

UNIVERSITÉ DU QUÉBEC À MONTRÉAL

A WATERSHED-SCALE ASSESSMENT OF AQUATIC CARBON EMISSIONS, EXPORT, AND BURIAL IN
TWO BOREAL LANDSCAPES

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ÉVALUATION À L'ÉCHELLE DU BASSIN VERSANT DES ÉMISSIONS, DE L'EXPORTATION ET DU
STOCKAGE DU CARBONE AQUATIQUE DANS DEUX PAYSAGES BORÉAUX

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COMME EXIGENCE PARTIELLE

DE LA MAÎTRISE EN BIOLOGIE

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RESUMÉ

Les eaux intérieures jouent un rôle majeur dans le cycle global du carbone (C) en traitant, émettant, exportant et stockant activement le carbone d'origine terrestre. Toutefois, leur contribution demeure encore mal comprise dans les paysages boréaux. Cette incertitude est particulièrement marquée dans les régions caractérisées par des réseaux denses de lacs et de cours d'eau, une forte connectivité hydrologique et une variabilité saisonnière prononcée en hydrologie. Cette thèse adopte une approche ascendante (bottom-up) à l'échelle du bassin versant afin d'examiner la manière dont les devenir du carbone aquatique s'intègrent dans des systèmes boréaux contrastés. Les bassins versants sont considérés comme des unités spatiales hydrologiquement pertinentes permettant de partitionner le carbone aquatique selon trois voies fondamentales : (1) l'émission de dioxyde de carbone (CO_2) et de méthane (CH_4) vers l'atmosphère, (2) transport latéral du carbone organique et inorganique dissous (COD et CID), et (3) le stockage à long terme par l'enfouissement du carbone organique dans les sédiments lacustres.

Deux études de cas complémentaires ont été analysées : le bassin versant du lac Laflamme, un petit bassin de tête dominé par un lac avec un seul exutoire et sans réseau amont, et le bassin versant de la rivière Bernard, un système plus vaste et hétérogène composé d'un réseau hiérarchisé de cours d'eau et de plusieurs lacs. Dans les deux bassins, les flux de carbone ont été quantifiés en tant que : (i) transport de COD et de CID aux exutoires des bassins ou sous-bassins, (ii) émissions diffuses de CO_2 et de CH_4 provenant des lacs et des cours d'eau, et (iii) enfouissement du carbone organique dans les sédiments lacustres à partir d'analyses de carottes sédimentaires. Des mesures à haute fréquence, combinées à des campagnes d'échantillonnage ponctuelles, des reconstructions hydrologiques annuelles et des séries temporelles à long terme ont été intégrées afin de capter la variabilité saisonnière et interannuelle. L'ensemble des flux étant normalisé à la surface du bassin versant pour permettre une comparaison directe entre les voies.

Les résultats démontrent que le devenir du carbone aquatique est fortement contrôlé par la taille du bassin versant, la complexité du réseau aquatique et l'hydrologie. Le bassin versant du lac Laflamme (superficie de drainage de $0,7 \text{ km}^2$) est dominé par les pertes atmosphériques provenant du réseau aquatique ($26,15 \text{ g CO}_2\text{-C m}^{-2} \text{ an}^{-1}$), avec un stockage à long terme limité du carbone dans les sédiments ($1,54 \text{ g C m}^{-2} \text{ an}^{-1}$) et un export contrôlé par l'hydrologie de $2,04 \text{ g COD-C m}^{-2} \text{ an}^{-1}$ à l'exutoire du bassin versant. À l'inverse, le bassin versant de la rivière Bernard (superficie de drainage de 56 km^2) présente une partition spatiale et temporelle plus marquée du carbone le long de son continuum aquatique, avec des émissions de carbone de $36,40 \text{ g CO}_2\text{-C m}^{-2} \text{ an}^{-1}$ provenant des cours d'eau et des lacs, un export de carbone de $14,64 \text{ g COD-C m}^{-2} \text{ an}^{-1}$ à l'exutoire du bassin versant, et un stockage de $4,68 \text{ g C m}^{-2} \text{ an}^{-1}$ dans les lacs du bassin de la rivière Bernard. Ces patrons reflètent des temps de résidence prolongés et un traitement accru du carbone au sein du réseau aquatique. Ensemble, ces études de cas mettent en évidence les eaux intérieures comme des réacteurs dynamiques du carbone plutôt que comme de simples conduits passifs, et démontrent la pertinence des cadres d'analyse à l'échelle du bassin versant pour intégrer les flux aquatiques dans les bilans de carbone boréaux. Ce travail fournit une compréhension empirique du cycle du carbone aquatique dans des systèmes boréaux éloignés et contribue à l'amélioration des évaluations régionales et globales des échanges de carbone entre la terre et l'atmosphère.

Mot des clés: eaux intérieures, cycle du carbone aquatique, paysages boréaux, bilan du carbone à l'échelle du bassin versant, connectivité terrestre-aquatique, export du carbone, émissions de gaz à effet de serre carbonés, enfouissement du carbone.

ABSTRACT

Inland waters play a disproportionate role in the global carbon (C) cycle by actively processing, emitting, exporting, and storing terrestrially derived C, yet their contributions remain poorly constrained in boreal landscapes. This uncertainty is particularly acute in regions characterized by dense lake–stream networks, strong hydrological connectivity, and pronounced seasonal variability in hydrology. This thesis adopts a watershed-scale, bottom-up framework to examine how aquatic C fates integrate across different boreal systems. Watersheds are treated as hydrologically meaningful spatial units that allow the partitioning of aquatic C among three fundamental pathways: emission of carbon dioxide (CO₂) and methane (CH₄) to the atmosphere, lateral export of dissolved organic and inorganic C (DOC and DIC), and long-term storage through organic C burial in lake sediments.

Two complementary case studies were examined: the Lac Laflamme watershed, a small headwater lake catchment with a single outflow and no upstream network, and the Bernard River watershed, a larger and more heterogeneous system composed of a hierarchically structured stream network and multiple lakes. Across both watersheds, C fluxes were quantified as (i) DOC and DIC export at watershed or sub-catchment outflows, (ii) diffusive CO₂ and CH₄ emissions from lakes and streams, and (iii) organic C burial in lake sediments derived from sediment core analyses. High-frequency monitoring and complementary discrete sampling, annual hydrological reconstructions, and long-term records were combined to capture seasonal and interannual variability, with all fluxes normalized to watershed area to enable direct comparison among pathways.

Results demonstrate that aquatic C fate is strongly controlled by watershed size, network complexity, and hydrology. The Lake Laflamme watershed (catchment area 0.7 km²) is dominated by atmospheric losses from the aquatic network (26.15 g CO₂-C m⁻² yr⁻¹), with limited long-term carbon storage in sediments 1.54 g C m⁻² yr⁻¹ and hydrologically driven export of 2.04 g DOC-C m⁻² yr⁻¹ at the watershed outflow. In contrast, the Bernard River watershed (catchment area 56 km²) exhibits greater spatial and temporal partitioning of C along its aquatic continuum with C emissions of 36.40 g CO₂-C m⁻² yr⁻¹ from streams and lakes, C export of 14.64 g DOC-C m⁻² yr⁻¹ at the watershed outflow and 4.68 g C m⁻² yr⁻¹ stored in the lakes within the Bernard River watershed, reflecting prolonged residence times and enhanced in-network processing. Together, these case studies highlight inland waters as dynamic C reactors rather than passive conduits and demonstrate the value of watershed-scale frameworks for integrating aquatic fluxes into boreal C budgets. This work provides empirical constraints on aquatic C cycling in remote boreal systems and contributes to improving regional and global assessments of land–atmosphere C exchange.

Keywords: Inland waters, aquatic carbon cycling, boreal landscapes, watershed-scale carbon balance, terrestrial-aquatic connectivity, carbon export, carbon greenhouse gas emissions, carbon burial.

INTRODUCTION

0.1 Context: role of inland waters in global carbon estimates

Carbon (C) is foundational to the building blocks of life and crucial to maintaining the Earth's atmosphere by trapping radiation from the sun. It is transported and distributed among the Earth's systems. It can be buried and stored, exported through aquatic continuums, and it can be respired by organisms, among others. These parameters are quantified and regularly evaluated in the global C budget conducted by the Intergovernmental Panel on Climate Change (IPCC, 2014).

A crucial component of the global C budget is how much C greenhouse gases (GHG), e.g., carbon dioxide (CO₂) and methane (CH₄), are emitted in a specified period (Keenan & Williams, 2018). In quantifying this budget, naturally occurring sources and sinks of C are considered. Ecosystems and landscapes can be identified as either C sources or sinks based on whether they contribute more C to the atmosphere than they remove or vice versa (Keenan & Williams, 2018).

Generally speaking, it is widely understood that major global carbon sinks are controlled primarily by terrestrial ecosystems and the oceans (Battin et al., 2009). For instance, it was found that the total forest C sink removed an estimated $2.4 \pm 0.4 \text{ Pg C yr}^{-1}$ from the atmosphere between 2007-2016 (Pan et al., 2011). Also, the oceanic sink had removed an estimated $2.5 \pm 0.6 \text{ Pg C yr}^{-1}$ around the same period of 2010-2019 (Friedlingstein et al., 2020). However, it has become well recognized by the scientific community that inland waters (e.g., lakes, rivers, streams, etc.) act as a large net source of C to the atmosphere despite only making up about 1% of the earth's surface (Battin et al., 2009; Raymond et al., 2013). Yet, the role and contributions of inland waters are still not well understood and not well represented in regional and global C estimates.

Until the 2000s, it was assumed that inland waters function as passive riverine pipes transporting C from land to sea. In fact, it has been shown that inland waters play a major role in the biogeochemical cycling of C where they emit, store, transport, and process large amounts of C and, consequently, greatly affect regional C dynamics (J. J. Cole et al., 2007). It is estimated that inland waters emit globally $\sim 4 \text{ Pg C yr}^{-1}$ (Drake et al., 2018). For comparison, anthropogenic CO₂ emissions from fossil fuel consumption and land-use change in 2019 were estimated to be $11.5 \pm 0.9 \text{ Pg C yr}^{-1}$ (Friedlingstein et al., 2020).

0.2 Uncertainty about the role of Inland waters in C balances

Due to the high connectivity of inland water with terrestrial ecosystems, C from terrestrial stocks can be transferred along the terrestrial-aquatic interface by lateral fluxes. Terrestrially derived C will then be partitioned into the various ecosystem roles that they assume within inland waters, e.g., transformation, emission, burial, and export (Chapin et al., 2006; Lovett et al., 2006). As research continues to be directed toward integrating aquatic and terrestrial networks in estimating land-atmosphere C exchanges, integrative case studies that effectively account for the hydrological connectivity between both systems are needed to improve C budgets.

It is often challenging to generate C budgets due to the large heterogeneity of landscapes and their interacting systems. Therefore, C mass balance studies are typically conducted at fine spatial scales focusing primarily on individual ecosystem types (e.g., forests, wetlands, lakes, streams), which derive total C inputs and outputs from all pathways in the ecosystem over a specified time, including all sources and sinks – physical, and biological (Chapin et al., 2006; Keenan & Williams, 2018). Focusing on single ecosystem types disregards the true heterogeneous nature of landscapes and fails to represent the interaction between terrestrial and aquatic systems (Casas-Ruiz et al., 2023). This is especially true for the boreal biome where the landscapes are characterized by complex fluvial networks that are closely connected to terrestrial ecosystems.

Canada is critical to the global C balance as it contains 50% of the earth's soil organic carbon pool (Schlesinger, 1997) and approximately 20% of the earth's freshwaters (McDonald & Brown, 2003) – out of which, a significant amount of the Canadian freshwaters exist in the boreal biome (Wells & Roberts, 2020). Furthermore, a typical boreal landscape can be composed of a mosaic of ecosystem types like forests, peatlands, lakes, and streams (Chi et al., 2020); and, each of these ecosystems are characterized by their own C dynamics and drivers (Casson et al., 2020; Hutchins et al., 2019).

Streams are generally the first points of contact between aquatic and terrestrial ecosystems, functioning as conduits and catalysts for biogeochemical reactions. Consequently, global rivers and streams are typically supersaturated with CO₂ and CH₄ (Bastviken et al., 2011; Marx et al., 2017; Raymond et al., 2013). Fluvial networks constitute a large portion of gas emissions and have the potential to offset their neighboring terrestrial C storage as has been seen in a 2016 study in subarctic Sweden (Lundin et al., 2016). However, this varies greatly across any given fluvial network as these emissions rely on their local

properties, e.g., stream order, topography, physical conditions, and groundwater input (Hutchins et al., 2020; Tank et al., 2018). Thus, determining the C budget for boreal landscapes is not straightforward and not easily measurable due to its remoteness, often leaving these estimates inaccurate.

There remain major challenges in defining the correct spatial scale for these assessments. Ecosystem and landscape boundaries remain largely ambiguous as biomes intersect and rely heavily on one another. Therefore, when utilizing a C mass balance approach, it is important that a universal spatial unit of measure be defined to make it hydrologically meaningful and applicable across scales.

Here, we use watersheds as the central spatial unit of measure for the mass balance, as watersheds already function as naturally occurring boundaries, reflecting the routing of water within the landscape (Casas-Ruiz et al., 2023). By using watersheds in this context, we can simplify the movement of water and overcome the limitations of assessing single ecosystem types. At a watershed scale, we can derive and estimate the different fates of C, since terrestrially derived C can be deposited in sediments, emitted into the atmosphere, and transported out of the watershed via the aquatic network (Butman et al., 2016; Pilla et al., 2022). By quantifying and estimating the C pools and fluxes associated with each of the pathways and ecosystem types within the watershed, we can constrain and integrate the role of the aquatic network within the watershed C balance.

For this thesis, we will conduct a C mass balance of the aquatic network at a watershed scale in two different watersheds in the Québec boreal region by (1) estimating CO₂ and CH₄ at a high spatiotemporal scale with high-frequency measurements; (2) determining the net C export at the watershed outflow; and (3) calculating lake C burial from sediment cores retrieved from the lakes. Our overall goal is to derive and estimate the aquatic C footprint in two different scaled watersheds. This thesis will contribute to the current knowledge of boreal aquatic C cycling and provide high-frequency observations to the global and regional C budget for these remote ecosystems.

0.3 Carbon biogeochemistry and functions

Inland waters are central components to the biogeochemical cycling of C as they are the primary vector through which terrestrially derived C is transported and processed before entering the oceans. For this reason, the terrestrial-aquatic interface is a hotspot for biogeochemical activity, where there is a disproportionately high processing of C and nutrients in these ecosystems (Laudon et al., 2011; McClain et

al., 2003). C can enter directly into inland waters as organic carbon (OC) in the form of organic matter, both dissolved and particulate, where surface runoff is the dominating form of transport (Drake et al., 2018). As well, C can enter in the form of dissolved inorganic carbon (DIC), such as CO_2 , as a product of respiration where groundwater is a major input. DIC can also derive from different processes like chemical and mechanical weathering with the production of carbonates (HCO_3^- and CO_3^{2-}). These different forms of C find the same fate: they can be stored in sediments, emitted into the atmosphere, or exported along the aquatic continuum (Fig. 0.1; Casas-Ruiz et al., 2023; Cole et al., 2007; Drake et al., 2018; Tank et al., 2018).



Figure 0.1 Diagram referenced from Casas-Ruiz et al. (2023) depicting the different C pathways in a watershed, and the most common source/sink roles of different terrestrial and aquatic ecosystems. NEE refers to the net ecosystem exchange for forests (F), inland waters (IW), agriculture (A), and wetlands (W). T refers to the lateral carbon flux due to harvesting and trading of wood and crops. R_{export} refers to the riverine export out of the watershed outflow. ΔC refers to ecosystem carbon accumulation (or loss). NWE refers to the net watershed exchange.

DIC is the sum of simple C compounds (e.g., CO_2 , HCO_3^- and CO_3^{2-}) that exist as aqueous C species within these systems. Within streams, sources of CO_2 are wide-ranging, as a product of biological and geological processing, or directly from terrestrial and aquatic processing. However, DIC (more specifically CO_2) in

boreal headwater streams generally originates from terrestrial areas either directly via groundwater or indirectly by biological processing of terrestrially derived C in the water column (Lupon et al., 2019). Headwater streams in these boreal regions are supersaturated with CO₂ and have the potential to offset their neighboring terrestrial C sink (Crawford et al., 2013; Venkiteswaran et al., 2014). This is mostly a reflection of large groundwater inputs of soil derived CO₂ combined with high rates of gas exchange with the atmosphere (Wallin et al., 2011). Of the C that is fluxed to the atmosphere, it is estimated, that globally inland waters emit ~4 Pg C yr⁻¹ and of which CO₂ is the dominating form (Table 1, Drake et al., 2018).

CH₄ has also been found to be saturated within streams and rivers in boreal landscapes (Lundin et al., 2013; Teodoru et al., 2009). It is primarily produced by anaerobic archaea in soils and sediments. Methanogenesis is a driving factor of CH₄ emissions in anoxic conditions and in the presence of sufficient organic C, e.g., in wetlands (Hope et al., 2004). Most recent studies estimate CH₄ emissions from rivers and streams to be 2-21 Tg CH₄ yr⁻¹ (Rosentreter et al., 2021). A synthesis of an inventory of 733 lakes in high northern latitudes found lakes to emit around 16.5 Tg CH₄ yr⁻¹ (12.4 Tg CH₄-C yr⁻¹; Wik et al., 2016).

The supersaturation of CO₂ and CH₄ in streams can also be attributed to the close connectivity with the surrounding terrestrial ecosystems that deliver large amounts of C to the aquatic network (Teodoru et al., 2009). The estimates of CO₂ and CH₄ flux to the atmosphere from streams have not been well quantified and there are few studies that conduct complete watershed scale C mass balances (Campeau & Del Giorgio, 2014; Taillardat et al., 2022). For instance, a recent 2022 study of a 3km boreal peatland headwater stream found that ~81% of in-stream CO₂ originated from porewater while the remaining originated from in-stream productivity (17%) and methane oxidation (2%) (Taillardat et al., 2022).

To describe the intensity of CO₂ and CH₄ exchange with the atmosphere, it is necessary to determine the gas transfer coefficient, or gas transfer velocity (k_{gas}). However, it is challenging to determine the right k since streams are so heterogeneous and dynamic in their morphology and along their continuum, resulting in differences in fluxes at small scales (Wallin et al., 2011, 2013b). In attempts to address this, models have been created to estimate k in streams and rivers that are slope-based and rely on other physical parameters (Natchimuthu et al., 2017; Raymond et al., 2012; Wallin et al., 2011).

As a highly mobile and reactive fraction across the soil-aquatic continuum, dissolved organic carbon (DOC) constitutes one of the planet's largest carbon reservoirs (Amado et al., 2006). In aquatic systems, DOC is continuously being altered by bacterial consumption and production. At the same time, photo-labile DOC

is subject to photodegradation and transformation. In boreal streams, it has been shown that CO₂ and DOC concentrations are positively related, indicating that DOC is an important component of C cycling in rivers and streams (J. F. Lapierre & Del Giorgio, 2012; Teodoru et al., 2009).

The rate of DOC production and removal is highly dependent on geological and ecological factors, such as land cover and temporal variables. For instance, it has been shown that wetlands and forest cover control DOC concentrations in boreal streams (Laudon et al., 2011). As well, in low-flow conditions, DOC predominately originates from wetlands and in high-flow, the major source of DOC originates from forested areas (Laudon et al., 2011). Since DOC is a measure of C content within dissolved organic matter (DOM), it is challenging to be able to derive its sources. DOM is a combination of plant, bacterial and algal material, and is characterized by a complex mixture of different compounds, and its role in the C cycle is not well understood (Singer et al., 2012).

To better understand these processes and their relationships, chromophoric dissolved organic matter (CDOM) measured with absorbance/fluorescence is often used to determine DOC concentration. CDOM is a fraction of the DOC pool that is light-absorbing (Rochelle-Newall & Fisher, 2002). Along a river continuum, the quality and concentration of DOM can transform and change. For instance, it has been shown that DOM properties in streams were strongly influenced by upstream lakes because of the longer residence time and the increased opportunities for processing in contrast to streams with no upstream lakes (Larson et al., 2007). By using CDOM absorbance/fluorescence to determine DOC concentration in stream water in boreal landscapes, we can better understand the contributions of terrestrially derived C to aquatic networks and how catchment characteristics drive organic matter export. As well, the analysis of DOM properties may provide insight into CO₂ production since their properties are related to photodegradation and bacterial mineralization (Amado et al., 2006). In fact, it has been shown that terrestrially derived DOM is a major contributor to CO₂ production (Fasching et al., 2014; Lapierre et al., 2013).

One often overlooked fate of C in aquatic systems is lake C storage through sedimentation. It is estimated that about 0.6 to 1.1 Pg C yr⁻¹ is stored within inland waters globally (Battin et al. 2009; Tranvik et al. 2009; Drake et al. 2018; Anderson et al. 2020). There is mounting evidence that carbon burial in inland waters represents a highly significant component of the overall continental carbon sink since a large fraction of that soil- and plant-derived carbon is laterally transported into aquatic networks, where lake sediments

act as long-term sequestration hot spots (J. J. Cole et al., 2007). The role of OC burial in the C cycle of boreal systems is important to consider and is crucial to watershed C balances as OC burial is one of the many fates that terrestrially derived C can assume. OC burial is controlled by several factors, but they are primarily dependent on lake morphology, i.e., lake size and shape (Downing et al., 2008; Ferland et al., 2012). There remain limited knowledge and success in modelling and predicting OC burial. It has been shown that there are relationships between lake bathymetry and the surrounding landscape in predicting the distribution of lake volume and depth (Heathcote et al., 2015). By modelling lake bathymetry and size distribution, there is an opportunity to model OC burial for boreal lakes and complete the C mass balance within these watersheds.

0.4 Overarching Objective

As discussed, the major fates of C in freshwater systems include the emission of C-GHG to the atmosphere, the reallocation of C across aquatic networks, and the storage of C in sediments as C burial. Still, these parameters are very poorly quantified, especially in boreal systems due to their complex and heterogeneous landscapes.

Here, we provide two separate case studies of the aquatic C footprint in the Lake Laflamme (LF) and the Bernard River watersheds in the Québec boreal region, as we attempt to answer how C fluxes integrate at the watershed scale. LF is constrained to one outlet and no inlets, with a small catchment size. LF functions as a funnel of C from the landscape, acting as an immediate collector of all C processes within the watershed (See Chapter 2). The Bernard River watershed, on the other hand, is characterized by a larger catchment size and a complex stream and lake network. Bernard captures the large heterogeneity that is so often observed in the boreal landscapes while allowing for the partitioning of C processes along its aquatic network (See Chapter 3). Additionally, Bernard is constrained to a single watershed outflow, allowing us to quantify the entire emission and export of the watershed. These two separate case studies present two different watersheds of different scales in terms of catchment size and stream network complexities.

To capture the aquatic C footprint of these two watersheds, we developed an aquatic C balance by integrating C-GHG emissions to the C export, and C burial of each of these respective aquatic networks and their sub-catchments. We achieved this by: (1) quantifying the annual watershed C export at the watershed or sub-catchment outlets on the basis of the DOC and DIC concentrations and the measured

discharge (in $\text{g C m}^{-2} \text{ yr}^{-1}$ of watershed area); (2) estimating CO_2 and CH_4 fluxes from the continuous and discrete sampling of the lake and streams in each watershed and their sub-catchments (in $\text{g C m}^{-2} \text{ yr}^{-1}$ of watershed area); and (3) calculating lake OC burial rates within the watershed and their sub-catchments from sediment cores collected during the sampling campaign (in $\text{gC m}^{-2} \text{ yr}^{-1}$ of watershed area). In this manner, I will derive three integrative metrics of aquatic C fluxes that are comparable: export, emission, and storage, all expressed in terms of the watershed area. These variables will be measured across three different field campaigns (June, August, and October) for the years 2021-2022 to capture the annual, and seasonal export, emissions, and storage. Our objective is to determine the balance between C export at the watershed outflow, C emissions from the entire aquatic network, and C burial in lake sediments, for these two watershed scenarios, and assess how this balance varies annually.

0.5 Chapter 1: Bernard River Watershed

In the Bernard River watershed, seven streams were continuously monitored from June to October for the years 2021 and 2022. In particular, the outflow of the watershed was monitored for temperature, discharge, CO_2 and CDOM (the latter in only 2 of the streams). Continuous measurements of CDOM allowed us to reconstruct the patterns of ambient DOC concentrations on a continuous basis, which together with the measured discharge allowed us to derive DOC export. We further reconstructed the annual pattern of discharge, beyond the measurement period, by extrapolating the hydrographs from monitored rivers within the region to the watershed outflow, and this allowed us to determine annual DOC and DIC export. Continuous monitoring was complemented with a discrete sampling of CH_4 and other parameters. Lake Bernard was sampled on a discrete basis for C-GHG, DOC, DIC, and other parameters following the regular field season campaigns. Lastly, sediment cores were collected from Lake Bernard and surrounding lakes for calculating OC burial rates within the Bernard River watershed.

By capturing these variables at various frequencies, we will reconstruct the export of DOC, DIC, and CO_2/CH_4 emissions from the watershed for the seasons and interannually. The entire aquatic network of the Bernard River watershed will be characterized using GIS by extracting stream network properties, slope, lake area, and elevation, among others. Our objective is to determine the balance between C export at the watershed outflow, C emissions from the entire aquatic network, and C burial in lake sediments.

0.6 Chapter 2: Lake Laflamme

The Lake Laflamme watershed is constrained to Lake Laflamme and its single outflow stream that extends 1 km downstream of the lake. LF is especially relevant for other headwater boreal watersheds that are remote and inaccessible and hence, the derived aquatic C balance from LF can be used as a reference for upscaling exercises. To achieve this, we will partition the fate of C within the LF watershed using the same approach described above. However, since there is no headwater stream network in LF, a buoy was installed to continuously measure the surface water CO₂, to provide a continuous record of aquatic CO₂ fluxes from the lake. The outflow of the lake has been continuously monitored for discharge and sampled weekly for DOC and other parameters for over two decades, allowing us to reconstruct the patterns of discharge and export of the outflow stream. The continuous buoy measurements were accompanied by discrete sampling within the lake and in the outlet stream for CH₄ and CO₂ dynamics across the seasons and years. Lastly, we collected a sediment core from the lake to determine OC burial within the watershed.

0.7 Overarching Hypothesis:

By quantifying these two watershed scale mass balances, we aim to provide two robust case studies that may inform and engage both terrestrial and aquatic scientists to consider this holistic approach. One important distinguishing characteristic between LF and Bernard is the residence time (RT) of DOC within the watershed, where Bernard will feature a much longer RT that can be attributed to its larger catchment size. Therefore, we hypothesize that the longer residence time in Bernard will provide more opportunity for the degradation of DOC and for increased production of CO₂ within the fluvial network. Furthermore, we hypothesize that the ratio of DOC export to C-GHG emissions will be higher in Bernard than LF. Lastly, we hypothesize that the contribution of each of these processes will shift in relevance depending on the seasonal dynamics in hydrology and climate. Since the Bernard River exists within a complex stream network, the net balance between C export, emission and storage will be driven by temporal variation in export. This hypothesis can be tested by assessing the balance of these three components on a seasonal and interannual basis, where hydrology varies greatly, and therefore, the export will also vary greatly.

CHAPTER 1

QUANTIFYING THE AQUATIC CARBON BUDGET OF A BOREAL WATERSHED: THE BERNARD RIVER WATERSHED CASE STUDY

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N.B. References cited in this chapter are presented at the end of the thesis

1.1 Context

Boreal landscapes store a substantial fraction of the Earth's terrestrial carbon (C) and play a disproportionate role in regulating exchanges between land, inland waters, and the atmosphere (Chi et al., 2020; Kasischke, 2000). While upland forests, peatlands, and wetlands have long been recognized as dominant C reservoirs, growing evidence demonstrates that inland waters are critical, yet often underrepresented, components of C budgets (Battin et al., 2009; J. J. Cole et al., 2007; Raymond et al., 2013). Streams, rivers, and lakes do not simply transport terrestrially derived C downstream, but actively transform, mineralize, and redistribute it among atmospheric, lateral, and sedimentary pathways (Cole et al., 2007). As a result, inland waters may offset terrestrial C sequestration through carbon dioxide (CO₂) and methane (CH₄) emissions, while simultaneously exporting dissolved organic and inorganic C (DOC and DIC) and sequestering C in sediments (Bastviken et al., 2011; Casas-Ruiz et al., 2021; Vachon et al., 2023). Quantifying the relative importance of these competing C fates remains a central challenge in constraining boreal and global C balances.

