



UMEÅ UNIVERSITY

# Biophysical controls on CO<sub>2</sub> evasion from Arctic inland waters

Gerard Rocher-Ros

Department of Ecology and Environmental Science  
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Dissertation for PhD

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*« Research has to be a game,  
because only when playing  
we are happy »*

Ramón Margalef

May 16<sup>th</sup> 1919 – May 24<sup>th</sup> 2004

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The thesis is based on the following chapters:

**Chapter I:** Large lakes dominate CO<sub>2</sub> evasion from lakes in an arctic catchment.

**Gerard Rocher-Ros**, Reiner Giesler, Erik Lundin, Shokoufeh Salimi, Anders Jonsson and Jan Karlsson (2017).

*Geophysical Research Letters*, 44(24), 12-254.

**Chapter II:** Landscape process domains drive patterns of CO<sub>2</sub> evasion from river networks.

**Gerard Rocher-Ros**, Ryan A. Sponseller, William Lidberg, Carl-Magnus Mörtz and Reiner Giesler (2019).

*Limnology and Oceanography: Letters*, 1-9, doi: 10.1002/lol2.10108

**Chapter III:** Stream metabolism controls diel patterns and evasion of CO<sub>2</sub> in Arctic streams.

**Gerard Rocher-Ros**, Ryan A. Sponseller, Ann-Kristin Bergström, Maria Myrstener and Reiner Giesler.

*Submitted.*

**Chapter IV:** Photosynthesis overrides photo-oxidation in CO<sub>2</sub> dynamics of Arctic permafrost streams.

**Gerard Rocher-Ros**, Tamara K. Harms, Ryan A. Sponseller, Maria Väisänen, Carl-Magnus Mörtz and Reiner Giesler.

*Manuscript.*

## **Author contributions**

**Chapter I:** GRR, JK and RG designed the study. GRR, AJ and EL contributed with field data. SS and GRR performed the GIS analysis. GRR performed the statistical analysis and upscaling. GRR wrote the paper with help from RG and JK. All authors commented the manuscript and helped with the interpretation of the results.

**Chapter II:** GRR, RG and RAS designed the study and wrote the paper. GRR carried out the field work, processed and analyzed the data and WL provided the wetness data. CMM and WL provided scientific insight to the analysis and interpretation of the data. All authors commented on the earlier versions of this manuscript.

**Chapter III:** GRR, RG, RAS and AKB designed the study. GRR performed the fieldwork with support of MM. GRR processed and analyzed the data and wrote the paper, with help of RG and RAS. AKB and MM provided scientific insight to the interpretation of the data. All authors commented on the manuscript.

**Chapter IV:** GRR, RG and TKH designed the study. GRR performed the fieldwork with support of RG and MV. TKH and CMM provided logistical support and analyzed the samples. GRR processed and analyzed the data with insights from RG and RAS. GRR wrote the paper with inputs of all authors.

## **Author abbreviations:**

**AKB:** Ann-Kristin Bergström, **RG:** Reiner Giesler, **TKH:** Tamara K. Harms, **AJ:** Anders Jonsson, **JK:** Jan Karlsson, **WL:** William Lidberg, **EL:** Erik Lundin, **MM:** Maria Myrstener, **CMM:** Carl-Magnus Mörth, **GRR:** Gerard Rocher-Ros, **SS:** Shokoufeh Salimi, **RAS:** Ryan A. Sponseller, **MV:** Maria Väisänen

# Abstract

CO<sub>2</sub> evasion to the atmosphere from inland waters is a major component of the global carbon (C) cycle. Yet spatial patterns of CO<sub>2</sub> evasion and the sources of C that fuel evasion remain poorly understood. In this thesis, I use detailed measurements of biological and physical drivers of CO<sub>2</sub> evasion to assess how C is transformed and evaded from inland waters in the Arctic (Northern Scandinavia and Alaska). I found that lake size was a master variable controlling lake CO<sub>2</sub> evasion in an Arctic catchment and that large lakes play a major role at the landscape scale. In stream networks, I found that catchment topography shapes patterns of CO<sub>2</sub> evasion by dictating unique domains with high lateral inputs of C, other domains where biological processes were dominant, and domains where physical forces promoted degassing to the atmosphere. Together, these topographically driven domains created a strong spatial heterogeneity that biases regional and global estimates of CO<sub>2</sub> evasion. Further, I found that photosynthetic activity in Arctic streams can produce a large change in CO<sub>2</sub> concentrations from night to day, and as a result CO<sub>2</sub> evasion is up to 45% higher during night than day. The magnitude of the diel change in CO<sub>2</sub> was also affected by the turbulence of the stream and photo-chemical production of CO<sub>2</sub>. Overall, this thesis offers important insights to better understand landscape patterns of CO<sub>2</sub> evasion from inland waters, and suggests that stream metabolic processes largely determine the fate of the C delivered from Arctic soils.

# Abbreviations

<b>C</b>	Carbon
<b>CO<sub>2</sub></b>	Carbon dioxide
<b>DOC</b>	Dissolved Organic Carbon
<b>ER</b>	Ecosystem Respiration
<b>GPP</b>	Gross Primary Production
<b><i>k</i></b>	Air-water gas transfer velocity
<b><i>k<sub>600</sub></i></b>	<i>k</i> standardized to a Schmidt number of 600
<b>NEP</b>	Net Ecosystem Production
<b>O<sub>2</sub></b>	Oxygen
<b>OC</b>	Organic Carbon
<b><i>p</i>CO<sub>2</sub></b>	Partial pressure of CO <sub>2</sub>
<b>Q</b>	Discharge



# Introduction

## Inland waters and the global carbon cycle

The global carbon (C) cycle is the thermostat of the planet. The concentration of CO<sub>2</sub> in the atmosphere is the key determinant of air temperature, and is thus a critical parameter that allows life on Earth (Schlesinger et al. 2011). CO<sub>2</sub> in the atmosphere is regulated through a series of mechanisms of the C cycle that can exchange CO<sub>2</sub> between the atmosphere, lithosphere, and oceans. Among all these major C compartments, inland waters are the pipes connecting them (Cole et al. 2007). More than conduits, inland waters are active components in the C cycle, processing, storing, and degassing large quantities of organic matter (Cole et al. 2007; Tranvik et al. 2009). Moreover, about 76% of the C received from land is evaded from inland waters to the atmosphere, therefore this water-atmosphere exchange represents an important flux in the global C cycle (Drake et al. 2017).

River networks play a disproportionate role in CO<sub>2</sub> evasion, emitting about 85% of the total CO<sub>2</sub> evaded from inland waters, while only covering 17% of the total inland water surface (Raymond et al. 2013). CO<sub>2</sub> evasion from streams and rivers is of the same order of magnitude as the net ocean CO<sub>2</sub> exchange with the atmosphere, while they cover 500 times less area than oceans. Hence, to improve our knowledge of the Earth's global C cycle we need a better understanding of the role of CO<sub>2</sub> evasion from inland waters to the atmosphere.

