# 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 rivers and streams 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 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 t C $yr^{-1}$ and to 2.9 g C $m^{-2}$ $yr^{-1}$, when normalised to the catchment area. Large temporal variations with maximum values during spring snowmelt and 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. 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). In addition, $pCO_2$ and subsequent

5    $CO_2$ outgassing fluxes typically decline rapidly from stream source areas to river sections further downstream (van Geldern et al., 2015;Hotchkiss et al., 2015). 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

10    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). 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.,

15    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.

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

20    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

25    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

30    $^{13}C/^{12}C$ 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 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 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

5   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

10   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

15   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 runoff intensity is more than double the other months' runoff intensities.

The forest consists of a spruce monoculture (*Picea abies*) and isolated patches of larch, beech and rowan trees (Sanda and

20   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

25   fluvial material, which embodies the main perennial aquifer (Sanda et al., 2014).
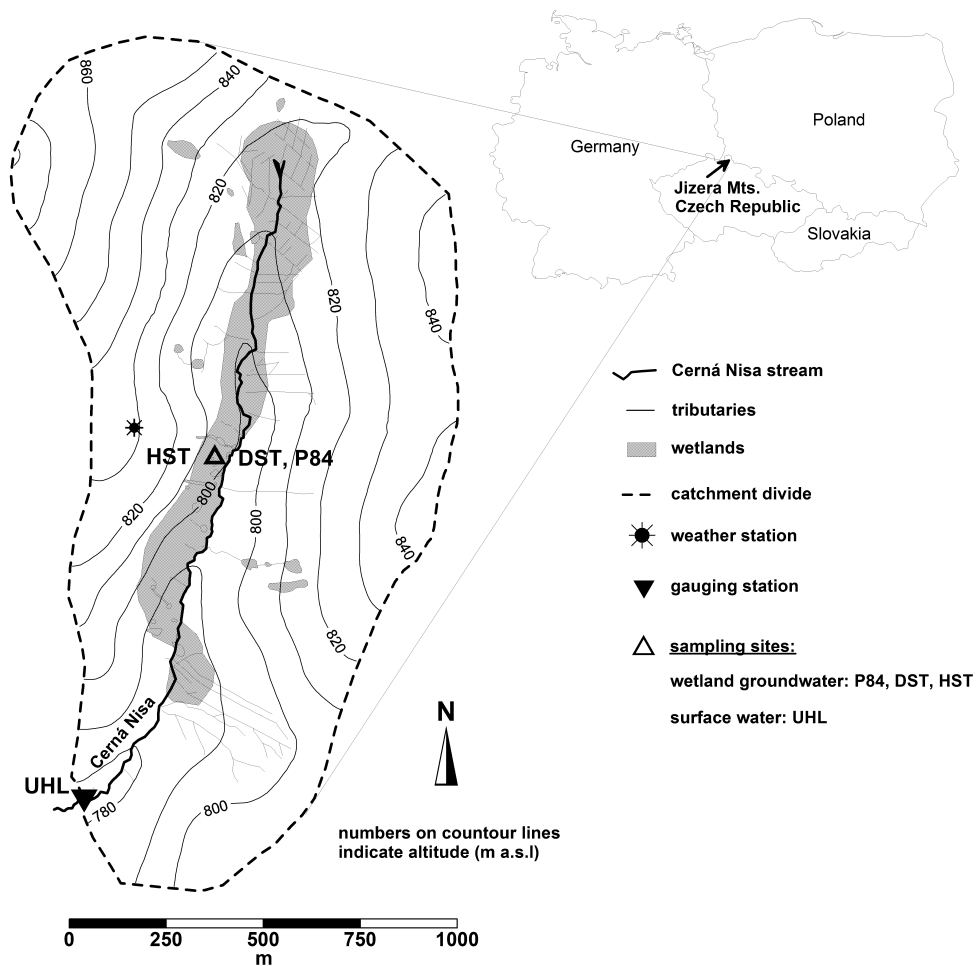
Figure 1: Location of the Uhlirska catchment and sampling sites modified from Sanda et al. (2014).

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$^2$ |
| Strahler stream order | 1 |
| Total stream length | 2.0 km |

| | |
|---|---|
| Stream flow (Q) | $Q_{median}$= 21.2 L s$^{-1}$ (2014-2016) |
| 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 |

**2.2 Water sampling and laboratory analyses**

Between September 2014 and April 2016 shallow wetland groundwater and stream water samples were collected on a monthly basis. The 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) (Marx et al., 2017b).