Recent syntheses emphasize that hydrology and network structure are first-order controls on aquatic C cycling in boreal regions (Hotchkiss et al., 2015; Raymond et al., 2013). Seasonal snowmelt, storm events, and moisture conditions regulate hydrological connectivity between organic-rich soils, wetlands, and channel networks, thereby controlling when and where terrestrial C enters aquatic systems (Ågren et al., 2008; Laudon et al., 2012). Once mobilized, C is subjected to repeated processing along hierarchical stream networks and across systems that differ widely in size, residence time, and metabolic balance (Tranvik et al., 2009; Ward et al., 2017). Low Strahler order streams often exhibit high partial pressures of CO₂ and CH₄ due to strong coupling with surrounding soils and short residence times that favor rapid mineralization, whereas higher-order streams and lakes integrate upstream signals while imposing additional physical and biogeochemical constraints on gas exchange and export (Wallin et al., 2013b). Despite this recognition, few studies have simultaneously quantified atmospheric evasion, lateral export, and sediment burial across boreal aquatic networks (Balathandayuthabani et al., 2023; Kokic et al., 2015; Wallin et al., 2013a).

The Bernard River Watershed, located in the boreal region of Québec, provides an ideal setting to resolve these interacting C pathways. The watershed encompasses a hierarchically structured stream network spanning first- to fifth-order channels, multiple lakes ranging in size and shape, and extensive bog- and wetland-influenced headwaters. This landscape heterogeneity promotes strong spatial gradients in hydrological integration, C source availability, and gas exchange conditions. Moreover, pronounced

seasonal hydrology driven by snowmelt and episodic discharge events creates periods of enhanced connectivity that are expected to disproportionately influence C mobilization, processing, and loss. Understanding how C is partitioned among evasion, export, and burial within such a system is critical for assessing the role of boreal aquatic networks as C reactors rather than passive conduits.

Here, we present an assessment of aquatic C fates in the Bernard River Watershed, integrating high-frequency and discrete measurements and reconstructions of hydrology, dissolved C dynamics, diffusive greenhouse gas fluxes, and sediment C burial. Specifically, we quantify (i) lateral C export as DOC and DIC at both local and integrated scales, (ii) diffusive CO₂ and CH₄ emissions from streams spanning multiple Strahler orders and from lakes across a broad size distribution, and (iii) long-term sediment C burial in the lakes within the Bernard River watershed derived from multi-decadal sediment records. By normalizing these fluxes to watershed area, we directly compare the relative magnitudes of atmospheric losses, downstream export, and long-term storage in lake sediments. By explicitly resolving these pathways within a single watershed framework, this study advances understanding of how boreal aquatic systems regulate C fate and provides a foundation for integrating aquatic fluxes into whole-watershed carbon mass balances that couple terrestrial and aquatic processes.

1.2 Materials and Methods

1.2.1 Study Site and Sampling

This study was conducted in the Bernard River watershed (Fig. 1.1; 50°51'33.2"N and 63°23'28.0"W), which is within the La Romaine River watershed (Côte-Nord Region, Québec, Canada). It is located at an elevation of ~315-500m above sea level. The predominant vegetation type for this watershed is needleleaf forest, accounting for ~80% of the watershed surface area. The watershed has a catchment area of 56 km² with a total lake surface area of 7.78 km² (13.9%) and a stream surface area of 0.14 km² (0.25%).

To establish a contemporary aquatic C budget, we partitioned the major C pathways in the Bernard River watershed into three components: (i) downstream export of DOC and DIC through the watershed outflow, (ii) stream and lake CO₂ and CH₄ emissions at the watershed scale, and (iii) contemporary sediment C burial since 1980 for the ensemble of lakes within the watershed. This study involved both discrete samples and high-resolution monitoring of the different components during 2021-2022.

The Bernard River Watershed stream network was delineated using a high-resolution digital elevation model (DEM) and classified according to Strahler stream order, spanning first- through fifth-order channels. Channel segments were extracted from the flow-accumulation grid and segmented at confluences to preserve order-specific geomorphic properties.

Continuous monitoring river sites ($n = 7$) was carried out at hourly timesteps for surface water partial pressure of CO_2 ($p\text{CO}_2$, μatm) and water height as a proxy for discharge, over the open-water season (June–October, Fig. 1.1). For each stream segment, we quantified key physical characteristics relevant to hydrological integration and biogeochemical processing (Fig. 1.2), including segment length (m), mean channel slope (unitless: rise/run), upstream contributing area (m^2), and modeled mean water velocity (m s^{-1} ; Eq. 1.4). These variables were selected to capture the hierarchical structure of the network and to provide spatial context for scaling C fluxes across stream orders.

The continuous measurements were accompanied by discrete sampling at the different stream sites and within the lake for partial pressure of CH_4 ($p\text{CH}_4$), $p\text{CO}_2$, DOC and DIC. Chromophoric Dissolved Organic Matter (CDOM) was continuously monitored at the watershed outflow and a first-order Bog Lake outflow (see Fig.1.7a-b) as a proxy for continuous DOC. Sediment cores were collected from six lakes of varying



Figure 1.1 Map of the Bernard River watershed (Orange dot; La Romaine Region, Québec, Canada) showing the delineated catchment boundary, stream network classified by Strahler order, and study sites (turquoise triangles).

size both within the Bernard River watershed ($n = 3$) and regional lakes within the La Romaine River watershed ($n = 3$) due to accessibility to lake sites.

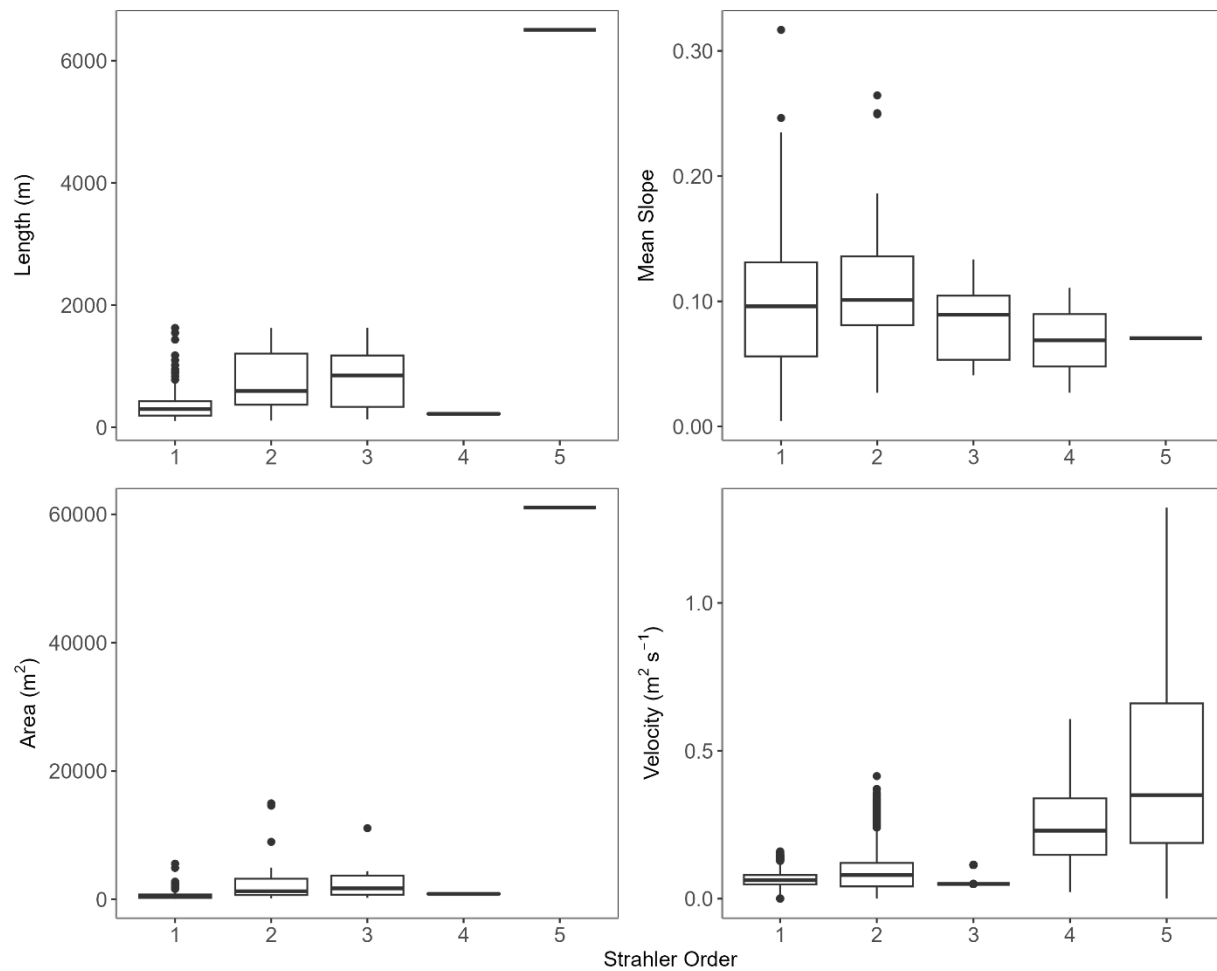


Figure 1.2 Geomorphological and hydraulic characteristics of the Bernard River watershed across Strahler stream orders. Panels show distributions of (a) segment stream length (m), (b) mean channel slope (unitless: rise/run), (c) upstream contributing area (m²), and (d) modeled mean mean water velocity (m² s⁻¹).

Stream segment length and upstream contributing area increased systematically with Strahler order, reflecting progressive network integration from headwaters to the watershed outflow. It should be noted that Stream Order 4 was a small stream connecting two big lakes within the watershed and is therefore not considered in the overall characterization of the stream orders within the Bernard River watershed. Mean channel slopes were predominantly moderate across the network and declining with increasing

stream order. Modeled mean water velocity increased with stream order, indicating that downstream hydraulic conditions were driven primarily by increasing discharge and channel integration rather than by increasing slope. Together, these stream characteristics illustrate a spatially heterogeneous boreal network in which headwater reaches are short, steeper, and weakly integrated, while higher-order channels exhibit longer lengths, larger contributing areas, and higher velocities.

1.2.2 Field and Laboratory Analyses

Discrete water samples for DOC and DIC were collected during three seasonal field campaigns between June and October in both 2021 and 2022. Samples were filtered using a 0.45- μm polyethersulfone membrane cartridge and subsequently stored at 4 °C in the dark until analysis at the Groupe de Recherche Interuniversitaire en Limnologie (GRIL) analytical laboratory at the Université du Québec à Montréal (UQAM). C concentrations were quantified using a total carbon analyzer (TOC1010, OI Analytical, USA) using high-temperature persulfate oxidation.

Surface water (~ 0.1 m) partial pressure of CO_2 and CH_4 were determined from discrete samples collected across each field campaign using the headspace technique (Kling et al., 1991). Water samples were collected in 140 mL syringes (three replicates), after which a headspace was created by replacing 40 mL of water by ultra-zero air (AI 0.0UZ, Praxair, Inc., Canada). Syringes were vigorously shaken for 2 minutes for equilibration of gas and water. The equilibrated headspace was then transferred to 12 mL exetainers (Labco Ltd, U.K.) for subsequent gas analysis. Concentrations of CO_2 and CH_4 were measured using a cavity ring-down spectrometer (CRDS) equipped with a small sample isotopic module (SSIM, Picarro G2201-i).

High-resolution continuous monitoring of DOC concentration, CO_2 and discharge was carried out using C-FLUOR Loggers (PME, CA, USA) for measuring CDOM, CO_2 probes (GMP343, Vaisala, Finland), U20 pressure loggers (Onset, USA) to measure water and atmospheric pressure (kPa) and temperature ($^{\circ}\text{C}$), and HOBO Micro Station Data Loggers (H21-USB, Onset, USA) to store field data, which were deployed at seven different streams spanning first- to fifth-order channels and catchment characteristics, including a headwater stream, a bog lake outflow, and the watershed outflow (Fig. 1.1). Stage-discharge rating curves were developed to estimate discharge from the continuous measurements of water height and discrete samples of discharge that were performed using the SonTek FlowTracker2 handheld Acoustic Doppler Velocimeter (ADV; geotech, Denver, CO, USA). All statistical analyses were performed in R (RStudio v2025.05.1.513).

1.2.3 Reconstructing annual discharge

Discharge was estimated from continuous measurements of water height and discrete samples of discharge that were performed using the SonTek FlowTracker2 handheld Acoustic Doppler Velocimeter (ADV; geotech, Denver, CO, USA). To retrieve continuous measurements of water height, U20 pressure loggers were deployed at all river sites ($n = 7$) both on the streambed and above water to detect the hydrostatic pressure of the water column above the sensor and calculating the difference between atmospheric pressure changes from the total pressure reading. Depth (m) was calculated as a function of the water-air pressure difference (Pa), and the density of water (ρ), which is a function of temperature. Discrete measurements of discharge were retrieved on each sampling occasion for 2021 and 2022 at each site ($n = 39$) along transects extending the full width of stream channel sites (80cm to >10m in width). A SonTek FlowTracker2 ADV was submerged at 10-20 cm under the surface water at multiple points along the transect to measure velocity and discharge (3-15 measurements; dependent on stream width). Total discharge (m^3) was calculated by taking the sum of all the transect measurements at the site.

Stage-discharge rating curves were generated for each site for 2021 and 2022 by plotting discrete measurements of discharge against the continuous measurements of water height. It should be noted that, instead of per site, a collective stage-discharge rating curve was generated for stream order 1 to achieve a significant relationship ($p < 0.05$). In 2021, solely ST5-WO measurements were heightened by a 3-4 fold difference than in 2022, even though stream characteristics had not changed and there were no major differences in precipitation patterns among the sampled years (Fig. 1.3). To correct measurements from this site, ST5-LO (an upstream site to ST5-WO) was used as a baseline standard for ST5-WO and a correction factor was developed by calculating the average difference between the two sites in 2022 when

measurements at both sites were correct. The derived correction factor (1.11) was applied to measurements at ST5-WO in 2021.

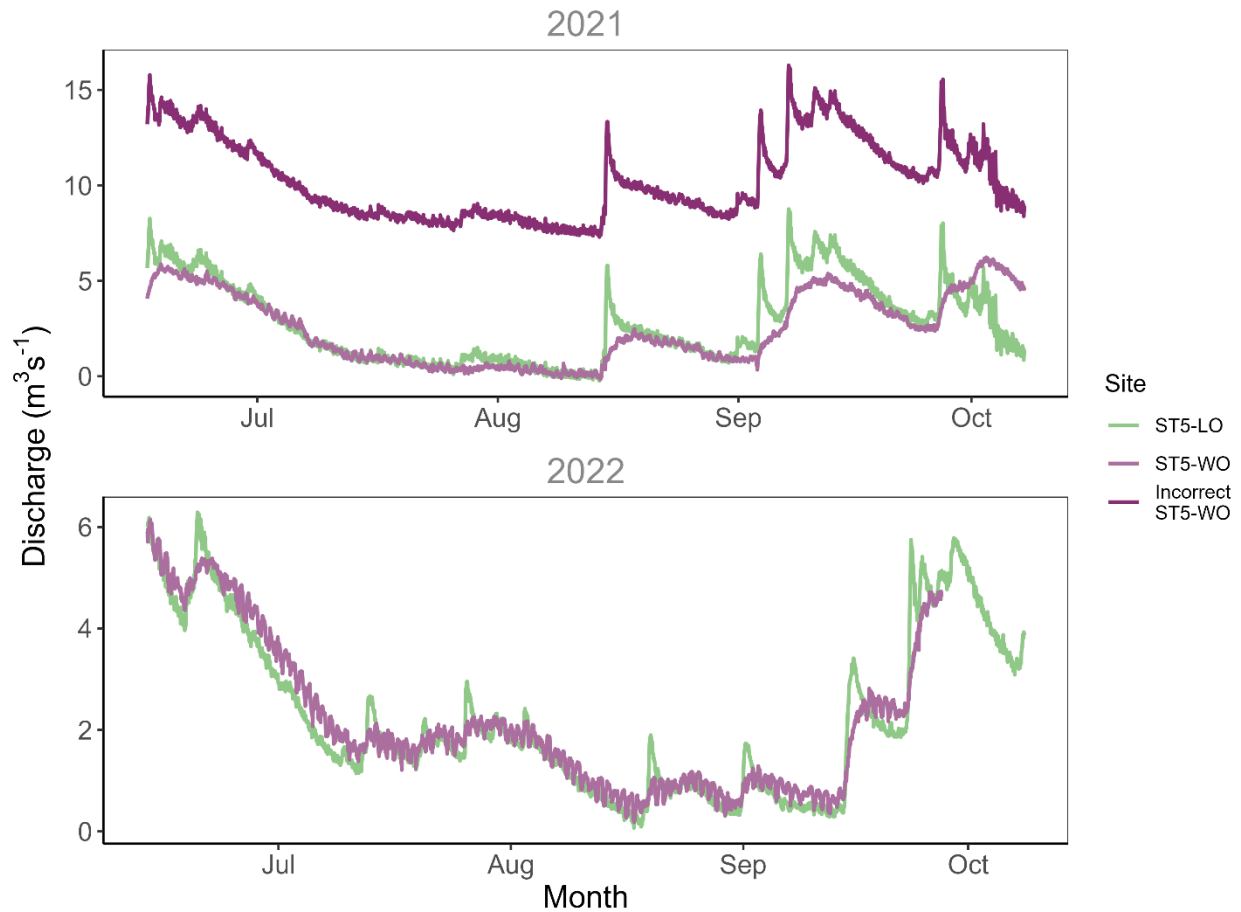


Figure 1.3 Comparison of estimated discharge before and after correction factor was applied to ST5-WO measurements in 2021. The correction factor was determined by calculating the average difference between ST5-LO and ST5-WO in 2022. Measured but deemed incorrect values at site ST5-WO are separately colour coded (dark purple) in 2021. ST5-WO (light purple) are values used for subsequent calculations : 2021 represent values after CF was applied, whereas 2022 are direct measurements.

Since the field campaigns only covered a portion of the ice-free season in 2021 and 2022, more specifically between June to October, important spring freshet and late autumn precipitation events, as well as the winter low flow period were not captured. To remedy this, the newest available regional hydrographs in the La Romaine River Watershed (Fig. 1.4a, Hydro-Québec) for the years 2014-2019 were used to capture annual hydrological patterns for the Bernard River watershed. It should be noted that three regional rivers of similar strahler order (fourth- and fifth-order) were selected for calculating the average hydrograph over the monitored years (Fig. 1.4a). Average annual regional discharge records revealed a highly coherent seasonal hydrological pattern, characterized by a pronounced spring freshet followed by declining summer

baseflow and episodic autumn recharge events across the monitored years (Fig. 1.4a). Despite differences in absolute discharge magnitude among stations, the timing of major hydrological phases was consistent across all three rivers, with peak flows occurring during late spring and secondary flow increases associated with fall precipitation. This provided a robust temporal framework for extrapolating discharge conditions to the study rivers during periods when site-specific measurements were unavailable. To do this, the daily percent contribution for each of the three surveyed rivers was calculated by dividing the average daily discharge of each day by the total annual discharge. The calculated percent contribution was averaged across the three rivers (Fig 1.4b) and applied to the two of our study rivers (the watershed outflow, ST5-WO, and the Bog lake outflow, ST1-BLO) to reconstruct annual discharge only for the period where there was missing measurements (Fig 1.5).

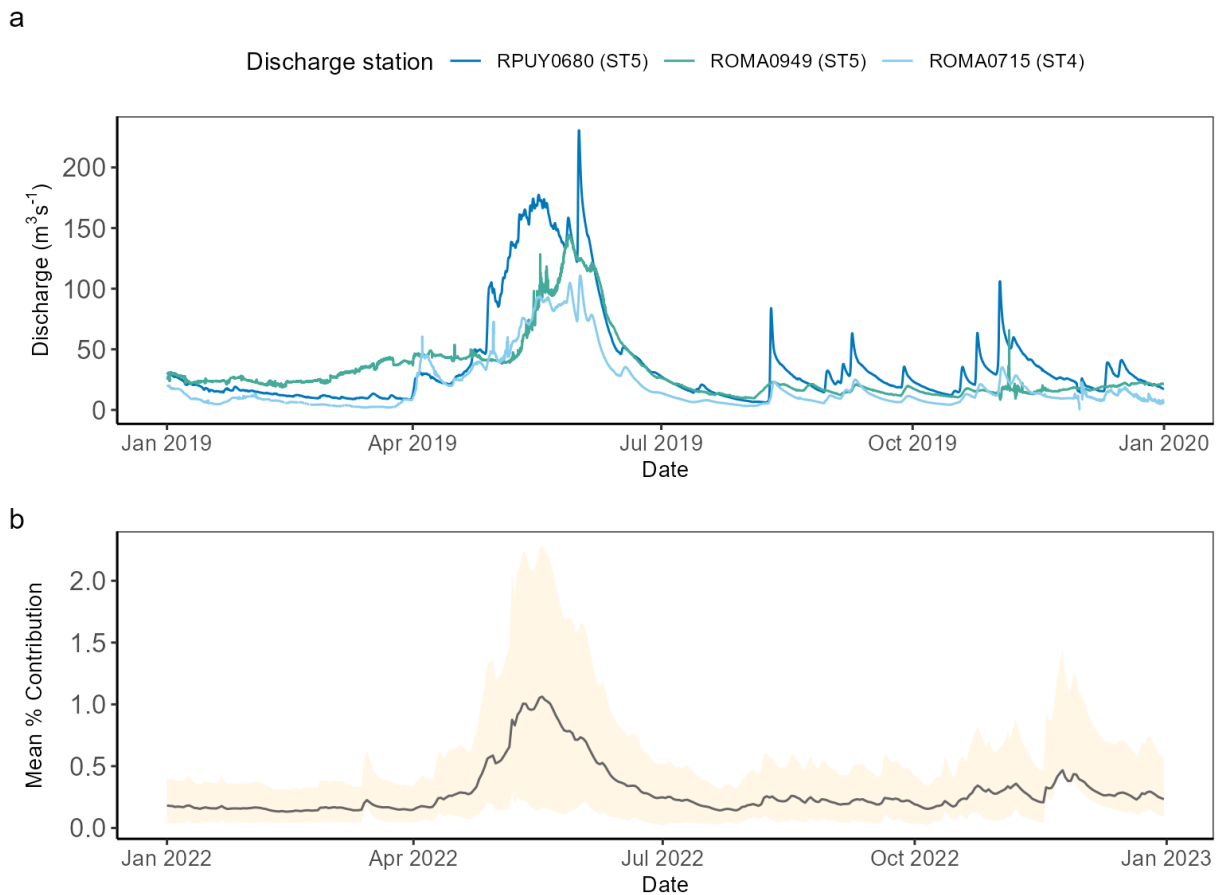


Figure 1.4 a) Regional discharge time series from three hydrometric stations in the La Romaine River watershed (RPUY0680, ROMA0949; fifth-order channels; and ROMA0715, fourth-order). b) represents the daily average percent contribution of the total discharge of the three rivers (black). Shaded areas represent the uncertainty bounds of the regional discharge estimate.

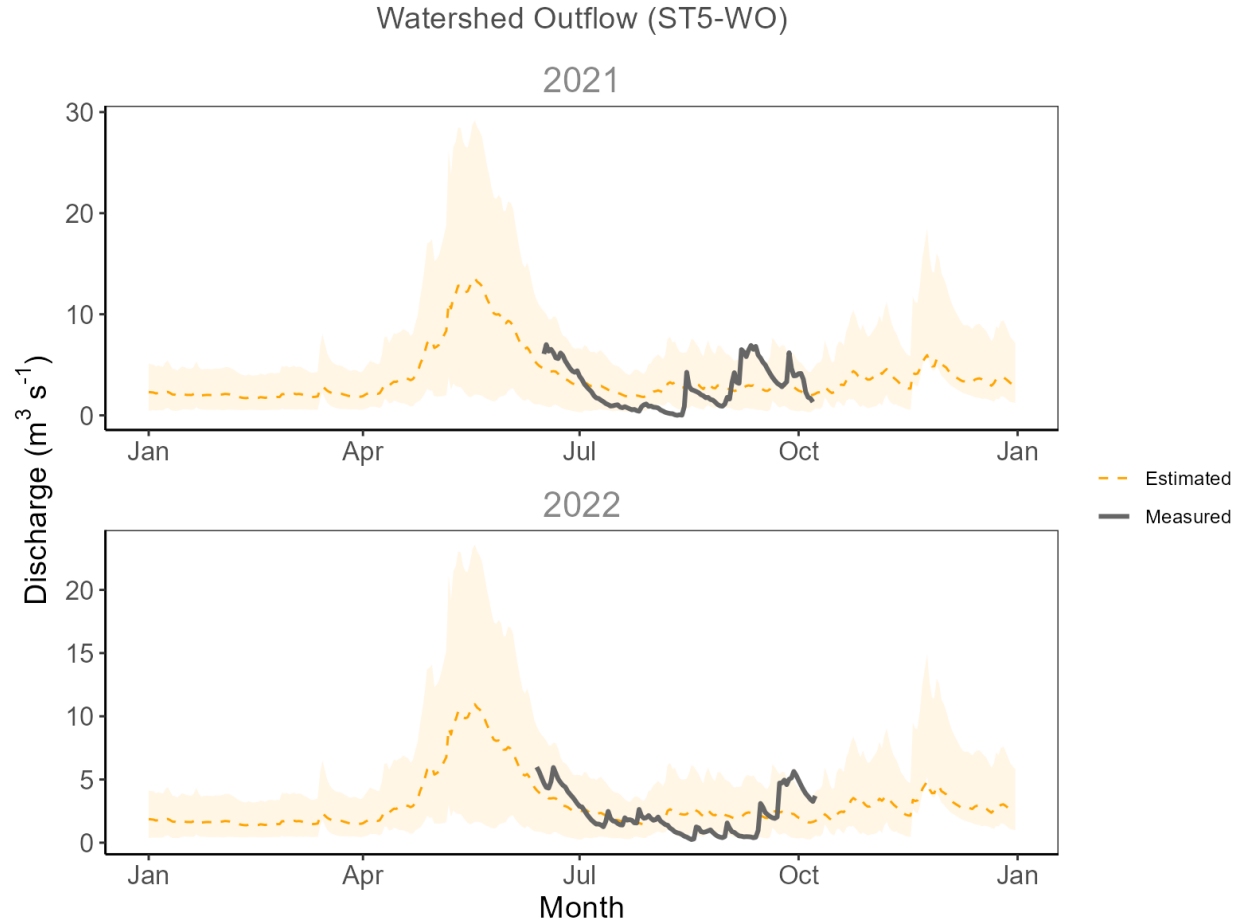


Figure 1.5 a) Average regional discharge time series from three hydrometric stations in the La Romaine River watershed between 2014-2019 (orange dashed line; RPUY0680, ROMA0949; fifth-order channels; and ROMA0715, fourth-order), and measured discharge from pressure loggers (black line). Shaded areas represent the uncertainty bounds of the regional discharge estimate. Panel a is discharge estimates for 2021 and Panel b are discharge estimates for 2022.