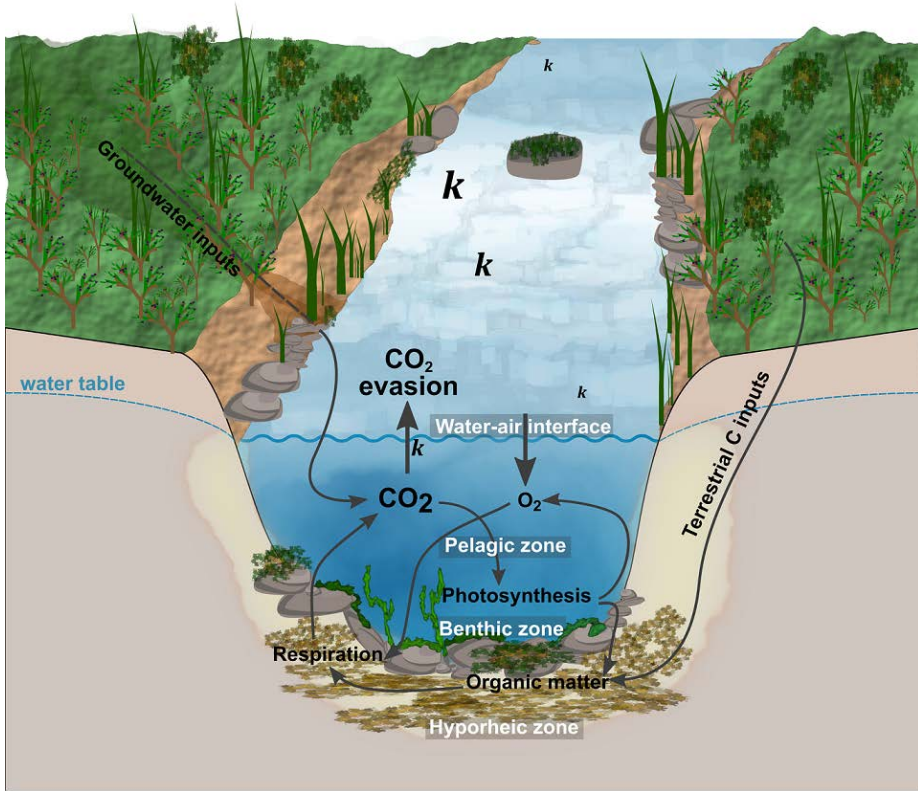
## The challenge of upscaling CO<sub>2</sub> evasion

Current estimates of CO<sub>2</sub> evasion from inland waters are largely unconstrained, with global estimates of riverine CO<sub>2</sub> evasion varying three-fold (0.7-1.8 Pg C yr<sup>-1</sup>; Raymond et al. 2013; Lauerwald et al. 2015), with a recent estimate of 3.9 Pg C yr<sup>-1</sup> for all inland waters (Drake et al. 2017). Thus, developing a mechanistical understanding of CO<sub>2</sub> evasion from inland waters is required to better constrain their role in the global C cycle. The goal of this thesis is to unravel the main drivers of CO<sub>2</sub> evasion from lakes (**Chapter I**) and streams (**Chapter II, III and IV**), and provide tools that can enhance our ability to understand landscape patterns in

CO<sub>2</sub> evasion. The evasion of CO<sub>2</sub> to the atmosphere depends on the concentration gradient of the gas and the diffusivity of the boundary layer. The evasion of CO<sub>2</sub> ( $E_{CO_2}$ ) can then be calculated using Fick's first law:

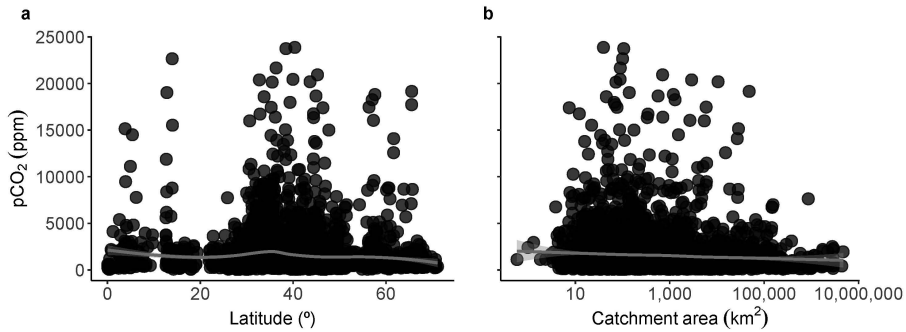
$$E_{CO_2} = k \times (pCO_{2water} - pCO_{2air}) \quad (1)$$

where  $k$  is the gas transfer velocity, which is a measure related to the turbulence of the water;  $pCO_{2water}$  and  $pCO_{2air}$  are the partial pressure of CO<sub>2</sub> in the water and in the air, respectively.



**Figure 1:** Different processes affecting CO<sub>2</sub> evasion in streams. CO<sub>2</sub> is supplied by respiration of organic matter or by groundwater inputs, while photosynthesis transforms CO<sub>2</sub> to organic matter. CO<sub>2</sub> evasion depends on the CO<sub>2</sub> concentration and the gas transfer velocity ( $k$ ), which is variable in space (font size indicates the magnitude of  $k$ ). Streams are usually a sink of O<sub>2</sub> and a source of CO<sub>2</sub> to the atmosphere. The different compartments of the stream ecosystem are shown in white.

Given that  $p\text{CO}_{2\text{air}}$  is stable (or used to be), the other two parameters of the equation can also be understood as the two key mechanisms of gas evasion: the physical forces that create turbulence in water-air interface ( $k$ ) and the balance of biological processes that produce and supply  $\text{CO}_2$  to the water (Figure 1). In this thesis, I use equation 1 across all chapters not only to calculate gas evasion, but also to understand the biological and physical controls on  $\text{CO}_2$  evasion.



**Figure 2:** Global trends of  $p\text{CO}_2$  across latitude (a) and catchment area (b) from the GLORICH database (Hartmann et al. 2014). The grey line is a LOESS fit of the data.

To accurately quantify and model  $\text{CO}_2$  evasion from inland waters we need a spatially explicit understanding of both factors ( $k$  and  $p\text{CO}_{2\text{water}}$ ). In the case of the  $k$  there are predictive tools that use topographic or meteorological information. For instance, in lakes the turbulence of the water is largely dependent on wind speed (Wanninkhof 1992) and lake size (Vachon et al. 2013), where larger lakes tend to be more wind exposed. For streams, the turbulence is mainly determined by the channel slope and water velocity which provide kinetic energy (Raymond et al. 2012). By comparison, landscape patterns of  $p\text{CO}_{2\text{w}}$  in inland waters are much harder to understand, particularly for streams and rivers. In a global database of water chemistry of rivers and streams (Hartmann et al. 2014),  $p\text{CO}_{2\text{water}}$  shows a large variability across a gradients in latitude and river size, two major drivers of ecosystem functioning (Figure 2). Patterns of terrestrial productivity should follow latitude, moving from tropical to polar regions, and thus C export to running waters should vary accordingly. River size is a common predictor of ecosystem functioning in rivers and connectivity to terrestrial ecosystems (Vanote et al. 1980). However, the large variability and weak

correlations between  $p\text{CO}_{2\text{water}}$  and these two important variables indicate that they are not useful predictors. This poses a great challenge to upscaling  $\text{CO}_2$  evasion from running waters. To move forward, we need better tools to predict landscape patterns of  $p\text{CO}_{2\text{water}}$  at meaningful spatial scales.

