

Riparian vegetation and open water carbon greenhouse gas fluxes of urban stormwater ponds

by

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A thesis

presented to the University of Waterloo

in fulfilment of the

thesis requirement for the degree of

Master of Science

in

Earth Sciences

Waterloo, Ontario, Canada, 2026

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Author's declaration

This thesis consists of material all of which I authored or co-authored: see Statement of contributions included in the thesis. This is a true copy of the thesis, including any final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

Statement of contributions

Chapter 2 of this thesis consists of a co-authored manuscript-format paper and will be modified for journal submission and reviewed by all co-authors. Chapter 3 is also in a manuscript-style format and is part of a larger co-authored data paper. In both these Chapters, I was primarily responsible for the study design, data collection, data analysis, and writing. The contributions of the listed co-authors are as follows for both Chapters: I conducted the field monitoring, performed the sample and data analysis with guidance from Dr. Fereidoun Rezanezhad, Dr. Philippe Van Cappellen, and Stephanie Slowinski. The gap-filling process were completed with the assistance of Dr. Jovana Radosavljevic. I drafted the original manuscript while all other authors provided critical feedback and contributions to shaping the research, analysis, and the manuscript. I am the sole author of all other chapters in this thesis.

Abstract

Stormwater ponds (SWPs) are a common stormwater management technology in new urban developments and have been suggested to be significant sources of the carbon greenhouse gases (GHGs); *e.g.*, carbon dioxide (CO₂) and methane (CH₄). However, they also sequester organic carbon (OC) and reduce the surface runoff of nutrients, hence, altering nutrient limitation patterns, trophic conditions, and GHG exchanges. Although numerous studies have focused on estimating open water GHG emissions in artificial ponds, there are limited studies that evaluate both open water and riparian vegetation fluxes from urban SWP systems comprehensively. This study quantified CO₂ and CH₄ fluxes from riparian vegetation and open water in two SWPs in the City of Kitchener, Ontario, located in residential (Activa pond) and industrial (Wabanaki pond) catchments.

In Chapter 2, the goal was to compare flux pathways and net source-sink status and assess how land use, spatial variability between forebay and main basin zones, and pond design influence the GHG dynamics. Using vegetation and floating chambers, CO₂ and CH₄ fluxes were measured bi-weekly across all seasons, capturing net ecosystem exchange (NEE), ecosystem respiration (ER), and gross primary production (GPP) from riparian vegetation, plus the diffusive and ebullitive fluxes from the open water surface.

Significant differences in the fluxes between the riparian vegetation and open water surfaces were observed. High photosynthetic activity allowed the riparian zone to function as a net carbon sink (-142.3 mol m⁻² yr⁻¹ for Activa and -140.5 mol m⁻² yr⁻¹ for Wabanaki). However, higher OC inputs from the industrial Wabanaki catchment enhanced sediment CH₄ production, particularly in the forebay, resulting in higher vegetation CH₄ emissions that weakened its GHG-sink strength relative to the residential Activa pond., resulting in CO₂-equivalent fluxes of -141.4 mol CO₂-eq

$\text{m}^{-2} \text{yr}^{-1}$ for Aactiva and only $-94.8 \text{ mol CO}_2\text{-eq m}^{-2} \text{yr}^{-1}$ for Wabanaki. Although Aactiva had greater per-area vegetation CO_2 -equivalent uptake, its small riparian zone limited whole-pond removal, whereas Wabanaki's extensive riparian area provided larger total CO_2 uptake ($-3.6 \text{ mol CO}_2\text{-eq m}^{-2} \text{yr}^{-1}$ for Aactiva and $-132.1 \text{ mol CO}_2\text{-eq m}^{-2} \text{yr}^{-1}$ for Wabanaki).

Open water fluxes were dominated by ebullitive CH_4 , which accounted for about 88% of the total CO_2 -equivalent flux ($125.6 \text{ mol CO}_2\text{-eq m}^{-2} \text{yr}^{-1}$ for Aactiva and $119.6 \text{ mol CO}_2\text{-eq m}^{-2} \text{yr}^{-1}$ for Wabanaki), making the open water surface a net GHG source. The forebay of the ponds consistently acted as carbon GHG hotspots due to higher carbon loading, nutrient enrichment, and reducing conditions, while larger, deeper main basins mitigated emissions.

Overall, both Aactiva and Wabanaki ponds ultimately acted as net GHG sources, with annual emissions of $189.6 \text{ kmol CO}_2\text{-eq yr}^{-1}$ at Aactiva and $349.9 \text{ kmol CO}_2\text{-eq yr}^{-1}$ at Wabanaki, driven primarily by CH_4 emissions. These findings highlight the combined influence of land-use-driven carbon loading, riparian zone extent, and the contrasting behaviour of forebays and main basins in controlling stormwater pond GHG dynamics.

In Chapter 3, the full dataset collected during the study period were presented. Based on field experience, we outline practical recommendations for municipalities, including linking monitoring objectives to decision-making, applying tiered spatial and temporal sampling, quantifying flux pathways, measuring key water and sediment drivers, integrating hydrologic data, and tracking vegetation cover for upscaling. Together, these approaches create a scalable, transparent framework for incorporating SWPs into city-scale GHG monitoring and management.

Acknowledgements

I would like to thank my supervisors Dr. Fereidoun Rezanezhad and Dr. Philippe Van Cappellen for your constant support and encouragement throughout my studies. The many opportunities you provided whether it was presenting at conferences or pursuing professional certifications enriched my academic experience. My visit to Vienna for the EGU 2025 conference is an experience I will always remember with great fondness. I would also like to thank my committee members Dr. Tonya DelSontro and Dr. Kevin Stevens for your valuable guidance, thoughtful suggestions, and crucial feedback to keep my research moving.

