Journal of Hydrology 595 (2021) 126060

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Research papers

Rainfall-driven and hydrologically-controlled variations in cave CO_2 sources and dynamics: Evidence from monitoring soil CO_2, stream flow and cave CO_2

Min Cao, Jiaqi Lei, Qiufang He, Ze Zeng, Xianfu Lü, Yongjun Jiang *

Chongqing Key Laboratory of Karst Environment & School of Geographical Sciences, Southwest University, Chongqing 400715, China

ARTICLE INFO

This manuscript was handled by Huaming Guo, Editor-in-Chief, with the assistance of Wenke Wang, Associate Editor

Keywords:
Rainfall
Cave air pCO_2
Carbon isotope
Stream degassing
Xueyu cave

ABSTRACT

Speleothems are used as a promising proxy for high-resolution paleoclimate reconstruction. Partial pressures of CO_2 (pCO_2) is one of the most important factors in the processes of speleothem formation in caves. The objective of our study was to monitor the CO_2 variations in the overlying soil, the cave air and the stream, and distinguish its sources and processes based on stable carbon isotopes in the Xueyu Cave system from October 2014 to February 2017. Overlying soil CO_2 was influenced by soil temperature and soil moisture. The cave air pCO_2 and equilibrium pCO_2 in the stream water during two years showed very similar seasonal variations, fluctuating with high values in wet seasons and low values in dry seasons. The average $\delta^{13}C_{soil\ air}$ value was -19.3 ± 0.8‰ and $\delta^{13}C_{cave\ air}$ value was -18.8 ± 0.4‰ in November; while the average $\delta^{13}C_{soil\ air}$ value was -23.9 ± 1.4‰ and $\delta^{13}C_{cave\ air}$ value was -23.3 ± 0.3‰ in June. Moreover, the contribution from soil during the transitional ventilation (in November) was calculated based on the two end-members model of stable carbon isotopes. On the contrary, in wet season, cave air CO_2 were mainly controlled by soil CO_2 inputs. The total amount of C from stream degassing was calculated, which was higher in June than in November. High-resolution monitoring of cave air CO_2 and its sources reveals the highly sensitive nature of CO_2 dynamics within cave environments, and highlights its sensitivity to hydrological conditions in the cave system.

1. Introduction

CO_2 concentrations in karst environments (epikarst and soil) largely affect karst landscapes that cover 7–12% of the Earth's continental area (Ford and Williams, 2007). CO_2-enriched shallow caves are widely distributed in the terrestrial environment (Faimon et al., 2006; Bourges et al., 2014; Covington and Vaughn, 2018). The earliest measurements for cave air CO_2 dated from 1859 CE (Ek and Gewelt, 1985). Modern sensors and logging techniques have been deployed to provide detailed records of CO_2, pressure, temperature and humidity in cave atmosphere (Spötl et al., 2005; Frisia et al., 2011; Bourges et al., 2014). However, the controls on CO_2 concentration variations in the karst system are still poorly quantified.

In most cases the cave air CO_2 concentration is higher than that in the open atmosphere, a proper understanding of the sources and dynamics of seasonality in cave air CO_2 is fundamental for speleothem palaeoclimatology (Fairchild and Baker, 2012). Caves with low CO_2 concentrations are always better ventilated (Bourges et al., 2014; Lang et al., 2015). In shallow or ventilated caves, CO_2 concentration is generally lower than that in the overlying soils, ranging from 500 to 10,000 ppmv, and most CO_2 concentration is no more than 6500 ppmv (Spötl et al., 2005; Faimon and Ličbinská, 2010; Pu et al., 2018). A few studies reveal that CO_2 concentration is very high in deep and confined karst, e.g. average vadose CO_2 concentration is between 10,000 and 40,000 ppmv, with a maximum of nearly 60,000 ppmv in boreholes near Nerja Cave, Spain (Benavente et al. 2010, 2015). Many studies have found that gas dynamics in caves often show seasonal variations in CO_2 concentration because of different temperatures in and out of caves (Liñán et al., 2008; Wong and Banner, 2010). In summer, the temperature out of the cave is higher, which increases CO_2 concentration in confined conditions. However, the thing is different in winter. The external air enters the caves by large openings or fractures when caves are better ventilated, which decreases CO_2 levels (Christelle et al., 2007). However, high CO_2 concentrations were observed in some Mediterranean caves with lower temperature but higher precipitation in winter (Mattey et al., 2016).

---

* Corresponding author.
E-mail address: jiangjyj@swu.edu.cn (Y. Jiang).

https://doi.org/10.1016/j.jhydrol.2021.126060
Received 28 July 2020; Received in revised form 29 September 2020; Accepted 1 February 2021
Available online 11 February 2021

The CO_2 concentrations in the karst caves are controlled by the input and output CO_2 fluxes (Lang et al., 2017). There are several main CO_2 inputs: (1) from soils/epikarst (e.g. Ek and Gewelt, 1985; Cuezva et al., 2011; Pla et al., 2017), (2) from dripwater/stream water degassing (Baldini et al., 2006; Breitenbach et al., 2015; Hao et al., 2018), and (3) anthropogenic inputs from visitors in some show caves (Faimon et al., 2006; Lang et al., 2015), (4) from microbial decay of organic matters (Atkinson, 1977; Mattey et al., 2016), (5) from deep magmatic or metamorphic sources (Bergel et al., 2017). Among these factors, soil inputs and atmospheric air are traditionally considered to be the most significant inputs for most of caves (Ridley et al., 2015; Lang et al., 2017). The cave outputs are controlled by cave ventilation mainly driven by cave geometry and temperature difference between the exterior and interior environment (Lang et al., 2017).

The production and transport of subterranean CO_2 within surface soils or subsurface cavities have been widely studied, especially the

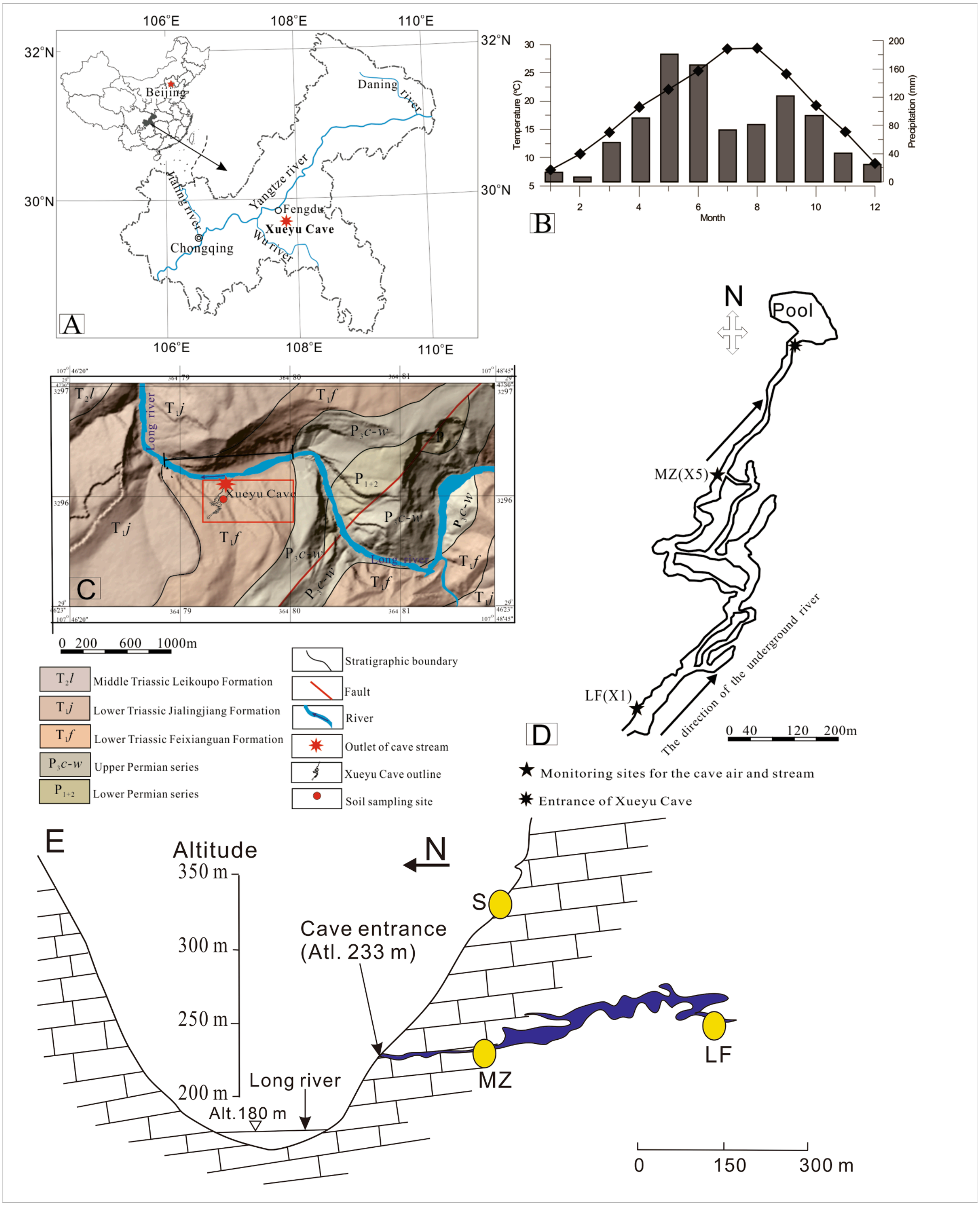

Fig. 1. (A) Chongqing Municipality, SW China and geographical location of study area (red shape), (B) monthly air and precipitation in Xueyu Cave, (C) the location of the Xueyu Cave, its surrounding strata and the soil sampling site (modified from Wu et al. (2015)), (D) sketch map of the Xueyu Cave and locations of the monitoring sites (LF and MZ), cross section of Xueyu Cave passages and the sampling locations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

