Response to Referee #2

Major Comments

This article uses environmental and isotope evidence from soil, stream water, and cave air to characterize the dynamics of carbon distribution in the Xueyu Cave system (China) and identify the contributions of potential reservoirs to overall cave air CO2. The work is important because it builds on a growing set of literature describing how and why cave air CO2 changes and has implications for interpretations of speleothem records used to reconstruct past climate. However, the paper is also missing key sections of the methodology, not all data is reported, and the discussion and data analysis are incomplete. The following areas require the authors' attention before publication:

1. **Manuscript grammar:** I appreciate that the authors may not be native English speakers, but sections of the manuscript are difficult to read. In particular, this hampered my understanding of the arguments the authors made in the discussion. I noted several sections that were unclear and need revision.

2. **Methodology:** Sections 2 and 3 are missing important information about sampling locations, sample collection (methodology, frequency, storage), and analysis methodology (instrumentation, standards). Measurements of $d^{13}C$ -atmosphere and $d^{13}C$ -plant material are reported but no methodology is provided.

3. **Data tables:** Not all data is reported in the tables, making it difficult to reproduce the authors' graphs and calculations. If there is not space in the main paper, data should be placed in a supplemental section or data repository.

4. **Discussion section:**

a. The mixing model employed for interpretation is not appropriate. Based on the authors' data, a model identifying CO2 sources must, at minimum, (1) include atmospheric CO2 and (2) consider the close relationship between stream- and cave air-CO2 concentration. The authors must also explain why they do not consider other potential sources listed in the introduction.

b. It is not clear to me that the November data really describe 'winter' conditions as cave air pCO2 does not drop to its 'winter baseline' until a week or two after the collection date. Do your isotope data represent baseline summer/winter cave conditions or only those during rain events?

c. The Discussion repeats information from the Results. I suggest a restructuring of the Discussion. In addition to your interpretation at this cave site the Discussion should focus on (1) comparison to previous studies of this nature and (2) the broader implications of the research for the cave community (e.g., studies of modern dripwater-calcite formation relationships and speleothem-based climate reconstructions).

Answer to the major comments:

We would like to say thanks to the referee for all his valuable comments for this paper, we added more background information in the methodology part.

1.We should say sorry that some parts of the manuscript are unreadable. We checked all the grammar problems in the revised version.

2. We added a new figure 2 in the text part to present the sampling locations, sample collection (methodology, frequency, storage), and analysis methodology (instrumentation, standards).

3. We would like to provide all the raw data in a supplementary table, and the data also exceed the excel limit, but it's difficult to list all.

4. a. From the introduction part, we know that there are several potential sources of cave air CO_2 including degassing from CO_2-rich groundwater, advection and diffusion of vadose air, human respiration, the decomposition of organic matter, deep geogenic sources etc. However, according to the seasonal variations of cave air CO_2 concentration and related stable carbon isotope, we can neglect the atmospheric CO_2. Because if atmospheric CO_2 outside the cave takes part in the mixing model, the carbon isotope should become positive with more inputs from the external air. However, this phenomenon in Xueyu Cave never happened. Besides, the human respiration and decomposition of organic matter are excluded according to the previous study (Pu et al., 2016). Though we could not exclude the carbon source from ground air, because we did not have samples from the boreholes. Actually, the soil and vadose air CO_2 show similar range of stable carbon isotopes. In general, the CO_2 from soil and vadose may hold similar values of stable carbon isotopes though ground air CO_2 shows more negative values of stable carbon isotopes according to the review from Baldini et al. (2018). We think that both are the endmembers with more negative $\delta^{13}C$.

b. Actually, the November data were collected at the transitional period when the cave air CO_2 concentration was decreasing during rain events. So it is not representative the 'winter baseline'. In the text, we use the specific months, instead of winter and summer.

c. We have written the Discussion where we added more information and widened the range of research implications.

Specific Comments

Title

A more informative title is “Constraining the source and dynamics of cave air CO2 in a cave system in Xueyudong, Southwest China through CO2 and $\delta^{13}C$ measurements”

Answer:

Thanks for your comments, we accepted it as “Constraining the sources and dynamics of cave air CO_2 in Xueyu Cave system, Southwest China through CO_2 and $\delta^{13}C$ measurements”

Abstract

Line 20

Your abstract suggests that we need studies like this one to interpret stalagmite records, but does not tell the reader how this study contributes to our understanding of how to interpret speleothem records.

Answer: We think that the monitoring of modern cave air CO_2 can help to interpret the carbon isotope proxy in speleothems. However, we never analyzed the speleothems in this manuscript. We cancelled this sentence finally.

1 Introduction

The introduction could focus more attention on why we care about CO_2 concentrations. I gather that you are interested in caves as a source of proxy records – spend more time explaining the connection between cave CO_2 and speleothem records (as well as the current gaps in knowledge). The introduction should lead the author logically to the final sentence of the section (line 85) where you state the aims of the paper.

Answer:

We arranged the introduction to make it more logical. Our logical structure: the current cave air CO_2, their sources and dynamics and carbon isotopes. We start the introduction part like this:

"In karst regions, carbon dioxide (CO_2) concentrations in epikarst (especially from soils) largely affect karst landscapes (Ford and Williams, 2007). Shallow caves are widely distributed in the terrestrial environment and contain a significant volume of underground air with high concentrations of CO_2 (Wood, 1985; Faimon et al., 2006; Bourges et al., 2014). According to Ek and Gewelt (1985) and Baldini (2010)'s reviews, the earliest measurements of CO_2 in cave air date from 1859. Modern sensors and logging techniques have been deployed to provide detailed records of CO_2, temperature and humidity in cave atmospheres (Spötl et al., 2005; Frisia et al., 2011; Bourges et al., 2014). In all cases the cave air CO_2 concentration is greater than in the open atmosphere, a proper understanding of the causes and dynamics of seasonality in cave air CO_2 is fundamental for speleothem palaeoclimatology (Fairchild and Baker, 2012)."

Line 69

Is this region dominated by C3 plants? Cite a reference for this if so.

Line 85

This section needs to be clearer. I suggest:

"The aim of this paper is to (1) identify the dynamics of carbon distribution and transfer between cave air CO2, soil air CO2, and stream CO2, and to (2) identify the contributions of major reservoirs to overall cave air CO2."

Line 88

Rephrase "The study area" to "Study area"

Line 89

More information is needed on the stream. Does it flow in/out of the cave? Or is it entirely underground? Pieces of information are available in the manuscript, but it should all be collected and put up front in this section.

Answers:

Line 69: The study area is dominated by C3 plants (evergreen broadleaf woods), the reference has been added. “The light end-member source should be located close to the roots of C3 type vegetation that is representative of evergreen broadleaf woods (Pu et al., 2016).”

Line 85: Thanks, we accepted it: “The aim of this paper is to (1) identify the dynamics of carbon distribution and transfer between cave air CO2, soil air CO2, and stream CO2 and (2) to identify the contributions of major reservoirs to overall cave air CO2.”

Line 88: Updated. “The study area” has been changed into “Study area”.

