

# Water Resources Research

## RESEARCH ARTICLE

10.1029/2020WR028806

### Key Points:

- Distinct land-water interfaces create unique seasonal patterns for different forms of carbon (dissolved organic carbon, carbon dioxide, and methane) supplied to boreal streams
- Different carbon forms have distinct flow-concentration relationships that together shift the composition of the stream carbon pool
- Shifts in dissolved to gaseous carbon delivered to streams drive temporal patterns in the share of emissions versus transported carbon

### Supporting Information:

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

### Correspondence to:

L. Gómez-Gener,  
[gomez.gener87@gmail.com](mailto:gomez.gener87@gmail.com)

### Citation:

Gómez-Gener, L., Hotchkiss, E. R., Laudon, H., & Sponseller, R. A. (2021). Integrating discharge-concentration dynamics across carbon forms in a boreal landscape. *Water Resources Research*, 57, e2020WR028806. <https://doi.org/10.1029/2020WR028806>

Received 11 SEP 2020

Accepted 2 AUG 2021

© 2021. The Authors.

This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial-NoDerivs License](https://creativecommons.org/licenses/by-nc-nd/4.0/), which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

## Integrating Discharge-Concentration Dynamics Across Carbon Forms in a Boreal Landscape

Lluís Gómez-Gener<sup>1,2,3</sup> , Erin R. Hotchkiss<sup>4</sup> , Hjalmar Laudon<sup>5</sup> , and Ryan A. Sponseller<sup>1</sup>

<sup>1</sup>Department of Ecology and Environmental Science, Umeå University, Umeå, Sweden, <sup>2</sup>Institute of Environmental Engineering, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland, <sup>3</sup>Centre for Advanced Studies of Blanes, Spanish National Research Council (CEAB-CSIC), Blanes, Spain, <sup>4</sup>Department of Biological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, VA, USA, <sup>5</sup>Department of Forest Ecology and Management, Swedish University of Agricultural Sciences (SLU), Umeå, Sweden

**Abstract** The flux of terrestrial carbon across land-water boundaries influences the overall carbon balance of landscapes and the ecology and biogeochemistry of aquatic ecosystems. The local consequences and broader fate of carbon delivered to streams is determined by the overall composition of carbon inputs, including the balance of organic and inorganic forms. Yet, our understanding of how hydrologic fluxes across different land-water interfaces regulate carbon supply remains poor. We used 7 years of data from three boreal catchments to test how different land-water interfaces (i.e., forest, wetland, and lake) modulate concentration-discharge (C-Q) relationships for dissolved organic carbon (DOC), carbon dioxide (CO<sub>2</sub>), and methane, as well as the balance among forms (e.g., DOC:CO<sub>2</sub>). Seasonal patterns in concentrations and C-Q relationships for individual carbon forms differed across catchments. DOC varied between chemostasis and transport limitation in the forest catchment, between supply limitation and chemostasis in the wetland catchment, and was persistently chemostatic in the lake outlet stream. Carbon gases were supply limited overall, but exhibited chemostasis or transport limitation in the forest and wetland catchments linked to elevated flow in summer and autumn. Unique C-Q relationships for individual forms reflected the properties of different interfaces and underpinned changes in the composition of lateral carbon supply. Accordingly, DOC dominated the carbon flux during snowmelt, whereas gas evasion increased in relative importance during other times of the year. Integrating the C-Q dynamics of individual carbon forms provides insight into the shifting composition of lateral export, and thus helps to predict how hydrologic changes may alter the fate of carbon supplied to streams.

**Plain Language Summary** Carbon transferred from soils to streams plays an important role in aquatic ecosystems and is relevant for carbon budget estimates at broader scales. The consequences and fate of carbon exported from land to water is influenced by the form of that carbon (e.g., dissolved organic carbon (DOC) or gases like carbon dioxide and methane). Yet, we still know little about what factors regulate the makeup of carbon that enters streams, including how it is influenced by the different “interface zones” that lie between soil sources and stream channels. We used seven years of data from a well-studied boreal research site to characterize the composition of carbon flux from three small streams dominated by different types of interfaces, including riparian forests, a large wetland, and a lake. Our results demonstrate that snowmelt periods are dominated by DOC and downstream transport, whereas high flow events in summer and autumn promote relatively greater carbon gas evasion to the atmosphere. DOC dominated export at all sites, but the relationships between water flow and the concentration of different carbon forms varied among sites and over time, reflecting differences in how interface zones regulate, store, and transform carbon before it reaches streams.

## 1. Introduction

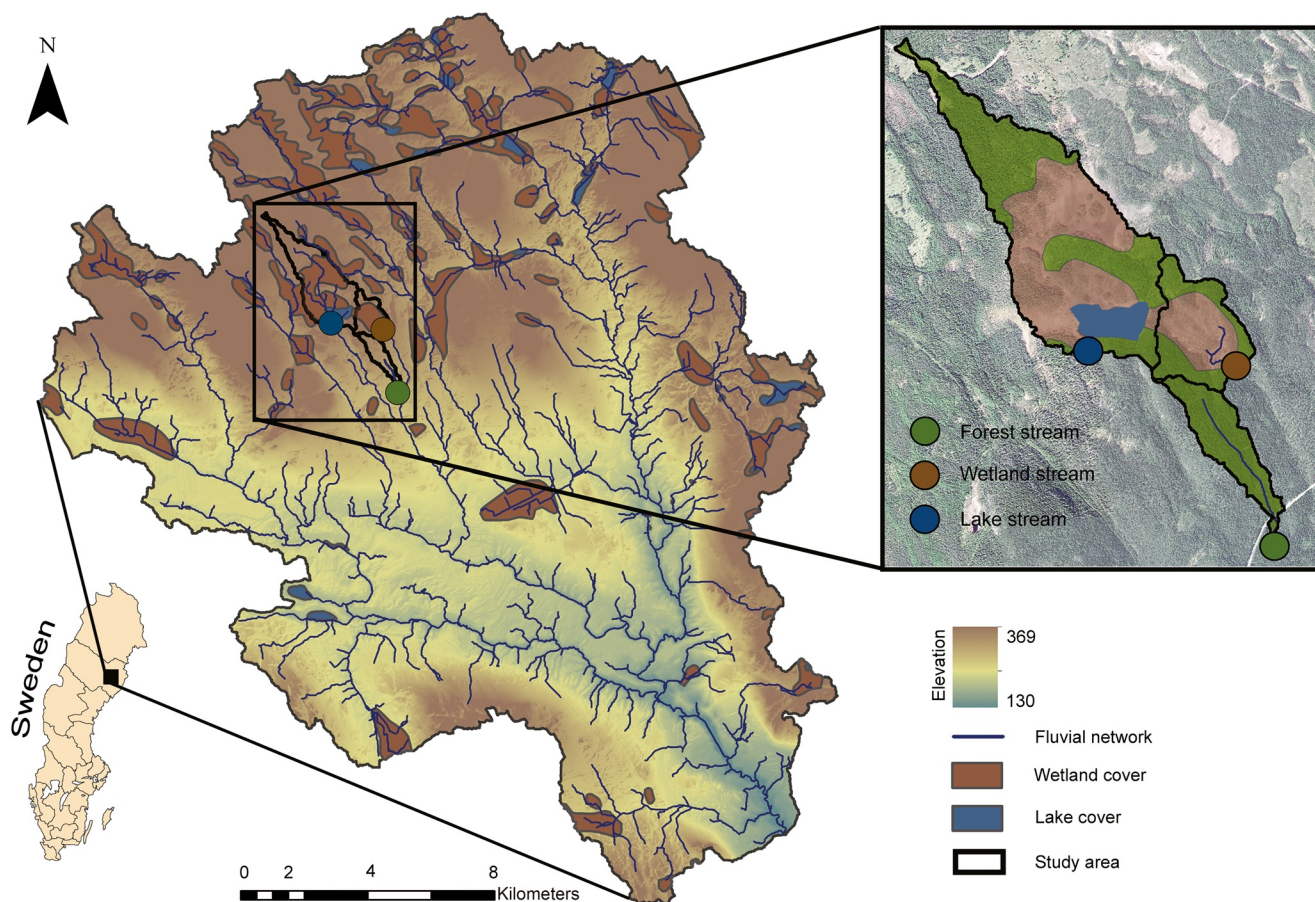
Headwater streams create the Earth's largest interface between terrestrial and freshwater systems. The flux of carbon across land-water interfaces is important for the carbon balance of regional landscapes (Webb et al., 2019) and central to the ecology and biogeochemistry of recipient streams and rivers (Tank et al., 2010). Even though decades of research have explored how catchment processes regulate the export of terrestrial carbon to streams, important gaps in our understanding remain. Most notably, studies to date have primarily focused on the dynamics and supply of individual organic or inorganic carbon species, but

efforts to assess the balance and proportions of different carbon forms delivered across land-water boundaries are relatively few (Tank et al., 2018).

Different carbon forms supplied to streams vary in chemical structure and biophysical reactivity, play unique biogeochemical roles, and have distinct downstream fates in drainage networks. For example, dissolved organic carbon (DOC) delivered from soils can be an important source of energy to in-stream heterotrophic microbes (Mineau et al., 2016), and a large fraction of this pool likely travels long distances (e.g.,  $10^3 - 10^5$  m) before it is mineralized (Casas-Ruiz et al., 2017; Kaplan et al., 2008), particularly during high flows (Raymond et al., 2016). By comparison, much of the carbon dioxide (CO<sub>2</sub>) delivered to streams can evade within meters of entry, a process that depends on the interplay between the stream turbulence and the degree of supersaturation of this gas into the water (e.g., Duvert et al., 2018; Öquist et al., 2009). Finally, methane (CH<sub>4</sub>) transported across ecosystem boundaries is more ephemeral still, as it can be rapidly oxidized along near-stream flowpaths that traverse low to high redox environments (Crawford et al., 2017; Lupon et al., 2019). Thus, variation in the forms of carbon moving across ecosystem boundaries will determine what biogeochemical processes may occur locally in recipient streams and, owing to differences in reactivity and turnover among forms, regulate the relative importance of downstream transport versus local emissions.

Capturing the forms and fates of the lateral carbon flux is particularly important in heterogeneous boreal landscapes, which store vast quantities of organic matter in soils (Bradshaw & Warkentin, 2015). While this storage can lead to high rates of carbon loading to streams (e.g., Aitkenhead & McDowell, 2000), the mosaic of forests, wetlands (mires), and lakes that define boreal landscapes can create important variation in soil-stream boundaries that alter the timing, magnitude, and forms of this exchange. This heterogeneity includes differences in vertical profiles of DOC, CO<sub>2</sub>, and CH<sub>4</sub> among soils at the interface with streams (Campeau et al., 2018), which potentially guide patterns of carbon mobilization in response to changes in groundwater levels and flow. For example, in forested catchments, increases in discharge often mobilize carbon from surficial riparian soils that are strong sources of DOC (Bishop et al., 2004; Ledesma et al., 2018), but relatively weak sources of carbon gases (Öquist et al., 2009). For wetlands, which are major sources of all carbon forms to boreal streams (e.g., Leach et al., 2016), hydrologic connections instead reflect preferential flowpaths that vary in their capacity to mobilize or dilute stream solutes and gases throughout the year (e.g., Holden et al., 2012; Sponseller et al., 2018). Finally, small headwater lakes, abundant in boreal landscapes, can also modify carbon fluxes to outlet streams through within-lake DOC processing, as well through periodic release of solutes and gases generated and stored in hypolimnetic waters (Crawford et al., 2014; Denfeld et al., 2018). While multiple studies in boreal landscapes have explored variable land-water connections for specific carbon forms (e.g., CO<sub>2</sub>; Wallin et al., 2010), especially during snowmelt (Laudon et al., 2011), little is known about how the relative contribution of multiple carbon forms is altered by the diversity of interfaces around headwater streams.

