Response to Referee #3

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 logging 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 CO_2 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.

Answer:

We would like to say thanks to the referee for all his valuable comments for this paper. We paid more attention to solve the problems about readability and the data explanation.

Major points

Throughout the text (e.g., line 9) when the authors write of 'p CO_2 of cave water'. To me, this sounds very sloppy and should be prevented. I mean, gaseous CO_2 (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 pCO_2 the cave water is in equilibrium with'. This wording is much more precise and should be applied throughout the whole text.

Answer:

$$PCO_2 = \frac{(HCO_3^-)(H^+)}{K_1 Kco_2}$$

Yes, pCO_2 is assumed to be in equilibrium with the sampled waters by the equation

I do not understand the 'the pCO_2 the cave water is in equilibrium with'.

The abstract should be reworked. In line 11 you are arguing that pc 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 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.

Answer:

Ok, we have to rewrite the abstract. The CO_2 production is mainly depending on temperature, but in hot summer, water is a very important factor to control it and the transport is also dominated by rainfall events. We wanted to make it more meaningful with the last sentence but it seems that it lacks some correlation. In the revised version, we cancelled it.

"Cave CO_2 plays an important role in carbon cycle in a karst system, largely influencing the formation of speleothems in caves. Gaseous CO_2 and aqueous CO_2 in Xueyu Cave were monitored from October 2014 to February 2017. The cave air pCO_2 and aqueous CO_2 over two years showed very similar variations in seasonal patterns, with high fluctuated CO_2 concentrations in the wet season and low steady CO_2 concentrations in the dry season. Soil CO_2 which is largely controlled by soil temperature and soil moisture as well as stream degassing are main origins for the Xueyu cave air pCO_2. The average values of $\delta^{13}C_{soil,}$ $\delta^{13}C_{DIC}$ in June were -23.9±2‰ and -13.4±0.3‰, respectively; $\delta^{13}C_{CO2}$ of atmospheric air was -10.0‰ and $\delta^{13}C_{CO2}$ of cave air was -23.3±0.3‰. The average values of $\delta^{13}C_{soil}$, $\delta^{13}C_{DIC}$ in November were -18.0±0.5‰ and -12.2±0.4‰, respectively; $\delta^{13}C_{CO2}$ of atmospheric air was -9.6‰ and $\delta^{13}C_{CO2}$ of cave air was -18.8±0.4‰. Moreover, the contribution from soil CO_2 is higher in June (78.8±13.0%) than in November (67.1±6.8%) based on the model of stable carbon isotopes. The contribution of C from the soil was larger in summer than in winter. The very similar (negative) values of carbon isotopes between soil and cave air CO_2 suggests that there were no potential geological/deeper sources which show more positive $\delta^{13}C_{CO2}$. Aqueous CO_2 degases from upper stream to downstream in the cave, resulting in slightly decreased pCO_2 but increased carbon isotope values in the downstream."

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 CO_2 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.

Answer:

Thanks for your suggestions, we added more information about the stream in the 'Study area' section. There are three lays in the cave space, which can be highly related to stream flow in different geological periods. In modern time, the stream flows through in the bottom layer. In the revised version, we will put more information about the geology and topography.

"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, the velocity of stream flow is 0.27 m/s on average."

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 CO_2 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]).

Answer:

We were planning to introduce the equipment in Line 111 and present the monitoring frequency in Line116.

"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)."

"Two sites inside the Xueyu Cave for pCO_2 monitoring of cave air and the subterranean stream have been located at LF (X1) and MZ (X5), respectively (Fig. 1). The data were recorded each quarter based on a GMM221 sensor (within the range 0~20000 ppm, precision ±1%) connected with RR-1008 data receiving terminal, which 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}~$20,000\times10^{-6}$ ppm). 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."

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 CO_2 might 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 CO_2 variations with respect to soil humidity under various temperature ranges, as soil pCO_2 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

Answer:

Ok, we will separate results and discussion. Yes, there is a time lag we did not pay more attention to. We have monitored but not put in this paper, the relationship between soil temperature, soil moisture and soil CO_2 on daily or seasonal scales.

