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RESEARCH ARTICLE
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Stream-Lake Connectivity Is an Important Control of Fluvial CO_2 Concentrations and Emissions in Catchments

Kaj Sand-Jensen[1], Tenna Riis[2], Johan Emil Kjær[1], and Kenneth Thorø Martinsen[1]

[1]Freshwater Biological Laboratory, Department of Biology, University of Copenhagen, Copenhagen, Denmark, [2]Institute of Biology, Aarhus University, Aarhus C, Denmark

Key Points:

- We show high spatial and temporal variability of CO_2 along 40 alkaline fluvial networks in Denmark
- In summer, the CO_2 decreases markedly upon transit through lakes, outlets having mean concentrations close to air saturation values
- CO_2 concentrations average 9.2-fold supersaturation at sites not influenced by lakes and daily mean emission for streams was 2.1 g CO_2-C m^{-2}

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

K. T. Martinsen,
kenneth.martinsen@bio.ku.dk

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Author Contributions:

Conceptualization: Kaj Sand-Jensen
Data curation: Kaj Sand-Jensen, Tenna Riis
Formal analysis: Kaj Sand-Jensen, Kenneth Thorø Martinsen
Funding acquisition: Kaj Sand-Jensen, Tenna Riis
Investigation: Kaj Sand-Jensen, Tenna Riis
Methodology: Kaj Sand-Jensen, Tenna Riis
Software: Kenneth Thorø Martinsen
Visualization: Johan Emil Kjær, Kenneth Thorø Martinsen

Abstract Streams in cultivated lowlands are commonly supersaturated with CO_2 and are a source of CO_2 to the atmosphere. Great uncertainties exist regarding the spatiotemporal variations of CO_2 concentrations and emission rates in stream-lake fluvial networks and small streams with variable plant cover. We studied this variability and the underlying mechanisms in 40 small, high-alkalinity Danish streams, including 5 catchments with lakes. Generally CO_2 concentrations were, on average, 9.2 times those of the atmosphere, declining downstream with rising water temperature, chlorophyll *a* concentration, and decreasing groundwater inputs. We furthermore observed that the concentrations of CO_2 in stream waters declined at the outlet of lakes to values close to or below air saturation due to phytoplankton uptake and atmospheric loss during the long water retention time in the lakes. Downstream, CO_2 concentrations were observed to decrease in summer and in the afternoons, which indicate plant uptake of CO_2. Sites with deeper water and few plants and low gas transfer velocity retained high CO_2 concentrations. Among 38 fluvial networks where emission could be calculated, it varied 10-fold (0.41–4.06 g C m^{-2} d^{-1}), but the overall mean was constrained to a narrow confidence interval (1.75–2.50 g C m^{-2} d^{-1}). Our results highlight that a complex of physical, chemical and biological processes cause highly variable carbon dynamics and CO_2 emissions in fluvial networks at local and catchment scales making upscaling challenging.

Plain Language Summary Freshwater streams are supersaturated in CO_2 and release high quantities of this gas into the atmosphere. We studied the spatial and temporal variation of CO_2 concentrations in 40 fluvial networks in Denmark; of these, five include lakes. We found that the concentration of CO_2 in streams is, on average, 9.2 times that of the atmosphere. However, CO_2 concentrations decrease (a) downstream of lakes, (b) in summer, and (c) in the afternoon. These spatial and temporal trends suggest that lakes and stream plants play a significant role in regulating the concentration of CO_2 in freshwater networks. Based on observations that CO_2 concentrations measured at the outlet of eutrophic lakes may vary up to 100 times between summer, when phytoplankton blooms, and winter, we conclude that biological activity strongly influence CO_2 freshwater uptake and emission in catchments.

1. Introduction

Small lowland streams in open agricultural landscapes are highly dynamic ecosystems due to variable hydrology, chemistry, and biology, both within and among streams (Borges et al., 2018; Fuß et al., 2017; Sand-Jensen & Staehr, 2012). These streams are usually supersaturated with carbon dioxide (CO_2) and release large quantities of CO_2 into the atmosphere (Cole et al., 2007; Raymond et al., 2013). Recurring revisions of carbon budget estimates reinforce and extend the global relevance of this source of carbon emissions (Drake et al., 2018). The surplus of CO_2 in streams is supplied partly by drainage water from land and partly by internal respiratory processing of terrestrially derived organic carbon (Crawford et al., 2016; Hotchkiss et al., 2015; Marx et al., 2017). This combination often leads to high emission rates from stream reaches (Wallin et al., 2011), especially when the gas transfer velocity is high and photosynthetic CO_2 consumption is low (Sand-Jensen & Staehr, 2012). The delivery of CO_2 from a catchment to associated streams varies at sub-daily to annual scales, due to variable CO_2 release by soil respiration, CO_2 consumption by weathering of carbonate and aluminum-silicate minerals, and changing runoff (Berner & Berner, 2012; Johnson et al., 2008; Maberly et al., 2015; Rebsdorf et al., 1991). Once water-borne, CO_2 distribution is influenced by photosynthetic and respiratory processes that change with light and water temperature during the day and night and with advective and diffusive export rates (Gómez-Gerner, 2021; Sand-Jensen & Frost-Christensen, 1998; Sand-Jensen & Staehr, 2012). Thus, alterations of catchment delivery of

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Writing – review & editing: Kaj Sand-Jensen, Tenna Riis, Johan Emil Kjær, Kenneth Thorø Martinsen

CO_2 and in-stream balances of photosynthesis and respiration may cause profound changes in CO_2 concentrations and emission rates along the stream (Crawford et al., 2016; Duvert et al., 2018).

Due to the unidirectional water flow and the relative decrease of terrestrial input through the fluvial network, the relative influence of metabolism increases downstream (Hotchkiss et al., 2015). In combination with the physical gas exchange at the air-water interface, this may push CO_2 concentrations toward air saturation and, consequently, emissions to lower levels. However, the decrease in CO_2 concentration downstream in small headwater streams characterized by high CO_2 influx from land and high emission rates to the atmosphere (Finlay, 2003; Liu & Raymond, 2018) may diverge from expectations if the water transits through reaches with particularly high or low rates of CO_2 supply or loss through in-stream processes (Maurice et al., 2017). Lake outlets may show particularly low CO_2 concentrations and emissions due to atmospheric and photosynthetic CO_2 losses during extended water retention time in the lakes (Brinkerhoff et al., 2021; Sand-Jensen & Frost-Christensen, 1998). Thus, lakes may strongly influence the water–atmosphere carbon dynamics, by lowering CO_2 concentrations and emissions in the streams over substantial distances downstream.