1.2.4 Downstream export of DOC and DIC through the watershed outflow

To continuously monitor DOC in the Bernard River watershed at a high-resolution, two C-FLUOR Loggers (PME, CA, USA) were deployed to measure CDOM - a proxy for DOC. The two streams that were instrumented include the Bernard River watershed outflow (ST5-WO) and a bog lake outflow (ST1-BLO). The watershed outflow was instrumented to be able to integrate DOC export at the watershed scale. The bog lake outflow was instrumented for two reasons: (i) to provide a case-study example of high-resolution monitoring of DOC export from a first order lake (catchment size: 0.45 km²); and, (ii) to capture the range of DOC export from a bog within the Bernard River watershed. Discrete samples of DOC and DIC were collected every sampling occasion in 2021 and 2022 ($n = 41$) to complement the continuous probe measurements. Discrete CDOM samples were measured at the UQAM GRIL Laboratory using a Duetta Spectrometer (Horiba, Kyoto, Japan) at a wavelength of 440 nm⁻¹ (Cuthbert & del Giorgio, 1992). A linear

model was developed using collected discrete samples of DOC and CDOM from all the Bernard River monitoring sites to assess the relationship between CDOM and DOC within the Bernard River Watershed (Fig. 1.6a; $R^2 = 0.86$, $p < 0.0001$). This relationship was consistent across headwater streams, intermediate reaches, and both lake and watershed outflows, with no systematic site-specific deviations from the overall trend. Although scatter increased at higher CDOM values, observed concentrations remained closely aligned with the fitted regression and within the associated confidence intervals. Together, these results demonstrate that CDOM provides a robust proxy for DOC concentration across spatial scales and hydrological conditions in the study system, a prerequisite for estimating DOM from sensor derived CDOM.

A dilution series was conducted between the C-FLUOR Loggers and laboratory derived DOC measurements (please refer to section 1.2.2 – Laboratory analyses) using water samples from 3 different sites with ambient DOC concentrations ranging 11 – 22 mg L⁻¹ to derive DOC from the continuous C-FLUOR Logger measurements (Fig. 1.6b; $R^2 = 0.96$, $p < 0.0001$). The derived equation was used to estimate DOC for our measured periods in 2021 and 2022 (Fig. 1.7c-d). It should be noted that DOC estimates at ST5-WO in 2022 were on average 2.5-5 mg L⁻¹ lower than 2021 values. This underestimation was believed to be the result of having placed the sensor in a new location within the stream due to unsafe currents that made access to our original site location inaccessible. To correct for this, correction factors for CDOM and DOC were generated by finding the average ratio between ST5-WO and ST1-BLO in 2022, since ST1-BLO site characteristics were unchanged across 2021 and 2022. Our measurements were multiplied by the correction factors (Fig 1.7; ST5-WO_{DOC-CF} = 2.37; ST5-WO_{CDOM-CF} = 1.74; light-purple line).

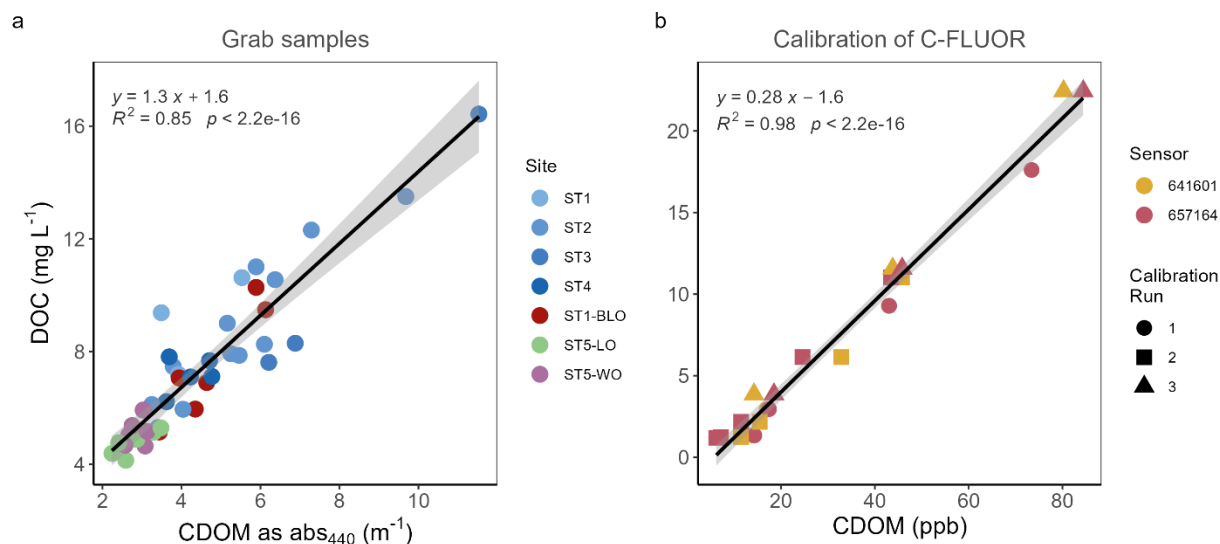


Figure 1.6 Relationship between grab-sample DOC concentrations and laboratory CDOM absorbance (panel a) and Calibration of CDOM fluorescence sensors (panel b). (a) Linear relationship between grab-sample DOC and CDOM absorbance at 440 nm across all monitoring sites ($R^2 = 0.85$). Shaded bands represent 95% confidence intervals. (b) Calibration curves for two C-FLUOR sensors (serial numbers 641601 and 657164) across three independent calibration runs (symbols), showing a strong linear relationship between laboratory DOC and in situ CDOM fluorescence ($R^2 = 0.96$).

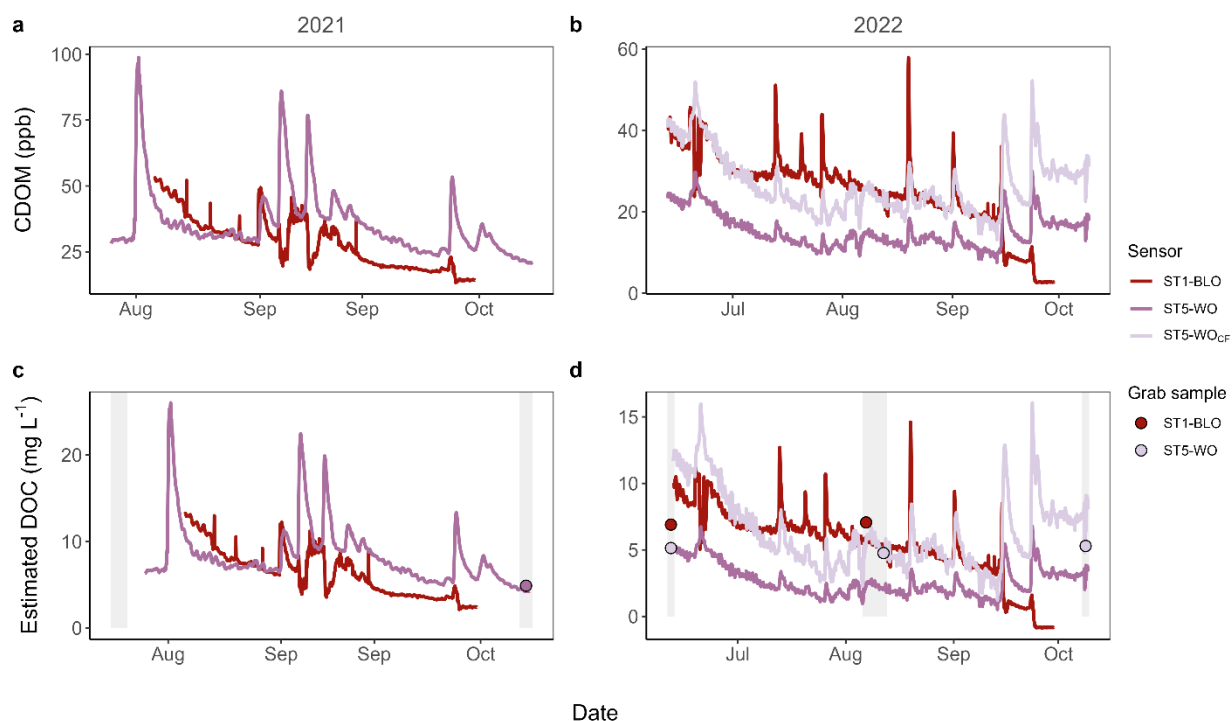


Figure 1.7 Continuous CDOM fluorescence and estimated DOC at two monitoring sites (ST1-BLO, red, and ST5-WO, purple) during 2021 (a, c) and 2022 (b, d). Panels (a–b) show CDOM fluorescence (ppb), and panels (c–d) show estimated DOC (mg L⁻¹) derived from laboratory sensor calibrations along with a corrected estimation (CF) from section 1.2.4 (light purple). Grey shaded areas indicate field-sampling campaigns when grab samples were collected (points).

To estimate DOC for the entire year, including periods where there are no continuous CDOM measurements, we had established: (i) relationships between CDOM and DOC (Fig. 1.6a; $R^2 = 0.85$, $p < 0.0001$); and, (ii) relationships between discharge and in situ measured CDOM (Fig. 1.8). These models provided the basis for modeling DOC from discharge measurements for the unsampled periods.

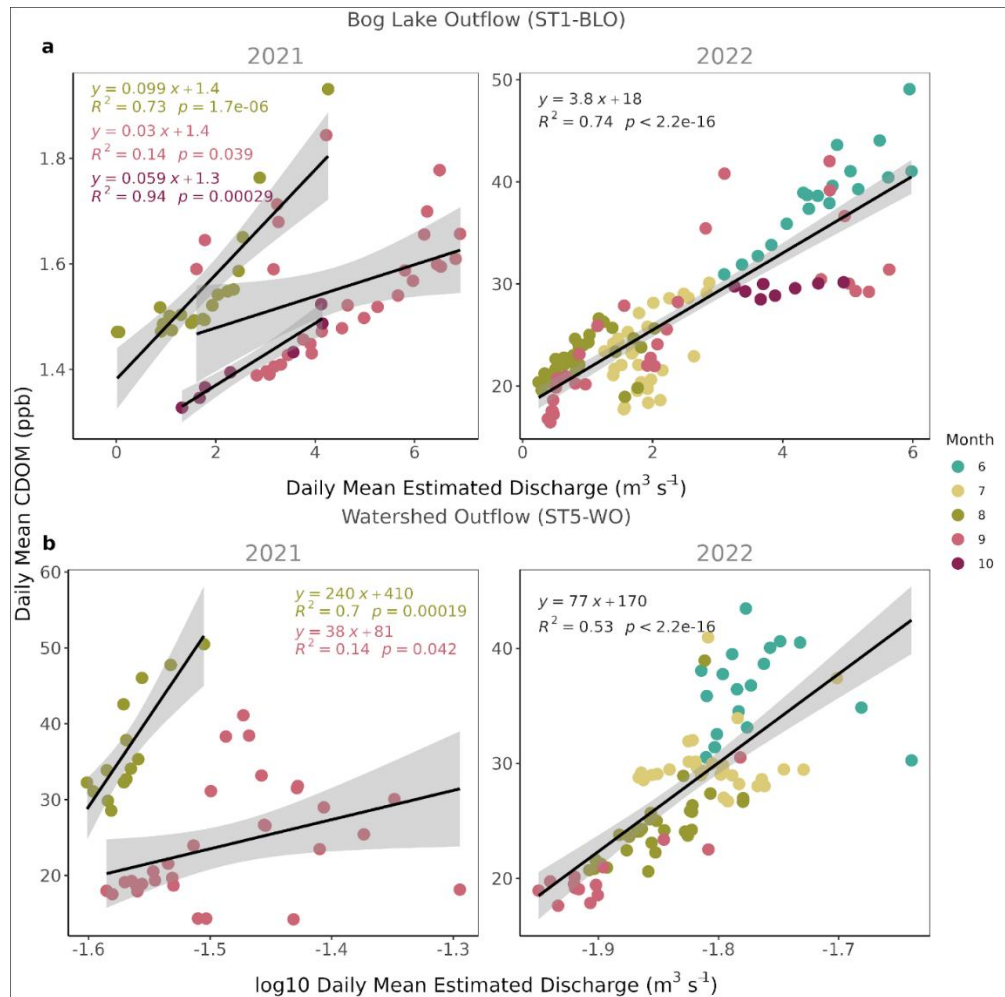


Figure 1.8 Relationships between daily mean CDOM and daily mean discharge at the upstream bog lake outflow (ST1-BLO) and the downstream watershed outflow (ST5-WO) during 2021 and 2022. (a) Linear regressions between daily mean CDOM fluorescence and discharge ($m^3 s^{-1}$) for the bog lake outflow, colored by month. (b) Linear regressions between daily mean CDOM fluorescence and $\log_{10}$ -transformed discharge for the watershed outflow, colored by month. Different lines in 2021 represent different hydrological conditions for 2021, whereas in 2022 a single model fit the data in both streams. Shaded bands represent 95% confidence intervals.

Watershed-scale export of DOC for the Bernard River watershed ($g \text{ DOC-C } m^{-2} \text{ yr}^{-1}$) was calculated using the following equation:

$$C_{export} = \frac{\sum_{i=1}^n [C]_i \times Q_i}{S} \quad (Eq. 1.1)$$

where $[C]_i$ represents DOC concentration (in mg L^{-1}) at time step i , Q_i represents discharge at the watershed outflow in the same time step (in $\text{m}^3 \text{d}^{-1}$), and S represents the watershed surface area (m^2). The sum of all the daily estimates provide the total annual DOC export at the watershed outflow, expressed in $\text{g DOC-C m}^{-2} \text{yr}^{-1}$ of watershed area. It should be noted that the DOC during the measured period was directly derived from continuous CDOM measurements while the unmonitored periods are estimated from discharge measurements using relationships described above.

DIC was also measured in order to quantify DIC export at the watershed outflow, however, there are no continuous measurements analogous to our estimated DOC export. DIC concentrations at the watershed outflow were measured from discrete samples for each sampling occasion in 2021 and 2022 ($n = 6$) using the same laboratory analyses for DOC (please refer to 1.2.2 Laboratory Analyses). Average DIC concentrations at the watershed outflow in the Bernard River watershed (ST5-WO) were multiplied by the annual discharge at the watershed outflow to derive the DIC export. This was upscaled to an entire calendar year and divided by the watershed area to derive the DIC export in $\text{g DIC-C m}^{-2} \text{yr}^{-1}$.

1.2.5 Stream and lake CO_2 and CH_4 emissions at the watershed scale

To quantify CO_2 and CH_4 emissions at the watershed scale for streams: we continuously monitored CO_2 using CO_2 probes (GMP343, Vaisala, Finland) in select first- to fifth-order streams (including the watershed outflow, ST5-WO, and the bog lake outflow, ST1-BLO, $n = 7$, Fig. 1.15); and additionally collected discrete samples of CO_2 and CH_4 at each site for each sampling occasion in 2021 and 2022 ($n = 41$) and concentrations were determined at the UQAM GRIL Laboratory using the same procedures mentioned in section 1.2.2. *Laboratory Analyses*.

Diffusive air-water fluxes of CO_2 and CH_4 were estimated for each sampling occasion using Fick's Law of diffusion, according to the equation:

$$F_{gas} = k_{gas} \times \Delta_{gas} \quad (Eq. 1.2)$$

where F_{gas} is CO_2 (F_{CO_2}) or CH_4 (F_{CH_4}) flux ($\text{mmol m}^{-2} \text{d}^{-1}$), k_{gas} is the gas transfer coefficient (m d^{-1}) adjusted for a given temperature, and Δ_{gas} is the concentration gradient of CO_2 or CH_4 from equilibrium with the

atmosphere (Δ_{CO_2} , Δ_{CH_4} , mmol m⁻³). Measured $p\text{CO}_2$ and $p\text{CH}_4$, were converted to concentrations using temperature corrected Henry's law constants.

For streams, k_{CO_2} and k_{CH_4} were estimated for each sampling occasion, from modeled standardized gas transfer coefficients (k_{600}) values following Raymond et al. (2012) equation 6 (equation 1.3 below):

$$k_{600} = 929 (\pm 141) \times (VS)^{0.75 \pm 0.027} \times Q^{0.011 \pm 0.016} \quad (\text{Eq. 1.3})$$

where V is stream water velocity (m s⁻¹), S is slope (unitless), and Q is discharge (m³ s⁻¹). Velocity was calculated following Casas-Ruiz et al. (2021) model, where flow velocity (m s⁻¹) was calculated using empirical relationships based on 173 streams and rivers across Quebec:

$$\ln V = 1.578 + (0.866 \times \ln Q) - (1.419 \times \ln W) \quad (\text{Eq. 1.4})$$

where V is velocity (m s⁻¹), Q is discharge (m³ s⁻¹), and W is stream width (m).

k_{600} was converted to gas-specific values using Schmidt numbers following (Jähne et al., 1987; Wanninkhof, 1992), assuming $n = 0.5$ (equation 1.5; Goldenfum, 2010):

$$k_{\text{CO}_2(\text{CH}_4)} = k_{600} \times \left(\frac{Sc_{\text{CO}_2(\text{CH}_4)}}{600} \right)^n \quad (\text{Eq. 1.5})$$

To scale fluxes to the entire watershed, monthly $p\text{CO}_2$ and $p\text{CH}_4$ values were averaged by stream order and assigned to all streams by their stream order; an average k_{gas} value was assigned by stream order; fluxes were then calculated (following equation 1.2, above) and multiplied by 212 days (assuming an ice-free period of 212 days); the sum of all the fluxes were calculated and divided by the watershed area (expressed as g C m⁻² yr⁻¹ of watershed area).

For lakes, diffusive fluxes of CO₂ and CH₄ were directly measured using a floating chamber connected to an Ultraportable Greenhouse Gas Analyzer (UGGA; Los Gatos Research, Inc., USA) for lakes within the Bernard River watershed and the regional La Romaine River watershed ($n = 78$ lakes). Fluxes were calculated from the linear change in gas concentrations of CO₂ and CH₄ in the chamber headspace over

time. For each site, a single chamber measurement was performed and fluxes were calculated according to the ideal gas law:

$$F = S \times 10^{-6} \times \frac{P \times V}{R \times T_{air\ chamber} \times A} \quad (Eq. 1.6)$$

where S is the temporal slope of CO_2 and CH_4 accumulation in the chamber over time ($ppm\ s^{-1}$); P is the atmospheric pressure (Pa); V is the total chamber and tubing volume (m^3); R is the ideal gas constant ($8.314\ Pa\ m^3\ K^{-1}\ mol^{-1}$); $T_{air\ chamber}$ is the air temperature within the chamber (K); A is chamber footprint area (m^2); and this is converted from seconds to days and mol to mmol.

To scale fluxes to the entire watershed, lakes within the watershed were categorized into 2 bins – small (lake area $< 4\ km^2$), and large lakes (lake area $> 4\ km^2$); average fluxes per lake size category were assigned to all the lakes within the watershed according to their lake size bin; lake fluxes were then multiplied by their lake surface area and multiplied by 212 days (assuming an ice-free period of 212 days); these fluxes were then summed for all of the lakes and divided by the watershed area to derive lake CO_2 and CH_4 fluxes in $g\ C\ m^{-2}\ yr^{-1}$ of watershed area.

1.2.6 Sediment C burial

Sediment carbon burial was estimated from sediment cores collected from 6 different lakes of varying size within the Bernard River watershed ($n = 3$) and the greater La Romaine River watershed ($n = 3$), using a gravity corer (NLA, Aquatic Research Instruments) with a 6.8 cm ID Plexiglass tube. Retrieved cores were sectioned at 1 cm intervals. Chronologies were established using gamma spectroscopy (^{210}Pb dating) at the Paleoecological Environmental Assessment and Research Laboratory (PEARL laboratory, Queen's University, Canada), with sediment accumulation rates modeled using the constant rate of supply (CRS) method (Baud et al., 2021). Elemental carbon and nitrogen concentrations were determined by combustion analysis on a Carlo Erba CN2500 analyzer (Hassan et al., 1997). Prior to OC analysis, samples were treated with 12 M HCl for 24 hours to remove carbonates (Meyers & Teranes, 2002). Inorganic C was calculated by difference, and molar C:N and OC:N ratios were computed. Cores were dated to derive historical burial rates and burial rate reconstructions retained all records between 1980s-2010s. Sediment layers younger than ten years were excluded from the analyses due to rapid loss of OC that happens within the first 10 years (Gälman et al., 2008).

The C and OC burial rates (*CBR* and *OCBR*; g C m⁻² yr⁻¹) were calculated as:

$$CBR = MAR \times \%Carbon \quad (Eq. 1.7)$$

where *MAR* is the mass accumulation rate (g of dry sediment m⁻² yr⁻¹) and *%Carbon* is the percentage of C or the percentage of OC.

The CBR and OCBR were corrected for the effect of sediment focusing (or sediment redistribution) to reflect whole-lake burial rates following Engstrom & Rose (2013). Sediment Focusing factors (*FF*) were determined by comparing measured sedimentary ²¹⁰Pb inventories (Bq m⁻² yr⁻¹) with expected atmospheric deposition estimated with local precipitation (eq 1.8 and eq. 1.9; Appleby, 2002).

$$^{210}Pb \text{ atmospheric fluxes} = \frac{100 \text{ Bq m}^{-2}}{1000 \text{ mm precipitation}} \times \frac{1}{\lambda(y)} \quad (Eq. 1.8)$$

$$FF = \frac{\text{sediment core } ^{210}Pb \text{ fluxes}}{\text{atmospheric } ^{210}Pb \text{ fluxes}} \quad (Eq. 1.9)$$

To quantify C burial for all the lakes within the Bernard River watershed, we categorized our six lake cores by lake size (bin = 2, lakes < 4 km² and lakes > 4 km²). Average C burial was calculated from our cored lakes using the equations above and values were assigned to all lakes within the Bernard River watershed according to their assigned size distribution (lakes < 4 km², n = 56; lakes > 4 km², n = 1). Lake Bernard represented the only large lake according to our size distribution within in our study (4.38 km²). Carbon burial rates were multiplied by their lake surface area (km²) and summed to retrieve a total C burial rate for the ensemble of lakes within the Bernard River watershed. This was normalized to the Bernard River watershed catchment surface area to be expressed in g C m⁻² yr⁻¹.

1.3 Results

1.3.1 Discharge

Discharge (m³ s⁻¹) was measured at seven sites within the Bernard River watershed during the 2021 and 2022 field seasons (Fig. 1.9). Time series represent hourly discharge estimates derived from pressure

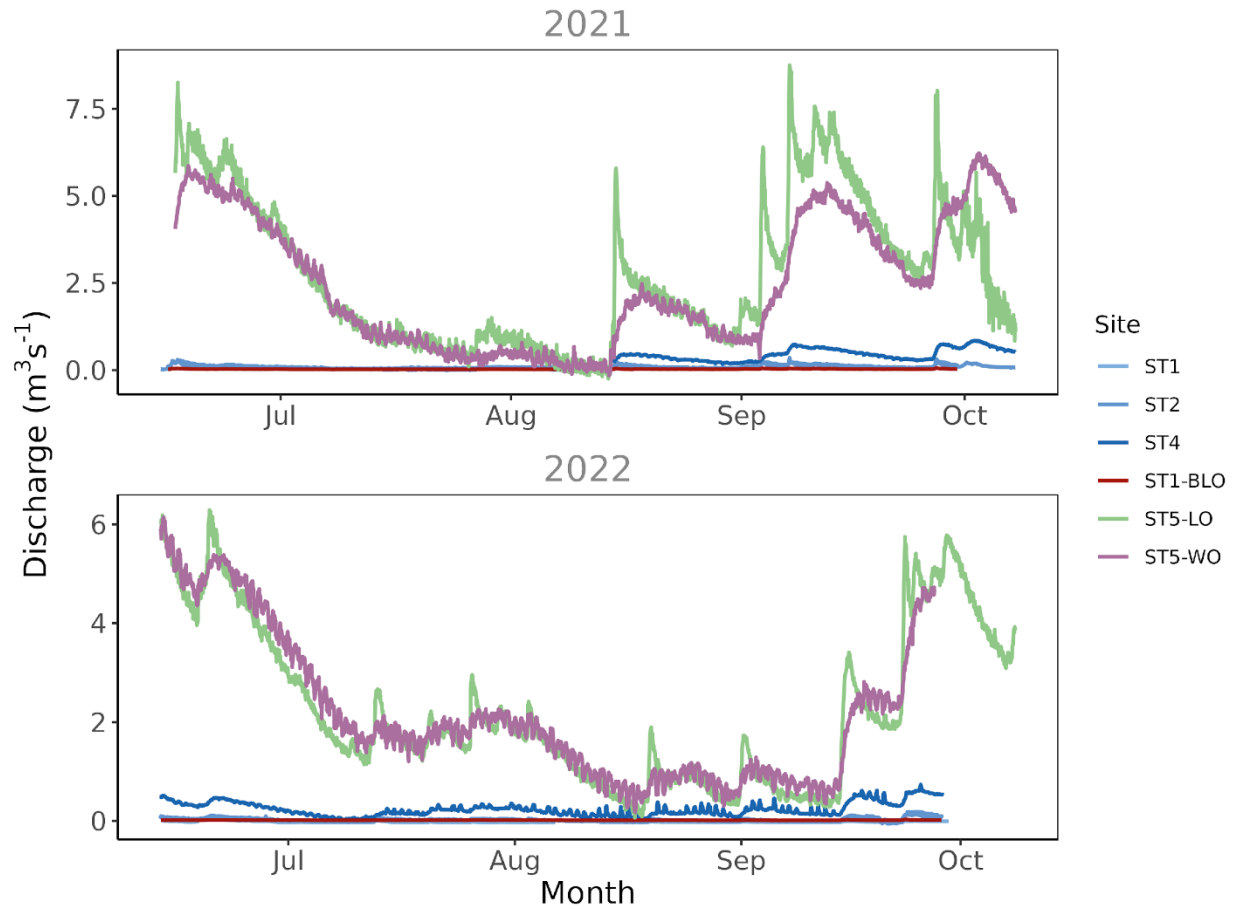


Figure 1.9 Seasonal discharge dynamics across the sampled boreal stream network during the 2021 and 2022 open-water seasons. Hourly discharge ($\text{m}^3 \text{s}^{-1}$) is shown for six monitoring sites spanning first- to fifth-Strahler order streams (ST1, ST2, ST4, ST1-BLO, ST5-LO, ST5-WO).

sensors and stage–discharge rating curves at first-order (ST1, ST1-BLO), second-order (ST2), fourth-order (ST4), and fifth-order (ST5-LO, ST5-WO) streams. It should be noted that one site was removed due to its intermittent behavior. We measured discharge over a total of 234 days (2021: 116d, 2022: 118d). Both years show characteristic early-season recession from snowmelt-driven high flows, punctuated by short-duration hydrologic pulses associated with summer and early-autumn precipitation events. Fifth-order sites displayed the greatest magnitude and variability in discharge ($2.43 \pm 1.79 \text{ m}^3 \text{s}^{-1}$), while first- and second-order streams remained near baseflow for most of the year ($0.04 \pm 0.03 \text{ m}^3 \text{s}^{-1}$). Interannual patterns reveal reduced early-season flow in 2022 compared to 2021, but similar late-season storm-driven increases (Fig. 1.9).

Using the regional hydrological context, continuous daily discharge was reconstructed for both the bog lake outflow (ST1-BLO) and the integrated watershed outflow (ST5-WO) for the 2021 and 2022 hydrological years (Fig. 1.10 and 1.11). Estimated discharge captured the dominant seasonal structure observed in regional rivers, including elevated spring flows, prolonged summer low-flow conditions, and renewed discharge variability in autumn. Where direct measurements were available, observed discharge closely followed the estimated seasonal trajectory, particularly during summer and fall, supporting the validity of the regional scaling approach. At both sites, measured values generally fell within the uncertainty bounds of the estimated discharge, with the largest discrepancies occurring during peak spring flows. Discharge magnitude differed between sites, reflecting contrasting hydrological integration.