Fig. 6: What exactly is plotted for the stream water? The measured d13C, ok. But howhave you determined the x-axis value? Is this the pCO_2 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 pCO_2 what comes from the stream is for sure lower than the pCO_2 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 CO_2 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.

Answer:

In Fig. 6, We updated the figure. The x-axis refers the inverted CO_2 concentration. The stream water is in equilibrium with pCO_2 value. Yes, 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 CO_2. However, there is no need to degas all, when it comes to be in equilibrium, no more aqueous CO_2 sources can transfer to gaseous CO_2.

The more positive values in the downstream (MZ) can indicate that degassing had occurred. Because more $d^{13}C$ was going to precipitate, and more negative $d^{13}C$ will degas into air. We use the Keeling plot to show that the contributions might be from soil and stream. Why these two sources? We excluded human respiration, deep source and atmospheric air according to their concentrations or carbon isotopes.

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.

Answer:

Thanks for your comments, that is true, what we said is just correct for some caves, especially the caves from the cited study. However, different cave modes show different circulation/ventilation characteristics, resulting in variations of cave CO_2.

“CO_2 concentrations in temperate karst soils range from 1000 to 15000 ppm, showing higher values in summer and lower values in winter in some caves (Spötl *et al*., 2005; Frisia *et al*., 2011).”

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

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”.

Answer:

Line 27-28, this sentence was going to explain how soil CO_2 goes into the cave system.

"The CO_2 inputs that penetrate caves and become part of the karstic atmosphere via directly in gaseous form, dissolved CO_2 in infiltrated waters from the soil matter" was changed into "Soil CO_2 can directly enter the cave by soil gaseous form or be dissolved in the water and move with the infiltration water'.

Line 32, 'Although' was cancelled.

"A few studies revealing very high CO_2 concentrations exist in deep and confined karst caves."

Line 64, 'Carbon' has been changed to 'carbon'.

"According to their study, carbon dioxide produced by the soil biomass is accumulated into underground voids due to gravitational drainage from cracks and fissures. As carbon dioxide is heavier than the other main atmospheric components, CO_2 accumulates in descending caves during the hot season due to the "cold trap effect".

Line 65, Ok, we accepted your expression, which is much clearer.

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 ….

Answer:

Line 73, cancelled. "Soil is commonly considered as the light end-member, and this assumption is correct as long as the CO_2 concentration in the cave is lower than the soil (Peyraube *et al*., 2013)."

Line 75, R/Ra should be '$^{226}Ra/^{228}Ra$', which is the isotopic ratios of Ra.

"Moreover, the $^{226}Ra/^{228}Ra$ versus $\delta^{13}C_{CO2}$ plot, traditionally used to estimate crustal versus mantle components of CO_2."

Line 76-77, new sentence is like this: "^{222}Rn is a radioactive isotope that is naturally produced within the ^{238}U decay chain. As it is heavier than air it is accumulating in the subterranean atmosphere and usually covaries with CO_2 concentration."

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

Answer:

Line 90, Yes, it should be expressed as ‘average annual precipitation’.

“This region has a typical subtropical monsoon climate with an average annual precipitation of approximately 1072 mm.”

Line 91, Ok, normally, speleothems are secondary carbonates.

“The geological formation and secondary carbonate deposits”

Line 93: We added the cave temperature in the Fig.3

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.

Answer:

We corrected in the revised version. X1 and X5 are LF and MZ (DK). We did not discuss drip water, so we have to remove the drip water sites in the Fig.1d.

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).

Answer:

Line 103, cancelled, the new sentence "The relationships between specific conductance (Spc), Ca^{2+} and HCO_3^- have been established and variations of CO_2 concentrations in the cave atmosphere and cave stream showed different changes in wet and dry season due to the ventilation".

Line 105, 106, 126, corrected. The changed sentences are

"(Pu *et al.*, 2015, 2018)."

"Seasonal variations of calcite growth rate are primarily controlled by variations of cave air pCO_2 and drip rate".