To estimate CO_2 emissions at large spatial scales, stream order categories have been used as aggregation units (Raymond et al., 2013). Other recent studies use catchment characteristics to interpolate CO_2 concentrations in the stream (Martinsen et al., 2020a). Lauerwald et al. (2015) produced high-resolution global maps of CO_2 concentrations and CO_2 emission, but excluded the smallest streams. Among other variables, Lauerwald et al. (2015) identified average catchment slope as an important predictor of CO_2 concentration. Catchment slope may influence changes in hydrological CO_2 input and it may influence atmospheric output due to the coupling between catchment slope and flow velocity with gas transfer velocity (Hutchins et al., 2019; Smits et al., 2017).

Our study is different because it includes short, small streams and mixed fluvial networks of streams and lakes, which characterize most agricultural lowland countries such as Denmark. The elevation is modest (<185 m), 75% of stream reaches are less than 2.5 m wide and they may support dense plant beds because of their shallowness (Sand-Jensen et al., 2006). About 30% of the Danish fluvial networks include eutrophic lakes that may reduce downstream CO_2 concentrations and emissions (Sand-Jensen, Riis, & Martinsen, 2022).

In this study, we present and discuss data for CO_2 concentration, water temperature, and flow velocity in 40 Danish streams, acquired in 1997–1998 as part of an extensive biodiversity campaign, complemented by biweekly measurements conducted from August 1995 to August 1996 in 18 sites along four streams that include lakes. We use an empirical relationship between flow velocity and gas transfer velocity (Sand-Jensen & Staehr, 2012) to calculate the stream-air CO_2 flux.

We show that: (a) CO_2 concentration and emission decrease along the main course of streams owing to increased stream dimension, water retention time, and water temperature and (b) CO_2 concentrations decrease extensively when water flows through phytoplankton-rich lakes.

2. Materials and Methods

2.1. Study Background

This study was originally part of an extensive analysis of plant species distribution and biodiversity conducted in 1997–1998 to evaluate local environmental conditions. The comprehensive measurements of inorganic carbon concentrations have not been previously analyzed, but they remain highly relevant even after 25 years, since no significant changes in hydrology and environmental conditions have occurred (Sand-Jensen et al., 2006). The atmospheric CO_2 concentration has increased from about 360 ppm in 1995 to 410 ppm in 2020 leading to a modest increase in the equilibrium concentration in the stream water from 15.8 to 18.0 µM, several-fold below the common CO_2 supersaturation (159 µM). Also, the temperature increase has been very modest (Rubek et al., 2020).

To establish the spatial differences in CO_2 concentrations and emissions, we examined 204 sites in 40 streams, 5 streams with lake influence, distributed between Denmark's three main geographical regions: Zealand (7 streams), Funen (4), and Jutland (29; Figure 1 and Table S1 in Supporting Information S1). Most streams are located in catchments with a mean annual runoff of 8–12 L s^{-1} km^{-2} for the 30 years period 1970–2000, though River Funder has a specific runoff exceeding 20 L s^{-1} km^{-2} catchment (Sand-Jensen et al., 2006). The largest catchment area (2,649 km^2) drains into the River Guden, while all other streams have catchment areas <611 km^2

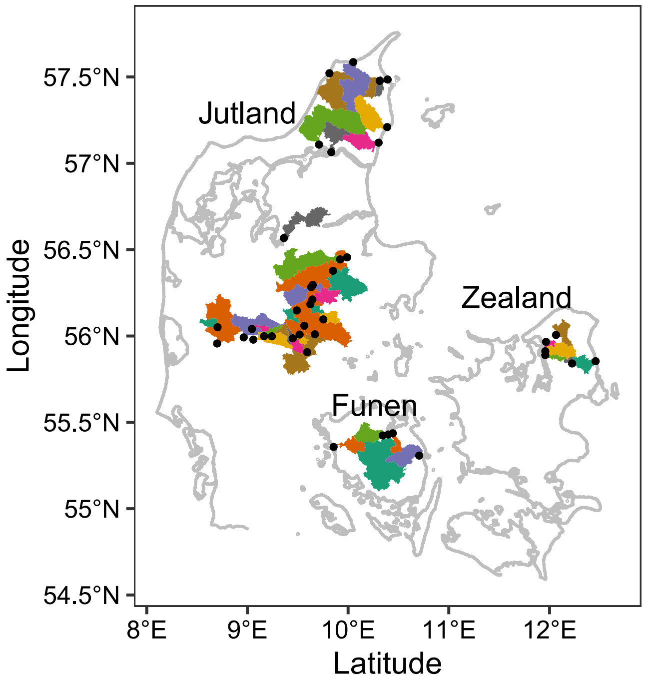

Figure 1. Map of Denmark with the 40 studied streams along the downstream course, and their corresponding, color-coded catchments in three regions. Stream outlets are marked by solid points.

(mean 226 km^2; Table S1 in Supporting Information S1). River Guden's main course was divided into an upper part with no lake influence and a lower part with prominent lake influence. We examined the downstream pattern for streams with sufficient number of examined sites (4–10) along the stream's main course (Table S2 in Supporting Information S1). Mean CO_2 emissions was calculated for 35 streams where flow velocity was available for all sites.

2.2. Sampling

All 204 sites were visited at least once in the summers of 1997 and 1998. Moreover, 18 sites in four streams on Zealand were visited biweekly the year before (August 1995-August 1996). To evaluate the suitability of using morning measurements (8:00–11:00) to represent the mean daily CO_2 concentration, the 18 sites were sampled five times during a diel cycle in July. This showed that calculated CO_2 concentrations at 9:30 (i.e., the middle of the time window 8:00–11:00), were only 8.7% (±5.7%, 95% CI) above the mean daily CO_2 concentration and, thus, our sampling approach was suitable to represent mean daily values at all 204 sites.

