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Hydrogeochemical responses of cave drip water to the local climate in the Liangfeng Cave, Southwest China

Xia Wu*, Moucheng Pan, Jianjun Yin, Meiliang Zhang and Jianhua Cao

Key Laboratory of Karst Dynamics, Institute of Karst Geology, No. 50 Qixing Road, Guilin 541004, China

*Corresponding author. E-mail: cugwuxia@126.com

ABSTRACT

The hydrogeochemistry of cave drip water is an important environmental index in cave systems, and drip water monitoring may be an essential solution for paleoclimate reconstructions. We measured the hydrogeochemical properties of the seasonal and perennial drip water and CO_2 concentrations from 2015 to 2019 in the Liangfeng Cave, Guilin, Southwest China. This study identified the difference in the regional environmental records in the perennial and seasonal drip water. By comparing the regional climate data recorded by the drip water, the results showed that the perennial drip water recorded regional climate information throughout the year, whereas the seasonal drip water only recorded the high precipitation periods. The precipitation during the 2015 dry season was abnormally high, and higher than the values in other rainy seasons. This indicates that hydrogeochemistry only represents changes in precipitation and not the alternation of dry and rainy seasons during this period.

Key words: CO_2, drip water, hydrogeochemistry, Liangfeng Cave, Southwest China

HIGHLIGHTS

- The first long-term monitoring study was performed in well ventilation Cave, Guilin, Southwest China.
- The purpose of this study was to interpret the precipitation and drought event signals recorded in hydrogeochemical properties of the cave water.
- The seasonal variation hydrogeochemical responses of the cave drip water can record regional climate information.

INTRODUCTION

Modern carbonate deposits are formed by drip water, which is the initial form of stalagmites in caves. Drip water can effectively record climatic changes outside caves, and is an important link between climate change and stalagmites (Bradley *et al.* 2010). Hence, drip water is important for the scientific interpretation of information recorded by stalagmites (Pape *et al.* 2010; Feng *et al.* 2014; Wu *et al.* 2014).

Previous studies have conducted systematic monitoring that focused on the migration process of ecological environmental information in the entire cave system (Chen & Li 2018; Yin *et al.* 2019; Baker *et al.* 2020). The suspended aquifer in the epikarst provides a store of water that sustains percolation flow to speleothems in caves and to cave streams over extended dry periods. Also, the characteristics of the epikarst strongly influence its capacity to absorb, store and transmit precipitation (Bakalowicz 2005; Williams 2008). Therefore, there have been many previous cave monitoring study attempts to improve the understanding of hydrology and chemistry in epikarst (Xiang *et al.* 2015; Zeng *et al.* 2015). Drip water is usually supplied by meteoric precipitation and a series of important hydrogeochemical processes (e.g., infiltrating water lagged and mixed, previously deposited calcite, strength of water–rock interaction, cave ventilation and so on) occur in the epikarst and inside the cave. For example, the infiltration of precipitation is affected by the original bedrock and soil materials at the top of the cave (Fairchild *et al.* 2000), the infiltration path (Oster *et al.* 2012) and the karstification intensity (Wong *et al.* 2011) during the infiltration process in the epikarst. Therefore, this series of complex hydrogeochemical processes can lead to uncertainties or limitations in the interpretation of climate proxy indicators in drip water and modern carbonate deposits (Finch *et al.* 2003; Li *et al.* 2011; Casteel & Banner 2015). Published monitoring results indicate that the pH, electrical conductivity (EC), Ca^{2+} and HCO_3^- concentrations of the drip water respond to changes in temperature and precipitation (Baker *et al.* 2000).

However, the increasing number of monitoring studies published in recent years indicates that the intensity of water–rock reaction, fresh–old water mixing and degassing (Zeng *et al.* 2015; Yin *et al.* 2021), dilution effect, the piston effect, prior calcite precipitation (Tooth & Fairchild 2003), the thickness of bedrock and the retention time of seeping water (Baker & Brunsdon 2003) are the principal factors in epikarst that interfere with the hydrogeochemical variations of drip waters. Moreover, different runoff paths lead to different response sensitivities at different drip water sites (Faimon *et al.* 2016). The EC of each drip water can vary on a site-specific basis that was affected by the water residence time within the aquifer (Miorandi *et al.* 2010; Sherwin & Baldini 2011), and it can reveal the highly sensitive nature of ventilation dynamics within the cave (Smith *et al.* 2015). In addition, the drip rate and CO_2 concentration in the cave air may also affect Mg^{2+} and Ca^{2+} concentrations in drip water after water infiltrates into the cave (Duan *et al.* 2012). Although drip water hydrogeochemistry was affected by the above factors, it can still effectively record outside climate information after the soil layer reaches saturation in the recharge zone (Kogovek 2007). Therefore, monitoring of drip water hydrochemistry characteristics can fully understand the precipitation infiltration process (McDonald *et al.* 2007), and is effective for determining the drip water response to regional climate (Treble *et al.* 2015). However, few studies have reported on the relationship between regional climate and perennial and seasonal drip water, all of which form modern carbonate deposits in Southwest China. Long-term cave monitoring is essential for obtaining an accurate understanding of the relationship between regional climate and changes in drip water hydrogeochemistry.

Cave system monitoring is an important method for effectively interpreting the response of drip water to regional climate. In this study, we investigated how perennial and seasonal drip water recorded regional climate using 5 years of cave monitoring data from the Liangfeng Cave (LF Cave) in Guilin, Southwest China. The main objectives of this study were to determine the hydrogeochemical variations of the perennial and seasonal drip water, and the relationships with regional atmosphere temperature and precipitation variations in ventilated caves.

