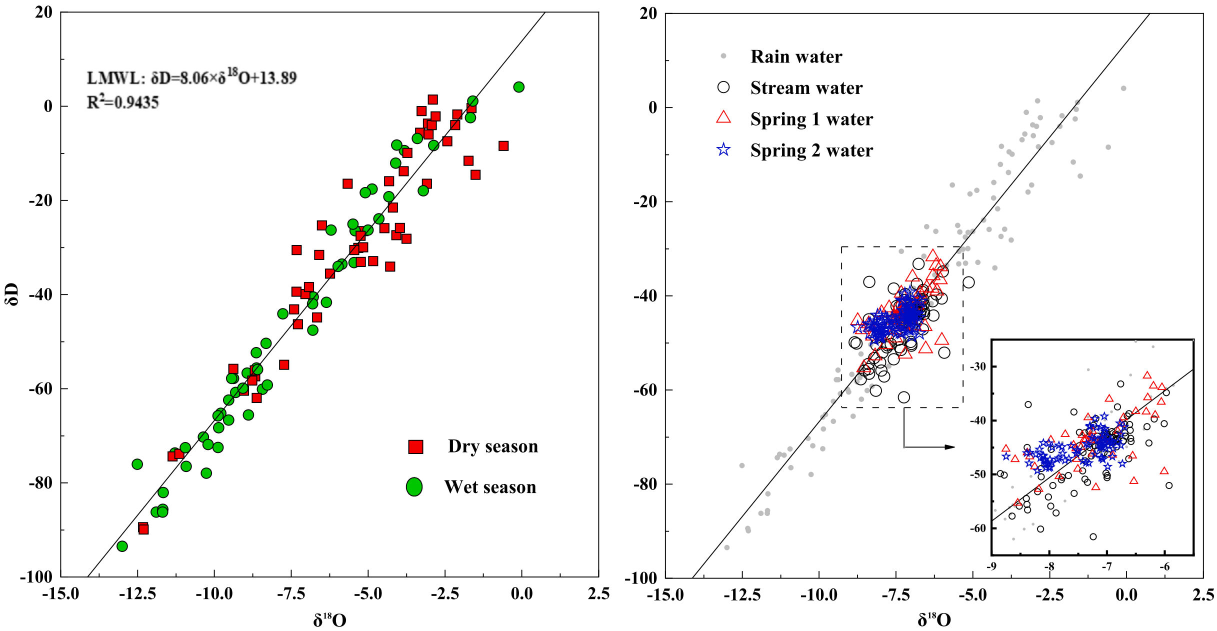

Fig. 3. Regression of local meteoric water line (LMWL) and δD vs. $\delta^{18}O$ of spring and stream waters.

rapid rises/falls in discharge and higher peak discharge of spring 1 indicates that the recharging of spring 1 was more sensitive to the variations in rainfall which means that the aquifer presented a relatively highly developed conduit system (Iacurto et al., 2020; Kresic and Panday, 2018) (Fig. 2). In addition, according to the comparison for the mean residence time between springs based on the displacement method (Fig. 6) (McGuire and McDonnell, 2006), we found that the mean residence time of spring 1 (22.9 weeks) was significantly smaller than spring 2 (200.9 weeks) which indicates the obvious hysteresis effect of spring 2. Spring 1 is an intermittent spring that discharges after a heavy rainfall event or sustained rainfall but dries up with short-term drought. In the study area, the mean thickness of the spring 2 epikarst (15.5 m) was greater than spring 1 (8.7 m), which resulted in a greater water storage capacity. Rusjan et al. (2019) suggested that the shorter mean residence time could be expected for karst aquifers without extensive deep groundwater storage. Conversely, the longer mean residence time indicates a larger groundwater storage and the intensive mixing and homogenization of water sources (rain water and groundwater) (Brkić et al., 2018; Kogovšek and Petrič, 2014). In the karstic study area, the aquifer was composed of a network of regularly distributed fractures, which resulted in sufficient mixing of different groundwater flows, despite the existence of rapid flow channels. These would account for the dampening of seasonal variations between rainwater and spring water isotopic compositions at spring 2. Moreover, the percentage of outcrop coverage at spring 1 (39.5%) was significantly greater than at spring 2 (6.8%). Wang et al. (2016) reported on the hydrological role of rock outcrops, in which water received by soil patches from rock runoff will equal the precipitation when the