In each of the 204 stream sites we measured the wetted cross-sectional area, in short, wetted area (A, m^2), flow velocity, and discharge. Along a 50 m reach at each site, we created 10 transversal sections and recorded water depth at 0.2 m intervals from shore to shore to determine A. Mean flow velocity (U, m s^{-1}) over the reach was measured by adding a pulse of dissolved NaCl above the reach and recording the transit time (T, s) of 50% of the added salt below the reach from the elevated specific conductivity above the background, measured every second ($U = 50\text{ m} \cdot T^{-1}$). Water discharge was determined as the product $U{\cdot}A$ ($m^3\ s^{-1}$). At a few sites characterized by very high discharge, the salt method was not applicable; thus, flow velocity, gas transfer velocity and CO_2 emission were not calculated for these sites (Tables S1 and S2 in Supporting Information S1). Across the 204 sites, stream width averaged 6.95 m (median 5.2 m, range 0.6–30.0 m) and discharge averaged 2.78 $m^3\ s^{-1}$ (median 0.63 $m^3\ s^{-1}$, range 0.013–26.0 $m^3\ s^{-1}$).

At each site we measured water temperature and collected water samples in the morning (8:00–11:00) for measurements of pH and inorganic carbon in airtight glass bottles, which were kept cool until measurements at 20°C could be conducted in the laboratory (typically within a few hours). Chlorophyll *a* concentrations were measured in water samples from all sites in the River Guden and below lakes in other streams (Table S1 in Supporting Information S1). Chlorophyll *a* is present in planktonic and suspended benthic microalgae. Chlorophyll *a* concentrations below lakes is a measure of phytoplankton biomass and primary production in the lakes.

2.3. Water Analyses and CO_2 Concentrations and Emissions

In the laboratory, conductivity and pH were measured by standard techniques. Chlorophyll *a* concentrations in the water was measured by passing water through glass microfibre filters, extracting the filters in ethanol and measuring chlorophyll absorbance by spectrophotometry (Jespersen & Christoffersen, 1987). Total alkalinity (Acid Neutralizing Capacity, ANC), dissolved inorganic carbon pool (DIC), and CO_2 were measured by Gran-titration (Gran, 1952). In 500 measurements at the stream sites, alkalinity was consistently high (mean 2.82 mEq. L^{-1}; range 0.13–6.42 mEq. L^{-1}) and only 23 measurements were below 1.0 mEq. L^{-1} and of those 3 were also below 0.5 mEq. L^{-1}. The minimum pH was 6.45 and only 3 measurements were below 7.0 (mean 7.6). No streams of low alkalinity and high content of dissolved organic carbon were included. Our calculation of CO_2 concentrations from alkalinity, pH, water temperature, and conductivity is very reliable because the interference of organic and mineral acids is negligible in waters of high alkalinity (>1 mEq. L^{-1}) and high pH (Abril et al., 2015; Rebsdorf et al., 1991). We confirmed this by showing close correspondence between direct DIC measurements and DIC calculated from Gran-titration (Table S3 in Supporting Information S1).

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The water-air CO_2 flux (F, mmol m^{-2} h^{-1}) at the field sites was calculated as the product of the water-air gradient (mmol m^{-3}) and the gas transfer velocity K (m h^{-1}):

$$F = K \cdot (CO_2 - CO_{2-sat}) \tag{1}$$

CO_2 is the calculated concentration in the water and $CO_{2\text{-sat}}$ is the CO_2 concentration in water at air saturation at the atmospheric CO_2 partial pressure and water temperature. K was calculated from U and water temperature according to the empirical relationship established from 55 mean daily values at different sites in two Danish lowland streams (Sand-Jensen & Staehr, 2012). K at 20°C (K_{20}, cm h^{-1}) was calculated from the relationship (SE in parenthesis):

$$\log(K_{20}) = 1.256(\pm 0.041) + \log(U) \cdot 0.0742(\pm 0.055) \tag{2}$$

K at ambient water temperature was calculated from K_{20} following Thyssen and Erlandsen (1987):

$$K = K_{20} \cdot \left(1.024^{\text{temp}-20}\right) \tag{3}$$

2.4. Groundwater and Catchment Delineation

Compared to inflow of surface and drainage water, groundwater inflow is much more constant over time, so the ratio of the annual median monthly minimum discharge to the annual median discharge is a suitable index of the groundwater contribution in Danish streams (Ovesen et al., 2000). We calculated this index for our catchments where daily discharge over 50 years (1970–2020) were available from national monitoring data (MFM & DCE, 2021).

Stream catchments boundaries were derived from the national digital elevation model (DEM) at 10 m resolution (SDFE, 2021). To condition the DEM for flow routing, the DEM was preprocessed using algorithms from the RichDEM Python library (Barnes, 2018); depressions and pits in the DEM were breached (Lindsay, 2016) followed by flat resolution, where a gradient is enforced on flat surfaces to ensure flow across the DEM (Barnes et al., 2014; Tarboton, 2017). Finally, D8 flow routing (O'Callaghan & Mark, 1984) and catchment delineation were performed using the TauDEM library (Tarboton, 2017). Spatial data analysis also used GDAL (GDAL/OGR contributors, 2021) and the *raster* (Hijmans, 2019) and *sf* R-packages (Pebesma, 2018).

2.5. Statistics

To test if CO_2 concentrations decreased from the first (upstream) to last (downstream) site along each stream, we used a Wilcoxon test for paired differences as differences were not normal distributed. We used linear regression models to examine the relationships between: (a) CO_2 concentration and chlorophyll *a* upstream and downstream of lakes, (b) CO_2 concentration, water temperature and chlorophyll *a* in River Guden, and (c) CO_2 emissions, groundwater index and catchment area. Non-normally distributed variables were $\log_{10}$-transformed prior to analysis to meet model assumptions. Model selection was performed by stepwise backwards elimination using F-tests. Quantile regression models were applied to examine the relationship between the CO_2 concentration and emission distributions and predictors using the *quantreg* R-package (Koenker, 2021). When quantile regression models were not significant we applied locally estimated scatterplot smoothing to visualize relationships. All statistics were done using statistical programming software R (R Core Team, 2021).

3. Results

3.1. Spatial Patterns in CO_2 Concentration Across Streams

Due to substantial variation of CO_2 concentrations between individual streams, combining all CO_2 measurements showed a wide scatter though with an overall decline from upstream sites to downstream sites described as a function of the wetted area (Figure 2). Three quantile regression models (0.1-, 0.5-, and 0.9-quantiles) were all highly significant ($p < 0.001$) showing that the upper-, median- and lower bounds of the $\log_{10}(CO_2)$ declined downstream in fluvial networks without lakes.