Concentration-discharge (C-Q) analysis has emerged as a powerful tool for understanding how lateral carbon fluxes to streams and rivers vary over space and time (Creed et al., 2015; Liu & Raymond, 2018; Zarnetske et al., 2018). C-Q relationships yield three main patterns that describe whether stream concentrations are invariant (i.e., chemostatic), or increase or decrease (i.e., chemodynamic) with increasing discharge (Moatar et al., 2017; Musolff et al., 2017). These patterns give insight into what limits the transfer of solutes and gases to streams. For example, a chemostatic C-Q relationship suggests a uniform distribution of solutes or gases in soils, such that changes in hydrological connections have no net influence on stream concentrations (Godsey et al., 2009). Positive C-Q relationships represent transport limitation, when the supply of a solute or gas is large enough for export to be limited by the strength of hydrological connections across ecosystem boundaries. In the context of carbon supply, positive C-Q relationships should emerge for forms that are concentrated near the soil surface (Bishop et al., 2004). By contrast, negative C-Q patterns represent source limitation and indicate that the supply of a solute is insufficient to keep pace with the increasing hydrologic flux, resulting in dilution of stream signals. Dilution can be expected if DOC or carbon gases are concentrated in deeper soils but decline toward the soils surface. C-Q analyses have been widely applied to understand DOC export, and in most cases have revealed either chemostatic patterns or transport limitation (e.g., Creed et al., 2015; Zarnetske et al., 2018). Application of this approach to CO<sub>2</sub> and CH<sub>4</sub> has revealed a broader set of responses (Aho & Raymond, 2019; Dinsmore et al., 2013; Horgby et al., 2019), with



**Figure 1.** Location of the Krycklan Catchment Study (KCS) in northeastern Sweden and the spatial distribution of major landscape units (i.e., forests, wetlands, and lakes; only wetlands and lakes are color coded due to the abundance of forests throughout the catchment). The black box highlights the location of three study headwater catchments within the KCS (catchment perimeters delineated with a black solid line) as well as the corresponding stream sampling locations (solid circles) and major landscape units. See Methods sections for more information.

both transport and supply limitation reported for gases when considered across large scales (Liu & Raymond, 2018). Here, we extend this approach to consider how unique C-Q relationships for different carbon forms, depending on catchment type and seasonal timing of flow, govern the overall composition of carbon supplied to boreal streams.

We quantified C-Q relationships for DOC, CO<sub>2</sub>, and CH<sub>4</sub> from seven years of monitoring data collected at three headwater streams in northern Sweden and evaluated how hydrological changes influenced the balance of these carbon species (i.e., DOC:CO<sub>2</sub> and CH<sub>4</sub>:CO<sub>2</sub>). The study streams are located close to each other, but drain catchments that differ in land cover: either completely forested, dominated by a large wetland, or drain a lake-wetland complex. We used our analyses to ask the following questions: (a) How do seasonal hydrological fluxes through riparian forest soils, wetlands, and lakes influence the supply and relative contribution of different carbon forms exported to streams? (b) How do C-Q relationships differ among high-flow events during snowmelt versus snow-free seasons? And finally (c) how do spatial and temporal variations in C-Q relationships ultimately govern the fate of carbon as either emissions or export?

## 2. Methods

### 2.1. Site Description

The study was conducted in the upper section of the Krycklan Catchment Study (KCS), in northern Sweden (64°14'N, 19°46'E, Figure 1). The KCS is part of the Svartberget Research Station, where research on



catchment hydrology and biogeochemistry have been ongoing since 1980 (see Laudon et al., 2013 for a full description of the study area). Briefly, climate at the KCS is characterized by long winters and short summers. Mean annual precipitation and temperature from 1980 to 2013 were 612 mm, and +1.7°C, respectively. Approximately 50% of annual precipitation falls as snow, and snow cover persists for 168 days per year on average, from the end of October to the beginning of May (Laudon & Ottosson Löfvenius, 2016). Snowmelt begins between mid and late April and ends between mid and late May (Laudon & Ottosson Löfvenius, 2016).

This study focused on three small first-order catchments located in the headwaters of the KCS (Figure 1). This part of the catchment is largely forested, with Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) as dominant species. Upland soils are primarily well-developed iron podzols, but thicker, organic-rich peat deposits are common in low-lying areas and along stream margins (Bishop et al., 1995). Open wetlands (mires) with extensive peat accumulation are also common in this part of the KCS, occupying more than 40% of area for some catchments (Laudon et al., 2013). The three catchments studied here drain glacial till soils, yet each is dominated by a distinct land-cover type of boreal landscapes: coniferous forests, wetlands, and lakes. The forest stream (C2) drains a 12-ha catchment with 99.9% forest cover. The wetland outlet stream (C4) drains an 18-ha catchment strongly influenced by a wetland (covering 44.1% of the total catchment area). Finally, the lake outlet stream (C5) drains a 65-ha catchment with mixed forest (54.1%) and wetland (39.5%) cover, but also a headwater lake covering 6.4% of its area. Water residence time of this lake is typically 4–6 months (e.g., Berggren et al., 2018; Denfeld et al., 2020). As is common in the region, a large fraction of this lake perimeter is fringed by a wetland ecosystem (Denfeld et al., 2018). The sampling stations for C4 and C5 are located approximately 50 m downstream of the wetland and lake outlets, respectively. Thus, carbon supply patterns for these sites are expected to primarily reflect how solutes and gases move across ecosystem boundaries rather than how in-stream processes or atmospheric exchange re-shape these pools during transport. For the C2 catchment, the channel upstream of the weir is slightly longer than in C4 and C5, and thus likely presents greater opportunity for in-stream processes to alter the observed chemical signals. However, unlike C4 and C5, which operate as point sources in the landscape, riparian soils at C2 supply water and solutes along this entire stream (e.g., see Lupon et al., 2019).

## 2.2. Stream Sampling and Laboratory Analysis

Stream DOC, CH<sub>4</sub>, dissolved inorganic carbon (DIC) and dissolved silica (DSi) were sampled at each site along with a suite of additional chemical and physical parameters as part of the KCS monitoring program. To cover a wide spectrum of hydrologic conditions, we compiled data from seven consecutive years (2010–2016). Samples were collected monthly during winter, every second week during summer and fall, and more intensively (approximately every third day) during the spring flood due to snowmelt (in total, ca. 210 sampling occasions).

Samples for DOC and DSi were filtered (0.45- $\mu$ m pore size; sterile PVDF membrane) into acid-washed 250-mL high-density polyethylene bottles (previously rinsed three times) and kept cold (<4°C) without headspace until laboratory analysis (<24 h after collection). The samples for DSi analysis were additionally preserved with ultrapure HNO<sub>3</sub> (1% v/v). DOC was analyzed by combustion using a Shimadzu TOC-V<sub>PCH</sub> following acidification to remove inorganic carbon. DSi was analyzed by inductively coupled plasma optic emission spectroscopy using a Varian Vista Ax Pro instrument. Samples for pH were collected in acid-washed 250-ml high-density polyethylene bottles (previously rinsed three times) and filled completely to avoid headspace. Samples were kept at similar temperatures as those measured in the field and upon return were immediately analyzed in the lab using an Orion 9272 pH meter. For DIC and CH<sub>4</sub>, a separate 5 ml sample of bubble-free water was taken and injected into a 22.5 ml glass vial (containing nitrogen gas (N<sub>2</sub>) at atmospheric pressure) sealed with a rubber septum. The vial was pre-filled with 0.1 ml of 85% phosphoric acid and N<sub>2</sub> at atmospheric pressure to shift the carbonate equilibrium toward CO<sub>2</sub>. Headspace CO<sub>2</sub> and CH<sub>4</sub> concentration were then analyzed by GC-FID (Perkin-Elmer Clarus 500) equipped with a methanizer operating at 250°C and connected to an autosampler (Turbo Matrix 110). Concentrations of the different species of DIC (i.e., CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>) were determined by combining the analytical headspace CO<sub>2</sub> with stream pH and temperature using temperature-dependent equations for carbonate equilibrium (Gelbrecht et al., 1998) and Henry's Law (Weiss, 1974). Similarly, we determined stream CH<sub>4</sub> concentration using the

analytical headspace CH<sub>4</sub> with the stream temperature following Henry's Law (Weiss, 1974). Free dissolved CO<sub>2</sub> was the predominant DIC form during the studied period (accounting for 94.3 ± 6.3%, 98.6 ± 6 0.9% and 98.0 ± 7.1% of the DIC pool in the forest, wetland and lake stream, respectively). Accordingly, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> were not included in our analysis due to their minor contribution to total DIC. Finally, we do not consider particulates, but previous studies in the Krycklan suggest that particulate organic matter typically represents a small percentage (on average <1%) of the total organic matter pool that is being transported (Laudon et al., 2011).

### 2.3. Hydrology and Season Delineation

At each stream, discharge (L s<sup>-1</sup>) was estimated at hourly intervals from stage height measured with pressure transducers installed at either a 90° V weir (C2 and C4) or an H-flume (C5) inside heated huts (allowing for year-round discharge monitoring; see Karlson et al., (2016) for details on hydrologic measurements, including rating curves to estimates discharge). To normalize and compare discharge among streams with different catchment areas, we report specific discharge (mm day<sup>-1</sup>). To explore seasonal changes in discharge-concentration relationships, we defined three seasons based on (a) hydrologic observations across the 7 years of the study (2010–2016) and (b) historical (1980–2008) seasonal records (see Laudon et al., 2011). In the end, we grouped observations into the most contrasting and characteristic hydrologic periods in this region (Figure S1): (a) the snow-covered period during winter (average length of 165 days), (b) the snowmelt period during spring (average length of 50 days) and (c) the snow-free period during summer and autumn (average length of 150 days). For visual interpretation of the seasonal dynamics of stream DOC, CO<sub>2</sub> and CH<sub>4</sub> concentrations, we computed Locally Weighted Scatterplot Smoothing (LOESS) models with a span (degree of smoothing) of 0.5. Additionally, to compare average concentrations of DOC, CO<sub>2</sub> and CH<sub>4</sub> concentrations across seasons, we used one-way analysis of variance. We then performed post-hoc comparisons (Tukey's Honest Significant Differences test) to evaluate the effect of season on the stream carbon concentrations across the three catchments. Both LOESS models and statistical analyses were conducted using the “stats” package in R statistical environment (R Core Team, 2018).

### 2.4. Concentration-Discharge Analysis

To understand how lateral inputs of different carbon forms vary with flow conditions and catchment, we generated concentration-discharge relationships (log C–log Q) across the full discharge range for each site (Thompson et al., 2011). C-Q relationships were analyzed as follows:

$$C = a Q^b \quad (1)$$

where C is concentration of each carbon form (mg L<sup>-1</sup>), a is the coefficient (mg L<sup>-1</sup>), Q is specific discharge (mm d<sup>-1</sup>), and b is a unitless exponent representing the slope of the log-transformed C-Q relationship (Moatar et al., 2017). Based on Meybeck and Moatar (2012), we used the b thresholds of -0.2 and 0.2 for respectively a negative chemodynamic behavior (indicating dilution or source limitation) and positive chemodynamic behavior (indicating concentration or transport limitation). Accordingly, a b between -0.2 and 0.2 would indicate a chemostatic behavior (i.e., and invariant response of the solute or gas with increasing discharge). We also used the coefficient of determination (r<sup>2</sup>), to determine the goodness of the fit of the linear log C–log Q relationships for the different carbon forms and the probability value (p-value) at α = 0.05 as the threshold for statistical significance (Godsey et al., 2009; Musolff et al., 2015).

In addition to evaluating C-Q relationships across the entire discharge range, we also decomposed the hydrograph above and below the median daily specific discharge (Q<sub>50</sub>) and calculated segmented C-Q relationships (and associated b, r<sup>2</sup> and p) for low and high discharge periods (following Meybeck & Moatar, 2012; Moatar et al., 2017; Figure S1). This decomposition of C-Q relationships provides a tool to evaluate solute dynamics during specific seasonal events, which are normally difficult to capture with entire range analysis due to nonlinearities and frequent hysteretic patterns (Meybeck & Moatar, 2012). In addition, to assess season-specific differences in the hydrological and biogeochemical functioning of the three studied streams, we analyzed the C-Q relationships (and associated b, r<sup>2</sup> and p) above Q<sub>50</sub> during two specific periods of the

year (the snowmelt and the snow-free period). Accordingly, decomposed or segmented C-Q relationships were analyzed as follows:

$$C_{Q50(t)} = \left[ \frac{Q_{50}}{10^{a_{50,t}}} \right]^{1/b_{50,t}} \quad (2)$$

where  $C_{Q50}$  is the average the carbon concentration at the median daily discharge ( $Q_{50}$ ),  $t$  is the specific period or season of interest (i.e., low discharge, high discharge during snowmelt and high discharge during snow-free), and the other terms are as defined in Equation 1. To compare the C-Q dynamics of the various carbon forms with those of a conservative weathering-derived element, we included the C-Q analysis for DSI. We generated linear log C-log Q models for the different carbon forms and its ratios using the “stats” and “vegan” packages in R statistical environment (R Core Team, 2018).