Study area

The LF Cave (Figure 1, 25 °11′55.93″ N, 110 °31′42.66″ E) is located in the Maocun Village, near the city of Guilin, Guangxi, Southwest China. The total area of the Maocun Village underground river basin is 14.23 km^2. The karst area is about 9.66 km^2, and accounts for 69.7% of the recharge area of the entire underground river system. In addition, the clastic area is about 4.57 km^2, and accounts for 30.3% of the recharge area of the entire underground river system. The underground water in the Maocun Village River basin is mainly carbonate karst water and bedrock fissure water. The Maocun Village underground river basin is mainly developed in the peak-cluster valley geomorphic area composed of carbonate rocks of Middle Devonian Donggangling Formation and Upper Devonian Rongxian Formation. The LF Cave is not a tourist cave; therefore, the interior environment of the cave is not directly affected by human activity. The bedrock lithology mainly composed limestone of the Upper Devonian Rongxian Formation (D_3^r). The range of coefficient percolation of precipitation is from 0.29 to 0.54 in limestone bedrock at the top of the cave. The entrance of the LF Cave is at an elevation of 183 m, and the main cave passage is approximately 80 m long, 2–7 m in height and 5–8 m wide. The entrance of the LF Cave formed due to a bedrock collapse at the top of the cave and many areas inside the cave are connected to the underground river system in places. The cave entrance floor is inclined downward into the cave. The bedrock at the top of the cave is ~20–30 m thick and the soil above the cave is 0–100 cm thick. The vegetation is mainly scrubland with sparse tree cover. Abundant stalagmites and stalactites are found within the cave. Owing to long-term weathering, these deposits have brown, yellow and black weathering crusts. In addition, the cave has many drip water sites where modern carbonate deposition occurs.

Drip water sample site numbers (LF-1, LF-3 and LF-9) were named from the outside to the inside. The LF Cave is on a slope of the mountain The thickness of the bedrock on the top of each drip water site increases gradually from the outside to the inside. LF-1 is situated about 15 m away from the cave entrance, LF-3 is situated in the middle of the cave approximately 30 m from the cave and LF-9 is situated at the innermost part of the cave approximately 70 m from the cave. Ding *et al.* (2019) investigated soil CO_2 seasonal variation in 30 and 60 cm on the top of the LF Cave from 2017 to 2019. The average soil CO_2 concentration at 30 cm was 5,774 ppm and the average soil CO_2 concentrations at 60 cm were 8,384 ppm during the wet season, and at 30 cm they were 3,288 ppm and at 60 cm were 4,856 ppm during the dry season.

The closest weather station to the cave is the Chaotian weather station in Chaotian town, which was 12 km away from the LF Cave. The Chaotian weather station recorded the average annual atmosphere temperature and average annual rainfall in the study area as 20.5 °C and 1,901 mm from 2000 to 2020 (Wu *et al.* 2021a, 2021b). The amount of annual average

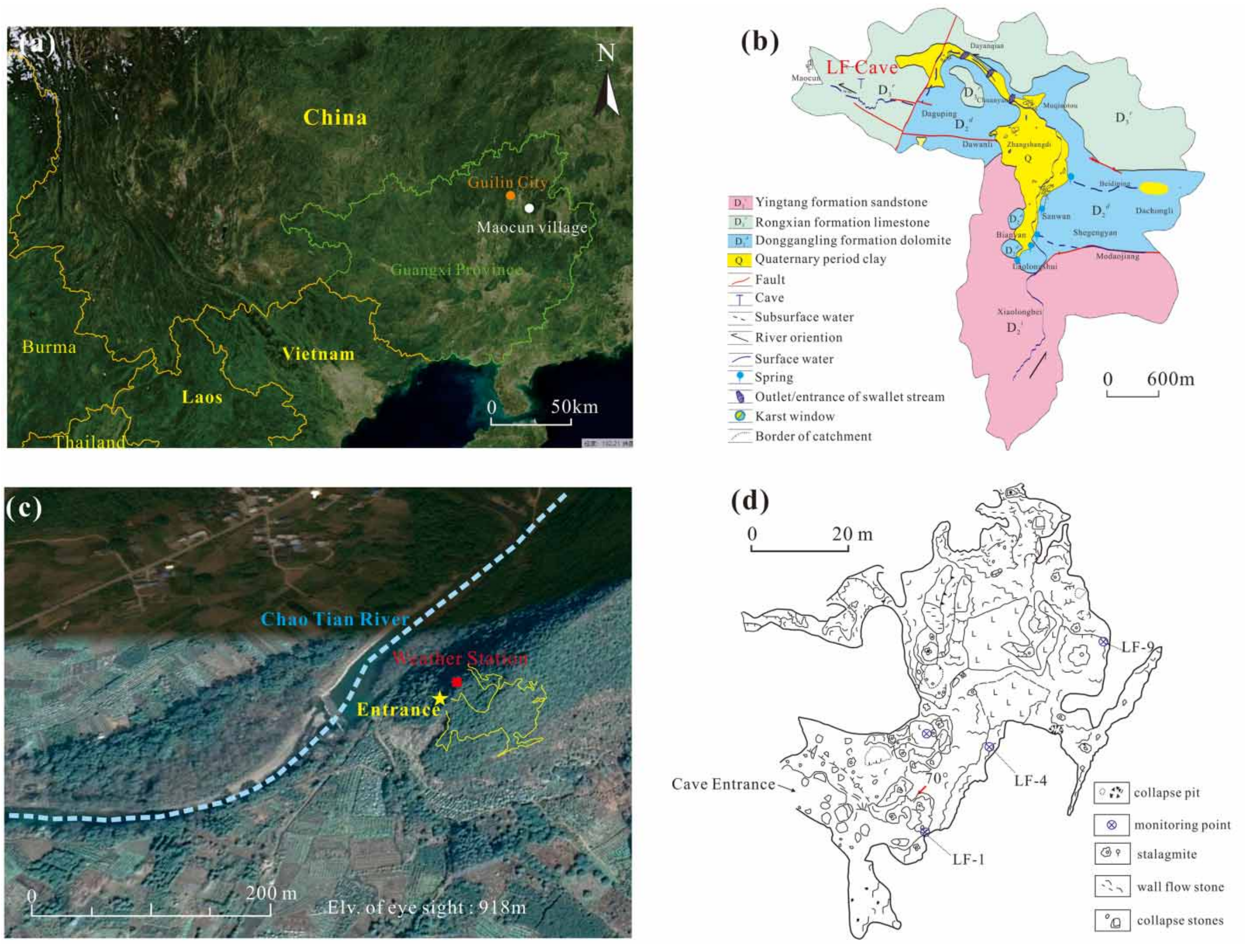

Figure 1 | Location of the study area. (a) Map showing the location of the LF Cave in Southwest China. (b) Hydrogeological map of the Maocun Village where the LF Cave is located. (c) Topographical map of the landscape around the LF Cave. White star indicates the cave entrance. (d) Plan view of drip water monitoring sites LF-1, LF-4 and LF-9 in the LF Cave. Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/nh.2022.015.

evaporation ranged from 1,490 to 1,905 mm. In the study area, the annual rainy season was from March to August, accounting for 61% of the total annual precipitation. The annual dry season was from September to the following February, during which precipitation decreases significantly. The inter-annual variations in precipitation in this region are directly related to monsoon strength.