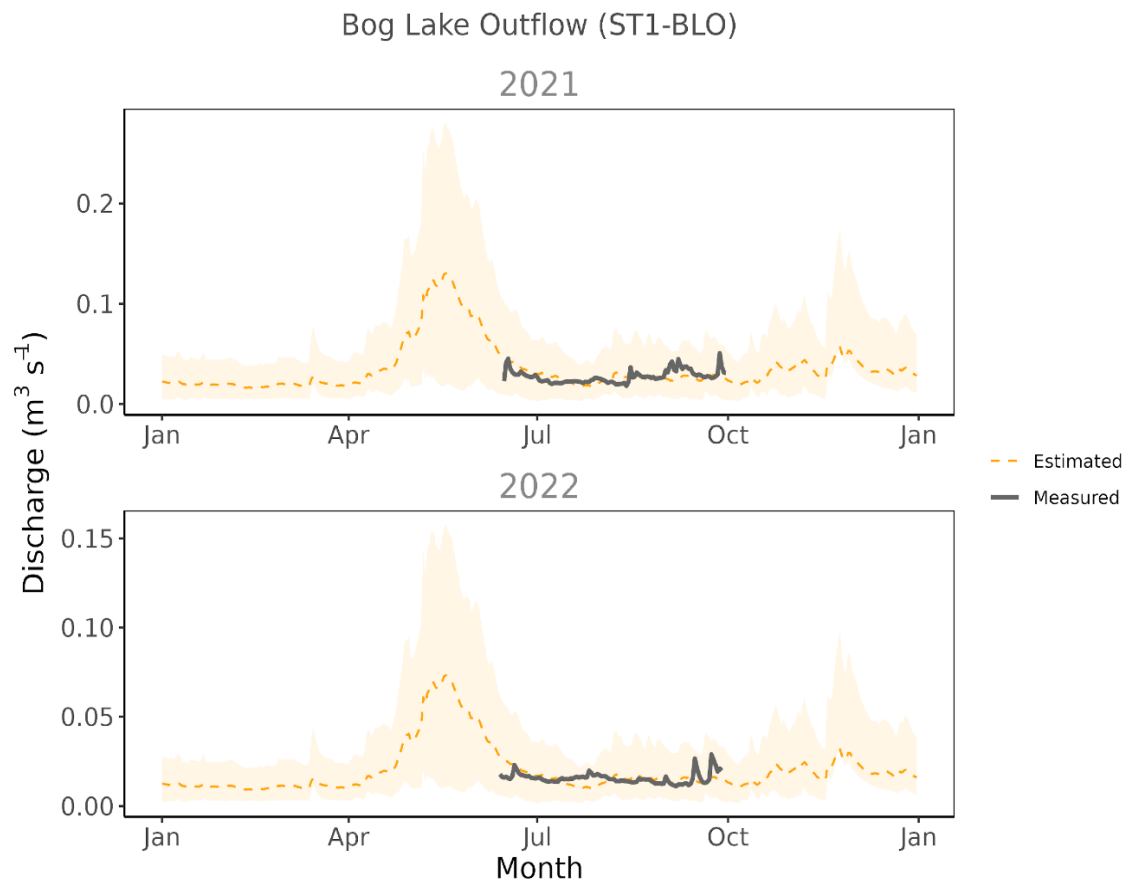


Figure 1.10 Measured discharge at the bog lake outflow (ST1-BLO; solid black line) with regionally estimated discharge derived from hydrometric records (Hydro-Québec; dashed orange line) for 2021 and 2022. Shaded areas represent the uncertainty bounds of the regional discharge estimate.

Bog Lake outflow exhibited low absolute discharge and muted variability, with spring freshet peaks one to two orders of magnitude lower than those observed at the watershed outflow (Fig. 1.10). In contrast, watershed outflow showed amplified discharge responses and greater event-scale variability, consistent with cumulative upstream contributions (Fig. 1.11). Discharge in the Bernard River watershed outflow showed pronounced interannual variability, with high-flow events exceeding $5.5 - 8 \text{ m}^3 \text{ s}^{-1}$ during spring snowmelt and storm events in fall (Fig. 1.11). Across the 2021-2022 record, daily discharge at the watershed outflow averaged at $3.73 \pm 2.80 \text{ m}^3 \text{ d}^{-1}$, while 2022 exhibited a lower-than-average mean discharge of $3.01 \pm 2.25 \text{ m}^3 \text{ d}^{-1}$ (Fig. 1.11). Total annual discharge at the watershed outflow averaged $1230.36 \pm 184.68 \text{ m}^3 \text{ yr}^{-1}$ over 2021-2022.

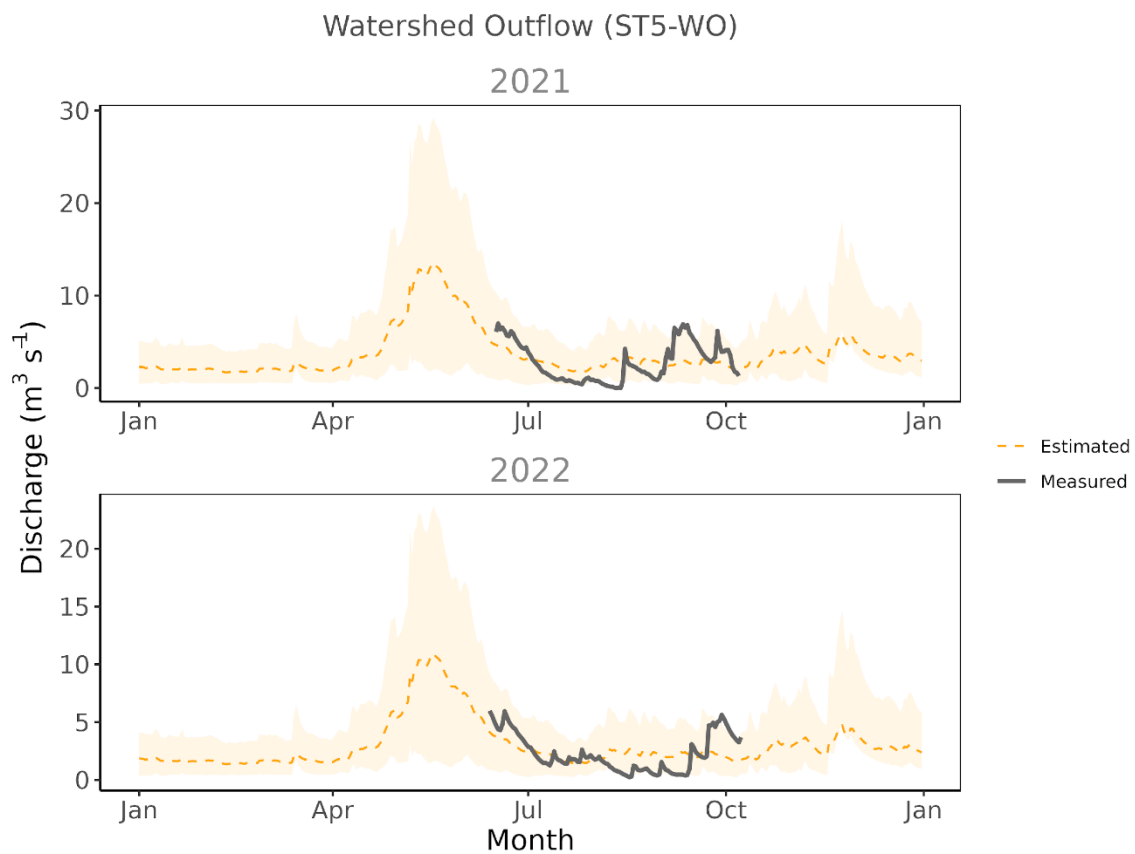


Figure 1.11 Measured discharge at the watershed outflow (ST5-WO; solid black line) with regionally estimated discharge derived from hydrometric records (Hydro-Québec; dashed orange line) for 2021 and 2022. Shaded areas represent the uncertainty bounds of the regional discharge estimate.

Together, these results demonstrate that regional river discharge records effectively constrain the seasonal hydrological regime of the study watershed and enable reconstruction of a complete hydrological year. This reconstructed discharge time series provides the foundation for subsequent analyses of seasonal and annual fluxes, allowing biogeochemical rates and exports to be interpreted within a continuous hydrological framework.

1.3.2 CDOM and DOC

Field grab samples confirmed a strong relationship between optically derived CDOM (4.56 ± 1.94 absorbance at 440 nm; abs_{440}) and DOC concentrations across all sampling sites (7.44 ± 2.69 g DOC-C mg L^{-1} , Fig. 1.6a). DOC increased linearly with CDOM absorbance, explaining a substantial proportion of observed variability ($R^2 = 0.85$, $p < 0.0001$). The strong agreement between laboratory calibration and field observations supports the use of continuous CDOM sensor data to resolve high-frequency DOC dynamics.

Laboratory calibration of the C-FLUOR loggers demonstrated a strong and highly significant linear relationship between sensor-reported CDOM (ppb) and measured dissolved organic carbon (DOC; mg L^{-1}) across all calibration runs and instruments (Fig. 1.6b). The combined calibration yielded a consistent slope with high explanatory power ($R^2 = 0.96$, $p < 0.0001$), indicating minimal inter-sensor variability and strong reproducibility among calibration runs. Calibration points spanned the full range of DOC concentrations observed in the field ($11 - 22 \text{ mg L}^{-1}$), supporting the applicability of the calibration across both low- and high-DOC conditions encountered in the study watershed.

Continuous CDOM fluorescence measurements revealed pronounced temporal variability at both the bog lake outflow (ST1-BLO) and the watershed outflow (ST5-WO) during the sample periods of 2021 and 2022 (Fig. 1.7a–b). At both sites, CDOM concentrations exhibited sharp, short-duration increases superimposed on a gradual seasonal decline from mid-summer into early autumn. These episodic peaks were more frequent and of greater magnitude at the watershed outflow, whereas CDOM dynamics at the bog lake outflow were comparatively dampened, reflecting differences in hydrological integration and upstream source complexity.

Applying the empirically derived CDOM–DOC relationships (Fig. 1.6b) to the continuous sensor records yielded high-resolution estimates of DOC concentrations (Fig. 1.7c–d). Estimated DOC closely tracked observed CDOM dynamics, capturing both event-scale pulses and longer-term seasonal trends (when

correction factor was included). In both years, estimated DOC concentrations declined through the summer low-flow period and increased episodically during hydrological events, with higher absolute concentrations and variability at the watershed outflow relative to the bog lake outflow. Interannual differences were evident, with lower peak DOC concentrations and reduced variability in 2022 compared to 2021, consistent with the attenuated hydrological regime observed during that year.

Discrete grab samples collected concurrently with sensor deployment aligned well with the estimated DOC time series and generally fell within the temporal period of sensor-derived values (Fig. 1.7c–d). This agreement supports the applicability of the calibration and field relationships for translating continuous CDOM observations into DOC concentrations across sites and years. Together, these results demonstrate that calibrated CDOM sensors provide a robust basis for resolving high-frequency DOC dynamics, enabling subsequent analyses of event-driven and seasonal carbon export.

Daily mean CDOM concentrations exhibited a positive relationship with discharge at both the bog lake outflow (ST1-BLO) and the watershed outflow (ST5-WO, Fig. 1.8), although the strength and form of this relationship varied seasonally and between years. In 2021, CDOM at the bog lake outflow increased with discharge, with statistically significant relationships during early and mid-summer months and weaker or more variable responses later in the season. This is likely due to a smaller sample size as sensors were not deployed until the summer campaign in 2021 as there was a delay in shipment. Monthly regressions revealed pronounced differences in slope magnitude, indicating that CDOM sensitivity to discharge was highest during periods of elevated connectivity between the bog and downstream channel network.

At the watershed outflow, CDOM–discharge relationships were stronger and more consistent than at the bog lake outflow in 2021. Daily mean CDOM increased markedly with discharge across the observed range, particularly at lower flows, with diminishing sensitivity at higher discharge. Log-transformed discharge further highlighted this nonlinear response, with steeper CDOM increases occurring under low-to-moderate flow conditions and reduced incremental changes at higher flows, consistent with progressive source exhaustion or mixing effects.

In 2022, CDOM–discharge relationships were stronger and more coherent at both sites. At the bog lake outflow, CDOM scaled positively with discharge across the full seasonal range, explaining a substantial proportion of observed variability. Similarly, at the watershed outflow, CDOM increased linearly with discharge, with higher explanatory power than in 2021 and reduced scatter among months. Seasonal

clustering of data indicated that early-season flows were associated with higher CDOM concentrations for a given discharge relative to late-season conditions, reflecting temporal shifts in source availability and hydrological connectivity. Overall, these results demonstrate that discharge exerts a primary control on CDOM dynamics across spatial scales, while seasonal variability modulate the magnitude of CDOM response.

1.3.3 Carbon Export

Estimated DOC export exhibited strong temporal variability at both the bog lake outflow and the watershed outflow, with pronounced differences between sites and years (Fig. 1.12 and 1.13). At the bog lake outflow, DOC export during the late summer and early autumn of 2021 was characterized by elevated values early in the observation period, followed by a gradual decline punctuated by short-lived export pulses (Fig. 1.12). Peak DOC export exceeded $0.06 \text{ g m}^{-2} \text{ d}^{-1}$ during early September, coinciding with elevated discharge and CDOM concentrations, before declining toward October as flows and DOC concentrations decreased. In contrast, DOC export in 2022 at ST1-BLO was consistently lower than 2021 ($0.037 \pm 0.016 \text{ g m}^{-2} \text{ d}^{-1}$), rarely exceeding $0.03 \text{ g m}^{-2} \text{ d}^{-1}$, and exhibited reduced variability through the season ($0.018 \pm 0.007 \text{ g m}^{-2} \text{ d}^{-1}$) (Fig. 1.12).

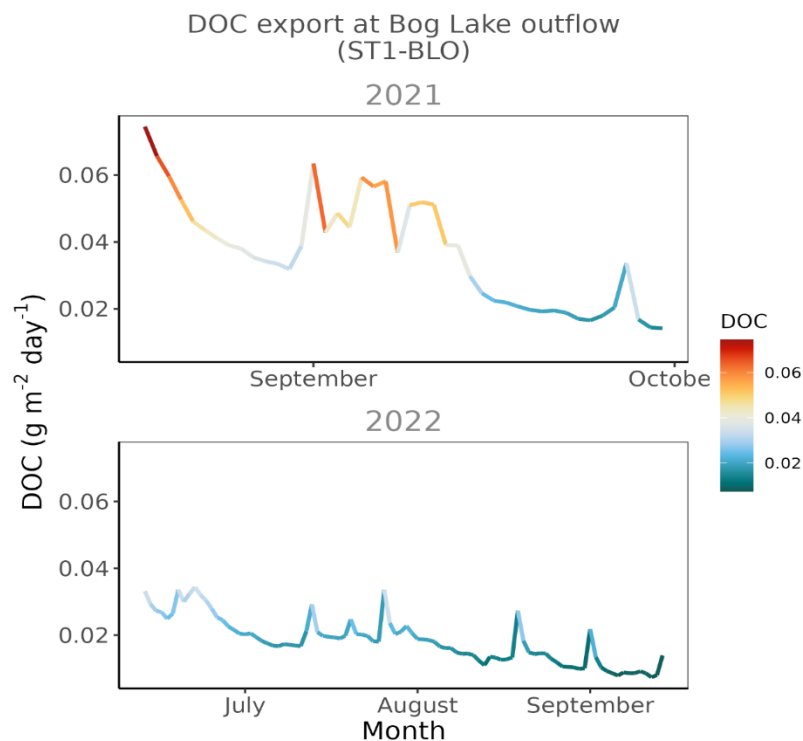


Figure 1.12 Daily DOC export at the bog lake outflow (ST1-BLO) during the 2021 and 2022 monitoring periods. Export ($\text{g m}^{-2} \text{ d}^{-1}$) was calculated from estimated DOC concentrations and measured discharge, with line color indicating DOC export.

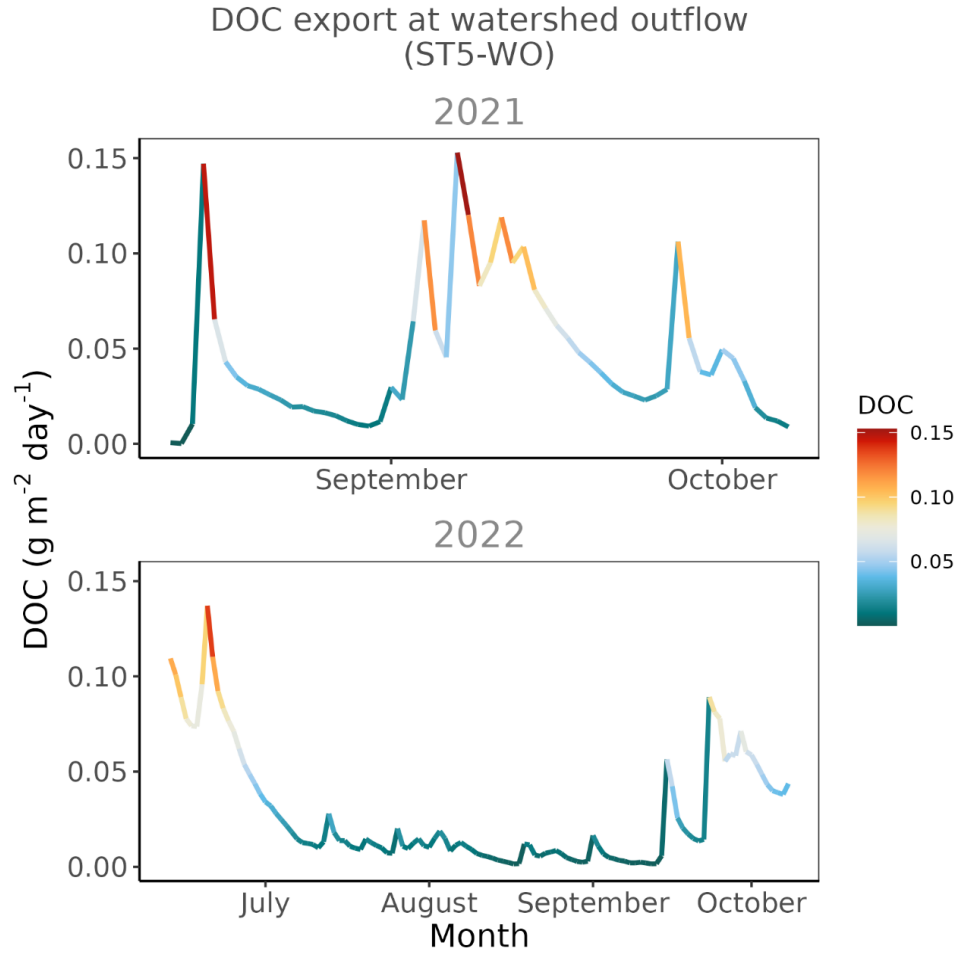


Figure 1.13 Daily DOC export at the watershed outflow (ST5-WO) during the 2021 and 2022 monitoring periods. Export rates ($\text{g m}^{-2} \text{d}^{-1}$) were calculated from estimated DOC concentrations and measured discharge, with line color scaled to DOC export.

At the watershed outflow (ST5-WO), DOC export magnitudes were substantially higher than those observed at the bog lake outflow in both years (Fig. 1.13). In 2021, DOC export showed pronounced event-driven peaks, with maximum values exceeding $0.1 \text{ g m}^{-2} \text{d}^{-1}$ during early and mid-September. These peaks were followed by rapid declines, reflecting the strong coupling between discharge variability and DOC transport at the watershed scale. Between events, DOC export remained elevated, highlighting the cumulative contribution of upstream sources and greater hydrological integration.

In 2022, DOC export at the watershed outflow was lower overall and more episodic than in 2021 (Fig. 1.13). Early summer export was elevated but declined into prolonged low-export conditions through mid-summer, with values frequently below $0.025 \text{ g m}^{-2} \text{d}^{-1}$. Late-season increases in DOC export occurred in response to discrete hydrological events in September and October, although peak magnitudes remained lower ($\sim 0.08 \text{ g m}^{-2} \text{d}^{-1}$) than those observed in the previous year. Across both sites, interannual differences

in DOC export mirrored differences in discharge regimes and CDOM–discharge relationships, with 2021 exhibiting higher export magnitudes and greater variability than 2022.

Collectively, these results demonstrate that DOC export is strongly modulated by hydrological conditions and site-specific integration. Event-scale variability dominated DOC export dynamics, particularly at the watershed scale, underscoring the importance of high-frequency discharge and DOC estimates for resolving carbon export patterns in boreal aquatic networks.

Reconstruction of continuous annual discharge using regional river hydrographs enabled estimation of full-year DOC export at both the bog lake outflow (ST1-BLO) and the watershed outflow (ST5-WO), including periods without direct discharge measurements (Fig. 1.14). At both sites, reconstructed discharge captured the dominant hydrological features of the year, most notably the spring freshet and lower baseflow, allowing DOC export to be resolved across hydrologically distinct seasons.

At the watershed outflow, reconstructed DOC export was dominated by the spring freshet, during which export rates increased sharply and exceeded $0.2 \text{ g C m}^{-2} \text{ d}^{-1}$. This short period contributed a disproportionate fraction of the annual DOC export (8.69 g C m^{-2} for the entire period), while extended summer baseflow was associated with comparatively low export rates, frequently below $0.02 \text{ g C m}^{-2} \text{ d}^{-1}$ (total of 3.33 g C m^{-2} during the measured period). During periods when discharge was directly measured, estimated DOC export closely tracked measured export, supporting the consistency between reconstructed and observed hydrological conditions. Combining the monitored and reconstructed periods yields a total export of $14.64 \text{ g C m}^{-2} \text{ yr}^{-1}$ from the watershed outflow in 2022. Final results from 2021 are not included in the estimates due to the uncertainty of the models.

At the bog lake outflow, reconstructed DOC export displayed a similar seasonal pattern but with lower absolute magnitude and reduced variability within the measured period. Peak export during the spring freshet approached $0.3 \text{ g C m}^{-2} \text{ d}^{-1}$ (total of 9.74 g C m^{-2} during this period), followed by a rapid transition to low and relatively stable export during summer and early autumn ($0.017 \pm 0.007 \text{ g C m}^{-2} \text{ d}^{-1}$, total of 1.72 g C m^{-2} during this period). Measured export during the summer period aligned with reconstructed values, indicating that regional discharge scaling effectively captured site-level hydrological forcing at the bog lake outflow. With the measured and estimated DOC, a total of $11.47 \text{ g C m}^{-2} \text{ yr}^{-1}$ was exported out of the bog lake outflow.

Across both sites, reconstructed periods (estimated discharge) and observed periods (measured discharge) exhibited coherent transitions in DOC export, with no abrupt discontinuities at the boundaries between measured and estimated intervals. This continuity supports the use of regional hydrographs to extend site-specific observations to the annual scale. Overall, these results demonstrate that hydrological reconstruction is essential for resolving annual DOC export, and that a small number of high-flow events account for a substantial portion of annual DOC export at both local and watershed scales.

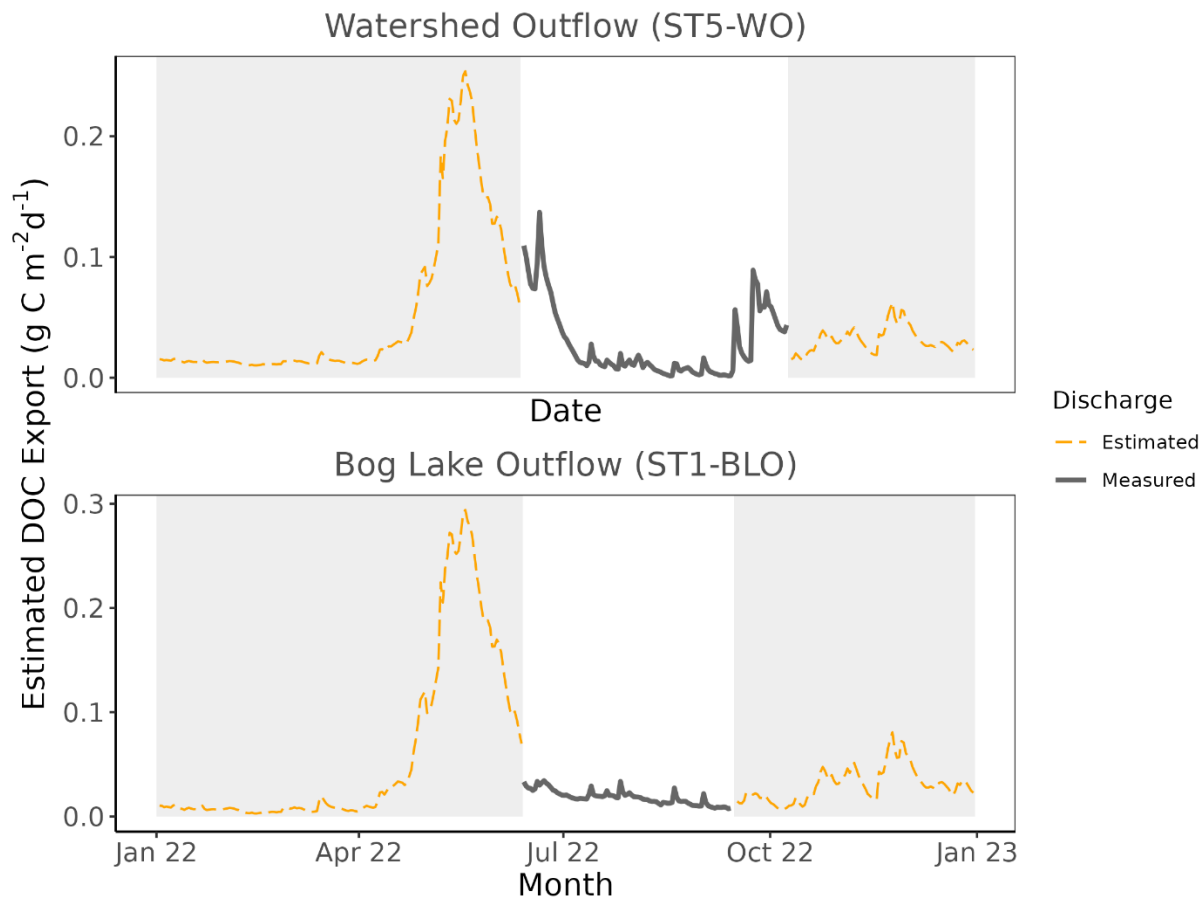


Figure 1.14 Estimated daily DOC export at the watershed outflow (ST5-WO; top) and bog lake outflow (ST1-BLO; bottom) for 2022. Solid black lines represent DOC export calculated using measured discharge and CDOM, while dashed orange lines represent DOC export estimated using regional hydrographs during periods without local measurements. Grey shaded regions indicate periods of missing discharge data.

To complete the C export pathway, DIC was also measured at the watershed outflow, however, it is only reported as a single annual estimate due to the lack of continuous measurements of DIC. DIC concentrations were measured from discrete samples for each sampling occasion in 2021 and 2022 ($n = 6$) to derive average DIC concentrations at the watershed outflow (ST5-WO). They were multiplied by the

annual discharge at the watershed outflow to derive the DIC export. This was upscaled to an entire calendar year and divided by the watershed area to derive a total DIC export of $3.83 \text{ g DIC-C m}^{-2} \text{ yr}^{-1}$.

1.3.4 CO₂ and CH₄ - Streams

Continuous $p\text{CO}_2$ measurements revealed substantial spatial and temporal variability across streams within the watershed during the ice-free periods of 2021 and 2022 (Fig. 1.15). Across all sites, $p\text{CO}_2$ values were consistently supersaturated relative to the atmosphere ($412 \text{ } \mu\text{atm}$), indicating persistent net CO₂ efflux potential from lotic environments. However, the magnitude and variability of $p\text{CO}_2$ differed markedly among site types and between years.

Headwater and upstream stream sites (ST1, ST2.1, ST2.2; first- and second-order channels) exhibited elevated $p\text{CO}_2$ values, with mean values typically exceeding $750\text{--}1200 \text{ } \mu\text{atm}$ and frequent short-term events above these levels. Variability at these sites were pronounced, with fluctuations occurring over sub-weekly timescales, particularly during mid- to late summer. Among these, ST2.2 consistently showed the highest $p\text{CO}_2$ levels, with sustained concentrations above $1000 \text{ } \mu\text{atm}$ in both years and episodic peaks approaching or exceeding $1500 \text{ } \mu\text{atm}$. In contrast, downstream stream sites (ST4, ST5-LO, ST5-WO) displayed lower mean $p\text{CO}_2$ values, generally ranging between 500 and $700 \text{ } \mu\text{atm}$, and exhibited comparatively reduced temporal variability.