Line 89: More information about the stream has been updated, as “Most parts of the cave are narrow, deep passages (canyon passages), which are developed along strata and is composed of three levels of passages: at 233–236 m (Level I), 249–262 m (Level II) and 281–283 m (Level III), separately. A cave stream flows at the bottom level (Pu et al., 2016). There is no allogenic stream sinking underground at the head of Xueyu Cave (Pu et al., 2015). The cave stream catchment is about 8–9 km^2. Previous investigations by Zhu et al. (2004) and Pu et al. (2016) have described the hydrogeological and hydrochemical functioning of the Xueyu Cave stream. The stream is the only entrance of Xueyu Cave with an explored length of 1644 m. The discharge of the underground river ranges from 4.1 L/s in dry period to 26.6 L/s in wet period.”

Figure 1

- Make all figure subsection labels (a, b, c, d) more obvious

- Legends on subsections b and c are too small

- 1C

o Is this figure after another paper? Needs to be cited if so

o Why is ‘location of measured geological section’ in here? You did not measure any sections o Rephrase ‘River/stream and its name’ as ‘River’

o Rephrase ‘The curves that frame the Xueyu Cave’ as ‘Xueyu Cave outline’

- 1D

o The pictures of equipment are too small. Include them as separate sections of the figure or put them in the supplemental material

o The map needs a north arrow and scale bar

o The location of the stream needs to be better defined. Where does it enter/exit the cave?

- Caption

o Describe the inset in part a (the small map of China)

o Where are monitoring sites DK, LF, and MZ? They must be labeled

Answer:

We have updated the figure 1, using large-scale labels.

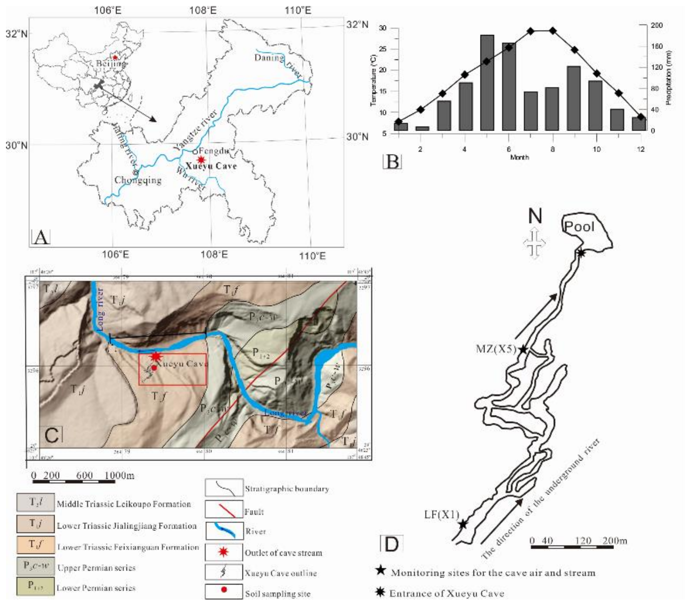


Figure 1

Fig.1C was modified from Wu et al. (2015), we put the citation notes. The ‘location of measured geological section’ should be related to another geological cross section from A to B. Here we did not use it and cancelled this part. ‘River/stream and its name’ and ‘The curves that frame the Xueyu Cave’ have been rephrased as ‘River’ and ‘Xueyu Cave outline’, respectively.

Fig.1D we would like to put the photos as supplementary material. A north arrow and scale bar have been posted. We labeled the entrance of the cave which is also the outlet of the cave stream (see the

Figure 1 above).

Fig.1A includes the maps of China and the province where Xueyu Cave is located. The sites LF and MZ correspond to X1 and X5, respectively. DK represents the MZ too. We make it consistent now.

3 Methods and Materials

All measurement types require more information so readers can assess the methodology.

For CO_2 concentration measurements:

- Automated measurements (CO_2-cave air, CO_2-soil, and CO_2-stream)

Were all measurements made with the GMM221 sensor?

o How was the sensor modified for measurement of CO_2-stream? List part numbers if direct from manufacturer.

o Who is the sensor made by? Vaisala?

o How frequently were measurements made? What time periods were measured?

o How were the sensors calibrated? How often were they calibrated?

o What was the depth of measurement for soil CO_2?

Answer:

Yes, all measurements were made with the GMM221 sensors. The original sensor is made by Vaisala.

-The measurements were performed every 15min, the reliability of sensor in the soil was calibrated on a monthly basis by the portable equipment that can insert into the soil for CO_2 measurement (portable pump-suction infrared CO_2 gas detector, measuring range 20×10^{-6}~$20,000\times10^{-6}$ pp with the precision≤±2%). Cave air CO_2 was determined with a calibrated CDU 440 CO_2 meter (measuring range 10×10^{-6}~$20,000\times10^{-6}$ ppm with the resolution of 10 ppm, made by Industrial Scientific, Pittsburgh, PA, USA). Besides, the sensor in the stream was difficult to be calibrated by another equipment, but logging data have been compared with pCO_2 that was calculated through equation: $PCO_2 = \frac{(HCO_3^-)(H^+)}{K_1 Kco_2}$.

-The depth for measurement in the soil is 40cm.

"A set of system for continuous and automatic soil CO_2 measurement with a CO_2 sensor was fixed in the soils above Xueyu Cave (Fig.2). The soil temperature and soil CO_2 concentrations were obtained from October 2014 by a composite measurement system, including a CO_2 sensor (GMM221, made by VAISALA in Finland with the resolution of 1 ppm and the range of 0-20000 ppm) and temperature and humidity sensor (AV-10T and AV-EC5 produced by AVALON, U.S.A with a resolution of 0.1 °C and 0.1%). All sensors were imbedded into the soil at the depth of 40 cm by drilling in the soil sampling site which is located about 40 m on the top with an elevation of about 300 m a.s.l. and 400 m a.s.l. in horizontal distance from the entrance of the cave (Fig.2). Above the cave, soils range from 0 to 50 cm in thickness. These soils are stony clays-rich and yellow soils that support evergreen forest and grainland (Field survey)."