Finally, we generated segmented C-Q curves and analyzed density distributions for the mass concentration ratios of both DOC to  $CO_2$  (DOC:CO<sub>2</sub>) and CH<sub>4</sub> to  $CO_2$  (CH<sub>4</sub>:CO<sub>2</sub>) for each stream to evaluate how the overall composition of the carbon pool shifted with changes in discharge across catchments and seasons. The DOC to  $CO_2$  ratio provides insight into the potential for carbon to be rapidly (and locally) lost from the system (e.g., via vertical  $CO_2$  emissions) or to have a more persistent, longitudinal influences downstream (e.g., if DOC dominates). Accordingly, increases in DOC:CO<sub>2</sub> with discharge represent a shift toward stronger longitudinal versus vertical carbon transport/loss. Additionally, CH<sub>4</sub>:CO<sub>2</sub> has been used as a proxy to understand the relative importance of anaerobic over aerobic metabolic processes (methanogenesis) in wetland (Segers, 1998) and stream ecosystems (Gómez-Gener et al., 2020; Stanley et al., 2016). In this study, CH<sub>4</sub>:CO<sub>2</sub> provides insight into the metabolic properties and redox conditions of different ecosystem interfaces that supply carbon to headwater streams. For example, decreases in CH<sub>4</sub>:CO<sub>2</sub> with discharge may be expected when rising water tables intersect increasingly oxic soil horizons. By contrast, increasing CH<sub>4</sub>:CO<sub>2</sub> with discharge should occur when/where expanding or contracting flowpaths intersect soils where anaerobic redox signals/pathways are dominant.

## 2.5. Annual and Seasonal Stream Carbon Evasion and Export

Our final goal was to evaluate the implications of different C-Q relationships for the annual and seasonal patterns of carbon gas emission and downstream carbon export. To do this, we first quantified the daily DOC downstream export flux for each site and date as the product of concentration and discharge, corrected for drainage area ( $g\ C\ m^{-2}\ d^{-1}$ ). We used export flux estimates to identify times and landscape types where downstream DOC fluxes were elevated, so that we could compare these windows with emissions (below). We grouped export fluxes by season and discharge condition to estimate the total annual and seasonal export ( $g\ C\ m^{-2}$ ) and relative contribution (%) of seasonal export for the different streams.

We then estimated the daily  $CO_2$  and CH<sub>4</sub> emission flux across the water-air interface ( $mmol\ m^{-2}\ d^{-1}$ ) for each stream and date using Fick's First Law of gas diffusion:

$$CO_2\ Emission\ Flux = k_{CO_2} (c_{CO_2,w} - c_{CO_2,a}) \quad (3)$$

$$CH_4\ Emission\ Flux = k_{CH_4} (c_{CH_4,w} - c_{CH_4,a}) \quad (4)$$

where  $c_{CO_2,w}$  and  $c_{CH_4,w}$  ( $mmol\ m^{-3}$ ) are the daily linearly interpolated molar concentrations of  $CO_2$  and CH<sub>4</sub> in stream water;  $c_{CO_2,a}$  and  $c_{CH_4,a}$  ( $mmol\ m^{-3}$ ) are the stream molar concentration of  $CO_2$  and CH<sub>4</sub> in the air. The  $k_{CO_2}$  and  $k_{CH_4}$  ( $m\ d^{-1}$ ) are the specific gas transfer velocities for  $CO_2$  and CH<sub>4</sub>. Positive values of  $CO_2$  and CH<sub>4</sub> emission flux represent gas efflux from the water to the atmosphere, while negative values indicate gas influx from the atmosphere to the water.

We used Equation 3 in Raymond et al. (2012) to estimate the mean daily gas transfer velocity from stream hydraulics:

$$k_{600} = 1162\ s^{0.77}\ v^{0.85} \quad (5)$$

where  $k_{600}$  ( $\text{m d}^{-1}$ ) is the standardized gas transfer velocity at 20°C. The segment slope ( $s$ ;  $\text{m m}^{-1}$ ) and the mean stream water velocity ( $v$ ;  $\text{m s}^{-1}$ ) derived from measured daily discharge ( $\text{L s}^{-1}$ ) and stream cross-section ( $\text{m}^2$ ). We then transformed  $k_{600}$  to  $k_g$  (i.e.,  $k_{\text{CO}_2}$  and  $k_{\text{CH}_4}$ ) following:

$$k_g = k_{600} \left( \frac{Sc_g}{600} \right)^{-1/2} \quad (6)$$

where  $Sc$  (dimensionless) is the Schmidt number for  $\text{CO}_2$  or  $\text{CH}_4$  at the measured water temperature (Wanninkhof, 1992). The applicability of indirect estimates of  $k_{600}$  based on stream morphometric and hydrologic variables (Raymond et al., 2012) was supported by comparison with direct gas tracer releases within these same streams by Wallin et al. (2011) ( $n = 28$ ; Figure S5). We then converted daily molar  $\text{CO}_2$  and  $\text{CH}_4$  emission fluxes ( $\text{mmol CO}_2$  and  $\text{CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ ) to carbon mass units ( $\text{g C m}^{-2} \text{ d}^{-1}$ ) and grouped them by season and discharge condition to estimate the total annual and seasonal emission fluxes ( $\text{g of C m}^{-2}$ ) and obtain the relative contribution (%) of seasonal emissions fluxes for the different streams.

### 3. Results

#### 3.1. Temporal Patterns of Different Carbon Forms Across Catchments

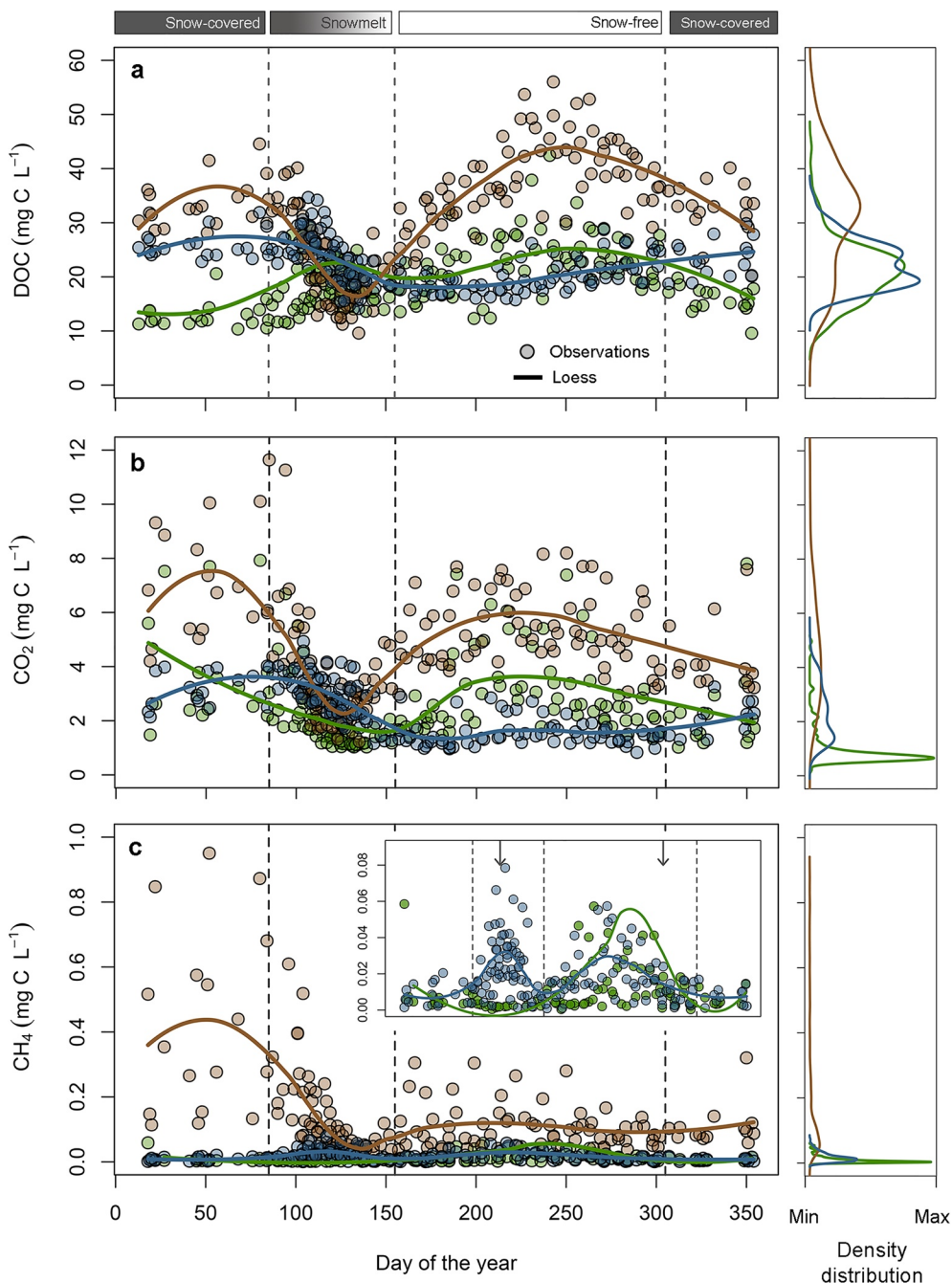
Analysis of 7 years of stream DOC,  $\text{CO}_2$  and  $\text{CH}_4$  concentration data revealed distinct but repeated patterns among streams and C forms (Figures 2 and S2). Specifically, the DOC (Figure 2a) in the forest stream increased from the snow-covered winter period (median:  $14.1 \text{ mg L}^{-1}$ ) to the snowmelt period ( $17.9 \text{ mg L}^{-1}$ ) and subsequently to the snow-free in summer and fall ( $23.2 \text{ mg L}^{-1}$ ). By contrast, DOC in the wetland outlet stream declined during snowmelt (from  $33.0$  to  $21.4 \text{ mg L}^{-1}$ ), but increased again to a median of  $38.5 \text{ mg L}^{-1}$  during the snow-free period. Finally, DOC concentrations in the lake outlet stream remained relatively stable across snow-covered and snowmelt periods ( $24.9$  and  $23.4$ , respectively), but, unlike the other sites, decreased to a median of  $19.5 \text{ mg L}^{-1}$  during the snow-free period.

$\text{CO}_2$  concentrations (Figure 2b) decreased during snowmelt in the forest stream (from  $2.4$  to  $1.7 \text{ mg L}^{-1}$ ) and wetland outlet stream (from  $5.4$  to  $3.0 \text{ mg L}^{-1}$ ), but increased at both sites during the snow-free period (to  $2.5$  and  $5.1 \text{ mg L}^{-1}$ , respectively), and remained relatively constant throughout winter. Consistent with DOC patterns, median  $\text{CO}_2$  in the lake outlet did not differ significantly between the snow-covered ( $2.6 \text{ mg L}^{-1}$ ) and the snowmelt period ( $2.8 \text{ mg L}^{-1}$ ) but decreased during the snow-free period (to  $1.4 \text{ mg L}^{-1}$ ).

$\text{CH}_4$  concentrations (Figure 2c) in the forest stream were constant throughout the snow-covered and snowmelt periods ( $2.0$  and  $1.7 \text{ } \mu\text{g L}^{-1}$ , respectively), but doubled during the snow-free period ( $5.6 \text{ } \mu\text{g L}^{-1}$ ). Similar to DOC and  $\text{CO}_2$ ,  $\text{CH}_4$  concentrations in the wetland outlet stream decreased during snowmelt (from  $133.0$  to  $81.5 \text{ } \mu\text{g L}^{-1}$ ). However, in contrast to these other forms,  $\text{CH}_4$  in the wetland outlet remained constant after snowmelt ( $82.8 \text{ } \mu\text{g L}^{-1}$ ). Finally,  $\text{CH}_4$  concentrations in the lake outlet stream increased more than twofold from the snow-covered ( $8.3 \text{ } \mu\text{g L}^{-1}$ ) to the snowmelt period ( $19.2 \text{ } \mu\text{g L}^{-1}$ ) and snow-free period ( $15.3 \text{ } \mu\text{g L}^{-1}$ ).