MATERIALS AND METHODS

Local climate monitoring

Cave air temperature and humidity in the study area were recorded using automatic recording instruments (HOBO U-30; Onset Computer Co.). The recording interval was 1 h, the cave air temperature measurement accuracy was 0.2 °C and the cave air humidity measurement accuracy was 2.5%. The weather station began recording on May 5, 2015.

Drip water monitoring

Drip water samples were collected every 15 days from May 2015 to December 2016, and every 30 days from January 2017 to December 2019. The physical and chemical properties of the drip water were analyzed in the field using a HACH HQ40D water quality multi-parameter analytical instrument (Germany). The water temperature, pH and EC of drip water at each drip water site were average measurement uncertainty of 0.1 °C, 0.1 (pH) and 0.1 μS/cm, respectively. Simultaneously, the mass concentrations of HCO_3^- and Ca^{2+} were titrated in the field using a basalimeter and hardness tester (Merck KGaA, Darmstadt, Germany) at resolutions of 0.1 mmol/L and 2 mg/L, respectively. Three drip water sites were monitored located from the entrance to the deepest part of the cave, with site numbers LF-1, LF-4 and LF-9. The LF-1 site was seasonal drip water, whereas LF-4 and LF-9 sites were perennial drip water.

Cave pCO_2 monitoring

Cave CO_2 concentrations were collected (at 10:00 AM) from May 2015 to December 2019. The gas collecting device was a diaphragm pump connected to a gas sampling bag that includes a pre-suction pump to remove gas from the bag before use. To avoid the influence of artificial respiration, sampling was conducted from the outside to the inside of the cave, and the sampler was kept at a distance of 3–4 m from the air inlet during operation. Gas samples collected were analyzed using a Picarro G2131-iCO_2 isotope analyzer (Picarro, Inc.), at the Institute of Karst Geology at the Chinese Academy of Geological Sciences. Errors in $\delta^{13}C$ measurements were less than 0.3‰. Errors in CO_2 concentration measurements were less than 0.1‰.

RESULTS

Local climate characteristics

Atmospheric temperatures and precipitation data outside the LF Cave from May 2015 to December 2019 were obtained from a weather station located near the cave, as shown in Figure 2. Over the monitoring period, there was a total range in average

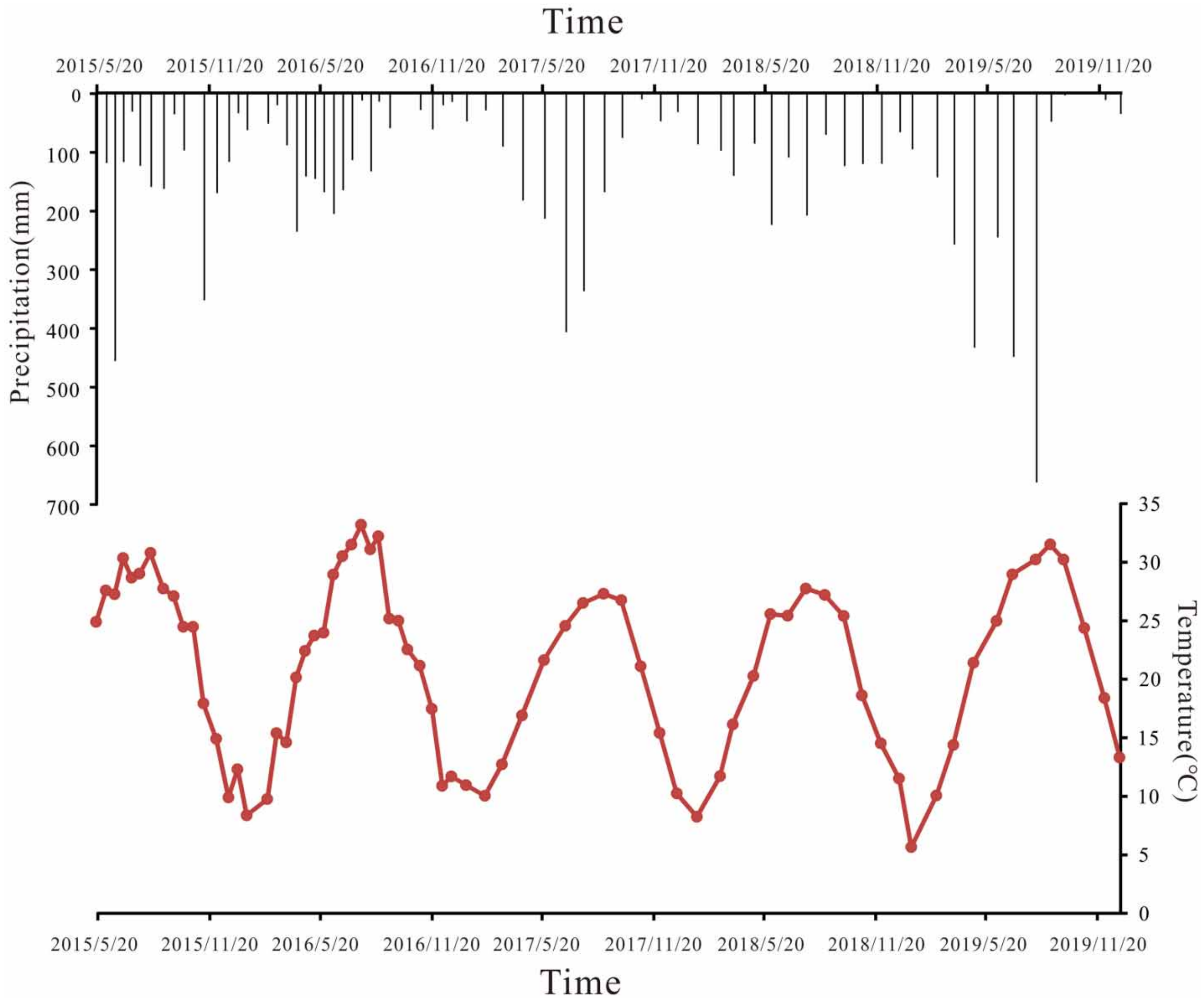

Figure 2 | Atmospheric temperatures (red line) and precipitation amounts (black histogram) outside the LF Cave from May 2015 to December 2019. The sampling periods of precipitation and temperature were the same as that of the cave drip water monitoring. Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/nh.2022.015.