surface-atmosphere CO_2 exchanges (Davidson et al., 1998). Soil CO_2, one of the most important sources of cave air, can directly enter the cave by gaseous form or by aqueous solution (Wood, 1985; Baldini et al., 2006; Cuezva et al., 2011). On one side, water moves downward via fissures and fractures, some of it enters caves as drips and seepage and some of it as shaft flow and stream water (Ford and Williams, 2007); on the other side, air moves around in a more complex pattern, which may circulate rapidly through high-permeability conduits or slowly as 'ground air' in the vadose zone (Benavente et al., 2010). Specifically, there may be CO_2 contributions from decomposition of organic matter in the caves (Mattey et al., 2016; Pla et al., 2017).

The importance of understanding specific cave ventilation mechanisms has been well highlighted in previous studies (Kowalczk and Froelich, 2010; Mattey et al., 2010; Benavente et al., 2015; Breitenbach et al., 2015). The magnitude and variability of soil CO_2 production is mainly driven by soil temperature (Pumpanen et al., 2003) and soil water content (Vargas et al., 2012). In this case, soil CO_2 and dissolved CO_2 in karst settings always display seasonal variability (Atkinson, 1977; Pu et al., 2014). The cave stream water had initially higher pCO_2 during high-flow periods (summer) and has degassed along its flow path in the cave system (Anthony et al., 2003; Pu et al., 2014; Cao et al., 2019).

The stable carbon isotope is a useful tool to understand the mixing process inside a cave. Some authors used the Keeling plot (Keeling, 1958) to consider cave air as a mix between two end-members (Spötl et al., 2005; Kowalczk and Froelich, 2010; Frisia et al., 2011). The light end-member source is with high pCO_2 but depleted $\delta^{13}C_{CO2}$ value (Mattey et al., 2010; Peyraube et al., 2013), close to the $\delta^{13}C$ values ($-30‰ \sim -24‰$) from roots of C3 type vegetation (Vogel, 1993). Both bulk and root-free soil respired $\delta^{13}C_{CO2}$, exhibiting depleted values ranging from $-29‰$ to $-26‰$ (Unger et al., 2010). Soil air CO_2 is enriched by about 4.4‰ due to a different diffusion coefficient for $\delta^{12}C$ and $\delta^{13}C$ compared to root respired and decomposed CO_2 (Cerling et al., 1991). The $\delta^{13}C_{CO2}$ derived from geothermal sources (e.g., magmatic or metamorphic sources) typically ranges from 2‰ to 6‰ (Faure, 1986).

In this study, we have investigated the data of soil CO_2 concentration, stream pCO_2, and cave air pCO_2 with their $\delta^{13}C$ values in high frequency from Xueyu Cave, SW China during the period of October 2014 and February 2017. The aim of this paper is to (1) identify the main factors that drive dynamics of carbon distribution and transfer between cave air CO_2, soil air CO_2, and stream CO_2 and (2) identify how they respond to hydrological processes in a karst cave.

2. Study area

Xueyu Cave (29°47′00″ N, 107°47′13″ E) is located in Fengdu County, Chongqing, China (Fig. 1A), where a typical subtropical monsoon climate is dominant with an average annual precipitation of approximately 1072 mm and a mean annual cave air temperature of 17.2 °C (Fig. 1B) and without seasonality (Xu, 2013; Pu et al., 2016). The vegetation is mainly composed of evergreen, broad-leaf forests and shrubs. Overlying soils range averagely from 20 cm to 50 cm in thickness, and the land use types are forests and dry lands reclaimed from croplands.

Xueyu Cave develops in the northwest wing of the Fangdou anticline that is consisted of the Lower Triassic Feixianguan Formation (T_1f) limestone with argillaceous rocks at the base and silt rocks at the top, the Lower Triassic Jialingjiang Formation (T_1j) dolomitic limestone with salt dissolution breccias at the top, and the Middle Triassic Leikoupo Formation (T_2l) argillaceous limestone embedded with silty shales (Fig. 1C). The thickness of the roof rocks of Xueyu Cave is over 150 m. The cave system has only one entrance at 233 m above sea level (Fig. 1E) and the space of the cave chambers has been 18040 m^3 (Xu, 2013).

The geological formation and secondary carbonate deposits, including soda straw, stalactites, stalagmites, cave flags, cave shields were explored in the cave (Zhu et al., 2004). The systemic study of the links between the host rock, water and speleothems has been performed to explain the universal cementation of magnesium-bearing minerals (Wu et al., 2015). Most parts of the cave are narrow and deep passages (canyon passages), which are developed along strata and composed of three levels: Level I (233–236 m), Level II (249–262 m) and Level III (281–283 m) (Pu et al., 2014). There is no allogenic stream sinking underground at the head of Xueyu Cave (Pu et al., 2015). A cave stream with the explored length of 1644 m and the total length of 8 km flows at the bottom Level I and out of Xueyu Cave with only one natural opening (Pu et al., 2016). Previous investigations have described the hydrogeological and hydrochemical functioning of Xueyu Cave stream (Zhu et al., 2004; Pu et al., 2016). The discharge of the subterranean stream ranges from 4.1 L/s in dry period to 26.6 L/s in wet period. Meteoric water recharges the karst aquifer through carbonate matrix and conduits.

As a show cave, Xueyu Cave receives a great number of visitors every year, especially in summer. Two doors have been installed at the cave entrance in order to prevent frequent exchange of indoor and outdoor gas. The cave is not well ventilated in most of the time. The relationships between specific conductance (Spc), Ca^{2+} and HCO_3^- have been established and variations of CO_2 concentrations in the cave atmosphere and cave stream showed different changes in wet and dry season due to the ventilation (Pu et al., 2015, 2018). High ^{222}Rn and CO_2 concentrations typically occur during the warm summer, and low concentrations are typical in cold winter (Yang et al., 2013; Pu et al., 2018). Xueyu Cave presents "chimney effect" based on monitoring of seasonal radon pattern (Wang et al., 2019), which is consistent with seasonality of cave air CO_2 concentration. As changes in radon production are expected to be small within the cave, the ventilation process is the main factor controlling changes of radon concentrations in the cave (Przylibski, 1999). Storms result in the most dramatic stream pCO_2 variations for a short time (Pu et al., 2018; Cao et al., 2019).

3. Methods and materials

Meteorological data including precipitation (with the precision of 0.01 mm) and temperature (with the precision of 0.1 °C) were recorded every 15 min using a Devis VP-2 weather station. The continuous and automatic measurement of soil air CO_2 with a CO_2 sensor (GMM221) was fixed at 40 cm depth in the soil profile above Xueyu Cave from October 2014 (seeing the site S in Fig. 1E and Fig. S1). The soil temperature and moisture were obtained by a temperature and humidity sensor (AV-10T and AV-EC5). CO_2 recordings were calibrated using a handheld probe (GT901).

Two sites (LF and MZ) in Xueyu Cave have been selected for the monitoring of CO_2 from cave air and the subterranean stream (Fig. 1E), using GMM221 sensors with RR-1008 data logging that was calibrated by CDU 440 CO_2 meter. Stream pCO_2 values calculated by hydrochemical parameters are used to compare with continuous logging data. To obtain the detailed hydrochemical variations, a CDTP300 multiparameter water quality meter was installed to record water temperature, water level, Spc and pH, respectively. The data from CO_2 measurement system and water quality data logger was set at the same time-interval of 15 min (See more details about these instruments in Supplementary material).