## Sources of $\text{CO}_2$ in running waters

A key step to improve estimates of  $\text{CO}_2$  evasion is to understand what regulates the supply of  $\text{CO}_2$  in aquatic systems. Stream networks are open systems and depend on external inputs of organic energy from terrestrial ecosystems (Fisher and Likens 1973). The supply of C from land should therefore determine  $\text{CO}_2$  evasion, but quantifying this lateral flux is elusive (Drake et al. 2017; Tank et al. 2018). C can enter aquatic systems in different forms: directly as  $\text{CO}_2$  and (methane)  $\text{CH}_4$  dissolved in water, as particulate or dissolved organic C (OC), or other inorganic dissolved forms ( $\text{HCO}_3^-$  or  $\text{CO}_3^{2-}$ ). Each of these C forms will be susceptible to unique processes in the aquatic systems at distinct spatial and temporal scales. For instance, direct supply of  $\text{CO}_2$  is related to groundwater inputs, which occur in discrete locations in the landscape, where gases rapidly evade to the atmosphere (Lupon et al. 2019). OC may also enter streams through groundwater or surface inputs (Likens and Borman 1974), but will persist in aquatic systems, be transported over potentially great distances, and be subject to biological processing and mineralisation (Hotchkiss et al. 2015). Understanding how, where and when OC becomes  $\text{CO}_2$  is therefore necessary to develop a mechanistic understanding of the riverine C cycle.

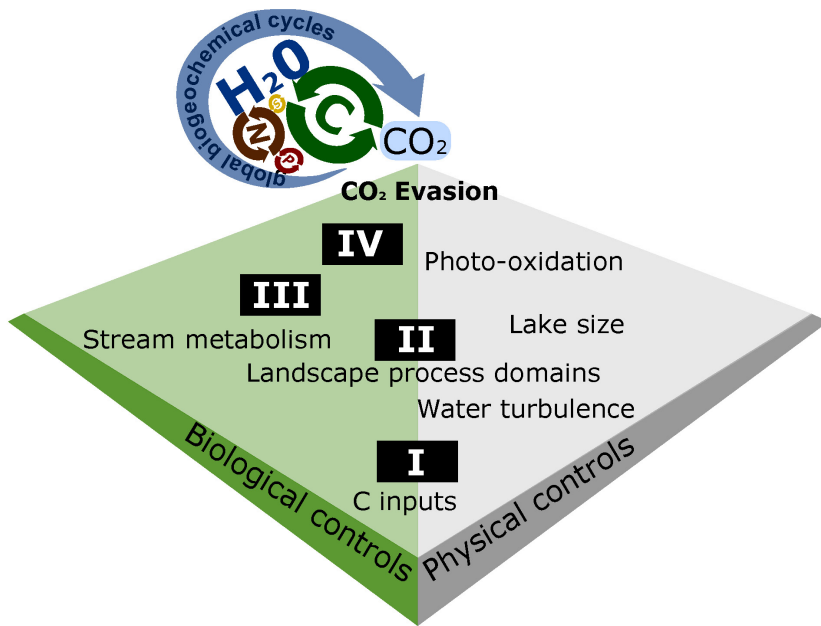
Biological processes can be important for the transformation of OC in streams (Rasilo et al. 2016), and have a dual effect on  $\text{CO}_2$  concentrations (Figure 1). On one hand gross primary production (GPP) will take up  $\text{CO}_2$ , while on the other hand ecosystem respiration (ER) will mineralise organic matter to  $\text{CO}_2$  (Odum 1956). The balance between both processes is the net ecosystem production (NEP), and, together with the external  $\text{CO}_2$  inputs, will determine whether the stream ecosystem is a source or sink of  $\text{CO}_2$ . Given the strong dependence on external inputs from land (Fisher and Likens 1973), stream ecosystems generally have  $\text{ER} > \text{GPP}$  (Hoellein et al. 2013) and therefore are net sources of  $\text{CO}_2$  to the

atmosphere. Despite the major importance of ER, GPP can still strongly affect CO<sub>2</sub> concentrations particularly at short temporal scales (from night to day). The contribution of stream metabolism to the C cycle is thought to be relevant in small streams (Rasilo et al. 2016; Demars 2018; Lupon et al. 2019). However, studies of coupled measurements of metabolism and CO<sub>2</sub> dynamics are generally lacking (Hotchkiss et al. 2015), and debate over the role of stream processes in the C cycle remains.

## **Aims**

The overarching aim of the thesis is to investigate the biological and physical controls on CO<sub>2</sub> evasion from inland waters (Figure 3). More specifically, I studied:

- **Chapter I:** The role of lake size on CO<sub>2</sub> evasion. Particularly, how the interaction of size-dependent physical ( $k$ ) and biogeochemical properties (terrestrial inputs) shape landscape patterns of CO<sub>2</sub> evasion from lakes.
- **Chapter II:** The effect of catchment topography in CO<sub>2</sub> evasion from streams. In this study, I explored how network-scale CO<sub>2</sub> evasion is affected by local geomorphic conditions and how we can use this information for upscaling.
- **Chapter III:** The control of stream metabolism on CO<sub>2</sub> evasion. Here I study to what extent ER sustains CO<sub>2</sub> evasion in streams, and how GPP and  $k$  affect diel patterns in CO<sub>2</sub> concentrations.
- **Chapter IV:** The interaction between photosynthesis and photo-oxidation shaping diel patterns in CO<sub>2</sub> concentrations in Alaska. Here, I studied the role of photo-oxidation compared to biotic processes in DOC-rich Arctic streams.



**Figure 3:** Conceptual diagram of different biological and physical controls on CO<sub>2</sub> evasion considered in this study. The black boxes represent each chapter of the thesis.

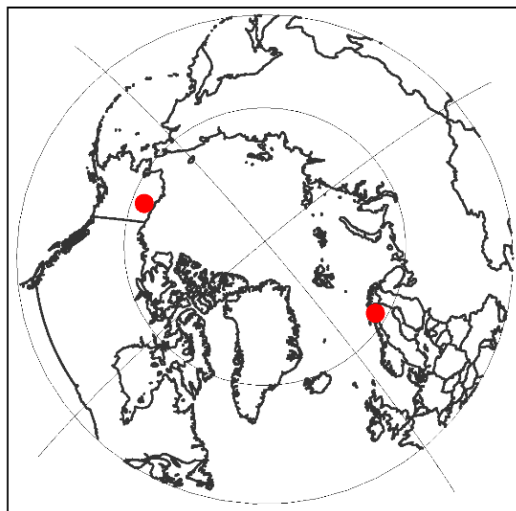
# Locations and Methods

## The Arctic

The research presented in this thesis was carried out in the Arctic region of Sweden (Chapters I, II and III) and Alaska (Chapter IV). The Arctic is characterized by long and cold winters, lasting more than 6 months and a similarly long snow cover. The snowmelt in spring typically occurs in May-June and results in a spring flood that is characteristic of high-latitude catchments.

Following snow melt, the growing season lasts for *circa* three months (from June to August), which is the period when most of the primary production occurs, at least in the terrestrial ecosystems. The landscape is often divided by the treeline: below which a sparse forest covers the land, and above which we find tundra vegetation, where the growth of trees is hindered by the harsh climatic conditions.