atmospheric temperatures and total precipitation of 18.7–21.5 °C and 1,426–2,901 mm, respectively. The overall average atmosphere temperature in 2019 had relatively small variations. The atmospheric temperatures in Guilin increased from May to September, with the highest atmospheric temperatures occurring in July and August and the lowest atmospheric temperatures occurring in December and January. Although plenty of precipitation occurs in the study area, seasonal droughts also occur that were caused by uneven precipitation. Precipitation in the monitoring area mainly occurred during the rainy season (May–September) and accounted for 56.7–84.9% of the total annual precipitation. In contrast, precipitation from October to the following April was relatively low, accounting for 15.1–43.3% of the total annual precipitation. The study area has obvious climatic characteristics of rain and heat that occur during the same season (Table 1). Moreover, the atmospheric precipitation during October 2016, 2017 and 2019 was less than 8 mm. Therefore, the drip rate in the LF Cave decreased during these periods and the effect of water inflow decreased sharply after October during the monitoring period. The seasonal drip point (LF-1) also stopped dripping until the following March. The LF Cave air humidity monitoring point was maintained at 100%.

Seasonal hydrogeochemical characteristics of drip water

Over the monitoring period, there was a total range in EC, pH, temperatures, Ca^{2+} and HCO_3^- of 201–532 μS/cm (average of 379 μS/cm), 7.56–8.70 (average of 8.18), 11.8–22.1 °C (average of 18.6 °C), 30–116 mg/L (average of 80 mg/L), 1–5.8 mmol/L (average of 3.9 mmol/L), respectively. The EC, pH and temperatures of drip water at sites LF-1, LF-4 and LF-9 had significant seasonal variations. However, there were differences in the hydrogeochemical variations between the different drip sites (Figure 3). LF-1 is the seasonal drip site that only drips during the rainy season, but stops during the dry season. Its ability to respond quickly to heavy precipitation events may be influenced by joints and fractures in the bedrock at the top of the cave (Wu *et al.* 2018a, 2018b). LF-3 is a perennial drip site with a large amplitude variation of drip rates. LF-9 is a perennial drip site with a small amplitude variation of drip rates and likely connected to a relatively large water reservoir in the epikarst zone to maintain a perennial and small amplitude variation drip rate. The variations in EC, pH and water temperature were synchronized with the regional alternating dry and rainy seasons (Table 2). Both EC and water temperature exhibited slow increases during the rainy season and rapid decreases during the dry season. Generally, the pH value was lower during the rainy season and higher during the dry season. Ca^{2+} and HCO_3^- were the main ions observed at the three drip water sites. In general, higher Ca^{2+} and HCO_3^- concentrations were observed during the rainy season, whereas lower concentrations were observed during the dry season. Furthermore, heavy precipitation months (e.g., November 2015) and seasonal drought months (e.g., October 2016, 2017 and 2019) had obvious influences on the hydrogeochemistry of the drip water.

Seasonal pCO_2 variations

The pCO_2 varied from 417 to 707 ppm, with an average of 533 ppm, during the monitoring period (Table 3). As an important indicator of the cave environment, cave pCO_2 can inhibit or promote modern calcite deposit formation in caves (Whitaker *et al.* 2009). Differences in cave pCO_2 were observed between sites LF-1, LF-4 and LF-9 and exhibited seasonal characteristics: high during the rainy season and low during the dry season (Figure 4). LF Cave temperature seasonal variations were significantly lower than that of the atmospheric temperature (Wu *et al.* 2019). Due to temperature differences inside and outside the cave, the thermal/density differences derived cave ventilation. Owing to the ventilation of the cave, the pCO_2 concentrations were similar to those of the outside atmosphere. In addition, cave pCO_2 did not change in magnitude

Table 1 | Average surface air temperatures and precipitation during the rainy and dry seasons from May 2015 to December 2019

	Surface air temperature (°C)		Precipitation (mm)			
Year	Rainy season	Dry season	Rainy season	% of whole year	Dry season	% of whole year
2015	26.8	15.3	1,970	67.9	930.8	32.1%
2016	28.5	14.5	1,369	79.2	360.0	20.8%
2017	24.0	13.4	1,370	84.9	242.3	15.1%
2018	25.3	13.5	808	56.7	617.6	43.3%
2019	27.9	14.4	1,828	77.5	530.4	22.5%