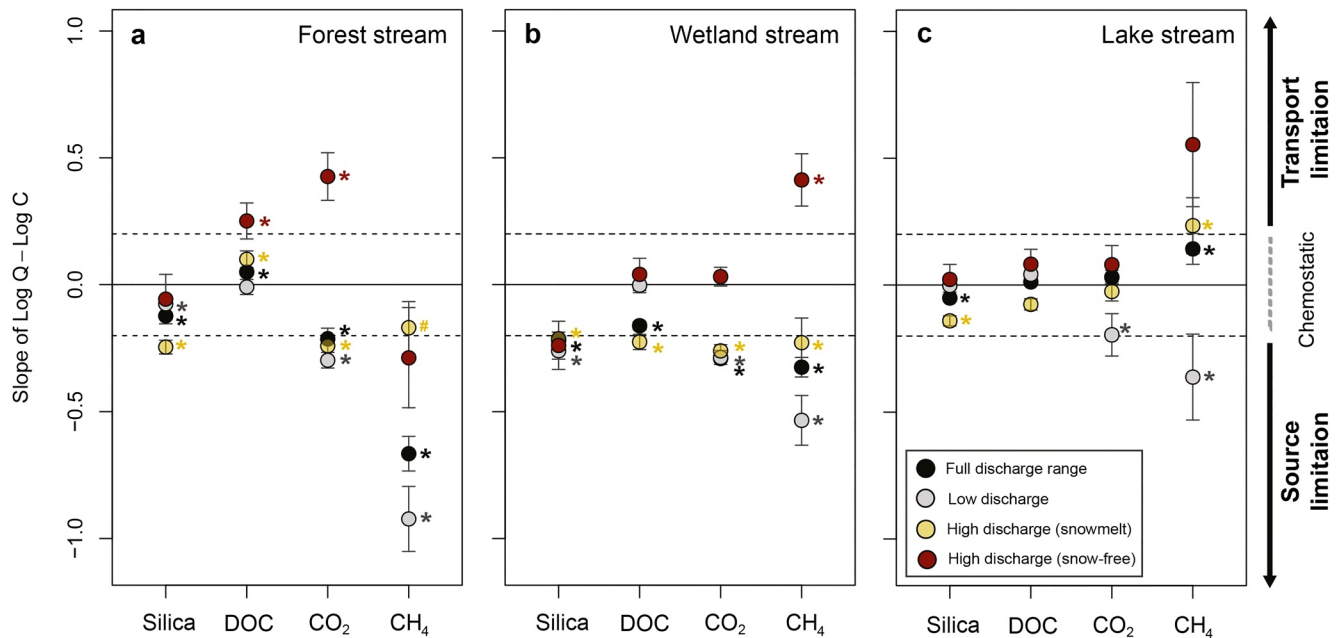
#### 3.2. Concentration-Discharge Dynamics of Individual Carbon Forms

The C-Q analysis for the full discharge range (Figure S3 and Table S1) differentiated the forest and wetland streams from the lake outlet. Specifically, C solutes tended to be correlated with discharge (i.e., intermediate to high  $b$  and  $r^2$ ) for the forest and wetland outlets, but there was no clear pattern for the lake outlet (i.e.,  $b$  between  $0.01$  and  $0.14$ ;  $r^2 \leq 0.03$ ). Segmenting C-Q relationships at median flow ( $Q_{50}$ ) revealed emergent C-Q patterns that were not detected when assessing the full discharge range (Figures 3 and S3, and Table S1). Trends above and below  $Q_{50}$  varied depending on stream type (forest vs. wetland outlet vs. lake outlet), carbon form (DOC,  $\text{CO}_2$ , or  $\text{CH}_4$ ), and season of flood events (snowmelt vs. snow-free). Specifically, the only significant C-Q relationships with a negative slope that remained constant above and below  $Q_{50}$  were for  $\text{CO}_2$  and  $\text{CH}_4$  in the wetland and forest streams, but only during snowmelt (Figures 3 and S3). In fact, either no significant C-Q relationship (for  $\text{CH}_4$  in the forest stream and  $\text{CO}_2$  in the wetland stream), or a positive C-Q relationship (for  $\text{CH}_4$  in the wetland stream and  $\text{CO}_2$  in the forest stream) was detected at these sites when evaluating high discharge (i.e., above  $Q_{50}$ ) during the snow-free period (Figures 3 and S3).



**Figure 2.** Intra-annual variability and density distributions of stream (a) dissolved organic carbon (DOC), (b) carbon dioxide (CO<sub>2</sub>) and (c) methane (CH<sub>4</sub>) concentrations (mg C L<sup>-1</sup>) for the study period (2010–2016) in the forest stream (green), the wetland outlet stream (brown) and the lake outlet stream (blue). Solid color lines in the time series plots are locally weighted regression model fittings (Loess) for a visual interpretation of the temporal dynamics. Horizontal bars in the top of (a) and vertical dashed bars within each time series plot delineate the most contrasting and characteristic hydrologic periods (see Method section and Figure S1 for a more detailed information). Inset in (c) represents zoomed-in intra-annual variability of the forest stream and the lake outlet stream for a range of CH<sub>4</sub> concentrations from 0.0 to 0.12 mg C L<sup>-1</sup>. Black solid arrows indicate the timing of most contrasted vertical mixing episodes in the lake.





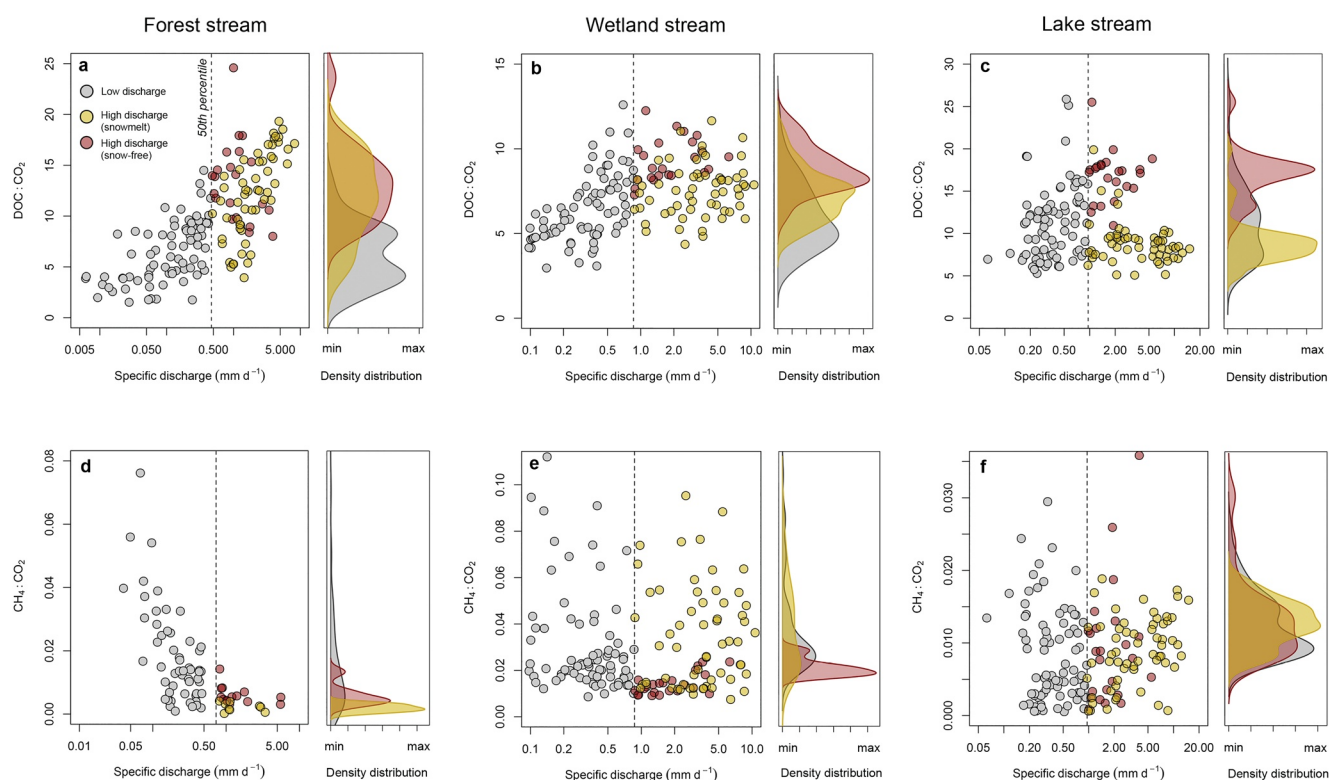
**Figure 3.** The slopes of the concentration-discharge (C-Q) relationships for dissolved organic carbon (DOC), carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) in the (a) forest stream, (b) wetland outlet stream and (c) lake outlet stream. Note that dissolved silica is included here as a reference because it is a conservative and weathering-derived element. Black circles represent slopes (b) of the C-Q relationships for the full discharge range. For C-Q regressions segmented at median Q, gray circles for low discharge conditions, yellow circles for high discharge during snowmelt and red circles for high discharge during the snow-free period. Error bars represent the standard error of the slope coefficient derived from C-Q relationships. Asterisks indicate statistically significant linear regression models ( $p < 0.05$ ). The horizontal solid reference line represents a slope = 0 (a net chemostatic C-Q relationship). Horizontal dashed lines at slopes -0.2 and 0.2 represent the slope thresholds for respectively a negative chemodynamic behavior (indicating dilution or source limitation) and positive chemodynamic behavior (indicating concentration or transport limitation) as in Meybeck and Moatar (2012). See Figure S3 and Table S1 for more a detailed information about the C-Q analyses.

There were also different C-Q patterns for DOC at high and low discharges compared to carbon gases, but again these relationships were more often predictable when segmenting C-Q relationships at  $Q_{50}$ . Specifically, below  $Q_{50}$  there was no relationship between DOC and discharge in the forest and wetland streams, but catchment-specific C-Q trends emerged above  $Q_{50}$ , and depended on the timing of the high flows (snowmelt vs. snow-free periods). For example, in the forest stream, we detected a positive C-Q relationship above  $Q_{50}$  during the snow-free but not snowmelt period. In contrast, for the wetland stream, we observed a strongly negative C-Q relationship during snowmelt, but no relationship at all for high discharge (above  $Q_{50}$ ) during the snow free period.

In contrast to C-Q relationships in the forest and wetland outlet streams, high dispersion across the full discharge range at the lake outlet indicated that the variability of carbon solutes was not driven by catchment hydrology (Figure S3). Instead, C-Q dynamics of the lake outlet stream, including chemostasis (for CO<sub>2</sub>) and transport limitation (for CH<sub>4</sub>) during snowmelt, appear more reflective of the physical and biogeochemical processes occurring in the lake (e.g., gas storage in the hypolimnion and release through vertical mixing events; Figures 2c and S4).

### 3.3. The Ratio of Carbon Concentrations Across Catchments and Hydrological Conditions

Evaluating the ratio of carbon forms across discharge conditions provided richer insight into how land-water connections distinctly supplied carbon among headwater catchments. For example, the ratio of DOC:CO<sub>2</sub> increased gradually across the whole discharge range in the forest stream and showed similar responses to flooding, regardless of season (Figure 4a). In contrast, DOC:CO<sub>2</sub> remained relatively unchanged across discharge conditions in the wetland outlet (Figure 4b). Finally, DOC:CO<sub>2</sub> varied considerably, but was also unrelated to discharge in the lake outlet stream (Figure 4c). In this case, the timing of flood events (snowmelt vs. snow-free) determined the relative proportion of DOC:CO<sub>2</sub> in the lake outlet stream carbon pool,