Soil and cave air samples for $\delta^{13}C_{CO2}$ analyses were collected using a pump and carefully sealed in the 100 mL trace gas bags. All samples were stored at room temperature before analysis. The measurement was performed at the Environmental Stable Isotope Lab, Chinese Academy of Agricultural Sciences (CAAS), where $\delta^{13}C_{CO2}$ in the bags was introduced to Delta V Plus. $\delta^{13}C_{DIC}$ samples from the stream were filtered and injected in 15 mL brown bottles without bubbles and two drops of $HgCl_2$ were added in order to prevent microbial activities. Analyses were performed using a Delta plus XL continuous-flow isotope ratio mass spectrometry. The results of carbon isotope were reported relative to V-PDB based on comparison to known carbonate standards and the analysis precision was better than 0.15‰ (1σ).

4. Results

During Oct. 2014 and Feb. 2017, the monthly air temperature ranged from 3.3 °C to 39.5 °C with an average of 19.5 ± 7.2 °C (Fig. 2A). Mean annual rainfall amount was over 1100 mm. Moreover, there were few rainfall events in August every year because of the strong effect of Northwest Pacific subtropical high pressure (Fig. 2B). The mean atmospheric CO_2 concentration during the study period was 467 ± 33 ppmv with a significant seasonal trend (low values in summer but high values in winter). The soil temperature ranged from 8.0 °C in December to 24.0 °C in August with a mean value of 18.5 ± 5.1 °C (Fig. 2A). The soil moisture varied between 0.5% and 24.0% with a mean value of 9.4 ± 4.4%, showing low values in winter and high values in summer, which is highly correlated with local rainfall events (Fig. 2C).

The complex cave geometry with three layers strongly influences airflow direction and velocity in different parts of the cave, but the inner cave temperatures are stable with the average temperature of 17.2 ± 0.2 °C throughout the year. The stream water temperatures ranged from 16.0 °C to 18.7 °C. During 150 days from May to October, the external temperature was above the cave temperatures and only 90 days from December to March, the external temperature was below the cave temperature (Fig. 2A). The correlations between different monitored items have been listed in Table 1, showing good correlations between soil temperature and soil CO_2, cave air pCO_2 and stream pCO_2.

The soil CO_2 concentrations obtained *in situ* are highly correlated with the results from the spectrometric analysis in the laboratory ($R^2 = 0.93$, $p < 0.01$, $n = 46$). Soil CO_2 at 40 cm depth showed noticeable seasonal variations throughout the annual cycle. The soil CO_2 concentrations ranged from 4000 ppmv in December to 17,000 ppmv in June with a mean value of 8890 ± 4576 ppmv, showing higher values in wet summer than in dry summer (Fig. 2D).

In winter, cave air pCO_2 was relatively steady and low (<1000 ppmv), similar to caves in Texas and Florida in the US that experience fastest ventilation in winter (Banner et al., 2007; Kowalczk and Froelich, 2010); whereas, it fluctuated largely and increased to be relatively abundant in summer (>6000 ppmv). Cave air pCO_2 showed the mean value of 5691 ppmv at LF (the innermost part in the cave) and that of 4447 ppmv at MZ (the entrance part) (Fig. 2D). Stream water pCO_2 showed a mean value of 6873 ppmv at LF and of 5558 ppmv at MZ. The continuous variational trend of stream pCO_2 at MZ are very similar to that at LF. pCO_2 values in the cave and the stream are generally lower than those in the soil. To make lines that depict pCO_2 trends more distinctive, we only showed monitoring results of stream pCO_2 from LF in the Fig. 2D.

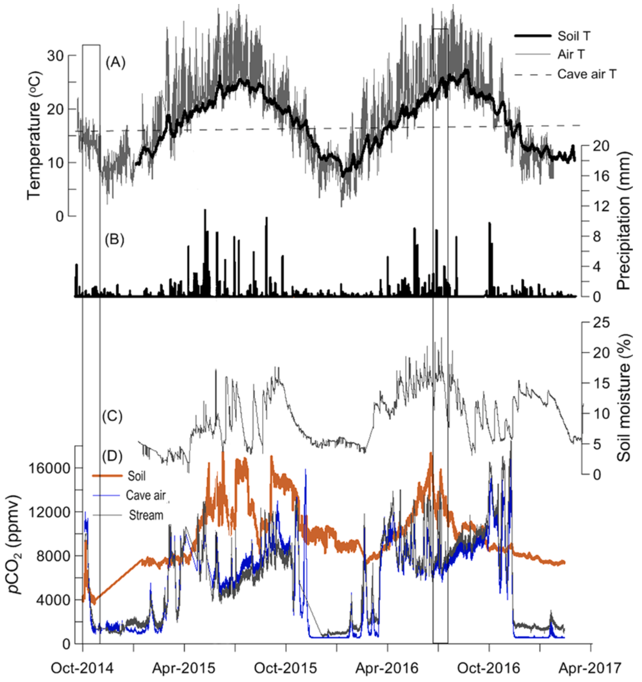

Fig. 2. (A) air temperature and soil temperature, (B) precipitation, (C) soil moisture, (D) pCO_2 values in the soil air, cave air and stream water of Xueyu system between Nov. 2014-Feb. 2017.

Specifically, abrupt changes of cave air and stream pCO_2 occurred at the moments of transitional seasons (autumn to winter or spring to summer) with large variational magnitudes, e.g. cave air CO_2 concentrations had increased to 16,000 ppmv and decreased to 1000 ppmv within several days in November 2015 and 2016. During the rainfall events, cave air and stream pCO_2 responded quickly to rainfall events (Fig. 3). At the end of October 2014, soil CO_2 concentrations increased gradually from 4000 ppmv to 9000 ppmv at the beginning of the rainfall event and then decreased gradually to below 5000 ppmv. On the contrary, cave air pCO_2 at LF and MZ were higher than soil CO_2, ranging from 8000 ppm to 12000 ppm. However, we did not grasp the initial increasing changes that corresponded to the onset of rainfall events because the equipment for the monitoring in the stream started to work only when the pCO_2 had increased and kept on the high level (Fig. 3D). That is, cave air and stream were initially characterized by high pCO_2 values and $pCO_{2\ (stream)} > pCO_{2\ (cave\ air)}$ at LF. With the external air entering the cave, cave air and stream pCO_2 decreased below 2000 ppmv in the next several days. Low cave air CO_2 concentrations indicated beneficial conditions for gas exchange and low-concentration recharge was gradually predominant in the cave (Fig. 3D). $pCO_{2(cave\ air)}$ was only slightly lower than $pCO_{2(stream)}$ at LF, while at MZ, $pCO_{2(cave\ air)}$ was the lowest, confirming that ventilation near the cave entrance is more significant.

In June 2016, before the rainfall, stream water pCO_2 was equilibrium with cave air pCO_2, showing increasing pCO_2 responding to rainfall events. Rainwater dissolved soil CO_2 and brought more CO_2 to the stream. The main source of cave air pCO_2 was rarely related to external air due to poor ventilation. Stream and cave pCO_2 were in equilibrium before rainfall and they increased along rainfall events, stream pCO_2 > cave pCO_2 at LF and MZ sites and stream pCO_2 was higher at LF than at MZ. All pCO_2 decreased in the flood recession period. Finally, stream pCO_2 at MZ was the highest.

The $\delta^{13}C_{air}$ values of background atmospheric air CO_2 were from −10.0‰ to −9.6‰. During the two high-resolution monitoring intervals, $\delta^{13}C$ value was −19.3‰±0.8‰ in the overlying soil gas in November but −23.9 ± 1.4‰ in June on average.

$\delta^{13}C_{cave\ air}$ values ranged from −18.8‰ (-19.4‰ ~ −18.2‰) in November to −23.3‰ (−23.6‰ ~ −22.7‰) in June at LF and MZ sites during rainfall events. There was no significant difference of $\delta^{13}C_{cave\ air}$ at both sites. $\delta^{13}C_{DIC}$ in the stream ranged from −11.9‰ (−12.6‰ ~−10.6‰) in November to −13.3‰ (−13.9‰ ~ −12.8‰) in June at MZ; from −12.7‰ (−13.1‰ ~ −12.2‰) in November to −13.5‰ (−13.9‰ ~ −13.2‰) in June at LF. The average value of $\delta^{13}C_{CO2}$ from stream degassing at MZ should be −21.0‰ and −22.3‰ in November and June, respectively, considering carbon isotopic fractionation of 9‰ between water and gas (Zhang et al., 1995). Similarly, the average value of $\delta^{13}C_{CO2}$ from stream degassing at LF was −22.4‰ in November to −23.9‰ in June at LF, respectively (Table 2).