The Bog Lake outflow site (ST1-BLO) was characterized by consistently higher $p\text{CO}_2$ than most stream reaches. ST1-BLO exhibited the highest $p\text{CO}_2$ values across the network, with mean concentrations exceeding $2400 \text{ } \mu\text{atm}$ in both years and frequent peaks above $3000 \text{ } \mu\text{atm}$. These elevated levels persisted throughout the observation period, although short-term variability increased in late summer and early autumn. In contrast, downstream lake and outflow sites (ST5-LO, ST5-WO) showed more moderate but still supersaturated $p\text{CO}_2$, with mean values near $600 \text{ } \mu\text{atm}$.

Interannual differences were evident across several sites. In 2022, $p\text{CO}_2$ variability increased at multiple locations, particularly at ST1-BLO, where higher peak values and greater short-term fluctuations were observed relative to 2021. Mean $p\text{CO}_2$ levels at higher stream order sites remained relatively stable between years, with only minor shifts in central tendency. Across the network, no abrupt discontinuities in $p\text{CO}_2$ were observed within seasons, indicating coherent temporal dynamics rather than isolated measurement artifacts.

Overall, these results demonstrate strong spatial structuring of $p\text{CO}_2$ across the watershed, with consistently higher concentrations in headwater streams and bog-influenced waters relative to higher stream order sites. The pervasive supersaturation observed at all sites establishes a robust basis for subsequent estimation of CO_2 evasion fluxes and for comparison with methane emissions across aquatic ecosystem types.

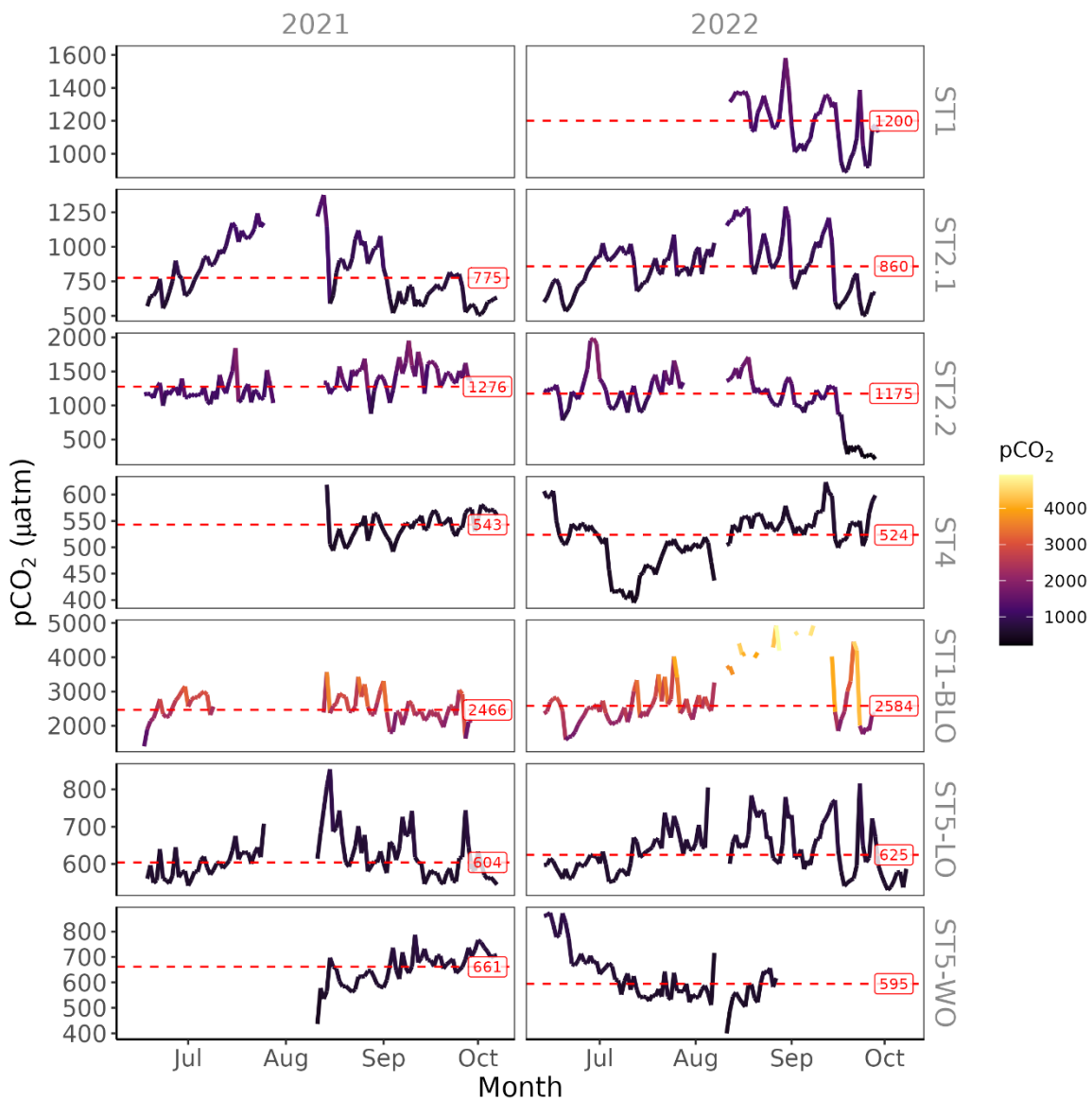


Figure 1.15 Partial pressure of CO_2 ($p\text{CO}_2$, μatm) across seven monitored stream and outflow sites during the 2021 and 2022 field seasons. Sites are ordered from headwaters (ST1, ST2.1, ST2.2) to mid-order streams (ST4) and outflow sites (ST1-BLO, ST5-LO, ST5-WO). Color gradients represent instantaneous $p\text{CO}_2$ values, while red dashed lines and labels indicate site-specific means.

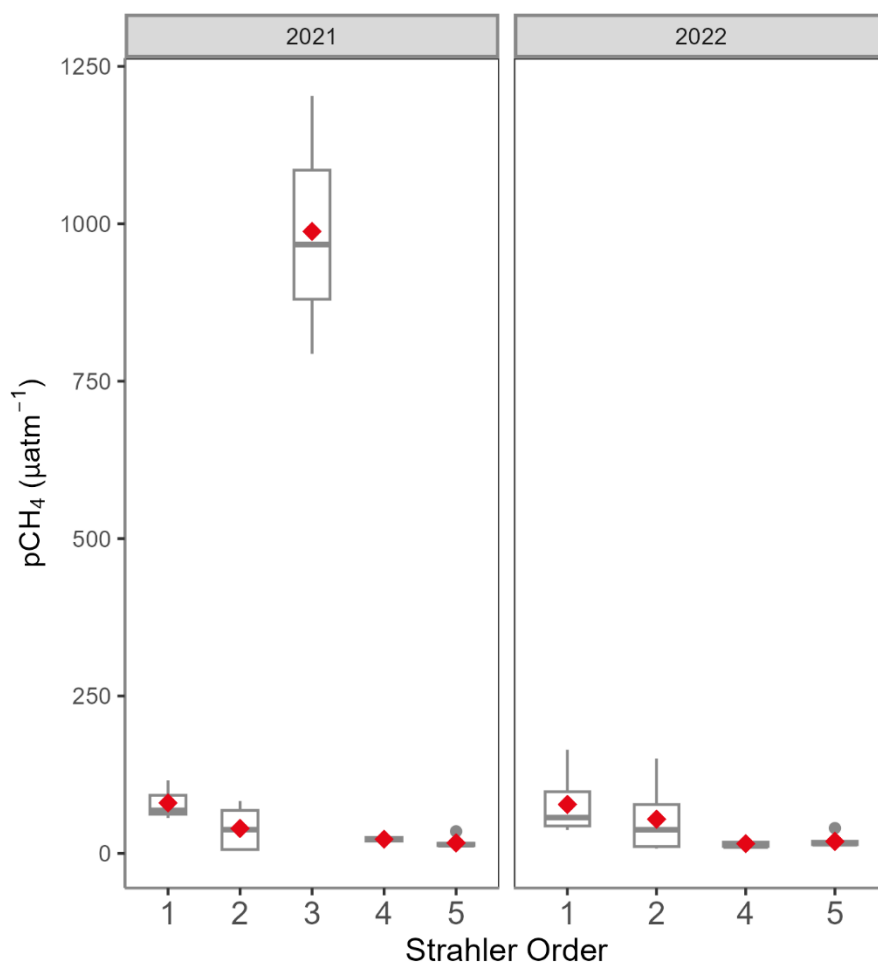


Figure 1.16 Distribution of partial pressure of methane ($p\text{CH}_4$, μatm) across Strahler stream orders during 2021 (left) and 2022 (right). Boxplots display the median and interquartile range for each order and red diamonds indicate mean values.

Partial pressure of methane ($p\text{CH}_4$) exhibited strong spatial structuring across the stream network, with pronounced differences among Strahler orders and between years (Fig. 1.16). It should be noted that $p\text{CH}_4$ samples were collected on a discrete basis during field campaigns - not continuous measurements. In 2021, $p\text{CH}_4$ concentrations were highest in low-order streams, particularly third-order reaches, where values were markedly elevated relative to all other stream orders. This site (stream order 3) had to be later removed in 2022 due to flooding from a downstream beaver pond, which is believed to have caused the elevated $p\text{CH}_4$ observed in 2021. Median $p\text{CH}_4$ at third-order sites approached 1000 μatm , with substantial variability and frequent observations above this level. In contrast, first- and second-order streams exhibited moderate $p\text{CH}_4$ concentrations ($53.2 \pm 39.1 \mu\text{atm}$), while higher-order streams (fourth and fifth order) consistently showed the lowest $p\text{CH}_4$ values ($18.2 \pm 8.94 \mu\text{atm}$).

In 2022, $p\text{CH}_4$ concentrations were generally similar to values measured in 2021 (Fig. 1.16; panel b). First- and second-order streams exhibited modest $p\text{CH}_4$ values, averaging $66.1 \pm 52.4 \mu\text{atm}$, while higher-order reaches again displayed the lowest concentrations ($17.9 \pm 9.52 \mu\text{atm}$). We were unable to measure a strahler order 3 stream in 2022, due to inaccessibility of the stream visited in the prior year.

The $p\text{CH}_4$ values tended to decrease with increasing Strahler order across both years, indicating reduced methane supersaturation in downstream reaches. Red diamonds representing mean $p\text{CH}_4$ further highlight elevated methane concentrations in low-order streams. Together, these results demonstrate that methane dynamics are heterogeneous at the watershed scale, with interannually consistent trends of decreasing methane with stream order.

The estimated gas transfer coefficients (k) for both CO_2 (k_{CO_2}) and CH_4 (k_{CH_4}) varied systematically across Strahler stream order (Fig. 1.17). In both 2021 and 2022, k values increased with stream order, with the lowest transfer velocities observed in first- and second-order streams and progressively higher values in larger downstream reaches. This pattern was consistent for both gases, although the magnitude and variability of k differed between CO_2 and CH_4 . The low k_{CO_2} and k_{CH_4} observed at the stream order 3 site are likely attributable to the beaver pond, which reduces turbulence and gas exchange in the downstream reach.

In 2021, k_{CO_2} exhibited moderate values in low-order streams, averaging at $35.6 \pm 14.6 \text{ m}^{-1} \text{ d}^{-1}$ in first- and second-order reaches, followed by a marked increase in fourth- and fifth-order streams with average k_{CO_2} values at $74.9 \pm 38.6 \text{ m}^{-1} \text{ d}^{-1}$ and increased variability. Fifth-order streams displayed the widest distribution of k_{CO_2} , indicating strong spatial and temporal heterogeneity in gas exchange conditions. In 2022, overall k_{CO_2} values were lower across all stream orders compared to 2021, but the monotonic increase with stream order was preserved. Average k_{CO_2} remained lowest in headwater streams ($20.7 \pm 10.8 \text{ m}^{-1} \text{ d}^{-1}$) and highest in fourth and fifth-order reaches ($60.5 \pm 31.8 \text{ m}^{-1} \text{ d}^{-1}$), with a slight reduction in variability compared to the previous year.

Patterns in k_{CH_4} mirrored those observed for k_{CO_2} but with consistently higher absolute values. In 2021, k_{CH_4} increased sharply from low-order to high-order streams, with average values rising from approximately $29.3 \pm 3.92 \text{ m}^{-1} \text{ d}^{-1}$ in the first-order streams to greater than $101.9 \pm 45.3 \text{ m}^{-1} \text{ d}^{-1}$ in fifth-order reaches. In 2022, k_{CH_4} values were again lower overall but retained the same spatial structure, with higher transfer velocities in larger streams and reduced variability in headwater reaches.

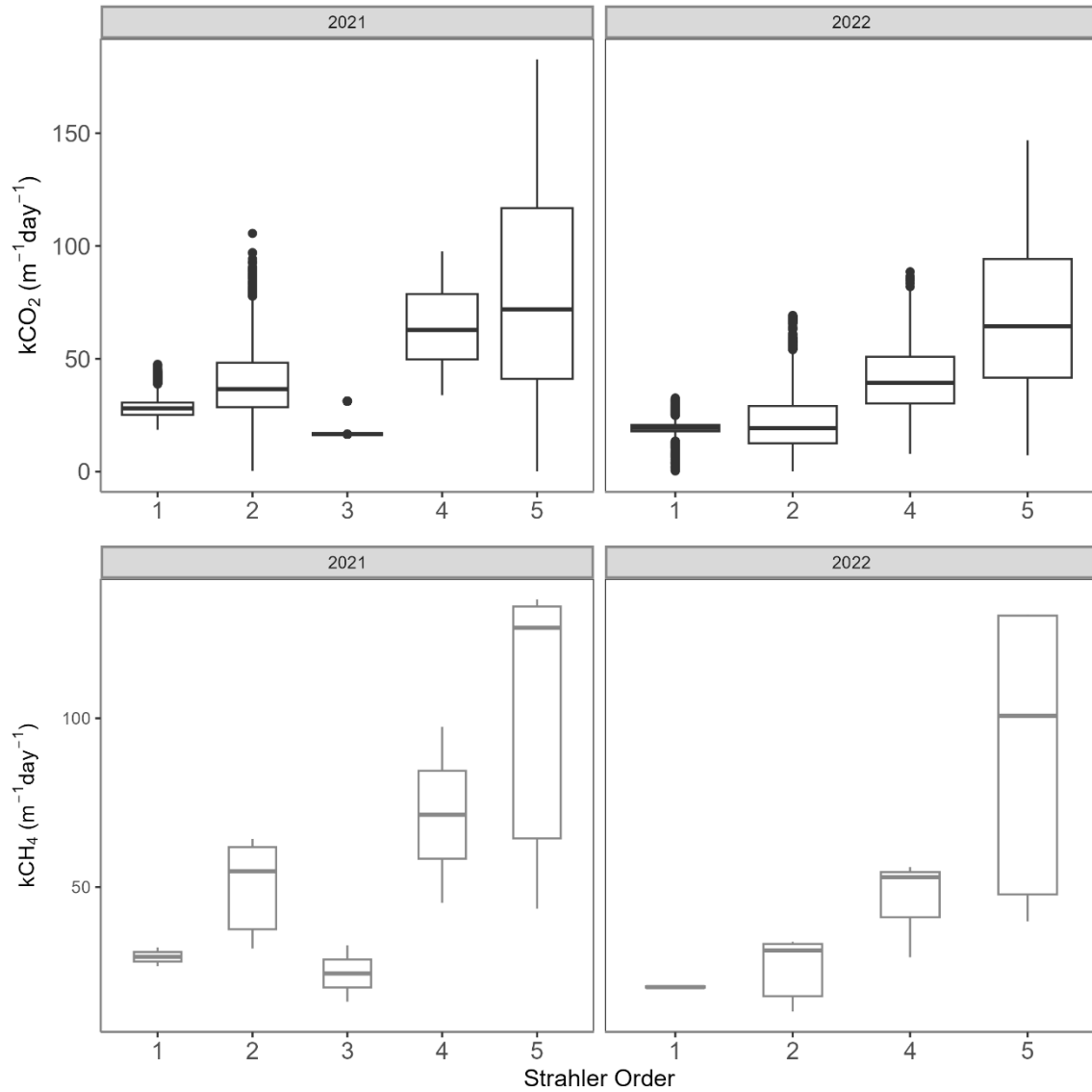


Figure 1.17 Spatial variation in modeled gas transfer velocities ($\text{m}^{-1} \text{d}^{-1}$) for CO_2 (k_{CO_2} ; top panels) and CH_4 (k_{CH_4} ; bottom panels) across Strahler stream orders during 2021 (left) and 2022 (right).

Across both years, k_{CH_4} consistently exceeded k_{CO_2} within the same stream order, reflecting gas-specific differences in transfer dynamics. The strong dependence of gas transfer coefficients on stream order, combined with pronounced interannual variability, highlights the importance of accounting for spatial heterogeneity in k when estimating CO_2 and CH_4 evasion across the watershed.

CO_2 fluxes were first calculated as daily areal fluxes ($\text{g C m}^{-2} \text{d}^{-1}$) for each stream segment. Mean fluxes by stream order were then computed as area-weighted averages across segments, such that each square

meter of stream surface contributed equally to the order-level estimate. Area-weighted and unweighted mean fluxes were nearly identical across stream orders, indicating limited covariance between segment surface area and areal CO₂ flux. Daily mean areal CO₂ fluxes decreased from first-order streams ($26.90 \pm 9.01 \text{ g C m}^{-2} \text{ d}^{-1}$) to fourth-order streams ($3.90 \pm 2.35 \text{ g C m}^{-2} \text{ d}^{-1}$), with intermediate fluxes observed in second-, third-, and fifth-order channels ($10.30 - 10.50 \text{ g C m}^{-2} \text{ d}^{-1}$).

Annual diffusive CO₂ and CH₄ emissions for streams are shown in Figure 1.18 as a function of Strahler stream order for 2021 and 2022. For each stream order, annual emissions were calculated by integrating daily areal fluxes over an ice-free period of 212 days, summing emissions across all stream segments belonging to that order, and normalizing the totals to watershed area. This approach yields watershed-normalized annual fluxes ($\text{g C m}^{-2} \text{ yr}^{-1}$ for CO₂; $\text{mg C m}^{-2} \text{ yr}^{-1}$ for CH₄) representing the contribution of each stream order to the watershed-scale gas budget. In 2021, estimated CO₂ emissions were highest in first-order streams, reaching $5.61 \text{ g C m}^{-2} \text{ yr}^{-1}$, and were lowest in third-order reaches ($0.82 \text{ g C m}^{-2} \text{ yr}^{-1}$). Fifth-order streams exhibited intermediate fluxes ($2.49 \text{ g C m}^{-2} \text{ yr}^{-1}$). The same overall pattern among stream orders was preserved in 2022; however, CO₂ fluxes were generally lower ranging from 0.36 to $2.92 \text{ g C m}^{-2} \text{ yr}^{-1}$.

It is believed that the lower CO₂ and CH₄ fluxes observed in 2022 for the Strahler order 1 stream are attributed to the installation of a new monitoring site that year (ST1; Fig. 1.15), which exhibited lower daily mean $p\text{CO}_2$ than the other headwater site (ST1-BLO), and an intermittent hydrological regime, resulting in reduced annual CO₂ efflux. The stream order 4 site was excluded from the analysis due to

geomorphological characteristics that differed substantially from other fourth-order channels in the watershed, rendering it unrepresentative for this study.

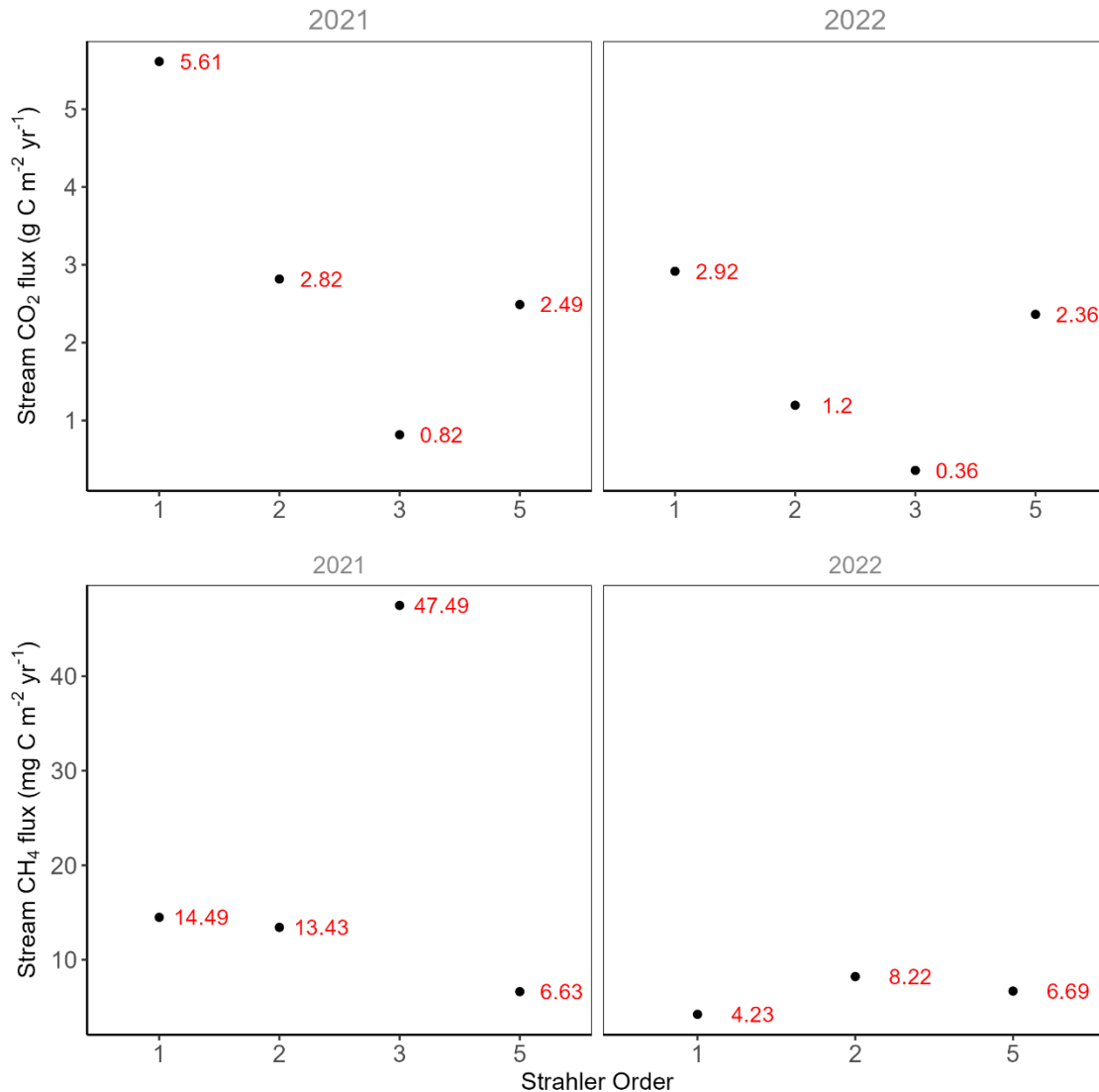


Figure 1.18 Annual diffusive carbon gas fluxes for CO₂ (g C m⁻² yr⁻¹, top panels) and CH₄ (mg C m⁻² yr⁻¹, bottom panels) across Strahler stream orders for 2021 (left) and 2022 (right). Red text indicates the estimated annual mean flux for the stream order.

Annual CH₄ emissions exhibited substantially greater spatial heterogeneity than CO₂ and showed strong interannual variability. In 2021, third-order streams dominated watershed-normalized CH₄ emissions, which emitted 47.49 mg C m⁻² yr⁻¹. First- and second-order streams exhibited intermediate CH₄ fluxes (14.49 and 13.43 mg C m⁻² yr⁻¹, respectively), while fifth-order streams had the lowest fluxes (6.63 mg C m⁻² yr⁻¹). There were no strahler order 3 streams sampled in 2022, regardless, CH₄ emissions were uniformly

lower across all stream orders, ranging from 4.23 to 8.22 mg C m⁻² yr⁻¹. These interannual differences were reflected in the overall average among stream orders of 6.38 mg C m⁻² yr⁻¹ in 2022, compared to 11.52 mg C m⁻² yr⁻¹ in 2021 (average without strahler order 3).

Across both gases, first-order streams consistently contributed disproportionately to the watershed-scale emissions relative to their position in the network, reflecting elevated gas concentrations despite lower transfer velocities (Fig. 1.15 - 1.17). In contrast, higher-order streams exhibited moderate CO₂ fluxes driven by higher gas transfer coefficients but lower *p*CO₂ and *p*CH₄. Interannual variability was more pronounced for CH₄ than CO₂, with a marked reduction in methane emissions in 2022 across all stream orders.

To estimate whole-watershed diffusive emissions from streams, watershed-normalized fluxes (reported in Fig. 1.18) were summed across stream orders and averaged across the 2021-2022 period, yielding mean diffusive emissions of 9.31 g C m⁻² yr⁻¹ for CO₂ and 0.05 g C m⁻² yr⁻¹ for CH₄. Together, these results demonstrate that diffusive greenhouse gas emissions from the stream network are strongly structured by stream order and exhibit strong interannual variability, with distinct spatial patterns for CO₂ and CH₄. These quantified fluxes provide the basis for integrating stream emissions into the watershed-scale carbon budget.

1.3.5 CO₂ and CH₄ - Lakes

Lake surface area within the watershed was strongly right-skewed, with the majority of lakes occupying areas < 0.1 km² and a small number of larger lakes contributing disproportionately to total lake area (Fig. 1.19). This size structure motivated a size-class approach for scaling diffusive greenhouse gas emissions across the lentic network.

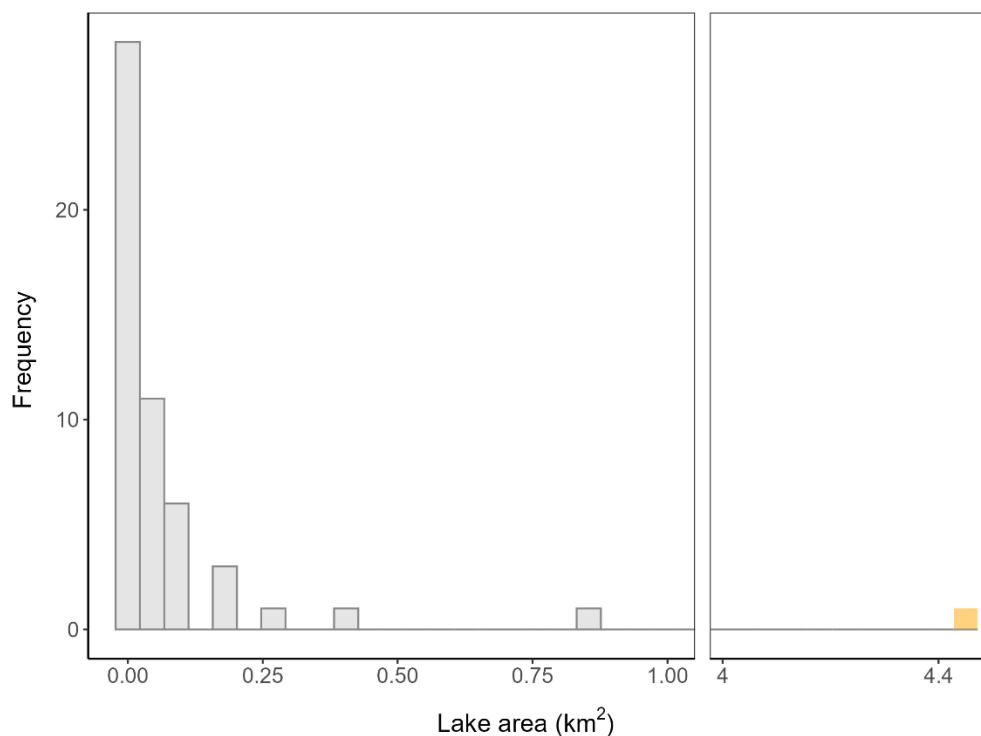


Figure 1.19 Histogram showing the frequency distribution of lake surface area (km²) across all mapped lakes in the watershed. Lake Bernard (highlighted in orange) represents the one larger lake in the watershed (right panel).