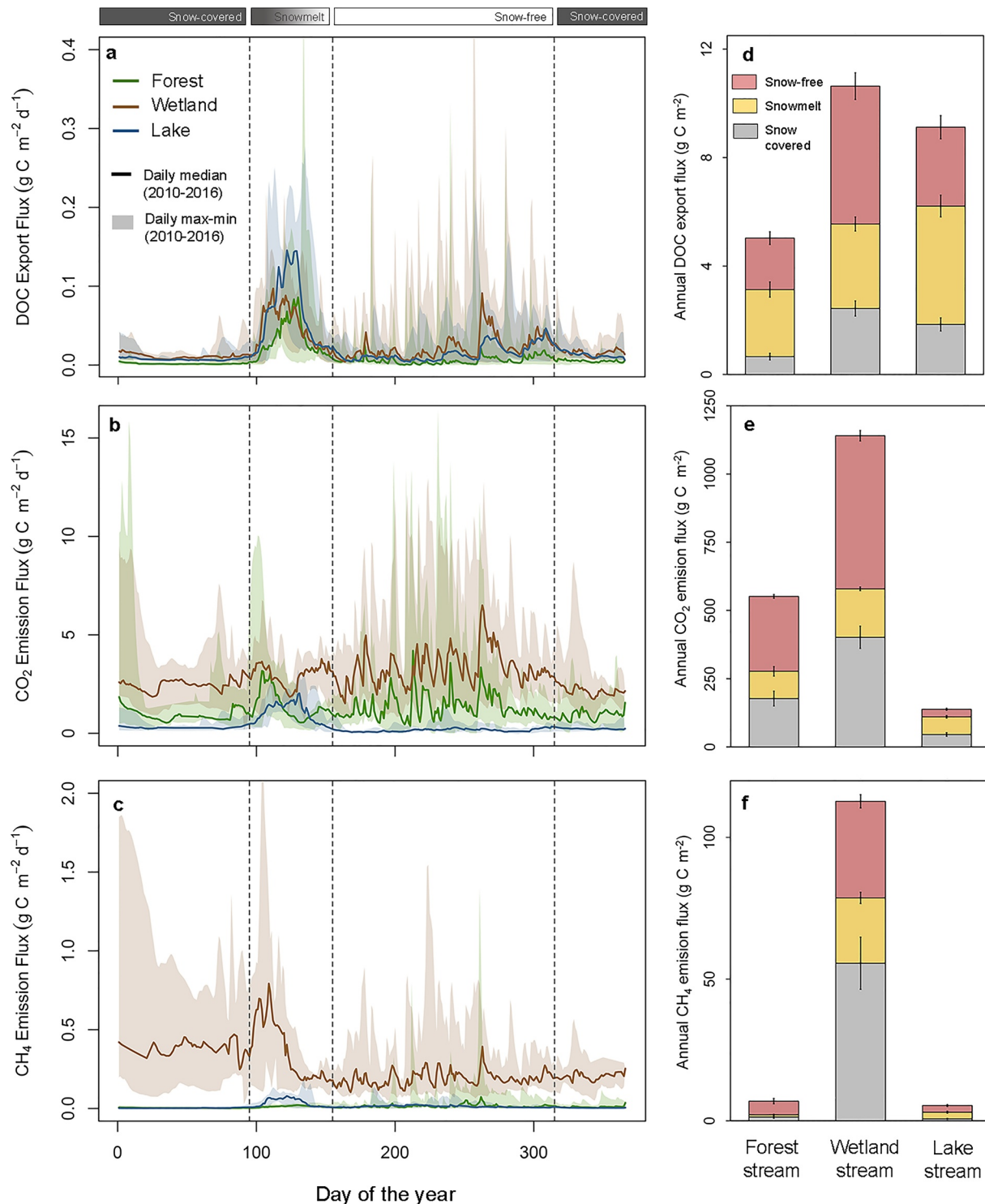
**Figure 4.** Relationships between the mass concentration ratio of dissolved organic carbon (DOC) to carbon dioxide ( $\text{CO}_2$ ) (upper panels,  $\text{DOC}:\text{CO}_2$ ) and specific discharge ( $\text{mm d}^{-1}$ ) at the (a) forest, (b) wetland and (c) lake streams. Relationships between the mass ratio of methane ( $\text{CH}_4$ ) to  $\text{CO}_2$  (lower panels,  $\text{CH}_4:\text{CO}_2$ ) and specific discharge at the (d) forest, (e) wetland and (f) lake streams. Colors of the circles and density plots represent specific seasonal events: gray for low discharge conditions, yellow for high discharge during snowmelt, and red for high discharge during the snow-free period. Vertical dashed lines represent the median discharge ( $Q_{50}$ ) of the different streams for all the study period that was used to split between high and low Q analyses. Note that axis ranges are adjusted to the results for the type of headwater stream and ratio.

resulting in a marked bimodal distribution of this ratio at high discharges. Specifically, flood events during snow-free periods enriched the carbon pool with DOC, while snowmelt flood events resulted in the opposite pattern (Figure 4c).

The ratio of  $\text{CH}_4$  to  $\text{CO}_2$  decreased across the low discharge range in the forest stream, but remained relatively stable in response to high discharges, regardless of season (Figure 4d). For the wetland outlet stream the opposite pattern was observed, with unchanged  $\text{CH}_4:\text{CO}_2$  across the low range of discharge, but the ratio differed for high discharge during the snowmelt and snow-free seasons. Specifically, flood events during snow-free periods were characterized by a pool of carbon with significantly lower  $\text{CH}_4:\text{CO}_2$  than flood events occurring during snowmelt periods (Figure 4e). Finally, the  $\text{CH}_4:\text{CO}_2$  in the lake outlet stream did not change in response to discharge (Figure 4f).

### 3.4. Annual, Seasonal and Episodic Apportionment of Stream Carbon Emissions and Export

The total annual DOC export and its seasonal apportionment varied across the three catchments (Figure 5a). On an annual basis, DOC exported from the wetland (median  $\pm$  sd =  $10.1 \pm 1.7 \text{ g C m}^{-2} \text{ y}^{-1}$ ) and the lake outlet (median  $\pm$  sd =  $8.7 \pm 2.0 \text{ g C m}^{-2} \text{ y}^{-1}$ ) was two times greater than that exported by the forest stream ( $4.6 \pm 1.2 \text{ g C m}^{-2} \text{ y}^{-1}$ ). Seasonally, DOC export fluxes during the snow-melt period contributed to about half of the annual exports in the forest and lake outlet stream (median  $\pm$  sd =  $2.8 \pm 0.7 \text{ g C m}^{-2}$ , 49% and  $4.4 \pm 1.1 \text{ g C m}^{-2}$ , 48%; Figure 5d). In contrast, the snow-free period DOC export contributed to 48% ( $4.7 \pm 1.3 \text{ g C m}^{-2}$ ) of the total export flux from the wetland outlet, whereas the snow-free period DOC exports only contributed 27% ( $1.9 \pm 0.6 \text{ g C m}^{-2}$ ) and 32% ( $2.6 \pm 1.1 \text{ g C m}^{-2}$ ) of the total annual DOC export flux from the forest and lake outlet stream, respectively (Figure 5d).



**Figure 5.** Intra-annual variability of the (a) downstream dissolved organic carbon (DOC) export flux ( $\text{g C m}^{-2} \text{d}^{-1}$ ), (b) carbon dioxide ( $\text{CO}_2$ ) emission flux ( $\text{g C m}^{-2} \text{d}^{-1}$ ), (c) methane ( $\text{CH}_4$ ) emission flux ( $\text{g C m}^{-2} \text{d}^{-1}$ ) in the three studied headwater streams: forest stream (green), wetland outlet stream (brown) and lake outlet stream (blue). Solid color lines represent the daily medians for the study period (2010–2016). Color shading includes the range of daily inter-annual minimums and maximums for the study period. Horizontal bars at the top of panel (a) and vertical dashed bars within time series plots delineate the most contrasting and characteristic hydrologic periods in the catchment (see the Method section and Figure S1 for a more detailed information). Annual and seasonal median (d) DOC export flux ( $\text{g C m}^{-2}$ ), (e)  $\text{CO}_2$  emission flux ( $\text{g C m}^{-2}$ ) and, (f)  $\text{CH}_4$  emission flux ( $\text{g C m}^{-2}$ ) for the three studied headwater streams. Error bars represent the inter-annual variability for the study period (2010–2016).

The total annual CO<sub>2</sub> and CH<sub>4</sub> emission fluxes and their seasonal apportionment also varied substantially for the three catchments (Figures 5b and 5c). In absolute terms, the CO<sub>2</sub> emitted annually from the wetland outlet stream (median ± sd = 1,087 ± 104 g C m<sup>-2</sup> y<sup>-1</sup>) was 1.9 times and 8.4 times higher to that in the forest (551 ± 97 g C m<sup>-2</sup> y<sup>-1</sup>) and lake outlet stream (128.8 ± 23 g C m<sup>-2</sup> y<sup>-1</sup>), respectively. Similar to CO<sub>2</sub> emissions, the total annual CH<sub>4</sub> emissions from the wetland outlet stream (114 ± 26 g C m<sup>-2</sup> y<sup>-1</sup>) were 13.5 times and 13.1 times higher than those from the forest (8 ± 4 g C m<sup>-2</sup> y<sup>-1</sup>) and lake outlet stream (8 ± 3 g C m<sup>-2</sup> y<sup>-1</sup>), respectively. Seasonally, the CO<sub>2</sub> and CH<sub>4</sub> emission fluxes during the snow-free period dominated annual emissions in the forest stream (median ± sd = 315 ± 22 g C m<sup>-2</sup>, 49% and 7 ± 3 g C m<sup>-2</sup>, 71%; Figures 5e and 5f). Similarly, the snow-free period CO<sub>2</sub> emissions contributed to 49% (584 ± 38 g C m<sup>-2</sup>) of the total annual efflux from the wetland outlet, whereas snow-free period CH<sub>4</sub> emission only contributed 30% (33 ± 5 g C m<sup>-2</sup>) of the total annual CH<sub>4</sub> emissions from the same stream (Figure 5). In the wetland stream, up to 51% (60 ± 23 g C m<sup>-2</sup>) of the total annual CH<sub>4</sub> flux was emitted during the snow-covered winter period (Figure 5). Finally, in the lake outlet stream, the temporal contribution of CO<sub>2</sub> to the total annual CO<sub>2</sub> emission flux was equally distributed across seasons (Figure 5). This was not the case for total annual CH<sub>4</sub> emission flux from the lake outlet, where summer CH<sub>4</sub> emissions contributed up to 51% (4 ± 2 g C m<sup>-2</sup>) of the total annual CH<sub>4</sub> emission.

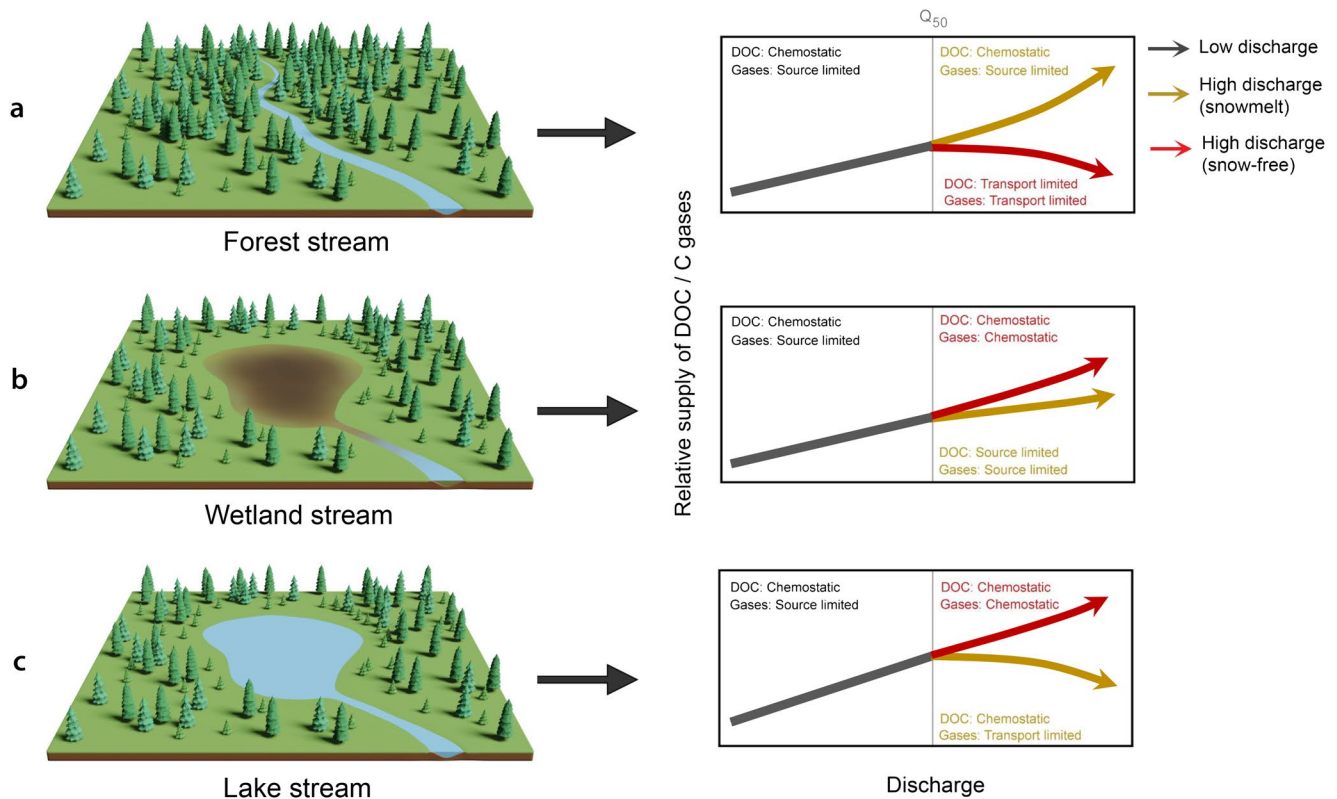
## 4. Discussion

The mosaic of patches within landscapes creates a diversity of land-water interfaces that regulate the lateral transfer of carbon from soils to river networks. For boreal regions, the heterogeneity of interfaces is determined by the areal extent and spatial arrangement of forests, wetlands, and lakes in the landscape. Our results show that unique C-Q relationships for DOC, CO<sub>2</sub>, and CH<sub>4</sub> across headwater streams with different land cover features likely emerged from differences in physical, chemical, and hydrological properties among these interfaces. Further, within streams, differences in C-Q relationships across seasons and among carbon forms underpin shifts in the relative contribution of dissolved versus gaseous carbon inputs to aquatic ecosystems (Figure 6). While our relatively coarse sampling frequency precludes detailed assessment of individual flow event responses (e.g., Knapp et al., 2020), seasonal shifts in the composition of carbon inputs highlight time windows where the fate of terrestrial carbon is more strongly linked to local gas evasion versus longitudinal transport through the aquatic network.

