

## ***Interactive comment on “Groundwater data improve modelling of headwater stream CO<sub>2</sub> outgassing with a stable DIC isotope approach” by Anne Marx et al.***

### **Anonymous Referee #2**

Received and published: 24 November 2017

Review of ‘Groundwater data improve modelling of headwater stream CO<sub>2</sub> outgassing with stable DIC isotope approach’

Summary: The manuscript by Dr. Marx and co-authors describes how the inclusion of GW d13C DIC data can improve the modelling of stream CO<sub>2</sub> evasion estimates from small headwater streams, that contribute substantially to global freshwater evasion fluxes (Aufdenkampe et al., 2011, Raymond et al., 2013). For this, GW isotope data is incorporated into a stream degassing model that considers isotope fractionation (d13C) to estimate degassing. This approach is different than the most commonly applied method for estimating CO<sub>2</sub> evasion. Commonly this flux is estimated

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by combining measurements of pCO<sub>2</sub> in streams with modelled and/or measured gas-transfer coefficients (k) (Dinsmore et al., 2013, Raymond et al., 2013, Wallin et al., 2013, Schelker et al., 2016). Thus the study aims to provide an alternative way to validate previous methods and to give a methodologically independent estimate of CO<sub>2</sub> evasion from a small, acidic headwater stream.

Overall I find the work to be reasonably well performed and as such a possible basis for a publication. However, at present there are several points that hamper the story to me as a reader. Therefore I would ask the authors to rethink and revise the manuscript following the comments provided below.

Main comments:

1) There appears to be little data. The stream sampling covers only one single stream at very coarse temporal resolution (4-weeks interval for two years). Similarly, GW data is only from one single GW well (1) at three different depth. As a comparison, a similar study covering also POC and DIC stable isotope data (Polsenaere et al., 2013) measured 9 streams for one year at 2-weeks interval. That is ~9 times more data than presented in this study. There is not much the authors can do about this now, but in case any other relevant datasets are available I would strongly encourage the authors to include any additional relevant material in the analysis.

2) The analysis clearly demonstrates the strong dependence of stream CO<sub>2</sub> evasion estimates to the respiration of the stream ecosystem. Within the analysis a wide range of R-values is used; scenarios cover a very large range from 14 to 75%. As such, the methods for estimating stream metabolism from dissolved oxygen dynamics are well established and developed (Odum, 1956, Fisher & Likens, 1973, Demars et al., 2015) and some formulations have even explicitly considered the potential for GW inflows (Hall & Tank, 2005). The relevant measurement can for example be done by a dissolved oxygen logger for ~1000 USD (for example from ONSET HOBO) that would have logged dissolved O<sub>2</sub> dynamics continuously. Unfortunately, it appears no oxygen

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measurements were applied in parallel to the C-isotope sampling that would allow an estimation of ecosystem respiration for this specific stream. Here I would at least expect that a literature analysis on streams with similar characteristics is performed to narrow down the possible range of respiration. However, in the paper only 'scenarios' for different contributions of ER to CO<sub>2</sub> evasions are used and little is provided on this matter.

3) What is the exact topic of the paper? As such the material could provide a number of different angles. However, it appears as if the authors cannot really decide on which topic to choose. At present, the work is presented as a methodological advancement paper of the method of using stable C isotopes of GW to improve stream CO<sub>2</sub> estimates. To really anchor the paper in the literature, an additional estimate of evasion fluxes by the more commonly used gas-transfer equation (Raymond et al., 2013) would have been required. Only then, one could conclude the true value of the new approach. Second, the paper is presently also placed as a contribution to the global literature on CO<sub>2</sub> evasion estimates from headwater streams. For this, there is in fact very little data (only one stream) with a low temporal resolution (only one sample per month). Thus and despite the fact that this new approach is interesting and promising, I find only limited use of the manuscript in this context.

So in simple words: At present, I see the paper as 'neither apples nor oranges' and suggest the authors to revise the focus of the paper as good as it is possible.

4) The overall quality of the writing can be improved and is sometimes unprecise. There are many examples where statements are not clear, especially in the discussion. I have given some indications for these in my detailed comments below. Please rework the discussion. Also, make sure all the text is past-tense.

Minor comments:

Title: Good.