5. Discussion

The cave air CO_2 concentration at a given time is the result of the balance between CO_2 fluxes into and out the cave (Breecker et al., 2012). Seasonal variations in cave air CO_2 could be related to changes in different sources and transport mechanisms. According to monthly monitoring results, the seasonality of cave CO_2 variations occurred, cave CO_2 concentration was generally higher in summer and lower in winter

Table 1
The correlation matrix of environmental parameters in Xueyu system.

	Soil M	Soil T	Prep	Cave T	Soil CO_2	Discharge	pH	MZ stream CO_2	MZ air CO_2	LF stream CO_2	LF air CO_2	Spc	TOC
Soil M	1												
Soil T	$.285^{**}$	1											
Prep	$-.023^{**}$	$-.013^{**}$	1										
Cave T	$.326^{**}$	$.367^{**}$	$-.040^{**}$	1									
Soil CO_2	$.263^{**}$	$.639^{**}$	$-.027^{**}$	$.116^{**}$	1								
Discharge	$-.062^{**}$	.011*	$.217^{**}$	$-.122^{**}$	$-.027^{**}$	1							
pH	$.044^{**}$	0.0033	$-.094^{**}$	$.296^{**}$	$-.052^{**}$	$-.278^{**}$	1						
MZ stream CO_2	$.791^{**}$	$.416^{**}$	$.073^{**}$	$-.192^{**}$	$.294^{**}$	$.224^{**}$	$-.735^{**}$	1					
MZ air CO_2	$.781^{**}$	$.518^{**}$	$.052^{**}$	$-.795^{**}$	$.683^{**}$	$.222^{**}$	$-.989^{**}$	$.868^{**}$	1				
LF stream CO_2	$.030^{**}$	$.402^{**}$	$.054^{**}$	$-.237^{**}$	$.263^{**}$	$.304^{**}$	$-.926^{**}$	$.876^{**}$	$.877^{**}$	1			
LF air CO_2	$-.030^{**}$	$.423^{**}$	$.059^{**}$	$-.210^{**}$	$.237^{**}$	$.253^{**}$	$-.904^{**}$	$.768^{**}$	$.963^{**}$	$.952^{**}$	1		
Spc	$.134^{**}$	$.227^{**}$	$.077^{**}$	$-.305^{**}$	$.062^{**}$	$.253^{**}$	$-.740^{**}$	$.610^{**}$	$.957^{**}$	$.749^{**}$	$.710^{**}$	1	
TOC	$.190^{**}$	$-.540^{**}$	$-.023^{**}$	$-.447^{**}$	$-.176^{**}$	$-.046^{**}$	$-.194^{**}$	$-.717^{**}$	$-.727^{**}$	$-.080^{**}$	$-.209^{**}$	$.111^{**}$	1

**$P<0.01$; *$P<0.05$; Soil M=soil moisture, Soil T=soil temperature, Prep=precipitation, Cave T=cave temperature.

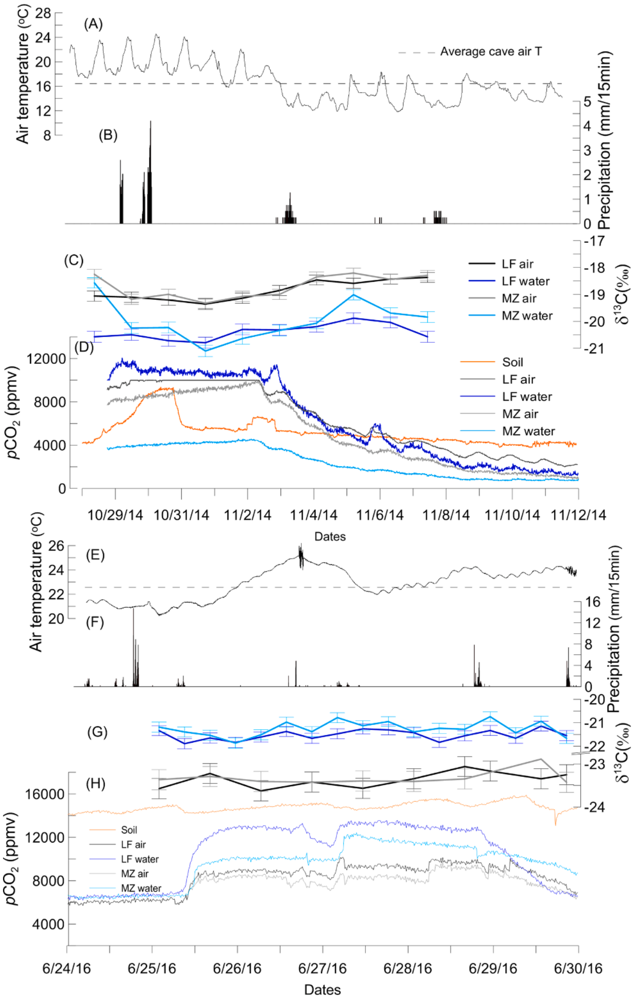

Fig. 3. Variations of monitoring items (precipitation, temperature, $\delta^{13}C$ and pCO_2) during rainfall events in October-November 2014 and June 2016.

(Wang et al., 2016; Pu et al., 2018). Our data provide further high-frequency records of temperatures, precipitation and CO_2 variations that allow us to see the details of variations and the processes in the cave.

5.1. Sources and variations of CO_2 concentrations in Xueyu soil-cave system

5.1.1. CO_2 production and variation in Xueyu soils

The time series of seasonal soil CO_2 concentrations suggest that the seasonality of soil CO_2 concentrations above Xueyu Cave were generally corresponding to the variations in soil temperature (Fig. 2A, 2D). Soil CO_2 is the combination of CO_2 produced by root respiration and microbial decomposition of organic matter (Breecker et al., 2012). Normally, soil CO_2 peaks in wet and warm summer in subtropical area. Soil CO_2 production rates will rise with temperature when soil moisture is not limited (Fang and Moncrieff, 2001). However, the study area always suffered summer drought in August due to the control of West Pacific Subtropical High (WPSH), which results in high air temperature but low precipitation (Zhou et al., 2009), leading to lower soil moisture during the dry period (Fig. 2C). Lower soil CO_2 concentrations could be due to reduced CO_2 production rates or greater gas permeability in dry environment, which also facilitates the escape of CO_2 to the surface (Mattey et al., 2016). Soil moisture enhances CO_2 production when soils are not saturated with water (Moyano et al., 2013).

The soil CO_2 concentrations of the study area were increased along with soil moisture in plant-growth period. Gibraltar soil CO_2 concentrations were minimum in the late summer each year, consistent with dry soil and died vegetation and rose in winter with abundant precipitation (Mattey et al., 2016). However, the effect of soil moisture on soil CO_2 concentrations was not always positive (Fig. 2C). For example, during rainfall events, soil CO_2 concentrations might rise up (Fig. 3D) or just decreased (Fig. 3H). The reason for the increase could be that mineralization of carbon containing compound enhances the microbial activities and activate their metabolism, more CO_2 is trapped and concentrated in soil under suitable temperature and moisture. While the reason for the decrease would be that too much water in the soil pores prevents the microbial activities and finally limits soil respiration.

5.1.2. CO_2 in Xueyu cave air

Although the drivers on cave air CO_2 are complex, many studies have confirmed that high cave air CO_2 concentrations are mainly imputable to high soil CO_2 (Wong and Banner, 2010; Frisia et al., 2011). Air CO_2 in Xueyu Cave is maximum in rainy seasons (April-October). The site near the entrance has more variable cave air CO_2 concentration, indicating that the influence of external air is greatest near the cave entrance where air exchanges in and out of the cave. In many previous studies about caves, the dominant sources of cave CO_2 are mixed with soil respiration and atmospheric air (Ek and Gewelt, 1985; Baldini et al., 2008). Low CO_2 production in the overlying soils in winter aggravates the scarcity of CO_2 in the cave. External air temperature drops below the internal cave

Table 2
The $\delta^{13}C$ values from cave air and stream and the contribution of cave CO_2 from soils.