### 4.1. Variation in Carbon Supply Among Dominant Interfaces

In forested landscapes, the riparian soils adjacent to small streams represent the most spatially extensive land-water interface. For boreal regions, these soils tend to be highly organic and thus serve as major carbon sources to streams (Ledesma et al., 2018), with the timing and magnitude of supply driven by the vertical arrangement of solutes and gases (i.e., supply) in relation to the fluctuating water table (i.e., transport; Bishop et al., 2004). This juxtaposition between supply and transport creates unique C-Q relationships among carbon forms (Figures 3 and S3), which together determine the overall composition of the carbon pool that is supplied to streams. For example, chemostasis for DOC in the forest stream indicates a rather uniform vertical distribution of supply across the riparian soil profile (Godsey et al., 2009). Compared to DOC, CO<sub>2</sub> and CH<sub>4</sub> tend to have different vertical patterns in riparian forest soils (Campeau et al., 2018) and thus generate distinct hydrological responses. CO<sub>2</sub> concentrations typically increase gradually with soil depth (Leith et al., 2015; Öquist et al., 2009), which gives rise to moderate dilution (i.e., supply limitation) when high flows mobilize water from more surficial soil strata. By comparison, CH<sub>4</sub> requires more specific redox conditions to accumulate, and is thus restricted to even greater soil depths, and is even more strongly diluted when considering the entire range of flows. In addition to these overall trends, resolving Q-C relationships by season and flow also revealed non-stationarities for all carbon forms, which either shifted toward chemostasis (for CH<sub>4</sub>) or even transport limitation (for CO<sub>2</sub> and DOC) between the snowmelt and snow free seasons (Figures 3a and S3). These shifts are consistent with carbon production and accumulation in seasonally disconnected surface soils during summer (e.g., Winterdahl et al., 2011) but also highlight the biogeochemical distinctiveness of rain-driven episodes, which have garnered less attention than snowmelt in high latitude landscapes. More broadly, a recent assessment at the same forested stream monitoring site shows that long-term changes in the concentration and vertical distribution of DOC in riparian soil





**Figure 6.** Conceptual diagram illustrating the seasonal shifts in the relative importance of downstream flux versus emission losses across headwaters with different land-water interfaces in the boreal landscape ((a), forest; (b), wetland; and (c), lakes). Patterns in the relative supply of dissolved organic carbon (DOC) and carbon gases emerge from superimposing the seasonal changes in the individual concentration-discharge (C-Q) relationships for DOC and C gas concentrations. In the right panels, the colored text describes the individual C-Q relationships (based on Figure 3), while the lines represent the hypothetical changes in the balance of forms during low flow (gray) and for high flow episodes during snow melt (yellow) and snow free (red) seasons.

solution has reduced the occurrence of transport limitation in favor of chemostasis over the last 20 years (Fork et al., 2020). Finally, a major consequence of distinct C-Q relationships among carbon forms is an emergent pattern in the overall composition of supply with changing discharge (Figure 4a). Specifically, the carbon pool in the forest stream shifted from a nearly equal representation of inorganic and organic forms at low flows (e.g., the DOC:CO<sub>2</sub> = 2–5) to a pool that is, overwhelming dominated by DOC at high discharge (DOC:CO<sub>2</sub> > 10 (Figure 4a).

Headwater wetlands (mires) are abundant in boreal landscapes (Nilsson et al., 2001) and act as a source for all carbon forms to the streams they feed (Leach et al., 2017). Indeed, compared to riparian soils, wetlands support higher concentrations of carbon that can be mobilized to streams, including CO<sub>2</sub> and CH<sub>4</sub> that accumulate with depth in anoxic peat layers (Campeau et al., 2018). However, wetlands tend to be less uniformly drained than riparian soils, with surficial and deep preferential flowpaths (Holden et al., 2012; Peralta-Tapia et al., 2015) that regulate chemical responses during high flow events in outlet streams (e.g., Sponseller et al., 2018). During snowmelt, rapid flushing along superficial preferential flowpaths can dilute all carbon forms in the wetland outlet (see Laudon et al., 2011). However, hydrological events during other times of the year generate different chemical responses: chemostatic patterns for DOC and CO<sub>2</sub> and transport limitation for CH<sub>4</sub> (Figures 3b and S3). These observations indicate that rates of carbon production and accumulation in hydrologically active peat layers during summer and autumn are sufficiently high to at least keep pace with hydrological throughput during non-snowmelt high flows. Despite seasonal differences, the overall variability in C-Q responses in the wetland outlet was dampened relative to the forest stream (Figure S3). Similarly, DOC:CO<sub>2</sub> in the wetland outlet (Figure 4b) was considerably lower than for the forest stream (Figure 4a), with values commonly between five and 10. The reduced variability in C-Q metrics and the ratio of forms suggests that the distribution and activation of preferential flowpaths draining wetlands

influences the mobilization of dissolved and gaseous carbon forms in similar ways. While our results reflect the dynamics of a single catchment, the abundance of wetlands differs both locally and regionally across the boreal biome (Gorham, 1991), which we expect to generate even larger-scale heterogeneity in landscape arrangements and carbon sources beyond the Krycklan watershed.

Small, headwater lakes are abundant in boreal landscapes and, compared to forested riparian zones and wetlands, represent a unique interface between terrestrial carbon sources and downstream river networks (Leach & Laudon, 2019). These lakes receive particulate, dissolved, and gaseous carbon from soils and through physical and biological processes can transform, store, and emit such inputs before delivery to outlet streams (Vachon et al., 2021). The potential for within-lake processing to control the magnitude and forms of carbon downstream is related to external inputs and lake water residence time (e.g., Evans et al., 2017), and our results suggest that the presence of lakes in stream networks can dampen downstream C-Q relationships. DOC and CO<sub>2</sub> in the lake outlet stream were essentially chemostatic across all flow conditions, and only for CH<sub>4</sub> did we observe a more dynamic shift between source and transport limitation (Figures 3c and S3). In addition, our results indicate that lake processes, including the timing of stratification and the accumulation of gases in the hypolimnion (e.g., Denfeld et al., 2016; Ducharme-Riel et al., 2015), regulated the seasonality and composition of carbon supplied downstream. This effect was again clearest for CH<sub>4</sub>, which increased during each snowmelt season, consistent with the release of gases stored beneath the ice during the long winter and/or mobilized from adjacent wetlands during thaw (Denfeld et al., 2018; Jammet et al., 2015). The potential influence of lake physical processes on downstream reaches was also reflected in the seasonal shift in the DOC and CO<sub>2</sub> pools in the outlet (Figure 4c). Specifically, the spring flood favored the mobilization of carbon gases relative to DOC (DOC:CO<sub>2</sub> = 6–10), likely because of the release of CO<sub>2</sub> and CH<sub>4</sub> accumulated at depth during winter and the concomitant dilution of surficial DOC from the wider landscape. By comparison, floods of similar magnitude during summer appeared to be more important for DOC transport, with DOC:CO<sub>2</sub> ratios similar to those observed in the forest stream (DOC:CO<sub>2</sub> > 15). Thus, the role of headwater lakes as ecosystems that mediate carbon transfer from soils to streams varies strongly throughout the year and appears linked to the timing of flow events relative to lake stratification processes that promote internal gas storage.

Variations in stream CH<sub>4</sub>:CO<sub>2</sub> highlight biogeochemical differences among ecosystem interfaces, particularly in their capacity to support methanogenesis (Stanley et al., 2016). While several studies have suggested that CH<sub>4</sub>:CO<sub>2</sub> is relatively constrained in northern streams (e.g., Campeau & Del Giorgio, 2014; Wallin et al., 2014), we observed considerable variability among sites and dates, from ratios less than 0.001 to nearly 0.12, which is high relative to estimates made in surface headwaters elsewhere (median of 0.006; Stanley et al., 2016). Not surprisingly, this ratio was greatest in the stream draining the wetland, ecosystems well known to support methanogenesis (Segers, 1998). Yet, we also observed clear shifts in CH<sub>4</sub>:CO<sub>2</sub> across seasons. For example, high flows in the wetland outlet during the snow-free season led to increases in CH<sub>4</sub>:CO<sub>2</sub>, likely reflecting hydrologic connections to low-redox flowpaths within the wetland and/or comparatively upregulated rates of CH<sub>4</sub> production in peat soils during warmer summer periods (e.g., Gómez-Gener et al., 2020; Hopple et al., 2020). By contrast, in the forest stream, increases from low to median flows exponentially depressed CH<sub>4</sub>:CO<sub>2</sub>, likely because CH<sub>4</sub> supply is greatest from deeper, perpetually anoxic riparian soils (Campeau et al., 2018), and this signal is lost as the water table rises and more water flows through surficial, oxidized strata. In this case, elevated flows may also affect the magnitude and distinct pathways of methanogenesis (hydrogenotrophic vs. acetolactic methanogenesis; Stanley et al., 2016) or enhance methane oxidation in stream and near stream sediments by increasing oxygen resupply (Trimmer et al., 2009, 2015). Finally, the CH<sub>4</sub>:CO<sub>2</sub> in the lake outlet was the lowest of all streams and had no clear temporal signal. While we know that CH<sub>4</sub> can be produced, stored and emitted in boreal lakes (Juutinen et al., 2009), recent studies indicate that a large fraction of CH<sub>4</sub> may be oxidized within the lake itself (Denfeld et al., 2016) and during initial transport to outlet streams (Lupon et al., 2019). The widespread flow-induced variability in CH<sub>4</sub>:CO<sub>2</sub> highlights a critical need to better understand how hydrologic fluxes across distinct soil-stream boundaries modulate changes in the supply and fate of carbon to streams.

#### 4.2. Implications of C-Q Relationships for Landscape Carbon Cycling and Fluxes

The C-Q trends for CO<sub>2</sub> and CH<sub>4</sub> reflected distinct seasonal patterns in the magnitude of gas evasion across streams. In general, events and seasons that support chemostatic or transport-limited CH<sub>4</sub> and CO<sub>2</sub> dynamics are moments of relatively high gas emissions, because this is when stream concentrations and air-water gas exchange are simultaneously elevated. Thus, hydrological events during the snow-free period supported pulses of CO<sub>2</sub> evasion from the forest and wetland outlet streams that were not observed during the spring flood, when gases were diluted by meltwaters. A similar dynamic was observed for CH<sub>4</sub> in the wetland outlet, where hydrological events during the snow-free season generated positive C-Q relationships and thus pulses of evasion. Because of the seasonal changes in C-Q relationships, gas losses during the summer and autumn accounted for a large fraction of the annual efflux from the forest and wetland outlet streams (e.g., >50% for CO<sub>2</sub>). In fact, only CH<sub>4</sub> evasion from the wetland outlet was high throughout the winter and at the onset of spring flood, despite low discharge during this period. Deep groundwater sources likely support streamflow in the wetland-dominated catchment throughout winter, when reduced solutes accumulate in preferential flowpaths (Sponseller et al., 2018). While this merits further study, our results suggest that deeper flowpaths also supply the stream with large amounts of CH<sub>4</sub> and that gases stored in preferential flowpaths are rapidly mobilized at the onset of snowmelt. Overall, recognizing the significance of seasonally shifting C-Q dynamics for CH<sub>4</sub> and CO<sub>2</sub> could help predict the consequences of future hydrologic change for stream carbon emissions and the carbon balance of landscape mosaics. In this context, the combination of C-Q patterns and evasion fluxes suggest that future changes in summer and autumn flood regimes are likely to be far more important to carbon emissions from streams than changes to the spring snowmelt.

Finally, seasonal changes in C-Q relationships for gases, when superimposed with patterns of DOC export, reveal likely shifts in the relative importance of downstream flux versus emission losses across headwater catchments (Figure 6). For example, even though the contribution of stream C losses to the annual net landscape carbon balance in the Krycklan is highest during the spring flood (8%; compared to other three seasons (2.4%–4.8%)) (Chi et al., 2020), these events support comparatively low rates of gas evasion and, are instead dominated by downstream DOC flux. Snow melt floods thus maximize upstream-downstream “carbon connectivity” via DOC transport, as represented by other conceptual frameworks (e.g., Raymond et al., 2016). However, because carbon gases have different C-Q relationships during the snow-free season (e.g., chemostasis and/or transport limitation), hydrological events during snow-free periods induce considerably higher emission rates, indicating that a larger fraction of the total carbon pool is evaded locally rather than transported downstream. Our results further suggest that seasonal changes in the strength of longitudinal versus vertical carbon fates are more pronounced for the forest and wetland catchments, and are potentially dampened by headwater lakes. Regardless, such shifts in the contribution of different carbon forms supplied during episodes acts to either expand or contract the spatial scale at which the overall carbon pool is cycled and transported in river networks.

