Hydrogeochemical Responses of Cave Drip Water to the Local Climate in Liangfeng Cave, Southwest China

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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 CO₂ concentrations from 2015 to 2019 in Liangfeng Cave, Guilin, Southwest China. This study identified the difference in the regional environmental records in perennial and seasonal drip water. By comparing the regional climate data recorded by the drip water, the results showed the perennial drip water recorded regional climate information throughout the year, while the seasonal drip water only recorded the high precipitation periods. The precipitation during the 2015 dry season was abnormally high, which not sure what index is 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.

1. Introduction

Cave stalagmites can provide high-resolution data for paleoclimate reconstructions to determine past global climatic changes (Wong et al. 2015). Stalagmites record a variety of high-resolution paleoclimate information that can be used to accurately depict the evolution of paleoclimate (Liu et al. 2013; Duan et al. 2016; Li et al. 2021). 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 et al. 2018; Yin et al. 2019; Baker et al. 2020). Drip water is usually supplied by meteoric precipitation and a series of important hydrogeochemical processes 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. Therefore, this series of complex hydrogeochemical processes can lead to uncertainties or limitations in the interpretation of climate proxy indicators in stalagmites or modern carbonate deposits (Finch et al. 2003; Li et al. 2011; Casteel and Banner 2015). Published monitoring results indicate that the pH, electrical conductivity (EC), and Ca²⁺ and HCO₃⁻ concentrations of the drip water respond to changes in temperature and precipitation (Baker et al. 2000). However, drip water can also effectively record outside climate information after the soil layer reaches saturation in the recharge zone (Kogovek et al. 2007). Moreover, different runoff paths lead to different response sensitivities at different drip water sites (Faimon et al. 2016). In addition, cave drip water hydrogeochemistry is affected by the dilution effect, the piston effect, and prior calcite precipitation (Tooth et al. 2003). The thickness of the bedrock at the top of the cave and the retention time of seeping water also affect the hydrogeochemical index (Baker et al. 2003). The drip rate and CO₂ concentration in the cave air may also affect Mg²⁺ and Ca²⁺ after water infiltrates into the cave (Duan et al. 2012). Therefore, cave monitoring is effective for determining the drip water response to regional climate and its effect on modern carbonate deposits (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. 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 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 their relationships with regional temperature and precipitation variations in ventilated caves. This study also compared the hydrogeochemistry of the drip water with regional extreme precipitation events and seasonal drought events, which can advance our understanding of the sensitivity of drip water hydrogeochemistry to regional climate variability.

2. Study Area

Liangfeng Cave (Fig. 1, 25°11'55.93" N, 110°31'42.66" E) is located in Maocun Village, near the city of Guilin, Guangxi, southwest China. The cave is not a tourist cave; therefore the interior environment of the cave is not directly affected by human activity. The bedrock lithology is mainly composed of Upper Devonian limestones. The entrance of the LF Cave is at an elevation of 183 m, and the main cave passage is ~ 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 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.

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 an average annual precipitation of 1596 mm from 1981 to 2010 and an annual evaporation ranging from 1490 to 1905 mm. In the study area, the annual rainy season was from March to August, accounting for 61% of the 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.

3. Methods

3.1 Local climate monitoring

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 temperature measurement accuracy was 0.2°C, and the humidity measurement accuracy was 2.5%. The weather station began recording on May 5, 2015.

3.2 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 measured at resolutions 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 basimeter and hardness tester (Merck KGaA, Darmstadt, Germany,) at resolutions of 0.1 mmol/L and 2 mg/L,

respectively. There 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. LF-1 site was seasonal drip water, LF-4 and LF-9 were persistent drip water.

3.3 Cave pCO₂ monitoring

Cave CO₂ were collectted (at 10:00 AM) from May 2015 to December 2019. The gas collecting device was a self-made pump connected to a gas sampling bag that includes a pre-suction pump that removes 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 collect were analyzed using a Picarro G2131-iCO₂ isotope analyzer (Picarro, Inc.), at the Institute of Karst Geology at the Chinese Academy of Geological Sciences.

