On behalf of all authors, I thank the referees for the evaluation and constructive comments. In the text and tables below, responses to the points raised by the referees 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.	*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.* *In contrast, the normalization procedure of the Aurora TIC-TOC analyzer relies on CO_2 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 decribes the system in detail.* *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 δ^{13}C-DIC and δ^{13}C-DOC typically relies on CO_2 that is completely liberated from*

	organic reference materials. *We revised the method description and provide more details on the analytical procedure.*
P.6 L.6. The same applies for the d13C of POC. Also, I am sceptical that the Aurora-IRMS 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.	*The reviewer is correct and we apologize for the confusion. The methods section is about DIC and only the last sentence refers to POC. For the POC method we refered 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:* *“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‰ 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* $\delta^{13}C_{POC}$*.”*
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.	HCO_3^- *was calculated with measured DIC, pH and dissociation constants with equations 1 and 2 being inserted in equation 3 and solved for* HCO_3^- *(Dickson et al. 2007).* $K1=\frac{[H^+][HCO_3^-]}{[H_2CO_3]} \rightarrow [H_2CO_3]=\frac{[H^+][HCO_3^-]}{[K1]}$ (1) $K2=\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \rightarrow [CO_3^{2-}]=\frac{[K2][HCO_3^-]}{[H^+]}$ (2)

	DIC= $[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$ *(3)* *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.* *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 ±21 % for* pCO_2*. We consider this as a worst-case scenario that is also indicated in Figure 2 and 3.* *We added these aspects and the relevant literature to the manuscript.*
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.	*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.*
P.6 L.24. The authors state that they use δ^{13}C of POC instead of the d13 of SOM. In soils, DOC is often more important than POC and CO2 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.	*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.*
P.6 L.28. Why is the term R not part of the modelling with groundwater?	*The original model computes the isotopic composition of soil* CO_2 *from the isotopic composition of soil organic matter (*δ^{13}*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 CO_2 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.*

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 CO_2 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.

Response to Anonymous Referee #2:

Summary: The manuscript by Dr. Marx and co-authors describes how the inclusion of GW d13C DIC data can improve the modelling of stream CO2 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 CO2 evasion. Commonly this flux is estimated by combining measurements of pCO2 in streams with modelled and/or measured gastransfer 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_2 evasion form 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.

The authors thank the reviewer for the positive and constructive evaluation of the manuscript.

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.

The sampling for isotopes in the investigated catchment was performed over a period of 20 months. We noticed that the study by Polsenaere et al. (2012) used more data points (in terms of time and space), however, in our study of the Uhlirska headwater catchment only one representative stream exists in the catchment. By interpolating values of total alkalinity and groundwater $\delta^{13}C_{DIC}$ *(linear interpolation), which serves as model input, we were able to use additional data and thus could considerably increase our data to a total of 84 samples.*
Groundwater data is from three different wells in the wetland. The wells have different depths with 2.7, 3.7 and 5.2 m below ground level. Calculated averages for the three wells are used for modeling. We assume that these wells do best reflect carbon inputs to the stream. Groundwater wells in headwater catchments are largely uncommon and thus to provide original groundwater data that are often not available in other studies are the best we can offer. In the conclusion chapter, we argue that more representative groundwater data are certainly necessary to strengthen the model.

2) The analysis clearly demonstrates the strong dependence of stream CO2 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 O2 dynamics continuously. Unfortunately, it appears no oxygen 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 CO2 evasions are used and little is provided on this matter.

In the streamCO$_2$*-DEGAS model the term R stands for the proportion of CO*$_2$ *coming from respiration in water along the entire river course (Polsenaere & Abril, 2012, eq. (1)). This is different from ecosystem respiration and cannot be quantified by dissolved oxygen methods; R has to be considered together with isotope changes caused by diffusion. If the CO*$_2$ *stems from respiration in the unsaturated zone, its isotope composition changes by up to 4.4 ‰ by diffusion. If the CO*$_2$ *originates from respiration in water, its isotope composition is identical to soil organic matter and diffusion does not apply. Therefore the term R indicates the relative contributions of respiration from saturated and unsaturated zones. In our model, R was varied between 10 and 75 %.*

3) What is the exact topic of the paper? As such the material could provide a number of different angels. 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 CO2 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 CO2

evasion estimates form 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.

We agree with the reviewer that the estimation of CO_2 fluxes by gas-transfer equations is a common approach. However, in our study we decided not to include CO_2 fluxes calculated by the gas transfer velocity k (Raymond et al., 2012) for comparison with our model results, because the use of k values is not recommended for headwater streams and exhibit very large uncertainties (Huotari et al. 2013, Wallin et al. 2011). Thus, these estimates should not be the basis to evaluate the value of our approach. Nevertheless we included Fluxes determined with k values in the revised manuscript. Overall, our study is a methological manuscript, in which we present, model and test actual data from a real-world headwater catchment. It contributes to the global CO_2 evasion discussion by providing an advanced method, however, we are not claiming to improve global datasets with this study alone.

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.

The authors appreciate the reviewer's detailed and constructive comments that we will address in detail in the table below.

Minor comments:
Title: Good.

Below we reply on each specific comment.

Comment by reviewer	***Answer/ action by authors***
Abstract: L14/15: appears contradicitive: 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?	*We changed the text as recommended.*
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).	*Done.*
P2, L4: suggest to also reference (Schelker et al., 2016) for the statement on gas transfer	*We added the reference.*

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.	*We replaced the reference by Stets et al. (2017).*
P2, L11, Schelker et al., 2016 would again,fit well.	*We added the suggested reference.*
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 donwstream.	*We added the reference as recommended by the referee.*
P3, L1: "the aim was" - past tense.	*We changed the text as recommended.*
P3, L2: Please add "and their stable isotope signature" to "measured groundwater contributions"	*Done.*
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 in Table 1.	*Sentence is changed to: „However, during snowmelt the monthly average discharge doubles (>50 L s^{-1}) compared to the other months' discharge (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.	*The referee is correct. The data is insufficient to cover the relevant runoff episodes. As mentioned before, we were able to increase the data. For instance, instread of one sample we now have 7 samples for March, when most of the snowmelt occurred.*
P5, L4: no need to cite anything here. Remove ref, or give the reader some information, why this ref is relevant here.	*We deleted the reference.*
P5, L23: replace 'usually multiplied by 1000' with 'expressed as per mill'	*Due to comments of referee #1 the methods section was thouroughly revised. We replaced the term as suggested.*
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.	*We shifted the first sentence to the end of the section and start section 2.3 with an explanation of model choices:* *"At the Uhlirska headwater catchment the original streamCO$_2$-DEGAS model was*

	applied to calculate stream CO$_2$ outgassing for different scenarios with varying values of river respiration (R) with 10, 19, 25, 50, and 75 % to test the model sensitivity to these values. In a second approach we modified the streamCO$_2$-DEGAS model as follows: instead of soil organic matter ($\delta^{13}C_{SOM}$) we used groundwater $\delta^{13}C_{DIC}$ data to better constrain initial CO$_2$ values and to reduce the model uncertainty."
P6, L11: I am not convinced that the a-priori assumption that there is no relevant primary production is reasonably, 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.	*We changed the text accordingly:* *"The Uhlirska catchment meets the assumption of the streamCO$_2$-DEGAS model with (i) stream waters being acidic with pH values between 4.7 and 6.8 (Table 2), and for our study we assumed that (ii) waters in the stream are unproductive. This means that secondary processes such as photosynthesis by algae or biofilms and DOC degradation to CO$_2$ are neglected. This is a plausible assumption because high runoff and short residence times often leave insufficient time for substantial degradation of DOC (Raymond et al., 2016;Catalan et al., 2016). However, the potential of temperature-dependent aquatic bio- and photodegradation (Demars et al., 2011;Moran and Zepp, 1997) particularly during summer cannot be entirely excluded in the Uhlirska catchment."* *This was also considered in the discussion section.*
P6, L22: The precise statement in the reference by Hotchkiss et al is:" Median internal CO2 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.	*In the revised manuscript we did the modeling with R= 10 % and R= 19% to reflect the range instead of the median value suggested by Hotchkiss et al. 2015 (also see our comment above).*
P7, L5 methods well described. Also great to see that one can extract a k-value that is then comparable to other studies.	*We appreciate the given credit.*

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.	*The nomenclature is now consistent and changed throughout the text.*
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.	*We thank the reviewer for pointing this out. We went through the entire manuscript and revised the complete results and discussion section.* *This section now starts with:* *“Our study shows that the uncertainty of the respiration parameter (R) can be circumvented by incorporating wetland groundwater $\delta^{13}C_{DIC}$ into the streamCO$_2$-DEGAS model. In a first step the original CO$_2$-DEGAS model was run with an R value of 10, 19, 25, 50, and 75 %. In a second step fractionation-corrected groundwater $\delta^{13}C_{DIC}$ was incorporated into the model. Thus the isotope composition of the initial CO$_2$ was better constrained and the uncertainty on the isotope fractionation in soils was reduced.* *In addition, we were able to estimate DIC export with modelled CO$_2$ outgassing and calculated lateral export of HCO_3^-, CO_2* as well as of total DIC (Table 3). These data cover a period of 20 months and measurements took place at the catchment outlet, whereas modelling results relate to CO$_2$ outgassing between the stream source and the catchment outlet (UHL).”*
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 CO2 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	*We moved the sentence to the methods and changed it according to:* *“To allow for inter-catchment comparisons the carbon losses were normalised to the stream surface area. In addition, to avoid often imprecise stream lengths and surface areas, the carbon losses were also normalised to the catchment area.”* *The mean stream surface area of 1.49 km^2 (calculated from stream geometry) was added to Table 1. Fluxes normalized to stream surface area were added to the*

	results section.
L20, averaged	*We think „mean values“ would be the more precise term here. We changes “averages” to “mean values”.*
P9, L1: interesting numbers!	*We agree. This means that a large amount of inorganic carbon is outgassed in the form of CO_2.*
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 din the discussion section.	*The reviewer is correct and we apologize for this inconsistency of the structure. For better readability we now revised the manuscript and merged the result and discussion sections.*
L4 and 5: Is there any relationship of k600 and Q? Most studies assume this (Raymond et al., 2012), as higher Q means higher flow velocity and therefore turbulence and gasexchange.	*The correlation of k600 values obtained with our model versus Q has an R^2 of 0.6 and for modeling with groundwater data the R^2 is 0.4 (see Figures below).* *However, the k600 values from our model depend on discharge. The reason is that k600 is calculated from F which is the flux that is calculated by multiplying the modeled concentration by discharge.* *For this reason we prefer Figure 4, which displays model results (CO_2 loss in mg/L) versus discharge rather then a plot of Q vs. k600.*
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).	*The fact that two different approaches were used is now outlined at the beginning of section 2.3 in the revised manuscript (see comment above).*
L13, please be precise. Concentration of what? As a reader I only know what relationship this is, after looking at the figure!	*We changed the sentence to:* *“Moreover, for CO_2 loss in mg L^{-1} and daily average discharge in L s^{-1} a negative concentration-discharge relationship was observed (Fig. 4).”*
L15: revise to ‘does not follow this proposed relationship’. The observation as such is very interesting.	*As mentioned above, for better readability in the revised manuscript the results and discussion sections were merged.*
L16: again, no references nor comparisons within the results!	*See answer above.*
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 section “result and discussion” now starts with:* *“Our study shows that the uncertainty of*

the forthcoming discussion. At present there is no red line here.	*the respiration parameter (R) can be circumvented by incorporating wetland groundwater $\delta^{13}C_{DIC}$ into the streamCO$_2$-DEGAS model. In a first step the original CO$_2$-DEGAS model was run with an R value of 10, 19, 25, 50, and 75 %. In a second step fractionation-corrected groundwater $\delta^{13}C_{DIC}$ was incorporated into the model. Thus the isotope composition of the initial CO$_2$ was better constrained and the uncertainty on the isotope fractionation in soils was reduced.* *In addition, we were able to estimate DIC export with modelled CO$_2$ outgassing and calculated lateral export of HCO_3^-, CO_2* as well as of total DIC (Table 3). These data cover a period of 20 months and measurements took place at the catchment outlet, whereas modelling results relate to CO$_2$ outgassing between the stream source and the catchment outlet (UHL).”*
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 pCO2 represents soil pCO2? This is how I read this sentence. Instead of making such bold statements, the authors should discuss, why they believe this is the case. . .	*We rephrased our statement to:* *“The streamCO$_2$-DEGAS model assumes that the modelled initial pCO$_2$ represents soil pCO$_2$ (Polsenaere and Abril, 2012). For the Uhlirska catchment this would mean that soil pCO$_2$ values ranged between…”*
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 pCO2 are larger contributions of CO2-enriched GW to stream water. . . ” does not make sense! How would GW flowing into the stream affect soil pCO2 in a positive way, meaning increasing it?	*The referee correctly identified an inconstistent line of argument. We corrected the statement to the fact that higher respiration rates exist in summer due to warmer temperatures.*
L20-24: There is in fact some literature that has raised this point: (Pacific et al., 2008, Boodoo et al., 2017)	*These helpful references were incorporated into the revised version:* *“Although this type of respiration was not measured directly, we can assume a large potential of respiration in waters of the organic-rich wetland and of riparian soils with peak values during late summer and*

	early fall (Pacific et al., 2008). In addition, respiration in gravel bar waters along the stream (Boodoo et al., 2017) can lead to an exceedance of 19 % for R along the Cerna Nisa stream."
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.	*We changed the sentences to:* *"Total alkalnity was low with 218 and 196 µmol* L^{-1} *in the Uhlirska catchment during June and July 2015. In contrast,* $\delta^{13}C_{DIC}$ *values and in situ* pCO_2 *were increased with –15.8 and –16.2 ‰ as well as 2225 and 2411 ppmV, respectively."*
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!	*We agree. We included this point to the beginning of the section:* *"Our study shows that the uncertainty of the respiration parameter (R) can be circumvented by incorporating wetland groundwater* $\delta^{13}C_{DIC}$ *into the streamCO*$_2$*-DEGAS model…" (Also see comment above).*
L17 and following: These comparisons are good and interesting. How about a tbale 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.	*A table with corresponding values was added.*
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 CO2 per volume may be countered on a per area.	*We agree that a comparison with other studies would be beneficial. However, the term of* CO_2 *loss is model-specific and the model would then first have to be applied to other catchments. By calculating fluxes normalized to stream surface areas (e.g. mg* m^{-2} *month*$^{-1}$*)* CO_2 *loss would have to be multiplied by runoff. Thus this flux term would not be independent of runoff and a plot against runoff not advisable (see answer above). No changes done.*
Conclusions: P13, L25 L27: 'the Uhlriska' is redundant here and can be removed.	*We removed 'the Uhlriska' at the end of the sentence.*