"During 2015-2016, the mean annual rainfall amount was 1149 mm, …"

Line 128-131, Line 133-134, we will separate better the results without comments.

Fig. 2: Please indicate the cave air temperature.

Answer: we added the cave air temperature in new Figure 3

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 -18 permill to -23.9.

Answer:

Line 137, corrected. "**Figure 3:** (a) Precipitation, (b) air temperature and soil temperature, (c) soil moisture, (d) pCO_2 values in the soil air, cave air and stream water of Xueyu system in the years 2015-2016."

Line 146-147, we rewrote the sentence "According to Pu et al. (2018), the seasonality of cave CO_2 variations occurred based on monthly monitoring, showing high values in summer and low values in winter."

Line 156-163, we moved this part to the discussion part and improved like this "During the transitional periods between different seasons, CO_2 concentration varied sharply. Especially with rainfall events, cave CO_2 concentrations changed largely due to increased high-CO_2 flow. A high-frequency monitoring in November 2014 and June 2015 showed the detailed changes of pCO_2 and carbon isotopes during rainfall events."

Line 169, corrected. "The $\delta^{13}C$ values of background atmospheric CO_2 ranged from -9.6 to -10.0‰."

Line 170, yes, we were talking about soil gas. It is descripted as "During the two monitoring intervals, $\delta^{13}C$ values were -18.0‰±0.8‰ in the overlying soil gas in October-November but -23.9±0.9‰ in June on average."

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 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.

Answer:

Line 183-185, there was a little rain in October, but we mainly monitored the rainfall event at the end of October. Of course, it is not so convincing with one/two rainfall events. However, it needs a lot of work to monitor many rainfall events. At present, we have monitored several rainfall events. However, we do not have enough samples for analysis of carbon isotopes. The decreasing trend of CO_2 concentrations are significant in the season transitional period.

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 endmember 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.

Answer:

Line 186-188, It is in Figure3

Line 205, ‘i’ in the equation was edited by equation editor, now we used the non-text expression.

$$\delta^{13}C_{CO2} = \sum_{0}^{i} (mC_i)(\delta^{13}C_i) / \sum_{0}^{i} (mC_i)$$

Line 207-209, We excluded other endmembers. Atmospheric input is not considered as a direct input due to the carbon isotope. If atmospheric input lowers the winter CO_2 concentration, the cave CO_2 concentration and isotope should have closed to atmospheric end. We excluded human interference and geological sources based previous field exploration, monitoring and also the stable carbon isotopes.

Line 211-212, cited. “Zhang, J., Quay, P.D., Wilbur, D.O.: Carbon isotope fractionation during gas–water exchange and dissolution of CO_2. Geochim. Cosmochim. Acta, 59, 107-114, https://doi.org/10.1016/0016-7037(95)91550-D, 1995.”

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 $d^{13}C$ of soil gas, cave air and DIC (or degassed CO_2) of the stream. The problem then is that the difference between stream degassed CO_2 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.

Answer:

Line 212-216, yes, the calculation is difficult as the $d^{13}C$ values from stream degassing and soil are not largely different. However, they are not the same even considered errors. We put the error zone in the figure 3.

Line 230, yes, no obvious roots were found in the cave, we removed this part.

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

Answer:

Line 280, corrected. "Increased CO_2 absorption from the slow-moving or stagnant cave air by carbonate weathering and potentially the stream might explain the low cave-air pCO_2, which is similar to the observation in Bunker Cave of India (Riechelmann *et al*., 2017)."

Line 292, we said they are in equilibrium because the variations in aquatic and air CO_2 are very similar in Figure 3. Actually, they are not in equilibrium, we can see that they fluctuated within 1000 ppm in most of time, resulting in degassing or absorbing. We can say that degassing occurred during the two intervals, but we do not know if it is true throughout the year. However, we can make sure that there is exchange between air and water during the monitoring intervals. We think that aqueous and gaseous CO_2 should be always in dynamical balance.

Line 308, the response time means that the time it takes to be in equilibrium. We can see rainfall events make the large difference of CO_2 concentrations between air and water, degassing does not always take place until its concentration become stable.