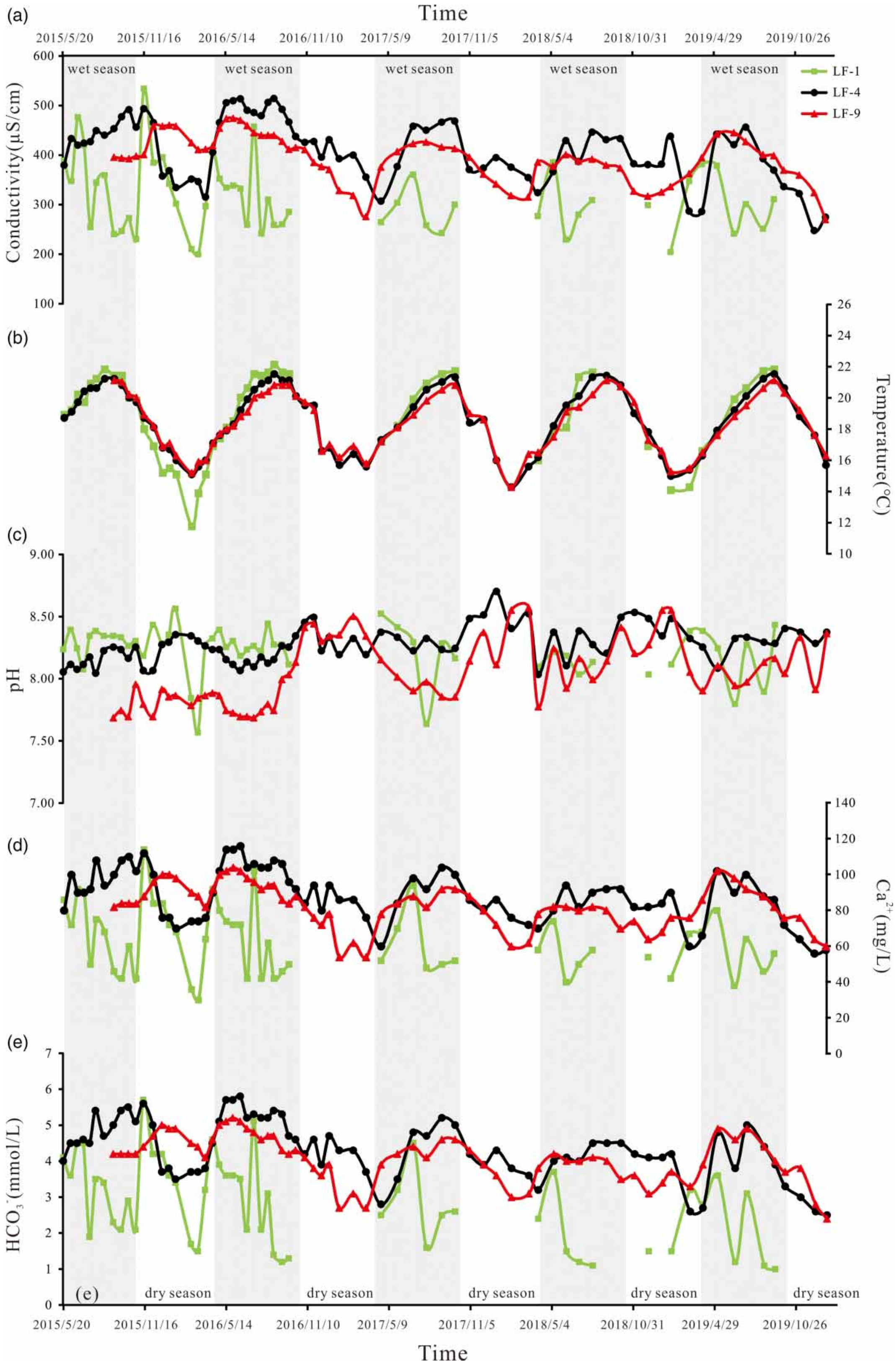

Figure 3 | The seasonal variations in hydrogeochemistry of the drip water from May 2015 to December 2019. (a) Drip water EC, (b) temperature, (c) pH, (d) Ca^{2+} concentrations and (e) HCO_3^- concentrations. Gray columns indicate the rainy season and white columns indicate the dry season. Please refer to the online version of this paper to see this figure in colour: https://dx.doi.org/10.2166/nh.2022.015.

Table 2 | Maximum, minimum and mean EC, temperature, pH, Ca^{2+} and HCO_3^- concentrations of drip water from May 2015 to December 2019 in the LF Cave

	Conductivity (μS/cm)			Temperature (°C)			pH			Ca^{2+} (mg/L)			HCO_3^- (mmol/L)		
	LF-1	LF-4	LF-9	LF-1	LF-4	LF-9	LF-1	LF-4	LF-9	LF-1	LF-4	LF-9	LF-1	LF-4	LF-9
Max	532	512	473	22.1	21.5	21.1	8.6	8.7	8.6	114	116	104	5.7	5.8	5.2
Min	201	248	270	11.8	14.3	14.3	7.6	8.0	7.2	30	56	54	1.0	2.5	2.4
Mean	314	410	394	18.8	18.6	18.4	8.2	8.3	8.0	63	89	83	2.8	4.3	4.1

Table 3 | Maximum, minimum and mean values of pCO_2 at monitoring sites LF-1, LF-4 and LF-9 from May 2015 to December 2019

Sample no.	Max (ppm)	Min (ppm)	Mean (ppm)	Standard deviation	Coefficient of variation (%)
LF-1 cave air	707	417	530	77.9	14.7
LF-4 cave air	668	430	531	62.4	11.8
LF-9 cave air	707	430	540	65.8	12.2

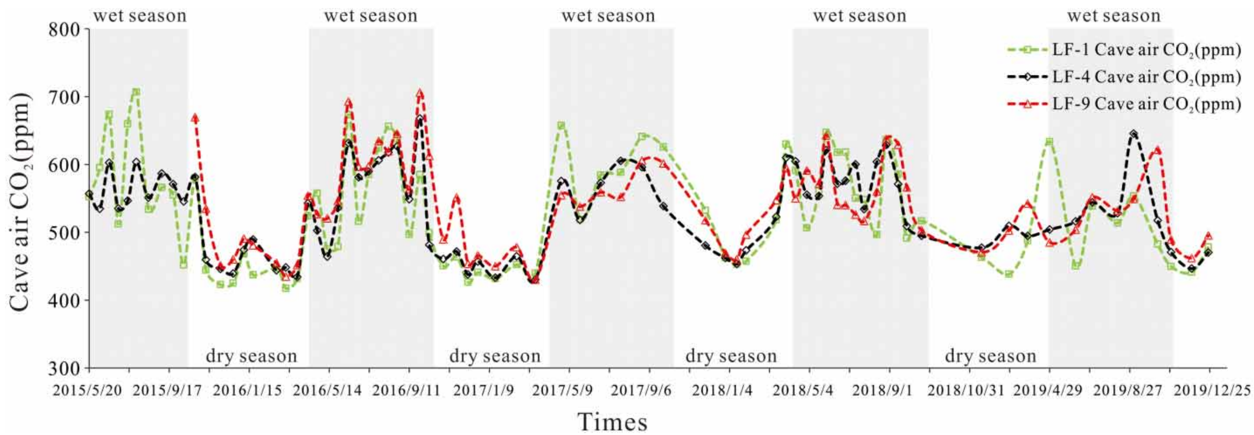

Figure 4 | Cave pCO_2 at monitoring sites LF-1, LF-4 and LF-9 during the monitoring period.

between the dry and rainy seasons. The pCO_2 variation coefficients at the three monitoring points were 14.7, 11.8 and 12.2, respectively, indicating a small degree of pCO_2 data dispersion in the cave.

