

## 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 CO<sub>2</sub>. The work is important because it builds on a growing set of literature describing how and why cave air CO<sub>2</sub> 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 d13C-atmosphere and d13C-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 CO<sub>2</sub> sources must, at minimum, (1) include atmospheric CO<sub>2</sub> and (2) consider the close relationship between stream- and cave air-CO<sub>2</sub> 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 pCO<sub>2</sub> 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 would check all the grammar problems in the revised version.

2. We added a new figure and also 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 data in supplementary table.

4. a. From the introduction part, we know that there are several potential sources of cave air CO<sub>2</sub> including degassing from CO<sub>2</sub>-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<sub>2</sub> concentration and related stable carbon isotope, we can neglect the atmospheric CO<sub>2</sub>. Because if there atmospheric CO<sub>2</sub> outside the cave takes part in the mixing model, the carbon isotope should become positive with more inputs from the external air. However, in Xueyu Cave, we never found this phenomenon. 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<sub>2</sub> show similar range of stable carbon isotopes. In general, the CO<sub>2</sub> from soil and vadose may hold similar values of stable carbon isotopes though ground air CO<sub>2</sub> shows more negative values of stable carbon isotopes according to the review from Baldini et al. (2018).

b. Actually, the November data were collected at the transitional period when the cave air CO<sub>2</sub> concentration was decreasing during rain events. So it is not representative the 'winter baseline'.

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 CO<sub>2</sub> in a cave system in Xueyudong, Southwest China through CO<sub>2</sub> and δ<sup>13</sup>C measurements"

**Answer:** Thanks for your comments, we accepted it as "Constraining the sources and dynamics of cave air CO<sub>2</sub> in Xueyu Cave system, Southwest China through CO<sub>2</sub> and δ<sup>13</sup>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<sub>2</sub> 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<sub>2</sub> concentrations. I gather that you are interested in caves as a source of proxy records – spend more time explaining the connection between cave CO<sub>2</sub> 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. We focused on explaining the sources and influencing factors of cave air CO<sub>2</sub> in previous version.

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 CO<sub>2</sub>, soil air CO<sub>2</sub>, and stream CO<sub>2</sub>, and to (2) identify the contributions of major reservoirs to overall cave air CO<sub>2</sub>.”

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.

**Answer:**

Line 69: The study area is dominated by C3 plants (evergreen broadleaf woods), the reference has been added.

Line 85: Thanks, we accepted it.

Line 88: Updated.

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 can be divided into three broad levels at 233–236 m (Level I), 249–262 m (Level II) and 281–283 m. (Level III) above sea level. A cave stream flows only in 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<sup>2</sup>. 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 cave 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.

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'.

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.

Fig.1A include 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<sub>2</sub> concentration measurements:

- Automated measurements (CO<sub>2</sub>-cave air, CO<sub>2</sub>-soil, and CO<sub>2</sub>-stream)
  - Were all measurements made with the GMM221 sensor?
  - o How was the sensor modified for measurement of CO<sub>2</sub>-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<sub>2</sub>?

**Answer:**

Yes, all measurements were made with the GMM221 sensor. The original sensor is made by Vaisala. But the equipment has been optimized when used in the stream.

-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<sub>2</sub> measurement (portable pump-suction infrared CO<sub>2</sub> gas detector, measuring range  $20 \times 10^{-6} \sim 20,000 \times 10^{-6}$  pp with the precision  $\leq \pm 2\%$ ). Cave air CO<sub>2</sub> was determined with a calibrated CDU 440 CO<sub>2</sub> meter (measuring range  $10 \times 10^{-6} \sim 20,000 \times 10^{-6}$

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  $p\text{CO}_2$  that was calculated by

$$p\text{CO}_2 = \frac{(\text{HCO}_3^-)(\text{H}^+)}{K_1 K_{\text{CO}_2}}$$

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

- Precipitation and temperature

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

**Answer:**

Regarding to "Precipitation and temperature", I do not understand the "part number(s) for the HOBO weather station", do you mean the 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  $\text{CO}_2$  concentration determined for the discrete samples of cave air, soil  $\text{CO}_2$ , and DIC (i.e., data in Figure 6)