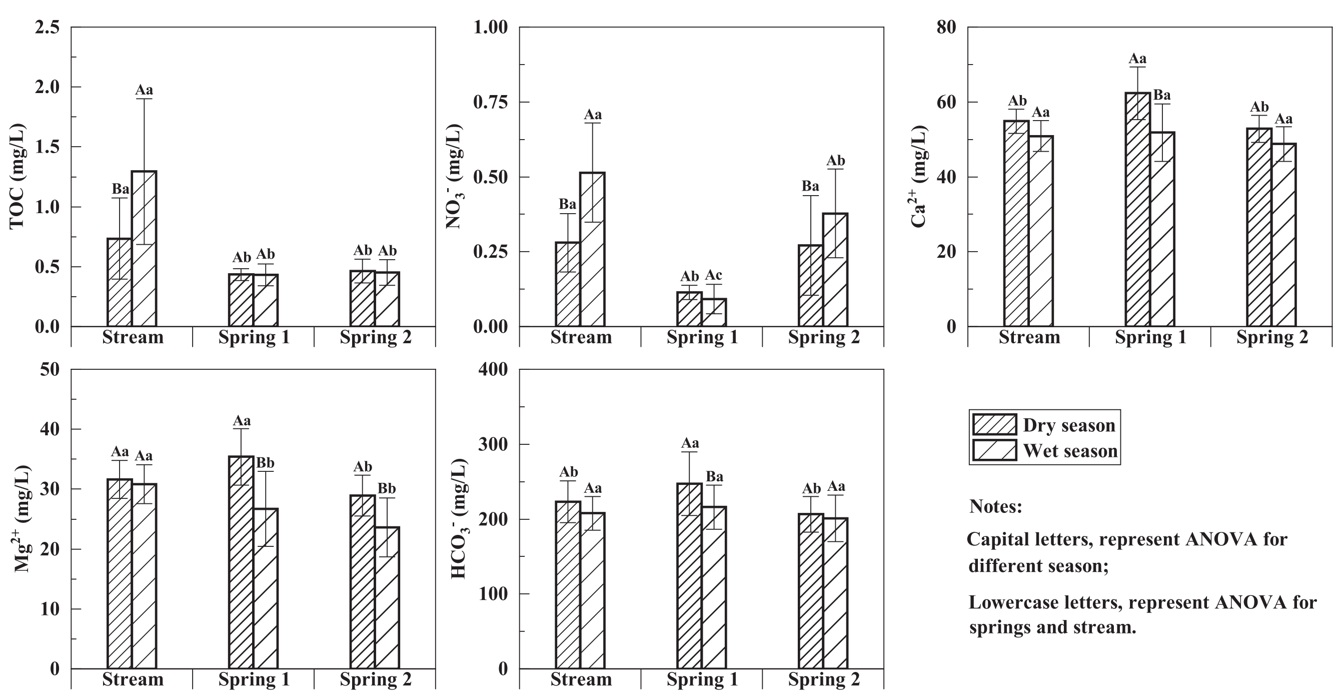

Fig. 4. Statistics of isotopes and chemical components in dry and wet seasons at different sampling sites.

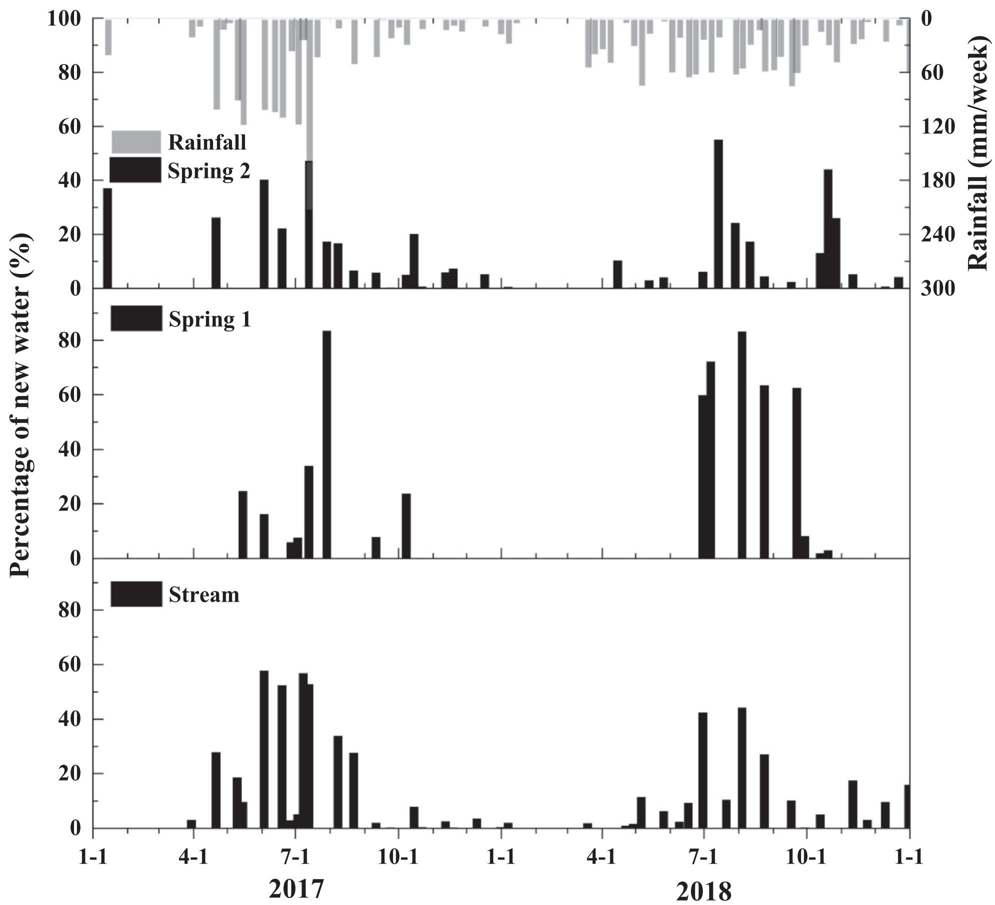

Fig. 5. Seasonal variations in new water recharging springs and streams.

outcrop area reaches 70% of the ground surface. Therefore, greater outcrop coverage at spring 1 area may have resulted in more and faster infiltration, thereby increasing the contribution and influence of recent rainwater.

The seasonal variation of hydrochemistry underlines the important roles of the saturated zone (dominated by mineralization) and the unsaturated zone (dominated by soil biochemistry) in the hydrogeological functioning of karst aquifers. PCA of all samples showed that spring 1 was more enriched in mineralized parameters (Ca^{2+}, Mg^{2+}, and HCO_3^-) and the distribution of various parameters in spring 2 was relatively balanced (Fig. 7). This indicates that generate flow of spring 1 was controlled by the saturated zone and spring 2 was affected by the coaction of unsaturated and saturated zones during whole study period (Mudarra and Andreo, 2011). TOC-Mg^{2+} diagram shows that springs had constant TOC independent of Mg^{2+} which showed higher variability (Fig. 8). As Fig. 8 shows, similar trends for NO_3^--Mg^{2+} were observed for spring 1; however, a weak inverse relation between NO_3^- and Mg^{2+} was observed for spring 2 (Fig. 8). Therefore, we suggest that NO_3^- was the typical parameter for tracing the effect of unsaturated zone for the mineralized effect of karstic bedrock on TOC. The variability of NO_3^--Mg^{2+} raised from the facts that the unsaturated zone in spring 2 was more important than spring 1 in recharge processes (Batiot et al., 2003). In our study sites, a more continuous soil layer with a mean thickness of 0.57 m around spring 2 area covered an epikarst system which indicates that most of rain water must infiltrate through the soil to recharge groundwater. This could account for the higher effect of the unsaturated zone at spring 2 than spring 1. In addition, all mineralized parameters exhibited a decreasing trend from dry season to wet season, and they were negatively correlated to NO_3^- and TOC which were the indicators of soil biochemistry in spring 2 (Fig. 4 and Fig. 9). They indicate that the effect of the unsaturated zone increased from the wet season to the dry season (Bicalho et al., 2012). Conversely, the relatively discrete distribution of all the parameters indicates a similar role of the unsaturated and saturated zones with a high karstic degree which could account for the rapid response to rainfall in spring 1. Moreover, Fig. 8 also exhibits that water samples of spring 2 contained high Mg^{2+} values while the NO_3^- values were low, which indicates that the flow discharged during dry season remained longer in the saturated zone than during the wet season (Emblanch et al., 2003).

