

On behalf of all authors, I thank the referee for the evaluation and constructive comments. In the text and tables below, responses to the points raised by the referee are answered in green and italic.

Response to Anonymous Referee #1:

General comments: The authors of this manuscript apply an already existing model to assess the CO₂ loss from a small silicate based watershed in Czech Republic. The novelty resides in the fact that their study is simplified by the fact that the watershed drains silicate rocks only and they use real data for the groundwater end-member instead of using literature values. The results from this manuscript are important since there are very few reliable data of CO₂ emissions from first order streams to estimate global CO₂ emissions from aquatic systems. I thus recommend the publication of this manuscript provided that the authors address the following specific comments.

We thank the reviewer for the positive and constructive evaluation of our manuscript.

Comment by reviewer	Answer/ action by authors
P.6 L. 3-4. The authors mention that the d13C-DIC data have been normalized to the VPDB scale by assigning +1.95 to NBS19 and -46.6 to LSVEC. These are solid carbonate materials which are very difficult to dissolve in water. It is thus unlikely that the authors have used these materials to normalize the raw data and if they did, they have likely broken the "identical treatment" principle. Here, the internal reference materials with their values and uncertainties need to be stated.	<p><i>The reviewer is correct. The description of the normalization procedure for the Aurora 1030W analyzer was not correct. We did not use NBS19 and LSVEC here, as NBS19 would not dissolve in water (LSVEC would). We deleted that sentence and apologize for the confusion.</i></p> <p><i>In contrast, the normalization procedure of the Aurora TIC-TOC analyzer relies on CO₂ liberated from organic substances that readily dissolve in water, such as sugar, which in turn were normalized to VPDB by EA-IRMS via international reference materials USGS 40, USGS41 and IAEA CH-6. The precision of the internal control standard (C3-sugar) is stated in the text. For details on this instrumental setup we refer to St Jean (2003) (for the reference see the manuscript) that describes the system in detail.</i></p> <p><i>Further, the referee is correct that we did not apply the "identical treatment" principle in a strict sense here. This is simply because of the facts that no international DIC reference material exist and that for this peripheral the normalization procedure for δ¹³C-DIC and δ¹³C-DOC typically relies on CO₂ that is completely liberated from organic reference materials.</i></p> <p><i>We revised the method description and provide more details on the analytical procedure.</i></p>
P.6 L.6. The same applies for the d13C of POC. Also, I am sceptical that the Aurora-IRMS	<i>The reviewer is correct and we apologize for the confusion. The methods section is about DIC and only the last sentence refers</i>

<p>system was used to measure d13C of POC. Unless the authors mean TOC, the usual method is to use an EA online with an IRMS. The authors should clarify.</p>	<p><i>to POC. For the POC method we referred to Barth et al. (2017). The POC was indeed measured on an EA-IRMS system and we now provide the full details on this analytical procedure in the methods section:</i></p> <p><i>“POC samples were analyzed for $\delta^{13}C_{POC}$ using a Costech Elemental Analyzer (ECS 4010; Costech International, Pioltello, Italy; now NC Technologies, Bussero, Italy) coupled in continuous flow mode to a Thermo Scientific Delta V plus IRMS. The data sets were corrected for linearity and instrumental drift during the run. Values were normalized for carbon to VPDB by analyses of internal reference materials (C_4 sugar and KHP) that were calibrated directly versus USGS-40 and USGS-41 (L-glutamic acid). Assigned values to USGS-40 and USGS-41 were -26.39‰ and $+37.63\text{‰}$ for $\delta^{13}C$, respectively. For precision and accuracy two laboratory standards (acetanilide and tartaric acid) were measured in each run. Precision, defined as the standard deviation of the control standard was better than 0.1‰ (1s) for $\delta^{13}C_{POC}$.”</i></p>
<p>P.6 L.15. In Equation 2, HCO₃ was not measured. The authors should state how they have calculated HCO₃ from the measured data and propagate their uncertainties.</p>	<p><i>HCO₃⁻ was calculated with measured DIC, pH and dissociation constants with equations 1 and 2 being inserted in equation 3 and solved for HCO₃⁻ (Dickson et al. 2007).</i></p> $K1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \rightarrow [H_2CO_3] = \frac{[H^+][HCO_3^-]}{[K1]} \quad (1)$ $K2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \rightarrow [CO_3^{2-}] = \frac{[K2][HCO_3^-]}{[H^+]} \quad (2)$ $DIC = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \quad (3)$ <p><i>Dissociation constants are temperature-dependent and were calculated according to Plummer & Busenberg (1982). The uncertainty of the calculation depends on the measurement uncertainties of DIC, pH and T.</i></p> <p><i>The largest uncertainty is usually caused by pH measurements as they are on a logarithmic scale. For instance, the uncertainty for pH is typically smaller than ± 0.1 causes a maximum uncertainty of $\pm 21\%$ for pCO_2. We consider this as a worst-case scenario that is also indicated in Figure 2 and 3.</i></p> <p><i>We added these aspects and the relevant</i></p>

	<i>literature to the manuscript.</i>
P.6 L.21. Even though the authors explain in depth their choice of an R value of 14% later in the discussion, they should explain here their choice of this value since there is no uncertainty associated to this value in the original cited paper.	<i>In a study about 187 streams and rivers the original paper (Hotchkiss et al. 2015) indicated a range between 10 and 19 % with 14 % being a median value for headwater streams. In our calculations we worked with this median value, but the revised version of the manuscript we now work with the range between 10 and 19 % to better reflect possible respiration.</i>
P.6 L.24. The authors state that they use $\delta^{13}\text{C}$ of POC instead of the d13 of SOM. In soils, DOC is often more important than POC and CO ₂ is more often linked to DOC than POC. Please explain why you use d13C of POC and not DOC or TOC. If d13C-POC = d13C-SOM, then explain.	<i>In our opinion, POC is the best representative of soil organic matter in the catchment. It is the material that is closest to the original plant and soil material. We did not choose DOC, because it is known to have recalcitrant phases that are poorly decomposed (Cauwet and Sidorov 1996; Laudon et al. 2011). This would introduce a non-representative value for organic matter input.</i>
P.6 L.28. Why is the term R not part of the modelling with groundwater?	<i>The original model computes the isotopic composition of soil CO₂ from the isotopic composition of soil organic matter ($\delta^{13}\text{C}$-SOM) (see eq. (1) in Polsenaere & Abril, 2012). In unsaturated soils the respiration related fractionation is large and variable (up to 4-5 ‰) and thus Polsenaere & Abril included R in eq. (1). We skipped this step with its high uncertainty by using groundwater data instead. During respiration in waterlogged soils and groundwaters the isotopic fractionation of CO₂ is much smaller (near 1 ‰, O'Leary, 1984). Thus we included 1 ‰ fractionation to the groundwater input. We changed the text passage in the manuscript.</i>

References

Cauwet, G., and I. Sidorov (1996), The biogeochemistry of Lena River: Organic carbon and nutrients distribution, Mar. Chem., 53(3-4), 211-227, doi: 10.1016/0304-4203(95)00090-9.

Dickson, A. G. S., C.L.; Christian, J.R. (Ed.) (2007), Guide to best practices for ocean CO₂ measurements. PICES Special Publication 3, 191 pp.

Laudon, H., M. Berggren, A. Agren, I. Buffam, K. Bishop, T. Grabs, M. Jansson, and S. Kohler (2011), Patterns and Dynamics of Dissolved Organic Carbon (DOC) in Boreal Streams: The Role of Processes, Connectivity, and Scaling, Ecosystems, 14(6), 880-893, doi: 10.1007/S10021-011-9452-8.