The climate in the Arctic is rapidly changing: temperature is rising two times faster than the rest of the globe, and precipitation is expected to increase more than 20% by the end of the century (ACIA 2004). These rapid changes in climate are having dramatic effects on Arctic ecosystems, by altering the physical and chemical template of the landscape. For instance, river discharge into the Arctic is increasing (Peterson et al. 2002) and the length of the lake ice cover is being reduced (Callaghan et al. 2010; Surdu et al. 2014). These changes are occurring in a landscape characterized by C rich permafrost soils, a C pool that is twice as large



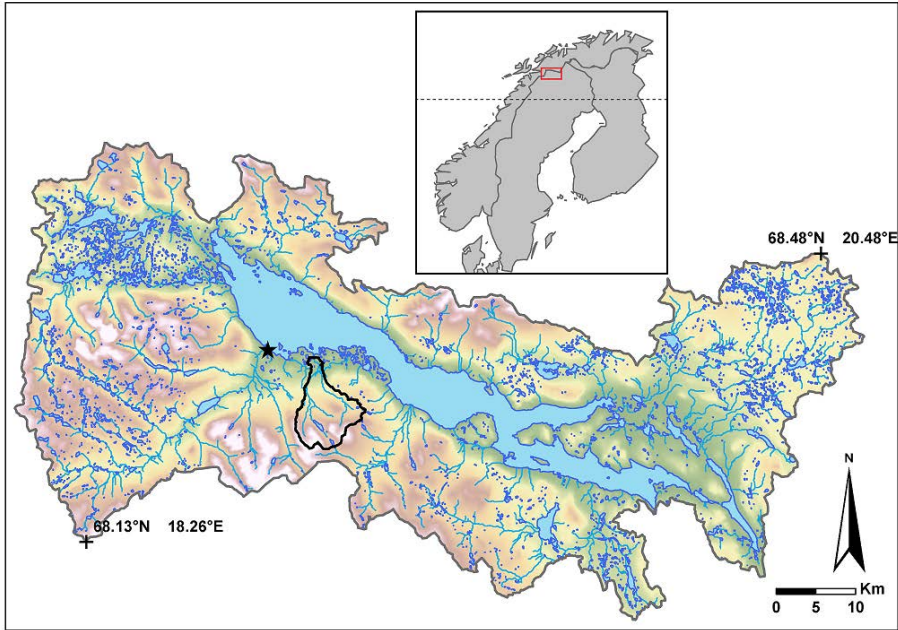
**Figure 4:** The Arctic, with the two locations where fieldwork for this thesis has been done (red dots). The inner circle denotes the Arctic circle.

as the atmospheric C content. The C stored in the permafrost is vulnerable to thaw since it can be mobilized by mineralization and evaded to the atmosphere (Schuur et al. 2015). Thus, the Arctic is not just being more affected by climate change, but also is an important feedback that can enhance global warming by releasing more C to the atmosphere previously stored in the soils.

### ***Torneträsk catchment***

The Torneträsk catchment covers large area (3290 km<sup>2</sup>) in northern Sweden, and is comprised of several river networks that drain into Lake Torneträsk (Figure 5). Located in the Scandinavian Mountains (Scandes), it is a mountainous catchment that includes peaks of 1750 meters above sea level (m.a.s.l) and several glaciers. Lakes cover about 15% of the catchment area, of which 69% corresponds to Lake Torneträsk. The lakes are generally clear, with dissolved organic carbon (DOC) concentrations ranging from 0.7 mg C L<sup>-1</sup> at high elevations to 10 mg C L<sup>-1</sup> in forested areas or mire-influenced areas, where lakes are slightly more coloured (Jonsson et al., 2003; Karlsson et al., 2001). The mean annual air temperature is 0°C (1995–2006), measured at the Abisko Scientific Research Station, which is located at the southern shore of the Lake Torneträsk. There is a clear precipitation gradient from west to east, with high precipitation (~900 mm) in the western part (Åkerman & Johansson, 2008). This causes a more continental climate that is drier on the eastern side of the catchment, with a precipitation minimum in the Abisko valley (340 mm). Forests are dominated by mountain birch (*Betula pubescens* spp. *czerepanovii*) in the lower altitudes with some patches of Scots pine (*Pinus sylvestris*) in the east. The tree line is around 650 m (Holmgren & Tjus, 1996), and tundra vegetation is found above the tree line. Discontinuous permafrost can be found above 800 m (Gisnås et al., 2017) and on mires at lower altitudes (Åkerman & Johansson, 2008).





**Figure 5:** The Torneträsk catchment in northern Sweden. The lakes in this catchment were studied in chapter I, and the streams in the Miellajokka catchment (the contour marked in black) were studied in the chapters II and III. The black star denotes the Abisko Research Station.

The Torneträsk region is a focus for Arctic research, where the Abisko Research Station has been a major hub for scientists for more than a century. Over the past two decades, there have been extensive studies of lake C cycling in arctic and subarctic lakes in the region (Jonsson et al. 2003; Karlsson et al. 2005; Lundin et al. 2013), and together with unpublished data of the Lake Torneträsk, we upscaled CO<sub>2</sub> evasion for all lakes in this catchment (**Chapter I**).

### ***Miellajokka catchment***

**Chapter II** and **III** were performed in the Miellajokka catchment, a sub-catchment within the Torneträsk catchment (Figure 5, 68° 21' 14" N, 18° 56' 16" E). The catchment covers 51.5 km<sup>2</sup>, and the elevation ranges between 384 and 1731 m above sea level. The morphology of the catchment is largely determined by the effect of several glaciations across millennia, causing U-shaped valleys and several deposits of coarse materials and moraines. The glacial imprint also

determines a general pattern for the flow of water: starting in steep peaks, followed by a plateau, a sustained, moderately sloped terrain ending in flat area, and finally draining into the lake Torneträsk. The catchment is defined by four large streams which flow northwards, with two distinct headwater systems in the western side of the catchment. The total stream network amounts to 44.6 km, ranging from 1st Strahler order streams to the 4th order stream at the outlet. There are two lakes that feed the main stream in the catchment. Flow-weighted DOC concentrations in the outlet are 3.2 mg C L<sup>-1</sup> and for DIC 2.2 mg C L<sup>-1</sup>.

The catchment has a large variation in landscape cover, starting with mostly bare rock at elevations above 1200 m a.s.l. including several permanent snow fields. Between 700 and 1200 m the landscape is characterized by tundra vegetation and extensive cryoturbation (Becher et al., 2013). The tree line is approximately at 700 m where sparse cover of mountain birch (*Betula pubescens* spp. *Czerepanovii*) is intermingled with treeless tundra heath vegetation. Below 400 m there are several areas with more productive birch forest with a denser canopy cover. The soil permafrost is discontinuous at higher elevations and sporadic at low elevation areas (Gisnås et al., 2017). The bedrock in the region is dominated by weakly metamorphic sedimentary rocks such as schist and dolomite in the central and western areas of the catchment, whereas more of quartzitic and phyllitic hard schist and salic igneous rocks form the bedrock on the eastern tributary. The catchment is mostly undisturbed by human activity, with a road and a railroad crossing the catchment at about 1.5 km south of the catchment outlet.

### ***Kuparuk catchment***

The study sites of **chapter IV** are in the Kuparuk catchment, located in the North Slope of Alaska and near the Toolik Lake field station. The terrestrial landscape in the Kuparuk catchment is dominated by tundra ecosystems. Permafrost extent is continuous and with a thickness of ~200 m, indicating that water flow is mostly superficial (Shaver et al., 2014) and groundwater inputs are restricted to springs (Bowden et al., 2014). Permafrost thaws in summer to depths of 0.3 to up to 2 m. depending on the topography. Tussock tundra dominates the landscape, with patches of wet sedges and heath vegetation (Shaver et al., 2014). The riparian

vegetation near streams consists of sporadic shrubs such as dwarf birch (*Betula nana*) and willow (*Salix* spp.), but with heights of < 1 m and without shading the stream. The Kuparuk river originates at mountain peaks in the Brooks Range, at elevations of 1500 meters above sea level but without major glaciers in the catchment. DOC concentrations dominate the C pool in the water, with mean concentrations of 6.4 mg C L<sup>-1</sup> while DIC concentrations are about 3.7 mg C L<sup>-1</sup> (Peterson et al., 1986).