Thanks to Steph Slowinski for all the support in the field and in the lab, as well as for all the insightful advice and continual encouragement throughout my research journey. I would also like to thank Dr. Jovana Radosavljevic and Bhaleka Persaud for their assistance with data analysis and figure preparation. Thanks to Marianne Vandergriendt, Dr. Shuhuan Li, Hang Nguyen, Kayla Martin, and all the co-cp students for assistance with field sampling and laboratory analyses, including Sam Smith, Camille Barre, Katie Miller, Ben Depetris, Laura Hammond, Devine Samoth, Melissa LeBlonc, Emily Zelenyt, Miles Yoshida, and William Dolson.

This research would not have been possible without the support of our funding sources: the Natural Sciences and Engineering Research Council of Canada (NSERC) Alliance Missions grant to the project “Adaptive management of green stormwater infrastructure to reduce greenhouse gas emissions from urban watersheds” (Grant No: ALLRP 577124-2022), the Global Water Futures (GWF) program funded by the Canada First Research Excellence Fund (CFREF), and the Global Water Futures Observatories (GWFO) program funded by Canada Foundation for Innovation-Major Science Initiatives (CFI-MSI).

Finally, thank you to all the fellow members of the Ecohydrology Research Group for your thoughtful questions and valuable feedback during group meetings, as well as all the coffee breaks and office conversations over the years. I am deeply grateful to my family for your unwavering confidence and encouragement throughout my research, and to my friends and my boyfriend, Yizhou Sun, for your continual emotional support and help in everyday life. This thesis is dedicated to my parents.

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List of abbreviations

GHG	Greenhouse gas
OM	Organic matter
CO ₂	Carbon dioxide
CH ₄	Methane
OC	Organic carbon
SWP	Stormwater pond
COK	City of Kitchener
N ₂ O	Nitrous oxide
WMO	World Meteorological Organization
IG ³ IS	Integrated Global Greenhouse Gas Information System
IPCC	Intergovernmental Panel on Climate Change
GPC	Global Protocol for Community-Scale
NEE	Net ecosystem exchange
ER	Ecosystem respiration
GPP	Gross primary production
FAIR	Findable, Accessible, Interoperable, and Reusable
PAR	Photosynthetically active radiation
GWP	Global warming potential
LUE	Light use efficiency
GAW	Global Atmosphere Watch
DIC	Dissolved inorganic carbon
DO	Dissolved oxygen

DOC	Dissolved organic carbon
GC	Gas chromatography
TOC	Total organic carbon
YSI	Yellow Springs Instruments
EC	Electrical conductivity
ORP	Oxidation-reduction potential

List of symbols

F	Flux
S	slope obtained from the concentrations of CO ₂ and CH ₄ measured by the LI-COR analyzer over 5 minutes
V	Chamber volume
mV	Molar volume
A	Surface area of chamber
C	Conversion factor to convert seconds into days
CO ₂ -eq	CO ₂ equivalents
ε_g	Effective light use efficiency
ε_0	Maximum light use efficiency
GPP_{max}	Maximum GPP flux observed at each collar
T_{scalar}	Scalars of temperature
W_{scalar}	Scalars of water
P_{scalar}	Scalars of plant phenology on photosynthesis
T_{min}	Minimum air temperature
T_{max}	Maximum air temperature
T_{opt}	Optimum air temperature
n_{sam}	Total moles of CO ₂ and CH ₄ in the original pond water sample
n_{HS}	Total moles of CO ₂ and CH ₄ in the headspace
n_w	Total moles of CO ₂ and CH ₄ in the water
n_{gas}	Total moles of CO ₂ and CH ₄ in the field air
Chl- <i>a</i>	Chlorophyll- <i>a</i>

1 Introduction

1.1 Greenhouse gas emissions from small waterbodies

Inland waters are an essential component of the global carbon cycle, acting as both sources and sinks of greenhouse gases (GHGs) through processes of organic matter (OM) mineralization and sediment carbon sequestration (Downing *et al.*, 2008; Raymond *et al.*, 2013; Rosentreter *et al.*, 2021). While past research has focused primarily on large lakes, rivers, and wetlands, small inland waters such as ponds have historically received less attention due to challenges in quantifying their global abundance and contribution to emissions (Raymond *et al.*, 2013). However, small waterbodies are ubiquitous across landscapes, and their cumulative surface area is substantial enough to exert a disproportionate influence on global carbon budgets (Holgerson & Raymond, 2016; Gorsky *et al.*, 2019).

Holgerson and Raymond (2016) estimated that ponds smaller than 0.001 km² comprise only 8.6% of total lake and pond surface area, yet they may account for roughly 15% of inland water carbon dioxide (CO₂) emissions and 40% of diffusive methane (CH₄) fluxes. Similarly, Peacock *et al.* (2021) found that artificial ponds and ditches are significant sources of CO₂ and CH₄, with the smallest systems showing the highest fluxes. These patterns reflect both higher organic carbon (OC) burial rates and greater metabolic activity in small waterbodies (Downing *et al.*, 2008; Taylor *et al.*, 2019). Collectively, these findings suggest that the contribution of small aquatic systems to the global carbon cycle is substantially underestimated.

The ecological importance of small artificial ponds has grown alongside rapid urbanization, agricultural intensification, and industrial expansion (Peacock *et al.*, 2021). For example, the

number of artificial small waterbodies in the United States increased more than 450-fold between 1934 and 2005 (Grinham *et al.*, 2018), mirroring global trends. Because these systems are anthropogenic, their emissions are included in national GHG inventories under the Intergovernmental Panel on Climate Change (IPCC, 2019), unlike natural lakes or wetlands. Consequently, understanding GHG fluxes from small-constructed ponds, such as urban stormwater management ponds, agricultural retention basins, and industrial runoff ponds, is crucial for improving emission inventories, guiding urban design, and informing climate adaptation and mitigation strategies.