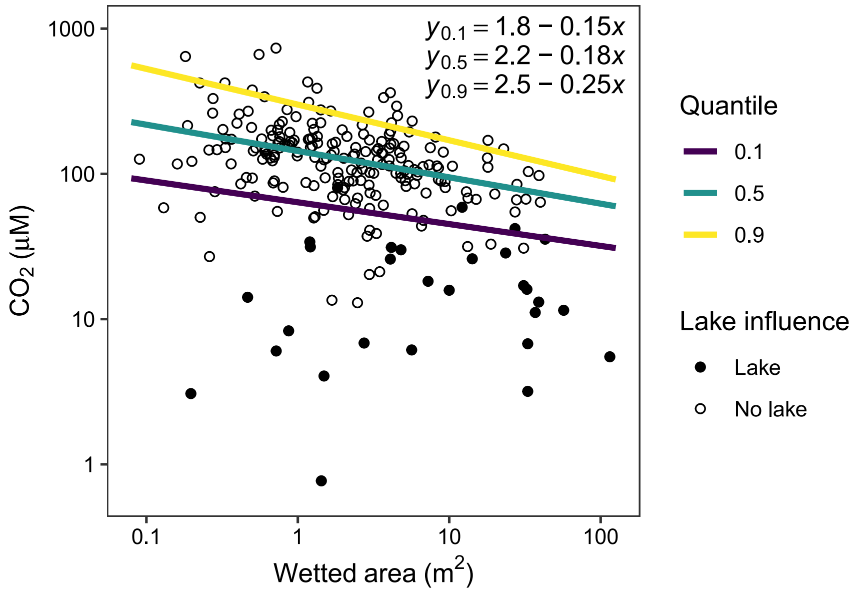

Figure 2. CO_2 concentrations during summer at many sites with distant or no influence of lakes (open circles) and below lakes (closed circles) along the stream course. Solid lines are quantile regression models (0.1-, 0.5-, and 0.9-quantiles, for all parameter estimates $p < 0.001$). Stream sites with lake influence (solid point) are not included in the regression analysis.

In 168 sites from 35 Danish streams with no lake influence, CO_2 concentrations on summer mornings were markedly supersaturated (mean ± 95% CI: 159 ± 15 µM; 9.2-fold supersaturated). In 22 of these streams (with 4–10 sites distributed along the main stream course), CO_2 concentrations decreased (Wilcoxon test, $V = 271$, $p < 0.001$) downstream, while only one stream (River Vindinge) that was artificially widened at its upper site tended to have increasing CO_2 concentrations downstream (Table S2 in Supporting Information S1).

The concentrations of CO_2 measured in proximity of the inlet were markedly higher than those in the stream waters at the outlet of lakes (Figure 3). Lower CO_2 concentrations were measured both in lake outlets and in the following downstream sites (River Mølle and River Guden; Figure 3). In these streams with one or more lakes, mean CO_2 concentrations measured in the morning were supersaturated upstream of the lakes (152.1 µM), but close to air saturation in lake outlets (16.8 µM; Table S4 in Supporting Information S1). With higher phytoplankton chlorophyll *a* concentrations in the lakes, CO_2 concentrations were markedly lower in lake outlets (Figure 4; linear regression model reported as parameter estimate (±SE), $\log_{10}(CO_2) = 2.0(\pm 0.31) - 0.9(\pm 0.21) \cdot \log_{10}$ (chlorophyll *a*), $R^2 = 0.47$, $N = 24$, $p < 0.001$).

River Guden is a large network of streams and lakes with 10 tributaries and several lakes in a 2,649 km^2 catchment. Increasing water temperatures and chlorophyll *a* from upstream to downstream sites were strong predictors of decreasing CO_2 concentrations (Figure 5). A regression model of measurements of CO_2 at 61 sites in the network of streams and lakes showed a strong significant negative influence of both higher chlorophyll *a* and water temperature ($\log_{10}(CO_2) = 2.99(\pm 0.134) - 0.055(\pm 0.011) \cdot$ water temperature $-0.523(\pm 0.065) \cdot \log_{10}$ (chlorophyll *a*), $R^2 = 0.72$, $N = 122$, interaction not significant).

3.2. Seasonal Variation in CO_2 Concentrations

Four neighboring streams on Zealand were sampled biweekly for a full year (Figure 6). Mean CO_2 concentrations in outlets from four phytoplankton-rich lakes were, on average, 3-fold lower during mid-summer (June–August, mean 28 µM, range 2–62 µM) compared to the rest of the year (mean 91 µM, range 31–139 µM). Fourteen sites with no lake influence in the same streams had much higher mean CO_2 concentrations that were only 1.2-fold lower during mid-summer (mean 220, range 160–345 µM) than the rest of the year (mean 266, range 196–422 µM).

The biweekly CO_2 concentrations are shown for the River Pøle (Figure 7). CO_2 concentrations were high at upstream sites 1 and 2 with few plants (annual means 335 and 286 µM), while concentrations were significantly