4.2. Recharge mechanism of the stream

Stream flow was generated from the mixing of rain water, and the recharge sources showed no measurable effect of evaporation on the isotopic composition, as inferred through the comparison of LMWL and stream water line (Fig. 2 and Fig. 3). Similarly, Riechelmann et al. (2017) also reported that evaporation in the soil, epikarst, and cave generated no significant imprint on drip water isotopic signature which suggested a draining of a karst reservoir with meteoric recharge origin (Wassenaar et al., 2011). In addition, the hydrograph separation results suggested that stream discharge was still dominated by pre-event water (old water, 93.3%) despite the proportion of new water up to 57.6% during certain period with heavy rainfall (Fig. 5). Rainwater might be sufficiently mixed with the old water or there was a relatively large volume of water in the subsurface storage that rain water did not substantially displace, which led to the negligible variability of isotopic values.

The NO_3^- and TOC contents plotted against the Mg^{2+} corroborate the high variability of these natural tracers of the stream water, which is in line with the findings of Batiot et al. (2003) (Fig. 8). This indicates that the saturated and unsaturated zones participated in the functioning of the catchment system. Furthermore, recharge sources exhibited

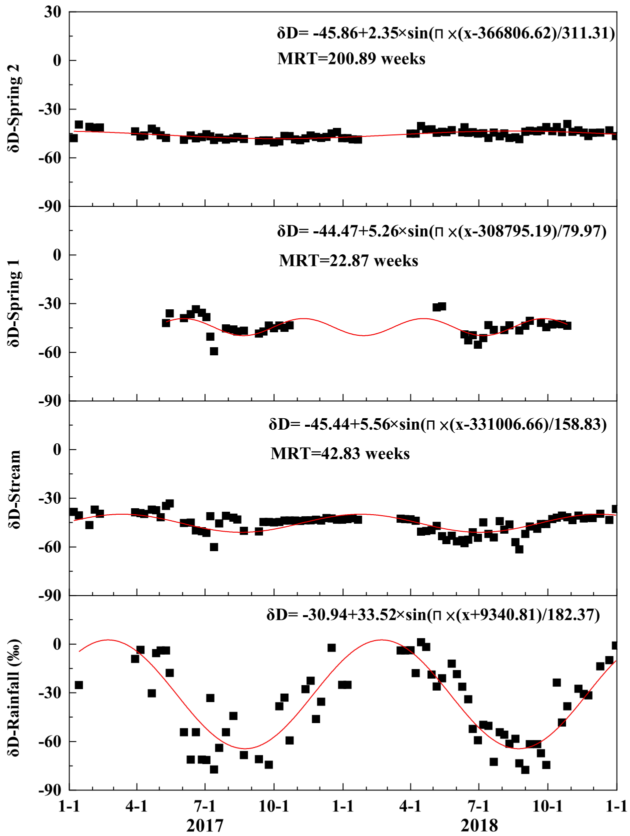

Fig. 6. Evaluations of the mean residence time of springs and stream waters with a sine wave model.

seasonal variation (Fig. 9), namely, that recharge source from unsaturated zone dominated the hydrochemical characteristic of stream water during the wet season. Conversely, a relatively constant water source from the saturated zone recharge stream was apparent (Doctor et al., 2006). Previous work has shown that soil was the source of TOC and NO_3^- (Emblanch et al., 2003). However, although soil layer in the depression is deeper than that on slopes, its composition mainly consists of clay, which results in a lower drainage efficiency and lower hydraulic conductivity (Fu et al., 2015a, 2015b; Yang et al., 2016). Two paths were assumed to supply the water sources with high TOC and NO_3^- contents. One was the erosion from surface soil by water flow and rainfall, and the other was the subsurface flow generated from hillslope to depression. Similarly, Wu et al. (2018) have found that the erosion processes and amount of soil nutrients would be enhanced during heavy rainfall and flood events and such recharge events occur over short time periods. Thus, the variations of TOC and NO_3^- were unstable during the wet season, whereas rainfall frequency and amount decreased with the onset of the dry season, causing the mean level of groundwater to decline. Therefore, without surface erosion and subsurface leaching, the mean concentration of TOC and NO_3^- tends to decline significantly in the dry season (Paces and Wurster, 2014). Although soil layers influenced the rechanging of the stream in the wet season, the hydrological function of the epikarst was also important. The lack of significant variation in the mean concentrations of Mg^{2+}, Ca^{2+}, and HCO_3^- between the dry and wet seasons (Fig. 4) indicates that these tracers were controlled by water–rock interactions without significant dilution by new water. Other studies, such as those of Moore et al. (2009) and Zhao et al. (2018), previously revealed that the dilution effect of precipitation is largely due to the pronounced development of conduit and fissure networks. In our study catchment, the conduit network was poorly developed (Fu et al., 2016) and the rainwater sufficiently mixed with pre-event water in the epikarst accompanying water–rock interactions, even during the high-flux period.

In the study catchment, waters from intermittent spring and perennial spring were not the main recharge sources of stream. According to data from the discharge monitoring, the mean contribution proportions were 0.2% and 2.6% during the whole study period despite the contribution proportion reaching up to 21.4% (spring 2) during the late dry season (Fig. 2). Most of water sources generated from a hillslope would recharge a stream through underground flow. Most studies have suggested that the variation of spring flow represents the recharge process of hillslope groundwater (Vardanjani et al., 2017; Winston and Criss, 2004). However, high spatial heterogeneity of hydrogeological conditions of karst aquifers present the challenge for identifying the recharge area of springs (Iacurto et al., 2020). Moreover, there were significant differences in the dynamics and hydrochemistry of spring waters under different hydrogeological conditions, even for the adjacent springs (Filippini et al., 2018). Moreover, Hu et al. (2015) and Zhang et al. (2020) found evidence for a damping effect from depression storage deficits and from depression soil components between hillslope flow to stream flow. Therefore, it was challenging to quantify the multiple water sources in the catchment. In our study, the mean