4 Results

4.1 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 Fig. 2. The annual average temperatures near the LF cave from 2015 to 2019 were 20.9°C, 21.5°C, 18.7°C, 19.4°C, and 21.2°C, respectively, and the overall average temperature in 2019 had relatively small variations. The temperatures in Guilin increased from May to September, with the highest temperatures occurring in July and August and the lowest temperatures occurring in December and January. The total precipitation in Guilin from 2015 to 2019 was 2901 mm, 1729 mm, 1613 mm, 1426 mm and 2359 mm, respectively, and precipitation was mainly concentrated from April to September, and the dry season occurred from October to the following March. Although plenty of precipitation occurs in the study area, seasonal droughts caused by uneven precipitation also occur. Precipitation in the monitoring area mainly occurred during the rainy season (May to September) and accounted for 56.7–84.9% of the annual precipitation. In contrast, precipitation from October to the following April was relatively low, accounting for 15.1–43.3% of the 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%.

Table 1 Average surface air temperatures and precipitation during the rainy and dry seasons.

	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	1970	67.9%	930.8	32.1%
2016	28.5	14.5	1369	79.2%	360.0	20.8%
2017	24.0	13.4	1370	84.9%	242.3	15.1%
2018	25.3	13.5	808	56.7%	617.6	43.3%
2019	27.9	14.4	1828	77.5%	530.4	22.5%

4.2 Seasonal hydrogeochemical characteristics of drip water

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 (Fig. 3). The variations in EC, pH, and water temperature were synchronized with the regional alternating dry and rainy seasons (Table 2). The variations in drip water conductivity and temperature were 201–532 $\mu\text{S}/\text{cm}$ (average of 379 $\mu\text{S}/\text{cm}$) and 11.8–22.1 $^{\circ}\text{C}$ (average of 18.6 $^{\circ}\text{C}$), respectively. Both EC and water temperature exhibited slow increases during the rainy season and rapid decreases during the dry season. The pH varied from 7.56 to 8.70, with an average of 8.18. 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. Ca^{2+} varied from 30 to 116 mg/L (average of 80 mg/L) and HCO_3^{-} varied from 1 to 5.8 mmol/L (average of 3.9 mmol/L). In general, higher Ca^{2+} and HCO_3^{-} concentrations were observed during the rainy season, while 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.

Table 2 Maximum, minimum, and mean electrical conductivity, temperature, pH, and Ca^{2+} and HCO_3^{-} concentrations of drip water in Liangfeng Cave.

	Conductivity ($\mu\text{S}/\text{cm}$)			Temperature ($^{\circ}\text{C}$)			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.

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

4.3 Seasonal pCO_2 variations

As an important indicator of the cave environment, cave $p\text{CO}_2$ can inhibit or promote modern carbonate sediment formation in caves (Whitaker et al. 2009). Differences in cave $p\text{CO}_2$ 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 (Fig. 4). The $p\text{CO}_2$ varied from 417 to 707 ppm, with an average of 533 ppm, during the monitoring period. Owing to the ventilation of the cave, the $p\text{CO}_2$ concentrations were similar to those of the outside atmosphere. In addition, cave $p\text{CO}_2$ did not change in magnitude between the dry and rainy seasons. The $p\text{CO}_2$ variation coefficients at the three monitoring points were 14.7, 11.8, and 12.2, respectively, indicating a small degree of $p\text{CO}_2$ data dispersion in the cave.

5 Discussion

5.1 Relationship between 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 (Fig. 3). During the rainy season, the EC, Ca^{2+} and HCO_3^- concentrations, and water temperature increased gradually with increasing temperature and precipitation, while 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 average soil CO_2 concentration at 30 cm was 5774 ppm and the average soil CO_2 concentration at 60 cm was 8384 ppm overlying the cave (Ding et al. 2019). The main water source for the cave was the vertical infiltration of meteoric water (Wu et al. 2018). 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 result indicates that the overlying soil CO_2 concentrations had a significant effect on the pH of the drip water (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 (Spötl et al. 2005). High concentrations of soil CO_2 were transported into the cave by precipitation, which increased the cave air CO_2 concentrations (Fig. 4). Although the LF Cave was affected by the ventilation effect during the rainy season, the overlying soil CO_2 concentrations were dozens 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 temperature and precipitation, while the pH increased. The average soil CO_2 concentrations at 30 and 60 cm were 3288 ppm and 4856 ppm, respectively. 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 (Tooth et al. 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 CO₂, 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 thereby susceptible to the mixing process. This implies that precipitation and runoff pathways will affect the degree of the hydrogeochemical response to external climate changes (Ban et al. 2008; Wu et al. 2015; Faimon et al. 2016). The cave water temperature, EC, and Ca²⁺ and HCO₃[−] 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 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 Ca²⁺ concentrations in the drip water. Therefore, Ca²⁺ of drip water differences between the rainy and dry seasons can be used as a proxy for interpreting variations in precipitation. Drip water Ca²⁺ and HCO₃[−] concentrations can indicate changes in precipitation and 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 CO₂ 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.