The climate in the upper Kuparuk catchment is characterized by a long cold season, with a snow cover that spans for ~8 months a year. The mean annual air temperature recorded in the Toolik Field Station for the period 1989-2010 was -8.5 °C (Cherry et al., 2014). The mean air temperature for the same period in July, the month when this study was performed, was 9.9 °C, with a mean maximum temperature of 16.1 °C and a mean minimum temperature of 3.0 °C. July is also the month with the highest precipitation (65 mm for the period 1989-2010), accounting for 44% of the mean annual precipitation (149 mm; Cherry et al., 2014).

## Methods

### *Gas transfer velocity*

The gas transfer velocity ( $k$ ) is the depth of water column that equilibrates with the overlying air per unit time. It is a key parameter to estimate both CO<sub>2</sub> evasion and metabolism, as it regulates the exchange of gases between the water and the atmosphere. It is a difficult to directly measure in the field, which typically involves adding a tracer gas not present in the water (e.g., propane, C<sub>3</sub>H<sub>8</sub>; sulphur hexafluoride, SF<sub>6</sub>, or argon, Ar) and measure the rate at which this degasses to the atmosphere (Wanninkhof et al. 1990; Cole et al. 1998). However, using this approach poses a severe constraint on measuring  $k$  to large spatial scales, as it involves performing many gas releases which are time-consuming. Fortunately, research in this field has been active in the past decade and currently there are

studies that show empirical relationships of  $k$  with multiple physical parameters of streams or lakes (Raymond et al. 2012; Vachon et al. 2013).

To upscale  $k$  in lakes, we used a relationship between  $k$  and lake size together with wind measurements, which have been established in a previous study (Vachon et al. 2013). To upscale  $k$  in streams, we measured multiple hydraulic parameters (width, depth, discharge and slope), and estimated  $k$  based on hydraulic equations from a recent synthesis (Raymond et al. 2012).

This approach to estimating  $k$  is sufficient for upscaling at multiple spatial scales (Chapter I and II); however, more detailed studies in specific streams (Chapter III and IV) required more precise and time variable estimates. For the latter studies, we relied on another approach to estimate  $k$ , which involved studying the patterns in  $O_2$  concentrations at sunset – the so called night-time regression method (Odum 1956; Hornberger and Kelly 1975). Briefly, at sunset when GPP approaches zero,  $O_2$  in water decreases as there is no more biological input. The rate of decrease in  $O_2$  concentrations is therefore dependent of the rate at which  $O_2$  can reach a new equilibrium with the atmosphere, and thus proportional to  $k$ . During the period when this occurs,  $k$  is approximated by the slope of the relationship between the rate of change in  $O_2$  concentration and the  $O_2$  deficit in the water (Odum 1956), and this can be converted to  $k$  (Hornberger and Kelly 1975). After obtaining  $k$  for a given set of days, we then related these estimates to discharge, as it usually is a good predictor of  $k$  for a specific site (Raymond et al. 2012). Through this relationship with discharge, I was able build predictive models for  $k$  among sites and over time.

### ***Estimating $CO_2$ evasion***

$CO_2$  evasion from streams and lakes was estimated following eq. 1. To quantify the  $CO_2$  concentrations in water we relied on direct measures of  $pCO_{2w}$  (Johnson et al. 2010). This method is highly preferred compared to other methods based on indirect measurements of pH and alkalinity, as they can cause large biases (Golub et al. 2017). In all studies, stream  $CO_2$  concentrations were measured using infrared gas analysers (IRGA) adapted for wet environments. We used

Vaisala (GMT220 sensor, Vaisala, Helsinki, Finland) and eosGP CO<sub>2</sub> probes (Eosense Inc. Dartmouth, Canada), covered with a PTFE layer highly permeable to dissolved gasses but not to water, following (Johnson et al. 2010).

### ***Stream metabolism***

Stream metabolism was modelled based on the open channel diel oxygen method (Odum 1956). Stream NEP is the balance between GPP and ER, and these two processes affect the diel oxygen concentration. These diel patterns can be used to estimate GPP and ER by analysing O<sub>2</sub> time series. We used a Bayesian inverse model from Hall and Hotchkiss (2017), governed by the following equation:

$$O_{2t} = O_{2t-1} + \left( \frac{GPP}{z} \times \frac{PAR_{t-1}}{\sum_{t=0}^{t=24} PAR} \right) + \frac{ER \times \Delta t}{z} + \frac{k_{O_2}}{z} \times (O_{2sat(t-1)} - O_{2(t-1)}) \times \Delta t \quad (2)$$

where  $O_{2t}$  is the oxygen concentration at time  $t$  (in g O<sub>2</sub> m<sup>-3</sup>),  $z$  is the channel depth (in m),  $PAR$  is the photosynthetic active radiation (in mol m<sup>-2</sup> s<sup>-1</sup>),  $k_{O_2}$  is the gas transfer velocity of  $k_{O_2}$  (in m d<sup>-1</sup>),  $\Delta t$  is the time steps of the time series (10 minutes) and  $O_{2sat}$  is the concentration of O<sub>2</sub> in the water if it would be 100% saturated.

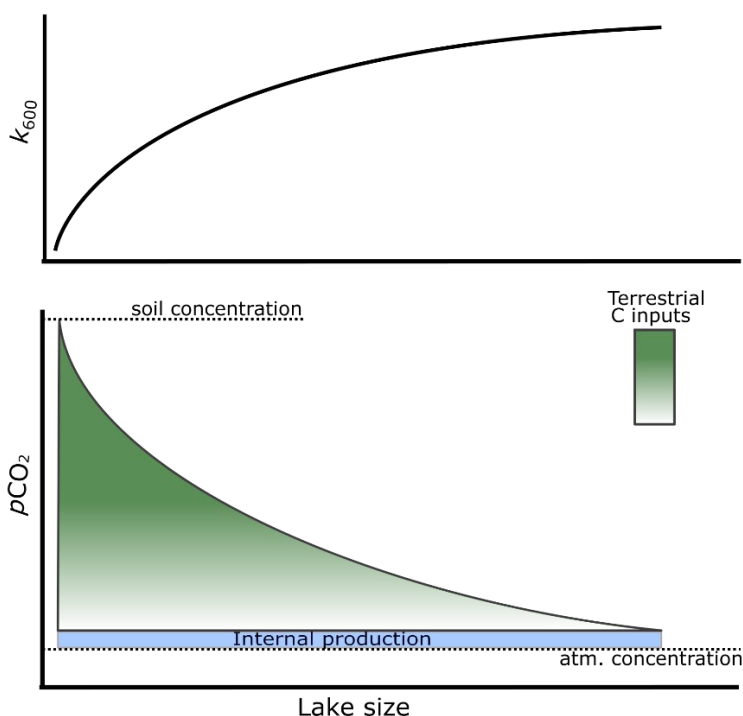
We modelled the three parameters (GPP, ER and  $k_{O_2}$ ), but used constrained priors for  $k$  based on relationships with discharge described above. Models that predict the three parameters avoid errors associated with estimating  $k$  empirically (Aristegi et al. 2009; Holtgrieve et al. 2016), but can give multiple solutions where different combinations of GPP, ER and  $k_{O_2}$  reproduce the same O<sub>2</sub> data, so-called equifinality (Appling et al. 2018). A solution for this is to relate  $k$  to hydrological measures such as discharge, which should be a proxy for  $k$  within a site (Appling et al. 2018). We used the relationship between  $k$  and discharge ( $Q$ ) from each site obtained from the night-time regression method, to obtain an approximate  $k$  for each day with its error associated. Then, for each day, the prior distribution of  $k$  was informed by the  $k \sim Q$  relationship. Metabolism computations were

performed following Hall and Hotchkiss (2017) for **chapter III** using a modified version of the R script available in that publication, while for **chapter IV** we used a new package in R (*streamMetabolizer*; version 0.10.9) that contains a more refined implementation of the same method (Appling et al. 2018).