1.2 Stormwater ponds and knowledge gap

Stormwater ponds (SWPs) are widely constructed in urban areas as integral infrastructure for managing runoff and mitigating flood risk. By providing detention and storage capacity, they attenuate peak flows and reduce downstream flooding (USEPA, 2021). They are particularly important in the context of Canadian cities, where, according to a study by Gaur *et al.*, 2019, between 40% and 60% of urban areas are projected to experience increased flooding frequencies. As climate change increases the frequency and intensity of rainfall events, SWPs are becoming increasingly important components of urban adaptation and resilience strategies (Abduljaleel *et al.*, 2023; Esraz-UI-Zannat *et al.*, 2024). Beyond flood control, these systems contribute to groundwater recharge, baseflow maintenance, pollutant removal, and habitat provision, aligning with the principles of nature-based solutions and sustainable urban water management (USEPA, 2021). For example, the City of Kitchener (COK) in Ontario manages more than 150 stormwater management ponds across a variety of catchments (City of Kitchener, 2021), highlighting the

extent to which these systems are now embedded in urban infrastructure and hydrologic management.

A typical SWP comprises the embankment, which stabilizes pond margins and prevents overflow, and the open water zone, representing the permanent pool that regulates hydraulic residence time and sedimentation (City of Toronto, 2015; USEPA, 2021). In this study, the riparian zone is defined and delineated based on field observations as the vegetated transitional area between open water and the embankment, characterized by emergent plant stands such as *Phragmites australis* and *Typha spp.* These zones differ in hydrology, vegetation cover, and sediment biogeochemistry, all of which influence GHG fluxes (Figure 1-1a).

Numerous studies have demonstrated that SWPs emit both CO₂ and CH₄, with flux magnitudes varying across sites and climatic regions (Gorsky *et al.*, 2019; Peacock *et al.*, 2021; Goeckner *et al.*, 2022). Vegetated zones often exhibit higher total respiration due to enhanced microbial and root activity (Ström *et al.*, 2007; D’Acunha & Johnson, 2019), while photosynthesis can partially offset these emissions by assimilating CO₂. However, quantitative assessments integrating both open water and riparian vegetation fluxes remain limited. Nitrous oxide (N₂O) fluxes are generally minor, accounting for less than 1% of total GHG emissions from SWPs in CO₂-equivalents (Blaszczyk *et al.*, 2018; Badiou *et al.*, 2019; Gorsky *et al.*, 2019), justifying a focus on CO₂ and CH₄ as dominant carbon-based GHGs in this study (Figure 1-1b).

1.3 CO₂ and CH₄ flux pathways from open water surface

In SWPs, OM decomposition consumes oxygen and generates anaerobic conditions near the sediment-water interface. Under these anoxic conditions, methanogenic archaea produce CH₄ through methanogenesis, the final step in anaerobic carbon degradation involving low-energy-yield redox reactions (Lyu *et al.*, 2018). At the same time, methanotrophic oxidation acts as the main CH₄-consuming process, converting part of the produced CH₄ back to CO₂ within the water column. CH₄ emitted from the pond surface originates through two principal mechanisms: diffusion and ebullition. Diffusive CH₄ flux occurs when dissolved CH₄ escapes gradually across the air-water interface, while ebullitive emissions result from the buildup of CH₄ bubbles in sediments that rise through the water column and release directly to the atmosphere. Due to CH₄'s low solubility in water (~22 mg L⁻¹ at 25°C, over 100 times lower than that of CO₂), bubbles form readily once saturation is exceeded (NCBI, 2025). Ebullition typically accounts for 50-90% of total CH₄ emissions, though the relative contribution depends on temperature, sediment composition, and OM availability (Malyan *et al.*, 2022).

CO₂ fluxes, in contrast, are primarily driven by respiration and OC mineralization. CO₂ is produced by microbial oxidation of dissolved and particulate OC, as well as respiration by algae and aquatic macrophytes (Gorsky *et al.*, 2019; Malyan *et al.*, 2022). Shallow urban ponds often exhibit high CO₂ production because of their large surface-to-volume ratios and continuous inputs of terrestrial OM from stormwater runoff (Holgerson, 2015). These inputs include allochthonous carbon from surrounding catchments and autochthonous carbon produced internally by aquatic vegetation and algae. During daylight, photosynthetic organisms, such as algae, submerged plants, and cyanobacteria, consume CO₂ to produce oxygen and biomass, reducing surface CO₂ concentrations.

However, photosynthesis can also stimulate CH₄ oxidation by supplying oxygen to methanotrophs, thereby linking CO₂ and CH₄ fluxes within the pond system (Oswald *et al.*, 2015). Overall, open water CO₂ and CH₄ emissions in stormwater ponds reflect a complex balance among production, oxidation, diffusion, and ebullition processes controlled by hydrological and biogeochemical conditions.

1.4 CO₂ and CH₄ flux pathways from riparian vegetation

Riparian vegetation zone influence both CO₂ and CH₄ fluxes by altering sediment redox conditions and OM dynamics. Net ecosystem exchange (NEE) represents the overall balance of CO₂ exchange between the ecosystem and the atmosphere, integrating ecosystem respiration (ER), which is the release of CO₂ through microbial and plant respiration, and gross primary production (GPP), which is the uptake of CO₂ via photosynthesis. The magnitude of NEE varies spatially and seasonally, depending on vegetation structure, biomass, and environmental conditions (Bonneville *et al.*, 2008; Zhou *et al.*, 2009; Jimenez *et al.*, 2012; Han *et al.*, 2013).