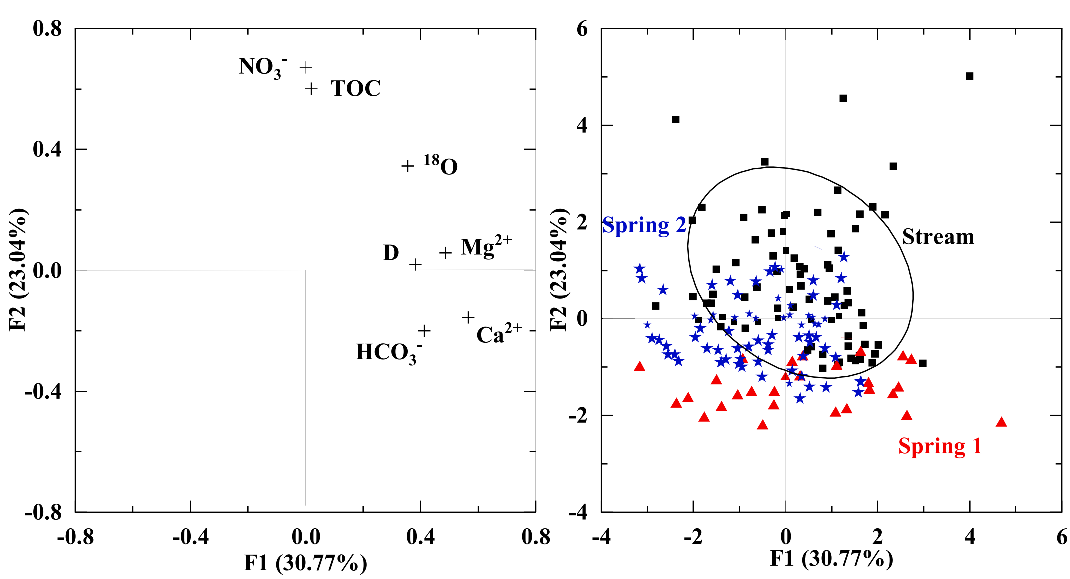

Fig. 7. Principal component analysis (PCA) conducted with all tracer data of spring 1, spring 2 and stream. Left: variable space; Right: sample space.

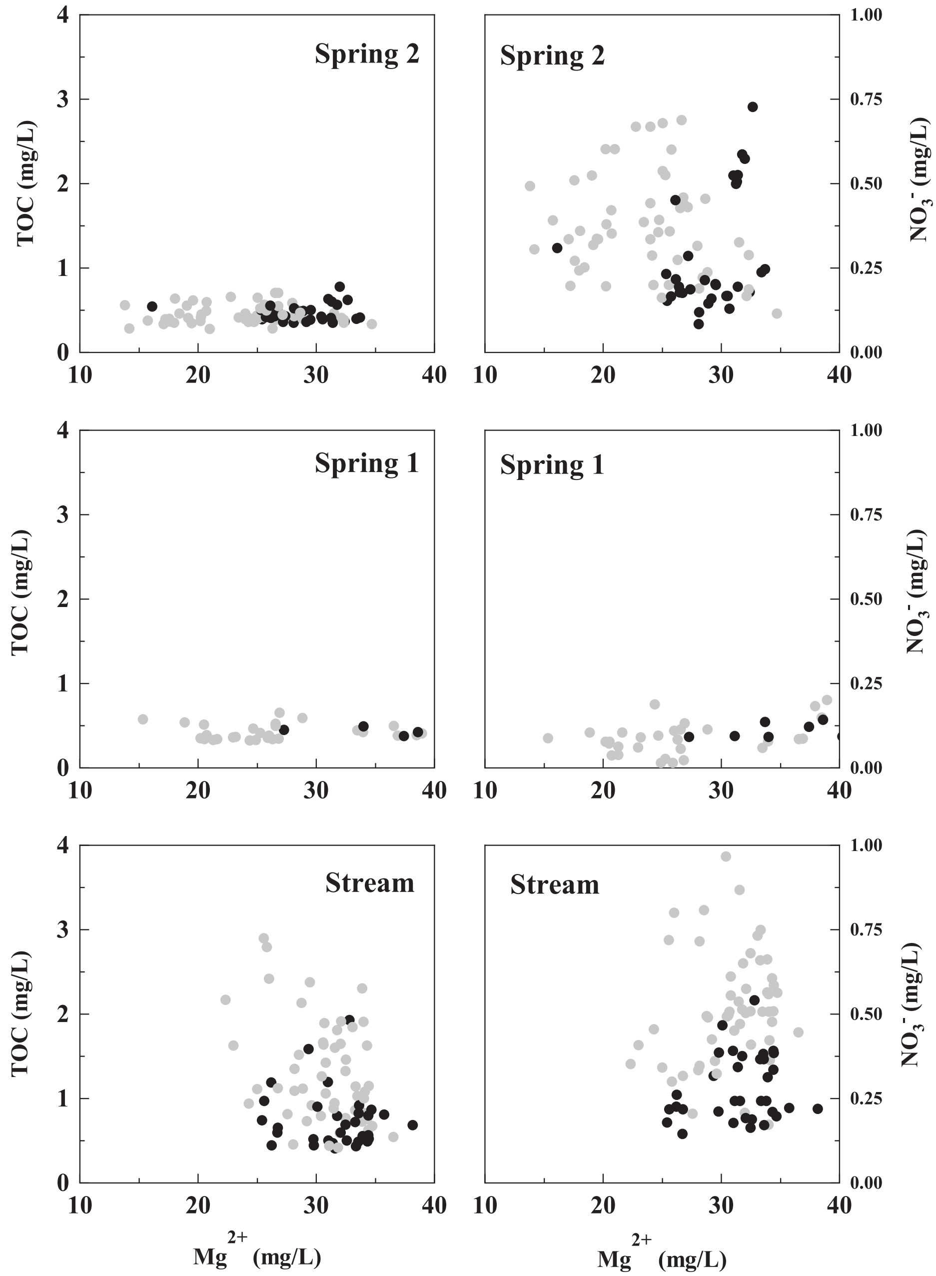

Fig. 8. Diagrams of the Mg^{2+} content versus total organic carbon (TOC) and NO_3^-.

residence time of stream water (42.8 weeks) was higher than spring 1 and significantly lower than spring 2 (Fig. 6). Therefore, the stream water was mainly recharged by the water sources which experienced the similar hydrological processes of spring 1.