# Results and Discussion

## CO<sub>2</sub> evasion across lake sizes

In **chapter I** we assessed the effect of lake size on CO<sub>2</sub> evasion from lakes in the Torneträsk catchment. Here,  $k$  increased with lake size (Vachon et al. 2013) as larger water bodies are more exposed to wind and can develop larger waves, promoting faster gas exchange with the atmosphere. In contrast,  $p\text{CO}_2$  has been shown to decrease with lake size (Humborg et al. 2010; Kankaala et al. 2013; Holgerson and Raymond 2016), as small lakes are strongly connected to land and susceptible to larger C inputs from terrestrial ecosystems. We hypothesized that both factors would cancel each other out, resulting in scale invariant CO<sub>2</sub> evasion rates (Figure 6).



**Figure 6:** Conceptual representation of the changes of  $k_{600}$  and  $p\text{CO}_2$  with lake size.  $p\text{CO}_2$  generally decreases with lake size, although large variability exists due to variable C inputs from land. The  $k_{600}$  increases with lake size as the water surface can harness more energy from wind and therefore higher turbulence.

Despite the opposing patterns of  $k$  and  $p\text{CO}_2$  with lake size, their interaction resulted in a decrease of  $\text{CO}_2$  evasion areal rates with increasing lake size, as observed in other studies (Kankaala et al. 2013; Holgersson and Raymond 2016; Zwart et al. 2018). The largest lake, Torneträsk, had three-fold lower evasion rates compared to the small ponds. However, at the landscape scale the large water bodies accounted for the most areal coverage, and therefore the single Lake Torneträsk was responsible for 53% of the  $\text{CO}_2$  evaded from lakes in the whole catchment. By comparison, there were approximately 27,000 ponds (lakes  $<0.001 \text{ km}^2$ ), but these only contributed 1.8% to the total lake area and  $<6\%$  to the total  $\text{CO}_2$  evasion from lakes in this catchment.

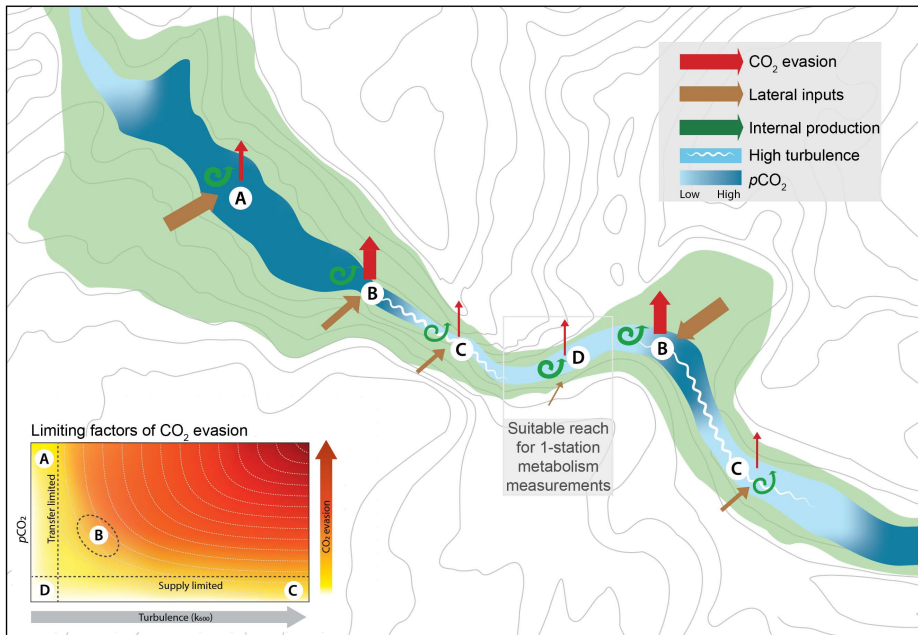
Our results show that incorporating size-dependent properties when upscaling  $\text{CO}_2$  evasion from lakes can be a simple and powerful tool to assess regional C budgets from lakes. In this catchment, the larger lake was the main source of  $\text{CO}_2$ , and therefore an accurate quantification of its role is necessary to refine the overall contribution of lakes in the regional C cycle. Further, we also observed strong daily changes in  $\text{CO}_2$  concentrations in Lake Torneträsk, causing the lake to be a sink of  $\text{CO}_2$  during the day and a source during the night. If we would have relied on grab samples (most likely taken during the day) rather than continuous measurements of  $p\text{CO}_2$ , the conclusion reached would have been that Lake Torneträsk is a sink of C, profoundly affecting the regional C budget. Thus, our results stress the need to incorporate estimates of  $\text{CO}_2$  evasion from lakes at multiple spatial and temporal scales.

## **Landscape patterns of $\text{CO}_2$ evasion from streams**

In **chapter II** we explored the spatial patterns of the two main controls of  $\text{CO}_2$  evasion across a whole river network:  $p\text{CO}_{2\text{water}}$  and  $k$ . We found that high  $k$  and high  $p\text{CO}_{2\text{water}}$  did not coexist across the landscape (yellow zone in inset in Figure 7), and therefore  $\text{CO}_2$  evasion could be either transfer limited (low  $k$ ), supply limited (low  $p\text{CO}_{2\text{water}}$ ) or both (low  $k$  and low  $p\text{CO}_{2\text{water}}$ ). Thus,  $\text{CO}_2$  evasion from different stream reaches across the catchment were limited by distinct controls. These results suggested that the fine-scale topography of the catchment had a



major role regulating  $\text{CO}_2$  evasion, by dictating distinct domains in the landscape where lateral C supply to streams is the dominant process driving gas evasion as well other domains where turbulent flow is paramount (Figure 7). The result is a strong spatial variability of  $\text{CO}_2$  evasion rates, which poses a challenge to understand large scale patterns in  $p\text{CO}_2$  (Figure 2).



**Figure 7:** Landscape process domains shaping  $\text{CO}_2$  evasion in streams. The spatial arrangement of C inputs and turbulent areas determines the controls and the magnitude of  $\text{CO}_2$  evasion. Thus,  $\text{CO}_2$  evasion will be either transfer limited (A), supply limited (C) or both (D). Hotspots of  $\text{CO}_2$  evasion can then occur when supply is high and there is enough turbulence to degas the water (B). Further, stream metabolism studies are often restricted to sites without lateral inputs of water and low turbulence (D), these sites can have relatively low rates of  $\text{CO}_2$  evasion, and therefore a major contribution of internal  $\text{CO}_2$  production to evasion than the average at the landscape scale (Chapter II and III).

