Comments for Cao et al. "Constraining the soil carbon source to cave-air CO_2: evidence from the high-time resolution monitoring soil CO_2, cave-air CO_2 and its $\delta^{13}C$ in Xueyudong, Southwest China"

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_2. The work is important because it builds on a growing set of literature describing how and why cave air CO_2 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 CO2 sources must, at minimum, (1) include atmospheric CO_2 and (2) consider the close relationship between stream- and cave air-CO_2 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).

Specific Comments
Title
A more informative title is "Constraining the source and dynamics of cave air CO_2 in a cave system in Xueyudong, 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.

1 Introduction

The introduction could focus more attention on why we care about CO2 concentrations. I gather that you are interested in caves as a source of proxy records – spend more time explaining the connection between cave CO2 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.

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_2, soil air CO_2, and stream CO_2, and to (2) identify the contributions of major reservoirs to overall cave air CO_2."

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.

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

3 Methods and Materials

All measurement types require more information so readers can assess the methodology.
For CO2 concentration measurements:
- Automated measurements (CO2-cave air, CO2-soil, and CO2-stream)

- o Were all measurements made with the GMM221 sensor?
- o How was the sensor modified for measurement of CO2-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 CO2?
- Precipitation and temperature
  - o List the part number(s) for the HOBO weather station
- 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)
  - o D13C-cave air CO2
    - What precautions were taken to avoid sampling your own breath?
  - o D13C-soil CO2
    - What were the depths of collection?
    - How much soil air was collected? Sampling soil air has the potential to introduce gas advection and destroy the d13C signal that you are attempting to measure
  - o D13C-DIC stream water
    - How were samples collected and what preservation techniques were used? Were samples filtered, was air headspace eliminated, were samples refrigerated/stored in the dark, were microbes poisoned with a substance like MgCl2? This is critical for the d13C-DIC measurements as improper storage can substantially alter the d13C-DIC and render interpretation unviable.
  - o D13C-atmosphere
    - This needs to be included in the methodology
    - What precautions were taken to avoid sampling your own breath?
  - o D13C-plants
    - This needs to be included in the methodology
    - What plants and parts of plants were sampled? Why were these particular samples chosen?
- Analysis
  - o What is the methodology for d13C analyses?
  - o What standards were used for d13C measurement?

Line 112
Be clear that samples collected for d13C-CO2 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 d13C-cave air and –stream DIC

- Why were these time periods chosen?
- Why are there data gaps in the d13C data (e.g., DK air of Figure 3)?

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 pCO2 is high but soil moisture is low (July-Aigust).

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 d13C 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)

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.

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.

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 d13C-cave air) should be the same line color and type
- Include error bars on d13C measurements
- "LF" and "DK" are not defined before Figure 3. Where are these sites?
- Caption
  - Rephrase to "during rainfall events in *October-November* 2014"

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 repaced at this time?
- Where are the d13C measurements?
- The same materials (e.g., CO2-cave air and d13C-cave air) should be the same line color and type
- Include error bars on d13C measurements
- Caption
  - Rephrase to "during rainfall events in *June-July* 2014"

Line 168
Rephrase "4.4 The carbon isotope d13C 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 d13C 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 d13C are mentioned. Information about plant collection and measurement should go in the methodology
- What is the range of d13C-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

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)

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 d13C-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 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.

Figure 6
- The y-axes on both plots should be the same to allow easy comparison
- The left plot has 'Steam CO_2 degassing,' which should be 'St**r**eam'

- The 'Stream CO2 degassing' data reported in this figure appear to be d13C-DIC values. Reporting these data as the d13C 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)

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 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?

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.
  - You consider CO2 contributions from soil, stream, and human breath
  - 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 d13C-DIC of the stream is controlled by flow rate (Line 174). Is there a relationship between stream flow rate and cave air CO2 or d13C?
- The discussion repeats results and repeats itself in sections. It should be edited for clarity and structure. I suggest the following general structure:
  - Interpretation of what is occurring at Xueyu Cave
  - Comparison to other studies of this nature
  - Implications for developing paleoclimate records from speleothems (here and elsewhere)

Line 211
Is d13C-soil referring to soil organic matter or soil air CO2? If it refers to soil air CO2, keep in mind that d13C-soil air CO2 changes with depth. Justify using a single value.

Line 211-212

- A citation and explanation are needed for the 'd13C-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'

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 d13Cco2' should be 'more negative d13C'

Line 228
How does water degassing CO2 not precipitate calcite?

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

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

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

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

- 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'

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

Table 1
- The time transgressive values do not give the reader the idea that a single value of d13C-soil CO2 is assumed for the whole time period
- The table should include the d13C values for cave air, stream DIC, and calculated CO2 in equilibrium with stream DIC

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