As vegetation grows and senesces, it contributes OC to the sediments, promoting microbial respiration and creating anoxic microzones favorable for methanogenesis (Bansal *et al.*, 2020). Conversely, vascular wetland plants have adaptive mechanisms that transport oxygen from shoots to roots through aerenchyma tissues. This radial oxygen loss reoxidizes reduced compounds such as Fe²⁺ and SO₄²⁻, thereby inhibiting CH₄ production by creating competition for carbon substrates and stimulating aerobic CH₄ oxidation by methanotrophic bacteria (Bansal *et al.*, 2020; Bodmer *et al.*, 2024). Temperature is a key control on these processes: microbial metabolism and methanogenesis rates increase exponentially with temperature, typically doubling or quadrupling

with every 10°C rise (van Winden *et al.*, 2012). Thus, warmer soils and sediments often exhibit elevated CH₄ emissions. CH₄ transport from sediments to the atmosphere occurs through diffusion at the soil surface and through both diffusive and convective pathways within the plant. Diffusion involves passive movement of dissolved CH₄ through the plant's internal air channels, while convective (pressurized) flow actively transports CH₄ from the rhizosphere to the atmosphere through aerenchyma tissues in emergent macrophytes such as *Typha* and *Phragmites* (Vroom *et al.*, 2022; Ge *et al.*, 2024). Together, these processes create a dynamic interface where vegetation simultaneously facilitates CO₂ uptake and CH₄ release, making riparian zones key regulators of carbon exchange in stormwater ponds.

1.5 Thesis objectives

This thesis investigates the role of urban SWPs in GHG exchange, focusing on CO₂ and CH₄ fluxes from both open water and riparian vegetation zones. The overarching goal is to quantify the carbon-based GHG fluxes and evaluate whether these engineered systems act as net sources or sinks within urban landscapes.

Specifically, Chapter 2 quantifies CO₂ and CH₄ fluxes from riparian vegetation and open water surfaces in two SWPs located in the City of Kitchener, Ontario: Aactiva pond (residential catchment) and Wabanaki pond (industrial catchment). The study aims to (1) compare open water and riparian vegetation fluxes to determine their net source or sink status, (2) assess spatial variability in fluxes between forebay and main basin zones to understand hydrological and biogeochemical controls, and (3) evaluate the influence of land use on the carbon dynamics of the studied ponds. Chapter 3 builds upon the findings from previous chapter by presenting a standardized, open-access dataset

encompassing all field measurements collected between September 2023 and March 2025. This dataset, covering CO₂ and CH₄ fluxes, dissolved gases, and supporting physicochemical parameters, was compiled following FAIR (Findable, Accessible, Interoperable, and Reusable) data principles. The objective was to promote data transparency, reproducibility, and integration into municipal-scale GHG monitoring and reporting frameworks, thereby enabling future research on carbon cycling and climate mitigation in urban stormwater systems.

1.6 Thesis outline

This thesis is comprised of four chapters, including the current Chapter 1. Chapter 2 is in a manuscript-style format which has been modified for this thesis and will be submitted for publication to the *Journal of Geophysical Research: Biogeosciences*. Chapter 2 quantifies CO₂ and CH₄ fluxes from riparian vegetation and open water in two stormwater ponds to assess spatial, seasonal, and land-use controls on GHG dynamics. Chapter 3 is also in a manuscript-style format and is part of a larger data paper that will be submitted for publication to *Scientific Data*. Chapter 3 provides a standardized, open-access dataset of these measurements to support reproducible research and municipal-scale GHG monitoring. Chapter 4 summarizes research findings from this thesis and proposes recommendations for future research. Appendices I and II contain supplementary materials for Chapters 2 and 3, respectively.

Riparian vegetation and open water carbon greenhouse gas fluxes of urban stormwater ponds

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A modified version of this chapter will be submitted to the *Journal of Geophysical Research:*

Biogeosciences

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2.1 Introduction

Inland waters are a critical component of the global carbon cycle and greenhouse gas (GHG) emissions, acting as potential source of GHGs to the atmosphere or sink through the sediment sequestration (Downing *et al.*, 2008; Raymond *et al.*, 2013; Rosentreter *et al.*, 2021). Research has traditionally been focused on larger bodies like rivers, lakes, and wetlands, often overlooking small inland waters (*e.g.*, ponds) due to the difficulty in quantifying their global distribution (Raymond *et al.*, 2013). However, these waterbodies are common in various landscapes, and their combined surface area is substantial. The knowledge gaps in GHG emissions from small waterbodies such as urban residential ponds, industrial ponds, and agricultural ditches have recently been reported (Holgerson and Raymond, 2016; Grinham *et al.*, 2018; Gorsky *et al.*, 2019; Peacock *et al.*, 2021; Goeckner *et al.*, 2022). Holgerson and Raymond (2016) estimated that although ponds with less than 0.001 km² surface area constitute 8.6% of lake and pond habitats' total area, they could disproportionately contribute to 15.1% of carbon dioxide (CO₂) and 40% of diffused methane (CH₄) emissions from inland waters. In a study by Peacock *et al.* (2021) on artificial ponds and ditches, they also found that these smaller waterbodies are significant CO₂ and CH₄ sources, with the smallest exhibiting the highest emissions. The disparity in carbon GHG emissions relative to size of the waterbodies is matched by higher organic carbon (OC) burial rates in small waterbodies compared to larger ones, indicating a complex and size-dependent dynamic in carbon cycling within these ecosystems (Downing *et al.*, 2008; Taylor *et al.*, 2019). These findings point to a substantial underestimation of the carbon budget from inland waters and highlight the importance of small artificial waterbodies in the global carbon cycle.

The growing awareness of the ecological importance of small artificial waterbodies has coincided with their increasing numbers, driven by urban development, agricultural expansion, and mining activities (Peacock *et al.*, 2021). In the United States alone, the number of artificial small waterbodies have increased 450-fold from 1934 to 2005 (Grinham *et al.*, 2018), a trend that reflects broader global patterns. Given these insights, the study of small-constructed ponds has become particularly valuable. Natural inland waterbodies are included within Intergovernmental Panel on Climate Change (IPCC) guidelines on carbon cycling and emissions, whereas artificial ponds have not been explicitly accounted for in national GHG inventories (IPCC, 2019). This underscores the need for comprehensive research to understand the carbon dynamics and GHG emissions of the small-constructed ponds for developing informed environmental policies and strategies to mitigate their impact on climate change.