**Answer:**

o The regular measurements of hydrochemistry, samples for  $d^{13}\text{C}_{\text{DIC}}$  analysis took place every month but samples for  $d^{13}\text{C}_{\text{soil}}$  and  $d^{13}\text{C}_{\text{cave air}}$  were collected only at the two periods (October-November 2014 and June-July 2015) on a daily basis. DIC Samples were stored at  $4^\circ\text{C}$  in the portable refrigerator and in the refrigerator in the lab. The

gas samples were kept at the room temperature ( $10\text{-}25^\circ\text{C}$ ).

o The measurement of gas isotope took place after the two concentrated sampling periods. Whereas the  $d^{13}\text{C}_{\text{DIC}}$  was analyzed every 6 months.  $\text{CO}_2$  concentrations of discrete samples for cave air, soil  $\text{CO}_2$  and DIC analyses were recorded by portable equipment that we mentioned above (in the method part).

o The air gas was absorbed into a trace gas bag by a pump from open air to avoid the influence of human respiration. While the measurement of soil was more complex. 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.

o The depth 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.

o Water samples for  $d^{13}\text{C}_{\text{DIC}}$  analysis were filtered and injected in 15ml brown bottles. Two drops of  $\text{HgCl}_2$  were added in order to prevent microbial activities. Then the bottle was sealed to make sure there were no bubbles inside. The samples were stored at

4°C in the refrigerator until analysis. All processes followed the standards from the lab.

o The methods for  $\delta^{13}\text{C}$ -cave air and  $\delta^{13}\text{C}$ -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.

- Analysis

o What is the methodology for  $\delta^{13}\text{C}$  analyses?

o What standards were used for  $\delta^{13}\text{C}$  measurement?

**Answer:**

The measurement was performed at the Environmental Stable Isotope Lab, CAAS. The  $\delta^{13}\text{C}$  of  $\text{CO}_2$  in the trace gas bags was introduced to Delta V Plus. Internal laboratory  $\text{CO}_2$ -in-air standards were calibrated against calcium carbonate standards. The samples for DIC were stored at 4 degrees Celsius in the fridge until analyses which 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‰ ( $1\sigma$ ). Plant leaves were collected in summer and winter 2014. The measurement of  $\delta^{13}\text{C}$  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.  $\text{CO}_2$  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‰.

Line 112

Be clear that samples collected for  $\delta^{13}\text{C}$ -  $\text{CO}_2$  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  $\delta^{13}\text{C}$ -cave air and –stream DIC

- Why were these time periods chosen?

- Why are there data gaps in the  $\delta^{13}\text{C}$  data (e.g., DK air of Figure 3)?

**Answer:**

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  $\text{CO}_2$  decreasing. In Figure 3, there are no data gaps for DK. The reason should be explained that in the excel some samples in DK lack of “-”, resulting in a no continuous line for DK. We update the figure.

#### 4 Results

Line 127

“Soil  $\text{CO}_2$ ” needs to be “Soil  $\text{CO}_2$ ”

Line 129

Soil CO<sub>2</sub> concentrations bottom out around 4000 ppm in November 2014

Line 130

Why do you compare soil CO<sub>2</sub> 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<sub>2</sub> is high but soil moisture is low (July-August).

**Answer:**

Line 127, corrected.

Line 129, corrected

Line 130, we just want to show the range of soil concentration.

Line 131, corrected

Line 134, we think that soil moisture is very important. Regarding to periods when pCO<sub>2</sub> 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 δ<sup>13</sup>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 will improve 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, but we can put it in the new version.