DISCUSSION

Relationship between the local climate and drip water hydrogeochemistry

During the monitoring period, the drip water hydrogeochemical properties exhibited seasonal variations in the cave that were synchronized with the changes between the rainy and dry seasons in the study area (Figure 3). During the rainy season, the EC, Ca^{2+} and HCO_3^- concentrations, and water temperature increased gradually with increasing atmospheric temperature and precipitation, whereas the pH decreased. CO_2 in the soil layer overlying the cave increased because of plant root respiration and intensified microbial activity during the rainy season. The main water source for the cave was the vertical infiltration of meteoric water (Wu *et al.* 2018a, 2018b). Therefore, the precipitation transported a large amount of CO_2 into the cave with increased precipitation during the rainy season and caused a decrease in the pH. Therefore, this monitoring data indicates that the overlying soil CO_2 concentrations had a significant effect on the pH of the drip water. Infiltrating water dissolves soil CO_2 and generates HCO_3^- and H^+ which react with carbonate bedrock and influence the pH (Baldini *et al.* 2006; Frisia *et al.* 2011; Wu *et al.* 2015). This enhanced the dissolution of the carbonate bedrock, which increased the Ca^{2+} concentrations in the drip water. The groundwater would have lower pH values but higher concentrations of Ca^{2+}

when the carbonate dissolution occurs under open-system conditions with respect to soil CO_2 (Owen *et al.* 2018; Fohlmeister *et al.* 2020). High concentrations of soil CO_2 were transported into the cave by precipitation, which increased the cave air CO_2 concentrations (Figure 4). Although the LF Cave was affected by the ventilation effect during the rainy season, the overlying soil CO_2 concentrations were a dozen times that of atmospheric CO_2. Accordingly, soil CO_2 was the main factor that affected cave CO_2 during the rainy season.

During the dry season, the EC, Ca^{2+} and HCO_3^- concentrations, and water temperature decreased gradually with decreasing atmosphere temperature and precipitation, whereas the pH increased. Soil CO_2 concentrations were lower than those in the rainy season, which was affected by plant root respiration and weaker microbial activity. With the decrease in precipitation, the dissolution capacity and amount of seepage water formed weakened and decreased, resulting in decreased Ca^{2+} and HCO_3^- concentrations in the drip water. Seeping water evolution from soil matrix and preferential flow solutions have exerted an important control on karst water chemistries (Tooth & Fairchild 2003). Due to decreased soil CO_2 concentrations and weak seepage water migration capacity, atmospheric CO_2 was the main factor affecting cave CO_2 during the dry season.

The cave drip water temperature, EC, and Ca^{2+} and HCO_3^- concentrations increased slowly during the rainy season. This could be attributed to a mixture of seepage water and 'old water' in the epikarst. The infiltrating water transported more CO_2, which resulted in the enhancement of water–rock interactions during the transition from the dry season to the rainy season. However, due to infiltrating water mixing with 'old water' in the epikarst, the drip water hydrogeochemistry was susceptible to the mixing process. This monitoring result implies that precipitation and runoff pathways will affect the degree of the hydrogeochemical responses to external climate changes. The hydrodynamic system and flow path are the main factors affecting the spatial variation in discharge, and this can influence the hydrogeochemical properties contained in this flow recharge (Ban *et al.* 2008; Wu *et al.* 2015; Faimon *et al.* 2016). Wu *et al.* (2018a, 2018b) analyzed the differences in δD and δ^{18}O isotopes in extreme precipitation event and drip water in the LF Cave. δD and δ^{18}O values of drip water showed smaller variations than precipitation, which was attributed to the drip water being mixed with 'old water' in the epikarst zone of the cave during this time. The cave water temperature, EC, and Ca^{2+} and HCO_3^- concentrations all decreased rapidly during the dry season. Precipitation also decreased sharply during the dry season, and precipitation was less than 8 mm during October 2016, 2017 and 2019. Lower precipitation was completely absorbed by the unsaturated soil layer during the dry season, but the drip water mainly recharged by 'old water' in the epikarst zone still dripped continuously during the dry season. This result indicated that the drip water was only recharged by seasonal precipitation in the LF Cave. Lower precipitation resulted in less water seepage into bedrock pipes or fissures, which is the only recharge water source for the LF Cave. The dissolution of the surrounding rock was reduced, resulting in decreased Ca^{2+} concentrations in the drip water. Therefore, Ca^{2+} of drip water differences between the rainy and dry seasons can be used as a proxy for interpreting variations in precipitation. Drip water Ca^{2+} and HCO_3^- concentrations can indicate changes in precipitation and atmospheric temperature, but their ranges are synergistically influenced by water–rock interactions, mixing, runoff pathway and other factors. Consequently, drip water hydrogeochemistry responds to changes in precipitation and CO_2 in the overlying soil. This provides further evidence that a regional climate signal could be recorded by drip water hydrogeochemistry in a ventilated cave and can be used to reconstruct rainy and dry seasonal variations.