L30: The point that snowmelt puts out more CO2 would be much clearer, if the per stream area values would be compared (see earlier comment)	*We agree with the referee and will add a time series figure of CO_2 flux normalized to the area to the Figures we transferred from the supplement to the main text.*
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!	*We advocated direct pCO_2 measurements here, because we think that they provide better inputs than its calculation via DIC, pH and T.* *Chambers are mentioned here because they can be used to directly measure (time-weighted average) pCO_2 values. In our opinion this determination of stream pCO_2 has smaller uncertainties than its calculation via DIC, T and pH.*
Figures: Figure 1: I can't really see the large map of Germany, Poland etc. lines too thin.	*We shaded the country areas to highlight the borders.*
Figure 2 and 3: Essentially these two show the same thing: A timeseries of the different model scenarios (different Rs and the model with GW) as well as the respective uncertainties. Thus I suggest to merge the figures into one. Uncertainty ranges can then be shown by background shading of different pattern and/or color.	*We updated Figure 2 (now Figure 3) with R = 10 – 19 %. Due to the complexity of the figure we suggest to keep Figure 3 and 3 separated and instead combine them into a single Figue 3 with the revised figures as Figures 3A and 3B (see below).*
Other comments: F2 caption: 'do not apply to'. Also, remove last sentence, as redundant, especially if figures are merged.	*Done.*
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 CO2 loss defined as a term? I may have overlooked it, but its important that the reader knows if this is equal to CO2 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.	*The outlier relates to a model result, where no convergence was reached and the model largely overestimates CO2 loss. Thus it does not show CO_2 release related to runoff generation.* *We decided to plot the figure without the outlier. We included only data were the convergence was attained and included a regression line. Please find the revised Figure 4 below.* *The term of CO_2 loss basically is the model result and equals the loss of CO_2 via outgassing upstream of the measurement point.* *We revised the figure caption.*

	For the answer regarding the unit of ‘loss’ see above.
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.	*The reviewer is right. We changed the stream length to 2.1 km as it is the correct value.* *Regarding runoff seasonality we added: “Snowmelts in 2015 and 2016: Q> 50 L s^{-1}”*
T3: caption: these are not parameter, but results! Please revise. One option would be to write ‘DIC partitioning according to the . . . model’	*We changed the caption as recommended by the reviewer.*
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.	*They now appear in the main text as Figure 2.*
TS1: please add a note on missing values	*We revised the supplement according to the new modelling with more data.*

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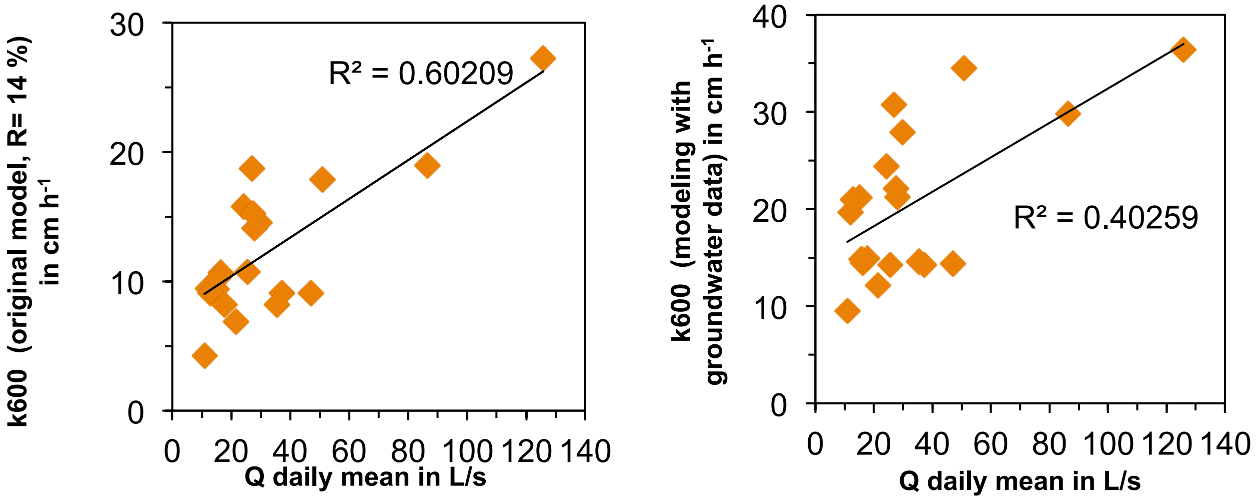
Figures



Figures are provided to support the answer to reviewer comment ‘P9 L4 and L5’ about the relationship between k600 and Q.

Groundwater data improve modelling of headwater stream CO_2 outgassing with a stable DIC isotope approach

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Abstract. A large portion of terrestrially derived carbon outgasses as carbon dioxide (CO_2) from streams and rivers to the atmosphere. Particularly, the amount of CO_2 outgassing from small headwater streams was indicated as highly uncertain. Conservative estimates suggest that they contribute 36 % (i.e., 0.93 petagrams C yr^{-1}) of total CO_2 outgassing from all fluvial ecosystems~~rivers and streams~~ on the globe~~worldwide~~. In this study, stream pCO$_2$, dissolved inorganic carbon (DIC) and $\delta^{13}C_{DIC}$ data were used to determine CO_2 outgassing from an acidic headwater stream in the Uhlirska catchment (Czech Republic). This stream drains a catchment with silicate bedrock. The applied stable isotope model is based on the principle, that the $^{13}C/^{12}C$ ratio of its sources and the intensity of CO_2 outgassing control the isotope ratio of DIC in stream water. It avoids the use of the gas transfer velocity parameter (k) that is highly variable and mostly difficult to constrain. Model results indicate that CO_2 outgassing contributed more than 80 % to the annual stream inorganic carbon loss in the Uhlirska catchment. This translated to a CO_2 outgassing rate from the stream of ~~5.2~~34.9 kg~~t~~ C m^{-2} yr^{-1}~~ and to 2.9 g C m^{-2} yr^{-1}~~, when normalised to the ~~catchment~~ stream surface area. Large temporal variations with maximum values shortly before ~~during~~ spring snowmelt and in summer emphasise the need for investigations at higher temporal resolution. We improved the model uncertainty by incorporating groundwater data to better constrain the isotope compositions of initial DIC. Due to the large global abundance of acidic, humic-rich headwaters, we underline the importance of this integral approach for global applications.

1 Introduction

Rivers and streams are the main carbon pathways from the continents to the oceans and thus constitute an important link in the global carbon cycle. In the process of transport, large amounts of carbon – mostly in the form of CO_2 – outgas from the water surface to the atmosphere (Cole et al., 2007;Aufdenkampe et al., 2011;Regnier et al., 2013;Wehrli, 2013). Globally, this form of CO_2 contributions to the atmosphere was estimated between 0.6 to 2.6 petagrams (Pg) of carbon per year (Raymond et al., 2013;Lauerwald et al., 2015;Sawakuchi et al., 2017;Marx et al., 2017a). The lower value of this range by Lauerwald et al. (2015) excluded streams of Strahler stream numbers ~~(Strahler, 1952)~~ below ~~3~~three. This is because of sparse coverage of actual direct measurements of the partial pressure of CO_2 (pCO_2) in headwater streams. Note that, the upper value of the range still lacks a representative contribution from headwater streams (Marx et al., 2017a).

The contributions of headwater streams are considered as a major unknown factor in these estimates of global carbon budgets for inland waters (Cole et al., 2007;Raymond et al., 2013). The main reasons are uncertainties of groundwater input as well as poorly defined surface areas and gas transfer velocities (Marx et al., 2017a;Schelker et al., 2016). In addition, pCO_2 and subsequent CO_2 outgassing fluxes typically decline rapidly from stream source areas to river sections further downstream (van Geldern et al., 2015;Stets et al., 2017). Poor definition of these gradients adds another uncertainty to the global carbon budget. The enormous number of small headwater streams making a significant contribution on a basin scale and thus in the continents combined with the scarcity of data led to the term *aqua incognita* (Bishop et al., 2008).

Various direct and indirect approaches to determine CO_2 fluxes exist. Most often fluxes are calculated from pCO_2 and gas transfer velocities (Teodoru et al., 2009;Raymond et al., 2012;Lauerwald et al., 2015;van Geldern et al., 2015). However, because of large variabilities of gas transfer velocities on spatial and temporal scales, this type of determination remains arguable, especially for small-scale applications (Marx et al., 2017a;Regnier et al., 2013;Schelker et al., 2016). For applications in small streams and during changing flow conditions also direct methods such as floating chamber approaches exhibit major drawbacks such as altered outgassing behaviour because of artificially created currents inside anchored chambers (Lorke et al., 2015;Bastviken et al., 2015). In addition, rapid downstream losses of CO_2 often imply that CO_2-rich groundwater inputs are lost before actual measurements can take place (Reichert et al., 2009).

Recent approaches have used stable carbon isotopes of dissolved inorganic carbon to reliably quantify CO_2 outgassing from streams and rivers (Polsenaere and Abril, 2012;Venkiteswaran et al., 2014), in which the model by Venkiteswaran et al. (2014) is a parsimonious, simpler version of the model by Polsenaere and Abril (2012). Both apply inverse modelling to calculate the amount of CO_2 lost upstream of a sampling point within a stream or at a catchment outlet. One clear advantage when compared to conventional methods is, that these stable isotope approaches account for the potentially high CO_2 outgassing upstream of any sampling point. Moreover they incorporate groundwater seeps in first-order headwaters, particularly at low discharge (Polsenaere and Abril, 2012). These factors are typically not covered by conventional methods.

The integrative models exploit the fact, that the stable isotope ratios of dissolved inorganic carbon (expressed as $\delta^{13}C_{DIC}$) in stream water are controlled by $^{13}C/^{12}C$ ratios of its sources and the intensity of CO_2 outgassing. One important input is the stable isotope ratio of soil CO_2 that in turn depends on the plants' pathways used for photosynthesis and the organic matter sources fuelling plant and microbial respiration (Mook et al., 1983;Vogel, 1993). In general, this soil-internally produced CO_2 has a $\delta^{13}C_{CO_2}$ value close to the initial substrate, which has a range from –30 to –24 ‰ for the most commonly occurring C3 plants (Ehleringer and Cerling, 2002). After entering the stream, CO_2 outgassing to the atmosphere increases $^{13}C/^{12}C$ ratios in the remaining DIC pool because of the well-known equilibrium isotopic fractionation between CO_2, HCO_3^-, and CO_3^{2-} (Myrttinen et al., 2015, 2012;Mook et al., 1974). This predictable and temperature-related process is calculated by the models of Polsenaere and Abril (2012) and Venkiteswaran et al. (2014). They are independent of the gas transfer velocity *k* and account for the upstream portion of a sampling site in headwater streams.

The aim of this work ~~is~~ was to model stream CO_2 outgassing on the basis of the stable isotope approach by Polsenaere and Abril (2012) and to extend their method by including measured groundwater ~~contributions~~ stable isotope signatures in order to reduce modelling uncertainties. Our study utilizes data from the well-studied Uhlirska catchment in the Jizera Mountains (Czech Republic) (Dusek et al., 2012;Sanda et al., 2014;Vitvar et al., 2016;Marx et al., 2017b). Since the background geology of the catchment consists of silicate rocks, carbonate weathering as CO_2 source can be virtually excluded. The CO_2 saturation is then exclusively controlled by the mobilization of terrestrial respired organic carbon and by the input of shallow groundwater (Humborg et al., 2010;Amiotte-Suchet et al., 1999).