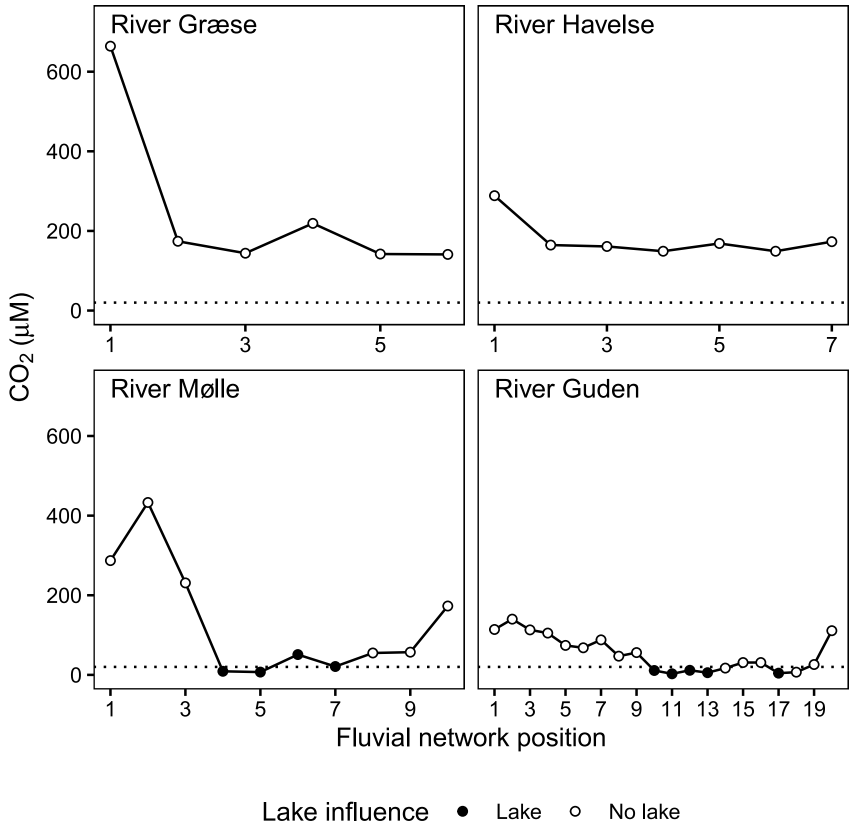

Figure 3. CO_2 concentrations on summer mornings along two streams without lakes (River Græse and River Havelse) and two streams with lakes (River Mølle and River Guden, tributaries omitted). The dotted line is the approximate CO_2 concentration at air saturation.

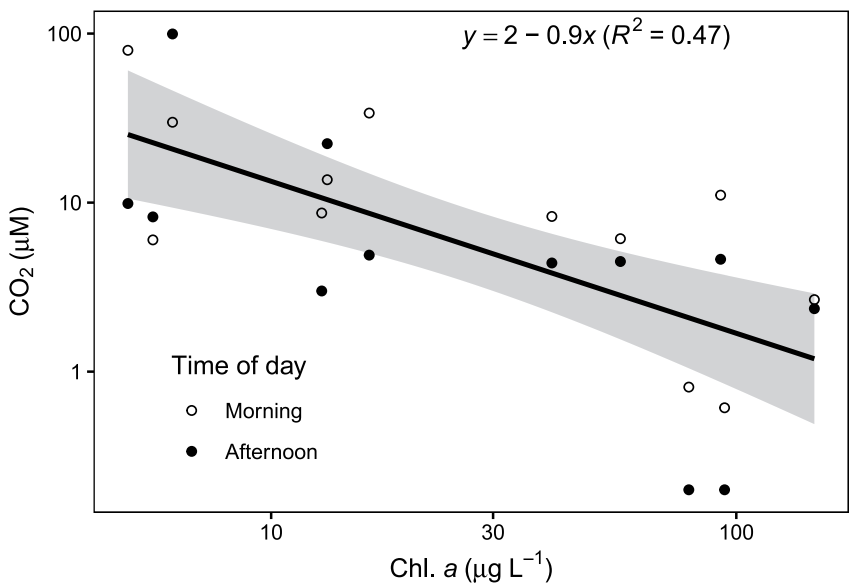

Figure 4. CO_2 concentrations in outlets from 12 lakes measured in the morning (8:00–11:00, open circles) and later in the afternoon (14:00–17:00, closed circles) as a function of the phytoplankton biomass (as chlorophyll *a*) in the lakes. Solid line is a linear regression model with 95% CI shown in gray. The *x*- and *y*-axis are $\log_{10}$-transformed.

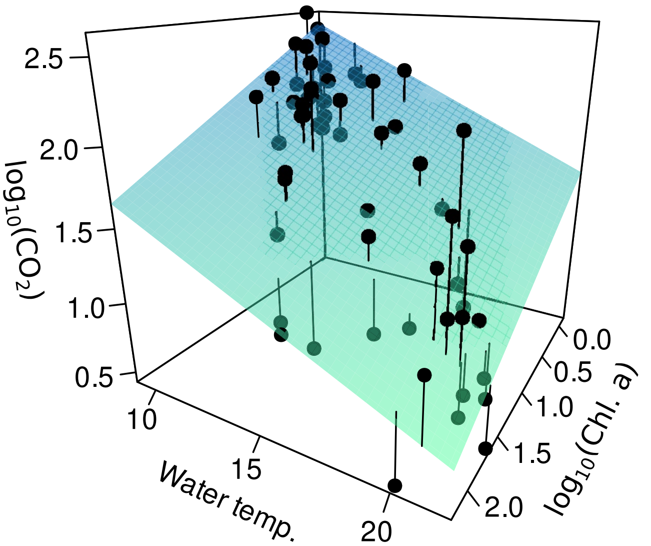

Figure 5. 3-D plot showing morning $\log_{10}(CO_2)$ at 61 sites in the River Guden stream-lake network as a function of water temperature and $\log_{10}$(chlorophyll *a*). The plane is the fitted regression model of $\log_{10}(CO_2)$ as a function of $\log_{10}$(chlorophyll *a*) and water temperature ($n = 61$, $R^2 = 0.75$).

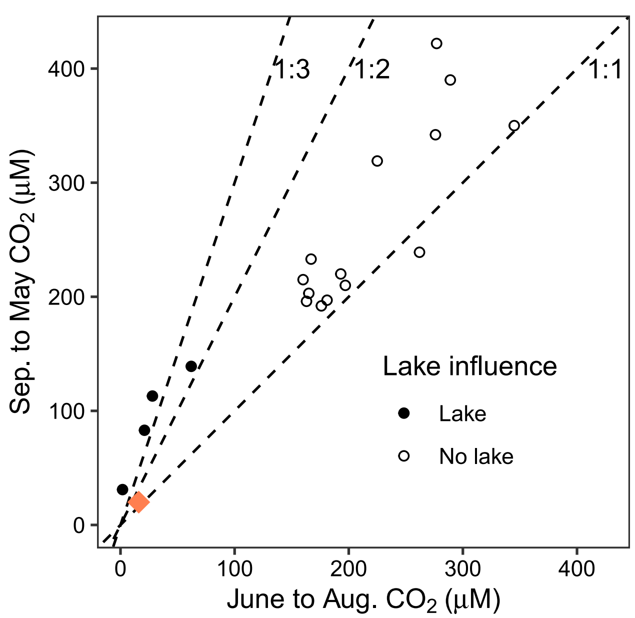

Figure 6. CO_2 concentrations influenced by season and the presence or lack of lakes. Mean CO_2 concentrations at sites in four neighboring streams located in northern Zealand measured in the summer (June–August, *x*-axis) versus the rest of the year (September–May, *y*-axis). Four of the sites were located downstream of lakes (closed circles) and 14 sites were not influenced by lakes (open circles). The red diamond is the approximate CO_2 concentration at air saturation. The three lines represent CO_2 concentrations in summer (*x*) compared to the rest of the year (*y*) of 1:1, 1:2 and 1:3.