Differences between seasonal and perennial drip water responses

As shown in Figure 3, EC, Ca^{2+} and HCO_3^- concentrations, water temperature and the pH of the seasonal drip water (LF-1) and perennial drip water (LF-4 and LF-9) sites responded to regional climatic changes during the monitoring period, but had significantly different ranges of change between the sites. This monitoring result reflects there were significant differences in intensity and timing of responses to regional climate records in different drip water responses. The migration process, thickness and water retention of the epikarst play important roles in initiating the drip water response (Genty & Deflandre 1998; Guo *et al.* 2015). Field monitoring results indicate that LF-1 dripped during the rainy season, but stopped dripping during the dry season. Moreover, drip water did not respond to precipitation early in the rainy season when precipitation is preferentially absorbed by the unsaturated soil layer. The precipitation amount required to activate cave drip water at the beginning of the rain season is the amount required to raise the soil moisture content from near wilting point to field capacity values (Kogovek 2007; Nathan *et al.* 2011). When the soil moisture content in the replenishment area was saturated, seasonal drip water hydrogeochemistry responded to regional precipitation. The hydrogeochemical properties of the seasonal drip water increased with the rapid inflow of mixed water, then decreased due to the dilution effect of increased precipitation during the rainy season. The sharp variations in EC and Ca^{2+} and HCO_3^- concentrations indicate that dense fissures and large fractures in the overlying bedrock generated high permeability. The hydrological behaviors can be related to sudden hydrochemical changes through preferential flow that were caused by the intense precipitation events (Guo *et al.* 2015). The LF-4 and LF-9 hydrogeochemical properties increased during the rainy season and decreased during the dry season, water dripped continuously, and modern carbonate deposits formed throughout the year. This may be caused by sparse fissures and small fractures in the overlying bedrock that generated low permeability and thick epikarst. The hydrogeochemical properties of the seasonal drip water first increased and then decreased during the rainy season, but these values continuously and slowly increased in perennial drip water (Figure 3 and Figure 5). This difference resulted from differing thicknesses of the overlying bedrock and the flow path at each drip site. Consequently, the hydrogeochemistry of the different types of drip water had different responses to regional climate. The difference in the hydrological conditions at the different drip sites were not consistent in their response to the external climate (Roberts *et al.* 1998; Fairchild *et al.* 2000; Treble *et al.* 2003; Gregory *et al.* 2009). This yielded different hydrogeochemical values (Mcdonald *et al.* 2007), but did not change the response of the drip water to regional climate.

In addition, LF-1 can record regional climate information for the entire year using hydrogeochemistry and modern carbonate deposits in high precipitation year (e.g., 2015). However, this site can only record regional climate information during the rainy season in seasonally dry years (e.g., 2016, 2017 and 2019). Accordingly, speleothems from this site would merely record

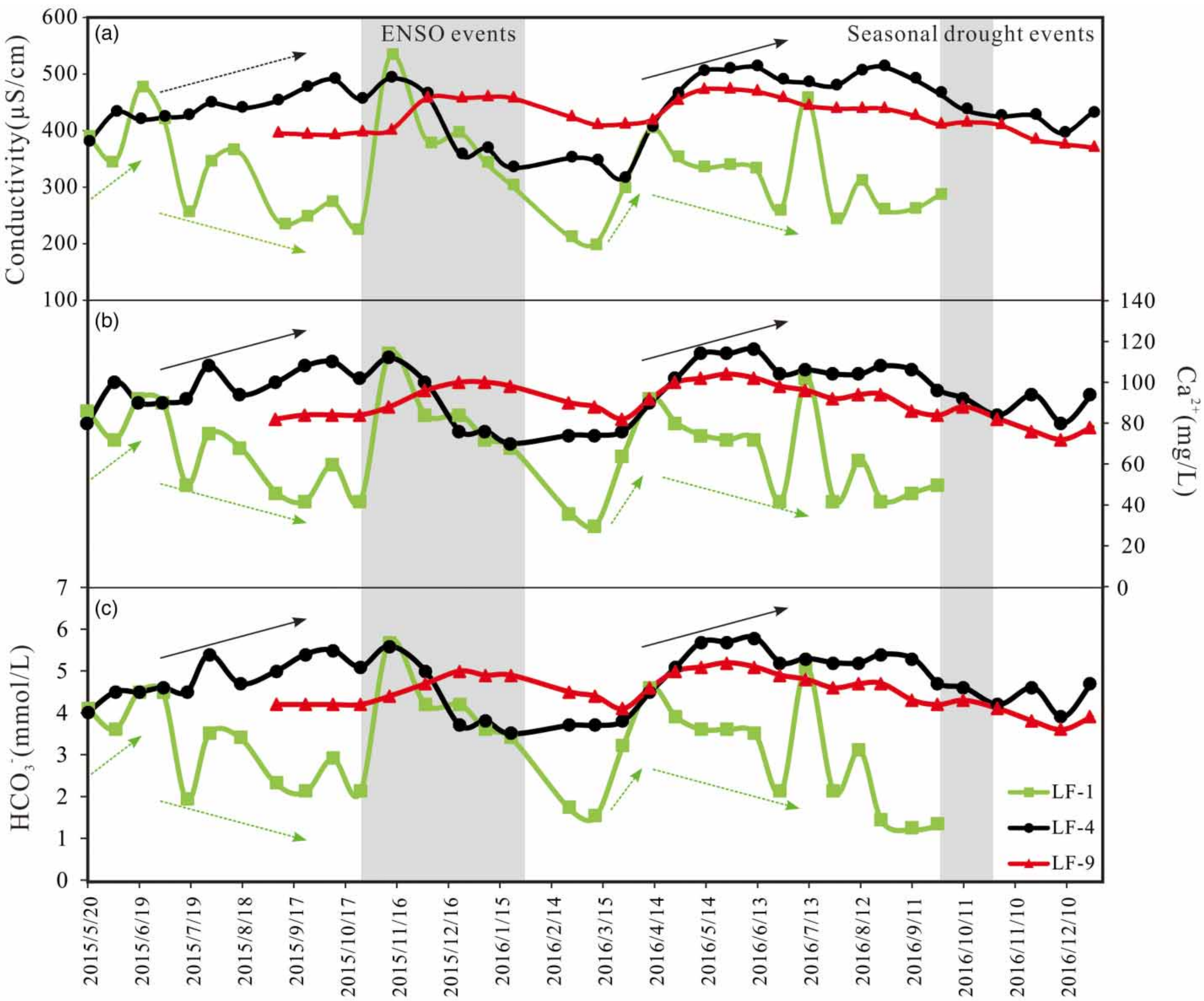

Figure 5 | Variations in drip water hydrogeochemistry during local drought and extreme precipitation events. The arrows show the trend of each drip site in different seasons: (a) drip water EC, (b) Ca^{2+} concentrations and (c) HCO_3^- concentrations.

years with heavy precipitation or rainy seasons on annual and seasonal scales that were formed by seasonal drip water. Perennial drip water can record regional climate information throughout the year. However, there were differences in the response times and variation amplitudes between the two perennial drip water sites caused by differences in hydrodynamic processes, water–soil interactions, water–rock interaction times and material sources. This indicates that different drip water samples record different climate information in the same cave. If only a single speleothem from this cave was used to reconstruct the paleoclimate, a significant amount of uncertainty would be introduced to quantitative calculations.

