

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 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.

Answer:

We would like to say thanks to the referee for all his valuable comments for this paper. We will pay more attention to solve the problems.

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.

Answer:

Yes, pCO₂ is assumed to be in equilibrium with the sampled waters by the equation

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

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 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 CO₂ 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 will add some discussion in the text.

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.

Answer:

Thanks for your suggestions, we added more information about the stream in the 'Study area' section. There are three layers 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.

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]).

Answer:

We were planning to introduce the equipment in Line 111 and present the monitoring frequency in Line 116. The soil temperature and soil CO₂ concentrations were obtained since May 2013 by a composite measurement system, including a CO₂ 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.1). 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 pCO₂ monitoring of cave air and the subterranean stream have been selected 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 \pm 1%) connected with RR-1008 data receiving terminal, which were installed in the cave and stream to measure CO₂ concentrations. The sensor in the soil was calibrated on a monthly basis by the portable equipment that can insert into the soil for CO₂ measurement (portable pump-suction infrared CO₂ gas detector, measuring range 20×10^{-6} ~ $20,000 \times 10^{-6}$ ppm with the precision $\leq \pm 2\%$). Cave air CO₂ was determined with a calibrated CDU 440 CO₂ meter (measuring range 10×10^{-6} ~ $20,000 \times 10^{-6}$ 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 *p*CO₂ 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, 0.01 cm, 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 CO₂ 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 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

Answer:

Ok, we will separate results and discussion. Yes, there should be 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 CO₂ on daily or seasonal scales.

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:

Answer:

In Fig. 6, we just wanted to show the difference of stable carbon isotope between two sites in the stream (upstream and downstream). The more positive values in the downstream 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 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 CO₂.

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 CO₂ goes into the cave system. ‘The CO₂ inputs that penetrate caves and become part of the karstic atmosphere via directly in gaseous form, dissolved CO₂ in infiltrated waters from the soil matter’ was changed into ‘Soil CO₂ can enter the cave soil gaseous form directly or be dissolved in the water and move with the water’.

Line 32, ‘Although’ was cancelled.

Line 64, ‘Carbon’ has been changed to ‘carbon’.

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’.

Line 75: 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: ‘ ^{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 : : :’.

Answer:

Line 73, cancelled.

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

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 ^{222}Rn is a radioactive gas that is naturally produced from the decay of uranium and other radioactive atoms in the carbonate host-rock in caves, which is accumulated 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’.

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

Line 93: We update in the 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.

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

Line 105, 106, 126, corrected.

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

Fig. 2: Please indicate the cave air temperature.

Answer: we will do.

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.

Answer:

Line 137, corrected.

Line 146-147, According to Pu et al. (2018), the seasonality of cave CO₂ variations occurred based on monthly monitoring with 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, CO₂ concentration varied sharply. Especially with rainfall events, cave CO₂ concentrations changed largely due to increased high-CO₂ flow. A high-frequency monitoring in October-November 2014 and June-July 2015 showed the detailed changes of pCO₂ and carbon isotopes during rainfall events.’

Line 169, corrected.

Line 170, yes, we were talking about soil gas.

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 were a little rain in October, but we mainly monitored the rainfall event at the end of October. We will mark it in Fig. 2. DK-d¹³C changed during the rainfall event. 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 could not afford to do such things.

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, we will present in a figure.

Line 205, 'i' in the equation refers to different sources, in this paper, soil CO₂ and stream degassing.

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 CO₂ concentration, the cave CO₂ concentration and isotope should have closed to atmospheric end.

Line 211-212, cited.

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.

Answer:

Line 212-216, We will put the error bars in the figures.

Line 230, yes, no roots 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.

Line 292, we said they are in equilibrium because the difference between aquatic and air pCO₂ are not so large. Actually, they are not in equilibrium, we can see that they fluctuated within 1000 ppm in most of time. 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. 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 $p\text{CO}_2$ between air and water, degassing does not always take place until its concentration become stable.