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:**

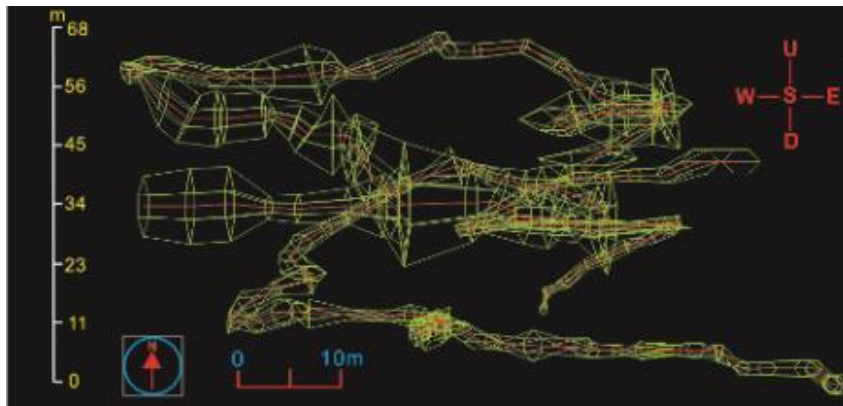
Line 139, updated.

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.

It's true that the average cave temperatures are different from the one presented in line 93. Because the previous one uses the general average value while the latter averages are based on the new records from 2014-2016. We will make it consistent in the new version.

“three layers” –we explain in “Study area”, it is as following figure



The three-lay structure of Xueyu cave

Line 147

Typo “stream000000”

Line 151

Does cave CO<sub>2</sub> decrease to atmospheric levels? It looks like it does from Figure 2

Line 157

- Could low cave CO<sub>2</sub> 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, cancelled as ‘stream’.

Line 151, cave CO<sub>2</sub> 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<sub>2</sub>. 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<sub>2</sub>, but the rainfall events could disturb the seasonality and also bring variations in cave air CO<sub>2</sub>.

Line 162, “less variability?” means that variational magnitudes in soil CO<sub>2</sub> concentration are less than that in cave air and stream pCO<sub>2</sub>.

### 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., CO<sub>2</sub>-cave air and d<sup>13</sup>C-cave air) should be the same line color and type
- Include error bars on d<sup>13</sup>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 will combine the two figures and adjusted the colors, direction and redraw it with error bars. LF and DK labels have been explained in the method section.

**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<sup>13</sup>C measurements?
- The same materials (e.g., CO<sub>2</sub>-cave air and d<sup>13</sup>C-cave air) should be the same line color and type
- Include error bars on d<sup>13</sup>C measurements
- Caption
  - o Rephrase to “during rainfall events in June-July 2014”

**Answer:**

The precipitation label has been changed and about the y axis, we will adjust it. The high temperatures during the period 6/29-7/22 are normal because the air temperatures here are not the inside cave temperatures. d<sup>13</sup>C measurements in details will be added. We also accept other detailed comments, including to update the colors, caption and add error bars.

Line 168

Rephrase “4.4 The carbon isotope d<sup>13</sup>C in cave air and stream water” to “4.4 Carbon isotopes in cave air, stream water, and soil”

Line 169

Why cite Matthey et al. (2010) for atmospheric d<sup>13</sup>C measurements at the Rock of Gibraltar? There are long-term records of atmospheric CO<sub>2</sub> that would be more directly relevant to your site

Line 170

- This is the first time that measurements of plant d<sup>13</sup>C are mentioned. Information about plant collection and measurement should go in the methodology
- What is the range of d<sup>13</sup>C-soil CO<sub>2</sub>?
- Remind readers of the depth of soil CO<sub>2</sub> collection as this is a critical parameter for interpretation

**Answer:**

Line 168, rephrased.

Line 169, to cite Matthey et al. (2010) for atmospheric  $\delta^{13}\text{C}$  measurements at the Rock of Gibraltar is just to say that our results are very similar the value observed in the Rock of Gibraltar. Anyway, it is not so much matter.

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

The range of  $\delta^{13}\text{C}$ -soil  $\text{CO}_2$  is from -18.0‰ to -23.9‰ at 40cm depth.

Line 173, changed.