5. Conclusions

In this study, we used weekly collected isotope and hydrochemistry data, combined with daily-collected hydrological data of waters from precipitation, two springs, and a stream in a dolomite–karst catchment to investigate the spring and stream recharge mechanisms, to discuss the recharge relationship between springs and stream. We observed distinct seasonal variations in the ^{18}O and D isotopes of rainwater, ranging from −13.4‰ to −0.5‰ for $\delta^{18}O$ and −108.5‰ to 16.6‰ for δD. However, the variations in the springs (δD: −57.9‰ to −31.7‰; $\delta^{18}O$: −12‰ to −3.3‰) and stream (δD: −61.6‰ to −28.7‰; $\delta^{18}O$: −8.8‰ to −5.1‰) isotopic compositions were relatively stable. Compared to the LMWL, springs and stream waters were generated from the mixing of rainfall water without a significant evaporation effect. The weekly hydrograph separation exhibited that the mean recharge proportions of old water were 93.9% (spring 1), 94.4% (spring 2), and 93.3% (stream), which is indicative of the homogeneous mixing processes of rainfall and groundwater for recharging springs and stream.

The mean residence time of spring 1 (22.8 weeks) was significantly lower than spring 2 (200.9 weeks) based on the sine wave fitting model on the seasonal variation of D isotope. Combined with PCA on hydrochemistry and NO_3^--Mg^{2+} distribution analysis, we found the rapid response of spring 1 flow to rainfall was attributed to the smaller storage and the well-developed karstification of spring 1 aquifer. Moreover, a continuous and relatively thick soil layer covered the epikarst in spring 2 area which resulted in the seasonal variation of the recharge function between the unsaturated zone and the saturated zone. Thus, spring 2 maintained a continuous flow.

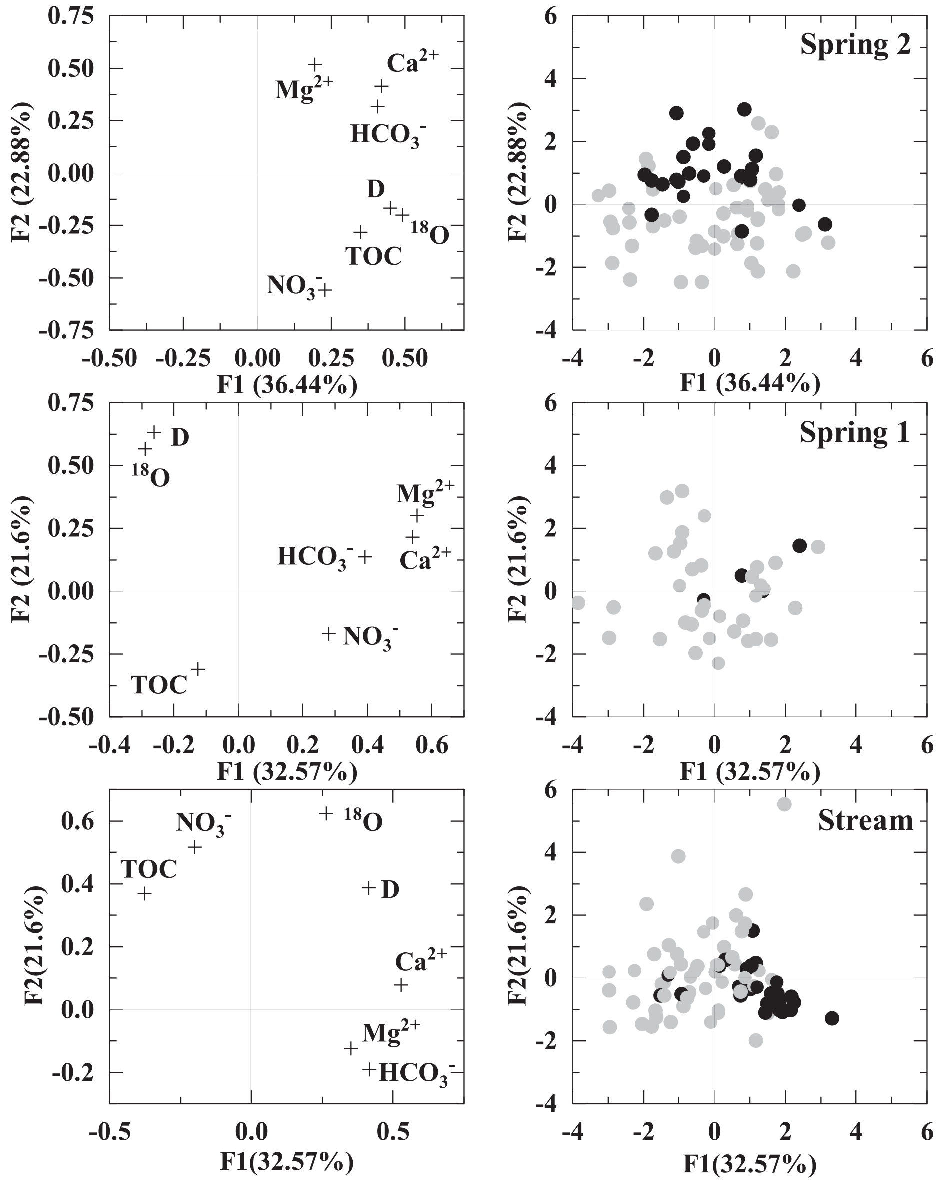

Fig. 9. Principal component analysis (PCA) conducted with all tracer data of different seasons from spring 1, spring 2 and stream. Left: variable space; Right: sample space.

PCA of stream hydrochemistry indicated that the dominant recharge processes of stream water exhibit seasonal variation. The unsaturated zone influenced by the soil layer dominated the recharging processes with surface and subsurface flow during the wet season. On the contrary, water from the saturated zone dominated by weathered bedrock (or epikarst) was the main sources recharging stream during the dry season. Based on the hydrological monitoring, most of water sources were recharged through underground rather than springs. Given the damping effect of depression on water flow transit, the mean residence time of stream water (42.8 weeks) was higher than spring 1 but significantly lower than spring 2. Thus, we suggest that water like spring 1 was the dominant water sources from the hillslope through depression to recharge stream.

6. Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

CRediT authorship contribution statement

Fa Wang: Conceptualization, Methodology, Software, Writing - original draft, Investigation. **Hongsong Chen:** Conceptualization, Supervision, Funding acquisition, Writing - review & editing. **Jinjiao Lian:** Resources, Funding acquisition, Writing - review & editing. **Zhiyong Fu:** Investigation, Resources. **Yunpeng Nie:** Resources, Visualization.

Declaration of Competing Interest

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

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References

Adji, T.N., Haryono, E., Fatchurohman, H., Oktama, R., 2016. Diffuse flow characteristics and their relation to hydrochemistry conditions in the Petoyan Spring, Gunungsewu Karst, Java, Indonesia. Geosci. J. 20 (3), 381–390.

Bahir, M., Ouazar, D., Ouhamdouch, S., 2018. Characterization of mechanisms and processes controlling groundwater salinization in coastal semi-arid area using hydrochemical and isotopic investigations (Essaouira basin, Morocco). Environ. Sci. Pollut. Res. 18, 1–13.

Bailly-Comte, V., Jourde, H., Roesch, A., Pistre, S., Batiot-Guilhe, C., 2008. Time series analyses for Karst/River interactions assessment: case of the Coulazou river (southern France). J. Hydrol. 349 (1–2), 98–114.

Bailly-Comte, V., Jourdé, H., Pistre, S., 2009. Conceptualization and classification of groundwater–surface water hydrodynamics interactions in karst watersheds: Case of the karst watershed of Coulazou river (southern France). J. Hydrol. 376, 456–462.

Bakalowicz, M., 2005. Karst groundwater: a challenge for new resources. Hydrogeol. J. 13 (1), 148–160.

Barberá, J., Andreo, B., 2015. Hydrogeological processes in a fluviokarstic area inferred from the analysis of natural hydrogeochemical tracers. The case study of eastern Serranía de Ronda (S Spain). J. Hydrol. 523, 500–514.

Batiot, C., Emblanch, C., Blavoux, B., 2003. Total Organic Carbon (TOC) and magnesium (Mg2+): two complementary tracers of residence time in karstic systems. Comptes Rendus Geoscoence, 335(2): 205-214.

Bicalho, C., Batiot, G., Taupin, J. D., Patris, N., Van Exter, S., Jourde, H., 2017. A conceptual model for groundwater circulation using isotopes and geochemical tracers coupled with hydrodynamics: A case study of the Lez karst system, France. Chemical Geology, 10.1016/j.chemgeo.2017.08.014.

Bicalho, C., Batiot, G., Seidel, J., Van Exter, S., Jourde, H., 2012. Geochemical evidence of water source characterization and hydrodynamic responses in a karst aquifer. Journal of Hydrology, 450-451: 206-218.

Brenot, A., Benoît, M., Carignan, J., France-Lanord, C., 2015. Insights into stable isotope characterization to monitor the signification of soil water sampling for environmental studies dealing with soil water dynamics through the unsaturated zone. C.R. Geosci. 347, 317–327.

Brkić, Ž., Kuhta, M., Hunjak, T., 2018. Groundwater flow mechanism in the well-developed karst aquifer system in the western Croatia: insights from spring discharge and water isotopes. Catena 161, 14–26.

Chang, Y., Wu, J.C., Jiang, G.H., 2015. Modeling the hydrological behavior of a karst spring using a nonlinear reservoir-pipe model. Hydrogeol. J. 23 (5), 901–914.

Chen, H.S., Hu, K., Nie, Y.P., Wang, K.L., 2017. Analysis of soil water movement inside a footslope and a depression in a karst catchment. Southwest China. Scientific Reports 7 (1), 2544.

Chu, H.B., Wei, J.H., Wang, R., Xin, B.D., 2017. Characterizing the interaction of groundwater and surface water in the karst aquifer of Fangshan, Beijing (China). Hydrogeol. J. 25 (2), 575–588.

De Giglio, O., Caggiano, G., Apollonio, F., Marzella, A., Brigida, S., Ranieri, E., Lucentini, L., Uricchio, V.F., Montagna, M.T., 2018. The aquifer recharge: an overview of the legislative and planning aspect. Ann Ig 30 (1).

Doctor, D.H., Alexander Jr., E.C., Petric, M., Kogovsek, J., Urbanc, J., Lojen, S., Stichler, W., 2006. Quantification of karst aquifer discharge components through endmember mixing analysis using natural chemistry and isotopes as tracers. Hydrogeol. J. 14, 1171–1191.

Emblanch, C., Zuppi, G.M., Mudry, J., Blavoux, B., Batiot, C., 2003. Carbon 13 of TDIC to quantify the role of the unsaturated zone: the example of the Vaucluse karst systems (Southeastern France). J. Hydrol. 279 (1–4), 262–274.

Filippini, M., Squarzoni, G., De Waele, J., Fiorucci, A., Vigna, B., Grillo, B., Riva, A., Rossetti, S., Zini, L., Casagrande, G., 2018. Differentiated spring behavior under changing hydrological conditions in an alpine karst aquifer. J. Hydrol. 556, 572–584.

Fu, T.G., Chen, H.S., Wang, K.L., 2016. Structure and water storage capacity of a small karst aquifer based on stream discharge in southwest China. J. Hydrol. 534, 50–62.

Fu, T.G., Chen, H.S., Zhang, W., Nie, Y.P., Peng, T., Wang, K.L., 2015a. Spatial variability of surface soil saturated hydraulic conductivity in a small karst catchment of southwest China. Environmental Earth Sciences 74 (3), 2381–2391.

Fu, T.G., Chen, H.S., Zhang, W., Nie, Y.P., Wang, K.L., 2015b. Vertical distribution of soil saturated hydraulic conductivity and its influencing factors in a small karst catchment in Southwest China. Environ. Monit. Assess. 187 (3), 92.

Geyer, T., Birk, S., Liedl, R., Sauter, M., 2008. Quantification of temporal distribution of recharge in karst systems from spring hydrographs. J. Hydrol. 348 (3–4), 452–463.

Guo, X.X., Jiang, G.H., Gong, X.P., Yin, J.J., Xia, W., 2015. Recharge processes on typical karst slopes implied by isotopic and hydrochemical indexes in Xiaoyan Cave, Guilin, China. J. Hydrol. 530, 612–622.