Time	Cave air (‰)		Stream DIC (‰)		Stream degassing (‰)		The proportion from soil	
October-November	MZ	LF	MZ	LF	MZ	LF	MZ (%)	LF (%)
2014/10/30–09:00	−18.2	−19.1	−10.6	−12.9	−19.6	−21.9	43.9	48.9
2014/10/31–09:00	−19.2	−19.1	−12.2	−12.8	−21.2	−21.8	50.1	49.1
2014/11/1–09:00	−19.0	−19.2	−12.2	−13.0	−21.2	−22.0	48.3	50.1
2014/11/2–09:00	−19.3	−19.4	−12.1	−13.1	−21.1	−22.1	49.9	49.3
2014/11/3–09:00	−19.1	−19.1	−12.6	−12.6	−21.6	−21.6	48.4	49.1
2014/11/4–09:00	−19.0	−18.9	−12.3	−12.6	−21.3	−21.6	44.9	48.6
2014/11/5–09:00	−18.3	−18.5	−12.1	−12.5	−21.1	−21.5	45.4	45.8
2014/11/6–09:00	−18.4	−18.6	−11.0	−12.2	−20.0	−21.2	49.7	46.4
2014/11/7–09:00	−18.4	−18.4	−11.7	−12.3	−20.7	−21.3	49.8	45.8
2014/11/8–09:00	−18.3	−18.4	−11.8	−12.9	−20.8	−21.9	44.9	44.8
Mean values	−18.7	−18.9	−11.9	−12.7	−20.9	−21.7	47.5	47.8
June								
2016/6/24-09:00	−23.4	−23.6	−13.2	−13.3	−22.2	−22.3	82.0	87.2
2016/6/25-09:00	−23.3	−23.2	−13.4	−13.9	−22.4	−22.9	76.3	58.8
2016/6/25-21:00	−23.4	−23.6	−13.5	−13.6	−22.5	−22.6	78.6	84.7
2016/6/26-09:00	−23.4	−23.4	−13.9	−13.8	−22.9	−22.8	70.3	72.9
2016/6/26-21:00	−23.4	−23.6	−13.5	−13.6	−22.5	−22.6	78.6	86.5
2016/6/27-09:00	−23.4	−23.3	−13.0	−13.2	−22.0	−22.2	83.7	78.0
2016/6/27-21:00	−23.3	−23.1	−13.4	−13.7	−22.4	−22.7	76.3	61.2
2016/6/28-09:00	−22.7	−23.2	−12.8	−13.5	−21.8	−22.5	66.1	70.1
2016/6/28-21:00	−22.9	−23.3	−13.1	−13.3	−22.1	−22.3	66.8	77.1
2016/6/24-09:00	−23.4	−23.3	−12.9	−13.3	−21.9	−22.3	84.2	75.2
Mean values	−23.3	−23.4	−13.3	−13.5	−22.3	−22.5	76.3	75.2

*The average $\delta^{13}C$ values of soils in November and June are −18.5 ± 0.4‰ and −23.9 ± 1.4‰ respectively.

air temperature causing cold dense air to flow inwards, resulting in a decline in cave temperature and CO_2 levels (Breecker et al., 2012). However, the sites in Xueyu Cave except the one near the entrance (MZ) have relatively steady cave air temperature.

CO_2 concentrations in cave air were sometimes higher than in contemporaneous soil air in transitional periods, suggesting a deeper source for cave air CO_2 (Benavente et al., 2010, 2015). Atkinson (1977) proposed that ground air CO_2 could be related to slow and steady decomposition of particulate organic matter of soils washed down by infiltrating water. The contribution to cave C source from old organic matter oxidation was emphasized too (Noronha et al., 2015). Similar phenomenon was also found but in winter in Gibraltar karst caves, which was considered to be a source of CO_2 from vadose zone (Mattey et al., 2016). A previous study of chromophoric dissolved organic matter (CDOM) in Xueyu Cave stream showed that CDOM was mainly from autochthonous source (Fan et al., 2019), which confirms that cave air CO_2 is only partly influenced by decomposition of soil organic matter. The delay of CO_2 concentration peaks in Xueyu Cave would be attributed to the slow movement of CO_2 that stores in karst fissures and voids in the vadose zone though the contemporaneous soil CO_2 concentration might be low (Fig. 4).

One of the most striking features of the CO_2 time series is the similar trend of cave air CO_2 and stream CO_2 (Fig. 2D). However, they still show some contradictions when we focus on the pCO_2 difference in water and

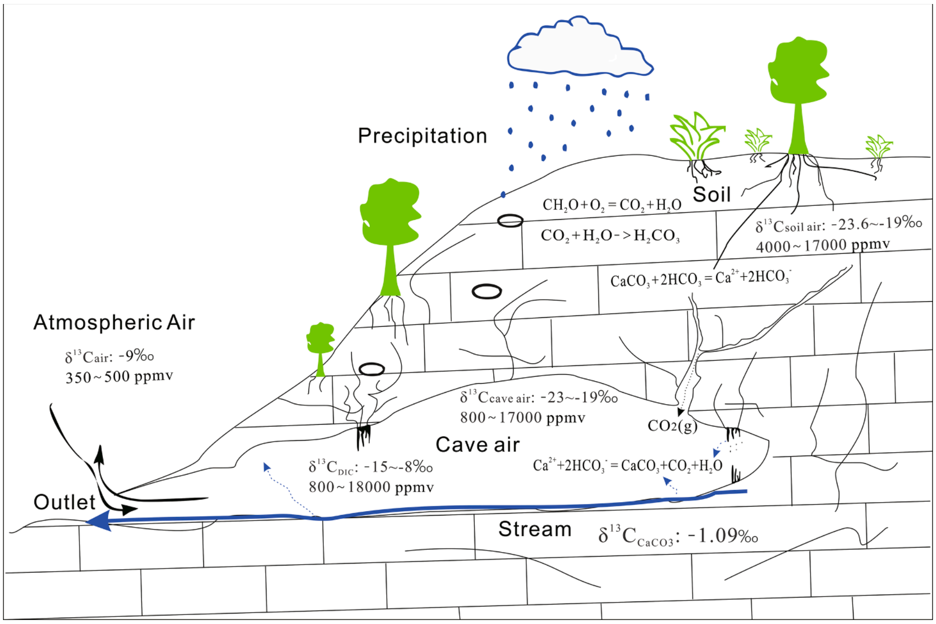

Fig. 4. Conceptual model for subsurface carbon cycling in Xueyu karst cave (modified from Kowalczk and Froelich, 2010). CO_2 respired in soils is transported into caves by gaseous form or infiltrated in rainwater. Changes of ventilation patterns which might be correlated to soil moisture overlying can help to accumulate cave air CO_2 or make it dispersed in summer and winter. Sketch of the seasonally controlled airflow of the Xueyu Cave system and resulting in pCO_2 changes.

gas (Fig. 5). Troester and White (1984) showed that seasonal degassing from a cave stream contributes to cave air CO_2. In Xueyu Cave, stream flow may also play an important role for variations of cave air pCO_2 as CO_2 degassing and absorption by stream water, like in Ballynamintra Cave (Baldini et al., 2006). Strong stream flow can induce air velocities proportional to that of the stream via friction between water and air (Cigna, 1968; Fairchild and Baker, 2012; Breitenbach et al., 2015). Degassing rates are greatest when cave air pCO_2 is lowest in winter. In other seasons, it is uncertain whether degassing occurs or not. Monitoring data from LF and MZ sites showed that stream pCO_2 variations were consistent with that of the cave air on the seasonal scale (Fig. 2D). Specifically, the higher stream pCO_2 at LF than that at MZ confirmed CO_2 degassing from the upstream (LF) to the downstream (MZ). Other C sources for the cave air CO_2 can be neglected, e.g. the effect of human respiration in the cave is of minor importance based on CO_2 measurements in peak tourist seasons (Wang et al., 2010).

5.2. Cave air CO_2 dynamics controlled by rainfall events

Soil CO_2 is considered as an important component in the chemical weathering of limestone. Previous studies in Xueyu Cave have revealed that precipitation rather than temperature exerts a significant impact on cave CO_2 variations on the storm scale (Pu et al., 2014; Wang et al., 2016; Cao et al., 2019). During storms, soil CO_2 dissolves in water and enters the karst system to dissolve limestone. The higher the precipitation, the higher the dissolution rate is; the higher the rainfall intensity, the higher the variations in stream and cave air pCO_2. Stream pCO_2 variations are considered as the most important control on the variation of dissolution rates and higher rates are observed with the high-pCO_2 flow during summer (Covington and Vaughn, 2018). The stream starts at a high pCO_2 level and then would enhance dissolution along the flow path in a closed system condition (Ford and Williams, 2007; Covington and Vaughn, 2018).

At the beginning of November, both the degassing and ventilation are responsible for the decrease of stream and cave air pCO_2. Because of the ventilation, MZ is the most striking part for air exchange, which could explain the lowest concentration of cave air pCO_2. The epi-karstic porous system is not water saturated in the cold and dry seasons, opening paths are beneficial for CO_2 movement (Fig. 4). The mechanism is depending on water that seals the pores where gas transport through the overlying soil is determined by the pore size distribution, interparticle porosity and water content (Cuezva et al., 2011). Large pCO_2 difference between stream water and cave air will result in faster degassing rates (Fig. 5). This pCO_2 difference started to become large at the beginning of rainfall events as the dissolution increased. Stream water interacted with cave atmosphere to get equilibrated with the cave air CO_2 within 3–4 days from the beginning of the rainfall events (Fig. 3D and 3H).