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Abstract:

L14/15: appears contradictive: they (small headwaters) contribute 36%... from all rivers and stream worldwide. How about changing 'all rivers and streams worldwide' with 'fluvial ecosystems on the globe' or something similar?

Introduction:

P1, L33: suggest to revise to "excluded streams of Strahler order below three" and leave the reference to Strahler out, as this is common knowledge, at least in hydrology. Also numbers below six should be spelled out (that's at least what I learned back in the days).

P2, L4: suggest to also reference (Schelker et al., 2016) for the statement on gas transfer velocities.

P2, L6: the Hotchkiss et al., reference does not appear to be a good reference here. It is a modeling paper that is based on a large number of streams.

P2, L11, Schelker et al., 2016 would again, fit well.

P2, L16: (Reichert et al., 2009) would be a good reference, as they provide estimates of the upstream length that significantly contributes to what is measured at the sampling location x downstream.

P3, L1: "the aim was" - past tense.

P3, L2: Please add "and their stable isotope signature" to "measured groundwater contributions"

Methods:

L17: How is 'runoff intensity' defined and what unit would this variable have? This is not a standard term in hydrology! A sum of discharge? Or peak-discharge? Besides the need to clarify the term (or replacing it), I suggest to provide some numbers for this

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in Table 1.

P5, L2: As pointed out in my main comment, it is unfortunate, that there is so little data. A monthly sampling for a stream with a nival flow regime, essentially means, that all relevant runoff episodes will, if at all, just be sampled by chance and then only one. If one is unlucky, there is not a single sample from the spring freshet. For me this is a major drawback of this dataset and of this study.

P5, L4: no need to cite anything here. Remove ref, or give the reader some information, why this ref is relevant here.

P5, L23: replace 'usually multiplied by 1000' with 'expressed as per mill'

P6, L7: The first sentence of this section is not well placed. This can go somewhere at the end of the section, as it is not very relevant. Instead a sentence or two that outline the model choices with a reasoning would be much more appropriate.

P6, L11: I am not convinced that the a-priori assumption that there is no relevant primary production is reasonable, as for example many northern streams have relevant PP, at least during summer lowflow, at the same time as the climate is similar to the stream of this study (Fisher & Likens, 1973). Anyhow, for the sake of the paper I suggest the authors to write something along the lines of 'For our study we assume that . . .' rather than claiming that there is no PP without providing explicit evidence from this specific stream.

P6, L22: The precise statement in the reference by Hotchkiss et al is: "Median internal CO<sub>2</sub> production increases from 14% (credible range = 10–19%) [. . .]". So as a matter of fact, this study does not give a single value, but rather a possible range of R. I suggest to consider this range, rather than a single value here and in other instances of the manuscript where R is discussed.

P7, L5 methods well described. Also great to see that one can extract a k-value that is then comparable to other studies.

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P7, L12: Be sure to know the difference between a model parameter and an input variable and use the terms accordingly. At least in hydrological modelling, a measured value is not a parameter.

Results:

P8, L5: Please improve the writing here. If you begin a new section, add a topic sentence so that the reader knows what is described in the following paragraph. At present, this is just a horrible start of a results section. Similarly, please try to describe the results as such, and not just in which table/figure these are presented.

P8, L14: This sentence belongs to the methods, but not the results. Also, even if data normalized to the catchment area is interesting (and maybe better), most other studies on CO<sub>2</sub> evasion have used the normalization by stream surface area. Thus I suggest to provide both these numbers (catchment and stream surface area normalized), so that the reader can compare with past results. Finally, I may add, that the argument for normalization by stream surface area has been, that remote sensing techniques can provide stream surface areas for large and remote areas and thus allow upscaling.

L20, averaged

P9, L1: interesting numbers!

P9, L4 please do not use any references in the results. Here only the data from this study is discussed, whereas any similarities and dissimilarities with other studies should be discussed in the discussion section.

L4 and 5: Is there any relationship of k<sub>600</sub> and Q? Most studies assume this (Raymond et al., 2012), as higher Q means higher flow velocity and therefore turbulence and gas-exchange.

L6: Unfortunatly it is only here, that the reader understands that now some different models (or scenarios) are compared. Please add the purpose of these different scenarios/models to the methods section (see earlier comment).