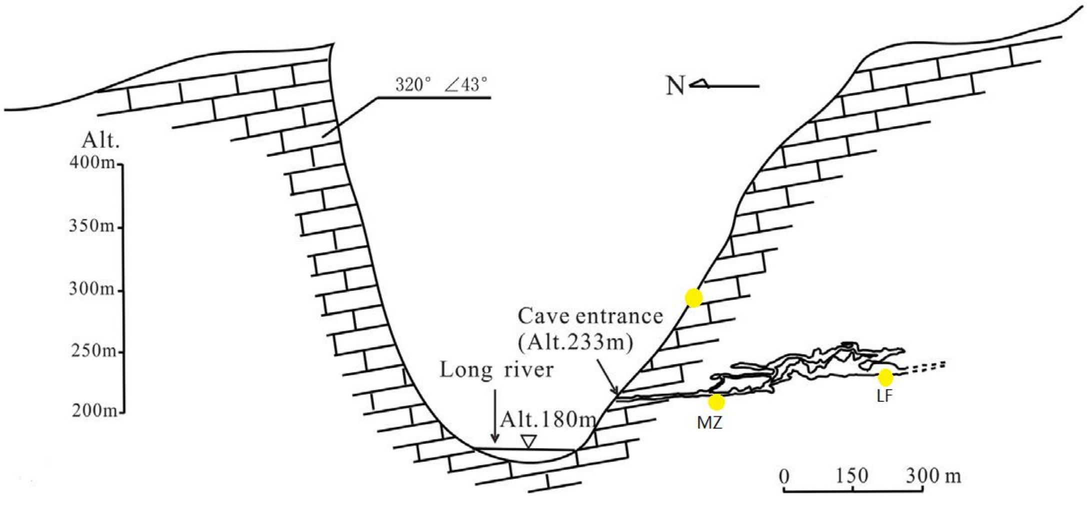


Figure 2 Cross section of Xueyu Cave passages and the sampling locations

"Two sites inside the Xueyu Cave for monitoring of cave air and the subterranean stream were located at LF (X1) and MZ (X5) (Fig. 2). GMM221 sensors with RR-1008 data logging were installed in the cave and stream to measure CO_2 concentrations. The sensor in the soil was calibrated on a monthly basis by the portable equipment that can insert into the soil for CO_2 measurement (portable pump-suction infrared CO_2 gas detector, measuring range 20×10^{-6}~$20,000\times10^{-6}$ pp with the precision≤± 2 %).Cave air CO_2 was determined with a calibrated CDU 440 CO_2 meter (measuring range 10×10^{-6}~$20,000\times10^{-6}$ ppm with the resolution of 10 ppm, made by Industrial Scientific, Pittsburgh, PA, USA). The sensor in the stream was difficult to be calibrated by another equipment, but logging data have been compared with pCO_2 that was calculated by hydrochemical parameters. To obtain the detailed hydrochemical variations, a CDTP300 multi-parameter water quality meter (made in Greenspan Corporation in Australia) was installed to record water temperature, water level, Ec and pH with resolutions of 0.01 °C, 0.01cm, 0.01 μS/cm and 0.01 pH units. Both the CO_2 measurement system and the water quality data logger were set at the same time-interval of 15 min."

- Precipitation and temperature

o List the part number(s) for the HOBO weather station

Answer:

We added in the text:

"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 HOBO weather station (H21-SYS-A)."

- Discrete samples

o All discrete samples

When were measurements made (list months, not summer/winter)?

What was the time period of sampling (two 10-day periods)

What were the frequency of measurements (1/day)?

How were samples stored and transported? How much time elapsed between collection and measurement?

How was CO2 concentration determined for the discrete samples of cave air, soil CO2, and DIC (i.e., data in Figure 6)

Answer:

o The regular sampling took place every month, but the samples for $\delta^{13}C_{CO2}$ analysis were collected in several days of November 2014 and June 2015. The measurement of gas isotope was carried out after the two concentrated sampling periods. CO_2 concentrations of discrete samples for cave air, soil CO_2 and DIC analysis were recorded by portable equipment that we mentioned above (in the method part). The air gas was absorbed into a trace gas bag by a pump from open air to avoid the influence of human respiration. The depth for soil CO_2 was at 40cm from surface and 100ml gas was collected. The quantity of soil gas is actually too small and the advection can be neglected. The methods for d^{13}C-cave air and d^{13}C-plants have been updated. The leaves of plants (Pinus massoniana Lamb., Ficus virens, Bauhinia championii) were sampled for analysis as they are dominant in the catchment.

"A steel tube with holes at the bottom end was inserted into the soil at 40cm, the top end was sealed with a plastic cap. The gas was pumped into a trace gas bag (100ml) next day. Soil and cave air/stream samples for $\delta^{13}C_{CO2}$ analyses were collected using a pump and carefully sealed in the 100ml trace gas bags, and shipped to the Southwest University in during two periods (10th-20th, June and 30th October-8th November) on a daily basis. All samples were stored at 4 ℃ before pretreatments for analysis. The measurement was performed at the Environmental Stable Isotope Lab, CAAS. The δ^{13}C of CO_2 in the bags was introduced to Delta V Plus. Internal laboratory CO_2-in-air standards were calibrated against calcium carbonate standards. DIC samples were filtered and injected in 15ml brown bottle without bubbles and 2 drops of $HgCl_2$ were added in order to prevent microbial activities, the samples then were stored at 4℃ in the portable refrigerator and in the refrigerator in the lab.

Analyses were performed using a Delta plus XL. The results were reported using V-PDB as the reference and the analysis precision was better than 0.15‰ (1σ). Plant leaves were collected in summer and winter 2014. The measurement of δ^{13}C in plants was based on vario PYRO cube elemental analyzer combined with ISOPRIME-100. The samples were combusted in a flow-type combustion flask under a continuous oxygen flow after being ground and passed through 100-mesh sieve. The oxygen gas containing the combustion products was carried by helium into successive magnesium perchlorate. CO_2 was separated through absorption column and injected into the IRMS. Lab standards were injected every 12 samples for calibration with the long standard deviation of 0.2‰."

- Analysis

o What is the methodology for d^{13}C analyses?

o What standards were used for d^{13}C measurement?

Answer:

The δ^{13}C of CO_2 in the trace gas bags was introduced to Delta V Plus. Internal laboratory CO_2-in-air standards were calibrated against calcium carbonate standards. The measurement of $\delta^{13}C$ in plants was based on vario PYRO cube elemental analyzer combined with ISOPRIME-100. Lab standards were injected every 12 samples for calibration with the long standard deviation of 0.2‰. The detailed information added in the text can be seen from the last answer.

Line 112

Be clear that samples collected for $d^{13}C$- CO_2 analyses are not the same samples as those from the continuous collection regime.

Be more precise than "in summer and winter, respectively." The samples were collected once a day during two 10 day periods in November 2014 and June 2015. Also:

- Note that these are the same collection periods for $d^{13}C$-cave air and –stream DIC
- Why were these time periods chosen?
- Why are there data gaps in the $d^{13}C$ data (e.g., DK air of Figure 3)?

Answer:

Yes, samples collected for $d^{13}C$-CO_2 analyses are not the same samples as those from the continuous collection regime.

We make the periods more specific. The main reasons to choose the periods in October 2014 are due to the rainfall events and the transitional time for cave CO_2 decreasing. In Figure 3, there are no data gaps for DK (we use MZ to refer it now), the problem in the figure is a mistake that the raw data are in wrong form, which results in no recognition. The figures can be seen in the following answers.

4 Results

Line 127

"Soil CO2" needs to be "Soil CO_2"

Line 129

Soil CO2 concentrations bottom out around 4000 ppm in November 2014

Line 130

Why do you compare soil CO2 concentration at your site to these other studies? Do they have similar climate and vegetation regimes?

Line 131

Be consistent in using “soil moisture” instead of “humidity.”

Line 134

If soil moisture controls respiration when temperature is suitable, what is occurring in summer 2015? It looks like there are time periods when pCO_2 is high but soil moisture is low (July-August).

Answer:

Line 127, corrected. “Soil CO2” needs to be “Soil CO_2”.

Line 129, corrected, “The soil concentrations ranged from 4000 ppm in December to 17000 ppm in June with the mean soil CO_2 being 8890±4576 ppm.”

Line 130, we just want to show the range of soil concentration in other places in the world.

Line 131, corrected, “soil moisture varied between 0.5% and 24.0% with the minima occurring in spring months (March 2015) and dry summer (July-August, 2015-2016)”.

Line 134, we think that soil moisture is very important. Regarding to periods when pCO_2 is high but soil moisture is low, we would like to explain it because of time lag.