In contrast, the system of epi-karstic fissures in the warm and wet seasons is almost temporarily saturated with water, making the host rock membrane impermeable to prevent the CO_2 diffusion from the cave. Ventilation is minimized and cool stagnant air could accumulate, resulting in higher CO_2 concentration in the cave. Noticeably, stream water CO_2 was higher at MZ than LF. Inputs from different water sources or increased dissolution rates may explain for a higher stream pCO_2 along flow path from LF to MZ. A drip water in nearby site from MZ showed its pCO_2 nearly two times higher, suggesting high-pCO_2 drip water and air seepage as plausible sources (Pu et al., 2018). During the flood recession period of rainfall events, the dissolution of calcite took CO_2 from cave air, which decreased the cave air pCO_2 but increased the stream pCO_2 at MZ.

5.3. $\delta^{13}C$ isotope calculating contributions from soil to cave air CO_2

Mean $\delta^{13}C_{CO2}$ in the overlying soil of Xueyu Cave was $-21.5‰\pm 0.5‰$, ranging from $-23.9‰$ to $-18.5‰$. It indicates that C_3 plants are responsible for most of the biogenic CO_2 production. In the soil and cave air, $\delta^{13}C_{CO2}$ was generally lower in the summer than other seasons (Wang et al., 2016). In the karst cave, HCO_3^- constituted the main DIC with the pH values above 7.4. The $\delta^{13}C$ of DIC ($\delta^{13}C_{DIC}$) in Xueyu stream was generally higher in dry seasons and lower in wet seasons. As the degassing occurs and pH increases, lighter $\delta^{13}C$ would be going to the cave air and the remaining $\delta^{13}C_{DIC}$ becomes heavier. Our observation has shown that soil CO_2 concentration with seasonality was similar to that from other soil sites in the study area, which was enriched from shallow to deep soil (Wang et al., 2016). Soil CO_2 was transported by advection and diffusion. The former would be changed by temperature variations (Mattey et al., 2016), while the latter always results in reduced CO_2 concentrations and increased $\delta^{13}C$ values relative to the root respiration (Cerling, 1984). Besides, transport by diffusion is slower than advection.

The identification of $\delta^{13}C$ compositions of the end-member components in each reservoir has been carried out to completely understand the underlying processes that control the generation and dispersal of CO_2 in karst systems. The source of the isotopically light end-member CO_2 in the standard model is soil respiration that is dominant in cave air (Baldini et al., 2006; Frisia et al., 2011; Breecker et al., 2012). Other potential sources include degassing from CO_2-riched groundwater, deep-sourced CO_2 (Breecker et al., 2012). In Xueyu Cave, there is a linear relationship between $\delta^{13}C_{CO2}$ and $1/CO_2$ during the transitional period, indicating a mixing process (Fig. 6). The mixing model has two end members, one of which from the degassing of stream water or soil inputs (ground air) is isotopically light and the other from the external air (Fig. 6). Within the linear relationships, the cave air $\delta^{13}C_{CO2}$ values

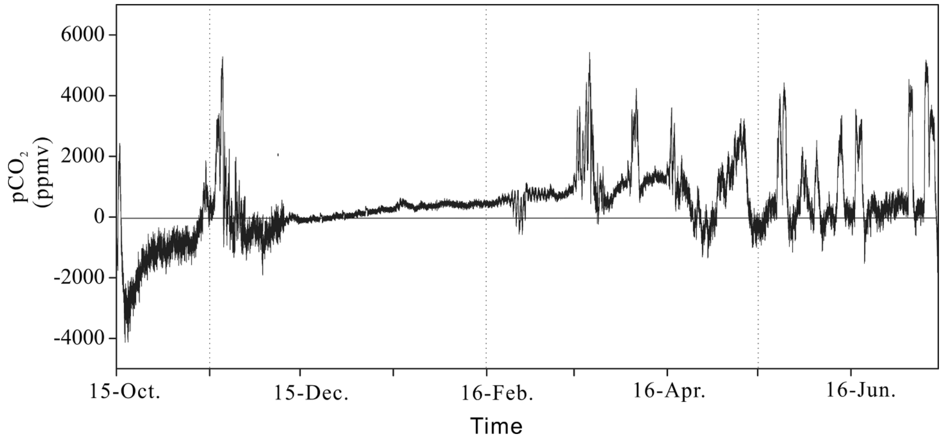

Fig. 5. The pCO_2 difference of stream and cave air at MZ in the Xueyu.

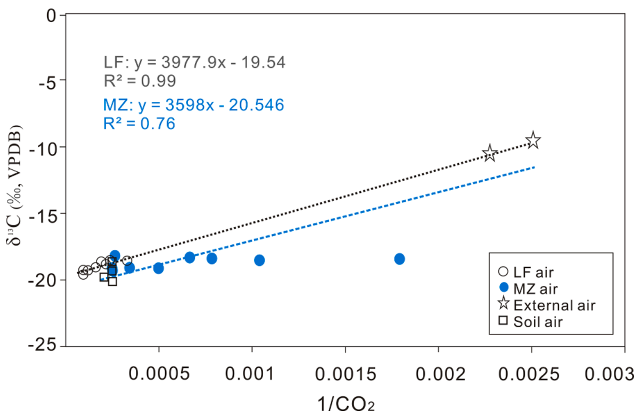

Fig. 6. The relationships between $\delta^{13}C_{V\text{-}PDB}$ and $1/CO_2$ during the CO_2 decline period from October to November 2014.

are extremely close to soil air values that are far from the data of exterior air. The lowest cave air pCO_2 and heaviest $\delta^{13}C_{CO2}$ occurred in the more exterior-influenced sites (MZ) inside the cave. The Keeling plot shows that the linear regression of the CO_2 transported via diffusive movement resulted in a higher intercept value (-19.5) than that dominated by advection (-20.5). With the influence of degassing, the sample collected at MZ the last time deviated far from the mixing line.

Soil $\delta^{13}C$-CO_2 agrees well with that in cave air, especially in June. There is no linear relationship between $\delta^{13}C_{CO2}$ and $1/CO_2$ to indicate a mixing process. However, the lighter values of cave air $\delta^{13}C$ from the beginning of the rainfall events might confirm a direct contribution from soil CO_2. Cave air $\delta^{13}C$ values only slightly changed along with the large variations in CO_2 concentrations. Here we excluded other sources such as human respiration that contributed very little CO_2 concentration (Wang et al., 2016). Besides, the contribution from deep sources can be neglected as it has more positive $\delta^{13}C$ value. Soil CO_2 would dominate the cave air CO_2 in wet summer (Table 2). This indicates that CO_2 is gradually accumulated in the cave due to increased soil inputs that are induced by high infiltration during storms.

5.4. Implications

The Xueyu, a karstic cave, could be representative of a series of natural shallow caves in vadose zone. The analysis of this particular cave summarized the complex relationships between the outdoor atmosphere, the soil/rock membrane and the underground atmosphere, which comprise a multicomponent system. Results presented in this study demonstrate the seasonality and processes of cave air pCO_2 dynamics occurring in Xueyu Cave. Changes of ventilation is controlled by a mixed effect of temperature difference in and out of the cave and rainfall events. Synchronous sharp variations in cave water and cave air pCO_2 of two locations in the cave from March to April or from October to November were recorded. The cave is assumed to be closed in summer despite small exchanges with the external air take place. The main source of cave air pCO_2 is overlying soil. However, more contributions from external air and degassing may dominate in pCO_2 variations from November. This study grasped the declining process of stream and cave air pCO_2, suggesting how the mixing occurred within several days. However, there are still limitations to our current quantitative understanding of the distribution of cave CO_2 production and transport from more than two sources.

6. Conclusions

Soil air pCO_2, cave air pCO_2 and stream pCO_2 as well as soil temperature, soil moisture and precipitation have been monitored at high resolution above and in Xueyu Cave. Importantly, the high CO_2 values of cave air and stream and the similarity of their seasonal patterns indicate fast exchange of CO_2 in water–gas state and they are always in dynamical equilibrium. The production and transport of soil CO_2 control the main variations in cave CO_2. Rainfall events can largely influence the CO_2 fluctuations, thus high-flow periods are always consistent with high pCO_2.

The temperature difference between external and inside cave seems to work as the threshold of ventilation for air in and out of Xueyu Cave. During the transitional period, ventilation regimes had changed and the entering of external air contributed more to the total cave air CO_2, especially the sites near the entrance. Cave air pCO_2 near those observed outside were found after several days of a strong winter ventilation. The contribution from external air is still below 20% in better-ventilated winter.