lower and seasonally variable at the mid-stream site 3, which contains many submerged plants only in summer (annual mean ± 95% CI; 106 ± 30 µM). At the deeper downstream site 4 with no plants, CO_2 was higher and less variable seasonally (169 ± 26 µM). The River Pøle flows into the hypertrophic Lake Arre (site 5), which showed very low CO_2 concentrations (<1 µM) below air saturation during mid-summer and appreciably higher mean CO_2 concentrations above air saturation (mean 58 µM), during winter. The outlet from Lake Arre (site 6) had CO_2 concentrations closely resembling those in the middle of the lake basin (Figure 7).

The much stronger lowering of CO_2 concentrations downstream of lakes during summer than the rest of the year was not restricted to Lake Arre. The same seasonal pattern was found in the other three lakes on Zealand that were sampled biweekly over the year (seasonal means in Figure 6, biweekly data not shown).

3.3. CO_2 Emission

The CO_2 emissions were proportional to CO_2 concentrations (Figure S1 in Supporting Information S1) and varied extensively but tended to be highest at up- and mid-stream sites and lowest at downstream sites (Figure 8a) in accordance with the falling CO_2 concentrations downstream (Figure 2). The upper emission rates decreased with water temperatures between 8 and 24°C, but rates were highly variable close to 8°C, and less variable at water temperatures close to 20°C (Figure 8b). Downstream of phytoplankton-rich lakes, CO_2 fluxes were particularly low across the whole temperature range and often directed from air to water due to CO_2 undersaturation (Figure 8).

The mean daily CO_2 emissions from stream sites with no or distant lake influence ranged ten-fold, from 0.41 to 4.06 g C m^{-2} (Table S1 in Supporting Information S1). Emissions were systematically higher in streams with high input of CO_2-rich groundwater. Thus, for 32 streams for which the groundwater index could be calculated, a linear regression model showed a significant positive relationship of CO_2 emission to the groundwater index ($p = 0.02$) and an almost significant negative relationship to the catchment area ($\log_{10}$-transformed, $p = 0.08$; CO_2 emission = 2.09 (±1.12) + 2.72(±1.13) · groundwater index – 0.78(±0.43) · $\log_{10}$(catchment area), $R^2 = 0.18$, $N = 32$; Figure S2 in Supporting Information S1).

4. Data Interpretation and Discussion

4.1. Spatiotemporal Variation of Stream CO_2 Concentrations

Generally, CO_2 concentrations in streams are highly influenced by the CO_2 supply from land and the atmospheric loss (Marx et al., 2017; Wallin et al., 2013). All Danish streams are short and there are no sharp distinction between steep headwater sites and river valley sites as in very large rivers deriving from inland mountains. The two Danish streams, Funder and Salten, with most headwater sites and steep downstream slope have a high groundwater index (0.85–0.91) and a high daily loss of CO_2 to the atmosphere (3.9–4.1 g C m^{-2}), while two streams, Odense and Ryå with headwater sites of lower slopes, have lower groundwater indices (0.51–0.59) and CO_2 emissions (0.8–1.2 g C m^{-2}; Table S2 in Supporting Information S1). Further, headwaters receiving much CO_2-rich groundwater, according to stream temperatures (8–12°C; Figure 5) close to Danish groundwater temperature of 8°C had the highest CO_2 levels, a characteristic also observed in other

