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Interactive comment on "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" *by* Min Cao et al.

Anonymous Referee #3

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Review of manuscript: bg-2019-66 by Cao et al.

about a cave research study entitled 'Constraining the soil carbon source to cave-air CO2: evidence from the high-time resolution monitoring soil CO2, cave-air CO2 and its δ13C in Xueyudong, Southwest China'

In this contribution, the authors measured partial pressure of cave and soil gas CO2 and DIC concentrations in a cave stream. Those measurements were complemented by temperature (cave, soil and atmosphere) and precipitation observations. The log-

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ging was performed for more than two years. Furthermore, they provide the stable C isotopic composition of various components (stream water, soil and cave air) for two shorter periods of time in lower resolution (10 days, one sample per day). The aim of this study is to investigate the major sources of CO2 in the cave.

Unfortunately, the manuscript is relatively difficult to read and I am not always sure, I understood what the authors wanted to say. In a possible revision, one focus should be on improvements with respect to the readability. Apart from this, I think, the study is not in a shape to be published. To my opinion, the text should be considerably improved before it could be considered for publication. There are many details, which should be improved and some sections should be reworked. However, I want to emphasize, that I think that a lot of the findings appear to not to be valid but that there are some potential within the data, to make it a quite nice contribution to the scientific community, which is worth to publish once the problems are solved, the text reworked and new ideas implemented.

Major points

Throughout the text (e.g., line 9) when the authors write of 'pCO2 of cave water'. To me, this sounds very sloppy and should be prevented. I mean, gaseous CO2 (which can be well expressed as pCO2) is dissolved in water and then forms the different carbon species often referred to as dissolved inorganic carbon (DIC). The DIC cannot be expressed as pCO2. It is all dissolved and should be expressed in terms of concentrations. To my opinion the authors most likely want to express with their wording something similar to: 'the pCO2 the cave water is in equilibrium with'. This wording is much more precise and should be applied throughout the whole text.

The abstract should be reworked. In line 11 you are arguing that pCO2 of the cave air depend on wet and dry periods. But as I understood your data, the main influence is on the temperature. Only if temperature is warm enough, the wet/dry relationship is important. The last sentence of the abstract, appears weird for me as well after having

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read the whole paper. In this sentence, you are referring to stalagmite records and what your findings imply for those. However, in the manuscript you did not discuss the influence of the important cave processes on the stalagmite stable carbon proxy. So either you should delete this sentence or add some discussion about this in the text. I guess the latter would be the more valid approach, as this way your story will have more impact.

As the stream seems to play an important role in the cave, I think it is important to let the reader know some more details. E.g., for which distance the stream is in contact with the cave atmosphere, how much water is transported, how fast is its velocity and something like that. This could be well included in Section 2. This is important, as this way other researchers investigating other caves can set their observations in better context and comparison with your results is easier.

I recognized that the cave is ascending into the host rock. However, with respect to cave CO2 and the derived ventilation regime, it behaves, according to your data, like those caves which are going downwards into the rock. This is quite interesting and could be much more emphasized. Maybe the stream is the key for this behavior? You should put some efforts here and elaborate more on this.

Section three should be completely reworked, as some information are given twice (e.g., about the CO2-sensor; Line 111 and 116) and others incomplete (How was soil CO2 measured? How was the sampling performed for soil gas d13C analysis? How was the pCO2, the stream water is in equilibrium with, determined?) or no information at all (e.g., about measurements of cave and soil temperature, soil moisture, d13C values of plants [according to line 170 they have been measured]).

Within the manuscript you are claiming: 'When the temperature is suitable in summer, soil moisture works as the main constraining factor for variations in soil CO2.' (e.g., Line 134). First, please don't discuss this in the results, but put it to the discussion and please be more detailed here. By eye, it is easily visible, that soil gas CO2 might

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be changed by soil moisture during the warm season. However, there seem to be a clear time delay between soil moisture and pCO2. I feel, you have to discuss this. Where is this delay coming from? Please, do some statistics, e.g., calculate correlation coefficient, determine time lag, ... You might be even able to make some statements about the sensitivity of soil CO2 variations with respect to soil humidity under various temperature ranges, as soil pCO2 seems also to react on soil humidity under lower temperatures. However, the sensitivity appears to be different when the variations in the cold and warm seasons are compared. This all, will have some influence on section 5.2.

Fig. 6: What exactly is plotted for the stream water? The measured d13C, ok. But how have you determined the x-axis value? Is this the pCO2 value, the stream water is in equilibrium with? But not all of this C can degas from the stream (due to the chemical limits of degassing) and thus cannot contribute to the cave air CO2. So the pCO2 what comes from the stream is for sure lower than the pCO2 value the water is in equilibrium with. Thus, those values should be put more to the right (the question is how much?). Due to all this, I think, providing this stream C source in the Keeling plot this way is quite bold without arguing why this can be done. This is then changing the available CO2 which can degas and is thus also changing the according mCi in your equation (line 205). As those plots contain the basis of your argumentation according to your present discussion, a change here, might have major influences on your final findings.

Technical comments:

Line 26: 'always with higher values in summer and lower values in winter' I want to point out that this is not true. This is only true for caves, which lead downwards with increasing distance from the entrance. For those caves, which leads upwards, the opposite will be observed. But you have indicated this correctly, e.g., in line 43. So please, be consistent and more precise here.

Line 27-28: Unfortunately, I do not understand this sentence. Can you reword this?