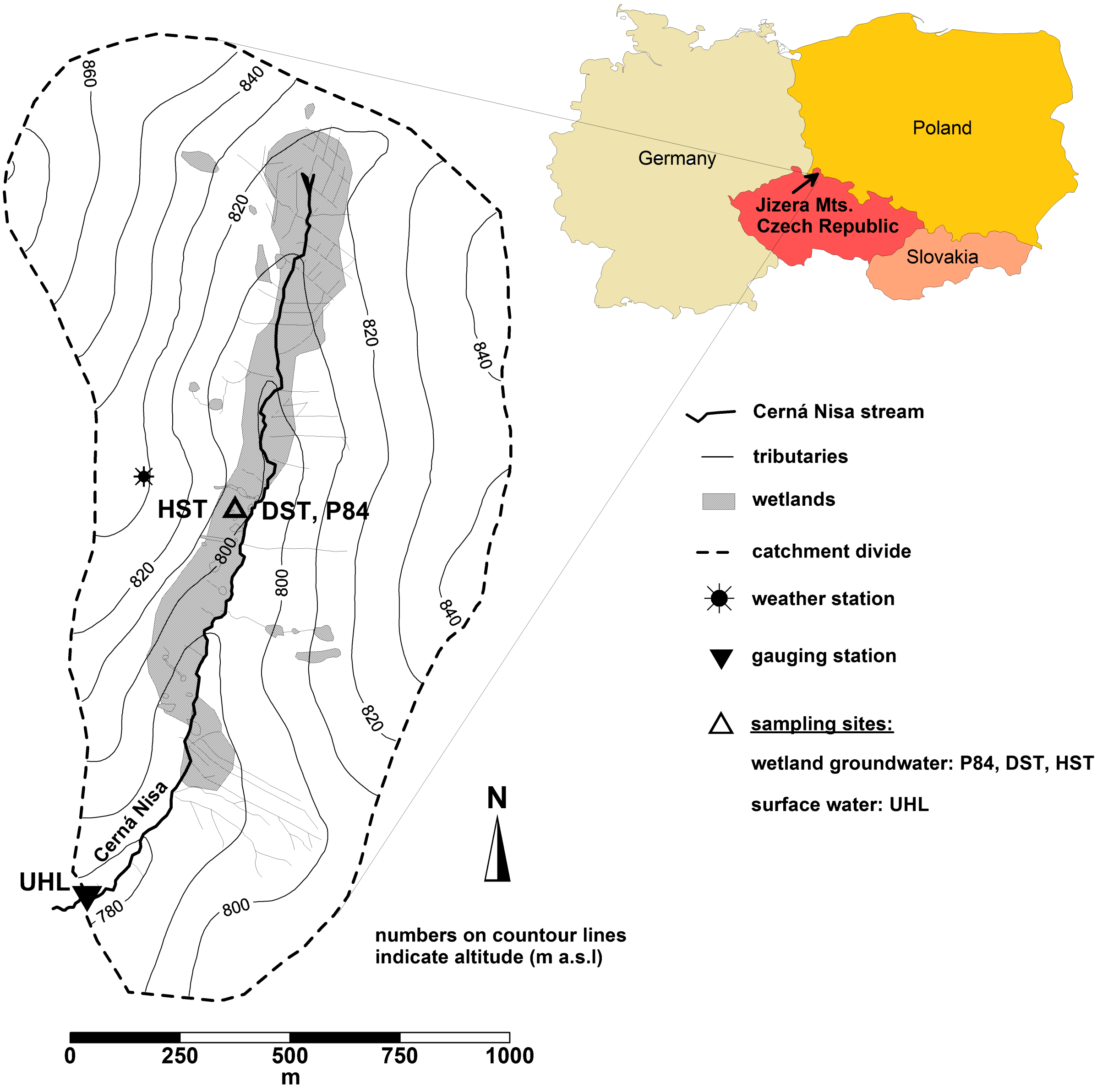
2 Materials and methods

2.1 Study site

The Uhlirska catchment is situated in the northern Czech Republic, 9 km northeast of the city of Liberec (Fig. 1). The stream Cerna Nisa flows in the catchment valley and is a tributary of the Luzicka Nisa River that later merges with the Odra River and flows towards the Baltic Sea. The stream length in this experimental catchment is about 2100 meters and water travel times are less than one hour from the spring to the catchment outlet.

Table 1 lists the main characteristics of the Uhlirska catchment. The annual average precipitation exceeds 1200 mm yr^{-1} and the annual average temperature is 5.5°C (1996-2009). Snowcover typically prevails during 6 months of the year, mostly between November and March (Hrncir et al., 2010). During our study period from September 2014 to April 2016 snowcover prevailed only between January and March. However, during snowmelt the monthly average ~~runoff~~ discharge ~~intensity is more than~~ doubles (>50 L s^{1}) compared to the other months' ~~runoff~~discharge ~~intensities~~ (Table 1).

The forest consists of a spruce monoculture (*Picea abies*) and isolated patches of larch, beech and rowan trees (Sanda and Cislerova, 2009). Purely granitic bedrocks underlie this type of C3 vegetation. The catchment has two basic types of soils. On the hillslopes, about 60-90 cm deep and highly heterogeneous soil profiles consist of dystric Cambisols, Podzols or Cryptopodzols that developed on weathered and fractured bedrocks. These soil types cover approximately 90 % of the catchment area. The valley bottom soils consist of a layer of peat of mostly Histosol-types with depths up to 300 cm. The latter soils cover approximately 10 % of the catchment area, make up small wetlands along the stream and lie on top of fluvial material, which embodies the main perennial aquifer (Sanda et al., 2014).



~~Figure 1: Location of the Uhlirska catchment and sampling sites modified from Sanda et al. (2014).~~

Table 1: Characteristics of the Uhlirska catchment and Cerna Nisa stream.

Location	15°09’E, 50°49’N
Altitude range	776-886 m above sea level
Drainage area	1.78 km^2
Stream surface area	1490 m^2
Strahler stream order	1

Total stream length	2.1~~0~~ km
Stream flow (Q)	Q_{median}= 21.2 L s^{-1} (2014-2016)
	Snowmelts in 2015 and 2016: Q> 50 L s^{-1}
Mean slope	2.3 %
Annual average air temperature	5.5°C (1996-2009)
Annual average precipitation	1212 mm (1996-2009)
Dominant vegetation	95 % Norway spruce, 5 % grassland
Dominant soil type	Cambisols, Podzols, Cryptopodzols, Histosols, Gleysols
Bedrock	Granite, deluviofluvial sediments, glacial tills

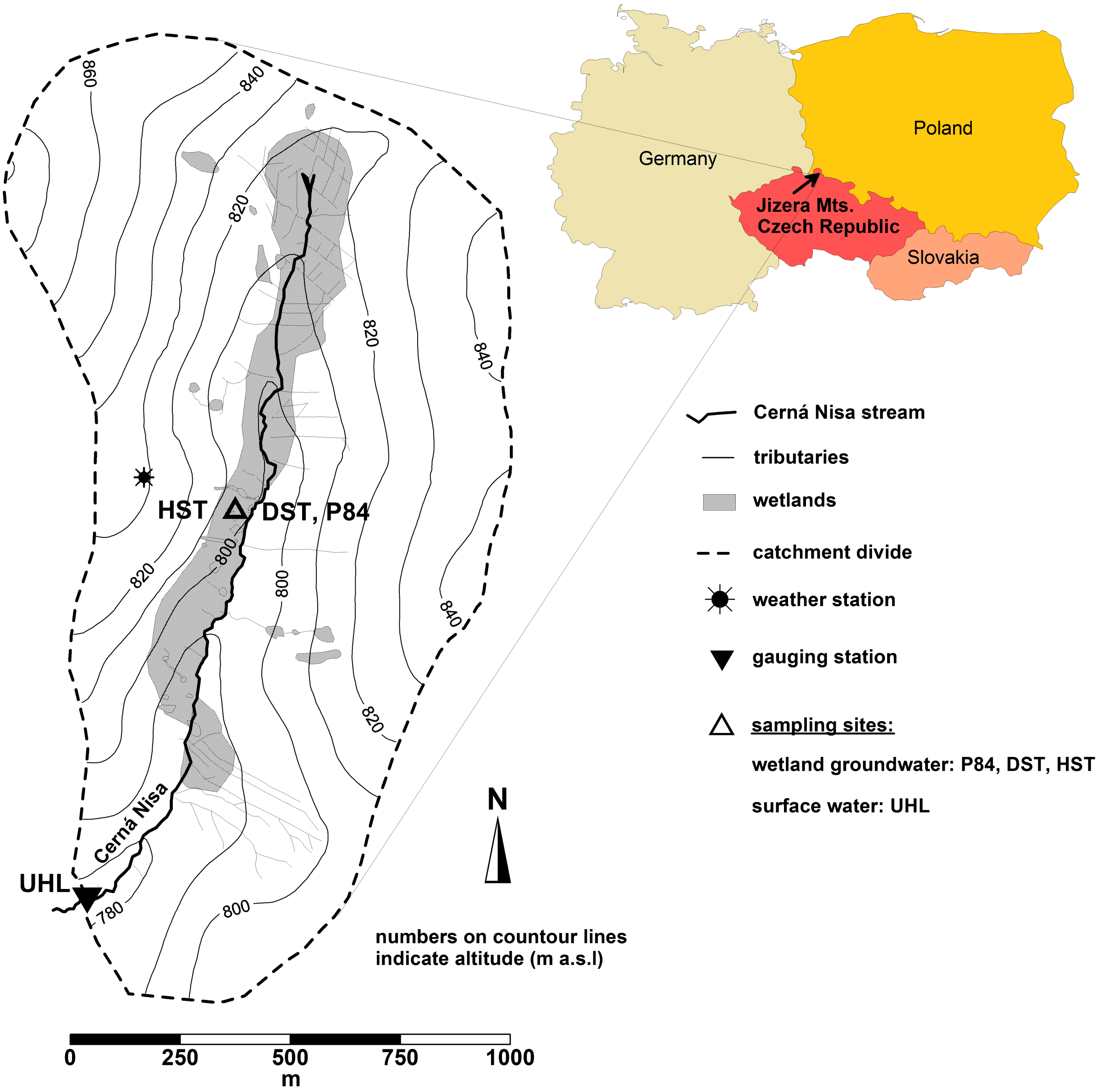


Figure 1: Location of the Uhlirska catchment and sampling sites modified from Sanda et al. (2014).

2.2 Water sampling and laboratory analyses

Between September 2014 and April 2016 shallow wetland groundwater was ~~and stream water samples were~~ collected on a monthly ~~basis.~~ and stream water on approximately a weekly basis. ~~The s~~Sampling points are shown in Figure 1.

The stream discharge was determined at a V-notch weir at the catchment outlet (site UHL, see Fig. 1)~~-~~. Temperature (T), pH and total alkalinity (TA) were determined in the field with portable HACH equipment that included a multi-parameter instrument and a digital titrator (all HACH Company, Loveland, CO, USA). The measured parameters exhibited a precision of 0.1 pH units, 0.1 °C (2σ) for T and was better than 2 % (2σ) per 100 titration steps for TA (Marx et al., 2017b). Water samples were collected from the stream approximately 10 cm below the water surface and from boreholes with a peristaltic pump approximately 24 hours after purging the boreholes.

Particulate organic carbon (POC) was sampled on 0.7 μm pore size glass fibre filter papers and analysed according to Barth et al. (2017). All other samples were filtered via syringe disk filters with 0.45 μm pore size (Minisart HighFlow PES, Sartorius AG, Germany) in the field. Before filtration, both syringe and membrane were pre-washed with sample water. Samples for the analysis of dissolved inorganic carbon (DIC) concentrations and isotopes were collected in 40 mL amber glass vials without headspace. The vials fulfil specifications of the US Environmental Protection Agency (EPA) and were closed with butyl rubber/PTFE septa and open-hole caps, with butyl rubber side showing towards the sample. Vials were poisoned with 20 μL of a saturated $HgCl_2$ solution to avoid ~~any~~ biological activity after sampling. After collection, all samples were kept in the dark at 4°C until analyses.

Water samples were analysed for their carbon stable isotope ratios of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) and dissolved organic carbon ($\delta^{13}C_{DOC}$) by an OI Analytical Aurora 1030W TIC-TOC analyser (OI Analytical, College Station, Texas) that was coupled in continuous flow mode to a Thermo Scientific Delta V plus isotope ratio mass spectrometer (IRMS) (Thermo Fisher Scientific, Bremen, Germany). The sample was reacted with 1 mL of 5% phosphoric acid (H_3PO_4) at 70°C for 2 min to release the dissolved inorganic carbon (DIC) as CO_2. The evolved CO_2 was purged from the sample by helium. In a second step 2 mL of 10% sodium persulfate ($Na_2S_2O_8$) were reacted for 5 min at 98 °C to oxidize the DOC to CO_2 that was subsequently purged from the solution by helium. A trap and purge (T&P) system was installed for the analysis of low concentrations. Details of the coupling of the TIC/TOC analyser to IRMS are described in St-Jean (2003).

All values are reported in the standard δ-notation in per mil (‰) vs. Vienna Pee Dee Belemnite (VPDB) according to~~Carbon isotope values are reported in the standard δ-notation as deviations in per mil (‰) from the corresponding reference material:~~

$$\delta=\frac{R_{\text{sample}}}{R_{\text{reference}}}-1\ , \qquad (1)$$

where R is the ratio of the numbers (n) of the heavy and light isotope of an element (e.g. $n(^{13}C)/n(^{12}C)$) in the sample and the reference (Coplen, 2011). The data sets were corrected for instrumental drift during the run and linearity. The data were normalized to the VPDB scale by two laboratory reference materials (C_4 sugar and KHP) measured in each run. The in-house reference materials were calibrated directly against USGS-40 (L-glutamic acid) and IAEA-CH-6 (sucrose) by using an elemental analyser (Costech ECS 4010). A value of –26.39 ‰ and –10.45 ‰ was assigned to USGS-40 and IAEA-CH-6, respectively. Concentration was determined from the signal of the OI Aurora 1030W internal non-dispersive infrared sensor (NDIR) and a set of calibration standard with known concentrations prepared from analytical (A.C.S.) grade potassium hydrogen phthalate (KHP). Areas of the sample peaks are directly proportional to the amount of CO_2 generated by the reaction of the sample with acid (DIC) or sodium persulfate (DOC). Analytical precision based on the repeated analyses of a control standard (C_3 sugar) during all runs was better than ±0.3‰ for $\delta^{13}C$ and better than 5% for concentrations (1σ).