Figure 2

- Make the data gaps more obvious. Note in the text where these are and why they occurred
- The x-axis is difficult to read. Label it by month instead?
- Mark the $d^{13}C$ sampling intervals on here so it is obvious where to look for the ‘zoomed-in’ sections presented in Figures 3 and 4
- 2A

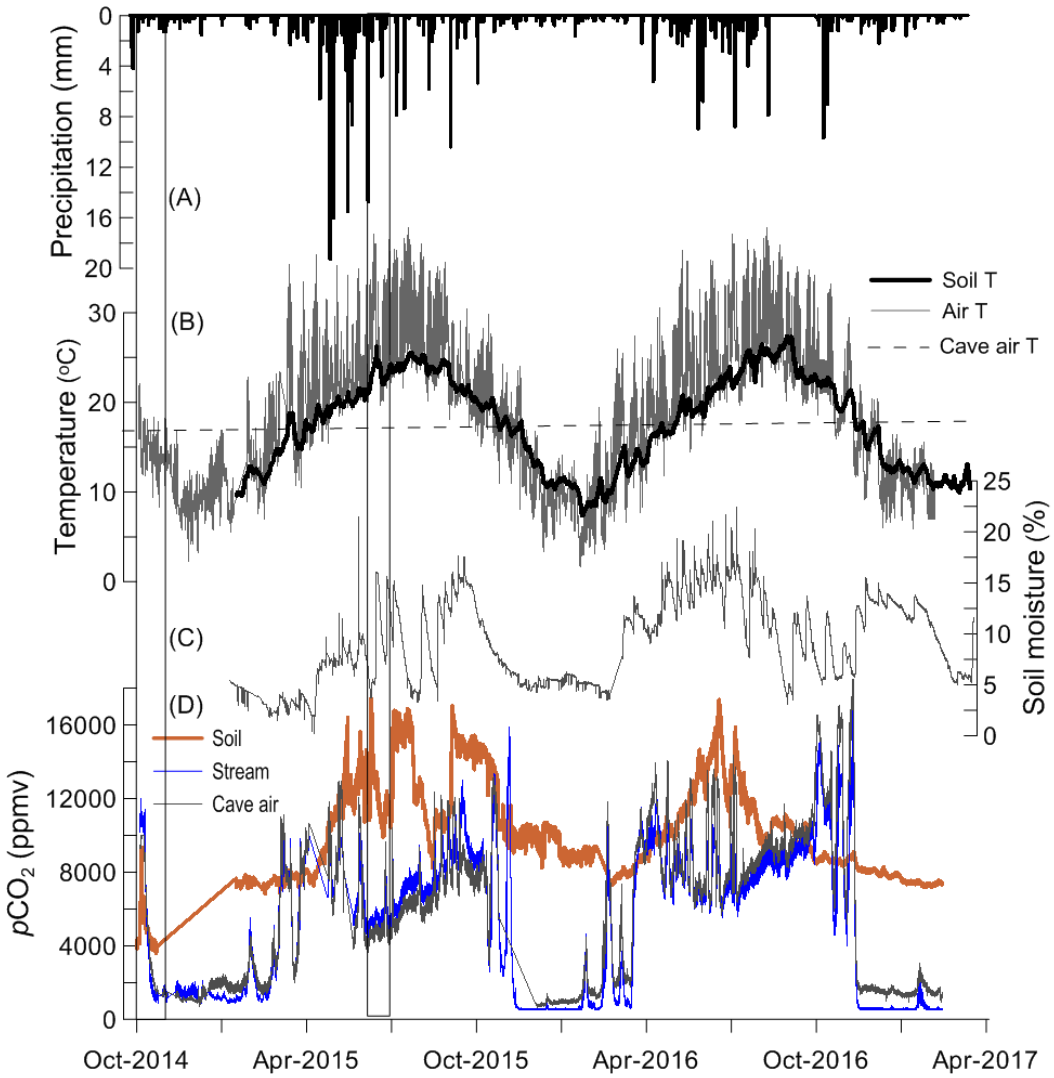
o I find the inverted y-axis confusing - precipitation should logically increase upwards

- 2B

o Include cave temperature on here as well (or at least the average)

Answer:

We updated the figure to make x axis much clearer and also to mark the intervals in Fig.3 and Fig.4. Normally, precipitation should logically increase upwards, we used inverted y axis just to save space. But this kind of layout can be found in climatic figures. Cave temperature is very stable, nearly horizontal.



Line 139

Rephrase "Cave parameters" to "Environmental measurements"

Line 140-141

- What are the "upper layer" and "lower layer?"
- The average cave temperatures are different from the average presented on line 93.
- Include cave temperature in Figure 2B
- What are the "three layers" – this is the first time this is mentioned in the text.

Answer:

Line 139, updated. We use "Environmental measurements".

Line 140-141, they are not actually "upper layer" and "lower layer?", two sites are located in the deepest cave and the entrance of the cave, respectively. I want to say the upper stream and down stream.

It’s true that the average temperatures are different from the one presented in line 93. Because the previous one refers to the cave temperature and the latter refer to temperature of cave stream water. “The cave stream temperatures at LF (the innermost part in the cave) ranges from 16.0 °C to 18.7 °C with a mean value of 16.2±0.2 °C, while from 16.3 °C to 16.8 °C at MZ (the entrance part) with a mean value of 16.6±0.1 °C.”

“three layers” –we explain in “Study area”, “Most parts of the cave are narrow, deep passages (canyon passages), which are developed along strata and is composed of three levels of passages: at 233–236 m (Level I), 249–262 m (Level II) and 281–283 m (Level III), separately.”

Line 147

Typo “stream000000”

Line 151

Does cave CO2 decrease to atmospheric levels? It looks like it does from Figure 2

Line 157

- Could low cave CO2 concentrations be related to effective transport of cave air to the outside?
- In any event, this kind of interpretation should be left to the Discussion section

Line 157-159

I’m not clear on the meaning of this sentence.

Line 162

What is “less variability?” Define this.

Answer:

Line 147, we cancelled 000000, which is additional inputs (a mistake), now as ‘stream’ in the textgg.

Line 151, cave CO_2 decreased in winter, but still three times higher than atmospheric levels.

Line 157, the transport of cave air to the outside could be a reason to explain the low concentrations of cave air CO_2. We will move this part to the discussion section.

Line 157-159, the meaning of this sentence is that there is seasonal variation of cave air CO_2, but the rainfall events could disturb the seasonality and also bring variations in cave air CO_2.

Line 162, “less variability?” means that variational magnitudes in soil CO_2 concentration are less than that in cave air and stream pCO_2.