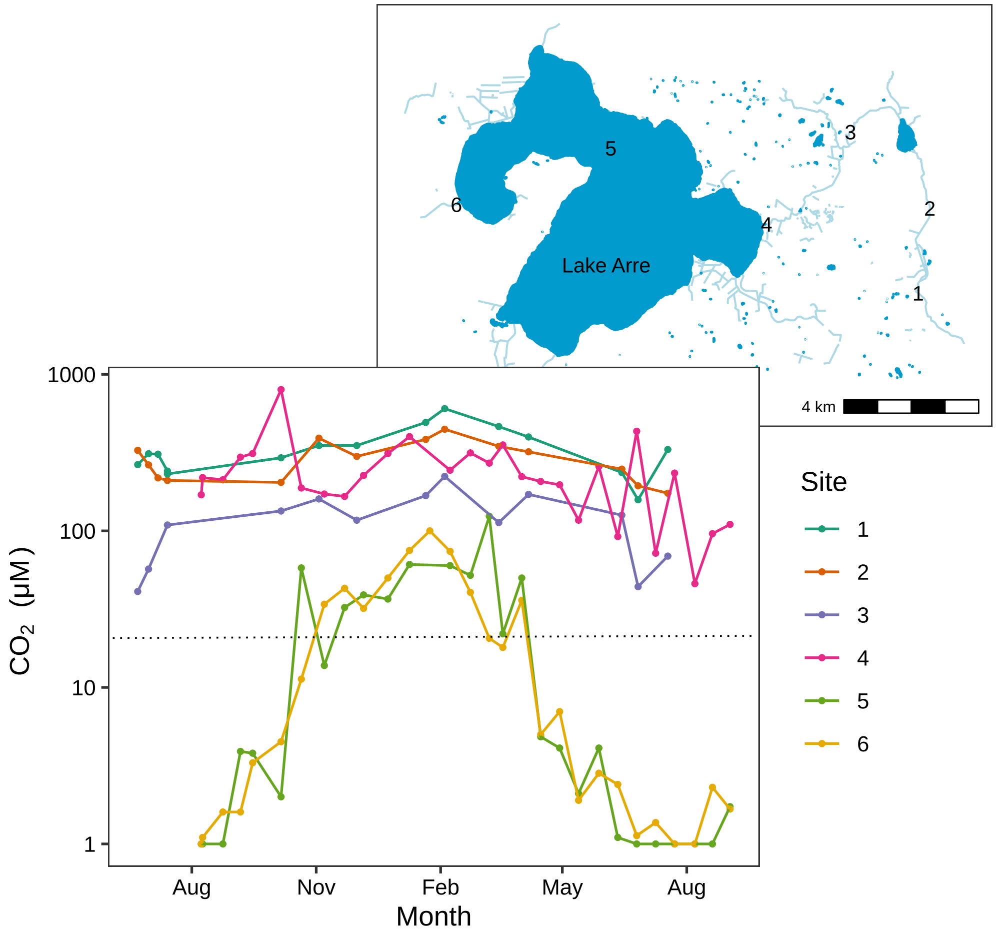

Figure 7. Seasonal changes of CO_2 concentrations at 6 sites located from upstream to downstream in the River Pøle-Lake Arre network. Sites 1 and 2 are located in the upper river; site 3 is downstream a shallow reach with fast flow and dense vegetation; site 4 is the deep inlet to Lake Arre, devoid of vegetation; site 5 is in the middle of hypertrophic Lake Arre; site 6 is the outlet from Lake Arre. Measurements taken twice monthly from Aug 1995 to Aug 1996. The dotted line is the approximate CO_2 concentration at air saturation. Lakes and streams shown in inset (OpenStreetMap contributors, 2021).

European groundwater-fed alkaline streams (Demars & Trémolières, 2009; Maberly et al., 2015). This effect was reflected in falling CO_2 concentrations during mid-summer in the River Guden's fluvial network as water temperature gradually increased above the groundwater temperature. The falling CO_2 concentrations with increasing water temperature from 8 to 22°C reflected the more downstream location of warmer sites and longer water retention time in the networks, leaving more time for dissolved CO_2 in the stream water to equilibrate with the atmosphere or to be consumed by photosynthesis.

The observed downstream decline of CO_2 concentrations was not homogeneous and constant in all observed streams, but were influenced by the density of vegetation and the atmospheric loss. Transit through shallow, fast-flowing reaches with high gas transfer velocity and CO_2 emission (Equation 1) or through reaches with dense plant stands and their associated high CO_2 consumption in photosynthesis, may lead to local minimum CO_2 concentrations (e.g., site 3 in River Pøle; Figure 7). In deeper downstream reaches (e.g., site 4 in River Pøle), CO_2 concentrations may have increased due to slower flow, 4-fold lower CO_2 transfer velocity to the atmosphere and fewer plants compared with site 3. Very marked changes were observed during the transit through lakes, bringing several-fold CO_2 supersaturation upstream of a lake all the way to below air saturation downstream from the lake. Thus, in Danish stream-lake networks (e.g., River Guden, River Mølle, and River Pøle-Lake Arre; Figures 3 and 7) as well as reported patterns from streams in England and France (Maberly et al., 2015; Neal et al., 1998), CO_2 concentrations show high spatial variability.

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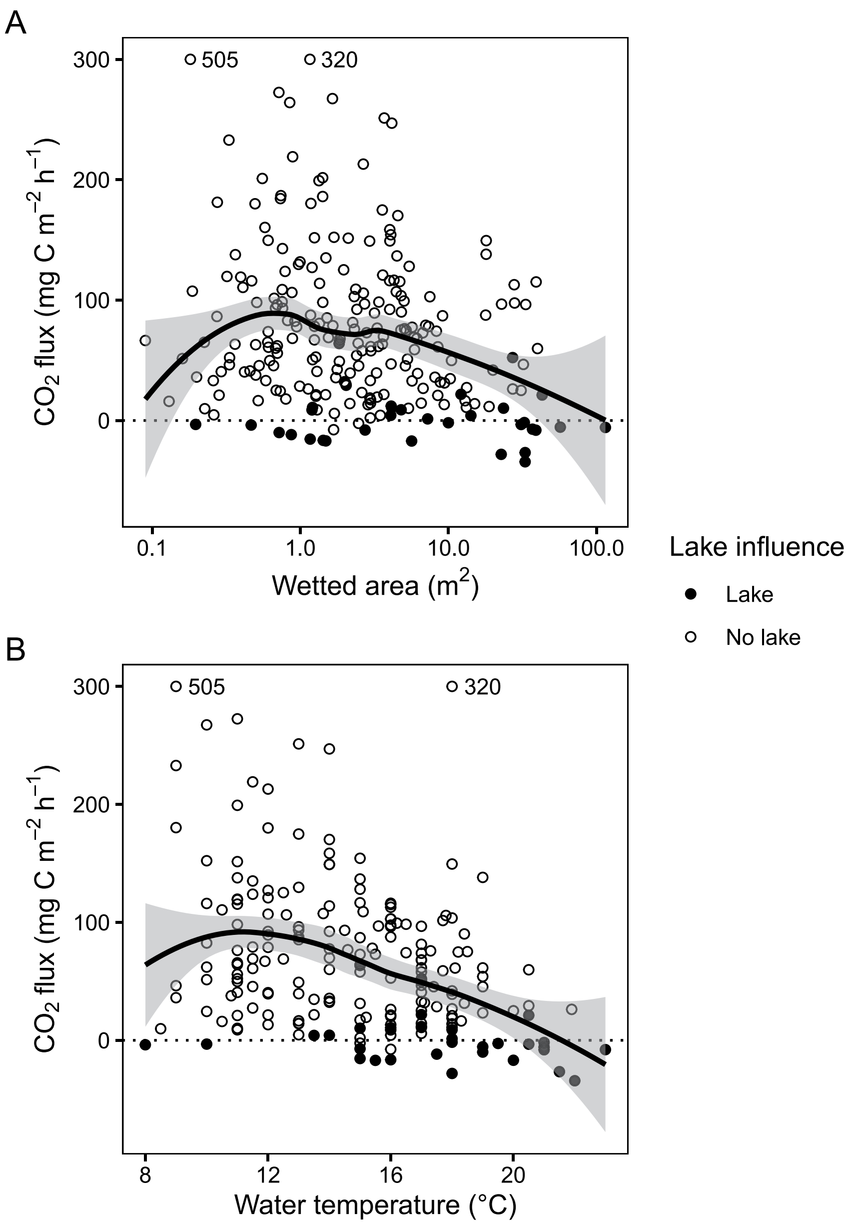

Figure 8. Predictors of stream CO_2 emission. (a) CO_2 flux from stream sites located either downstream of lakes (closed circles) or with no or distant influence from lakes (open circles) as a function of the wetted area. The trend in the point cloud is shown using a locally estimated scatterplot smoothing (LOESS) function (solid line) with 95% CI in gray. The *x*-axis is $\log_{10}$-transformed. (b) CO_2 flux from stream sites as a function of water temperature. The trend in the point cloud is shown using a LOESS smoothing function (solid line) with 95% CI in gray.