~~where *R* is the ratio of the heavy and light isotope numbers (*n*) of an element in the sample and the reference (Coplen, 2011). Here the ratio corresponds to $n(^{13}C/)/n(^{12}C)$ and the reference material is Vienna Pee Dee Belemnite (VPDB). This value is usually multiplied by 1000 to render small changes visible.~~

POC samples were analysed for $\delta^{13}C_{POC}$ using a Costech Elemental Analyser (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‰ 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‰ (1σ) for $\delta^{13}C_{POC}$. ~~DIC concentrations and $\delta^{13}C_{DIC}$ isotopes were measured with an Aurora 1030W instrument (OI Analytical, College Station, Texas, USA) coupled in continuous flow mode to a Delta V isotope ratio mass spectrometer (Thermo Fisher Scientific, Bremen)(St-Jean, 2003). The resulting $\delta^{13}C_{DIC}$ data were corrected for linearity effects and normalized to the VPDB scale by assigning a value of +1.95 ‰ and –46.6 ‰ to the international reference materials NBS 19 and LSVEC, respectively. The precision based on repeat analyses of a control standard (C_3 sugar) for concentrations and the carbon isotope values during all runs was better than ±5 % (1σ) and ±0.3 ‰ (1σ), respectively. For $\delta^{13}C_{POC}$ the precision was better than ±0.1 ‰ (1σ).~~

2.3 Calculations and model assumptions

~~All modelling approaches were executed via Matlab (MathWorks, Natick, MA, USA).~~

At the Uhlirska headwater catchment the original streamCO_2-DEGAS model was applied to calculate stream CO_2 outgassing for different scenarios with varying values of river respiration (R) with 10, 19, 25, 50, and 75 % to test the model sensitivity to these values. In a second approach we modified the streamCO_2-DEGAS model as follows: instead of soil organic matter ($\delta^{13}C_{SOM}$) we used groundwater $\delta^{13}C_{DIC}$ data to better constrain initial CO_2 values and to reduce the model uncertainty.

The Uhlirska catchment meets the ~~two~~ assumption~~s~~ of the ~~model by Polsenaere and Abril (2012) (~~streamCO_2-DEGAS~~)~~ model with (i) stream waters being acidic with pH values between ~~4.7~~3.9 and 6.~~8~~ 7 (Table 2), and

~~(ii)~~ for our study we assumed that (ii) waters in the stream ~~being~~ are unproductive. This means that secondary processes such as photosynthesis by algae or biofilms ~~can be~~and DOC degradation to CO_2 are ~~neglected~~neclected. This is a plausible assumption because high runoff and short residence times often leave insufficient time for substantial degradation of DOC (Raymond et al., 2016;Catalan et al., 2016). However, the potential of temperature-dependent in-stream bio- and photodegradation (Demars et al., 2011;Moran and Zepp, 1997), particularly during summer cannot be entirely excluded in the Cerna Nisa stream.

The original streamCO$_2$-DEGAS model by Polsenaere and Abril (2012) demands the input variables of total alkalinity (TA), $\delta^{13}C_{DIC}$, pCO_2 and temperature (Table 2) as well as the proportion of river respiration (R) and the carbon isotope composition of $\delta^{13}C_{SOM}$. Note that TA and groundwater $\delta^{13}C_{DIC}$ were only measured during monthly samplings and linear interpolated otherwise.

We used DIC concentrations to calculate HCO_3^- (Dickson, 2007) and together with pH and T we were able to calculate~~d the~~ pCO_2 values ~~from DIC concentration, pH and T~~ with the following ~~Eq. (2)~~equation (Plummer and Busenberg, 1982):

$$pCO_2 = \frac{\mathrm{HCO_3^-} \times \mathrm{H^+}}{\mathrm{K_H} \times \mathrm{K_1}}, \tag{2}$$

where HCO_3^- is the activity of bicarbonate, H^+ is 10^{-pH}, K_1 is the temperature-dependent first dissociation constant for the dissociation of H_2CO_3 (all variables in mol L^{-1}), and K_H is the Henry's law constant in mol L^{-1} atm^{-1}. The uncertainty of the calculation depends on the measurement uncertainties of DIC, pH and T. The largest uncertainty is caused by pH measurements as they are on a logarithmic scale. The pH measurement uncertainty is typically smaller than ±0.1 pH units and causes a maximum uncertainty of ±21 % for pCO_2. We consider this as a worst-case scenario that is also indicated in Figure 3.

~~The streamCO$_2$-DEGAS model demands the input parameters of total alkalinity (TA), $\delta^{13}C_{DIC}$, pCO_2 and temperature (Tables 2 and 3) as well as the proportion of river respiration (R) and the carbon isotope composition of soil organic matter ($\delta^{13}C_{SOM}$).~~

~~The~~ R ($0 < R < 1$) is the proportion of CO_2 resulting from respiration in water along the entire stream course (waterlogged soils, stream waters, and sediments) and was approximated by a range ~~with R~~ between ~~= 14 %~~0.1 and 0.19 (i.e., 10 to 19 %). This corresponds to the credible range of internal CO_2 production as a percentage ~~from~~ of median stream CO_2 emissions ~~in~~ from small streams (<0.01 m^3 s^{-1}) in the contiguous United States and was determined by Hotchkiss et al. (2015).
POC was considered as best representative of soil organic matter in the catchment. It is the material closest to the original plant and soil material. DOC has recalcitrant phases and thus would introduce a non-representative value for organic matter input (Laudon et al., 2011;Cauwet and Sidorov, 1996). Polsenaere and Abril (2012) chose a $\delta^{13}C_{SOM}$ ~~$\delta^{13}C_{SOM}$~~ of –28 ‰ that was determined as average annual ~~$\delta^{13}C_{POC}$~~ $\delta^{13}C_{POC}$ at their study site. In our study we also used the average annual stream $\delta^{13}C_{POC}$~~$\delta^{13}C_{POC}$~~. Thus the $\delta^{13}C_{SOM}$ ~~$\delta^{13}C_{SOM}$~~ was confined with –29.5 ‰ (Table 2). In addition, the average of wetland groundwater $\delta^{13}C_{DIC}$ ~~$\delta^{13}C_{DIC}$~~ with an assumed isotopic fractionation of +1 ‰ for movement of CO_2 in waterlogged soils, groundwaters, river waters and sediments (O'Leary, 1984), served as input of initial $\delta^{13}C_{DIC}$ ~~$\delta^{13}C_{DIC}$~~ (δ^{13}C-DIC$_{init.}$).

Measured $\delta^{13}C_{DIC}$ values ~~These were entered into the model with values ranging~~ranged between –25.~~9~~2 ‰ and –~~23~~10.1~~9~~ ‰ (~~Supplement~~ Table S1).~~). Note that the term R was not part of the modelling with groundwater data(O'Leary, 1984).~~

The model results are the partial pressure of initial CO_2 before gas exchanges (pCO_{2init}) with the atmosphere start and the fraction of stream DIC that has degassed into the atmosphere ($[DIC]_{ex}$). $[DIC]_{ex}$ corresponds to the CO_2 loss upstream of the sampling point and is given as a concentration (Polsenaere and Abril, 2012). ~~Monthly and annual~~ CO_2 fluxes~~losses~~ ~~are~~ were calculated by multiplication with average discharges that were established from daily values. To allow for inter-catchment comparisons the carbon losses were normalised to the stream surface area. In addition, to avoid often imprecise stream lengths and surface areas, the carbon losses were also normalised to the catchment area.

For comparison, the gas transfer velocity adjusted to the in situ temperature (k_T, in m d^{-1}) can be calculated from model results when assuming that the water pCO_2 ($pCO_{2,aq}$) is the average between the modelled soil pCO_2 and the in situ pCO_2 at the catchment outlet:

$$k_T = \frac{F}{K_H \times \left(pCO_{2,aq} - pCO_{2,air}\right) \times M_C}, \tag{3}$$

where F is the modelled CO_2 outgassing (in g m^{-2} d^{-1}), $pCO_{2,air}$ the partial pressure of CO_2 in the atmosphere considered with ~400 ppmV (ESRL/GMD, 2017), K_H is the Henry's law constant (in mol L^{-1} atm^{-1}) and M_C the molar mass of C (12.011 g mol^{-1}). k_T was then converted into the normalized gas transfer velocity of CO_2 at 20°C (k_{600}, in m d^{-1}) ~~with Eq. (4)~~according to:

$$k_{600} = \frac{k_T}{\left(\frac{Sc_T}{600}\right)^{-0.75}}, \tag{4}$$

where Sc_T is the Schmidt number at the measured in situ temperature (Raymond et al., 2012).

All modelling approaches were executed via Matlab (MathWorks, Natick, MA, USA).

2.4 Model input ~~parameters~~ variables from the Uhlirska catchment

Stream (UHL) and wetland groundwater (DST, HST, P84) pH values were always below 6.~~9~~7 during the entire study period (Table 2). In agreement with generally low stream pH values, the capacity of waters to buffer acidic inputs indicated by TA was generally low. ~~At the catchment outlet~~ The TA ranged around a median of ~~145~~ 130 μmol L^{-1} with a standard deviation (1σ) of ±~~110~~ 101 μmol L^{-1} at the catchment outlet (Table 2). Note, that in the following the standard deviations express the variation over the sampling period and not the measurement error. The $\delta^{13}C_{DIC}$ values ~~at UHL~~ had a median of –18.~~5~~ 4 ±~~2~~3.~~7~~ 3 ‰ with a range from –~~22~~25.~~4~~ 2 to –~~14~~10.1~~.0~~ ‰ (Table 2). The most negative values were measured in wetland groundwater with median values of –24.5 ‰, –28.7 ‰ and –24.3 ‰ in HST, DST, and P84, respectively (Fig. 1). The range of these groundwaters between –23.6 and –29.6 ‰ fits the range of $\delta^{13}C$ in C3 plants and associated soil organic matter. In the different water compartments (wetland groundwater and stream, Table 2), the DIC concentrations decreased with increasing $\delta^{13}C_{DIC}$ values. The lowest DIC concentrations were found at the catchment outlet (~~65~~ 31 to ~~261~~ 483 μmol L^{-1}) and the highest concentrations in wetland groundwater (284 to 540 μmol L^{-1}). The median stream pCO_2 determined at the catchment outlet was ~~1500~~ 1374 ±~~500~~ 710 ppmV with a range from ~~650~~ 450 to ~~2760~~ 3749 ppmV. Values in wetland groundwater were typically higher with median values of 5590, 4440, and 6210 ppmV at HST, DST, and P84, respectively. Stream water temperatures showed a characteristic annual trend with a range from 0.~~9~~ 8 °C to 13.~~0~~ 8 °C and a median of 4.~~3~~ 5 °C (Table 2).

Table 2: pH, total alkalinity (TA), temperature (T), pCO_2 values, DIC concentrations and $^{13}C/^{12}C$ ratios ~~for monthly samples from September 2014 to April 2016 in the Uhlirska catchment~~ expressed as median values with ± 1σ standard deviation and ranges given in parentheses. Site names are according to Figure 1.

Site ID	Description [sampling depth]	pH	TA μmol L^{-1}	T °C	DIC μmol L^{-1}	$\delta^{13}C_{DIC}$ ‰	pCO_2 ppmV	$\delta^{13}C_{POC}$ ‰
	Surface water							
UHL	Main stream outlet	~~6.1~~5.9 ±0.7~~5~~	~~145~~ 130 ±1~~100~~01	4.~~3~~ 5 ±3.~~8~~5	~~141~~114±~~5~~ 472	–18.4~~5~~±~~2~~3.~~7~~3	~~1520~~ 1374 ±~~520~~710	–29.5 ±0.~~5~~6
		(34.9-6.7)	(24-500)	(0.8~~0.9~~-13.8~~0~~)	(~~65~~31-~~261~~483)	(–~~22~~25.42- –~~14~~10.1~~0~~)	(~~650~~450-~~2760~~3749)	(–30.45- –~~28~~27.45)
	Groundwater							
HST	Wetland	5.9 ±0.2	180 ±57	6.4 ±2.1	424 ±46	–24.5 ±0.8	5590 ±1120	–28.6 ±1.0
	[2.7 m]	(5.7-6.4)	(120-350)	(4.3-11.3)	(349-509)	(–27.0- –23.6)	(3660-7860)	(–29.8- –25.6)
DST	Wetland	5.9 ±0.4	160 ±38	5.9 ±2.1	399 ±57	–28.7 ±0.7	4440 ±1410	–28.7 ±0.7
	[3.7 m]	(5.7-7.3)	(82-244)	(3.1-10.8)	(284-482)	(–29.8- –27.6)	(1080-6960)	(–29.8- –27.6)
P84	Wetland	5.9 ±0.5	158 ±33	6.8 ±1.4	499 ±58	–24.3 ±0.7	6210 ±1720	–29.2 ±0.6
	[5.2 m]	(5.0-7.3)	(110-222)	(3.3-9.6)	(299-540)	(–25.0- –22.1)	(980-7830)	(–29.9- –28.1)

3 Results ~~of carbon dioxide loss modelling~~and discussion

Our study shows that the uncertainty of the respiration parameter (*R*) can be circumvented by incorporating wetland groundwater $\delta^{13}C_{DIC}$ into the streamCO$_2$-DEGAS model. In a first step the original CO$_2$-DEGAS model was run with an *R* value of 10, 19, 25, 50, and 75 %. In a second step fractionation-corrected groundwater $\delta^{13}C_{DIC}$ was incorporated into the model. Thus the isotope composition of the initial CO_2 was better constrained and the uncertainty on the isotope fractionation in soils was reduced.