- A decreasing then increasing trend is significant in the 'DK water' and 'DK air' data, but in 'LF water' and 'LF air', the increasing trend is still significant though the decreasing trend is not obvious.

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.

### **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 will update the figure with error bars and a new table in the revised version. The high-resolutions periods are shown in Fig. 3 and 4, so we just showed the monthly data in Fig.5.

Locations of LF and MZ(DK) can be found in Fig.1.

## **5 Discussion**

Line 183

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

Line 184

- The values for  $\delta^{13}\text{C}$ -cave air need to be reported in a table and the collection+analysis method need to be described in the Methodology
- 'cave air  $\text{CO}_2$  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 d13C values'

Line 187

'the d13C-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.

Line 184, the background information has been put in the method section. 'cave air CO<sub>2</sub> 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 'LF water' data could be explained by the fractures that transport CO<sub>2</sub> in gas forms. In the above part, we explain why 'DK air' data do not cover the entire time period. Actually, the trends in DK water and air are very similar. The rainfall events will be added in the new Fig.5.

Line 185, sorry to bring so much troubles, we make it clear in the Figure 1. DK and LF sites are X1 and X5, we will check through all the text in the revised version.

Line 186, 'the variability of d<sup>13</sup>C values' means the variational magnitude.

Line 187, the answer is similar to the one in Line 184.

Line 189-191, we would like to say that stable carbon isotopes in cave air are very similar to that in soils. During the rainfall events, the variations can reflect the movement of soil CO<sub>2</sub>.

### **Figure 6**

- The y-axes on both plots should be the same to allow easy comparison
- The left plot has 'Stream CO<sub>2</sub> degassing,' which should be 'Stream'
- The 'Stream CO<sub>2</sub> degassing' data reported in this figure appear to be d13C-DIC values. Reporting these data as the d13C of CO<sub>2</sub> in equilibrium with stream DIC requires calculation of the fractionation factor between DIC and CO<sub>2</sub>
- 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 'Stream' has replaced the 'stream CO<sub>2</sub> degassing'. Other comments are all accepted for revised Figure 6.

Line 200

'heavier d13C' should be 'higher d13C'

Line 200-202

- This sentence is unclear – is your intent to relate the d13C of respired organic matter to d13C of soil air CO<sub>2</sub>?
- 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.

Line 200-202, we use our monitoring data for estimation. We cite the results from Gibraltar just to compare with our 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 CO<sub>2</sub> contributions from soil, stream, and human breath
  - o However, your introduction considers these additional sources important: atmospheric CO<sub>2</sub>, 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 CO<sub>2</sub> changes
- If >75 % of cave air CO<sub>2</sub> is from the soil, why is there much better seasonal correlation between CO<sub>2</sub>-cave air and CO<sub>2</sub>-stream? Do your results apply only to rain events or year round?
- What causes the overall U-shape in the cave air and stream CO<sub>2</sub> data every summer? Again, if soil CO<sub>2</sub> is controlling cave air CO<sub>2</sub>, why is this signal not visible in the soil CO<sub>2</sub> data?
- It is unclear to me from the discussion whether you think the soil, stream, or both are controls on cave air CO<sub>2</sub>. 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 CO<sub>2</sub> concentration data.
- You briefly describe that δ<sup>13</sup>C-DIC of the stream is controlled by flow rate (Line 174). Is there a relationship between stream flow rate and cave air CO<sub>2</sub> or δ<sup>13</sup>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 field monitoring, the magmatic/metamorphic sources and human breath can be excluded. We do not include the atmospheric CO<sub>2</sub> though it seems more reasonable to assume atmospheric CO<sub>2</sub> brings low CO<sub>2</sub> concentration in many caves. The reason is that if atmospheric CO<sub>2</sub> makes more contribution, the cave air CO<sub>2</sub> should show higher values of δ<sup>13</sup>C and low CO<sub>2</sub> concentration in November (which can be seen in the Figure 6).