Soil input is the main source of cave air CO_2 in summer. Higher discharge in the stream after storms is equilibrated by CO_2 degassing too as cave air pCO_2 increased to its peaks over one day after the stream pCO_2 peaks. Keeling plot were used to assess the different contributions from soil and external air in the strong mixing process. The combined effects of different CO_2 sources, ventilation conditions and the occurrence of rainfall events could impact the final variations of cave air CO_2 through a year. More attention should also be paid to estimates of extreme events and sub-daily flow variation given their significant impacts to cave air CO_2.

CRediT authorship contribution statement

Min Cao: Formal analysis, Visualization, Conceptualization, Writing-original draft, Writing-review & editing. **Jiaqi Lei:** Investigation, Methology, Software, Formal analysis. **Qiufang He:** Formal analysis, Funding acquisition, Writing-review & editing. **Ze Zeng:** Investigation, Formal analysis, Resources. **Xianfu Lü:** Investigation, Formal analysis. **Yongjun Jiang:** Data curation, Funding acquisition, Project administration, Supervision, Validation, Writing-review & editing.

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.

Acknowledgements

This research was supported by the National key research and developmental program of China (2016YFC0502306), the Fundamental Research Funds for the Central Universities (XDJK2020C013), the Chongqing Municipal Science and Technology Commission Fellowship Fund (CSTC2018jcyj-yszx0013, CSTC2017jcyj-ysxx0004), and the open project from Chongqing Key Laboratory of Karst Environment (Cqk201701). Thanks to Liuchan Hu and Sibo Zeng who helped with the field work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jhydrol.2021.126060.

References

Anthony, D., Groves, C.G., Meiman, J., 2003. Preliminary investigations of seasonal changes in the geochemical evolution of the Logdson River, Mammoth Cave, Kentucky. Speleogenesis and Evolution of Karst Aquifers 1, 1–6.
Atkinson, T.C., 1977. Carbon dioxide in the atmosphere of the unsaturated zone: an important control of groundwater hardness in limestones. J. Hydrol. 35, 111–123.

Baldini, J.U.L., Baldini, L.M., Mcdermott, F., Clipson, N., 2006. Carbon dioxide sources, sinks, and spatial variability in shallow temperate zone caves: evidence from Ballynamintra cave, Ireland. J. Cave Karst Stud. 68 (1), 4–11.

Baldini, J.U.L., Mcdermott, F., Hoffmann, D.L., Richards, D.A., Clipson, N., 2008. Very high-frequency and seasonal cave atmosphere P_{CO2}, variability: implications for stalagmite growth and oxygen isotope-based paleoclimate records. Earth Planet. Sc. Lett. 272 (1–2), 118–129.

Banner, J.L., Guilfoyle, A., James, E.W., 2007. Seasonal variations in modern speleothem calcite growth in Central Texas, USA. J. Sed. Res. 8, 615–622.

Benavente, J., Vadillo, I., Carrasco, F., Soler, A., Liñán, C., Moral, F., 2010. Air carbon dioxide contents in the vadose zone of a Mediterranean karst. Vadose Zone J. 9 (1), 126–136.

Benavente, J., Vadillo, I., Liñán, C., Rosal, Y.D., Carrasco, F., 2015. Influence of the ventilation of a karst show cave on the surrounding vadose CO_2, reservoir (Nerja, South Spain). Environ. Earth Sci. 74 (12), 7731–7740.

Bergel, S.J., Carlson, P.E., Larson, T.E., Wood, C.T., Breecker, D.O., 2017. Constraining the subsoil carbon source to cave-air CO_2 and speleothem calcite in central Texas. Geochim. Cosmochim. Acta 217, 112–127.

Bourges, F., Genthon, P., Genty, D., Lorblanchet, M., Mauduit, E., D“Hulst, D., 2014. Conservation of prehistoric caves and stability of their inner climate: Lessons from Chauvet and other French caves. Sci. Total Environ. 493, 79–91.

Breecker, D.O., Payne, A.E., Quade, J., Banner, J.L., Ball, C.E., Meyer, K.W., Cowan, B., 2012. The sources and sinks of CO_2 in caves under mixed woodland and grassland vegetation. Geochim. Cosmochim. Acta 96 (11), 230–246.

Breitenbach, S.F.M., Lechleitner, F.A., Meyer, H., Diengdoh, G., Mattey, D., Marwan, N., 2015. Cave ventilation and rainfall signals in dripwater in a monsoonal setting – a monitoring study from NE India. Chem. Geol. 402, 111–124.

Cao, M., Jiang, Y. J., Chen, Y., Fan, J. X., He, Q. F., 2019. Variations of soil CO2 concentration and pCO2 in a cave stream on different time scales in subtropical climatic regime. 185, 104280.

Cerling, T.E., 1984. The stable isotopic composition of modern soil carbonate and its relationship to climate. Earth Planet. Sc. Lett. 71 (2), 229–240.

Cerling, T.E., Solomon, D.K., Quade, J., Bowman, J.R., 1991. On the isotopic composition of carbon in soil carbon dioxide. Geochim. Cosmochim. Acta 55, 3403–3405.

Christelle, B.G., Jean-Luc, S., Hervé, J., Olivier, H., Vincent, B.C., 2007. Seasonal variations of CO_2 and ^{222}Rn in a Mediterranean sinkhole - spring (Causse d'Aumelas, SE France). Int. J. Speleol. 36 (1), 51–56.

Cigna, A.A., 1968. An analytical study of air circulation in caves. Int. J. Speleol. 3, 41–54.

Covington, M.D., Vaughn, K.A., 2018. Carbon dioxide and dissolution rate dynamics within a karst underflow-overflow system, Savoy Experimental Watershed, Arkansas, USA. Chem. Geol. S0009254118301219.

Cuezva, S., Fernandez-Cortes, A., Benavente, D., Serrano-Ortiz, P., Kowalski, A.S., Sanchez-Moral, S., 2011. Short-term CO_2(g) exchange between a shallow karstic cavity and the external atmosphere during summer: role of the surface soil layer. Atmos. Environ. 45 (7), 1418–1427.

Davidson, E.A., Belk, E., Boone, R.D., 1998. Soil water content and temperature as independent or confounded factors controlling soil respiration in a temperate mixed hardwood forest. Global Change Biol. 4, 217–227.

Ek, C., Gewelt, M., 1985. Carbon dioxide in cave atmospheres. New results in Belgium and comparison with some other countries. Earth Surf. Proc. Land. 10 (2), 173–187.

Faimon, J., Štelcl, J., Sas, D., 2006. Anthropogenic CO_2-flux into cave atmosphere and its environmental impact: a case study in the Císařská Cave (Moravian karst, Czech Republic). Sci. Total Environ. 369, 231–245.

Faimon, J., Ličbinská, M., 2010. Carbon dioxide in the soils and adjacent caves of the Moravian karst. Acta Carsol. 39 (3), 463–475.

Fairchild, I.J., Baker, A., 2012. Speleothem Science: From Process to Past Environments. Wiley, p. 450.

Fan, J.X., Jiang, Y.J., He, Q.F., Wang, J.N., He, R.L., Zhang, C.Y., Ma, L.N., Wang, Q.R., 2019. Effect of aquatic photosynthesis on CDOM in Karst water in Xueyu Cave. Environ. Sci. 40 (06), 167–176 (in Chinese with English abstract).

Fang, C., Moncrieff, J.B., 2001. The dependence of soil CO_2 efflux on temperature. Soil Biol. Biochem. 33, 155–165.

Faure, G., 1986. Principles of Stable Isotope Geology. John Wiley, New York, p. 175.

Ford, D., Williams, P.W., 2007. Karst hydrogeology and geomorphology. John Wiley & Sons Ltd., 158.

Frisia, S., Fairchild, I.J., Fohlmeister, J., Miorandi, R., Spötl, C., Borsato, A., 2011. Carbon mass-balance modelling and carbon isotope exchange processes in dynamic caves. Geochim. Cosmochim. Acta 75 (2), 380–400.

Hao, Y., Zhang, C., Wang, J., Liao, X., Jiang, Y., Xiao, Q., 2018. High-resolution monitoring and analysis of the abrupt change of P_{CO2} in Xueyu Cave around the end of autumn. Environ. Sci. Technol. 41 (1), 134–142 (in Chinese with English abstract).

Keeling, C.D., 1958. The concentration and isotopic abundances of atmospheric carbon dioxide in rural areas. Geochim. Cosmochim. Acta 13, 322–334.