In addition, we were able to estimate DIC export with modelled CO_2 outgassing and calculated lateral export of HCO_3^-, CO_2* as well as of total DIC (Table 3). These data cover a period of 20 months and measurements took place at the catchment outlet, whereas ~~DIC parameters including modelled CO_2 outgassing according to Polsenaere and Abril (2012) in the investigated period between September 2014 and April 2016 are listed in Table 3. M~~modelling results relate to CO_2 outgassing between the stream source and the catchment outlet (UHL). ~~Figure 2 displays modelled monthly CO_2 losses for the proportion of river respiration (*R*) inputs that were assumed with 14, 25, 50 and 75 %. It also displays results for the modified modelling with groundwater input. The shaded ribbon shows pCO_2 measurement uncertainties for modelling without groundwater data. Points that lay outside the measurement uncertainty did not fulfil the convergence criteria (Polsenaere and Abril, 2012). They were thus replaced by interpolated values in the discussion. Note that, for modelling with groundwater data the convergence criteria were not fulfilled only for February 2015 (Fig. 3).~~

~~For modelling with *R* = 14 % in May 2015 the modelled CO_2 outgassing was highest with 1531 kg C month^{-1} (Fig. 2). For the remaining months, CO_2 outgassing ranged from 15 kg C month^{-1} in April 2016 to 909 kg C month^{-1} in December 2014. The median CO_2 outgassing over the sampling period was 145 kg C month^{-1}. Translating these to annual carbon outgassing~~

~~yielded a mean of 4.8 t C for 12 consecutive months (Supplement Table S2). To allow for inter-catchment comparisons and to avoid often imprecise stream lengths and surface areas, the carbon losses were normalised to the catchment area. With this, the Uhlirska catchment lost a mean 2.7 g C m^{-2} yr^{-1} via the stream to the atmosphere.~~

~~On an annual basis, the DIC proportions of HCO_3^- export, CO_2* (i.e. the sum of $CO_{2(aq)}$ and H_2CO_3) export and CO_2 outgassing had averages of 0.7, 1.1 and 6.2 mg C L^{-1}, respectively (Table 3). This corresponds to the relative amounts of about 9:14:78 % HCO_3^- export, CO_2* export and CO_2 outgassing with respect to total inorganic carbon loss from the Uhlirska catchment outlet. Other studies found similar relationships and showed that the largest proportion of DIC entering a stream rapidly outgasses as CO_2 (Billett et al., 2004;Johnson et al., 2008;Davidson et al., 2010;Polsenaere and Abril, 2012).~~

~~Calculated k_{600} values varied between 1.0 and 6.5 m d^{-1} (Table 3), with higher values occurring during springtime and lower values during summer.~~

~~When including shallow wetland groundwater data in the model, median CO_2 outgassing was 84 kg C month^{-1} and ranged between 12 and 2656 kg C month^{-1}, with minimum and maximum values during April 2016 and June 2015 (Fig. 3 and Table 3). Corresponding annual carbon outgassing yielded 5.2 t C yr^{-1} and 2.9 g C m^{-2} yr^{-1} when normalized to the catchment area. With this calculation the relative proportions of DIC fractions were 7:12:81 % with 0.7, 1.1 and 7.8 mg C L^{-1} of HCO_3^- export, CO_2* export and CO_2 outgassing, respectively.~~

~~Derived k_{600} values from the latter approach ranged from 2.3 to 8.7 m d^{-1} (Table 3). Higher values occurred during springtime and lower values during summer.~~

~~Moreover, a negative concentration-discharge relationship was observed (Fig. 4). Higher pCO_2, modelled soil pCO_2 and modelled CO_2 loss occurred during low flow, when relative contributions of CO_2-enriched groundwaters to stream waters were high. One exception is the largest discharge of 0.138 m^3 s^{-1} that does not fit into this pattern. For this discharge in springtime 2015 also the computed upstream CO_2 loss ($[DIC]_{ex}$) was high with 11.6 mg L^{-1}. {Dinsmore, 2008 #1637}~~

3.1 Model sensitivity

The parameter of proportion river respiration (*R*) has a large impact on the results by the model. It is attributed to the average percentage of respiration occurring along the entire stream course (waterlogged riparian soils, stream waters, sediments and the hyporheic zone). Thus, it is important to evaluate the model sensitivity to assumed respiration. Modelled CO_2 outgassing and modelled initial pCO_2 values relate to an assumed *R* of 10 and 19 %, which corresponds to an average in-stream respiration as determined by Hotchkiss et al. (2015). However, this value does not account for respiration in groundwater and soil water. The contributions of these compartments are typically also considerable in headwaters. Although this type of respiration was not measured directly, we can assume a large potential of respiration in waters of the organic-rich wetland and of riparian soils with peak values during late summer and early fall (Pacific et al., 2008). In addition, respiration in gravel bar waters along the stream (Boodoo et al., 2017) can lead to an exceedance of 19 % for R along the Cerna Nisa stream.

In some cases the model was not able to produce reliable results and the convergence criteria were not fulfilled. The initial soil pCO_2 had to be extremely large (> 150000 ppmV) for selected sampling events to reach the convergence of both $\delta^{13}C_{DIC}$ and pCO_2 at the same iteration (Polsenaere and Abril, 2012). This was during few cases in February and March 2015 and during summer between May and September 2015. However, for an *R* of 10 to 19 % during 22 to 23 cases, for a *R* of 25 and 50 % during 26 cases and for a *R* of 75 % during 29 cases the convergence criteria were not attained. Consequently, with increasing *R* a necessary convergence was more often not possible due to exceeding reasonable boundaries. These findings suggest that 10 to 19 % are reasonable *R* values for most months, except for June to August in 2015. Low respiration values are plausible for springtime, however during summer an increased respiration can be assumed due to warmer temperatures and increased biological activity. One possible explanation for higher model uncertainty during summer is that the modelled CO_2 loss shows a strong non-linear dependence on in situ pCO_2 and $\delta^{13}C_{DIC}$ (Polsenaere and Abril, 2012). Thus, the relative error of modelled CO_2 loss increases with the modelled CO_2 loss itself. This is particularly the case for low TA (e.g. 0.1 mmol L^{-1} (Polsenaere and Abril, 2012)), where the $\delta^{13}C_{DIC}$ increase is not buffered by the HCO_3^- pool. According to Polsenaere and Abril (2012), large losses of CO_2 only occur with high in situ pCO_2 and with high $\delta^{13}C_{DIC}$. TA was low with 218 and 196 μmol L^{-1} in the Uhlirska catchment during June and July 2015. In contrast, $\delta^{13}C_{DIC}$ values and in situ pCO_2 were increased with on average –15.8 and –16.2 ‰ as well as 2225 and 2411 ppmV, respectively. Thus, increased $\delta^{13}C_{DIC}$ values together with the model's non-linear dependence on in situ pCO_2 and $\delta^{13}C_{DIC}$ may have caused an overestimation of modelled CO_2 losses and – as a consequence – led to failed convergence criteria during summer. Note that processes such as photosynthesis, which are not part of the model, may also lead to increased $\delta^{13}C_{DIC}$ and lower in situ pCO_2 values. This may further increase the uncertainty of model results.

3.2 Gas transfer velocities

A huge benefit of the applied isotope approach is, that the difficult to estimate gas transfer velocity parameter (*k*) is not needed for the calculation of CO_2 outgassing fluxes. On the other hand, k_{600} (gas transfer velocity of CO_2 at 20°C, eq. (4)) values could be estimated from model results when assuming the water pCO_2 being the average between the modelled soil pCO_2 and the in situ pCO_2 at the catchment outlet (Table 3; Figure 2).

For the original model calculated k_{600} values varied from 0.5 to 7.0 m d^{-1} and from 0.6 to 7.9 m d^{-1} for R = 10 and 19 % (Table 3), with higher values mostly occurring during springtime and lower values during summer (Fig. 2). These values were higher than k_{600} values that were determined in a lowland boreal landscape of Québec (Campeau et al., 2014)(Table 4). However, values were slightly higher than in the silicate Renet catchment in France (1.2 – 7.2 m d^{-1}) and were comparable to results from temperate silicate catchments in Germany (Halbedel and Koschorreck, 2013) (Table 4). They also equalled median values for boreal and arctic streams (latitude 50°-90°) determined by Aufdenkampe et al. (2011), whereas k_{600} values for Sweden, for the United States, and for this study - all determined with model equations (i.e., Raymond et al. (2012)) - showed higher values (Table 4). For modelling with groundwater data, we obtained lower k_{600} values than with the original model (Table 3). Values ranged from 0.1 to 5.4 m d^{-1} (Table 3) with higher values during springtime and lower values during summer (Fig. 2). The mean k_{600} value was similar to the value of 2.2 m d^{-1} calculated from gas transfer coefficients for propane in the temperate Zilllierbach stream in Germany (Table 4).

Table 3: DIC partitioning according to the streamCO$_2$-DEGAS model (Polsenaere and Abril, 2012) and calculated from DIC measurements from September 2014 to April 2016 in the Uhlirska catchment expressed as median/average values ± 1σ standard deviation and ranges given in parentheses. The total DIC export corresponds to the sum of HCO$_3^-$ export, CO$_2$* export and CO$_2$ outgassing. Initial soil pCO$_2$ was calculated from DIC$_{init.}$, pH and temperature. k_{600} was calculated from model results.

Concentrations	
HCO$_3^-$ from silicate weathering (mg L^{-1})	0.29/0.49 ±0.56 (0.001 – 3.44)
CO$_2$* dissolved in water (mg L^{-1})	1.04/1.09 ±0.44 (0.37 – 2.36)
CO$_2$ loss^a (mg L^{-1})	1.93/6.35 ±12.43 (0.01 – 72.52)
CO$_2$ loss^b (mg L^{-1})	1.34/7.47 ±14.99 (0.003 – 85.40)
Total DIC exported from land^a (mg L^{-1})	3.72/7.93 ±12.72 (0.38 – 74.64)
Total DIC exported from land^b (mg L^{-1})	2.88/9.04 ±15.37 (0.38 – 87.73)
Modelled soil pCO$_2$^{a} (pCO$_{2init.}$) (ppmV)	2790/7670 ±16490 (460 – 106770)
Modelled soil pCO$_2$^{b} (pCO$_{2init.}$) (ppmV)	2730/10360 ±22910 (460 – 131050)
Fluxes (normalised to the catchment area)	
HCO$_3^-$ from silicate weathering (mg C m^{-2} d^{-1})	0.36/0.40 ±0.35 (0.02 – 1.63)
CO$_2$* dissolved in water (mg C m^{-2} d^{-1})	1.27/1.91 ±1.89 (0.26 – 11.68)
CO$_2$ outgassed to the atmosphere^a (mg C m^{-2} d^{-1})	1.92/5.10 ±8.37 (0.03 – 57.07)
CO$_2$ outgassed to the atmosphere^b (mg C m^{-2} d^{-1})	1.66/4.93 ±8.42 (0.02 – 49.74)
Total DIC exported from land^a (mg C m^{-2} d^{-1})	4.89/7.42 ±8.26 (1.38 – 58.61)
Total DIC exported from land^b (mg C m^{-2} d^{-1})	4.04/7.24 ±8.18 (1.28 – 51.10)
Fluxes (normalised to the stream surface area)	
HCO$_3^-$ from silicate weathering (g C m^{-2} d^{-1})	0.43/0.48 ±0.42 (0.03 – 1.95)
CO$_2$* dissolved in water (g C m^{-2} d^{-1})	1.53/2.29 ±2.26 (0.31 – 13.98)
CO$_2$ outgassed to the atmosphere^a (g C m^{-2} d^{-1})	2.29/6.10 ±10.02 (0.03 – 68.29)
CO$_2$ outgassed to the atmosphere^b (g C m^{-2} d^{-1})	1.99/5.90 ±10.08 (0.02 – 59.52)
Total DIC exported from land^a (g C m^{-2} d^{-1})	5.85/8.87 ±9.88 (1.65 – 70.13)
Total DIC exported from land^b (g C m^{-2} d^{-1})	4.83/8.67 ±9.79 (1.54 – 61.15)
k_{600}^{a} (m d^{-1})	2.8/3.1 ±1.4 (0.5 – 7.9)
k_{600}^{b} (m d^{-1})	1.9/2.1 ±1.0 (0.1 – 5.4)

[a] Modelling with proportion river respiration (R) = 10 and 19 %.

[b] Modelling with groundwater data.