Figure 1.20 summarizes areal lake-surface fluxes used for parameterization, whereas watershed-normalized emissions are derived from size-class scaling and reported separately. Annual areal lake CO₂ and CH₄ fluxes (expressed per unit lake surface area) differed markedly in magnitude and variability (Fig. 1.20). CO₂ fluxes spanned more than two orders of magnitude, with small lakes exhibiting high variable emissions. In contrast, CH₄ areal fluxes were consistently lower than CO₂ across all lakes. Lake Bernard fell within the upper range of observed areal fluxes relative to the small-lake distribution.

To scale lake emissions to the Bernard River watershed, mean daily areal fluxes derived from a regional lake dataset were assigned to lake size classes and multiplied by the total lake surface area in each class within the watershed. Fluxes were summed across size classes, integrated over an ice-free period of 212 days, and normalized to total watershed area to yield watershed-normalized annual diffusive emissions (g C m⁻² yr⁻¹ of watershed area for CO₂; mg C m⁻² yr⁻¹ for CH₄). Summed across lakes and averaged across 2021-2022, lakes contributed 27.10 g C m⁻² yr⁻¹ (CO₂) and 68.36 mg C m⁻² yr⁻¹ (CH₄) to the watershed-scale

diffusive gas budget. Together, these results demonstrate that lake emissions are shaped by the watershed's lake-size distribution: small lakes dominate in abundance and contribute substantial variability in areal fluxes, whereas a small number of larger lakes can disproportionately influence total emissions due to their surface area.

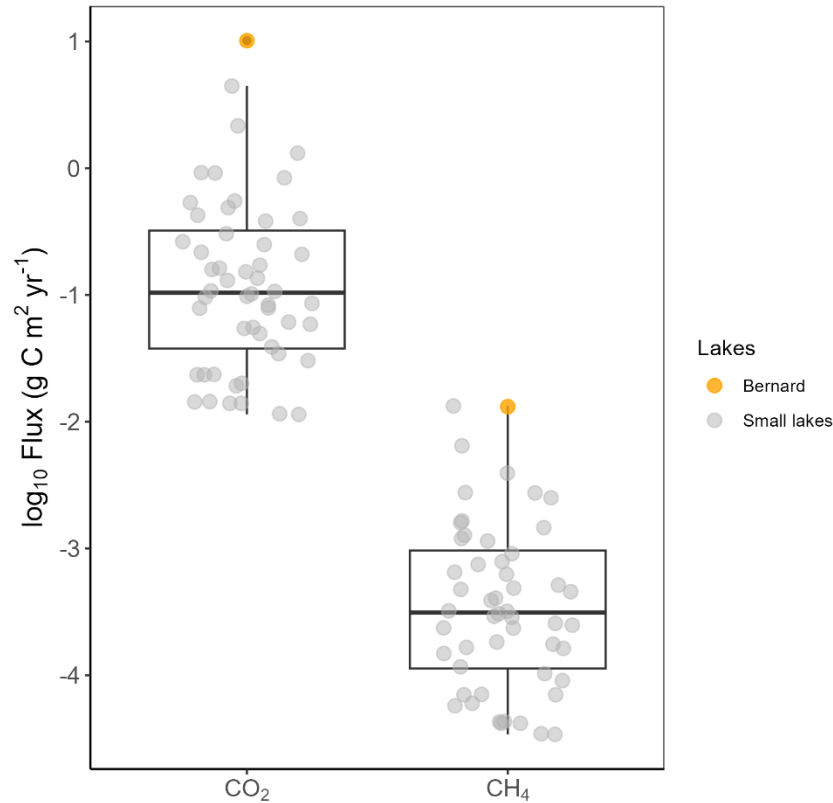


Figure 1.20 Boxplots showing the distribution of log₁₀-transformed areal CO₂ and CH₄ fluxes (g C m⁻² yr⁻¹) across lakes (per m⁻² lake surface area) in the watershed. Gray points represent individual small lakes, while the orange point denotes Lake Bernard. Boxes indicate the interquartile range with median values shown as horizontal lines, and whiskers represent 1.5x the interquartile range.

1.3.6 Sediment Carbon Burial

Sediment carbon burial was estimated from sediment cores collected from 6 different lakes of varying size within the Bernard River watershed (n = 3) and the greater La Romaine River watershed (n = 3) and rates were assigned to lakes within the Bernard River watershed according to their size categorization of small lakes (area < 4 km²) and large lakes (area > 4 km²). Small lakes made up the majority of lakes within the

Bernard River watershed (Fig. 1.19). Also, small lakes sediment carbon burial rates ranged 0.01 – 18.10 g C m⁻² yr⁻¹ of lake area.

Below, we provide an example of how lake organic carbon burial rates changed over the decades in Lake Bernard, expressed as g C m⁻² yr⁻¹ of watershed area (Table 1.1). Lake Bernard exhibited substantial interannual variability over the observational period, spanning more than three decades (1980–2011; Table 1). Estimated organic carbon burial ranged from 1.32 to 7.64 g C m⁻² yr⁻¹, with a long-term mean burial rate of 3.39 g C m⁻² yr⁻¹. The lowest burial rates were observed in 1980 (1.35 g C m⁻² yr⁻¹) and 1997 (1.32 g C m⁻² yr⁻¹), whereas a pronounced peak occurred in 2006 (7.64 g C m⁻² yr⁻¹). The most recent estimate (2011) indicated an intermediate burial rate of 3.26 g C m⁻² yr⁻¹, closely aligned with the long-term average.

To scale C burial rates to the entire watershed, average C burial rates from the retrieved sediment cores were assigned to lakes within the Bernard River watershed based on the lake size categories. The assigned average C burial rates for the ensemble of lakes within the Bernard River watershed were summed to achieve a watershed sediment C burial of 4.68 g C m⁻² yr⁻¹ (expressed in terms of watershed area).

Year	Organic Carbon Burial Rate (g C m ⁻² yr ⁻¹)
2011	3.26
2006	7.64
1997	1.32
1980	1.35
<i>Average Carbon Burial: 3.39 g C m⁻² yr⁻¹</i>	

Table 1.1 Lake Bernard sediments. Organic carbon burial (g C m⁻² yr⁻¹) at dated intervals from 1980 to 2011, based on sediment core analyses. Burial rates varied between 1.35 and 7.64 g C m⁻² yr⁻¹, with a long-term mean of 3.39 g C m⁻² yr⁻¹ of watershed area.

1.3.7 Whole-System Carbon Fates

When normalized to watershed area, the relative magnitudes of aquatic C fates in the Bernard River watershed reveal a clear dominance of atmospheric losses, followed by lateral export, with sediment burial representing a smaller but non-negligible sink (Table 1.2). Total CO₂ diffusive flux was the largest C fate, averaging 36.40 g C m⁻² yr⁻¹ (74.5% lake, 25.5% stream emissions), exceeding all other pathways by a substantial margin. In contrast, CH₄ diffusive flux contributed minimally to the overall C budget, with an areal flux of only 0.11 g C m⁻² yr⁻¹ (58 % lake, 42% stream emissions). It should be noted that ebullitive flux measurements are not accounted for in this study.

Lateral C export constituted the second most important set of pathways. DOC export averaged 14.64 g C m⁻² yr⁻¹, substantially exceeding DIC export, which averaged 3.83 g C m⁻² yr⁻¹. This imbalance highlights the dominance of organic forms in downstream carbon transport and underscores the strong coupling between terrestrial C inputs, hydrological connectivity, and aquatic C processing in this boreal watershed.

Sediment C burial for the lakes within the Bernard River watershed totaled 4.68 g C m⁻² yr⁻¹, comparable in magnitude to DIC export but an order of magnitude smaller than CO₂ evasion. Although burial represents a long-term sequestration pathway, its contribution to the overall aquatic C budget is modest relative to atmospheric and lateral losses. Taken together, these results demonstrate that the Bernard River watershed functions primarily as a conduit and a biogeochemical reactor for C, with most aquatic C returned to the atmosphere as CO₂ or exported downstream as DOC, while only a smaller fraction is retained through sediment burial on longer timescales.

This partitioning among C fates emphasizes the central role of gas exchange in regulating watershed-scale C balance and highlights the importance of integrating atmospheric fluxes with lateral export and burial to fully resolve C cycling in complex boreal aquatic networks.

Table 1.8 Annual carbon budget for the Bernard River watershed (2021-2022). Carbon fluxes and storage expressed in g C m⁻² yr⁻¹ of watershed area.

Aquatic CO ₂ Diffusive Flux (g C m ⁻² yr ⁻¹)	Aquatic CH ₄ Diffusive Flux (g C m ⁻² yr ⁻¹)	DOC Export (g C m ⁻² yr ⁻¹)	DIC Export (g C m ⁻² yr ⁻¹)	Sediment Carbon Burial (g C m ⁻² yr ⁻¹)
36.40	0.11	14.64	3.83	4.68
All values are normalized to watershed area				

1.4 Discussion

At the scale of the Bernard River watershed, aquatic C cycling is dominated by atmospheric losses, with lateral export and long-term sediment burial representing secondary pathways. When normalized to watershed area, diffusive CO₂ evasion from streams and lakes exceeded all other quantified C fates by a substantial margin, surpassing both dissolved C export and sediment burial. This dominance of CO₂ emissions reflects the strongly reactive nature of inland waters in boreal landscapes, where terrestrially derived carbon is efficiently mineralized during aquatic transport (Algesten et al., 2004; Lapierre et al., 2013). The Bernard River watershed is situated within the boreal biome and is characterized by a heterogeneous mosaic of landscape elements, including a hierarchically structured stream network spanning first- to fifth-order streams, large and small lakes, bog-influenced waters, wetlands, and coniferous forest uplands. Such landscape complexity promotes high hydrological connectivity and repeated processing of carbon across aquatic–terrestrial interfaces, reinforcing the role of inland waters as biogeochemical reactors rather than passive conduits (Hutchins et al., 2019).

The relative importance of CO₂ evasion observed here is consistent with boreal syntheses demonstrating that inland waters return a large fraction of terrestrial carbon inputs to the atmosphere, often at magnitudes comparable to or exceeding lateral export and long-term storage (Kokic et al., 2015; Wallin et al., 2013a). CO₂ emissions were consistently highest in first-order streams despite their lower gas transfer velocities, indicating that elevated $p\text{CO}_2$ concentrations were the dominant control on CO₂ efflux in headwaters (Fig. 1.15; Fig. 1.17; Fig. 1.18). This pattern supports a process-based interpretation in which low-order streams act as intense biogeochemical reactors, receiving high inputs of terrestrially derived DOC from soils, wetlands, and bog-influenced waters, which is then mineralized to CO₂ during short residence times (Crawford et al., 2013; Taillardat et al., 2022). Stream CO₂ flux generally decreased from headwaters to mid-reach channels before showing a moderate resurgence in downstream reaches (Figure 1.18). This non-linear pattern suggests a complex interplay between decreasing $p\text{CO}_2$ and higher gas transfer velocities downstream, signaling a shift to exchange-limited conditions that varies by stream size. Similar stream-order structuring of CO₂ emissions has been documented across Québec and eastern Canadian boreal networks, where headwater streams disproportionately contribute to total fluvial CO₂ evasion despite representing a small fraction of total channel area (Campeau et al., 2014; Wallin et al., 2013a), reinforcing the importance of resolving low-order channels when scaling emissions to the watershed or regional level. Together, the Bernard River watershed results emphasize that accurate

assessment of stream greenhouse gas emissions requires explicit consideration of stream order, hydrological variability, and source heterogeneity.

In contrast to CO₂, diffusive CH₄ emissions constituted a minor component of the watershed-scale carbon budget. However, it is important to note that the methane fluxes reported here account only for diffusive exchange and do not include ebullitive emissions, which can represent a substantial, and often highly variable, fraction of total CH₄ release from boreal streams, lakes, and wetlands (Baulch et al., 2011; DelSontro et al., 2016). Ebullition is known to be spatially patchy, episodic, and strongly controlled by sediment characteristics, organic matter availability, and hydrological or pressure fluctuations, making it difficult to quantify without dedicated measurements (Maeck et al., 2014; Praetzel et al., 2021). Studies across boreal and temperate systems have shown that ebullition can equal or exceed diffusive CH₄ fluxes in shallow lakes, peat-influenced waters, and low-gradient streams, while contributing little in deeper or more turbulent systems (DelSontro et al., 2016; Rasilo et al., 2015). Given the presence of bog lakes, wetlands, and low-order streams within the Bernard River Watershed, it is plausible that total methane emissions are underestimated in this study; however, the magnitude of this underestimation cannot be constrained with the available data. As a result, the low contribution of CH₄ to the total aquatic carbon budget should be interpreted as a conservative estimate, reflecting diffusive emissions only rather than the full spectrum of methane release pathways.

DOC export from the Bernard River watershed was strongly hydrology-driven, with watershed integration amplifying event signals and making a small number of high-flow periods disproportionately important for annual export. Results in this study show that DOC export at the watershed outflow (ST5-WO) in 2021 exhibited larger, sharper event-driven export peaks than 2022, mirroring the more dynamic discharge regime in 2021 (Fig. 1.14). Mechanistically, this pattern is consistent with "connectivity-first" controls on DOC mobilization in boreal mosaics: as discharge rises, hydrologic flowpaths expand into organic-rich riparian soils, wetlands, and peat-influenced areas, flushing recently produced and previously stored DOC to the channel network, whereas prolonged baseflow reflects a more limited set of deeper or less DOC-rich sources (Prijs et al., 2023). The stronger and more coherent CDOM–discharge relationships in 2022 support this interpretation (Fig. 1.8), suggesting that interannual differences in runoff generation and antecedent wetness can shift DOC sensitivity to discharge, not just the magnitude of export. This event-dominance and discharge sensitivity closely matches observations from other Canadian boreal systems, where DOC loads are often synchronized across catchments during the spring freshet and other high-

connectivity periods, indicating regionally coherent forcing superimposed on local landscape heterogeneity (Morison et al., 2022).

Lake CO₂ and CH₄ emissions in the Bernard River Watershed were strongly structured by lake size, reflecting systematic differences in C sources, processing capacity, and physical exchange regimes across the lentic network. Although small lakes dominated numerically, areal greenhouse gas fluxes varied widely among these systems, indicating substantial heterogeneity in biogeochemical functioning at relatively small spatial scales. This variability likely reflects differences in watershed-to-lake area ratios, hydrologic connectivity to wetlands and peatlands, and internal metabolic balance, all of which can strongly influence carbon loading and in-lake mineralization (Kankaala et al., 2013; Premke et al., 2016). Interestingly, Lac Bernard exhibited CO₂ and CH₄ emissions near the maximum of the observed distribution (Figure 1.20). While this contradicts the well-established pattern of decreasing gas flux with increasing lake area, it underscores the system's unique position. As the largest water body in the watershed, its elevated flux reflects a high reliance on upstream terrestrial carbon sources. Larger lakes in boreal regions often experience longer water residence times and greater opportunities for in-lake respiration of terrestrially derived DOC, leading to sustained CO₂ supersaturation even when areal CH₄ fluxes remain moderate (Algesten et al., 2004; Kankaala et al., 2013).

Methane emissions from lakes were consistently lower than CO₂ emissions across all size classes, yet displayed marked variability among small lakes, highlighting the importance of local controls on methanogenesis and gas transfer (Fig. 1.20). Small, shallow lakes are particularly prone to elevated CH₄ production due to warm sediments, frequent anoxia, and strong coupling between sediments and the water column, whereas larger and deeper systems often suppress diffusive CH₄ emissions through enhanced oxidation and stratification-driven decoupling of sediments from the surface mixed layer (Vachon et al., 2019; West et al., 2016). Observations from Québec and eastern Canadian boreal lakes similarly demonstrate that small lakes contribute disproportionately to regional methane emissions despite representing a minor fraction of total lake area, while larger lakes exert a stabilizing influence on watershed-scale flux estimates (Kankaala et al., 2013). Together, these patterns underscore the necessity of explicitly resolving lake size structure when scaling lentic greenhouse gas emissions and reinforce the view that boreal lake networks function as spatially heterogeneous but collectively important components of inland C cycling.

Sediment carbon burial in Lake Bernard represents a persistent, long-term carbon sink within the watershed, but one that is modest in magnitude relative to atmospheric and lateral fluxes (Table 1.1). Multi-decadal burial rates derived from sediment cores indicate substantial interannual variability, yet converge on a long-term mean that places Lake Bernard within the lower to moderate range reported for boreal lakes (Ferland et al., 2014). This variability suggests that burial efficiency is not constant through time, but instead reflects episodic enhancement driven by fluctuations in organic matter delivery, in-lake production, and sediment focusing, as well as post-depositional mineralization (Bindler et al., 2025; Radbourne et al., 2017). These findings align with observations from Québec and other eastern Canadian boreal regions, where lakes commonly act as net sources of atmospheric CO₂ while simultaneously accumulating organic carbon in sediments at lower rates (Ferland et al., 2014). In this context, Lake Bernard functions less as a dominant carbon sink and more as a long-term integrator of watershed processes, retaining a small but climatically relevant fraction of incoming carbon over centennial timescales. Taken together, these results reinforce the view that sediment carbon burial, though essential for closing inland water carbon budgets, plays a secondary role in regulating near-term carbon balance relative to faster and more responsive pathways such as evasion and export (Cole et al., 2007; Ferland et al., 2014).

The results from streams, lakes, and sediments support a conceptual model in which the Bernard River watershed functions as a tightly coupled, hydrologically driven C reactor embedded within a heterogeneous boreal landscape. C enters the aquatic network primarily as terrestrially derived DOC mobilized from forests, wetlands, and bog-influenced soils during periods of elevated hydrological connectivity, particularly during the spring freshet and storm-driven events. As carbon is routed through a hierarchically structured stream network, low-order channels release a disproportionate amount of CO₂ to the atmosphere relative to their surface area. This high headwater outgassing is primarily driven by the evasion of soil-derived CO₂ injected via groundwater. Downstream reaches and lakes further integrate and transform upstream C inputs, with larger systems such as Lac Bernard acting as processing hubs that sustain CO₂ emissions while retaining a small fraction of C through long-term sediment burial. Although burial provides a persistent sink on longer timescales, it remains secondary to the faster and more responsive pathways of evasion and export that dominate the near-term C balance. Hydrology ultimately regulates the strength and timing of all major C fates by controlling source activation, transport efficiency, and residence times across the network. In this framework, the Bernard River watershed exemplifies how boreal aquatic systems operate not as passive pipes of terrestrial C, but as dynamic, spatially structured

reactors in which hydrological variability governs the partitioning of C among atmospheric release, downstream export, and long-term storage.

1.5 Conclusion

This study provides a high-resolution complete assessment of aquatic C cycling in a boreal watershed, demonstrating that streams and lakes function as dynamic regulators of carbon fate rather than passive transport pathways (Lundin et al., 2013). Across the Bernard River watershed, hydrology emerged as the dominant organizing force linking terrestrial C mobilization to aquatic processing, with episodic high-connectivity periods disproportionately controlling DOC export and subsequent greenhouse gas emissions. Diffusive CO₂ evasion from streams and lakes constituted the largest aquatic C flux, particularly from low-order streams and integrative lake systems, while sediment C burial in Lake Bernard represented a smaller but persistent long-term sink. Methane emissions were comparatively minor when considering diffusive fluxes alone, though the absence of ebullitive measurements highlights an important source of uncertainty in fully resolving watershed-scale CH₄ dynamics. Collectively, these findings reinforce the view that boreal aquatic networks act as biogeochemical reactors that transform and release terrestrially derived C, thereby exerting a strong influence on landscape-scale C balance.

Importantly, the partitioning of C among evasion, export, and burial observed here underscores the need to explicitly represent spatial heterogeneity and network structure when scaling aquatic C fluxes (Kokic et al., 2015; Premke et al., 2016). Headwater streams, despite their limited surface area, played a disproportionate role in CO₂ emissions, while lake size structure governed both the variability and stability of lentic fluxes at the watershed scale. Sediment burial in Lake Bernard integrates C inputs over decadal timescales, providing a record of longer-term watershed dynamics, yet contributes only a modest fraction of total aquatic C retention relative to contemporary losses. These results place the Bernard River watershed squarely within the growing body of evidence from boreal and eastern Canadian systems indicating that inland waters substantially offset terrestrial C sequestration through mineralization and atmospheric release (Drake et al., 2018; Pilla et al., 2022).

A critical next step is the integration of these aquatic fluxes into a full watershed C mass balance that explicitly couples terrestrial and aquatic processes. Linking high-resolution aquatic measurements with terrestrial C stocks, soil respiration, forest productivity, and wetland C dynamics will allow quantification of how much landscape-derived C is retained on land versus exported or emitted via inland waters (Casas-

Ruiz et al., n.d.). Such an integrated framework would enable direct comparison of aquatic C losses with net ecosystem C balance estimates from upland forests and peatlands, improving constraints on boreal C budgets under current and future climatic conditions. Incorporating ebullitive methane emissions, winter fluxes, and long-term sediment accumulation across multiple lakes will further refine these estimates. Ultimately, embedding aquatic systems within whole-watershed C accounting is essential for accurately assessing the role of boreal landscapes in the global C cycle and for predicting how shifts in hydrology, climate, and land cover may alter C fate in the decades ahead.

CHAPTER 2

RECONSTRUCTING THE CONTEMPORARY AND HISTORICAL AQUATIC CARBON BALANCE OF THE LAFLAMME LAKE WATERSHED

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greenhouse gas emissions, carbon burial, carbon biogeochemistry.

N.B. References cited in this chapter are presented at the end of the thesis.

2.1 Context

Inland waters play a substantial role in the global carbon (C) cycle, processing and emitting up to 4 Pg of C annually (Drake et al., 2018) despite their relatively small areal extent (Biddanda, 2017). Lakes, in particular, act as both conduits and reactors for C, simultaneously transporting material downstream, emitting greenhouse gases to the atmosphere, and burying organic matter in sediments (Cole et al., 2007; Cole et al., 1994). The balance among these pathways determines whether a lake functions as a net source or sink of C (Anas et al., 2015), with important implications for regional and global C budgets (Prairie, 2008; Tranvik et al., 2009).

Boreal regions are especially critical to this balance. They contain dense networks of lakes and wetlands (Wells & Roberts, 2020), store substantial forest and soil organic C (Rapalee et al., 1998) and are experiencing rapid environmental change driven by climate warming, altered hydrology, and shifting vegetation (Bring et al., 2016; Gauthier et al., 2015; Gonzalez et al., 2010). Recent studies across northern latitudes suggest increasing dissolved organic carbon (DOC) concentrations (Couture et al., 2012; Monteith et al., 2007; Weyhenmeyer & Karlsson, 2009) and increased inputs of colored DOC from land to lakes (Lapierre et al., 2013), phenomena often described as “browning” (Meyer-Jacob et al., 2019). These trends highlight the need to understand not only contemporary fluxes but also long-term trajectories of C cycling in boreal headwater systems.

Although headwater streams have gained much attention due to their high C flux rates (Venkiteswaran et al., 2014), not many studies focus on small headwater lake catchments (Kokic et al., 2015; Stets et al., 2010). The emerging role of small lakes has been highlighted recently (Pi et al., 2022), and headwater lakes are particularly important because they represent the first point of entry for terrestrial C into aquatic networks. Their position in the landscape makes them sensitive to hydrological variability, catchment characteristics, and atmospheric forcing (Quinlan et al., 2003). Yet, their C budgets remain poorly constrained, as most long-term monitoring and process studies have focused on larger rivers and downstream systems. Consequently, uncertainties persist in how small boreal lakes partition C among export, emission, and burial pathways (Lundin et al., 2015).

This study aimed to quantify a contemporary and historical C budget in the Lac Laflamme watershed, a small headwater lake located in the Forêt Montmorency, Québec, Canada. By integrating long-term monitoring records (1983–2021), high-frequency buoy data, discrete sampling campaigns, and sediment

core analyses, we evaluate how C is distributed among major fluxes: (i) hydrological export of DOC and DIC, (ii) atmospheric efflux of CO₂ and CH₄, and (iii) organic C burial in sediments. We further assess temporal trends in DOC concentrations and *p*CO₂ to determine whether Lac Laflamme reflects broader patterns of browning and increased C emissions observed across boreal regions.

2.2 Materials and Methods

2.2.1 Study Site and Sampling

This study was conducted in the Lac Laflamme (LF) watershed (Fig. 2.1), which is in the Forêt Montmorency, Québec, Canada (47.19'23.5" N and 71.07'23.6" W). It is located at an elevation of ~640 m above sea level. The predominant vegetation type for this watershed is Balsam fir, accounting for ~90% of the vegetative stand. The LF watershed is constrained to Lac Laflamme and one outflow stream that extends 1 km downstream of the lake. The watershed has a catchment area of 0.7 km² and a lake surface area of 0.06 km².

To establish a present-day aquatic C budget, we partitioned the major C pathways in LF into three components: (i) atmospheric emissions of CO₂ and CH₄ from the lake, (ii) downstream export of DOC and DIC via the outflow, and (iii) sediment C burial within Lac Laflamme. However, since LF lacks upstream tributaries, a buoy was installed in 2021 for recording high-resolution, hourly measurements of surface water partial pressure of CO₂ (*p*CO₂, µatm), over the open-water season (July-November) of 2021. The continuous measurements were accompanied by discrete sampling within the lake and at the outflow for *p*CH₄ and *p*CO₂. DOC and DIC were sampled monthly through July - November 2021. The outflow of the lake was continuously monitored for discharge since 1999.

To place the contemporary budget into a historical context, the outflow of the lake was sampled weekly for DOC between 1999–2021 by Environment and Climate Change Canada (ECCC) and Ministère des Ressources naturelles et des Forêts (MRNF). Additional lake water measurements of DIC, pH, and conductivity from 1983–2021 were used to reconstruct long-term $p\text{CO}_2$ trends (please refer to section 2.2.2 for more information on how this was done). Finally, a sediment core was extracted from the lake to quantify organic C burial through time.

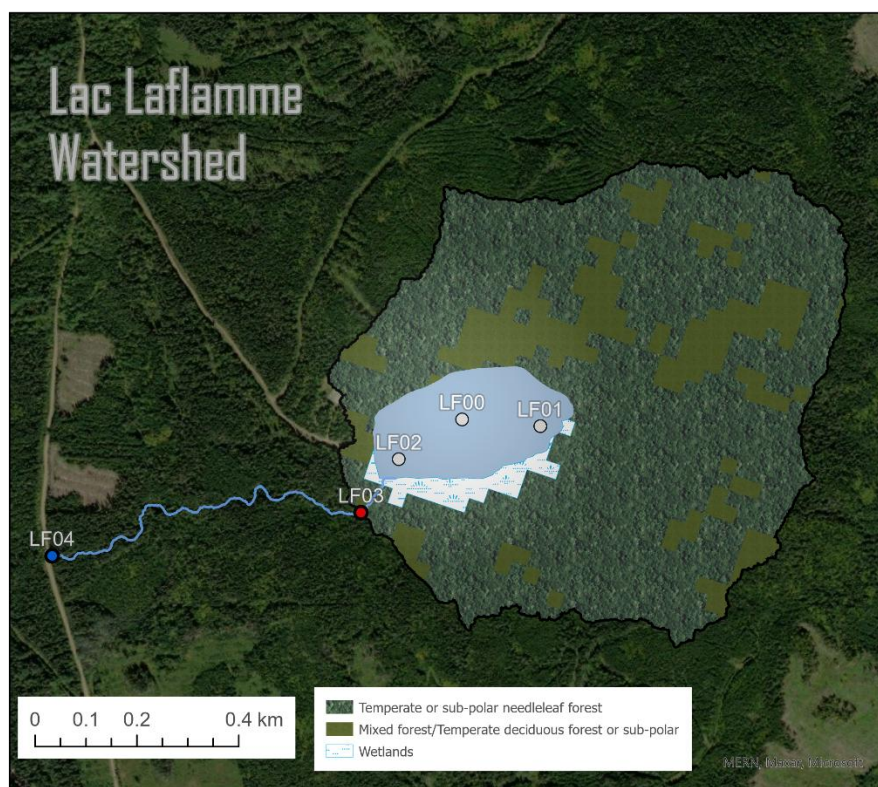


Figure 2.1 The Lac Laflamme watershed and predominant landcover types located in the Forêt Montmorency, Québec, Canada. The dots and labels mark the sampled sites in this study, where the red dot marks the lake outflow and the blue dot marks the extent of the Laflamme River.