Stormwater ponds (SWP), commonly constructed in urban areas, serve a vital function as infrastructure for managing stormwater and controlling urban flooding. By providing detention volume for stormwater runoff, they effectively reduce peak runoff levels, thus controlling flooding (USEPA, 2021). The SWPs are becoming increasingly important in urban planning as effective adaptation measures. The rising frequency and intensity of rainfall events associated with climate change have intensified flood risks (Abduljaleel *et al.*, 2023), underscoring the need for resilient stormwater infrastructure. As key components of nature-based solutions, SWPs are now widely integrated into urban resilience and sustainability strategies around the world (Esraz-Ul-Zannat *et al.*, 2024). The implementation of stormwater management plans encompasses more than just flood control. They also contribute significantly to groundwater conservation, maintenance of baseflow characteristics, enrichment of aquatic biodiversity, provision of recreational

opportunities, and most notably, improvement of water quality (USEPA, 2021). Therefore, SWPs face heightened risks from increased flooding and pollution compared to their natural counterparts. As a result, GHG emissions from the SWPs should not be directly equated with GHG originating from natural aquatic systems, given their different roles and behaviors within the ecosystem. (Peacock *et al.*, 2021).

Stormwater ponds can be divided into three distinct zones: the open water zone, defined as the permanent pool area that the pond is engineered to maintain; the riparian zone, delineated in this study based on field observations as the band of emergent vegetation between open water and the embankment, dominated by species such as *Phragmites* and *Typha*; and the embankment zone, which forms the sloped earthen perimeter designed for flood control, typically steeper than other zones and sometimes vegetated with deciduous trees and shrubs.

Greenhouse gas fluxes from SWPs vary widely across studies but consistently has been previously reported that these systems emit both CO₂ and CH₄ (e.g., Gorsky *et al.*, 2019; Peacock *et al.*, 2021; Goeckner *et al.*, 2022). While many studies focus on the open water zone of SWPs, SWPs can also be surrounded by a vegetated riparian zone around the margins of the pond. Vegetated ponds have been shown to exhibit higher total respiration rates than non-vegetated sites (Ström *et al.*, 2007; D’Acunha and Johnson, 2019). At the same time, vegetation can act as a carbon sink by absorbing CO₂ through photosynthesis. However, studies quantifying the combined GHG contributions of open water and riparian vegetation zones remain limited. In addition to carbon GHG emissions, numerous studies have shown that nitrous oxide (N₂O) flux is not a significant contributor to GHG emissions in SWPs (Błaszczak, *et al.*, 2018; Badiou *et al.*, 2019; D’Acunha and Johnson, 2019).

Gorsky *et al.* (2019) found that N₂O comprises less than 1% of GHG emissions in terms of CO₂ equivalent. Thus, it can be assumed that urban SWPs are unlikely to be a significant source of N₂O to the atmosphere. As a result, the focus of this study will primarily be on CO₂ and CH₄ fluxes.

In this study, we measured the CO₂ and CH₄ fluxes associated with the vegetated riparian zone and the open water surface of two SWPs in the City of Kitchener (COK), Ontario, Canada to compare the relative magnitudes of the fluxes and to determine whether the whole SWP systems, including the vegetated zones, function as net carbon sources or sinks, and whether they have a net climate warming or cooling effect. The main objectives of this study were to: 1) compare open water and riparian vegetation GHG fluxes in SWPs to assess their net source or sink status, 2) investigate spatial variability in GHG fluxes between forebay and main basin zones of SWPs to understand how hydrological and biogeochemical gradients influence carbon dynamics, and 3) examine how land use influences the carbon dynamics of the two SWPs.

2.2 Materials and Methods

2.2.1 SWP study sites

The study was conducted at two stormwater management ponds in the City of Kitchener, Ontario, Canada: Activa pond (43°24'28"N, 80°30'54"W) and Wabanaki pond (43°24'44"N, 80°26'00"W). These two SWPs differ in catchment land use, morphometry, and riparian vegetation. The Activa pond drains a catchment consisting of a residential subdivision, was constructed in 2000 and was last dredged in 2018, whereas the Wabanaki pond drains an industrial catchment, was constructed in 2011, and has not been dredged since construction. These contrasting land uses provide a framework for comparing how residential versus industrial inputs shape the carbon GHG fluxes.

Figure 2-1 shows the aerial imagery of the Activa and Wabanaki ponds. The Activa pond is divided into a forebay (482 m²) and a main basin (1028 m²). The pond has a small riparian zone (~26 m²) located near the middle, dominated by *Scirpus spp.* (bulrush) and *Nasturtium spp.* (watercress). In contrast, the remainder of the shoreline is surrounded primarily by shrubs and trees, resulting in limited riparian vegetation cover along the pond's margins. The Wabanaki pond is supplied by both a main inlet in the forebay and an overflow inlet into the main basin, with an outlet located on the opposite side of the main basin (Figure 2-1b). The Wabanaki pond consists of a forebay (294 m²) and a larger main basin (2631 m²). Its riparian zone is extensive (~1393 m²), dominated by *Phragmites australis* (common reed), *Typha spp.* (cattails), and *Scirpus spp.* (bulrush) (Table 2-1).