Figure 3

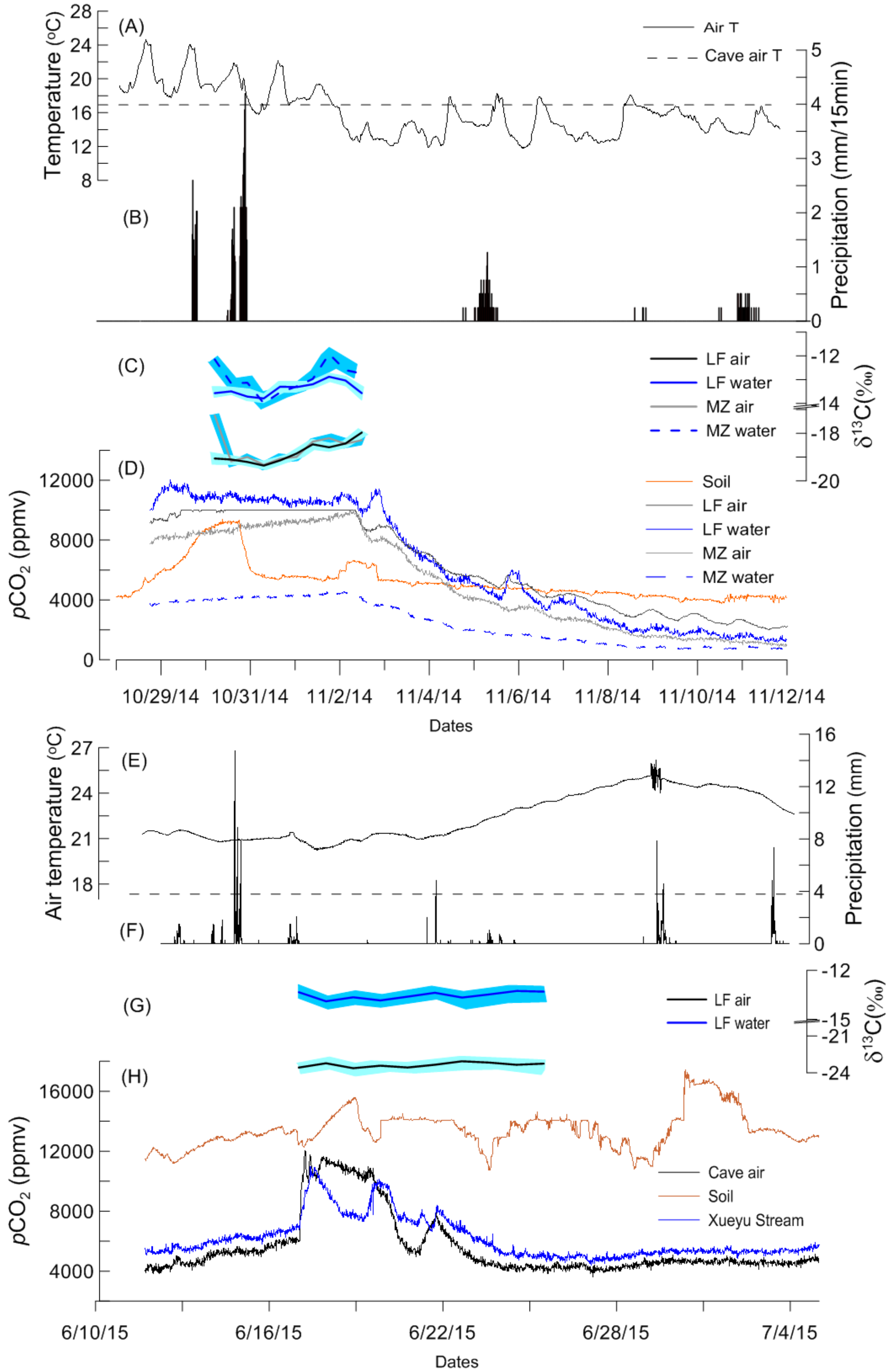
Figures 3 and 4 should be combined for ease of reference

- Precipitation should increase upwards
- Precipitation should be black, as in the other diagrams
- The same materials (e.g., CO2-cave air and $d^{13}C$-cave air) should be the same line color and type
- Include error bars on $d^{13}C$ measurements
- "LF" and "DK" are not defined before Figure 3. Where are these sites?
- Caption

o Rephrase to "during rainfall events in October-November 2014"

Answer:

We combined the Figure 3 and Figure 4, we also adjusted the colors. LF and DK labels have been explained in the method part and they are also labeled in Figure 1. The Caption was: "Variations of monitoring items (precipitation, temperature, $\delta^{13}C$ and pCO_2) during rainfall events in October-November, 2014 and June 2015."



(A)
(B)
(C)
(D)
(E)
(F)
(G)
(H)
Air T
Cave air T
Temperature (°C)
Precipitation (mm/15min)
LF air
LF water
MZ air
MZ water
δ13C(‰)
Soil
pCO2 (ppmv)
10/29/14
10/31/14
11/2/14
11/4/14
11/6/14
11/8/14
11/10/14
11/12/14
Dates
Air temperature (°C)
Precipitation (mm)
Cave air
Xueyu Stream
6/10/15
6/16/15
6/22/15
6/28/15
7/4/15

Figure 4

- The precipitation plot is labeled as air temperature

- Precipitation should increase upwards

- What are the high-frequency oscillations (6/29 and 7/22) in the cave temperature record? Were sensors replaced at this time?

- Where are the $d^{13}C$ measurements?

- The same materials (e.g., CO2-cave air and $d^{13}C$-cave air) should be the same line color and type

- Include error bars on $d^{13}C$ measurements

- Caption

o Rephrase to "during rainfall events in June-July 2014"

Answer:

The precipitation label has been changed in the above figure. The increasing temperatures (external air temperatures) during the period 6/29-7/22 are normal. The temperature in the cave is still stable (the discontinuous line). In the new figure, we only showed the period from 11^{th}, June to 24^{th}, June. Error bars of carbon isotopes were added. The caption was shown in the last Answer.

Line 168

Rephrase "4.4 The carbon isotope $d^{13}C$ in cave air and stream water" to "4.4 Carbon isotopes in cave air, stream water, and soil"

Line 169

Why cite Mattey et al. (2010) for atmospheric $d^{13}C$ measurements at the Rock of Gibraltar? There are long-term records of atmospheric CO2 that would be more directly relevant to your site

Line 170

- This is the first time that measurements of plant $d^{13}C$ are mentioned. Information about plant collection and measurement should go in the methodology

- What is the range of $d^{13}C$-soil CO2?

- Remind readers of the depth of soil CO2 collection as this is a critical parameter for interpretation.

Line 173

- Change "High-frequency" to "Daily".

- A decreasing then increasing trend is potentially seen in the 'DK water' data, but I do not see this trend in any of the other samples

Line 174

- Where is data for low/high streamflow? It is not mentioned before this point

Answer:

Line 168, rephrased.

“4.4 Carbon isotopes in cave air, stream water, and soil”

Line 169, we cited the results of atmospheric $d^{13}C$ measurements at the Rock of Gibraltar from Mattey et al. (2010) for comparison. However, as you pointed out that it is not suitable to cite in the results part. We cancelled in the revised version.

Line 170, in the updated version, we put more information about the measurement in the method section.

The range of $d^{13}C$-soil CO_2 is from -18.0‰ to -23.9‰ at 40cm depth.

“Plant leaves were collected in summer and winter 2014. The measurement of $\delta^{13}C$ in plants was based on vario PYRO cube elemental analyzer combined with ISOPRIME-100.”

Line 173, changed.

“Daily monitoring in November 2014 showed a decreasing trend and then an increasing trend of $\delta^{13}C$ values during rainfall events. The trend during the rainfall events in June 2015 was not significant.”

- In November, a decreasing then increasing trend is significant in the ‘DK water’ and ‘DK air’ data (now we use MZ), but in ‘LF water’ and ‘LF air’, the increasing trend is still significant though the decreasing trend is not obvious at the beginning (See Figure 3).

Line 174, the stream information has been added in the ‘Study area’ section. The high flow is related to periods with more rainfall events, which result in large discharge.

“A cave stream flows at the bottom level (Pu et al., 2016). There is no allogenic stream sinking underground at the head of Xueyu Cave (Pu et al., 2015). The cave stream catchment is about 8–9 km^2. Previous investigations by Zhu et al. (2004) and Pu et al. (2016) have described the hydrogeological and hydrochemical functioning of the Xueyu Cave stream. The stream is the only entrance of Xueyu Cave with an explored length of 1644 m. The discharge of the underground river ranges from 4.1 L/s in dry period to 26.6 L/s in wet period, the velocity of stream flow is 0.27 m/s on average.”