5    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.

10   Particulate organic carbon (POC) was sampled on 0.7 $\mu$m 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 $\mu$m 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

15   closed with butyl rubber/PTFE septa and open-hole caps, with butyl rubber side showing towards the sample. Vials were poisoned with 20 $\mu$L 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.

Carbon isotope values are reported in the standard δ-notation as deviations in per mil (‰) from the corresponding reference material:

$$\delta = \frac{R_{sample}}{R_{reference}} - 1 \; , \tag{1}$$

20   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.

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

5  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).

The Uhlirska catchment meets the two assumptions of the model by Polsenaere and Abril (2012) (streamCO₂-DEGAS) with

10  (i) stream waters being acidic with pH values between 4.7 and 6.8 (Table 2), and

(ii) waters in the stream being unproductive. This means that secondary processes such as photosynthesis by algae or biofilms can be neglected.

We calculated the $pCO_2$ values from DIC concentration, pH and T with the following Eq. (2) (Plummer and Busenberg, 1982):

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

15  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 streamCO₂-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 ($\delta^{13}C_{SOM}$).

20  The proportion of $CO_2$ resulting from respiration in water along the entire stream course (waterlogged soils, stream waters and sediments) was approximated with $R$ = 14 %. This corresponds to the internal $CO_2$ production as a percentage from median stream $CO_2$ emissions in small streams (<0.01 m³ s⁻¹) and was determined by Hotchkiss et al. (2015).

Polsenaere and Abril (2012) chose a $\delta^{13}C_{SOM}$ of –28 ‰ that was determined as average annual $\delta^{13}C_{POC}$ at their study site. In our study we also used the average annual stream $\delta^{13}C_{POC}$. Thus the $\delta^{13}C_{SOM}$ was confined with –29.5 ‰ (Table 2). In

25  addition, the average of wetland groundwater $\delta^{13}C_{DIC}$ 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 $\delta^{13}C_{DIC}$ ($\delta^{13}C\text{-}DIC_{init.}$). These were entered into the model with values ranging between –25.9 ‰ and –23.9 ‰ (Supplement Table S1). Note that the term $R$ was not part of the modelling with groundwater data.

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 $CO_2$ losses are calculated by multiplication with average discharges that were established from daily values.

5  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) and $M_C$ the molar mass of C (12.011 g mol$^{-1}$). $k_T$ was then converted into the normalized

10  gas transfer velocity of $CO_2$ at 20°C ($k_{600}$, in m d$^{-1}$) with Eq. (4):

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

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

### 2.4 Model input parameters from the Uhlirska catchment

Stream (UHL) and wetland groundwater (DST, HST, P84) pH values were always below 6.9 during the entire study (Table 2). In agreement with generally low stream pH values, the capacity of waters to buffer acidic inputs indicated by TA was

15  generally low. At the catchment outlet TA ranged around a median of 145 $\mu$mol L$^{-1}$ with a standard deviation (1σ) of ±110 $\mu$mol L$^{-1}$ (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 ±2.7 ‰ with a range from –22.4 to –14.0 ‰ (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

20  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 to 261 $\mu$mol L$^{-1}$) and the highest concentrations in wetland groundwater (284 to 540 $\mu$mol L$^{-1}$). The median stream $pCO_2$ determined at the catchment outlet was 1500 ±500 ppmV with a range from 650 to 2760 ppmV. Values in wetland groundwater were typically higher with median values of 5590, 4440 and 6210 ppmV at HST,

25  DST and P84, respectively. Stream water temperatures showed a characteristic annual trend with a range from 0.9 °C to 13.0 °C and a median of 4.3 °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 $\mu mol\ L^{-1}$ | T °C | DIC $\mu mol\ L^{-1}$ | $\delta^{13}C_{DIC}$ ‰ | $pCO_2$ ppmV | $\delta^{13}C_{POC}$ ‰ |
|---|---|---|---|---|---|---|---|---|
| | *Surface water* | | | | | | | |
| UHL | Main stream outlet | 6.1 ±0.5 | 145 ±110 | 4.3 ±3.8 | 141±54 | −18.5±2.7 | 1520 ±520 | −29.5 ±0.5 |
| | | (4.9-6.7) | (24-500) | (0.9-13.0) | (65-261) | (−22.4- −14.0) | (650-2760) | (−30.4- −28.4) |
| | *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

5 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. 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.

10 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.