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Line 32: It seems to me, that ‘although’ is not fitting here.

Line 64: ‘carbon’ with a small first letter.

Line 65: ’Especially, in descending caves where carbon dioxide is heavier than the other main atmospheric components . . .’ I am pretty sure you are meaning this differently than stated here. CO2 is always heavier than the main atmospheric components (O2 and N2), not only in descending caves. Maybe reword this to something like that: ‘As carbon dioxide is heavier than the other main atmospheric components, CO2 accumulates in descending caves during the hot season due to the “cold trap effect”.

Line 73: The ‘Thus’ does not seem to fit here, as the previous sentence does not provide a reason for what you are stating in the following sentence, which you begun with ‘Thus’.

Line75: Please define R/Ra. What is this?

Line 76-77: Please be more precise and reword this sentence as 222Rn is not produced from the decay of U and other radioactive atoms as you have stated here. It would be more precise to write something similar to: ‘222Rn is a radioactive isotope that is naturally produced within the 238U decay chain. As it is heavier than air it is accumulating in the . . .’.

Line 90: ‘multiyear average precipitation’ sounds a bit strange. Do you mean ‘average annual precipitation’?

Line 91: Is the term ‘secondary speleothems’ correct? It seems to me, you might mean ‘secondary carbonates’ instead?

Line 93: Please provide information, of how constant cave air T is. Give its variation throughout the year and plot it maybe even in Fig. 2

Fig. 1: It is not clear, why the monitored drip sites are shown in d), as these are not discussed in the text. In addition, I am very confused about the naming of your river

drip-sites. Here in Fig. 1 they are labelled as X1 and X5. In Tab. 1 they are labeled MZ and LF while throughout the text and in the figures they are labeled DK and LF. Please stay consistent.

Line 103: ‘cave’ appears to be unnecessary here.

Line 105: Please, replace ‘,’ by ‘.’ after ‘)’.

Line 106: ‘drip rate’ instead of ‘drip water rate’.

Line 126: ‘amount’ instead of ‘amounts’

Line 128 and 131: Here you quite often make some statements, which should be carefully discussed before. To my opinion those statements do not belong in the results section, but should be shifted towards the discussion section.

Line 133-134: This belongs also to the discussion and it is not quite clear, what ‘suitable’ is meaning here. Please, be more precise. I also wonder if this statement is justified (see above). Fig. 2: Please indicate the cave air temperature.

Line 137: Capital letters of ‘Air’ and ‘Soil’ should be small ones.

Line 146-147: Sorry, but I do not understand this sentence. Could you rewrite this under the correction of the ‘stream00000’ typo.

Line 156-163: This should be shifted to the discussion part. And I do not understand the sentence in Line 157. Also the following sentence (line 157-159) is not clear to me.

Line 169: Typo. Should be ‘-10 permil’, shouldn’t it?

Line 170: Please include here, that you are talking about soil gas, which has values of -18permill to -23.9.

Line 183-185: I am sorry. From my side, this does not look as contemporaneously as you described it. Please provide some shaded rectangles in the appropriate figures to allow to better follow your argumentation. For me it even seems, that there is no rain

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event in October, which was also covered with DIC and pCO2 measurements at DK. In November are some rain events, but there, I could not see the described relationship. DK-d13C is already decreasing before the rain event. Thus, it appears the decrease in d13C has nothing to do with the single rain event. And to be honest, the observation of such behavior (if there would be indeed one) during only one single event is not very convincing.

Line 186-188: Please also show this in a figure. With only seeing the numbers in the table, I am not able to follow.

Line 205: Please subscript the 'i' in the equation.

Line 207-209: Why has the mixing model only two endmembers? What is with the atmospheric input? Why can this be neglected. Please explain. But then, an end-member modelling with three sources is much more difficult. (even with the assumed two end-members, the equation in line 205 needs an additional equation to order to be solved. [Sum of all mCi = 1])

Line 211-212: Please, cite the work you are taking the fractionation factor from.

Line 212-216: Even with your two end-member modelling, I am somewhat confused, about your numbers for the contribution of the C sources to the cave air. There is quite some scatter in the d13C of soil gas, cave air and DIC (or degassed CO2) of the stream. The problem then is that the difference between stream degassed CO2 and soil air is quite small compared to the scatter in your values. This makes the calculation quite difficult. At least, I would require to give some error estimates in your values here.

Line 230: Why are you mentioning roots here. Are there roots in your cave? I assume not, otherwise I would have expected some description of them earlier in Section 2. So it is not clear to me, why you are mentioning them here with respect to other caves. This sentence is also completely out of context with the sentence before and after.

Line 280: Mawmluh cave was not investigated by Riechelmann et al., 2017. They

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investigate Bunker Cave. Please change the citation accordingly.

Line 292: Why do you say that cave CO2 and stream DIC are in equilibrium with each other? For me this looks quite different in Fig. 8. There is barely a time, when the difference between both is 0. Even if this would be the case, all your argumentation from above that the stream is a significant CO2 source is destroyed by this sentence. If both would be in equilibrium, no CO2 can be degassed from the stream and could not provide CO2 to the cave atmosphere. And if all the CO2 of the stream would have been degassed earlier, you could also not do any end-member modelling as you do not have the initial conditions of the water.

Line 308: Please define and explain, what the response time is. How have you calculated this? Can you show a plot of the observed relationship?

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