Figure 5

- Plot needs error bars

- Why are the high-resolution measurement periods not shown?

- Where are sites LF and MZ? Specify the ‘upstream’ and ‘downstream’ locations

- This data needs to be reported in a table (or in the supplemental information)

Answer:

We cancelled this figure as we have discussed the daily details in the two intervals and it is not necessary to put monthly data.

5 Discussion

Line 183

Rephrase ‘lighter $\delta^{13}C$ to ‘more negative $\delta^{13}C$.’ Values cannot be lighter or heaver. See, for example, table 2.1 in Sharp’s Stable Isotope Geochemistry (https://digitalrepository.unm.edu/unm_oer/1/). Fix throughout the manuscript.

Line 184

- The values for $d^{13}C$-cave air need to be reported in a table and the collection+analysis method need to be described in the Methodology

- ‘cave air CO2 decreased at the beginning of the rain and then increased during the process at DK site.’ There does not appear to be a strong initial decrease in the ‘LF air’ data and the ‘DK air’ data do not cover the entire time period. I suggest incorporating these observations into your interpretation

- When does the rain event start? This could be stated clearly here and be shown more clearly (vertical dotted lines?) in the graphs

Line 185

As noted above, it is not clear where the DK and LF sites are. I will not note further instances, but this needs to be addressed for the whole paper.

Line 186

Define ‘the variability of $d^{13}C$ values’

Line 187

'the d[13]C-DIC values of stream water at two sites decreased and then increased during the rainfall events.' Depending on exactly when the rainfall event occurred, this may be true for site MZ. However, I see no overall change in the values for site LF.

Line 189-191

This sentence is unclear and appears to contradict itself. Please clarify how you are interpreting the relationship between soil gas and cave air.

Answer:

Line 183, thanks for your recommendation. The sentence has been rephrased.

The sentence is "The interannual variability of carbon isotopes seems to be related to precipitation, resulting in more negative $\delta^{13}C$ values with more precipitation."

Line 184

-the background information of the collection and analysis of carbon isotopes has been put in the method section, which can be seen in answer for methodology.

-'cave air CO_2 decreased at the beginning of the rain and then increased during the process at DK (MZ) site.' There does not appear to be a strong initial decrease in the 'LF air' data and the 'LF water' data could be explained by the fractures that transport CO_2 in gas forms.

-In the above part, we explain why 'DK air' data do not cover the entire time period, just a mistake, the new Figure 3 presents the clear trend.

Line 185, sorry to bring so much troubles, we make it clear in the new Figure 1. LF and MZ sites are located in the in the deepest and the entrance of the Xueyu cave.

Line 186, 'the variability of $d^{13}C$ values' means the variational magnitude.

"Moreover, the variational magnitude of $\delta^{13}C$ values was larger at MZ than LF."

Line 187, we still support the idea that 'the $d^{13}C$-DIC values of stream water at two sites decreased and then increased during the rainfall events.' Because the $d^{13}C$-DIC decreased from -13.2‰ or -13.2‰ to -13.9‰, then increased back to 12.9 or 13.3‰. However, the trend is not so clear in the Figure 3(G) due to the large-range y axis. Actually, the variational changes of $d^{13}C$-DIC in LF and MZ are very similar.

Line 189-191, we think that stable carbon isotopes in cave air are very similar to that in soils. We think that soil gas can enter the cave space directly to show similarity of carbon isotopic values between them.

Figure 6

- The y-axes on both plots should be the same to allow easy comparison

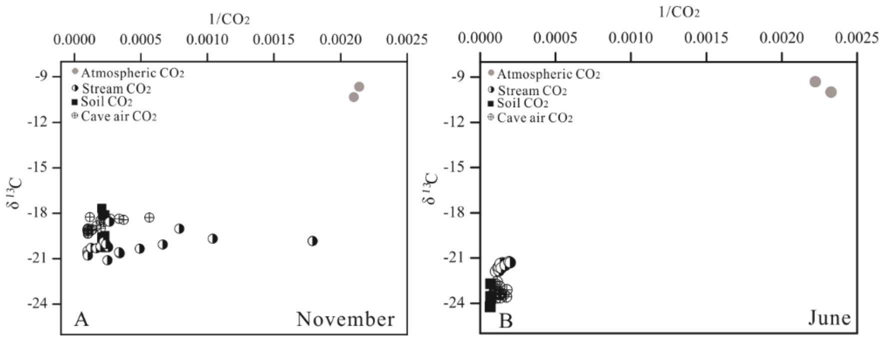
- The left plot has 'Steam CO2 degassing,' which should be 'St**r**eam'

- The 'Stream CO2 degassing' data reported in this figure appear to be d^{13}C-DIC values. Reporting these data as the d^{13}C of CO2 in equilibrium with stream DIC requires calculation of the fractionation factor between DIC and CO2

- Keep the order the same for all graphs. Show November and then June (June is shown first in Figure 6)

Answer:

We made the consistent y axes in both plots. The 'St**r**eam' has replaced the 'steam CO_2 degassing'. Other comments are all accepted for revised Figure 6, e.g. the values of d^{13}C-DIC in the figure contain the fractionation.



Line 200

'heavier d^{13}C' should be 'higher d^{13}C'

Line 200-202

- This sentence is unclear – is your intent to relate the d^{13}C of respired organic matter to d^{13}C of soil air CO2?

- Why are soil air measurements in Gibraltar relevant to your field site in SE China? Why not use your own measurements to make an estimate?

Answer:

Line 200, corrected. “Fractionation by diffusion in the pore space results in higher $\delta^{13}C$.”

Line 200-202, We cited the results from Gibraltar just to compare with our data. But now we cancelled the sentence as we think it is not necessary to cite any other data.

Line 205

I have the following issues with the discussion section:

- Why is a 2-endmember mixing model appropriate for your conceptual model? Several of your citations suggest a simple 2-endmember mixing model is inappropriate for understanding changes in cave air.

o You consider CO2 contributions from soil, stream, and human breath

o However, your introduction considers these additional sources important: atmospheric CO2, organic matter decay in the cave, magmatic/metamorphic sources

- Atmospheric air appears to be a particularly important endmember that this model does not address. The authors need to revise their data analysis to incorporate all of the information available from the dataset conceptual model of how/why cave air CO2 changes

- If >75 % of cave air CO2 is from the soil, why is there much better seasonal correlation between CO2-cave air and CO2-stream? Do your results apply only to rain events or year round?

- What causes the overall U-shape in the cave air and stream CO2 data every summer? Again, if soil CO2 is controlling cave air CO2, why is this signal not visible in the soil CO2 data?

- It is unclear to me from the discussion whether you think the soil, stream, or both are controls on cave air CO2. However, in the conclusions you definitively identify soil contributions as most important. Your position should be made clearer and should be supported by the isotope and CO2 concentration data.

- You briefly describe that $d^{13}C$-DIC of the stream is controlled by flow rate (Line 174). Is there a relationship between stream flow rate and cave air CO2 or $d^{13}C$?