2.2.2 Field and Laboratory Analyses

For all sites, DOC and DIC samples were collected monthly in 2021, kept on ice for 24–36 hours, and processed at the Groupe de Recherche Interuniversitaire en Limnologie (GRIL) analytical laboratory at the Université du Québec à Montréal (UQAM). Samples were filtered through 0.45- μm polyethersulfone cartridges, stored at 4 °C in the dark, and analyzed on a total carbon analyzer (TOC1010, OI Analytical, USA) using high-temperature persulfate oxidation.

Discrete CO₂ and CH₄ samples were collected monthly at the surface waters (0.1 m) during the 2021 field season using the headspace technique to determine $p\text{CO}_2$ and $p\text{CH}_4$ (Kling et al., 1991). Three 140 mL syringes of sample water were replaced by 40 mL of ultra-zero air (AI 0.0UZ, Praxair, Inc., Canada) and vigorously shaken for 2 minutes. The equilibrated headspace was transferred to 12 mL exetainers (Labco Ltd, U.K.). Gas concentrations were determined on a cavity ring-down spectrometer (CRDS) equipped with a small sample isotopic module (SSIM, Picarro G2201-i).

The buoy deployed in LF (LF00) was equipped with a MiniDOT (PME, California, USA) that continuously monitored surface water temperature (°C), DO concentration (mg L⁻¹, % saturation) at surface waters (0.2 m, hourly intervals). Additional sensors included a CO₂ Probe (GMP343, Vaisala, Finland), and a U20 Pressure Logger (Onset, USA) to measure atmospheric pressure (kPa) and temperature (°C), and HOBO Micro Station Data Loggers (H21-USB, Onset, USA) to store field data. Meteorological data (wind speed, air temperature) were extracted from the ERA 5 dataset (Hersbach et al., 2020).

The LF outflow (LF03) was sampled on a weekly basis by ECCC for lake color, pH, conductivity and concentrations of DOC and DIC. Water samples collected were kept cool and sent to their laboratories within 24-36 hours. Lake water pH and conductivity were measured potentiometrically using pH-meter (Accumet 50) and conductivity meters (Accumet model AB30), respectively (Rodríguez-Cardona et al., 2023). Samples were filtered with 0.45 μm filters prior to analyses and DIC and DOC were measured using oxidation with persulfate-ultraviolet radiation and detection by infrared spectrometry until 2013, then thermal oxidation techniques since 2014 (Rodríguez-Cardona et al., 2023).

DIC concentrations measured from samples taken from ECCC were used to reconstruct $p\text{CO}_2$ (Stumm & Morgan, 2013; Weyhenmeyer et al., 2012) following evidence that $p\text{CO}_2$ and pH show closer agreement with directly measured $p\text{CO}_2$ (Couture et al., 2012) (via headspace equilibration analyzed on a Picarro G2201-i) than estimates based on alkalinity and pH. Previous work further demonstrated that correcting pH, according to the approach of Liu et al. (2020), improve DIC-based CO₂ calculations and substantially reduces error in reconstructed $p\text{CO}_2$, even when alkalinity-based methods account for DOC contributions.

2.2.3 Downstream export of DOC and DIC through the Lake Outflow

The DOC and DIC export at the outlet of the watershed (g DOC-C, or DIC-C, m⁻² yr⁻¹) was calculated using the following equation:

$$C_{export} = \frac{\sum_{i=1}^n [C]_i \times Q_i}{S} \quad (Eq. 2.1)$$

where $[C]_i$ corresponds to the DOC or DIC concentration (in mg L^{-1}) at time step i , Q_i corresponds to the stream discharge at timestep i (in $\text{m}^3 \text{d}^{-1}$), and S corresponds to the catchment area (m^2). The sum of all the weekly estimates provide the total annual DOC export at the watershed outflow, expressed in $\text{g DOC-C m}^{-2} \text{yr}^{-1}$.

DIC was also measured in order to quantify DIC export at the watershed outflow, however, the long-term dataset of DIC is not represented in this study. DIC concentrations were measured from discrete samples for each sampling occasion in ($n = 6$) using the same laboratory analyses for DOC (please refer to 2.2.2 Laboratory Analyses). Average DIC concentrations at the Lac Laflamme outflow were multiplied by the annual discharge at the watershed outflow for 2021 to derive the DIC export. This was then upscaled to an entire calendar year and divided by the watershed area to derive the DIC export in $\text{g DIC-C m}^{-2} \text{yr}^{-1}$.

2.2.4 CO_2 and CH_4 Flux from Lake Laflamme

We calculated air-water fluxes of CO_2 and CH_4 for each sampling occasion using Fick's Law of diffusion, according to the equation:

$$F_{gas} = k_{gas} \times \Delta_{gas} \quad (Eq. 2.2)$$

where F_{gas} is the flux ($\text{mmol m}^{-2} \text{d}^{-1}$) of CO_2 (F_{CO_2}) or CH_4 (F_{CH_4}), k_{gas} is the gas transfer coefficient at a given temperature (m d^{-1}), and Δ_{gas} is the departure of CO_2 or CH_4 from equilibrium with the atmosphere (ΔCO_2 , ΔCH_4 , mmol m^{-3}). For equation (2.2) we used our measured $p\text{CO}_2$ and $p\text{CH}_4$, converted to concentrations using Henry's constant corrected for temperature. k_{CO_2} and k_{CH_4} were estimated for each sampling occasion, from modeled standardized gas transfer coefficients (k_{600}) values estimated following Vachon & Prairie (2013) equation:

$$k_{600} = 2.51(\pm 0.99) + 1.48(\pm 0.34) \times U_{10} + 0.39(\pm 0.08) \times U_{10} \times \log_{10} LA \quad (Eq. 2.3)$$

where U_{10} is the wind speed at 10 m height (m s^{-1}), and LA is the lake area (km^2). k_{600} was converted to gas-specific values using Schmidt numbers following (Jähne et al., 1987; Wanninkhof, 1992), with $n = 0.5$ for

wind speeds $>3 \text{ m s}^{-1}$ (equation 2.4; Goldenfum, 2010). Fluxes were scaled to the watershed area and expressed as $\text{g C m}^{-2} \text{ yr}^{-1}$ (assuming an ice-free period of 212 days).

$$k_{CO_2(CH_4)} = k_{600} \times \left(\frac{ScCO_2(CH_4)}{600} \right)^n \quad (Eq. 2.4)$$

It should be noted that CH_4 fluxes are calculated from discrete samples of pCH_4 ($n = 11$) following the procedures described above (please refer to section 2.2 – Field and Laboratory Analyses). An average pCH_4 was assigned to Lake Laflamme and scaled to the watershed area and expressed as $\text{g C m}^{-2} \text{ yr}^{-1}$ (assuming an ice-free period of 212 days).

2.2.5 Sediment Carbon Burial

Sediment burial was reconstructed using a gravity corer (NLA, Aquatic Research Instruments) with a 6.8 cm ID Plexiglass tube, deployed at the deepest point in the lake (LF00) as determined with a portable sonar. The core was sectioned at 1 cm intervals, yielding 15 samples for chronology and geochemistry. Gamma spectroscopy (^{210}Pb dating) was conducted at the Paleocological Environmental Assessment and Research Laboratory (PEARL laboratory, Queen's University, Canada) and modeled using the constant rate of supply (CRS) approach (Baud et al., 2021). Elemental composition (C, N) was analyzed via combustion on a Carlo Erba CN2500 analyzer (Hassan et al., 1997). Samples for OC analysis were acidified with 12 M HCl for 24 hours to remove carbonates (Meyers & Teranes, 2002). IC was calculated by difference, and molar C:N and OC:N ratios were derived. We successfully dated 11 samples to derive historical burial rates and retained all records between 1985-2018. It should be noted that sediment layers deposited within the last ten years were excluded from the analyses because OC is subject to rapid degradation during the initial post-depositional period (Gälman et al., 2008). The C and OC burial rates (CBR and OCBR; $\text{g C m}^{-2} \text{ yr}^{-1}$) were calculated as:

$$CBR = MAR \times \%Carbon \quad (Eq. 2.5)$$

where MAR is the mass accumulation rate ($\text{g m}^{-2} \text{ yr}^{-1}$). Sediment Focusing factors (FF) were estimated by comparing measured and atmospheric ^{210}Pb inventories ($\text{Bq m}^{-2} \text{ yr}^{-1}$; Appleby, 2002), following Engstrom & Rose (2013). Average burial rates were scaled to the watershed area.

$$^{210}\text{Pb atmospheric fluxes} = \frac{100 \text{ Bq m}^{-2}}{1000 \text{ mm precipitation}} \times \frac{1}{\lambda(y)} \quad (\text{Eq. 2.6})$$

$$FF = \frac{\text{sediment core } ^{210}\text{Pb fluxes}}{\text{atmospheric } ^{210}\text{Pb fluxes}} \quad (\text{Eq. 2.7})$$

2.2.6 Time series and trend analyses

Long-term variability in LF was examined using annual mean values of DOC, discharge, and reconstructed $p\text{CO}_2$ over the period of 1999–2021. Aggregation to annual means was used to minimize short-term variability and to emphasize persistent directional trends through time. Trends in discharge, DOC, and $p\text{CO}_2$ were evaluated using the non-parametric Mann–Kendall test, as implemented in the Kendall R package (McLeod, 2005), which is well suited for environmental datasets characterized by non-normal distributions and occasional missing values. The direction and magnitude of monotonic trends were described using Kendall’s tau (τ), which ranges from -1 to 1 , with negative and positive values indicating decreasing and increasing trends, respectively. Statistical significance was evaluated using two-sided tests.

To account for potential temporal autocorrelation in the time series and its influence on uncertainty estimates, confidence intervals for Kendall’s tau were obtained using a block bootstrap procedure. Bootstrap resampling was conducted with the `tsboot` function from the `boot` R package, employing fixed-length blocks to retain serial dependence within the data (Canty & Ripley, 2025; Davison & Hinkley, 1997). A block length of 40 observations was used, and 599 bootstrap iterations were generated following established recommendations for percentile-based inference. Percentile bootstrap confidence intervals (95%) were subsequently calculated using the `boot.ci` function, providing a robust, non-parametric estimate of uncertainty that accounts for serial correlation. All statistical analyses were carried out in R and RStudio (R version: 2025.05.1+513; Posit Team, 2025; R Core Team, 2025).

2.3 Results

2.3.1 Discharge

Discharge was measured over a total of 8,401 days, culminating in a long-term record spanning 23 years (LF03; 1999–2021). Discharge in the Lake Laflamme outflow showed pronounced interannual variability, with four high-flow events exceeding $20,000 \text{ m}^3 \text{ d}^{-1}$ during spring snowmelt and storm events in May 2011, 2014, and 2017 as well as November 2017 (Fig. 2.2a). Across the 1999–2021 record, daily discharge averaged at $1,511 (\pm 19,934) \text{ m}^3 \text{ d}^{-1}$, while 2021 exhibited a lower-than-average mean discharge of $882 (\pm 568.5) \text{ m}^3 \text{ d}^{-1}$ (Fig. 2.2b). No long-term temporal trend was found for daily discharge (Kendall's $\tau = -0.0002$, 95% CI $[-0.07, 0.08]$, p-value = 0.97, $n = 8,401$) or annually averaged discharge (Kendall's $\tau = 0.11$, p-value = 0.49, $n = 23$). Total annual discharge averaged $552,627 (\pm 118,510) \text{ m}^3 \text{ yr}^{-1}$ over the measured two decades.

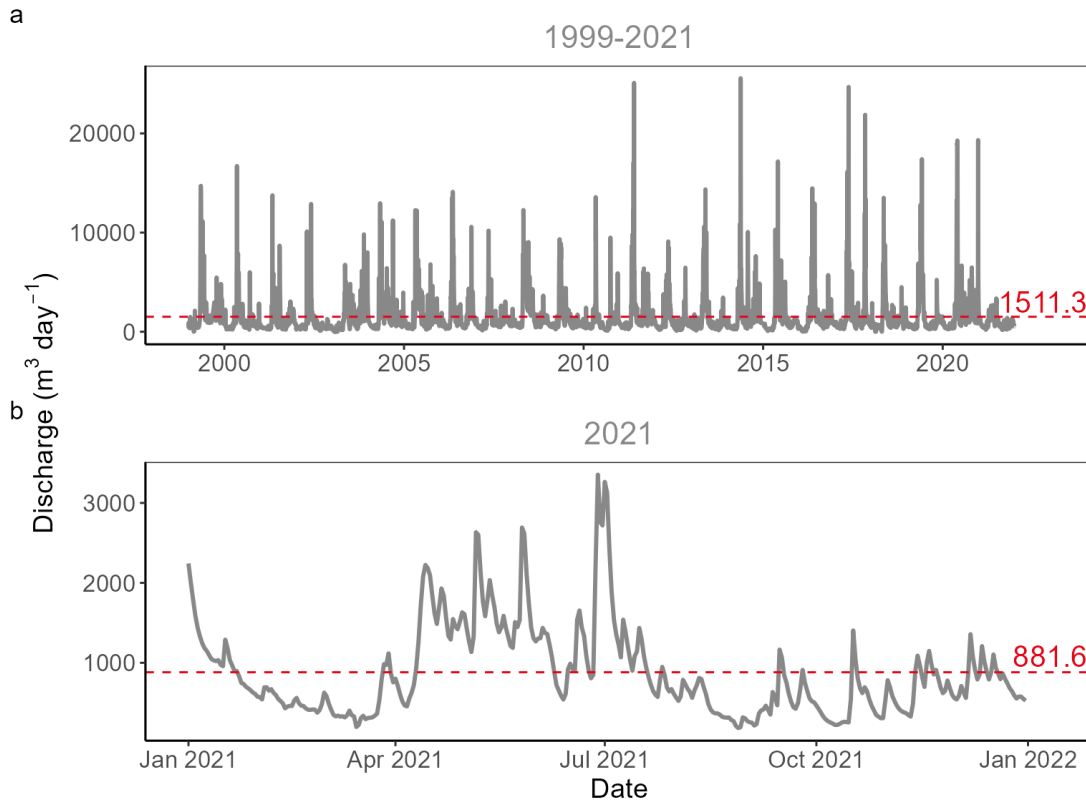


Figure 2.2 Long-term and contemporary discharge patterns in the Lake Laflamme watershed. (a) Daily discharge ($\text{m}^3 \text{ d}^{-1}$) from 1999–2021. The dashed red line indicates the long-term mean discharge ($1,511 \text{ m}^3 \text{ d}^{-1}$) (b) Daily discharge in 2021, averaging $882 \text{ m}^3 \text{ d}^{-1}$ (dashed red line).

2.3.2 DOC and DIC

Surface water carbon concentrations collected at all sites during 2021 were characterized by mean DOC of $4.7 (\pm 0.64) \text{ mg L}^{-1}$ and DIC of $1.6 (\pm 0.39) \text{ mg L}^{-1}$ (Fig. 2.3). DOC showed strong seasonal fluctuations, ranging from $3.2\text{--}6.7 \text{ mg L}^{-1}$, while DIC remained relatively stable ($1.2\text{--}2.3 \text{ mg L}^{-1}$) throughout the sample period. Over the long-term record (1999–2021), DOC concentration averaged $4.85 (\pm 1.22) \text{ mg L}^{-1}$ and increased significantly over time (Kendall's $\tau = 0.20$, 95% CI [0.09, 0.29], $p < 0.05$, $n = 1,122$), rising from ~ 4.5 to $> 5 \text{ mg L}^{-1}$ (Fig. 2.5). DOC was strongly driven by discharge ($R^2 = 0.30$, $p < 0.001$, $n = 8,690$), indicating a strong hydrologic control over DOC concentration across the measured years (Fig. 2.5).

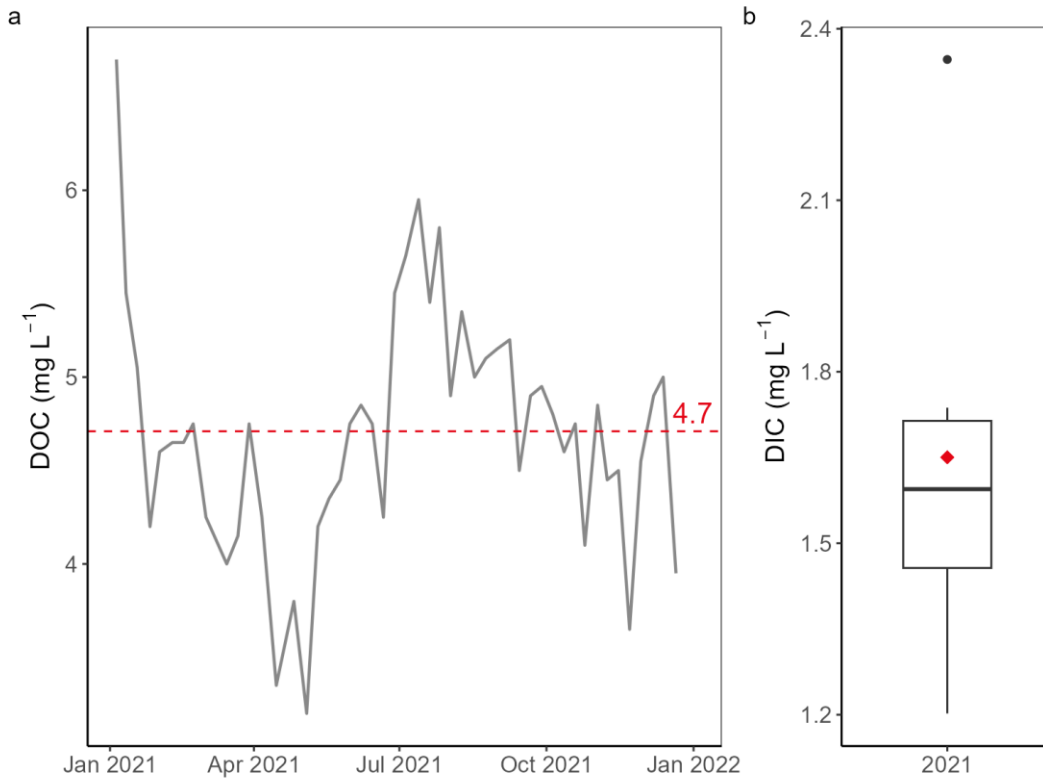


Figure 2.3 Dissolved carbon concentrations in Lac Laflamme during 2021. (a) Dissolved organic carbon (DOC) concentrations (mg L^{-1}) in 2021, with an annual mean of 4.7 mg L^{-1} (dashed red line). (b) Dissolved inorganic carbon (DIC) concentrations (mg L^{-1}) summarized as a boxplot for 2021, with a mean of 1.6 mg L^{-1} .

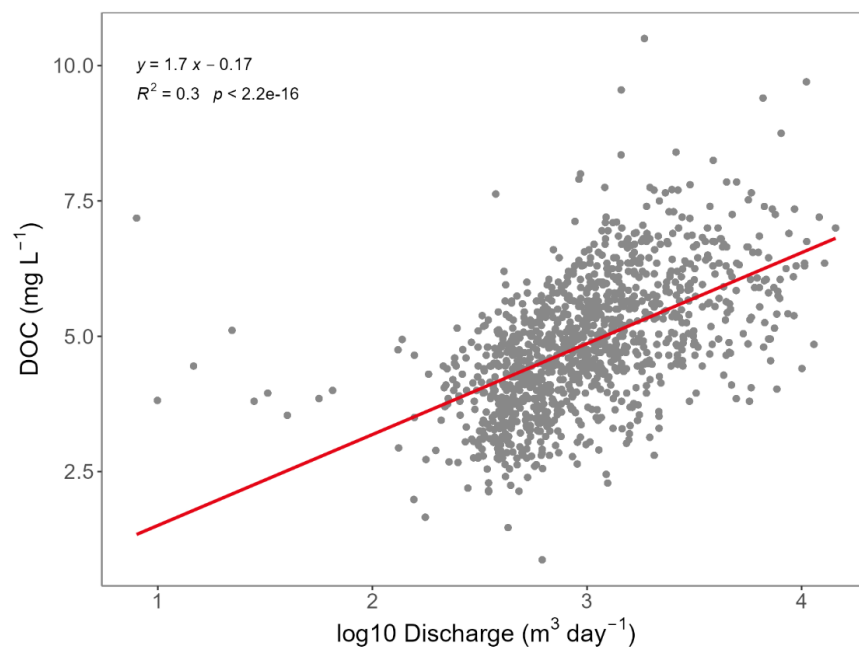


Figure 2.4 Relationship between discharge and DOC concentrations in Lac Laflamme (1999-2021). DOC concentrations (mg L^{-1}) plotted against $\log_{10}$ -transformed daily discharge ($\text{m}^3 \text{ day}^{-1}$). A positive relationship was observed (red regression line; $R^2 = 0.3$, $p < 0.00001$).

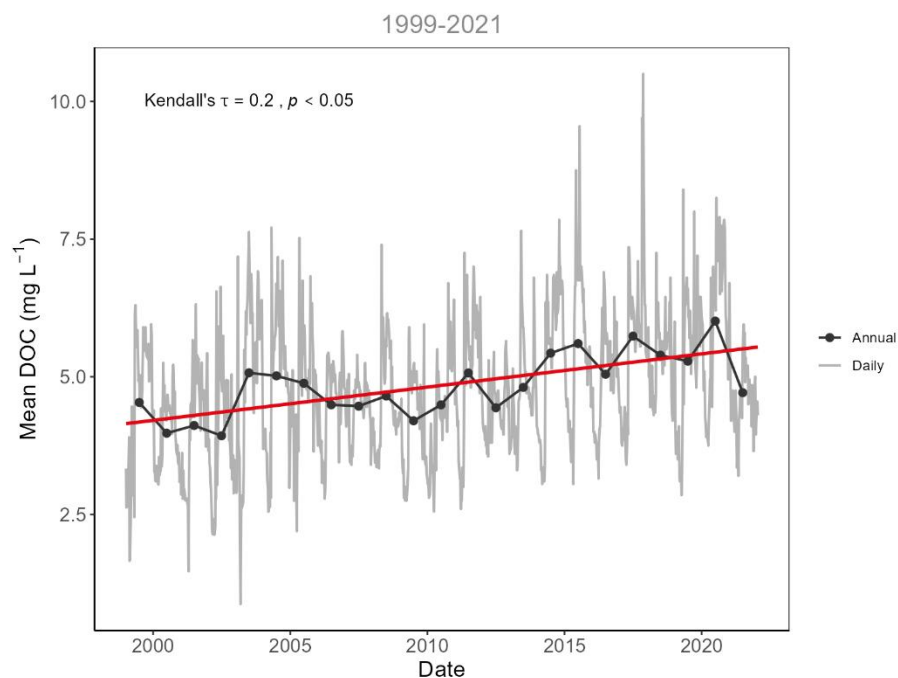


Figure 2.5 Long-term trends in DOC concentration in Lac Laflamme (1999-2021). Daily mean DOC concentrations (grey line) and annual means (in black) are shown with a fitted linear trend (red line). Mann-Kendall's test was performed to determine trends where Kendall's $\tau = 0.2$ ($p < 0.05$) and a 95% confidence interval of [0.09, 0.29].

2.3.3 Carbon Export

To calculate average annual DOC export for the long-term record between 1999–2021, average DOC concentrations were multiplied by average discharge (LF03). This was then scaled to an entire calendar year and normalized to the watershed area to derive an annual DOC export in $\text{g DOC-C m}^{-2} \text{ yr}^{-1}$. Annual DOC export averaged $4.1 (\pm 1.33) \text{ g C m}^{-2} \text{ yr}^{-1}$ between 1999–2021, with substantial year-to-year variability (Fig. 2.6a). Notably, DOC export was lower in 2021 than the long-term mean, averaging $0.006 \text{ g C m}^{-2} \text{ d}^{-1}$ (Fig. 2.6b). Although a slight upward trend can be observed until 2021, no statistically significant temporal trend was found for DOC export when 2021 was included (1999–2021: Kendall's $\tau = 0.24$, $p = 0.11$, $n = 23$), however, a significant positive trend was found for the 1999–2020 period (Kendall's $\tau = 0.33$, 95% CI [0.06, 0.5], $p < 0.05$, $n = 22$).

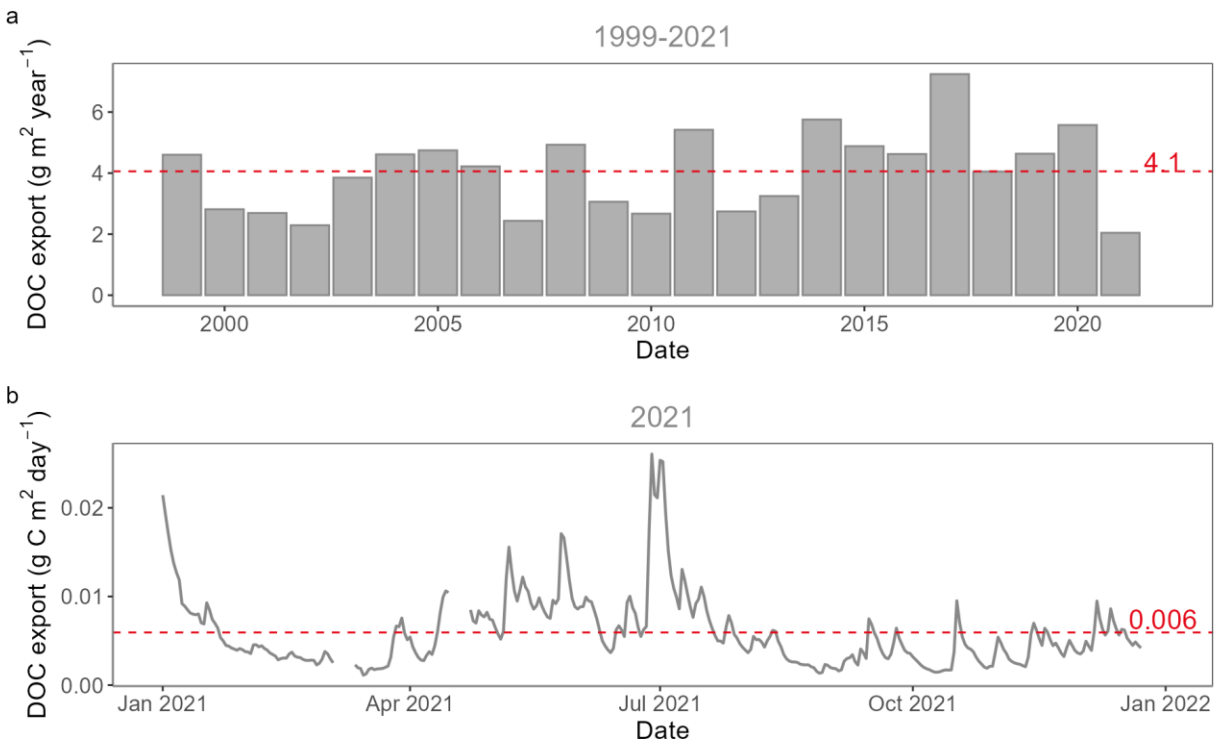


Figure 2.6 DOC export from the Lac Laflamme watershed. (a) Annual DOC export ($\text{g C m}^{-2} \text{ yr}^{-1}$) from 1999–2021, with a long-term mean of $4.1 \text{ g C m}^{-2} \text{ yr}^{-1}$ indicated by the dashed red line. (b) Daily DOC export ($\text{g C m}^{-2} \text{ yr}^{-1}$) during 2021, which averaged $0.006 \text{ g C m}^{-2} \text{ yr}^{-1}$ (dashed red line).