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L13, please be precise. Concentration of what? As a reader I only know what relationship this is, after looking at the figure!

L15: revise to 'does not follow this proposed relationship'. The observation as such is very interesting.

L16: again, no references nor comparisons within the results!

Discussion:

Please begin the discussion with describing the key result in a larger context. . . "This study shows/demonstrates. . .!" to create a red line for the forthcoming discussion. At present there is no red line here.

P12, L2: This first sentence is a prime example for my criticisms of unprecise writing. Have Polsanere and Abril really conclusively shown for this(!) catchment that initial pCO<sub>2</sub> represents soil pCO<sub>2</sub>? This is how I read this sentence. Instead of making such bold statements, the authors should discuss, why they believe this is the case. . .

L: 8 and following: I agree with the enhanced soil respiration, which is a function of temperature and humidity. However, the sentence: "The main reason for higher soil pCO<sub>2</sub> are larger contributions of CO<sub>2</sub>-enriched GW to stream water. . ." does not make sense! How would GW flowing into the stream affect soil pCO<sub>2</sub> in a positive way, meaning increasing it?

L20-24: There is in fact some literature that has raised this point: (Pacific et al., 2008, Boodoo et al., 2017)

P13, L3: Good english writing means that place and time are placed at the end of the sentence, and in the order given before. Here (and in some other instances) this is not the case.

L8-10: This is the core results of the study! Please present this somewhere more prominent, rather than here, in the middle of the discussion!

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L17 and following: These comparisons are good and interesting. How about a table that compares you findings on K600 with other studies. The advantage would be that the reader would actually get to see the other values and not just a 'in the range' statement. Obviously such a literature overview should only on stream of the same stream order, and somewhat similar characteristics.

On a similar matter and also concerning Figure 4: Here a comparison with other studies on a per-area (stream surface) would be great, as stream surface area and water volume increase with increasing discharge, so that the observed pattern of decreasing CO<sub>2</sub> loss per volume may be countered on a per area.

Conclusions:

P13, L25

L27: 'the Uhlriska' is redundant here and can be removed.

L30: The point that snowmelt puts out more CO<sub>2</sub> would be much clearer, if the per stream area values would be compared (see earlier comment)

P14, L7 and following: I don't really understand this. . . If the isotopes give such wonderful new possibilities, why are the authors then arguing that more chamber measurements should be done? Besides the fact that these have their own problems, the best would probably be chambers with C-isotopes, as it is already used in some terrestrial systems using a laser ring down spectroscopy analyzer. Please revise or remove. The results are not suggesting to do more bastviken-style chamber work!

Figures:

Figure 1: I can't really see the large map of Germany, Poland etc. lines too thin.

Figure 2 and 3: Essentially these two show the same thing: A timeseries of the different model scenarios (different R<sub>s</sub> and the model with GW) as well as the respective uncertainties. Thus I suggest to merge the figures into one. Uncertainty ranges can

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then be shown by background shading of different pattern and/or color.

Other comments: F2 caption: 'do not apply to'. Also, remove last sentence, as redundant, especially if figures are merged.

Fig4: A nice figure. Maybe add a little information, on the 'one outlier', that is the event with the highest flow either in the caption or directly in the figure (using an arrow). Also, how about plotting an exponential function to the data (maybe with the outlier removed), as this relationship seems pretty strong. Next, is CO<sub>2</sub> loss defined as a term? I may have overlooked it, but its important that the reader knows if this is equal to CO<sub>2</sub> evasion. Finally, please see my earlier comment, on the unit of 'loss' and how this pattern may change, if one takes a look at the entire stream reach.

Tables:

T1: Add runoff seasonality during the study years (see earlier comment). Also, stream length is 2.0km here, whereas it 2100m in the text.

T3: caption: these are not parameter, but results! Please revise. One option would eb to write 'DIC partitioning according to the . . . model'

Supplementary:

Fig.S1 and S2. These show some of the nice data of this work! Please compress these (for example discharge can be shown in all graphs in grey in the background) and present them as full figures in the manuscript. No reason to hide them.

TS1: please add a note on missing values

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Interactive comment on *Biogeosciences Discuss.*, <https://doi.org/10.5194/bg-2017-357>, 2017.