15 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 $CO_2$

20 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

5      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 $HCO_3^-$

10    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 $p$CO$_2$, modelled soil $p$CO$_2$ and modelled $CO_2$ loss occurred during low flow, when relative contributions of $CO_2$-enriched groundwaters to stream waters

15    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$^{-1}$. 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 streamCO₂-DEGAS model (Polsenaere and Abril, 2012) and calculated from DIC**
20    **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 HCO₃⁻ export, CO₂* export and CO₂ outgassing. Initial soil $p$CO₂ 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 $p$CO$_2$ [a] ($p$CO$_{2init.}$) (ppmV) | 4640/9850 ±14000 (850 – 56950) |
| Modelled soil $p$CO$_2$ [b] ($p$CO$_{2init.}$) (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.
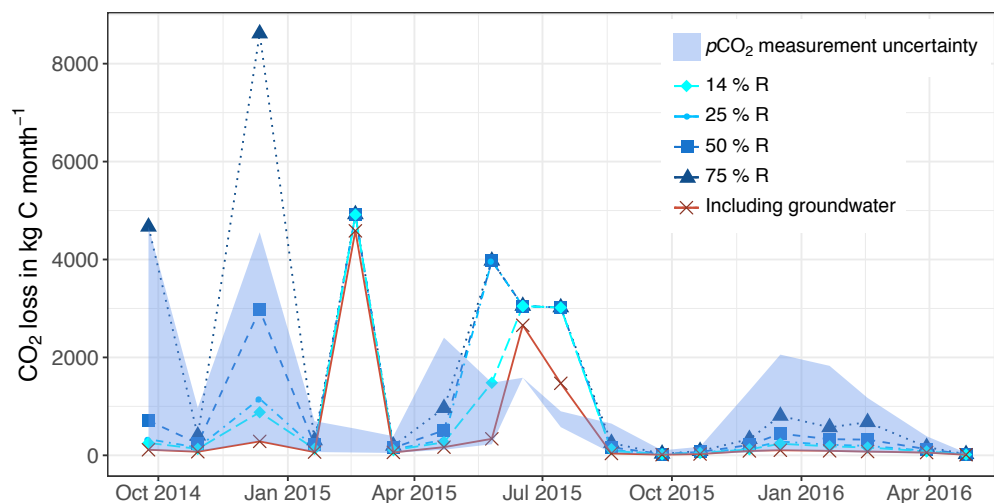
**Figure 2: Modelled monthly carbon dioxide loss via outgassing from the stream to the atmosphere upstream of the Uhlirska catchment outlet (UHL) based on the model by Polsenaere and Abril (2012) for proportion river respiration ($R$) between 14 and 75 % and modified with measured groundwater $\delta^{13}C_{DIC}$. 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.**
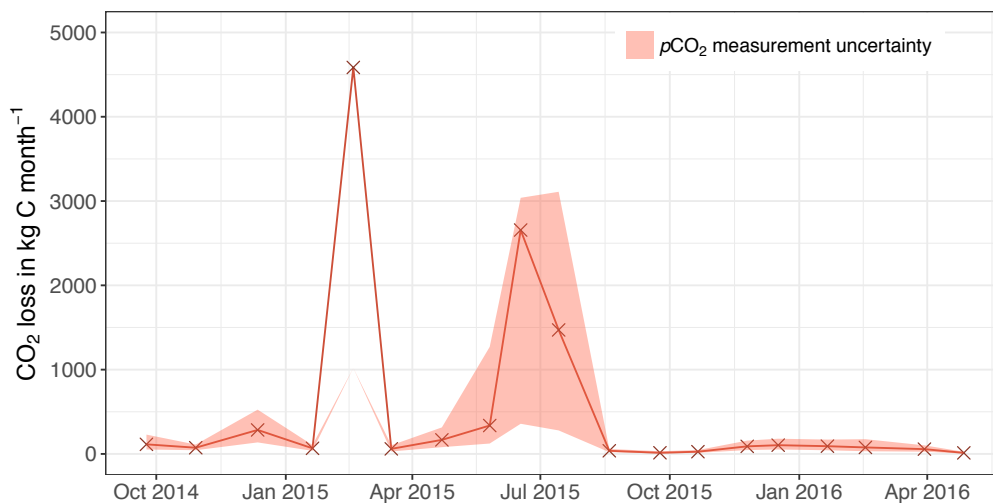
**Figure 3: Modelled monthly carbon dioxide loss via outgassing from the stream to the atmosphere upstream of the Uhlirska catchment outlet (UHL) based on the model by Polsenaere and Abril (2012) modified with measured groundwater $\delta^{13}C_{DIC}$. The red-shaded area indicates uncertainties in calculation of $pCO_2$ with ±21 %. Note that the model could not produce a reliable result for February 2015 (see Sect. 4).**
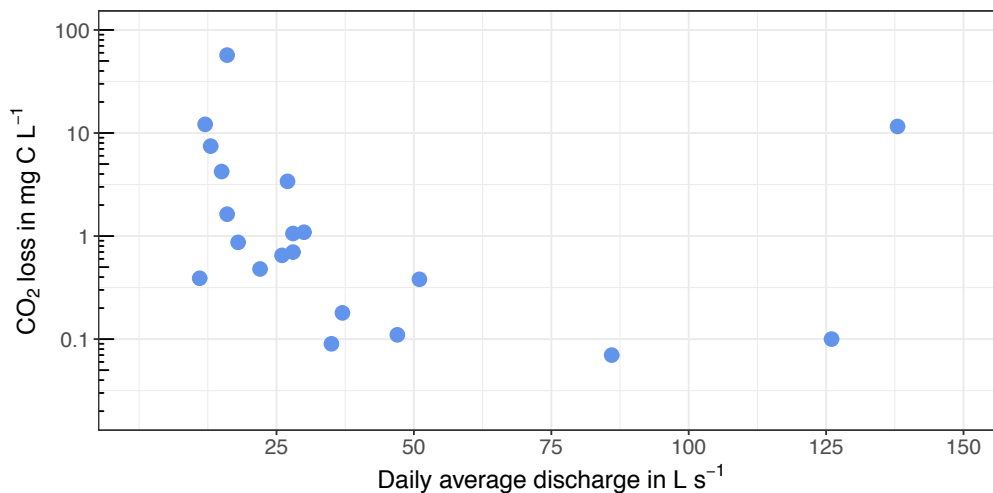
**Figure 4: Modelled $CO_2$ loss (Polsenaere and Abril, 2012) versus daily average discharge at the Uhlirska catchment outlet (UHL).**