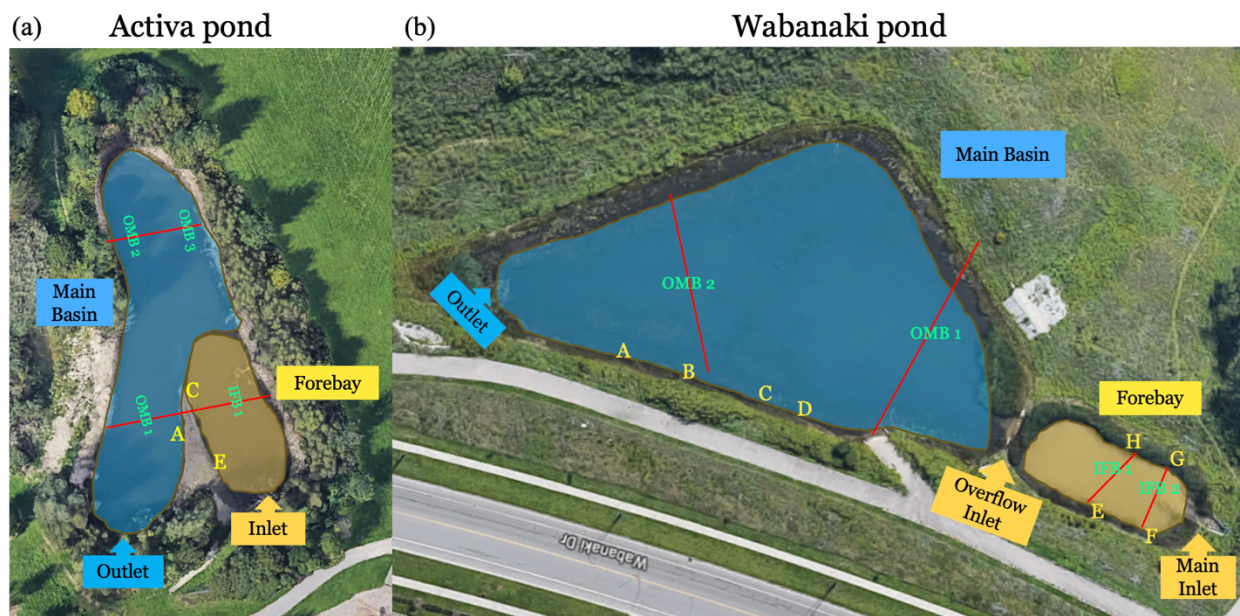


Figure 2-1: Aerial imagery of (a) Activa pond and (b) Wabanaki pond showing forebay (yellow) and main basin (blue) zones, with inlet and outlet locations marked. Sampling locations for both vegetation and open-water flux measurements are overlaid: yellow letters indicate vegetation collars, and green labels indicate open water flux sampling points.

Table 2-1: Morphological characteristics of Activa and Wabanaki ponds.

	Activa Pond	Wabanaki Pond
Catchment land use	Residential	Industrial
Forebay area (m²)	482	294
Main basin area (m²)	1,028	2,631
Riparian zone area (m²)	26	1,393
Dominant riparian vegetation	<i>Scirpus</i> spp. (bulrush); <i>Nasturtium</i> spp. (watercress)	<i>Phragmites australis</i> (common reed); <i>Typha</i> spp. (cattails); <i>Scirpus</i> spp. (bulrush)
Relative riparian extent	Small, localized patch near mid-pond	Large, continuous zone along shoreline

2.2.2 Data collection

2.2.2.1 Riparian vegetation flux measurements

The locations of the riparian vegetation flux collars and the open water flux locations are provided in Figure 2-1. The collars used for the vegetation flux measurements at both ponds were constructed from stainless steel, with a dimension of 60 cm × 60 cm. The fittings between the metal pieces of the collar were sealed with silicone sealant to ensure they were gas tight. The collars were installed in the sediment, around the vegetation, in the Fall of 2023 before flux measurements began to allow sufficient time for the collars to settle into the sediment so as to minimize disturbance to the flux measurements (Figure AI-1a). Depending on water level fluctuations, the collars could be submerged below the water surface or exposed above it. The vegetation collars were established to capture the dominant riparian plant communities at both ponds (Figure 2-1). At Activa pond, collars were placed within patches of *Scirpus* spp. (bulrush; Activa-C), and *Nasturtium* spp. (watercress; Activa-E), representing the limited riparian vegetation scattered among the otherwise shrub- and tree-dominated shorelines. A collar was also placed around a patch of *Salix* spp. (willow; Activa-A), which was technically located in the embankment zone and therefore not included in the upscaled calculations of riparian vegetation

fluxes. In contrast, Wabanaki pond supported a much broader range and greater extent of emergent riparian vegetation. Collars were positioned in stands of *Typha spp.* (cattails; Wabanaki-A and Wabanaki-F), *Scirpus spp.* (bulrush; Wabanaki-B and Wabanaki-E), and *Phragmites australis* (common reed; Wabanaki-C, Wabanaki-D, and Wabanaki-G). These arrangements highlight the ecological contrast between the two SWP sites: Activa pond is characterized by sparse and patchy small riparian vegetation, while Wabanaki pond is dominated by dense stands of emergent macrophytes, providing a stronger interface for carbon and GHG dynamics.

The closed vegetation flux chamber set-up was designed to accommodate vegetation of different heights. The flux chamber set-up consisted of two sizes of compartments made from clear acrylic boards: a bottom compartment which was not closed at the top (60 cm × 60 cm × 60 cm) and a top compartment (60 cm × 60 cm × 30 cm). In cases where vegetation was very tall (>120 cm), two bottom compartments plus a top compartment were used to increase the overall height of the assembled chamber set-up (Figure AI-1b). When 1 bottom and 1 top compartment were combined, the total volume was 324 L, when 2 bottom compartments and the top compartment were combined, the total volume was 540 L. Each chamber compartment was equipped with a fan to circulate air internally. The chamber was connected to a CH₄/CO₂/H₂O infrared gas analyzer (IRGA) (LI-7810, LI-COR Biosciences) by two tubes to measure CO₂ and CH₄ concentrations. After completing the vegetation fluxes, the clear chamber was removed for a short time to allow CO₂ and CH₄ concentrations to return to ambient levels and then a dark chamber covered by aluminum tape was repositioned to block out light (Figure AI-1c). During measurements, water was added to seal the connections between the top and bottom parts of the chamber, as well as between the bottom chamber and the collar. Each vegetation flux measurement by clear and dark chambers took 5