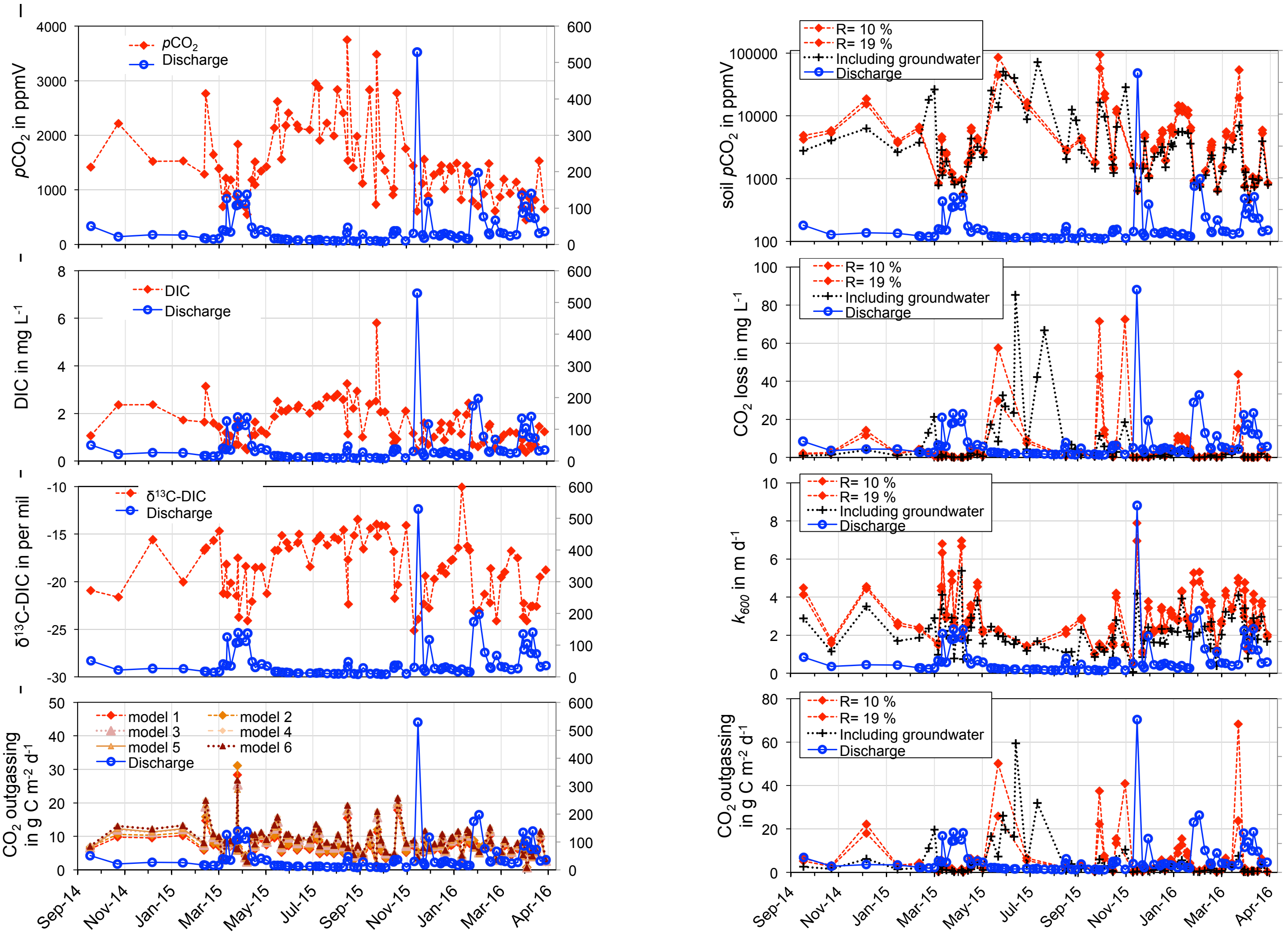


Figure 2: Data of measured discharge, in situ pCO$_2$, δ^{13}C$_{DIC}$, DIC concentrations, and CO$_2$ fluxes calculated via model equations in Raymond et al. (2012) for the Uhlirska catchment outlet (UHL) (left) and modelled soil pCO$_2$, CO$_2$ loss as well as from model results calculated k_{600} and CO$_2$ outgassing normalized to the stream surface area (right).

Table 4. Gas transfer velocities (k_{600}) normalized to a stream temperature of 20°C of low order streams. Values calculated from model results are displayed in Table 3.

Region	Stream order	k_{600} in m d^{-1}	Reference
Temperate streams (25°-50°)	-	4.8 $^{b, c}$	Aufdenkampe et al. (2011)
Uhlirska, Czech Republic	1	6.4 ^{a} 6.0 ^{b}	This study (model 1 – 6, Raymond et al. (2012)
Renet, France	-	2.9 ^{a}	Polsenaere and Abril (2012)
United States	<4	4.5 ^{b}	Butman and Raymond (2011)
Wiesent, Germany	-	6.3 ^{a}	van Geldern et al. (2015)
Rappbode, Germany	-	2.9 ^{a}	Halbedel and Koschorreck (2013)

Hassel, Germany	-	2.4[a]	Halbedel and Koschorreck (2013)
Zillierbach, Germany	-	2.2[a]	Halbedel and Koschorreck (2013)
Ochsenbach, Germany	-	2.5[a]	Halbedel and Koschorreck (2013)
Boreal and arctic streams (50°-90°)	-	3.1[b, c]	Aufdenkampe et al. (2011)
Québec, Canada	1	0.6[a]	Campeau et al. (2014)
Québec, Canada	2	0.6[a]	Campeau et al. (2014)
Québec, Canada	3	0.5[a]	Campeau et al. (2014)
Québec, Canada	4	1.4[a]	Campeau et al. (2014)
Alaska, United States	≦4	6.5[a]	Crawford et al. (2013)
Sweden	1	15.5[a]	Humborg et al. (2010)
Sweden	2	12.4[a]	Humborg et al. (2010)

[a] Mean values.

[b] Median values.

[c] Running waters in Aufdenkampe et al. (2011) have < 60 – 100 m width.

3.3 Soil $p\mathrm{CO}_2$

The streamCO$_2$-DEGAS model assumes that the modelled initial $p\mathrm{CO}_2$ represents soil $p\mathrm{CO}_2$ (Polsenaere and Abril, 2012). For the Uhlirska catchment, this would mean that soil $p\mathrm{CO}_2$ values ranged between 460 and 106770 ppmV for original model and between 460 and 131050 ppmV for modelling with groundwater input (Table 3). These were mostly within the range of values reported by Amundson and Davidson (1990) who determined $p\mathrm{CO}_2$ from 400 to 130000 ppmV for the upper metre of soils around the world. For three acidic catchments in France, modelled soil $p\mathrm{CO}_2$ varied between 2120 and 77860 ppmV (Polsenaere and Abril, 2012). In a temperate hardwood-forested catchment Jones and Mulholland (1998) modelled soil $p\mathrm{CO}_2$ values between 907 in winter and 35313 ppmV in summer. Higher soil $p\mathrm{CO}_2$ values were also modelled during summer in the Uhlirska catchment. The main reasons for elevated soil $p\mathrm{CO}_2$ in warmer seasons are higher temperatures with enhanced soil respiration in summer (Jones and Mulholland, 1998).

A clear positive correlation between soil $p\mathrm{CO}_2$ and CO$_2$ outgassing for modelling with groundwater inputs ($r^2 > 0.96$, Table S2) stresses the importance of soil $p\mathrm{CO}_2$ values and their dynamics for stream CO$_2$ loss.

3.4 CO$_2$ outgassing

Figure 3A displays modelled CO$_2$ outgassing for the proportion of river respiration (*R*) inputs that were selected with 10, 19, 25, 50, and 75 %. Figure 3B displays results for the modified modelling with groundwater input. Shaded areas show $p\mathrm{CO}_2$ measurement uncertainties. Points that plot outside the measurement uncertainty did not fulfil the convergence criteria (Polsenaere and Abril, 2012). They were thus replaced by interpolated values in the discussion. Note that, for modelling with groundwater data the fluxes where the convergence criteria were not fulfilled could get reduced by ~50 % (Fig. 3B).

For modelling with R = 10 % and 19 % the modelled CO_2 outgassing varied from 0.01 to 72.52 mg C L^{-1} and showed a mean of 6.35 mg C L^{-1} (Table 3). When normalised to the catchment area, fluxes showed a mean of 5.10 mg C m^{-2} d^{-1} with values from 0.03 to 57.07 mg C m^{-2} d^{-1}.

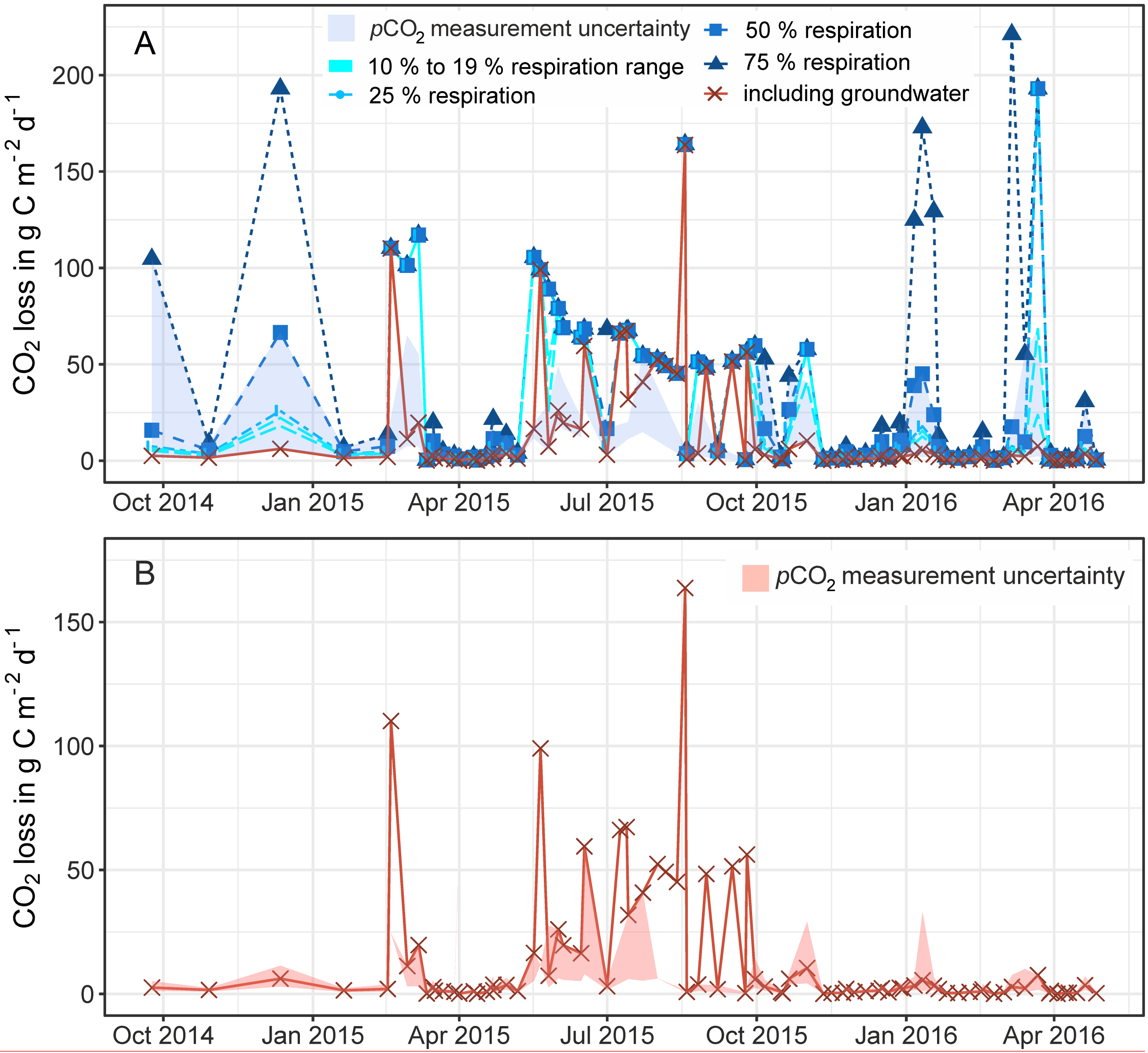
The highest fluxes > 30 mg C m^{-2} d^{-1} were modelled in May 2015, September 2015, November 2015, and March 2016 (Fig. 2). Translating these results to annual carbon outgassing fluxes yielded a mean of 23.9 to 34.5 g C m^{-2} yr^{-1} for 12 consecutive months and R = 10 and 19 %. Normalised to the stream surface area, an average of 28.6 to 41.3 kg C m^{-2} yr^{-1} were outgassed annually.

When including shallow wetland groundwater data in the model, the mean CO_2 outgassing was 1.34 mg C L^{-1} and varied from 0.003 to 85.40 mg C L^{-1}, with minimum and maximum values during April 2016 and June 2015 (Table 3). Corresponding fluxes with a mean of 8.8 kg C d^{-1} and a maximum of 88.5 kg C d^{-1} were smaller when compared to mean CO_2 losses of 952, 258, and 10671 kg C d^{-1} for similar organic-rich catchments in France calculated with the same model approach (Polsenaere and Abril, 2012). However, stream discharge in the French catchments was larger by at least one order of magnitude, thus yielding higher outgassing rates. When normalised to the catchment area, modelled CO_2 losses had a mean of 4.9 mg C m^{-2} d^{-1} and varied from 0.02 to 49.7 mg C m^{-2} d^{-1} in the Uhlirska catchment. These values translate to a mean 5.9 g C m^{-2} d^{-1} and a range between 0.02 and 59.5 g C m^{-2} d^{-1}, when normalised to the stream surface area. Those groundwater-improved CO_2 outgassing estimates yielded the same outgassing trend with slightly decreased values (Fig. 3).

The most used method to calculated CO_2 fluxes is via k values, which are predicted via slope, flow velocity, stream depth, and discharge (Raymond et al., 2012). Corresponding equations (1) to (6) yielded a mean flux of 8.1 g C m^{-2} d^{-1} with a range between 0.6 and 31.1 g C m^{-2} d^{-1} for the Uhlirska catchment. This mean value was larger than model results, whereas the range of fluxes was smaller (Table 3; Figure 2). Huotari et al. (2013) and Wallin et al. (2011) observed large uncertainties of calculated k values and corresponding outgassing fluxes on the temporal scale. For instance, in headwater streams Wallin et al. (2011) determined errors of up to 100 % in median outgassing rates compared to measured k values. Annual carbon outgassing for modelling with groundwater data yielded 34.9 kg C m^{-2} yr^{-1} when normalised to the stream surface area and was in the range between 32.7 and 42.9 kg C m^{-2} yr^{-1} of annual values obtained by equations for k in Raymond et al. (2012).

Results indicate that fluxes according to Raymond et al. (2012) yielded reasonable estimates for annual fluxes, but showed deficiencies in reproducing temporal variability (Fig. 2). The discrepancies are likely due to uncertainties in the selection of an appropriate k value in temporal highly variable headwater streams where variables such as slope, flow velocity, stream depth, and discharge are insufficient to predict the variability of k. ~~{Huotari, 2013 #1982@@author-year} {Wallin, 2011 #263@@author-year}~~

~~{Raymond, 2012 #366@@author-year}~~Moreover, for CO_2 loss ($[DIC]_{ex}$) in mg C L^{-1} and daily average discharge in L s^{-1}, a negative concentration-discharge relationship was observed (Fig. 4). Higher pCO_2, modelled soil pCO_2 and modelled CO_2 loss occurred during low flow, when relative contributions of CO_2-enriched groundwaters to stream waters were high. A similar concentration-discharge relationship was observed in a peatland stream, where deep soil and groundwater were considered as major CO_2 sources (Dinsmore and Billett, 2008).