Local drought and El Niño-Southern Oscillation events

An El Niño-Southern Oscillation (ENSO) event led to an abnormal increase in precipitation during the dry season in Guilin from October 2015 to January 2016 (Wu *et al.* 2021a, 2021b). In other years, precipitation in the dry season decreased significantly, especially in October. The abnormal changes in precipitation produced responses in the hydrogeochemical properties of the drip water in the LF Cave. The Ca^{2+} and HCO_3^- concentrations and EC of the drip water had increasing trends that were affected by ENSO events (Figure 5) The increased Ca^{2+} concentrations ranged from 4 to 72 mg/L, the HCO_3^- concentrations ranged from 0.2 to 3.6 mmol/L and EC ranged from 3 to 301 μS/cm. The pH and water temperature of the drip water both decreased over time. The pH decrease ranged from 0.12 to 0.28, and the decrease in the water temperature ranged from 1.1 to 1.8 °C. The pH value decreased because of the infiltration of large amounts of precipitation, which dissolved soil CO_2 and generated HCO_3^-. Moreover, this water can dissolve the carbonate bedrock and may have influenced the increase of Ca^{2+} in drip water (Wu *et al.* 2018a, 2018b). The drip water temperature decreased owing to precipitation derived from subsurface water percolating into the cave during ENSO events. The monitoring result indicates that event anomalous temperature signals are recorded by drip water. The sensitivity of drip water response to climate has been clearly identified in extreme temperature events (Guo *et al.* 2019). Therefore, the hydrogeochemistry of drip water can respond to ENSO events.

The EC and Ca^{2+} and HCO_3^- concentrations of the seasonal drip water changed more drastically due to ENSO events than perennial drip water, but the durations of these changes were shorter than those in perennial drip water. Moreover, seasonal drip water stopped dripping during seasonal drought events, whereas perennial drip water continued to drip. This indicates that the overlying bedrock at the seasonal drip water sites was highly permeable and had an active connection with the surface that led to hydrogeochemistry that was very sensitive to variations in precipitation (Musgrove & Banner 2004; Oster *et al.* 2012; Wu *et al.* 2014). During ENSO events, the hydrogeochemical values (EC, Ca^{2+} and HCO_3^- concentrations) of both types of drip water were greater than the maximum values observed during the other rainy seasons in the study period. Hydrological dynamics is one of the important processes governing the water–CO_2–rock interactions that was affected by the amount of precipitation during an ENSO event. Many studies have revealed that enhanced meteoric recharge could dissolve and deliver constant and larger amount of CO_2 from soil into epikarst, causing carbonate dissolution and thus higher EC and Ca^{2+} and HCO_3^- values (Baker *et al.* 2000; Tooth & Fairchild 2003; Zeng *et al.* 2015; Yin *et al.* 2021). Therefore, the hydrogeochemistry at these sites was controlled by the amount of precipitation during this time. Conversely, reduced meteoric recharge results in the lack of sufficient supply of seep water and soil CO_2 during local drought events (Guo *et al.* 2015; Wu *et al.* 2015; Chen & Li 2018). This caused lower EC and Ca^{2+} and HCO_3^- values to be observed during drought events. The alternating dry and rainy seasons could be determined using the chemistry of the drip water. However, ENSO events may obscure dry season information in drip water chemistry when such events occur.

In addition, perennial drip water recorded not only ENSO events (November 2015), but also seasonal drought events (October 2016, 2017 and 2019). The hydrogeochemistry of the perennial drip water did not exhibit abnormal decreases during seasonal drought events, and the amplitudes of the two drip water types were different. This mainly contributes to the difference in the retention time of seeping water. The spatial variations in the condition for retention time are mainly related to the heterogeneity of flow path and water movement across the epikarst to the vadose zone (Liu *et al.* 2004; Musgrove & Banner 2004). Therefore, monitoring multiple drip water sites in the same cave and analyzing their responses to climate are crucial for understanding this type of variability in climate records.

CONCLUSIONS

- The multi-year monitoring results for EC, Ca^{2+} and HCO_3^- concentrations, water temperature and pH at three drip water sites in the LF Cave recorded the regional climate in a seasonal scale. The response times and amplitudes of the drip water types were significantly different and were influenced by complex geochemical processes. However, this did not change the response of the hydrogeochemistry to the external climate.

- Different types of drip water had different responses to regional climate, and the ranges of the hydrogeochemical values also differed in a seasonal scale. The seasonal drip point (LF-1) quickly responded to changes in precipitation and was affected by high bedrock permeability. However, seasonal drip water can only record information during high levels of precipitation. The perennial drip water (LF-4 and LF-9) indicates alternating responses to the dry and rainy seasons, but their amplitudes were different due to different hydrogeological processes. In summary, the seasonal hydrogeochemical variability of the drip water samples in the LF Cave reflects changes during the dry and rainy seasons.
- The study area has abundant precipitation, and the overlying epikarst of the LF Cave has weak water storage capacity. The recorded hydrogeochemical variation patterns suggest that the variations were subject to multiple superimposed influences, including seasonal effects and single precipitation events. The monitoring demonstrated that the hydrogeochemistry of drip water can reflect ENSO and seasonal drought events in the LF Cave. Correspondingly, information regarding precipitation changes caused by ENSO events obscure the seasonal information during the dry season.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICTS OF INTEREST STATEMENT

The authors declare there is no conflict.

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