minutes, with flux calculations adjusted for the chamber's effective volume. Vegetation volume was estimated using observed stem counts combined with literature-derived minimum and maximum stem and leaf volumes for each species and growth stage, and the effective chamber volume was calculated as the maximum chamber volume minus the estimated volume of vegetation enclosed within the chamber. Additionally, for ground collars, the collar height above the ground was added to the chamber volume, while for submerged collars, the height above the water surface was subtracted. Photosynthetically active radiation (PAR) was measured using a PAR sensor (Apogee MQ-500: Full Spectrum Quantum Meter) before each clear chamber measurement. Additionally, air temperature of both the inside and outside of the chambers were measured using a temperature sensor (HOBO Pendant MX 2201 Temperature Data Logger) at the end of each flux measurement. From April 2024 to November 2024, the vegetation collars at Activa pond were sampled on a biweekly basis, whereas the larger number of collars at Wabanaki pond prevented completion within a single field day, resulting in each Wabanaki collar being sampled at least once per month. Consequently, Activa collars have 9 to 13 measurements per collar, while Wabanaki collars have 6 to 10 measurements.

2.2.2.2 Open water flux measurements

The floating chamber technique was used to measure the fluxes from the open water of the SWPs (Goeckner *et al.*, 2022). Similar to the vegetation flux measurements, open water flux measurements used both clear and dark chamber setups with a fan installed inside to enhance circulation (Figure A1-2). Each chamber encompassed an area of 0.0531 m² and maintained an effective volume of 14.57 ± 0.28 L (mean ± SD) from the chamber top to the midpoint of the floating noodle, corresponding to the water surface. Effective volumes showed minor variation among clear and dark chambers. An inflatable boat was used to access the ponds, and ropes

attached to wooden posts were deployed across the open water surface to stabilize the boat at the measurement locations and to avoid disturbing the sediments. Before deployment on the open water surface, the chambers were aired out to ensure that the CO₂ and CH₄ concentrations inside the chamber matched those of the outside air. CO₂ and CH₄ concentrations in the chamber were measured using a LI-COR CH₄/CO₂/H₂O IRGA connected to the chamber via tubing.

The floating chamber was deployed until a CH₄ ebullition event was detected, which appeared on the LI-COR software interface as a sudden CH₄ concentration spike. Because of the low CH₄ upper detection limit of the LI-COR analyzer, the chamber was removed from the open water surface after each CH₄ concentration spike to allow the air inside the chamber to return to ambient CH₄ concentrations. Up to six ebullition events were captured at each sampling location. Each measurement period prior to an ebullition event typically consisted of an initial phase characterized by a steady diffusive CH₄ flux, followed by one sudden CH₄ concentration spike that indicated an ebullition event. For each chamber deployment, total and diffusive CH₄ fluxes were calculated as the mean flux over the entire measurement period. The ebullitive CH₄ flux was then calculated as the difference between the total flux and the diffusive component. Diffusive CO₂ fluxes were estimated using the pre-ebullition portion of the time series, during which diffusion was more stable and not disrupted by ebullitive events. A negative flux indicated a net CO₂ or CH₄ absorption by the pond water column, while a positive flux signified a net CO₂ or CH₄ emission to the atmosphere. Each flux component (total, diffusive, and ebullitive CH₄, and diffusive CO₂) was calculated by averaging results from up to six chamber deployments capturing individual ebullition events and then further averaged across the sampling locations within each basin, as shown in Figure 2-1, to represent basin-scale fluxes for each measurement day.

The open water flux measurements were conducted bi-weekly from April 2024 until November 2024 to observe the seasonality in fluxes over the course of a year. Due to the presence of a frozen ice layer over the ponds, limiting gas exchange with the atmosphere, combined with the lack of live vegetation during the Winter, the flux measurements were only conducted during the Spring, Summer, and Fall seasons.

2.2.3 CO₂ and CH₄ flux calculations

The carbon fluxes of CO₂ and CH₄ in both vegetation and floating chambers were calculated using the following equation:

$$F = \frac{S \times V}{mV \times A} \times C \quad (2-1)$$

where F represents the flux in mmol m⁻² d⁻¹; S is the slope obtained from the concentrations of CO₂ and CH₄ measured by the LI-COR analyzer over 5 minutes expressed in ppm sec⁻¹; V denotes the chamber volume in L; mV is the molar volume in L mol⁻¹ derived from the Ideal Gas Law (Laugier and Garai, 2007); A is the surface area of the chamber in m²; and C is the conversion factor necessary to convert seconds into days.

To compare the CH₄ and CO₂ fluxes in terms of their climate impact, CH₄ fluxes were further converted to CO₂ equivalents (CO₂-eq) using a 100-year global warming potential (GWP₁₀₀) of 27 (Forster *et al.*, 2021). When expressed on a molar basis, this corresponds to a conversion factor of 9.84 mol CO₂-eq per mol CH₄.

2.2.4 Data analyses

The CO₂ fluxes measured in the clear vegetation chamber are used to estimate net ecosystem exchange (NEE), representing the overall CO₂ exchange with the atmosphere. The CO₂ fluxes measured in the dark vegetation chamber provide an approximation of ecosystem respiration (ER); although not a perfect measure of true ER, dark chamber fluxes are commonly used because they closely reflect respiration when photosynthesis is suppressed. The difference between clear and dark chamber fluxes (clear – dark flux) therefore isolates the photosynthetic component of CO₂ exchange, allowing gross primary production (GPP) to be estimated. Accordingly, GPP is calculated as $GPP = NEE - ER$. GPP quantifies the total CO₂ fixed by vegetation through photosynthesis over a given period. As ER contributes CO₂ to the atmosphere, its flux sign is positive. In contrast, GPP is marked with a negative sign, indicating CO₂ absorption by vegetation. The negative NEE indicates a net uptake of CO₂ from the atmosphere, when GPP surpasses ER. Conversely, positive NEE signifies a net release of CO₂ to the atmosphere, when ER exceeds GPP.