~~A similar concentration-discharge relationship was observed in a peatland stream, where deep soil and groundwater were considered as major CO_2 sources (Dinsmore and Billett, 2008).~~

~~Table 3: DIC parameters determined with the streamCO$_2$-DEGAS model (Polsenaere and Abril, 2012) and calculated from DIC measurements for monthly samples from September 2014 to April 2016 in the Uhlirska catchment expressed as median/average values ± 1σ standard deviation and ranges given in parentheses. The total DIC export corresponds to the sum of HCO_3^- export, CO_2* export and CO_2 outgassing. Initial soil pCO$_2$ was calculated from DIC$_{init.}$, pH and temperatures. k_{600} was calculated from model results.~~

~~*Concentrations*~~	
~~HCO_3^- from silicate weathering (mg L^{-1})~~	~~0.63/0.68 ±0.50 (0.02 – 2.03)~~

~~CO_2* dissolved in water (mg L^{-1})~~	~~1.16/1.12 ±0.39 (0.49 – 2.19)~~
~~CO_2 loss^a (mg L^{-1})~~	~~2.30/6.17 ±9.55 (0.17 – 38.12)~~
~~CO_2 loss^b (mg L^{-1})~~	~~1.20/7.83 ±20.47 (0.13 – 85.40)~~
~~Total DIC exported from land (mg L^{-1})~~	~~4.28/7.97 ±9.81 (1.10 – 40.20)~~
~~Modelled soil pCO_2^{a} ($pCO_{2init.}$) (ppmV)~~	~~4640/9850 ±14000 (850 – 56950)~~
~~Modelled soil pCO_2^{b} ($pCO_{2init.}$) (ppmV)~~	~~2990/13250 ±31770 (810 – 131050)~~
~~*Fluxes*~~	
~~HCO_3^- from silicate weathering (kg C $month^{-1}$)~~	~~37/38 ±19 (7 – 80)~~
~~CO_2* dissolved in water (kg C $month^{-1}$)~~	~~87/87 ±54 (14 – 256)~~
~~CO_2 outgassed to the atmosphere^a (kg C $month^{-1}$)~~	~~146/329 ±394 (16 – 1531)~~
~~CO_2 outgassed to the atmosphere^b (kg C $month^{-1}$)~~	~~84/299 ±639 (12 – 2656)~~
~~Total DIC exported from land (kg C $month^{-1}$)~~	~~290/454 ±387(91 – 1616)~~
~~k_{600}^{a} (m d^{-1})~~	~~2.5/3.0 ±1.3 (1.0 – 6.8)~~
~~k_{600}^{b} (m d^{-1})~~	~~4.9/4.9 ±1.9 (2.3 – 8.7)~~

~~[a] Modelling with proportion river respiration (*R*) = 14 % and $\delta^{13}C_{POC}$ = –29.5 ‰.~~

~~[b] Modelling with groundwater data. {Raymond, 2012 #366@@author-year}~~Figure ~~2~~3: Modelled ~~monthly~~ carbon dioxide loss via outgassing from the stream to the atmosphere upstream of the Uhlirska catchment outlet (UHL) based on the model by **Polsenaere and Abril (2012)** for proportion river respiration (*R*) between 140 and 75 % (A) and modified with measured groundwater $\delta^{13}C_{DIC}$ (A and B). The areas shaded in blue (A) and red (B) indicate~~s~~ uncertainties in calculation of pCO_2 with ±21 %. Convergence criteria were not fulfilled for data points that lie outside the shaded area (see Sect. ~~4~~3.1).

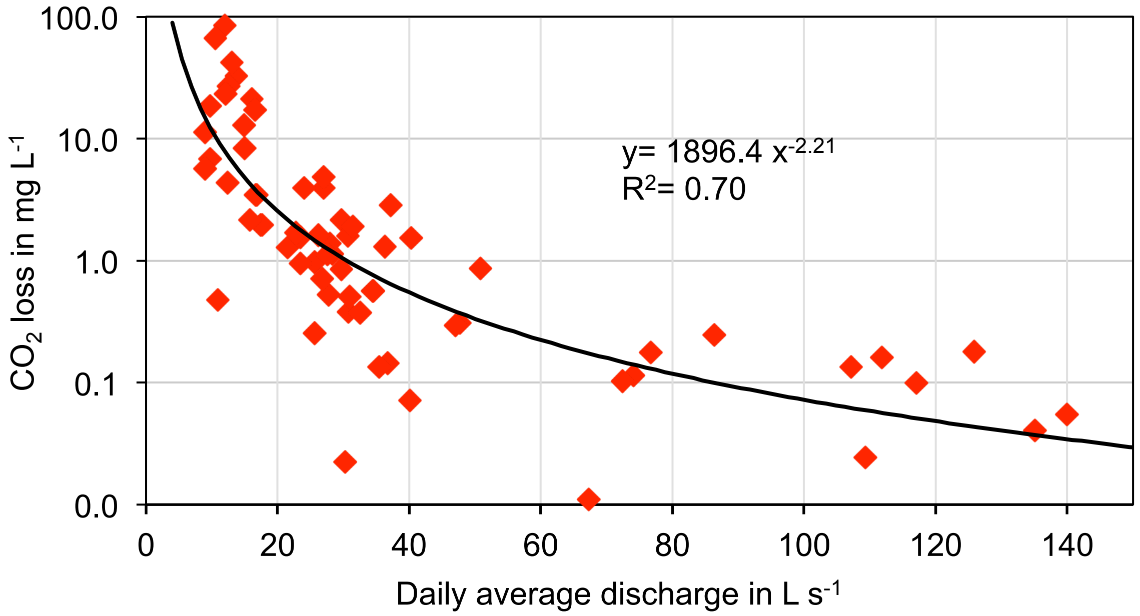
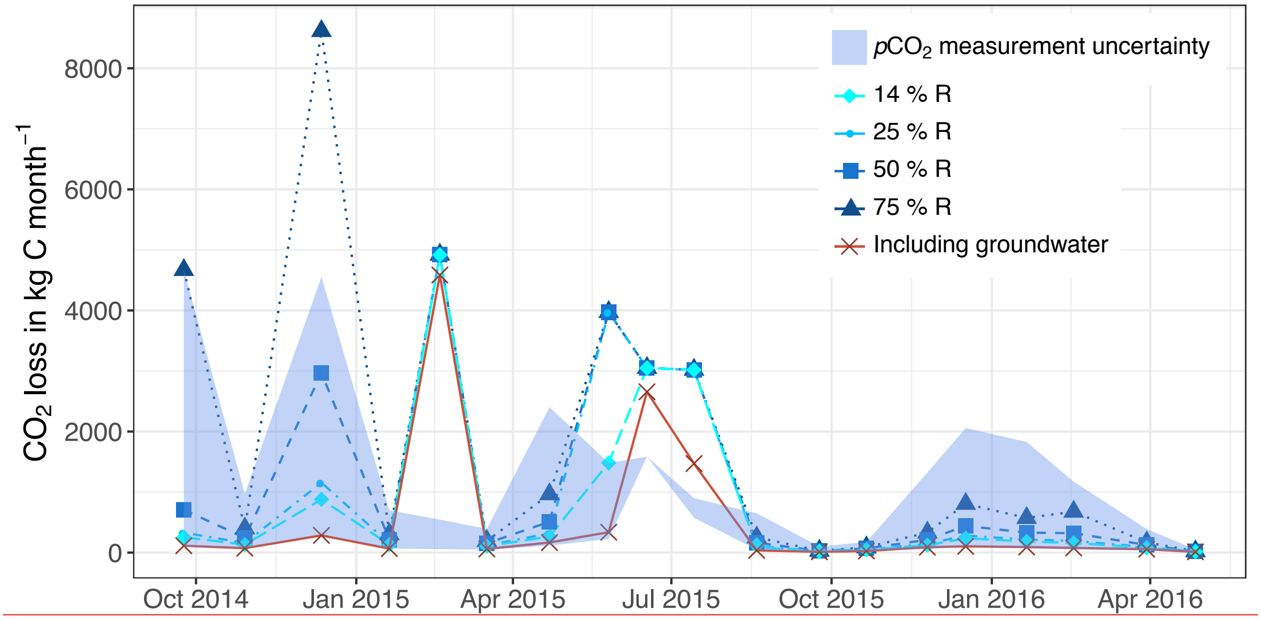


Figure 4: Modelled CO_2 loss via outgassing upstream of the measurement point (UHL) versus daily average discharge. Modelling results correspond to modelling with groundwater input.

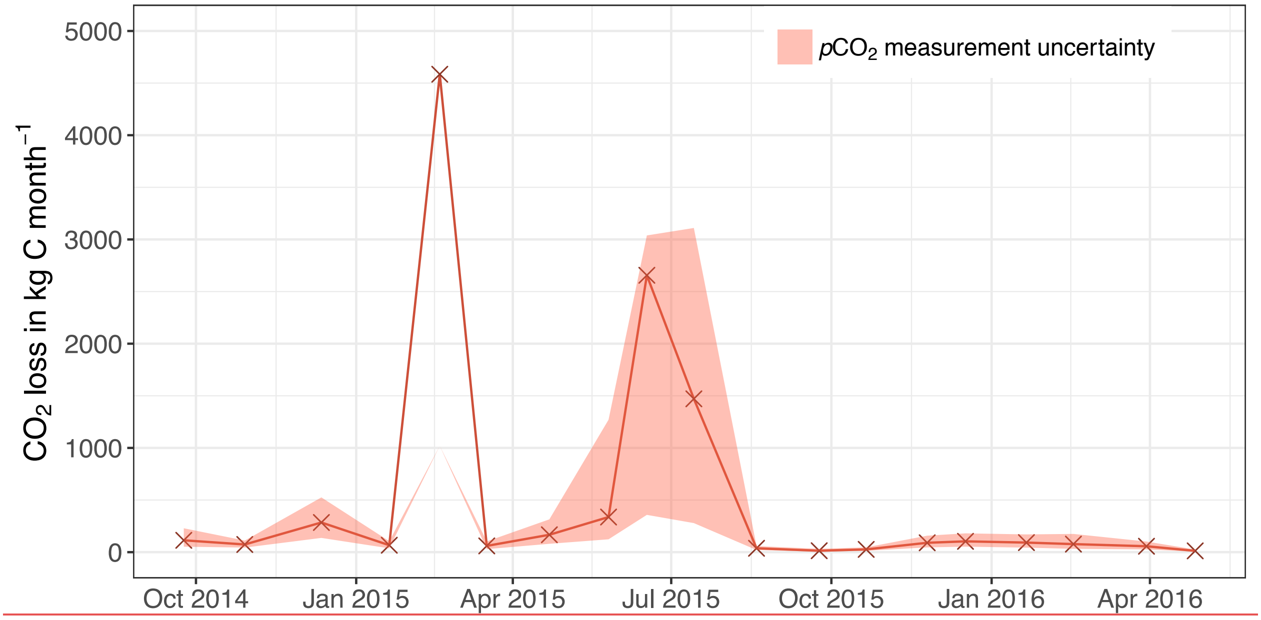


3.5 Export of DIC proportions

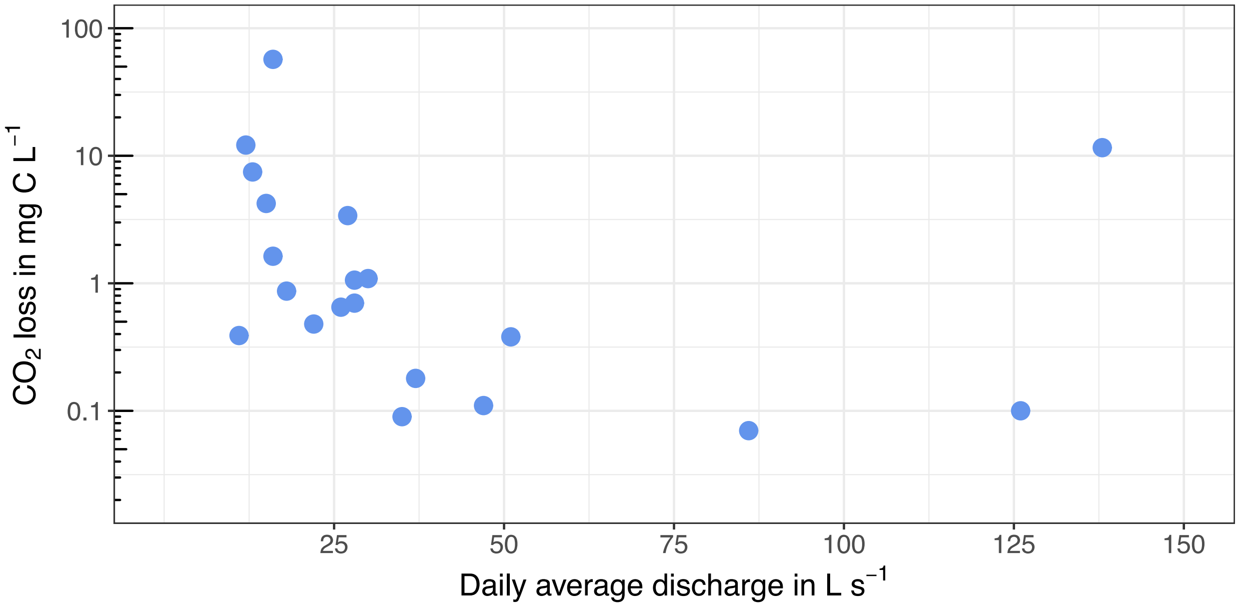
Measured DIC together with modelled CO_2 outgassing from the stream surface to the atmosphere allowed the calculation of exported DIC species distributions. On an annual basis, the DIC proportions of HCO_3^- export, CO_2* (i.e. the sum of $CO_{2(aq)}$ and H_2CO_3) export, and CO_2 outgassing had averages of 0.6, 1.2, and 7.1 to 10.3 mg C L^{-1} for CO_2 outgassing with *R* = 10 and 19 % (Table 3). This corresponds to the relative amounts of approximately 6:12:82 % HCO_3^- export, CO_2* export, and CO_2 outgassing with respect to total inorganic carbon loss from the Uhlirska catchment outlet.