75 % of cave air CO<sub>2</sub> is from the soil, which makes the background of cave air CO<sub>2</sub>, the close relationship between CO<sub>2</sub>-cave air and CO<sub>2</sub>-stream can be considered as the equilibrium between the air and water. The contribution calculation is based on rainfall events.

Soil CO<sub>2</sub> shows high correlations to temperature and soil moisture. The overall U-

shape in the cave air and stream CO<sub>2</sub> data every summer can be considered as accumulation of CO<sub>2</sub>, not only related to soil CO<sub>2</sub> source, but also the transport way and the cave geometry. We have a conclusion that soil and stream are controls on cave air CO<sub>2</sub> based on isotope similarity and the consistent change of stream-cave air CO<sub>2</sub>.

d<sup>13</sup>C<sub>DIC</sub> variations are mainly controlled by sources, the interaction between water and rock.

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. We will adjust the structure to separate discussion well from the results.

Line 211

Is d<sup>13</sup>C-soil referring to soil organic matter or soil air CO<sub>2</sub>? If it refers to soil air CO<sub>2</sub>, keep in mind that d<sup>13</sup>C-soil air CO<sub>2</sub> changes with depth. Justify using a single value.

**Answer:**

d<sup>13</sup>C-soil refers to soil air, we always collected samples at the same depth.

Line 211-212

- A citation and explanation are needed for the 'd<sup>13</sup>C-CO<sub>2</sub> from degassing -21.4 per mil due to isotopic fraction of 8 per mil.' Converting from DIC to the CO<sub>2</sub> 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.

'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-CO<sub>2</sub>

Line 219

'light d<sup>13</sup>Cco<sub>2</sub>' should be 'more negative d<sup>13</sup>C'

Line 228

How does water degassing CO<sub>2</sub> not precipitate calcite?

**Answer:**

Line 213, we checked that there was mismatch between the Table and the text. We should have put the contribution from stream contribution not the d<sup>13</sup>C<sub>DIC</sub> (considering the fractionation).

Line 214, 219, corrected.

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. There are other models in previous studies, however, few figures with streams. So 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 accompanying with rainfall events' refer to?

Line 283

The terms 'S-pCO<sub>2</sub>' and 'C-pCO<sub>2</sub>' are confusing. I recommend not using them

Line 287

Delete the final sentence of this paragraph

#### Answer:

Line 277-278, we should have described more better, I mean that high-temperature water infiltration in summer always accompany with the rainfall events.

Line 283, we accept the comments to avoid using the 'S-pCO<sub>2</sub>' and 'C-pCO<sub>2</sub>'. Instead, we use pCO<sub>2(cave air)</sub> and pCO<sub>2(stream)</sub>.

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 CO<sub>2</sub> 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
- Lines 311-316 do not seem to add to the section. If you are reporting results, they should be in the Results section

Line 309

'in consistent' should be 'inconsistent'

#### Answer:

Line 290, we will cancel 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 to present the trend.

Line 305, we want to find if there is relationship between cave air pCO<sub>2</sub> 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 make the balance between the stream and cave air CO<sub>2</sub>.

Line 309, we still think it should be 'in consistent', because here we want to express that high frequency and high amount of rainfall events help to maintain the high concentration of cave air CO<sub>2</sub>.

## **6 Conclusions**

Line 331

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

Line 322

'<sup>13</sup>C' should be ' $\delta^{13}\text{C}$ '

Line 333

The stated percentage contributions do not match Table 1

**Answer:**

Line 331, ok, we will accept this expression, that in two intervals not throughout the year.

Line 322, corrected.

Line 333, the table and the text are in consistent in the new one

### **Table 1**

- The time transgressive values do not give the reader the idea that a single value of  $\delta^{13}\text{C}$ -soil CO<sub>2</sub> is assumed for the whole time period
- The table should include the  $\delta^{13}\text{C}$  values for cave air, stream DIC, and calculated CO<sub>2</sub> in equilibrium with stream DIC

**Answer:**

Yes, we will add the mentioned one to this part.

### **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 will move 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.