To quantify the DIC export component of the watershed C budget, DIC concentrations were measured at the watershed outflow (LF03) using discrete water samples. Continuous DIC measurements were not available; therefore, export was estimated as a single annual value. DIC concentrations were determined

from individual sampling events conducted in 2021 ($n = 11$) and averaged to represent mean outflow conditions. These mean concentrations were combined with annual discharge to calculate DIC export, which was then extrapolated to a full calendar year and normalized by watershed area. This approach yielded an estimated DIC export of 1.5 ± 0.5 g DIC-C $\text{m}^{-2} \text{yr}^{-1}$.

2.3.4 Partial Pressure of CO_2 and CH_4

Lake water $p\text{CO}_2$ showed high variability across temporal scales. Long-term monitoring (1983–2019) revealed mean annual $p\text{CO}_2$ of $719 \mu\text{atm}$ (± 509) (Fig. 2.8a). In 2021, hourly buoy measurements captured strong seasonal increases, with mean $p\text{CO}_2$ of $880 \mu\text{atm}$ (± 213) and maxima $>2000 \mu\text{atm}$ during autumn (Fig. 2.8b). $p\text{CH}_4$ was generally heightened and averaged $64 (\pm 26) \mu\text{atm}$ across the year, whereas monthly mean values ranged 21–83 μatm , with September exhibiting elevated concentrations (Fig. 2.8c).

Frequency distributions of daily measurements in 2021 revealed positively skewed distributions for both $p\text{CO}_2$ and diffusive fluxes, with median values lower than means (Fig. 2.7). Median $p\text{CO}_2$ was $816 \mu\text{atm}$ (standard error (SE): ± 24) and median CO_2 flux was $1,129 \text{ mg C m}^{-2} \text{d}^{-1}$ (SE: ± 67). CH_4 fluxes averaged $7.22 (\pm 3.0) \text{ mg C m}^{-2} \text{d}^{-1}$ and followed the same seasonal trend as $p\text{CH}_4$. CH_4 flux was highest in September ($9.86 \pm 1.21 \text{ mg C m}^{-2} \text{d}^{-1}$), followed by July ($6.4 \pm 2.12 \text{ mg C m}^{-2} \text{d}^{-1}$) and November ($1.78 \pm 1.5 \text{ mg C m}^{-2} \text{d}^{-1}$).

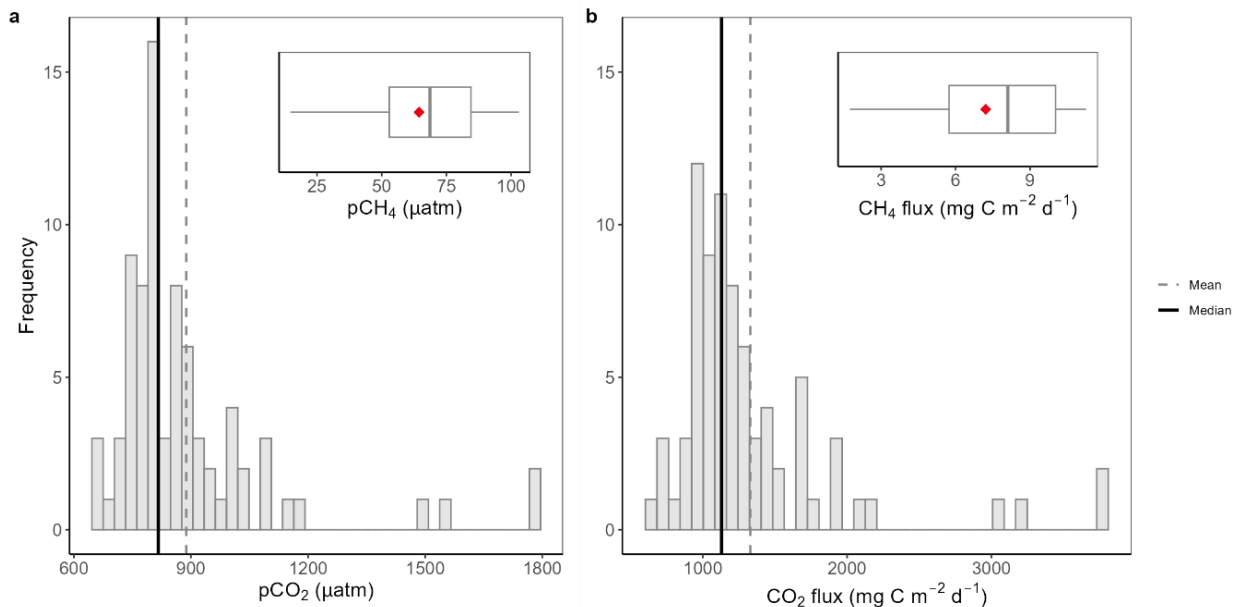


Figure 2.7 Frequency distributions of partial pressures and fluxes of CO_2 and CH_4 in Lac Laflamme during 2021. (a) Histogram of $p\text{CO}_2$ (μatm) with median (solid black line) and mean (dashed grey line) values indicated. The inset boxplot shows $p\text{CH}_4$ (μatm), with the red diamond marking the mean. (b) Histogram of diffusive CO_2 flux ($\text{mg C m}^{-2} \text{d}^{-1}$) with corresponding median (solid black line) and mean (dashed grey line). The inset boxplot shows CH_4 flux ($\text{mg C m}^{-2} \text{d}^{-1}$), with the red diamond indicating the mean. Both gases displayed positively skewed distributions, with means higher than medians due to episodic high values.

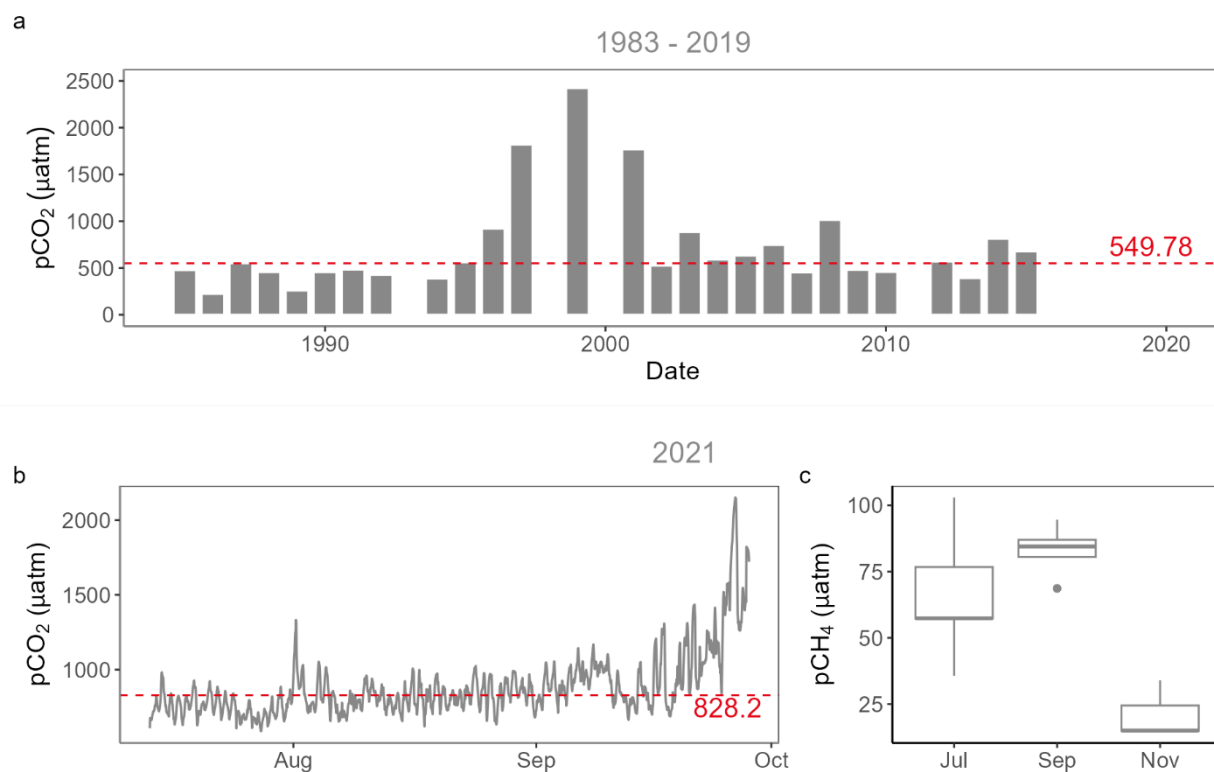


Figure 2.8 Partial pressure of CO₂ and CH₄ in Lac Laflamme. (a) Annual mean surface water $p\text{CO}_2$ (µatm) from 1983–2019, with the median value of 549.8 µatm shown as the dashed red line. (b) High-frequency buoy measurements of $p\text{CO}_2$ (µatm) during 2021. The median $p\text{CO}_2$ for 2021 was 828.2 µatm (dashed red line). (c) Boxplots of lake water $p\text{CH}_4$ (µatm) from discrete sampling campaigns in 2021.

2.3.5 Sediment Carbon Burial

Sediment C burial was derived from a single sediment core retrieved from Lake Laflamme in 2021. Sediment core analyses indicated stable organic C burial rates over the past 40 years (Table 1). Burial rates ranged from 1.3 to 1.8 g C m⁻² yr⁻¹, with a mean of 1.54 (± 0.18) g C m⁻² yr⁻¹ of watershed area. No clear monotonic trend in carbon burial was evident over time. Instead, burial rates averaged around a long-term mean of 1.54 g C m⁻² yr⁻¹, indicating relatively stable long-term sediment C accumulation in the lake - representing a persistent temporally stable carbon sink. The consistent C burial supports long-term sediment C sequestration and reflect cumulative watershed inputs and in-lake processing rather than short-term variability.

Table 2.1 Organic carbon burial rates in Lac Laflamme sediments. Organic carbon burial (g C m⁻² yr⁻¹) at dated intervals from 1985 to 2018, based on sediment core analyses. Burial rates varied between 1.33 and 1.83 g C m⁻² yr⁻¹, with a long-term mean of 1.54 g C m⁻² yr⁻¹.

Year	Organic Carbon Burial (g C m ⁻² yr ⁻¹)
1985	1.36
1992	1.83
1999	1.64
2005	1.56
2012	1.33
2018	1.50
<i>Average Carbon Burial: 1.54 g C m⁻² yr⁻¹</i>	

2.3.6 Whole-System Carbon Budget

The Integration of diffusive emissions, downstream export and sediment burial, reveals the dominant C pathways within the Lake Laflamme watershed in 2021 (Table 2.2). It is important to note that all values expressed here are in g C m⁻² yr⁻¹ of watershed area for 2021. First, diffusive CO₂ emissions represented the largest C flux of 26.15 g C m⁻² yr⁻¹ and had exceeded all other pathways by more than an order of magnitude. In contrast, CH₄ emissions contributed minimally to the C budget (0.14 g C m⁻² yr⁻¹). Downstream export of dissolved C played a minor role in comparison to CO₂ emissions, only accounting

for a combined $3.54 \text{ g C m}^{-2} \text{ yr}^{-1}$ ($2.04 \text{ g DOC-C m}^{-2} \text{ yr}^{-1}$; $1.50 \text{ g DIC-C m}^{-2} \text{ yr}^{-1}$) that was exported out of the watershed through the Lake Laflamme outflow. Sediment C burial represented a persistent but secondary C sink within the watershed, albeit with a sediment C burial rate of $1.54 \text{ g C m}^{-2} \text{ yr}^{-1}$. Burial rates were comparable to DOC and DIC export, indicating that long-term storage in sediments represent a non-negligible component of the watershed C balance. Overall, these results demonstrate that C losses from the aquatic system are dominated by atmospheric CO_2 emissions, with downstream export and sediment C burial playing complementary, but smaller, roles in regulating the fate of aquatic C within the Lake Laflamme watershed.

CO_2 Diffusive Flux ($\text{g C m}^{-2} \text{ yr}^{-1}$)	CH_4 Diffusive Flux ($\text{g C m}^{-2} \text{ yr}^{-1}$)	DOC Export ($\text{g C m}^{-2} \text{ yr}^{-1}$)	DIC Export ($\text{g C m}^{-2} \text{ yr}^{-1}$)	Sediment Carbon Burial ($\text{g C m}^{-2} \text{ yr}^{-1}$)
26.15	0.14	2.04	1.50	1.54

Table 2.2 Annual carbon budget for the Lac Laflamme watershed (2021). Carbon fluxes and storage are expressed in $\text{g C m}^{-2} \text{ yr}^{-1}$ of watershed area.

2.4 Discussion

Hydrology exerted a strong influence on DOC dynamics in the Lac Laflamme watershed. The positive correlation between discharge and DOC concentrations ($R^2 = 0.30$, $p < 0.001$; Fig. 2.5) mirrors patterns reported in other boreal catchments, where high-flow events mobilize terrestrially derived organic matter from soils and riparian zones (Laudon et al., 2011). Long-term monitoring revealed a significant increase in DOC concentrations (Fig. 2.4), consistent with the widespread “browning” phenomenon observed across northern lakes and streams (Meyer-Jacob et al., 2019; Monteith et al., 2007; Rodríguez-Cardona et al., 2025; Weyhenmeyer & Karlsson, 2009). Unlike larger rivers, where dilution during high-flow can reduce concentrations, the catchment characteristics of Lake Laflamme appear to amplify export pulses. This reinforces the notion that small headwater lakes function as responders to hydrological fluctuations, with disproportionately high C turnover relative to their size (Pi et al., 2022).

The year 2021 was notably drier than the long-term average, with mean discharge 40% lower than the 1999–2021 record of $1,511 \text{ m}^3 \text{ day}^{-1}$ (Fig. 2.2). This anomaly had measurable impacts on carbon dynamics: DOC export was lower than the multi-decadal mean (Fig. 2.6b), while in-lake $p\text{CO}_2$ remained elevated ($828 \mu\text{atm}$ on average; Fig. 2.8b). Such conditions highlight the sensitivity of small headwater lakes to interannual hydrological variability (Lepistö et al., 2008). Dry years reduce lateral transport of DOC, decoupling concentrations from export, and may shift the balance toward in-lake mineralization and

atmospheric efflux (Dinsmore et al., 2013; Kokic et al., 2015). Because long-term trends in DOC export were only significant when 2021 was excluded (Kendall's $\tau = 0.33$, 95% CI [0.06, 0.5], $p < 0.05$, $n = 22$), 2021 underscores the importance of hydrological extremes in shaping historical records and complicating the detection of directional trends. Given projections of more frequent summer droughts in boreal regions (Bring et al., 2016; Gauthier et al., 2015), years like 2021 may become increasingly representative of future conditions.

The Lake Laflamme C budget indicates that gaseous fluxes, particularly CO_2 efflux ($26.2 \text{ g C m}^{-2} \text{ yr}^{-1}$), overwhelmingly dominate C losses relative to aquatic export of DOC and DIC, and sediment C burial (Table 2.2). This aligns with studies across boreal lakes that emphasize the role of inland waters as net sources of CO_2 to the atmosphere (Lapierre et al., 2013; Prairie, 2008; Sobek et al., 2005). Although CH_4 contributed little to the annual budget ($0.14 \text{ g C m}^{-2} \text{ yr}^{-1}$), its seasonal variability and heightened $p\text{CH}_4$ in September and parts of July (Fig. 2.8c) may have disproportionate impacts on greenhouse gas radiative forcing due to the high global warming potential of CH_4 (Bastviken et al., 2004; Wik et al., 2016). The seasonal increase in $p\text{CO}_2$ during autumn (Fig. 2.8b) reflects both declining primary production and with enhanced organic matter mineralization, processes that are tightly linked to stratification and mixing dynamics (Karlsson et al., 2013; Vachon et al., 2016). In addition to processing organic C, the lake is likely degassing terrestrially derived CO_2 brought in by groundwater.

Sediment core analyses revealed stable OC burial rates ($1.54 \text{ g C m}^{-2} \text{ yr}^{-1}$ of watershed area) over the past four decades (Table 2.1). This long-term stability contrasts with other boreal systems where browning and increased terrestrial inputs have accelerated burial rates in recent decades (Anderson et al., 2019; Heathcote, et al., 2015). When normalized to the total catchment area, these burial values demonstrate that Lac Laflamme acts as a highly efficient regional funnel, sequestering a substantial mass of terrestrial carbon relative to the size of its watershed. This significant burial footprint indicates that long-term sediment accumulation is a major pathway for carbon mitigation in this landscape. Rather than functioning purely as passive conduits or exclusive 'reactors' that mineralize all incoming organic matter to CO_2 (Tranvik et al., 2009), these findings suggest a more balanced role for Lac Laflamme, where high atmospheric evasion coexists with robust, sustained landscape-level carbon sequestration.

Compared to regional averages, Lake Laflamme exhibits lower DOC export of an average $4.1 \text{ g C m}^{-2} \text{ yr}^{-1}$ for the period between 1999-2021 (Fig. 2.6a) but comparable CO_2 emissions (J.-F. Lapierre et al., 2013;

Vachon et al., 2017). This supports the view that headwater lakes, despite their small size, are disproportionate contributors to atmospheric C release (Pi et al., 2022; Raymond et al., 2013). The absence of a complex upstream network likely reduces cumulative DOC export while intensifying in-lake processing. Overall, Lake Laflamme reflects the emerging view that small boreal lakes are hotspots of C turnover, disproportionately contributing to atmospheric CO₂ release relative to their areal extent (Kankaala et al., 2013; Kokic et al., 2015).

2.5 Conclusion

This chapter provides a comprehensive assessment of hydrological controls and aquatic C fates within the Lake Laflamme watershed by integrating long-term discharge records (1999-2021), dissolved C dynamics (1999-2021), greenhouse gas concentrations and fluxes (1983-2021), sediment C burial (1985-2018), and a whole-system C budget. Over more than two decades of monitoring, discharge exhibited pronounced interannual variability but no long-term directional trend, emphasizing the importance of episodic hydrological events rather than gradual change in regulating C transport. In contrast, DOC concentrations increased significantly over time (Kendall's $\tau = 0.20$, 95% CI [0.09, 0.29], $p < 0.05$, $n = 1,122$), consistent with widespread browning trends observed across boreal regions (Rodríguez-Cardona et al., 2023). Together, these patterns indicate that while hydrology governs short-term variability in C mobilization, longer-term changes in C supply to the aquatic system are driven by shifts in terrestrial C pools and watershed biogeochemistry.

Hydrological variability emerged as a central control on C export and in-lake processing. Strong coupling between discharge and DOC concentrations highlights the role of high-flow events in mobilizing terrestrially derived organic matter (Fig. 2.5), whereas dry conditions, such as those observed in 2021, reduced lateral export despite elevated in-lake DOC concentrations (Fig 2.6). This decoupling illustrates how low-flow years can shift the balance of C processing away from downstream transport and toward in situ mineralization and atmospheric efflux. The sensitivity of DOC export trends to the inclusion of a single dry year underscores the importance of long-term records for detecting directional change and suggests that increasing hydrological variability may complicate future assessments of watershed-scale C export.

Greenhouse gas dynamics further demonstrate the dominance of in-lake processing within the Lake Laflamme system. Both long-term and high-frequency measurements revealed persistently elevated $p\text{CO}_2$ and substantial diffusive CO₂ emissions (Fig 2.7). Methane concentrations and fluxes were lower in

magnitude but exhibited strong seasonal variability, with elevated $p\text{CH}_4$ during late summer and early autumn (Fig. 2.8c). Although CH_4 contributed little to the annual C budget, its temporal variability and high global warming potential suggest that even modest fluxes may have disproportionate climatic relevance.

Sediment core analyses indicate that OC burial in Lake Laflamme has remained stable over the past four decades. Burial rates averaged $1.54 \text{ g C m}^{-2} \text{ yr}^{-1}$ and showed no evidence of an increasing trend despite rising DOC concentrations in surface waters. This stability contrasts with observations from similar lakes where increased terrestrial inputs have enhanced sediment carbon sequestration (Ferland et al., 2014), and instead suggests limited burial efficiency in Lake Laflamme. The majority of C entering the lake is therefore likely respired and returned to the atmosphere rather than stored long-term in sediments, reinforcing the role of the lake as a biogeochemical processor rather than a C sink.

Integration of all quantified C pathways highlights the overwhelming dominance of atmospheric CO_2 emissions within the watershed carbon budget. Diffusive CO_2 efflux ($26.15 \text{ g C m}^{-2} \text{ yr}^{-1}$) exceeded downstream DOC and DIC export and sediment C burial by more than an order of magnitude, while CH_4 emissions contributed only a minor fraction of total C losses. Lateral export and burial nonetheless represent meaningful secondary pathways, together accounting for a substantial portion of non-gaseous C fate. These results underscore that C losses from the Lake Laflamme watershed are governed primarily by in-lake mineralization and gas exchange with the atmosphere, rather than by downstream transport or long-term storage.

Overall, Lake Laflamme exemplifies the emerging view that small headwater lakes are hotspots of carbon emissions within boreal landscapes (Kankaala et al., 2013; Premke et al., 2016). Despite modest DOC export relative to regional averages, the lake exhibits CO_2 emissions comparable to larger systems, reflecting intense in-lake processing driven by hydrology, organic matter supply, and physical mixing dynamics. As climate change is expected to increase hydrological extremes and alter terrestrial C inputs across boreal regions, systems like Lake Laflamme are likely to play an increasingly important role in regulating watershed-scale C balances and atmospheric C exchange. This chapter provides a mechanistic foundation for integrating small lake processes into broader watershed and regional C budgets.

CONCLUSION

Together, these two case studies show that boreal aquatic networks function as highly active components of the landscape C cycle, where inland waters not only transport terrestrial C but repeatedly transform and redistribute it among atmospheric evasion, downstream export, and longer-term sediment storage. Across both the Bernard River watershed and Lac Laflamme (LF), the watershed-scale aquatic C footprint was dominated by C loss to the atmosphere, underscoring the broader implication that inland waters can potentially offset neighboring terrestrial C sequestration. By framing both budgets at the watershed scale and expressing fluxes in common units (per watershed area), this thesis provides a directly comparable synthesis across two end-member watershed configurations: a small, simple headwater lake catchment (LF) and a larger, networked stream–lake continuum (Bernard River watershed).

A central cross-system finding is that diffusive CO₂ evasion consistently exceeded DOC/DIC export and sediment burial. These results, on one hand, indicate that mineralization during aquatic transport and processing is a primary fate for terrestrially derived C entering boreal waters, and on the other hand, may reflect lateral influx of terrestrial CO₂ emitted in inland waters. In Bernard, CO₂ emissions were especially pronounced in low-order streams, where high $p\text{CO}_2$ (Fig. 1.15) drove efflux, consistent with headwaters acting as intense biogeochemical reactors supplied by organic-rich soils, wetlands, and bog-influenced waters. In LF, continuous lake $p\text{CO}_2$ remained elevated while annual CO₂ efflux (Fig. 2.7) overwhelmingly dominated the budget, reinforcing that even small headwater lakes can be persistent atmospheric CO₂ sources. The convergence of these patterns across contrasting watershed types strengthens the general conclusion that boreal aquatic systems are not passive “pipes,” but rapid-processing reactors that return a large fraction of mobilized C to the atmosphere.

Hydrology emerged as the shared organizing force controlling both the timing and the partitioning of C fates, particularly through its control on DOC mobilization and downstream export. In Bernard, a small number of high-flow, high-connectivity periods disproportionately governed annual DOC export, consistent with event-driven activation of riparian and peatland flowpaths that flush DOC to the channel network. In LF, discharge was also positively related to DOC concentration and export (Fig 2.5), and the small catchment geometry appeared to amplify export pulses rather than dilute them. Importantly, interannual variability highlighted how extreme hydrologic years can shift apparent trends and reorganize the balance among pathways: LF’s anomalously dry year reduced DOC export while maintaining elevated

$p\text{CO}_2$, suggesting a shift toward greater in-lake processing and atmospheric efflux when lateral transport is constrained.

The two watersheds nonetheless differed in how landscape structure and network complexity shaped where C was processed and how heterogeneity emerged. Bernard's hierarchical stream network and diverse lentic components created repeated opportunities for both transformation and addition along the aquatic continuum, with clear stream-order structuring of CO_2 dynamics: headwaters produced disproportionate emissions (Fig. 1.18), while downstream reaches reflected a transition toward exchange-limited conditions as gas transfer velocities increased and $p\text{CO}_2$ declined (Fig 1.15; Fig 1.17). In parallel, Bernard's lake network displayed strong size structuring of greenhouse gas emissions, with small lakes exhibiting high variability and larger systems acting as integrative processing hubs (Fig. 1.20). By contrast, LF's simpler topology concentrated transformation within a single lake, emphasizing the role of residence time and internal metabolism in regulating CO_2 supersaturation and efflux in headwater systems.

Across both case studies, methane represented a comparatively minor fraction of the annual C budget when considering diffusive fluxes alone, but with important caveats and implications. LF showed low annual diffusive CH_4 emissions yet episodic peaks that may be climatically disproportionate given methane's high radiative forcing. In Bernard, diffusive CH_4 emissions were also small relative to CO_2 , but the absence of ebullition measurements that are particularly relevant in small, shallow, peat- and wetland-influenced waters, means that total methane emissions likely remain underestimated. Taken together, these results suggest that CO_2 dominates the C mass balance in these boreal aquatic networks, while methane remains a key uncertainty for greenhouse forcing and a priority for future methodological integration.

Sediment C burial emerged in both watersheds as a persistent but secondary sink: climatically relevant over long timescales, yet modest relative to atmospheric and lateral fluxes. In LF, burial rates were stable over the past 40 years and represented a small share of total C losses (Table 2.1), indicating limited long-term sequestration capacity despite evidence for increasing DOC concentrations in the watershed. In Bernard, multi-decadal burial in Lake Bernard exhibited variability but converged on a long-term mean consistent with a role as a long-term integrator of watershed C delivery and processing rather than a dominant sink (Table 1.1) . This cross-system pattern reinforces a core conclusion for boreal landscapes:

burial is essential to close aquatic C budgets, but near-term watershed C balance is regulated more strongly by hydrologically responsive evasion and export.

The combined evidence supports a nuanced interpretation of residence time, network complexity, and hydrologic variability as co-controls on aquatic C fate. The expectation that the more complex Bernard system would provide greater opportunity for DOC degradation and CO₂ production is broadly consistent with the strong role of network processing, though both watersheds ultimately expressed atmospheric loss as the dominant pathway. The predicted contrast in the ratio of DOC export to greenhouse gas emissions is best viewed through the lens of hydrology and connectivity: export is episodic and highly sensitive to runoff generation, whereas CO₂ efflux can remain persistently large even when export is suppressed (as illustrated by LF during drought conditions, Fig. 2.4). Finally, the hypothesis that seasonal and interannual hydrology reorganizes the relative importance of export, emission, and storage is strongly supported across both systems, with event-driven connectivity and climate anomalies emerging as key determinants of when and where C is routed, processed, and ultimately released.

Overall, this thesis advances a watershed-scale, bottom-up framework for quantifying aquatic C footprints in boreal landscapes and demonstrates why resolving spatial heterogeneity (stream order, lake size structure) and temporal variability (events, droughts, seasonal mixing) is necessary for credible upscaling. The most important next step is to embed these aquatic budgets within full watershed C accounting that explicitly links terrestrial C stocks and fluxes (forests, wetlands, soils) with aquatic processing, thereby quantifying how much landscape-derived C is retained on land versus emitted or exported via inland waters. Methodologically, incorporating ebullitive methane emissions, winter fluxes, and a broader representation of lake burial across lake networks would refine closure and reduce uncertainty. Conceptually, these two Québec boreal case studies illustrate that future shifts in hydrology and climate are likely to alter not just the magnitude but the pathway partitioning of inland-water C, with direct consequences for regional and global C budget estimates.

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