Specifically, the variability observed at such a small scale has strong implications for upscaling  $\text{CO}_2$  evasion from fluvial systems. In this context, we show that the current global estimates may be biased if the effect of fine-scale topography is not considered. For instance, analysis of the same global dataset used in Figure 2, where patterns of  $p\text{CO}_{2\text{water}}$  are unclear, we show that  $p\text{CO}_{2\text{water}}$  is strongly affected

by the local  $k$  of the site. We further show that  $p\text{CO}_{2\text{water}}$  is the main parameter regulating the magnitude of evasion, and that without the capacity to predict landscape patterns of  $p\text{CO}_{2\text{water}}$  or lateral C inputs, our understanding of the role of inland waters in the C cycle is hampered.

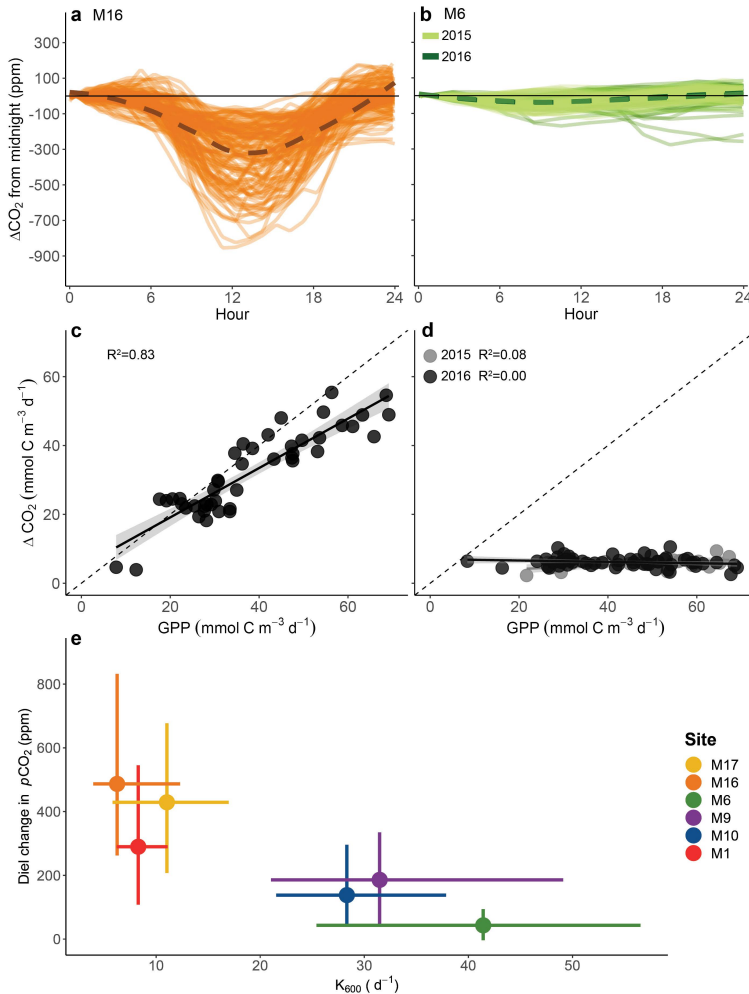
## **The role of biological processes on CO<sub>2</sub> evasion from streams**

In **chapter III** we combined measures of stream metabolism with high frequency CO<sub>2</sub> concentration, as well as a mass balance model, to assess the role of internal processing of C in streams as a driver of CO<sub>2</sub> evasion. We found that these Arctic streams are strongly heterotrophic (e.g.  $\text{ER} > \text{GPP}$ ) and net sources of CO<sub>2</sub> to the water column. Furthermore, the contribution of internally derived CO<sub>2</sub> to evasion was higher than external inputs, implying that CO<sub>2</sub> evasion from streams was largely controlled by in-stream metabolism. Surprisingly, in most of the streams, we found that the rate at which CO<sub>2</sub> is produced in the stream was higher than evasion, indicating that metabolic processes could cause an increase in  $p\text{CO}_2$  and subsequent export downstream.

However, this finding apparently conflicts with the results of chapter II, where lateral inputs of C were largely driving CO<sub>2</sub> evasion. The likely reason for this discrepancy is that stream sites used for metabolism modelling – by design – avoided locations that had high rates of groundwater input and/or had areas with very high gas exchange (e.g., waterfalls), which are both likely hotspots of C inputs or evasion (Figure 7). This explanation is supported by the fact that we found lower CO<sub>2</sub> evasion rates in the sites where we measured metabolism when compared to the whole stream network assessment performed in chapter II. Together, chapter II and III indicate that accurate estimates of the drivers of CO<sub>2</sub> evasion from streams need to combine measurements at fine spatial and temporal scales.

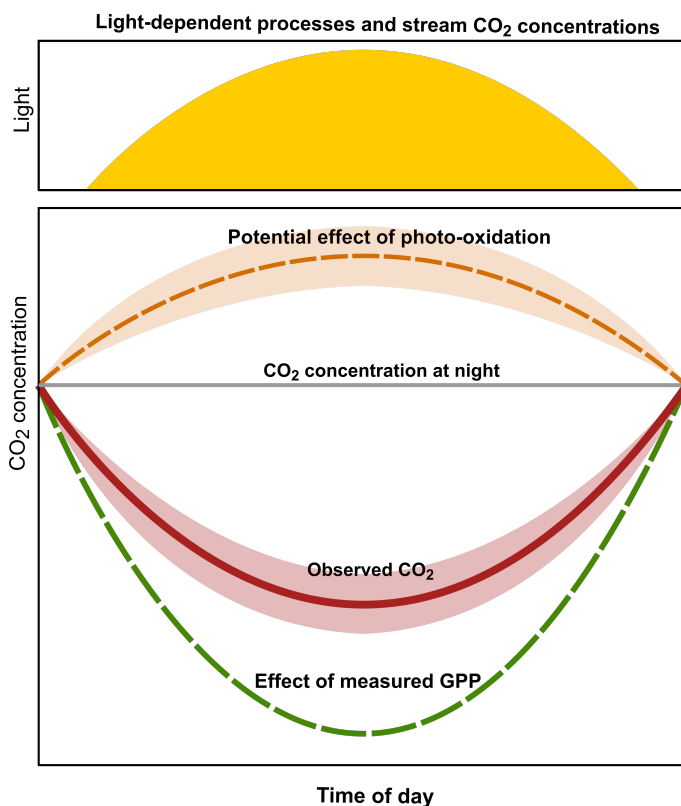
Despite the net heterotrophy observed in Abisko streams, which was a major source of CO<sub>2</sub>, the uptake by photosynthetic activity strongly impacted CO<sub>2</sub> concentrations, causing a marked decrease of  $p\text{CO}_2$  at day-time compared to night-time (Figure 8a, c). We observed this pattern in streams with lower  $k$ , while

sites with higher  $k$ , the turbulence likely masked the effect of GPP on diel changes of  $p\text{CO}_2$  (Figure 8b, d). Regardless, in five out of six streams the drawdown of  $\text{CO}_2$  by GPP impacted  $\text{CO}_2$  evasion, being 24–45% higher at night compared to day.