- The discussion repeats results and repeats itself in sections. It should be edited for clarity and structure. I suggest the following general structure:

o Interpretation of what is occurring at Xueyu Cave

o Comparison to other studies of this nature o Implications for developing paleoclimate records from speleothems (here and elsewhere)

Answer:

Line 205

-Two endmembers are simple. Though we introduced more sources, but from the filed monitoring, the magmatic/metamorphic sources and human breath can be excluded. The magmatic/metamorphic sources have very positive isotopic values. We do not include the atmospheric CO_2 though it seems more reasonable to assume atmospheric CO_2 brings low CO_2 concentration in many caves. The reason is that if atmospheric CO_2 makes more contribution, the cave air CO_2 would show higher values of $d^{13}C$ and low CO_2 concentration in November (which can be seen in the Figure 6A). The human respiration has been excluded as the previous monitoring from Xu et al. found that there is no linear relationship between the number of tourists and the carbon concentrations in the cave air. At last, the proportion from organic matter decay in the cave can be neglected too. In the Xuyue Cave environment, the organic matters are not abundant, even if they work as a source, the contribution will be very limited.

- Normally, atmospheric air appears to be a particularly important endmember in other caves. However, the sharply decreasing trend did not go along with increased carbon isotopic values, showing no marked influence from atmospheric CO_2 that has low CO_2 concentration but higher isotopic values.

-75 % of cave air CO_2 is from the soil, which makes the background of cave air CO_2, the close relationship between CO_2-cave air and CO_2-stream can be consider as the equilibrium between the air and water. The contribution calculation is based on two rainfall events, which confirms the contributions from both stream degassing and the diffusion of overlying soil or fractures. Though our results are observed from rainfall processes, the implication can be extended. Rainfall processes can reveal the changes in short period, which allow us to explore what happens inside the system.

- The overall U-shape in the cave air every summer (April-November) can be considered as accumulation of CO_2, not only related to soil CO_2 source, but also the transport way and the cave geometry. We think that the abundant soil concentrations can be dissolved in the infiltration water and finally to increase CO_2 in the stream. The degassing of stream CO_2 as well as the gaseous soil CO_2 entering the cave through fissures and fractures accumulate in the cave. The U-shape in summer can be also explained that most of karst spaces are filled with water, providing a relatively sealed environment. This environment maintains the stable CO_2 concentrations except during rainfall events. Soil CO_2 shows high correlations to soil temperature and soil moisture, no U-shape concentration.

- It is clear that the soil, stream, both are controlling on cave air CO_2 variations, which can be seen from the consistent variations of cave CO_2 and stream CO_2. And their contributions can be calculated from carbon isotopes.

-d$^{13}C_{DIC}$ variations are mainly controlled by sources, the interaction between water and rock. We do not know whether there is linear relationship between stream flow rate and cave air CO_2 because we did not measure corresponding flow rate.

-Thanks for your suggestion. The discussion not just repeats results, because we wanted to make the result part and the discussion part to be consistent. But we will adjust the structure to separate discussion well from the results:

5.1 Variations in cave air CO_2 in Xueyu Cave

We started with "The sharpness of the transitions during the seasons demonstrates that it responded immediately to the changes of external environments. The cave CO_2 values are comparable with the values in some other karst caves reported by Sánchez-Moral *et al.* (1999) for the Altamira Cave (6000 ppm), lower than extreme 60000 ppm (Benavente *et al.,* 2015). A high-frequency monitoring in November 2014 and June 2015 showed the detailed pCO_2 changes in the cave air and stream, and carbon isotopes during rainfall events. In November, low cave air CO_2 concentrations indicated the more open system for gas exchange or low-concentration recharge was predominant. During rainfall events in June, cave air CO_2 concentrations increased due to the increased high-CO_2 stream flow. Soil CO_2 concentrations did not show abrupt variations (Fig. 3). The similarity of variations in soil, cave air and stream CO_2 concentrations indicated that there are correlations between them. There are significant correltations between stream pCO_2 and cave air CO_2, especially at LF site (R^2=0.95, $p<0.01$). The correlation between soil CO_2 and soil temperature is significant too…"

"5.2 $\delta^{13}C$ isotope tracing the sources and their contributions to cave air CO_2

The $\delta^{13}C$ values of the cave stream generally showed seasonal fluctuations with the lowest values occurring in June and the highest values in November months (Fig. 5). It was consistent with previous observation that winter samples with relatively low pCO_2 were isotopically heavy (Spötl *et al.*, 2005). In October, the monitoring results of rainfall events showed that $\delta^{13}C$ values of the stream DIC and cave air CO_2 decreased at the beginning of the rain and then increased during the process at MZ site (near the entrance of the cave). However, at LF site (upstream) those $\delta^{13}C$ values were in an increasing trend (Fig. 3). Moreover, the variational magnitude of $\delta^{13}C$ values was larger at MZ than at LF."

Line 211

Is $d^{13}C$ -soil referring to soil organic matter or soil air CO2? If it refers to soil air CO2, keep in mind that $d^{13}C$ -soil air CO2 changes with depth. Justify using a single value.

Answer:

$d^{13}C$-soil refers to soil air, we always collected samples at the same depth at 40cm.

Line 211-212

- A citation and explanation are needed for the '$d^{13}C$-CO2 from degassing -21.4 per mil due to isotopic fraction of 8 per mil.' Converting from DIC to the CO2 in equilibrium with it is not a straightforward connection for unfamiliar readers
- 'fraction' should be 'fractionation'

Answer:

Line 211-212, more explanation about background of stream degassing has been added.

"The average values of $\delta^{13}C_{soil,}$ $\delta^{13}C_{DIC}$ in June were -23.9‰ and -13.4‰, respectively, the $\delta^{13}C_{CO2}$ from stream degassing -is 21.4‰ due to the fact that equilibrium isotopic fractionation of 8‰ is between liquid water and vapour at the air–water interfaces (DIC and CO_2) (Zhang et al., 1995)."

'fraction' was changed to 'fractionation'.

Line 213

I do not get the same output from your model using the values in Table 1

Line 214

Same as line 211-212 – a citation and explanation are needed for the fractionation between DIC-CO2

Line 219

'light $d^{13}C_{CO2}$' should be 'more negative $d^{13}C$'

Line 228

How does water degassing CO_2 not precipitate calcite?

Answer:

Line 213, we checked that there was mismatch between the Table and the text. We should have put the isotopic values of gas from stream not the $d^{13}C_{DIC}$ in aquatic form (considering the fractionation).

Line 214, changed, "The average values of $\delta^{13}C_{soil}$, $\delta^{13}C_{DIC}$ in November were -18.3‰ and -12.2‰, respectively (the $\delta^{13}C_{CO2}$ from stream degassing was -20.9‰ considering carbon isotopic fractionation of 8‰ between water and gas)."

Line 219, corrected, "The more negative $\delta^{13}C_{co2}$ in the Xueyu cave air are close to −23.3 ‰ in summer, , discarding the deep CO_2 and the human respired CO_2 as sources."

Line 228, normally, the degassing companies with precipitating calcite. We just said that the precipitation is not significant.

Figure 7

- How is this model different from those proposed/used by other you cite? Might be better just to cite/describe the model.

- I did not understand that the river flowed from inside the cave to outside the cave until this figure – this information should be up front in the study area description

Answers:

This figure was abstracted from our study area. We know that there are other models in previous studies, however, few figures with suitable streams. And we think this figure can help readers to understand the main text better. More information about the stream we also explained in the 'Study area' section.

Line 277-278

This sentence is unclear: what does 'resulting in warm surface air into the cave companying with rainfall events' refer to?

Line 283

The terms ‘S-pCO2’ and ‘C-pCO2’ are confusing. I recommend not using them

Line 287

Delete the final sentence of this paragraph.

Answer:

Line 277-278, we should have descripted it better, I mean that high-temperature water infiltration in summer always accompany with the rainfall events. “The stream running through Xueyu Cave increased its discharge dramatically in the wet season, companying with increased water temperature during storm events.”