Hartmann, A., Gleeson, T., Wada, Y., Wagener, T., 2017. Enhanced groundwater recharge rates and altered recharge sensitivity to climate variability through subsurface heterogeneity. Proc. Natl. Acad. Sci. 114 (11), 2842–2847.

Herman, E.K., Toran, L., White, W.B., 2009. Quantifying the place of karst aquifers in the groundwater to surface water continuum: a time series analysis study of storm behavior in Pennsylvania water resources. J. Hydrol. 376, 307–317.

Hu, K., Chen, H.S., Nie, Y.P., Wang, K.L., 2015. Seasonal recharge and mean residence times of soil and epikarst water in a small karst catchment of southwest China. Sci. Rep. 5, 10215.

Iacurto, S., Grelle, G., De Filippi, F.M., Sappa, G., 2020. Karst spring recharge areas and discharge relationship by oxygen^{-18} and deuterium isotopes analyses: A case study in southern latium region. Italy. Applied Sciences 10 (5), 1882.

Iván, V., Mádl-Szőnyi, J., 2017. State of the art of karst vulnerability assessment: overview, evaluation and outlook. Environmental Earth Sciences 76 (3), 112.

Jeelani, G., Kumar, U.S., Kumar, B., 2013. Variation of δ^{18}o and δD in precipitation and stream waters across the kashmir himalaya (india) to distinguish and estimate the seasonal sources of stream flow. J. Hydrol. 481, 157–165.

Jiang, Z.C., Lian, Y.Q., Qin, X.Q., 2014. Rocky desertification in Southwest China: impacts, causes, and restoration. Earth Sci. Rev. 132, 1–12.

Klaus, J., McDonnell, J., 2013. Hydrograph separation using stable isotopes: Review and evaluation. J. Hydrol. 505, 47–64.

Kogovšek, J., Petrič, M., 2014. Solute transport processes in a karst vadose zone characterized by long-term tracer tests (the cave system of Postojnska Jama, Slovenia). J. Hydrol. 519, 1205–1213.

Küry, D., Lubini, V., Stucki, P., 2017. Temperature patterns and factors governing thermal response in high elevation springs of the Swiss Central Alps. Hydrobiologia 793 (1), 185–197.

Kresic, N., Panday, S., 2018. Numerical groundwater modelling in karst. Geological Society, London, Special Publications 466 (1), 319–330.

Lee, E.S., Krothe, N.C., 2001a. A four-component mixing model for water in a karst terrain in south-central indiana, usa. using solute concentration and stable isotopes as tracers. Chem. Geol. 179 (1), 129–143.

Lee, E.S., Krothe, N.C., 2001b. Delineating the karstic flow system in the upper lost river drainage basin, south central indiana: using sulphate and $\delta^{34}S_{so4}$ as tracers. Appl. Geochem. 18, 145–153.

Li, G.Q., Goldscheider, N., Field, M.S., 2016. Modeling karst spring hydrograph recession based on head drop at sinkholes. J. Hydrol. 542, 820–827.

Li, Z., Chen, X., Liu, W.Z., Si, B.C., 2017a. Determination of groundwater recharge mechanism in the deep loessial unsaturated zone by environmental tracers. Sci. Total Environ. 586, 827–835.

Li, Z.W., Xu, X.L., Liu, M.X., Li, X.Z., Zhang, R.F., Wang, K.L., Xu, C.H., 2017b. State-space prediction of spring discharge in a karst catchment in southwest China. J. Hydrol. 549, 264–276.

Liu, F.J., Conklin, M.H., Shaw, G.D., 2017. Insights into hydrologic and hydrochemical processes based on concentration-discharge and end-member mixing analyses in the mid-Merced River Basin, Sierra Nevada. California. Water Resources Research 53 (1), 832–850.

Liu, L.H., Chen, X.H., Xu, G.Q., Shu, L.C., 2011. Use of hydrologic time-series data for identification of hydrodynamic function and behavior in a karstic water system in China. Hydrogeol. J. 19 (8), 1577–1585.

Luo, M., Chen, Z.H., Zhou, H., Zhang, L., Han, Z.F., 2018. Hydrological response and thermal effect of karst springs linked to aquifer geometry and recharge processes. Hydrogeol. J. 26 (2), 629–639.

McDonnell, J.J., 2003. Where does water go when it rains? moving beyond the variable source area concept of rainfall-runoff response. Hydrol. Process. 17, 1869–1875.

McGuire, K.J., McDonnell, J.J., 2006. A review and evaluation of catchment transit time modeling. J. Hydrol. 330 (3–4), 543–563.

Moore, P.J., Martin, J.B., Screaton, E.J., 2009. Geochemical and statistical evidence of recharge, mixing, and controls on spring discharge in an eogenetic karst aquifer. J. Hydrol. 376 (3–4), 443–455.

Mosquera, G.M., Célleri, R., Lazo, P.X., Vaché, K.B., Perakis, S.S., Crespo, P., 2016. Combined use of isotopic and hydrometric data to conceptualize ecohydrological processes in a high-elevation tropical ecosystem. Hydrol. Process. 30 (17), 2930–2947.

Mudarra, M., Andreo, B., 2011. Relative importance of the saturated and the unsaturated zones in the hydrogeological functioning of karst aquifers: the case of alta cadena (southern spain). Journal of Hydrology (Amsterdam) 397 (3–4), 263–280.

Mudarra, M., Hartmann, A., Andreo, B., 2019. Combining experimental methods and modeling to quantify the complex recharge behavior of karst aquifers. Water Resour. Res. 55 (2), 1384–1404.

Musgrove, M., Stern, L., Banner, J., 2010. Springwater geochemistry at Honey Creek State Natural Area, central Texas: implications for surface water and groundwater interaction in a karst aquifer. J. Hydrol. 388 (1–2), 144–156.

Nie, Y.P., Chen, H.S., Wang, K.L., Tan, W., Deng, P.Y., Yang, J., 2011. Seasonal water use patterns of woody species growing on the continuous dolostone outcrops and nearby thin soils in subtropical China. Plant Soil 341 (1/2), 399–412.

Paces, J.B., Wurster, F.C., 2014. Natural uranium and strontium isotope tracers of water sources and surface water–groundwater interactions in arid wetlands-Pahranagat Valley, Nevada, USA. J. Hydrol. 517 (5), 213–225.