**Figure 8:** Drivers of diel patterns in  $\text{CO}_2$  concentrations in two contrasting streams. (a) and (b) show the change in  $\text{CO}_2$  concentrations from midnight, for the two most contrasting sites in the Miellajokka catchment (all sites are presented in **chapter III**). Each solid line is one day, and the dashed line denotes the average. (c) and (d) show the linear relationship between GPP and the diel change in  $p\text{CO}_2$  (solid line), and the dashed line shows the 1:1 line. (e) Shows the average diel change in  $\text{CO}_2$  concentration for each site respective to the average  $K_{600}$ , the bars denote the 0.05 – 0.95 quantiles for both  $\Delta\text{CO}_2$  and  $K_{600}$ .

The effect of photosynthesis on  $p\text{CO}_2$  indicated that it is possible to study light-dependent processes of the C cycle by using high temporal resolution measures. Another important light-dependent process is the photo-oxidation of OC, which may account for a majority of the  $\text{CO}_2$  evaded from streams in Arctic Alaska, with dark waters and high DOC (Cory et al. 2014). In our study sites in northern Sweden this process may be minor, with clear water and low DOC concentrations and low light absorbance (Giesler et al. 2014). However, photo-oxidation studies in Alaska were based on measurements of OC mineralization in the water column (Cory et al. 2014), and the relative importance of photo-oxidation for  $\text{CO}_2$  production in the whole stream ecosystem, encompassing the benthic and hyporheic zones (Figure 1) is not well quantified.



**Figure 9:** The effect of light-dependent processes in stream  $\text{CO}_2$ . The diel change on  $\text{CO}_2$  concentrations (red line) is the balance of two opposing, light-dependent processes: photo-oxidation (orange line) produce  $\text{CO}_2$  while photosynthesis (green line) consume  $\text{CO}_2$ .

In **chapter IV** we studied streams in the same area in Alaska where photo-oxidation is suggested to be the major process producing  $\text{CO}_2$  in the water column (Cory et al. 2014). If this would be the case, we expected to detect an increase of  $p\text{CO}_2$  from night to day. Surprisingly, we found a consistent decrease of  $p\text{CO}_2$  at daytime, similar to streams in northern Sweden (Figure 8), that was also driven by rates of GPP. Yet, unlike the data from Sweden, we observed a mismatch between GPP and the diel change in  $p\text{CO}_2$ . Specifically, this relationship suggests more  $\text{CO}_2$  during the day than would be expected given rates of GPP, and this could partly be due to  $\text{CO}_2$  produced from photo-oxidation (Figure 9). Overall, when measuring light-dependent processes at a whole ecosystem scale, we find that photosynthesis played a larger role than photo-oxidation, also in the high DOC and coloured streams in Alaska. Moreover, stream metabolism in the streams in Alaska was also a major contributor to  $\text{CO}_2$  evasion, in line with our findings in streams in northern Sweden.

## Conclusions

In this thesis I studied how different biological and physical controls interact to shape patterns of CO<sub>2</sub> evasion from inland waters. I found that physically-driven processes are a major constraint on biological activity at multiple spatial and temporal scales. In lakes, increase in lake size shapes inputs of C and the potential for degassing, and despite larger lakes have lower CO<sub>2</sub> evasion rates, they play a major role at landscape level due to its size. In stream networks, catchment topography regulated the contribution of lateral inputs from terrestrial ecosystems and internal production to CO<sub>2</sub> evasion. I also showed that CO<sub>2</sub> concentrations in streams can be strongly affected by biological uptake – photosynthesis – but the magnitude of this effect was also controlled by the physical template of the stream. Both the spatial patterns of C inputs and temporal changes due to biological activity created high variability in CO<sub>2</sub> evasion rates, which are important to account for global estimates of CO<sub>2</sub> evasion from running waters. Also, in streams of northern Alaska underlined by permafrost, I showed that photosynthesis plays a larger role than the photo-degradation of organic C, which was previously thought to be the main contributor to CO<sub>2</sub> evasion in that region. Overall, I demonstrated that aquatic biological activity in streams can strongly regulate CO<sub>2</sub> evasion from high-latitude streams, and therefore stream metabolic processes are key drivers of the transformation and fate of terrestrial organic matter exported from Arctic soils.

## Acknowledgements

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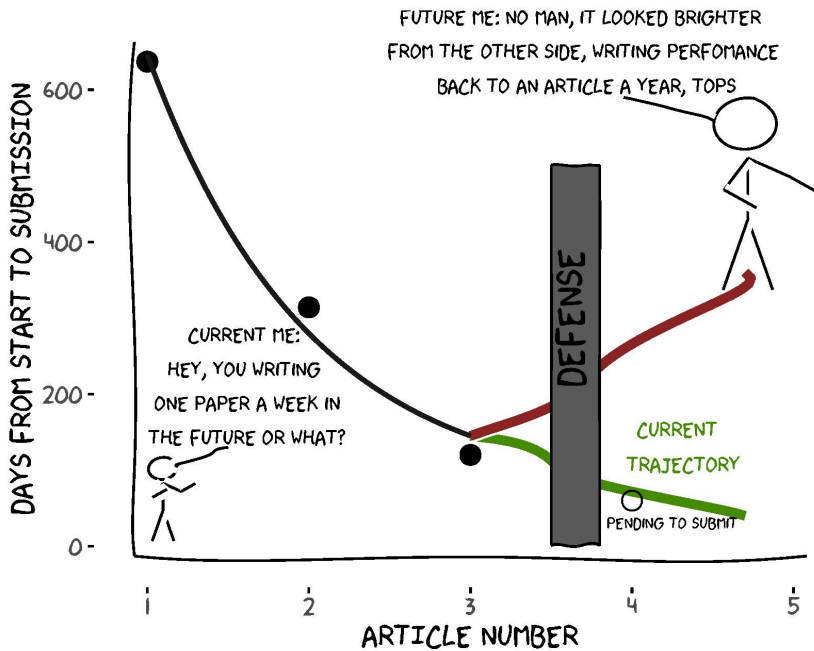


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**Figure n:** The effect of a hard deadline – such as the end of the thesis – on the productivity of a graduate student. The y-axis shows the number of days since the start of writing to submission of each article ( $n=3$ ). The solid black line represents an exponential fit ( $y = 1875 \times e^{-0.978X}$ ;  $R^2=0.98$ ), the green line is the current trajectory, while the red line represents the most likely scenario according to decades of experience of the scientific community, together with multiple night-time conversations with the future self.

Tribute to *xkcd* for a weekly source of distraction and procrastination along the PhD. Plot made with the R package “xkcd”. Code to reproduce the figure is available in: [https://github.com/rocher-ros/phd\\_trajectory](https://github.com/rocher-ros/phd_trajectory)



## ***Moltes gràcies***

Tomorrow I will send the thesis to print and the PhD will soon be over. It is late on a Sunday evening, I need to thank many people but most likely will forget an equal amount of them, but I will give it a try: Reiner, as a soil biogeochemist maybe you could not teach much about  $k$ , CO<sub>2</sub> evasion or metabolism. Most of it was new for you as it was for me, but you have been a great supervisor: you showed me what is to be a scientist, a writer, a teacher and a good person; more than giving me the fish you gave me the rod. Ryan, you are quite good at randomly coming to the office and say: *Hey, about that thing, maybe you should read these papers, and maybe try this and that (but I don't know to do it)*. All these little pushes and conversations is probably how I learnt about stream biogeochemistry and big ideas in ecology. Anki, you have always been in the backseat of the car and being really helpful along the twisted path of the PhD life in Umeå. Janne, with you I first worked here and discussed many ideas that eventually sprouted into this thesis.

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