Line 283, we accept the comments to avoid using the ‘S-pCO2’ and ‘C-pCO2’. Instead, we use $pCO_{2(cave\ air)}$ and $pCO_{2(stream)}$.

Line 287, the sentence has been cancelled.

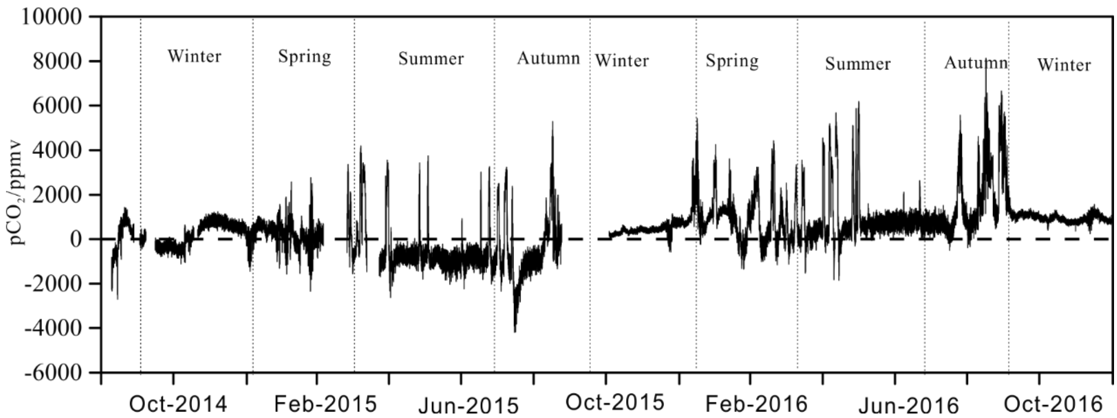
Figure 8

- Mark months of the year on the x-axis, not the 20th of each month

- Mark when the cave switches between summer and winter modes

Answer:

We accept the suggestions to mark the months and transitions.



Line 290

This section largely repeats what has been already said

Line 303

Where is the CO2 data for stream water at the two LF and DK sites? We are only presented with one dataset

Line 305

- This section is difficult to understand. I'm not sure what I am supposed to get out of it.

- Define the metrics 'before rain' and 'after rain,' response time, intensity, and equilibrium time

Line 309

-'in consistent' should be 'inconsistent'

Lines 311-316 do not seem to add to the section. If you are reporting results, they should be in the Results section

Answer:

Line 290, we cancelled the repeated part.

Line 303, the pattern between the air and water is similar in LF and DK, that is why we only put one (LF site) to present the trend.

Line 305, we want to find if there is relationship between cave air pCO_2 the intensity and amount of rainfall events. 'before rain' and 'after rain' just the time that we collected the data. Response time and intensity refer to the lasting time of the rainfall events and their intensity, equilibrium time refers to the time it takes to get balance between the stream and cave air CO_2.

Line 309, accepted, 'inconsistent' in the revised version.

"The accumulated rainfall amount in 2015 was higher than that in 2016, which was inconsistent with the general increasing trend of cave air pCO_2 variations during the two years."

6 Conclusions

Line 331

Measurements were made two times in the year, not 'throughout the year'

Line 322

'^{13}C' should be '$\delta^{13}C$'

Line 333 The stated percentage contributions do not match Table 1

Answer:

Line 331, ok, we accepted this expression, that in two intervals not throughout the year. 'throughout the year' has been cancelled.

Line 332, corrected. "$\delta^{13}C_{DIC}$ showed higher values in winter but lower values in summer."

Line 333, the table and the text are checked to make sure that the information is consistent.

Table 1

- The time transgressive values do not give the reader the idea that a single value of d[13]C -soil CO2 is assumed for the whole time period.

- The table should include the d[13]C values for cave air, stream DIC, and calculated CO2 in equilibrium with stream DIC

Answer:

We added the value of $d^{13}C$-soil CO_2 in the new table.

Table1 $\delta^{13}C$ 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 soils* (%)	
	MZ	LF	MZ	LF	MZ	LF	MZ	LF
2014/10/30-09:00	-18.2	-19.1	-10.6	-12.9	-18.6	-20.9	59.2	63.9
2014/10/31-09:00	-19.2	-19.1	-12.2	-12.8	-20.2	-20.8	48.2	61.3
2014/11/1-09:00	-19.0	-19.2	-12.2	-13.0	-20.2	-21	56.2	60.7
2014/11/2-09:00	-19.3	-19.4	-12.1	-13.1	-20.1	-21.1	57.9	56.7
2014/11/3-09:00	-19.1	-19.1	-12.6	-12.6	-20.6	-20.6	60.1	56.9
2014/11/4-09:00	-19.0	-18.9	-12.3	-12.6	-20.3	-20.6	58.1	68.3
2014/11/5-09:00	-18.3	-18.5	-12.1	-12.5	-20.1	-20.5	84.4	82.6
2014/11/6-09:00	-18.4	-18.6	-11.0	-12.2	-19	-20.2	61.8	74.2
2014/11/7-09:00	-18.4	-18.4	-11.7	-12.3	-19.7	-20.3	75.5	82.8
2014/11/8-09:00	-18.3	-18.4	-11.8	-12.9	-19.8	-20.9	85.8	88.2
Mean values	-18.7	-18.9	-11.9	-12.7	-19.9	-20.7	64.7	69.5
2015/6/15-09:00	-23.4	-23.6	-13.2	-13.3	-21.2	-21.3	82.4	89.7
2015/6/16-09:00	-23.3	-23.2	-13.4	-13.9	-21.4	-21.9	77.9	68.6
2015/6/17-09:00	-23.4	-23.6	-13.5	-13.6	-21.5	-21.6	81.6	90.6
2015/6/18-09:00	-23.4	-23.4	-13.9	-13.8	-21.9	-21.8	79.3	79.4

2015/6/19-09:00	-23.4	-23.6	-13.5	-13.6	-21.5	-21.6	81.2	88.1
2015/6/20-09:00	-23.4	-23.3	-13.0	-13.2	-21	-21.2	85.2	81.7
2015/6/21-09:00	-23.3	-23.1	-13.4	-13.7	-21.4	-21.7	80.3	64.5
2015/6/22-09:00	-22.7	-23.2	-12.8	-13.5	-20.8	-21.5	63.7	71.9
2015/6/23-09:00	-22.9	-23.3	-13.1	-13.3	-21.1	-21.3	65.1	81.1
2015/6/24-09:00	-23.4	-23.3	-12.9	-13.3	-20.9	-21.3	86.0	77.0
Mean values	-23.3	-23.4	-13.3	-13.5	-21.3	-21.5	78.3	79.3

*The average $\delta^{13}C$ values of soils in November and June are 18.0‰ and 23.9‰ respectively.

Table 2

- This table does not mean much to the reader as the parameters are not defined (intensity, response time, equilibrium time)

- This table can be moved to the supplemental information

Answer:

We moved this part to the supplemental material.

References:

Baldini, J. U. L., Bertram, R. A., & Ridley, H. E., (2018). Ground air: a first approximation of the earth's second largest reservoir of carbon dioxide gas. Science of The Total Environment, 616-617, 1007-1013.

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. Journal of Asian Earth Sciences, 119(2), 167-178.

Xu, S.Q., (2013). Thesis of master, Southwest University, China.