Parise, M., Gabrovsek, F., Kaufmann, G., Ravbar, N., 2018. Recent advances in karst research: from theory to fieldwork and applications. Geological Society, London, Special Publications 466, 1–24.

Pavlovskiy, I., Selle, B., 2015. Integrating hydrogeochemical, hydrogeological, and environmental tracer data to understand groundwater flow for a karstified aquifer system. Groundwater 53 (S1), 156–165.

Peng, T., Wang, S.J., 2012. Effects of land use, land cover and rainfall regimes on the surface runoff and soil loss on karst slopes in southwest China. Catena 90, 53–62.

Poulain, A., Watlet, A., Kaufmann, O., Van, C.M., Jourde, H., Mazzilli, N., Rochez, G., Deleu, R., Quinif, Y., Hallet, V., 2018. Assessment of groundwater recharge processes through karst vadose zone by cave percolation monitoring. Hydrol. Process. 32 (13), 2069–2083.

Riechelmann, S., Schröder-Ritzrau, A., Spötl, C., Riechelman, D.F.C., Richter, D.K., Mangini, A., Frank, N., Breitenbach, S.F.M., Immenhauser, A., 2017. Sensitivity of Bunker Cave to climatic forcings highlighted through multi-annual monitoring of

rain-, soil-, and dripwaters. Chem. Geol. 449, 194–205.
Rosenberry, D.O., LaBaugh, J.W., 2008. Field techniques for estimating water fluxes between surface water and ground water. Geological Survey (US) 135p.
Rusjan, S., Sapac, K., Petric, M., Lojen, S., Bezak, N., 2019. Identifying the hydrological behavior of a complex karst system using stable isotopes. J. Hydrol. 577, 123956.
Sprenger, M., Stumpp, C., Weiler, M., Aeschbach, W., Allen, S.T., Benettin, P., Dubbert, M., Hartmann, A., Hrachowitz, M., Kirchner, J.W., 2019. The demographics of water: A review of water ages in the critical zone. Rev. Geophys. 57, 3.
Stevanovic, Z., 2018. Global distribution and use of water from karst aquifers. In: Parise, M., Gabrovsek, F., Kaufmann, G., Ravbar, N. (Eds.), Advances in Karst Research: Theory, Fieldwork and Applications. Geological Society, London, Special Publications, pp. 217–236.
Tweed, S., Munksgaard, N., Marc, V., Rockett, N., Leblanc, M., 2015. Continuous monitoring of stream δ18o and δ2h and stormflow hydrograph separation using laser spectrometry in an agricultural catchment. Hydrol. Process. 30 (4), 648–660.
Vardanjani, H.K., Chitsazan, M., Ford, D., Karimi, H., Charchi, A., 2017. Initial assessment of recharge areas for large karst springs: a case study from the central zagros mountains, iran. Hydrogeol. J. 12, 1–14.
Wang, D.J., Shen, Y.X., Huang, J., Li, Y.H., 2016. Rock outcrops redistribute water to nearby soil patches in karst landscapes. Environ. Sci. Pollut. Res. 23, 8610–8616.
Wang, S.J., Zhang, M.J., Hughes, C.E., Crawford, J., Wang, G.F., Chen, F.L., Du, M.X., Qiu, X., Zhou, S.E., 2018. Meteoric water lines in arid Central Asia using event-based and monthly data. J. Hydrol. 562, 435–445.
Wassenaar, L.I., Athanasopoulos, P., Hendry, M.J., 2011. Isotope hydrology of precipitation, surface and ground waters in the Okanagan Valley, British Columbia. Canada. Journal of Hydrology 411 (1), 37–48.
Wexler, S., Hiscock, K., Dennis, P., 2011. Catchment-scale quantification of hyporheic denitrification using an isotopic and solute flux approach. Environ. Science Technol. 45, 3967–3973.
White, W.B., 2002. Karst hydrology: Recent developments and open questions. Eng. Geol. 65 (2–3), 85–105.
Winston, W. E., Criss, R. E., 2004. Dynamic hydrologic and geochemical response in a perennial karst spring. Water resources research, 40(5), p.W05106.1-W05106.11.
Wu, Y., Luo, Z.H., Luo, W., Ma, T., Wang, Y.X., 2018. Multiple isotope geochemistry and hydrochemical monitoring of karst water in a rapidly urbanized region. J. Contam. Hydrol. 218, 44–58.
Yang, J., Chen, H.S., Nie, Y.P., Wang, K.L., 2019a. Dynamic variations in profile soil water on karst hillslopes in Southwest China. Catena 172, 655–663.
Yang, J., Nie, Y.P., Chen, H.S., Wang, S., Wang, K.L., 2016. Hydraulic properties of karst fractures filled with soils and regolith materials: Implication for their ecohydrological functions. Geoderma 276, 93–101.
Yang, M.J., Taquian, J.A., Annable, M.D., Jawitz, J.W., 2019b. Karst conduit contribution to spring discharge and aquifer cross-sectional area. J. Hydrol. 578, 124037. https://doi.org/10.1016/j.jhydrol.2019.124037.
Yuan, D.X., 1994. Chinese Karstology. Geology Press, Beijing, pp. 1–200.
Yu, F.K., Huang, X.H., Liang, Q.B., Yao, P., Li, X.Y., Liao, Z.Y., Duan, C.Q., Zhang, G.S., Shao, H.B., 2015. Ecological water demand of regional vegetation: the example of the 2010 severe drought in Southwest China. Plant Biosystems-An International Journal Dealing with all Aspects of Plant Biology 149 (1), 100–110.
Zhang, J., Li, T.Y., 2019. Seasonal and interannual variations of hydrochemical characteristics and stable isotopic compositions of drip waters in furong cave, southwest china based on 12 years' monitoring. J. Hydrol. 572, 40–50.
Zhang, R., Chen, X., Zhang, Z., Soulsby, C., 2020. Using hysteretic behavior and hydrograph classification to identify hydrological function across the "hillslope-depression-tream" continuum in a karst catchment. Hydrol. Process. 1–71.
Zhao, M., Hu, Y.D., Zeng, C., Liu, Z.H., Yang, R., Chen, B., 2018. Effect of land cover on variations in stable hydrogen and oxygen isotopes in karst groundwater: A comparative study of three karst catchments in Guizhou Provience, Southwest China. J. Hydrol. 565, 374–385.