### 5. Conclusions

Efforts to integrate the lateral supply of different carbon forms in transit from soils to streams remain rare (Tank et al., 2018). Here we show that the type of ecosystem interface connecting soils and streams in boreal landscapes play a unique role in regulating not only the composition of the carbon pool supplied to aquatic ecosystems, but also its downstream fate. Landscape mosaics generate a diversity of interfaces that differ in how they store and process carbon internally as well as how and when they are connected to aquatic networks. In this context, exploring variation in carbon fluxes across landscapes with a greater diversity of land-water interfaces is a critical next step for characterizing landscape-scale carbon dynamics. Further, lateral fluxes in other biomes may be more influenced by hydrological pulses that create pronounced, but intermittent connections with adjacent floodplains or dry channels (e.g., Allen et al., 2020; Campo et al., 2019). Similarly, for many catchments, anthropogenic structures and activities could exert primacy over the timing and character of lateral carbon fluxes (e.g., Barnes et al., 2018; Fork et al., 2018). Regardless of the interface type, our results show how the consideration of landscape heterogeneity is required to understand the fluxes and fate of lateral carbon inputs to stream networks. Future research in ecosystem interfaces across heterogeneous landscape mosaics is necessary for real-world characterizations and predictions of biogeochemical cycling in complex and dynamic linked ecosystems.

## Data Availability Statement

All data can be accessed via [www.slu.se/Krycklan](http://www.slu.se/Krycklan) or by request to authors.

### Acknowledgments

We thank Peder Blomkvist, Kim Lindgren, Abdulmajid Mahomoud, Johannes Tiwari and the rest of Krycklan sampling crew for helping to generate and maintain this database. We also thank Emily Stanley for assistance with the MethDB database. This research was funded by the Swedish Research Council (FORMAS), SITES (VR), the Wallenberg Foundation (Branch-Point), the Kempe Foundation, and SKB.

### References

- Aho, K. S., & Raymond, P. A. (2019). Differential response of greenhouse gas evasion to storms in forested and wetland streams. *Journal of Geophysical Research: Biogeosciences*, *124*(3), 649–662. <https://doi.org/10.1029/2018JG004750>
- Aitkenhead, J. A., & McDowell, W. H. (2000). Soil C:N ratio as a predictor of annual riverine DOC flux at local and global scales. *Global Biogeochemical Cycles*, *14*(1), 127–138. <https://doi.org/10.1029/1999GB900083>
- Allen, D. C., Datry, T., Boersma, K. S., Bogan, M. T., Boulton, A. J., Bruno, D., et al. (2020). River ecosystem conceptual models and non-perennial rivers: A critical review. *WIREs Water*, *7*(5). <https://doi.org/10.1002/wat2.1473>
- Barnes, R. T., Butman, D. E., Wilson, H. F., & Raymond, P. A. (2018). Riverine export of aged carbon driven by flow path depth and residence time. *Environmental Science & Technology*, *52*(3), 1028–1035. <https://doi.org/10.1021/acs.est.7b04717>
- Berggren, M., Klaus, M., Selvam, B. P., Ström, L., Laudon, H., Jansson, M., & Karlsson, J. (2018). Quality transformation of dissolved organic carbon during water transit through lakes: Contrasting controls by photochemical and biological processes. *Biogeosciences*, *15*(2), 457–470. <https://doi.org/10.5194/bg-15-457-2018>
- Bishop, K., Lee, Y. H., Pettersson, C., & Allard, B. (1995). Terrestrial sources of methylmercury in surface waters: The importance of the riparian zone on the Svartberget Catchment. *Water, Air, & Soil Pollution*, *80*(1–4), 435–444. <https://doi.org/10.1007/BF01189693>
- Bishop, K., Seibert, J., Köhler, S., & Laudon, H. (2004). Resolving the Double Paradox of rapidly mobilized old water highly variable responses in runoff chemistry. *Hydrological Processes*, *18*(1), 185–189. <https://doi.org/10.1002/hyp.5209>
- Bradshaw, C. J. A., & Warkentin, I. G. (2015). Global estimates of boreal forest carbon stocks and flux. *Global and Planetary Change*, *128*, 24–30. <https://doi.org/10.1016/j.gloplacha.2015.02.004>
- Campeau, A., Bishop, K., Nilsson, M. B., Klemetsson, L., Laudon, H., Leith, F. I., et al. (2018). Stable carbon isotopes reveal soil-stream DIC linkages in contrasting headwater catchments. *Journal of Geophysical Research: Biogeosciences*, *123*, 149–167. <https://doi.org/10.1002/2017JG004083>
- Campeau, A., & Del Giorgio, P. A. (2014). Patterns in CH<sub>4</sub> and CO<sub>2</sub> concentrations across boreal rivers: Major drivers and implications for fluvial greenhouse emissions under climate change scenarios. *Global Change Biology*, *20*(4), 1075–1088. <https://doi.org/10.1111/gcb.12479>
- Campo, R., Gómez, R., & Singer, G. (2019). Dry phase conditions prime wet-phase dissolved organic matter dynamics in intermittent rivers. *Limnology and Oceanography*, *64*(5), 1966–1979. <https://doi.org/10.1002/lno.11163>
- Casas-Ruiz, J. P., Catalán, N., Gómez-Gener, L., von Schiller, D., Obrador, B., Kothawala, D. N., et al. (2017). A tale of pipes and reactors: Controls on the in-stream dynamics of dissolved organic matter in rivers. *Limnology and Oceanography*, *62*, S85–S94. <https://doi.org/10.1002/lno.10471>
- Chi, J., Nilsson, M. B., Laudon, H., Lindroth, A., Wallerman, J., Fransson, J. E. S., et al. (2020). The net landscape carbon balance—Integrating terrestrial and aquatic carbon fluxes in a managed boreal forest landscape in Sweden. *Global Change Biology*, *26*(4), 2353–2367. <https://doi.org/10.1111/gcb.14983>
- Crawford, J. T., Loken, L. C., West, W. E., Crary, B., Spawn, S. A., Gubbins, N., et al. (2017). Spatial heterogeneity of within-stream methane concentrations. *Journal of Geophysical Research: Biogeosciences*, *122*(5), 1036–1048. <https://doi.org/10.1002/2016JG003698>
- Crawford, J. T., Lottig, N. R., Stanley, E. H., Walker, J. F., Hanson, P. C., Finlay, J. C., & Striegl, R. G. (2014). CO<sub>2</sub> and CH<sub>4</sub> emissions from streams in a lake-rich landscape: Patterns, controls and regional significance. *Global Biogeochemical Cycles*, *28*(3), 197–210. <https://doi.org/10.1002/2013GB004661>
- Creed, I. I. F., Mcknight, D. D. M., Pellerin, B. A., Green, M. B., Bergamaschi, B. A., Aiken, G. R., et al. (2015). The river as a chemostat: Fresh perspectives on dissolved organic matter flowing down the river continuum. *Canadian Journal of Fisheries and Aquatic Sciences*, *14*, 1–1285. <https://doi.org/10.1139/cjfas-2014-0400>
- Denfeld, B. A., Klaus, M., Laudon, H., Sponseller, R. A., & Karlsson, J. (2018). Carbon dioxide and methane dynamics in a small boreal lake during winter and spring melt events. *Journal of Geophysical Research: Biogeosciences*, *123*(8), 2527–2540. <https://doi.org/10.1029/2018JG004622>
- Denfeld, B. A., Lupon, A., Sponseller, R. A., Laudon, H., & Karlsson, J. (2020). Heterogeneous CO<sub>2</sub> and CH<sub>4</sub> patterns across space and time in a small boreal lake. *Inland Waters*, *10*(3), 348–359. <https://doi.org/10.1080/20442041.2020.17877653382>
- Denfeld, B. A., Ricão Canelhas, M., Weyhenmeyer, G. A., Bertilsson, S., Eiler, A., & Bastviken, D. (2016). Constraints on methane oxidation in ice-covered boreal lakes. *Journal of Geophysical Research: Biogeosciences*, *121*, 1924–1933. <https://doi.org/10.1002/2016jg003382>
- Dinsmore, K. J., Wallin, M. B., Johnson, M. S., Billett, M. F., Bishop, K., Pumpanen, J., & Ojala, A. (2013). Contrasting CO<sub>2</sub> concentration discharge dynamics in headwater streams: A multi-catchment comparison. *Journal of Geophysical Research: Biogeosciences*, *118*(2), 445–461. <https://doi.org/10.1002/jgrg.20047>
- Ducharme-Riel, V., Vachon, D., del Giorgio, P. A., & Prairie, Y. T. (2015). The relative contribution of winter under-ice and summer hypolimnetic CO<sub>2</sub> accumulation to the annual CO<sub>2</sub> emissions from northern lakes. *Ecosystems*, *18*(4), 547–559. <https://doi.org/10.1007/s10021-015-9846-0>
- Duvert, C., Butman, D. E., Marx, A., Ribolzi, O., & Hutley, L. B. (2018). CO<sub>2</sub> evasion along streams driven by groundwater inputs and geomorphic controls. *Nature Geoscience*, *11*(11), 813–818. <https://doi.org/10.1038/s41561-018-0245-y>
- Evans, C. D., Futter, M. N., Moldan, F., Valinia, S., Froggbrook, Z., & Kothawala, D. N. (2017). Variability in organic carbon reactivity across lake residence time and trophic gradients. *Nature Geoscience*, *10*(11), 832–835. <https://doi.org/10.1038/NGEO3051>
- Fork, M. L., Blaszczyk, J. R., Delesantro, J. M., & Heffernan, J. B. (2018). Engineered headwaters can act as sources of dissolved organic matter and nitrogen to urban stream networks: Engineered headwaters can act as sources of DOM and N. *Limnology and Oceanography Letters*, *3*(3), 215–224. <https://doi.org/10.1002/lo2.10066>
- Fork, M. L., Sponseller, R. A., & Laudon, H. (2020). Changing source-transport dynamics drive differential browning trends in a boreal stream network. *Water Resources Research*, *56*(2), e2019WR026336. <https://doi.org/10.1029/2019WR026336>
- Gelbrecht, J., Fait, M., Dittrich, M., & Steinberg, C. (1998). Use of GC and equilibrium calculations of CO<sub>2</sub> saturation index to indicate whether freshwater bodies in north-eastern Germany are net sources or sinks for atmospheric CO<sub>2</sub>. *Fresenius' Journal of Analytical Chemistry*, *361*(1), 47–53. <https://doi.org/10.1007/s002160050832>