When CO_2 concentrations from all examined sites in Danish streams of widely different hydrology, geomorphology, and plant density were related to the wetted area across the stream, the spatial variability of CO_2 accounted for was low, though the overall downstream decrease was highly significant. Concurrently, CO_2 concentration also varied extensively between pronounced supersaturation at most stream sites and uptake in a few lake outlets. The CO_2 concentrations were low in lake outlets and even lower at sites several kilometers downstream. The CO_2 concentrations in lake outlets is reduced most during summer at high phytoplankton production and long water retention time, but even during winter at low phytoplankton production, CO_2 concentrations are much lower downstream than upstream as CO_2 continues to be emitted from the large lake surfaces (Figures 6 and 7).

CO_2 concentrations decreased in lake outlets log-log linearly with higher phytoplankton biomass and were markedly undersaturated (only 1 μM) in the highly eutrophic Lake Arre (Figure 7). This is a result of intensive summer phytoplankton production, which changes to CO_2 supersaturation for the same lakes between autumn and spring due to less incoming light, limited photosynthesis and net heterotrophy (Figure 6). The seasonal variations of CO_2 concentrations are most pronounced in outlets from eutrophic lakes such as Lake Arre with a 100-fold variation from mid-summer (1 μM) to mid-winter (100 μM). In comparison, humic forest lakes remain CO_2 supersaturated and net heterotrophic during the entire year due to combined light and nutrient limitation of phytoplankton production (Martinsen et al., 2020b; Staehr et al., 2010). While, no fluvial networks with forest lakes were included in our study of the primarily open, cultivated Danish landscape, such lakes are common over large forested areas in boreal regions (Nydahl et al., 2020; Sobek et al., 2003). Thus, high spatial variability along streams and localized influence of groundwater inflow, land use and lakes must be accounted for through a high spatial coverage when CO_2 emission rates are up-scaled to emissions budgets for individual streams or large geographical regions (Duvert et al., 2018).

4.2. CO_2 Emission Rates

CO_2 emission during summer varied between the shallow streams in the Danish landscape characterized by changing CO_2 input from land and in-stream respiration versus CO_2 loss to the atmosphere and consumption by photosynthesis of submerged plants and microalgae. The variability was particularly high in fluvial networks where CO_2 emission from streams upstream of lakes changed to CO_2 uptake downstream of lakes. However, shallow reaches with dense submerged plants can also support high summer gross photosynthetic rates (max. 2.8 g C m^{-2} d^{-1}; Alnoee et al., 2021) effectively reducing CO_2 emission during the daytime. Subsequently, CO_2 emission increases during nocturnal respiration and later during autumn degradation of organic carbon accumulated in the plant biomass (Kelly et al., 1983; Sand-Jensen, 1998). Both on daily and annual basis the Danish streams are generally net heterotrophic according to oxygen mass balances with in-stream respiration exceeding gross photosynthesis and generating a CO_2 surplus (Alnoee et al., 2021; Kelly et al., 1983; Simonsen & Harremoës, 1978).

Although mean CO_2 emission from streams with no lakes varied 10 times from minimum to maximum, the overall summer mean for all streams was constrained within a relatively narrow confidence interval (1.75–2.50 g C m^{-2} d^{-1}). Thus, it is possible to attain a reliable estimate of the mean value for Danish fluvial networks during summer, when, as in this study, several hundred sites are included representing the main geographical regions and fluvial networks (Gómez-Gerner, 2021). However, upscaling is challenged by the extreme spatial variability and the need to include numerous sites to account for the profound influence of: (a) lakes and their variable water retention time and phytoplankton productivity, (b) stream site location in the network and, thus, the variable downstream and lateral CO_2 input, and (c) variable in-stream autotrophic-heterotrophic balance.

We found that the mean summer emission rates per m^2 for Danish streams resembles global emissions for streams in temperate regions (Lauerwald et al., 2015). However, it remains uncertain how representative summer emissions are of annual emissions. Higher inflow of CO_2-rich soil water, including much drainage water from cultivated fields, during winter than summer as well as increasing respiration relative to photosynthesis in the fluvial network will generate a CO_2 surplus (Alnoee et al., 2021; Kelly et al., 1983; Simonsen & Harremoës, 1978). The increase of CO_2 concentrations and CO_2 emission from summer to winter is highest close to lake outlets and in lower reaches, while smaller changes are expected in groundwater-fed headwater streams with relatively constant CO_2 concentrations, water temperatures, and flow velocities (Sand-Jensen & Staehr, 2012).

It is important to determine annual CO_2 emissions in streams and validate the calculations by using different approaches. It is possible to combine continuously recording field sensors (e.g., flow velocity, depth, water temperature, CO_2, pH, and conductivity) and gas flux chamber measurements (Sand-Jensen & Staehr, 2012), and compare them with general calculations based on regional monitoring data (i.e., discharge, slope, channel dimensions, etc.; Raymond et al., 2013). It should be possible to check these direct and general calculations with a mass balance approach using radon as a tracer of groundwater inflow and gas emission from stream surfaces (Duvert et al., 2019).

While attempting to evaluate patterns of CO_2 concentration and emission in streams at regional and global scales, we must recall that availability of CO_2 at local stream sites also has a direct influence on species diversity and primary production of plants that, in turn, affect the flow, water chemistry and CO_2 emission (Demars & Trémolières, 2009; Sand-Jensen, 1998). Carbon dynamics remains a complexity of regulations and interactions at local and catchment levels in fluvial networks.

Data Availability Statement

Data on stream discharge and the national elevation model are publicly available from the sources cited in the main text. Data and scripts used for the analysis and figures are available from an online repository (https://doi.org/10.17894/ucph.108eeee5-131c-4eab-bc5a-0a338d729e77; Sand-Jensen, Riis, Kjær, & Martinsen, 2022).

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