Kowalczk, A.J., Froelich, P.N., 2010. Cave air ventilation and CO_2, outgassing by radon-222 modeling: how fast do caves breathe? Earth Planet. Sc. Lett. 289 (1), 209–219.

Lang, M., Faimon, J., Ek, C., 2015. The relationship between carbon dioxide concentration and visitor, numbers in the homothermic zone of the Balcarka Cave (Moravian Karst) during a period of limited ventilation. Int. J. Speleol. 44 (2), 167–176.

Lang, M., Faimon, J., Godissart, J., Ek, C., 2017. Carbon dioxide seasonality in dynamically ventilated caves: the role of advective fluxes. Theor. Appl. Climatol. 129 (3–4), 1355–1372.

Liñán, C., Vadillo, I., Carrasco, F., 2008. Carbon dioxide concentration in air within the Nerja Cave (Malaga, Andalusia, Spain). Int. J. Speleol. 37 (2), 99–106.

Mattey, D.P., Fairchild, I.J., Atkinson, T.C., Latin, J., Ainsworth, M., Durell, R., 2010. Seasonal micro- climate control of calcite fabrics, stable isotopes and trace elements in modern speleothem from St Michaels Cave, Gibraltar, in Pedley, H. M., Rogerson, M, eds., Tufas and Speleothems: Unravelling the Microbial and Physical Controls: Geological Society London, Special Publications 336, 23-344.

Mattey, D.P., Atkinson, T.C., Barker, J.A., Fisher, R., Latin, J.P., Durrell, R., Ainsworth, M., 2016. Carbon dioxide, ground air and carbon cycling in Gibraltar karst. Geochim. Cosmochim. Acta 184, 88–113.

Moyano, F.E., Manzoni, S., Chenu, C., 2013. Responses of soil heterotrophic respiration to moisture availability: An exploration of processes and models. Soil Biol. Biochem. 59, 72–85.

Noronha, A.L., Johnson, K.R., Southon, J.R., Hu, C.Y., Ruan, J.Y., McCabe-Glynn, S., 2015. Radiocarbon evidence for decomposition of aged organic matter in the vadose zone as the main source of speleothem carbon. Quater. Sci. Rev. 127, S0277379115002267.

Peyraube, N., Lastennet, R., Denis, A., Malaurent, P., 2013. Estimation of epikarst air P_{CO2} using measurements of water $\delta^{13}C_{TDIC}$, cave air P_{CO2} and $\delta^{13}C_{CO2}$. Geochim. Cosmochim. Acta 118, 1–17.

Pla, C., Cuezva, S., Martinez-Martinez, J., Fernandez-Cortes, A., Garcia-Anton, E., Fusi, N., Crosta, G.B., Cuevas-Gonzalez, J., Cañaveras, J.C., Sanchez-Moral, S., Benavente, D., 2017. Role of soil pore structure in water infiltration and CO_2 exchange between the atmosphere and underground air in the vadose zone: a combined laboratory and field approach. Catena 149, 402–416.

Przylibski, T.A., 1999. Radon concentration changes in the air of two caves in Poland. J. Environ. Radioactiv. 45 (1), 81–94.

Pu, J., Yuan, D., Zhao, H., Shen, L., 2014. Hydrochemical and P_{CO2} variations of a cave stream in a subtropical karst area, Chongqing, SW China: piston effects, dilution effects, soil CO_2, and buffer effects. Environ. Earth Sci. 71 (9), 4039–4049.

Pu, J., Wang, A., Yin, J., Shen, L., Sun, Y., Yuan, D., Zhao, H., 2015. Processes controlling dripwater hydrochemistry variations in Xueyu Cave, SW China: implications for speleothem palaeoclimate signal interpretations. Boreas 44 (3), 603–617.

Pu, J., Wang, A., Shen, L., Yin, J., Yuan, D., Zhao, H., 2016. Factors controlling the growth rate, carbon and oxygen isotope variation in modern calcite precipitation in a subtropical cave, Southwest China. J. Asian Earth Sci. 119 (2), 167–178.

Pu, J., Wang, A., Yin, J., Shen, L., Yuan, D., 2018. P_{CO2} variations of cave air and cave water in a subtropical cave, SW China. Carbonate. Evaporite. 33 (3), 477–487.

Pumpanen, J., Ilvesniemi, H., Hari, P., 2003. A process-based model for predicting soil carbon dioxide efflux and concentration. Soil Sci. Soc. Am. J. 67, 402–413.

Ridley, H.E., Baldini, J.U.L., Prufer, K.M., Walczak, I.W., Breitenbach, S.F.M., 2015. High-resolution monitoring of Yok Balum Cave, Belize: an investigation of seasonal ventilation regimes and the atmospheric and drip-flow response to a local earthquake. J. Cave Karst Stud. 77 (3), 183–199.

Spötl, C., Fairchild, I.J., Tooth, A.F., 2005. Cave air control on dripwater geochemistry, Obir Caves (Austria): implications for speleothem deposition in dynamically ventilated caves. Geochim. Cosmochim. Acta 69 (10), 2451–2468.

Troester, J.W., White, W.B., 1984. Seasonal fluctuations in the carbon dioxide partial pressure in a cave atmosphere. Water Resour. Res. 20 (1), 153–156.

Vogel, J.C., 1993. Variability of carbon isotope fractionation during photosynthesis. Stable Isotopes and Plant Carbon-water Relations 29–46.

Unger, S., Máguas, C., Pereira, J.S., David, T.S., Werner, C., 2010. The influence of precipitation pulses on soil respiration-assessing the “birch effect” by stable carbon isotopes. Soil Biol. Biochem. 42 (10), 1800–1810.

Wang, A.Y., Pu, J.B., Shen, L.C., He, Y., 2010. Natural and human factors of CO_2 concentration variations in Xueyu Cave, Chongqing. Tropical Geogr. 30 (3), 272–277 (in Chinese with English abstract).

Wang, X.X., Wu, Y.H., Shen, L.C., 2016. Influence of air CO_2 on hydrochemistry of drip water and implications for paleoclimate study in a stream-developed cave, SW China. Acta Geochim. 35 (2), 172–183.

Wang, Y., Luo, W., Zeng, G., Wang, Y., Yang, H., Wang, M., Zhang, L., Cai, X.L., Chen, J., Cheng, A., Wang, S.J., 2019. High ^{222}Rn concentrations and dynamics in Shawan cave, Southwest China. J. Environ. Radioactiv. 199–200, 16–24.

Wong, C., Banner, J.L., 2010. Response of cave air CO_2 and drip water to brush clearing in central Texas: Implications for recharge and soil CO_2 dynamics. J. Geophys. Res. Biogeosci. 115 (G4), 6291–6297.

Wood, W.W., 1985. Origin of caves and other solution openings in the unsaturated (vadose) zone of carbonate rocks: a model for CO_2 generation. Geol. 13, 822–824.

Wu, K.Y., Shen, L.C., Zhang, T.S., Xiao, Q., Wang, A.Y., 2015. Links between host rock, water, and speleothems of Xueyu Cave in Southwestern China: lithology, hydrochemistry, and carbonate geochemistry. Arab J. Geosci. 11, 8999–9013.

Vargas, R., Collins, S.L., Thomey, M.L., Johnson, J.E., Brown, R.F., Natvig, D.O., Friggens, M.T., 2012. Precipitation variability and fire in fluence the temporal dynamics of soil CO_2 efflux in an arid grassland. Global Change Biol. 18, 1401–1411.

Xu, S., 2013. Research on variations of cave air CO2 and water-gas C transfer in Xueyu Cave. Master dissertation, Southwest University (in Chinese with English abstract).

Yang, X.X., Zi, T., Chen, B., Xiang, X., Wang, X.X., 2013. Variation Characteristics of the Radon's Concentration and Protection to the Harm in the Xueyu Cave. Chongqing. Carsol. Sinica 32 (4), 472–479 (in Chinese with English abstract).

Zhang, J., Quay, P.D., Wilbur, D.O., 1995. Carbon isotope fractionation during gas–water exchange and dissolution of CO_2. Geochim. Cosmochim. Acta 59, 107–114.

Zhou, T., Yu, R., Zhang, J., Grange, H., Cassou, C., Deser, C., Hodson, D.L.R., Sanchez-Gomez, E., Keenlyside, N., Xin, X.G., Okumura, Y., Li, J., 2009. Why the Western Pacific Subtropical High has extended westward since the late 1970s. J. Clim. 22, 2199–2215.

Zhu, X., Zhang, Y., Han, D., Wen, R., Chen, B., 2004. Cave characteristics and speleothems in Xueyu Cave group, Fengdu, Chongqing city. Carsol. Sinica 23 (2), 85–90.