5.2 Differences between seasonal and persistent drip water responses

As shown in Fig. 3, EC, Ca²⁺, and HCO₃[−] concentrations, water temperature, and the pH of the seasonal drip water (LF-1) and persistent 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 result reflects the migration process, thickness, and water retention of the epikarst, which play important roles in initiating the drip water response (Genty et al. 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 (Kogovsek 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 Ca²⁺ and HCO₃[−] concentrations indicate that dense fissures and large fractures in the overlying bedrock generated high permeability (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 seasonal drip water first increased and then decreased during the rainy season, but these values continuously and slowly increased in persistent drip water (Figs. 3 and 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 was affected by hydrological conditions and had different responses to regional climate (Roberts et al. 1998; Treble et al. 2003; Fairchild et al. 2000; 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 years with heavy precipitation or rainy seasons on annual and seasonal scales that were formed by seasonal drip water. Persistent drip water can record regional climate information throughout the year. However, there were differences in the response times and variation amplitudes between the two persistent drip water sites caused by differences in hydrodynamic processes, water–soil interactions, water–rock interaction times, and material sources. This indicates that different drip waters 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.

5.3 Local drought and extreme precipitation events

An ENSO event led to an abnormal increase in precipitation during the dry season in Guilin from November 2015 to January 2016 (Wu et al. 2020). 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 extreme precipitation events (Fig. 3). 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 $\mu\text{S}/\text{cm}$. 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 decreasing of water temperature ranged from 1.1°C 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 Ca^{2+} of drip water increase (Wu et al. 2018). The drip water temperature decreased owing to precipitation derived from subsurface water percolating into the cave during extreme precipitation events (Guo et al., 2019). Therefore, the hydrogeochemistry of drip water can respond to extreme precipitation events.

The EC and Ca^{2+} and HCO_3^- concentrations of seasonal drip water changed more drastically due to extreme precipitation events than persistent drip water, but the durations of these changes were shorter than those in persistent drip water. Moreover, seasonal drip water stopped dripping during seasonal drought events, while persistent 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. During extreme precipitation 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. Therefore, the hydrogeochemistry at these sites was controlled by the amount of precipitation during this time. The alternating dry and rainy seasons could be determined using the chemistry of the drip water. However, extreme precipitation events may obscure dry season information in drip water chemistry when such events occur.

In addition, persistent drip water recorded not only extreme precipitation events (November 2015), but also seasonal drought events (October 2016, 2017, and 2019). The hydrogeochemistry of the persistent 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 (Musgrove et al. 2004; Liu et al. 2004). Therefore, monitoring multiple drip water sites in the same cave and analyzing their responses to climate is crucial for understanding this type of variability in climate records.

6 Conclusions

(1) The multi-year monitoring results for EC, Ca^{2+} , and HCO_3^- concentrations, water temperature, and pH at three drip water sites in Liangfeng Cave recorded the regional climate. 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.

(2) Different types of drip water had different responses to regional climate, and the ranges of the hydrogeochemical values also differed. 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) indicate 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 waters in Liangfeng Cave reflects changes during the dry and rainy seasons.

(3) 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 extreme precipitation and seasonal drought events in Liangfeng Cave. Correspondingly, information regarding precipitation changes caused by extreme precipitation events obscure the seasonal information during the dry season.

Declarations

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Figures

Figure 1

Location of the study area, (a) Map showing the location of Liangfeng Cave in Southwest China. (b) Topographic map of the landscape around Liangfeng Cave. Brown star indicates the cave entrance. (c) Plan view of drip water monitoring sites LF-1, LF-4, and LF-9 in Liangfeng Cave.

Figure 2

Atmospheric temperatures (red line) and precipitation amounts (black histogram) outside Liangfeng 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.

Figure 3

The seasonal variations in hydrogeochemistry of the drip waters. (a) Drip water electrical conductivity, (b) temperature, (c) pH, (d) Ca²⁺ concentrations, (e) and HCO₃⁻ concentrations. Gray columns indicate the rainy season and white columns indicate the dry season.

Figure 4

Cave pCO₂ at monitoring sites LF-1, LF-4, and LF-9 during the monitoring period.

Figure 5

Variations in drip water hydrogeochemistry during local drought and extreme precipitation events. (a) Drip water electrical conductivity, (b) Ca^{2+} concentrations, (c) and HCO_3^- concentrations.