- Godsey, S. E., Kirchner, J. W., & Clow, D. W. (2009). Concentration-discharge relationships reflect chemostatic characteristics of US catchments. *Hydrological Processes*, 23(13), 1844–1864. <https://doi.org/10.1002/hyp.7315>
- Gómez-Gener, L., Lupon, A., Laudon, H., & Sponseller, R. A. (2020). Drought alters the biogeochemistry of boreal stream networks. *Nature Communications*, 11(1), 1795. <https://doi.org/10.1038/s41467-020-15496-2>
- Gorham, E. (1991). Northern peatlands: Role in the carbon cycle and probable responses to climatic warming. *Ecological Applications*, 1(2), 182–195. <https://doi.org/10.2307/1941811>
- Holden, J., Smart, R. P., Dinsmore, K. J., Baird, A. J., Billett, M. F., & Chapman, P. J. (2012). Natural pipes in blanket peatlands: Major point sources for the release of carbon to the aquatic system. *Global Change Biology*, 18(12), 3568–3580. <https://doi.org/10.1111/gcb.12004>
- Hopple, A. M., Wilson, R. M., Koltun, M., Zalman, C. A., Chanton, J. P., Kostka, J., et al. (2020). Massive peatland carbon banks vulnerable to rising temperatures. *Nature Communications*, 11(1), 2373. <https://doi.org/10.1038/s41467-020-16311-8>
- Horgby, Å., Gómez-Gener, L., Escoffier, N., & Battin, T. J. (2019). Dynamics and potential drivers of CO<sub>2</sub> concentration and evasion across temporal scales in high-alpine streams. *Environmental Research Letters*, 14(12), 124082. <https://doi.org/10.1088/1748-9326/ab5cb8>
- Jammet, M., Crill, P., Dengel, S., & Friborg, T. (2015). Large methane emissions from a subarctic lake during spring thaw: Mechanisms and landscape significance. *Journal of Geophysical Research: Biogeosciences*, 120(11), 2289–2305. <https://doi.org/10.1002/2015JG003137>
- Juutinen, S., Rantakari, M., Kortelainen, P., Huttunen, J. T., Larmola, T., Alm, J., et al. (2009). Methane dynamics in different boreal lake types. *Biogeosciences*, 6(2), 209–223. <https://doi.org/10.5194/bg-6-209-2009>
- Kaplan, L. A., Wiegner, T. N., Newbold, J. D., Ostrom, P. H., & Gandhi, H. (2008). Untangling the complex issue of dissolved organic carbon uptake: A stable isotope approach. *Freshwater Biology*, 53(5), 855–864. <https://doi.org/10.1111/j.1365-2427.2007.01941.x>
- Karlsen, R. H., Grabs, T., Bishop, K., Buffam, I., Laudon, H., & Seibert, J. (2016). Landscape controls on spatiotemporal discharge variability in a boreal catchment: LANDSCAPE CONTROLS ON DISCHARGE VARIABILITY. *Water Resources Research*, 52(8), 6541–6556. <https://doi.org/10.1002/2016WR019186>
- Karlsson, J., Bergström, A.-K., Byström, P., Gudasz, C., Rodríguez, P., & Hein, C. (2015). Terrestrial organic matter input suppresses biomass production in lake ecosystems. *Ecology*, 96(11), 2870–2876. <https://doi.org/10.1890/15-0515.1>
- Knapp, J. L. A., von Freyberg, J., Studer, B., Kiewiet, L., & Kirchner, J. W. (2020). Concentration-discharge relationships vary among hydrological events, reflecting differences in event characteristics. *Hydrology and Earth System Sciences*, 24(5), 2561–2576. <https://doi.org/10.5194/hess-24-2561-2020>
- Laudon, H., Berggren, M., Agren, A., Buffam, I., Bishop, K., Grabs, T., et al. (2011). Patterns and dynamics of dissolved organic carbon (DOC) in boreal streams: The role of processes, connectivity, and scaling. *Ecosystems*, 14(6), 880–893. <https://doi.org/10.1007/s10021-011-9452-8>
- Laudon, H., & Ottosson Löfvenius, M. (2016). Adding snow to the picture - Providing complementary winter precipitation data to the Krycklan Catchment Study database. *Hydrological Processes*, 30(13), 2413–2416. <https://doi.org/10.1002/hyp.10753>
- Laudon, H., Taberman, I., Ågren, A., Futter, M., Ottosson-Löfvenius, M., & Bishop, K. (2013). The Krycklan Catchment Study - A flagship infrastructure for hydrology, biogeochemistry, and climate research in the boreal landscape. *Water Resources Research*, 49(10), 7154–7158. <https://doi.org/10.1002/wrcr.20520>
- Leach, J. A., Larsson, A., Wallin, M. B., Nilsson, M. B., & Laudon, H. (2016). Twelve year interannual and seasonal variability of stream carbon export from a boreal peatland catchment. *Journal of Geophysical Research: Biogeosciences*, 121(7), 1851–1866. <https://doi.org/10.1002/2016JG003357>
- Leach, J. A., & Laudon, H. (2019). Headwater lakes and their influence on downstream discharge. *Limnology and Oceanography Letters*, 4, 105–112. <https://doi.org/10.1002/lol2.10110>
- Leach, J. A., Lidberg, W., Kuglerová, L., Peralta-Tapia, A., Ågren, A., & Laudon, H. (2017). Evaluating topography-based predictions of shallow lateral groundwater discharge zones for a boreal lake-stream system. *Water Resources Research*, 53(7), 5420–5437. <https://doi.org/10.1002/2016WR019804>
- Ledesma, J. L. J., Futter, M. N., Blackburn, M., Lidman, F., Grabs, T., Sponseller, R. A., et al. (2018). Towards an improved conceptualization of riparian zones in boreal forest headwaters. *Ecosystems*, 21(2), 297–315. <https://doi.org/10.1007/s10021-017-0149-5>
- Leith, F. I., Dinsmore, K. J., Wallin, M. B., Billett, M. F., Heal, K. V., Laudon, H., et al. (2015). Carbon dioxide transport across the hillslope-riparian-stream continuum in a boreal headwater catchment. *Biogeosciences*, 12(6), 1881–1892. <https://doi.org/10.5194/bg-12-1881-2015>
- Liu, S., & Raymond, P. A. (2018). Hydrologic controls on pCO<sub>2</sub> and CO<sub>2</sub> efflux in US streams and rivers. *Limnology and Oceanography Letters*, 3(6), 428–435. <https://doi.org/10.1002/lol2.10095>
- Lupon, A., Denfeld, B. A., Laudon, H., Leach, J., Karlsson, J., & Sponseller, R. A. (2019). Groundwater inflows control patterns and sources of greenhouse gas emissions from streams. *Limnology and Oceanography*, 1, 1545–1557. <https://doi.org/10.1002/lno.11134>
- Meybeck, M., & Moatar, F. (2012). Daily variability of river concentrations and fluxes: Indicators based on the segmentation of the rating curve. *Hydrological Processes*, 26(8), 1188–1207. <https://doi.org/10.1002/hyp.8211>
- Mineau, M. M., Wollheim, W. M., Buffam, I., Findlay, S. E. G., Hall, R. O., Hotchkiss, E. R., et al. (2016). Dissolved organic carbon uptake in streams: A review and assessment of reach-scale measurements. *Journal of Geophysical Research: Biogeosciences*, 121(8), 2019–2029. <https://doi.org/10.1002/2015JG003204>
- Moatar, F., Abbott, A., Minaudo, F., Curie, F., & Pinay, G. (2017). Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions. *Water Resources Research*, 53, 5375–5377. <https://doi.org/10.1002/2013WR014979.Reply>
- Musolff, A., Fleckenstein, J. H., Rao, P. S. C., & Jawitz, J. W. (2017). Emergent archetype patterns of coupled hydrologic and biogeochemical responses in catchments. *Geophysical Research Letters*, 44(9), 4143–4151. <https://doi.org/10.1002/2017GL072630>
- Musolff, A., Schmidt, C., Selle, B., & Fleckenstein, J. H. (2015). Catchment controls on solute export. *Advances in Water Resources*, 86, 133–146. <https://doi.org/10.1016/j.advwatres.2015.09.026>
- Nilsson, M., Mikkilä, C., Sundh, I., Granberg, G., Svensson, B. H., & Ranneby, B. (2001). Methane emission from Swedish mires: National and regional budgets and dependence on mire vegetation. *Journal of Geophysical Research*, 106, 20847–20860. <https://doi.org/10.1029/2001JD900119>
- Öquist, M. G., Wallin, M., Seibert, J., Bishop, K., & Laudon, H. (2009). Dissolved inorganic carbon export across the soil/stream interface and its fate in a boreal headwater stream. *Environmental Science and Technology*, 43(19), 7364–7369. <https://doi.org/10.1021/es900416h>
- Peralta-Tapia, A., Sponseller, R. A., Ågren, A., Tetzlaff, D., Soulsby, C., & Laudon, H. (2015). Scale-dependent groundwater contributions influence patterns of winter baseflow stream chemistry in boreal catchments. *Journal of Geophysical Research: Biogeosciences*, 120(5), 847–858. <https://doi.org/10.1002/2014JG002878>
- Raymond, P. A., Saiers, J. E., & Sobczak, W. V. (2016). Hydrological and biogeochemical controls on watershed dissolved organic matter transport: Pulse-shunt concept. *Ecology*, 97(1), 5–16. <https://doi.org/10.1890/14-1684.1>

- Raymond, P. A., Zappa, C. J., Butman, D., Bott, T. L., Potter, J., Mulholland, P., et al. (2012). Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers. *Limnology & Oceanography*, 2, 41–53. <https://doi.org/10.1215/21573689-1597669>
- R Core Team (2018). *R: A language and environment for statistical computing*. Retrieved from <https://www.R-project.org/>
- Segers, R. (1998). Methane production and methane consumption: A review of processes underlying wetland methane fluxes. *Biogeochemistry*, 41, 23–51. <https://doi.org/10.1007/s12237-011-9381-y>
- Sponseller, R. A., Blackburn, M., Nilsson, M. B., & Laudon, H. (2018). Headwater mires constitute a major source of nitrogen (N) to surface waters in the boreal landscape. *Ecosystems*, 21(1), 31–44. <https://doi.org/10.1007/s10021-017-0133-0>
- Stanley, E. H., Casson, N. J., Samuel, T. C., Christel, J. T., Loken, L. C., & Oliver, S. K. (2016). The ecology of methane in streams and rivers: Patterns, controls, and global significance. *Ecological Monographs*, 86, 146–171. <https://doi.org/10.1890/15-1027.1>
- Tank, J. L., Rosi-Marshall, E. J. E., Griffiths, N. A., Entekin, S. A., & Stephen, M. L. (2010). A review of allochthonous organic matter dynamics and metabolism in streams. *Journal of the North American Benthological Society*, 29(1), 118–146. <https://doi.org/10.1899/08-170.1>
- Tank, S. E., Fellman, J. B., Hood, E., & Kritzbeg, E. S. (2018). Beyond respiration: Controls on lateral carbon fluxes across the terrestrial-aquatic interface. *Limnology and Oceanography Letters*, 3, 76–88. <https://doi.org/10.1002/lol2.10065>
- Thompson, S. E., Basu, N. B., Lascunari, J., Aubeneau, A., & Rao, P. S. C. (2011). Relative dominance of hydrologic versus biogeochemical factors on solute export across impact gradients. *Water Resources Research*, 47(7), 1–20. <https://doi.org/10.1029/2010WR009605>
- Trimmer, M., Hildrew, A. G., Jackson, M. C., Pretty, J. L., & Grey, J. (2009). Evidence for the role of methane-derived carbon in a free-flowing, lowland river food web. *Limnology and Oceanography*, 54(5), 1541–1547. <https://doi.org/10.4319/lo.2009.54.5.1541>
- Trimmer, M., Shelley, F. C., Purdy, K. J., Maanoja, S. T., Chronopoulou, P.-M., & Grey, J. (2015). Riverbed methanotrophy sustained by high carbon conversion efficiency. *The ISME Journal*, 9(10), 2304–2314. <https://doi.org/10.1038/ismej.2015.98>
- Vachon, D., Sponseller, R. A., & Karlsson, J. (2021). Integrating carbon emission, accumulation and transport in inland waters to understand their role in the global carbon cycle. *Global Change Biology*, 27(4), 719–727. <https://doi.org/10.1111/gcb.15448>
- Wallin, M., Buffam, I., Öquist, M., Laudon, H., & Bishop, K. (2010). Temporal and spatial variability of dissolved inorganic carbon in a boreal stream network: Concentrations and downstream fluxes. *Journal of Geophysical Research*, 115, G02014. <https://doi.org/10.1029/2009JG001100>
- Wallin, M. B., Lofgren, S., Erlandsson, M., & Bishop, K. (2014). Representative regional sampling of carbon dioxide and methane concentrations in hemiboreal headwater streams reveal underestimates in less systematic approaches. *Global Biogeochemical Cycles*, 28(4), 465–479. <https://doi.org/10.1002/2013GB004715>
- Wallin, M. B., Öquist, M. G., Buffam, I., Billett, M. F., Nisell, J., & Bishop, K. H. (2011). Spatiotemporal variability of the gas transfer coefficient ( $K_{CO_2}$ ) in boreal streams: Implications for large scale estimates of  $CO_2$  evasion. *Global Biogeochemical Cycles*, 25(3), GB3025. <https://doi.org/10.1029/2010GB003975>
- Wanninkhof, R. (1992). Relationship between wind speed and gas exchange over the ocean. *Journal of Geophysical Research*, 97(92), 7373–7382. <https://doi.org/10.1029/92JC00188>
- Webb, J. R., Santos, I. R., Maher, D. T., & Finlay, K. (2019). The importance of aquatic carbon fluxes in net ecosystem carbon budgets: A catchment-scale review. *Ecosystems*, 22(3), 508–527. <https://doi.org/10.1007/s10021-018-0284-7>
- Weiss, R. (1974). Carbon dioxide in water and seawater: The solubility of a non-ideal gas. *Marine Chemistry*, 2(3), 203–215. [https://doi.org/10.1016/0304-4203\(74\)90015-2](https://doi.org/10.1016/0304-4203(74)90015-2)
- Winterdahl, M., Futter, M., Köhler, S., Laudon, H., Seibert, J., & Bishop, K. (2011). Riparian soil temperature modification of the relationship between flow and dissolved organic carbon concentration in a boreal stream. *Water Resources Research*, 47(8), W08532. <https://doi.org/10.1029/2010WR010235>
- Zarnetske, J. P., Bouda, M., Abbott, B. W., Saiers, J., & Raymond, P. A. (2018). Generality of hydrologic transport limitation of watershed organic carbon flux across ecoregions of the United States. *Geophysical Research Letters*, 45(21), 11702–11711. <https://doi.org/10.1029/2018GL080005>