## 4 Discussion

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

5 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 $\mathrm{CO_2}$-enriched groundwater to the stream water during low flow together with enhanced soil respiration in summer (Dinsmore and Billett, 2008;Jones and Mulholland,

10 1998).

A clear positive correlation between soil $p\mathrm{CO_2}$ and $\mathrm{CO_2}$ outgassing ($r^2 > 0.9$, Supplement Table S3) stresses the importance of soil $p\mathrm{CO_2}$ values and their dynamics for stream $\mathrm{CO_2}$ loss. Modelled stream $\mathrm{CO_2}$ 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 $\mathrm{CO_2}$ losses for similar organic-rich

15 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 $\mathrm{CO_2}$ outgassing

20 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. It is therefore possible that $R$ exceeds 14 % along the Cerna Nisa stream.

25 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 $\delta^{13}\mathrm{C_{DIC}}$ 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

30 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 $\mathrm{CO_2}$ loss shows a strong non-linear dependence on in situ $p\mathrm{CO_2}$ and $\delta^{13}\mathrm{C_{DIC}}$ (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 $\mu$mol $L^{-1}$, $\delta^{13}C_{DIC}$ values and in situ $pCO_2$ were increased with –15.0 and –15.2 ‰

5   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

10   isotope fractionation in soils. For initial $\delta^{13}C_{DIC}$ ($\delta^{13}C\text{-}DIC_{init}$) 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

15   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.

20   (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).

## 5 Conclusions

Numerous studies have demonstrated the importance of $CO_2$ outgassing from rivers and streams to the atmosphere on global

25   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 isotope model was able to reproduce logical seasonal patterns of soil $pCO_2$ with a high variability of soil $pCO_2$ and $CO_2$ outgassing. It showed increased values in summer and during snowmelt 2015. Modelled $CO_2$ losses also negatively

30   correlated with stream discharge. Nonetheless, results indicate maximum values of $CO_2$ outgassing from the stream to the atmosphere 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.

The model sensitivity to changing parameters of streamCO$_2$-DEGAS model, such as the proportion of river respiration ($R$), in situ $p$CO$_2$ and $\delta^{13}$C$_{DIC}$, was high. This indicates that the potential to assess temporal variations becomes compromised by larger potential for errors.

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. Because of its decreased uncertainty future CO$_2$ modelling would further benefit from direct $p$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 is needed to better reproduce dynamics and quantities of CO$_2$ outgassing.

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