For modelling with groundwater, the relative proportion of CO_2 outgassing to annual DIC export was even higher. With concentrations of 0.6, 1.2, and 10.3 mg C L^{-1} of HCO_3^- export, CO_2* export, and CO_2 outgassing they were approximately 5:10:85 %. These values are comparable to relations found by other studies (Billett et al., 2004;Johnson et al., 2008;Davidson et al., 2010;Polsenaere and Abril, 2012) and largely differ from findings from a headwater stream in karstic bedrock, where <30 % of DIC was outgassed as CO_2 (Lee et al., 2017). The determined DIC proportions suggest that a very large proportion (>80 %) of DIC entering the headwater stream in the silicate Uhlirska catchment rapidly outgasses as CO_2.~~Figure 2: Modelled monthly carbon dioxide loss via outgassing from the stream to the atmosphere upstream of the Uhlirska catchment outlet (UHL) based on the model by Polsenaere and Abril (2012) for proportion river respiration (*R*) between 14 and 75 % and modified with measured groundwater $\delta^{13}C_{DIC}$. The area shaded in blue indicates uncertainties in calculation of *p*CO_2 with ±21 %. Convergence criteria were not fulfilled for data points that lie outside the shaded area (see~~

~~Sect. 4).~~ ~~Note that the values for modelling with groundwater are displayed here for comparison, but do not apply for the shaded blue area. For corresponding uncertainties refer to Figure 3.~~



~~Figure 3: Modelled monthly carbon dioxide loss via outgassing from the stream to the atmosphere upstream of the Uhlirska catchment outlet (UHL) based on the model by Polsenaere and Abril (2012) modified with measured groundwater $\delta^{13}\mathrm{C}_{\mathrm{DIC}}$. The red-shaded area indicates uncertainties in calculation of $p\mathrm{CO}_2$ with ±21 %. Note that the model could not produce a reliable result for February 2015 (see Sect. 4).~~



~~**Figure 4: Modelled CO_2 loss versus daily average discharge at the Uhlirska catchment outlet (UHL).**~~

~~4 Discussion~~

~~(Polsenaere and Abril, 2012)(Polsenaere and Abril, 2012)(Polsenaere and Abril, 2012)Polsenaere and Abril (2012)(O'Leary, 1984)(Halbedel and Koschorreck, 2013)Aufdenkampe et al. (2011){Raymond, 2012 #366@@author-year}In the Uhlirska catchment, modelled initial $p\mathrm{CO}_2$ can be assumed to represent soil $p\mathrm{CO}_2$ (Polsenaere and Abril, 2012). Computed values ranged between 850 and 56950 ppmV (Table 3). These lie within the range of values reported by Amundson and Davidson (1990) who determined $p\mathrm{CO}_2$ from 400 to 130000 ppmV for the upper metre of soils around the world. For three acidic catchments, modelled soil $p\mathrm{CO}_2$ varied between 2120 and 77860 ppmV (Polsenaere and Abril, 2012). In a temperate hardwood-forested catchment Jones and Mulholland (1998) modelled soil $p\mathrm{CO}_2$ values between 907 in winter and 35313 ppmV in summer. Also in the Uhlirska catchment higher soil $p\mathrm{CO}_2$ values were modelled in summer. The main reasons for higher soil $p\mathrm{CO}_2$ in warmer seasons are large relative contribution of CO_2-enriched groundwater to the stream water during low flow together with enhanced soil respiration in summer (Jones and Mulholland, 1998).~~

~~A clear positive correlation between soil $p\mathrm{CO}_2$ and CO_2 outgassing (r^2>0.9, Supplement Table S3) stresses the importance of soil $p\mathrm{CO}_2$ values and their dynamics for stream CO_2 loss. Modelled stream CO_2 outgassing varied between 0.17 and 38.12 mg L^{-1} (Table 3). Corresponding fluxes varied between 16 and 1531 kg C month^{-1} and between 8.69 and 860.32 mg C m^{-2} month^{-1} for the Uhlirska catchment. These values are smaller when compared to CO_2 losses for similar organic-rich catchments in France calculated with the same model (Polsenaere and Abril, 2012). However, stream discharge in the French catchments was larger by at least one order of magnitude, thus yielding higher outgassing rates.~~

~~The parameter of proportion river respiration (*R*) has a large impact on the results by the model. It is attributed to the average percentage of respiration occurring along the entire stream course (waterlogged riparian soils, stream waters, sediments and the hyporheic zone). Thus, it is important to evaluate the model sensitivity to assumed respiration. Modelled CO_2 outgassing and modelled initial $p\mathrm{CO}_2$ values relate to an assumed *R* of 14 %, which corresponds to an average in-stream respiration as determined by Hotchkiss et al. (2015). However, this value does not account for groundwater and soil water respiration. The contributions of these compartments are typically also high in headwaters. Although this type of respiration was not measured directly, we can assume a large potential of respiration in organic-rich wetland soils(Pacific et al., 2008). (Boodoo et al., 2017)It is therefore possible that *R* exceeds 14 % along the Cerna Nisa stream.~~

~~When running the model with an *R* value of 25, 50 and 75 % (Fig. 2, Supplement Table S2) the initial soil $p\mathrm{CO}_2$ had to be extremely large (> 150000 ppmV) for selected months to reach the convergence of both $\delta^{13}\mathrm{C}_{\mathrm{DIC}}$ and $p\mathrm{CO}_2$ at the same iteration (Polsenaere and Abril, 2012). This was the case during February 2015, June 2015 and July 2015 for an *R* of 25 to 75 %, in May 2015 for a *R* of 25 to 75 % and in December 2014 for a *R* of 75 %. In addition, with increasing *R* a necessary convergence was more often not possible due to exceeding reasonable boundaries. These findings suggest that 14 % is a reasonable *R* value for February, June and July 2015. This is plausible for springtime, however during summer an increased respiration can be assumed due to warmer temperatures and increased biological activity.~~

~~One possible explanation for the high model uncertainty during summer is that the modelled CO_2 loss shows a strong non-linear dependence on in situ pCO_2 and $\delta^{13}C_{DIC}$ (Polsenaere and Abril, 2012). Consequently, the relative error of modelled CO_2 loss increases with the modelled CO_2 loss itself. This is particularly the case for low TA (e.g. 0.1 mmol L^{-1} (Polsenaere and Abril, 2012)), where the $\delta^{13}C_{DIC}$ increase is not buffered by the HCO_3^- pool. According to Polsenaere and Abril (2012), large losses of CO_2 only occur with high in situ pCO_2 and with high $\delta^{13}C_{DIC}$. In the Uhlirska catchment during June and July 2015 the TA was low with 218 and 196 μmol L^{-1}, $\delta^{13}C_{DIC}$ values and in situ pCO_2 were increased with −15.0 and −15.2 ‰ as well as 2120 and 1910 ppmV, respectively. Thus, increased $\delta^{13}C_{DIC}$ values together with the model's non-linear dependence on in situ pCO_2 and $\delta^{13}C_{DIC}$ probably caused an overestimation of modelled CO_2 losses and – as a consequence – led to failed convergence criteria during summer.~~

~~The uncertainty of the respiration parameter (R) can be circumvented by incorporating wetland groundwater $\delta^{13}C_{DIC}$ into the model. This allows to better constraining the isotope composition of the initial CO_2 and reduces the uncertainty on the isotope fractionation in soils. For initial $\delta^{13}C_{DIC}$ (δ^{13}C-DIC$_{init.}$) we used the average wetland groundwater $\delta^{13}C_{DIC}$ with an assumed isotope fractionation of 1 ‰ for CO_2 in waterlogged soils, groundwaters, river waters and sediments (O'Leary, 1984). Those improved CO_2 outgassing estimates yielded the same outgassing trend with slightly decreased values (Fig. 2). In addition, the convergence criteria were more often fulfilled than for model runs with different respiration assumptions.~~

~~• A huge benefit of the applied isotope approach is, that the difficult to estimate gas transfer velocity (k) parameter is not needed for the calculation of CO_2 outgassing fluxes. On the other hand, k_{600} (gas transfer velocity of CO_2 at 20°C) values could be estimated from model results when assuming the water pCO_2 being the average between the modelled soil pCO_2 and the in situ pCO_2 at the catchment outlet (Table 3). These values lie in the range of the silicate Renet catchment in France (Polsenaere and Abril, 2012) and are comparable to results from a similar temperate silicate catchment (Halbedel and Koschorreck, 2013). They also match median values for boreal and arctic streams (latitude 50°-90°) by Aufdenkampe et al. (2011). For modelling with groundwater data, we obtained elevated k_{600} values (Table 3). Here the median k_{600} value equalled the median of 4.8 m d^{-1} determined by Aufdenkampe et al. (2011) for temperate streams (latitude 25°-50°) and the median of 4.5 m d^{-1} for streams with stream orders below 4 in the United States (Butman and Raymond, 2011).Other studies found similar relationships and showed that the largest proportion of DIC entering a stream rapidly outgasses as CO_2 (Billett et al., 2004;Johnson et al., 2008;Davidson et al., 2010;Polsenaere and Abril, 2012)~~.

~~Aufdenkampe et al. (2011)Raymond et al. (2012) Polsenaere and Abril (2012) Butman and Raymond (2011) van Geldern et al. (2015) Halbedel and Koschorreck (2013)Halbedel and Koschorreck (2013)Halbedel and Koschorreck (2013)Halbedel and Koschorreck (2013)Aufdenkampe et al. (2011) Campeau et al. (2014)Campeau et al. (2014)Campeau et al. (2014)Campeau et al. (2014) Crawford et al. (2013) Humborg et al. (2010)Humborg et al. (2010)Aufdenkampe et al. (2011)~~

~~5~~ 4 Conclusions

Numerous studies have demonstrated the importance of CO_2 outgassing from rivers and streams to the atmosphere on global carbon budgets and pointed out the restricted data on headwater catchments (Raymond et al., 2013;Lauerwald et al., 2015;Aufdenkampe et al., 2011). Here we present a new study that successfully applied, validated, and modified the CO_2 degassing model by Polsenaere and Abril (2012) to a carbonate-free headwater catchment~~ in Czech Republic, the Uhlirska~~. The modified isotope model was able to reproduce logical seasonal patterns of soil $p\mathrm{CO_2}$ with a high variability of soil $p\mathrm{CO_2}$ and CO_2 outgassing. It showed increased ~~values~~ fluxes in summer and during snowmelt 2015. Modelled CO_2 losses also negatively correlated with stream discharge. ~~Nonetheless, r~~Results indicate maximum values of CO_2 outgassing from the stream to the atmosphere shortly before~~during~~ snowmelt~~ in springtime because of the fact that the annual discharge is largely dominated by snowmelt~~.~~ During this time, monthly runoff intensities are more than double as compared to other months.~~ Modelled annual CO_2 outgassing was comparable to results obtained with model equations to calculate gas transfer velocities according to Raymond et al. (2012). However, results of the modified streamCO_2-DEGAS model showed larger variability, which indicates its potential to assess temporal CO_2 dynamics. ~~{Zhang, 2009 #1432}~~

The model sensitivity to changing parameters of streamCO_2-DEGAS model, such as the proportion of river respiration (*R*), in situ $p\mathrm{CO_2}$ and $\delta^{13}C_{DIC}$, was high. This indicates that the potential to assess temporal variations becomes compromised by a larger potential for errors. This was particularly the case during summer.

Because of its decreased uncertainty, future CO_2 modelling would further benefit from direct $p\mathrm{CO_2}$ measurement instead of its calculation. Such direct in situ methods include submerged infrared gas analysis (Johnson et al., 2010), equilibrator systems (Polsenaere et al., 2013), off-axis integrated cavity output spectrometer combined with a gas analyser (Gonzalez-Valencia et al., 2014) and nondispersive infrared sensors inside floating chambers (Bastviken et al., 2015;Lorke et al., 2015).

We circumvent the uncertainty of the respiration parameter (*R*) by incorporating wetland groundwater $\delta^{13}C_{DIC}$ into the model.

By using groundwater data, ~~to constrain the isotope composition of the initial CO_2 instead of its estimation,~~ the modelling results have shown substantial improvements when compared to modelling without groundwater data. We therefore stress the importance of adding more accurate groundwater measurements to such studies. This implies installation of more test wells in headwater catchments or the alternative use of local spring water as a proxy for groundwater. ~~Because of its decreased uncertainty future CO_2 modelling would further benefit from direct $p\mathrm{CO_2}$ measurement instead of its calculation. Such direct in situ methods include submerged infrared gas analysis (Johnson et al., 2010), equilibrator systems (Polsenaere et al., 2013), off-axis integrated cavity output spectrometer combined with a gas analyser (Gonzalez-Valencia et al., 2014) and nondispersive infrared sensors inside floating chambers (Bastviken et al., 2015;Lorke et al., 2015).~~ In addition, modelling on higher temporal resolution, particularly at the beginning of snowmelt, is needed to better reproduce dynamics and quantities of CO_2 outgassing.

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The authors declare that they have no conflict of interest.

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