As the vegetation flux measurements were conducted bi-weekly, all fluxes were gap-filled to generate continuous daily average values for each vegetation collar site. An exponential relationship between daily dark CO₂ fluxes and air temperature, as established by Kutzbach *et al.* (2007), was derived for each site using observed dark CO₂ fluxes and air temperature data. This relationship was then applied to continuous daily air temperature records from Environment and Climate Change Canada (Government of Canada, n.d.) to predict daily dark CO₂ fluxes. A similar type of relationship was also applied to predict vegetation CH₄ fluxes. At each vegetation collar, CH₄ fluxes measured under clear and dark chamber conditions were analyzed separately to establish two exponential relationships with air temperature, representing daytime and nighttime

flux behavior, respectively. Daily CH₄ fluxes were then estimated using these equations in combination with daylength data obtained from Time and Date AS (2024).

The clear – dark CO₂ fluxes, used to estimate GPP, were predicted using the light use efficiency (LUE) model, as described by the following equations (Schwalm *et al.*, 2006; Yan *et al.*, 2008; Kross *et al.*, 2016; Kang *et al.*, 2018;):

$$GPP = \frac{PAR * \epsilon_g * GPP_{max}}{PAR * \epsilon_g + GPP_{max}} \quad (2-2)$$

$$\epsilon_g = \epsilon_0 * T_{scalar} * W_{scalar} * P_{scalar} \quad (2-3)$$

$$T_{scalar} = \frac{(T - T_{min})(T - T_{max})}{(T - T_{min})(T - T_{max}) - (T - T_{opt})^2} \quad (2-4)$$

where ϵ_g represents the effective LUE (mmol CO₂ mol⁻¹ PAR); ϵ_0 is the maximum LUE; GPP_{max} is the maximum GPP flux observed at each collar; and T_{scalar} , W_{scalar} , and P_{scalar} are the scalars of temperature, water, and plant phenology on photosynthesis, respectively. W_{scalar} represents the limitation of photosynthesis imposed by water availability or moisture stress on vegetation. Due to consistent water saturation observed at the riparian zones of SWPs, a W_{scalar} of 1 was assumed, representing no water limitation on light use efficiency. T_{scalar} represents the temperature-dependent regulation of photosynthetic efficiency relative to optimal conditions. In accordance with the observed temperature regime at the study sites, the model parameters were set as follows: $T_{min} = 0^\circ\text{C}$, $T_{max} = 35^\circ\text{C}$, and $T_{opt} = 25^\circ\text{C}$. The maximum LUE (ϵ_0) was set to 52 mmol CO₂ mol⁻¹ PAR, based on literature and field conditions (Schwalm, *et al.*, 2006; Yan *et al.*, 2008). P_{scalar} is a dimensionless response modifier that scales light-use efficiency based on how effectively vegetation utilizes available light, reflecting canopy development, phenology, shading, and light saturation effects. P_{scalar} was set to 0 from December to April to represent the non-growing

season, when field observations indicated senescent or dormant vegetation and negligible photosynthetic activity. It was then increased linearly from 0 to 1 during May and June to reflect observed canopy development and rapid biomass accumulation, held at 1 in July and August during peak growing conditions when vegetation was fully developed (Kang *et al.*, 2018), and decreased from 1 to 0 from September to November to represent senescence and declining photosynthetic capacity. PAR data was obtained from the online MODIS dataset (NASA LP DAAC, 2025).

Open water fluxes of diffusive CO₂ and CH₄, and ebullitive CH₄ at the forebay and main basin of both SWPs were gap-filled using a regression-based multiple imputation approach. The imputation method involved pairing the observed flux measurements with continuous time series data of environmental variables which influence GHG fluxes: air temperature, wind speed, PAR, and cumulative precipitation over the 6 hours prior to each flux measurement. Observed flux data were used to calibrate gas-specific linear relationships with standardized predictors, which were trained on 70% of available data and validated on the remaining 30% to confirm predictive skill. Missing daily fluxes were then filled by generating multiple plausible realizations (30 imputations per gas), combining model predictions with randomly sampled residuals to preserve natural variability and uncertainty, while observed measurements were retained unchanged. Complete daily time series were produced for each imputation, and seasonal or annual flux estimates were calculated by averaging across imputations, with uncertainty quantified from within- and between-imputation variance. Plausibility of the gap-filled data was evaluated through validation performance, distributional comparisons, temporal coherence, and sensitivity to the number of imputations. More details about the open water gap-filling method are provided in Appendix I.

2.3 Results

2.3.1 Vegetation fluxes

2.3.1.1 CO₂ and CH₄ seasonal trends

Different collars had different carbon GHG flux magnitudes, as shown in the examples in Figure 2-2 for Activa collar A and Wabanaki collar A. Although the predicted fluxes were specific to each vegetation collar, they all showed clear seasonal trends, with higher CO₂ and CH₄ fluxes during the summer due to increased biological activity, and minimal fluxes during the cold winter season. As part of the gap-filling, the value of P_{scalar} was set to 0 during winter period (December to April), resulting in no photosynthetic activity and thus zero clear – dark CO₂. As vegetation growth resumed in May and temperatures increased, the clear – dark CO₂ flux also increased (*i.e.*, became more negative), peaking in late July to early August before gradually declining to zero as the system entered the dormant season again (Figures 2-2a and c). Dark CO₂ followed a similar seasonal trend (*i.e.*, became more positive), increasing with temperature and biomass. However, unlike the clear – dark CO₂, dark CO₂ continued at low levels during winter, contributing to small but consistent CO₂ emissions from soil processes. CH₄ fluxes also exhibited seasonal trends (Figures 2-2b and d), with elevated emissions during the warmer months and reduced values in winter, following a trend similar to dark CO₂ flux.

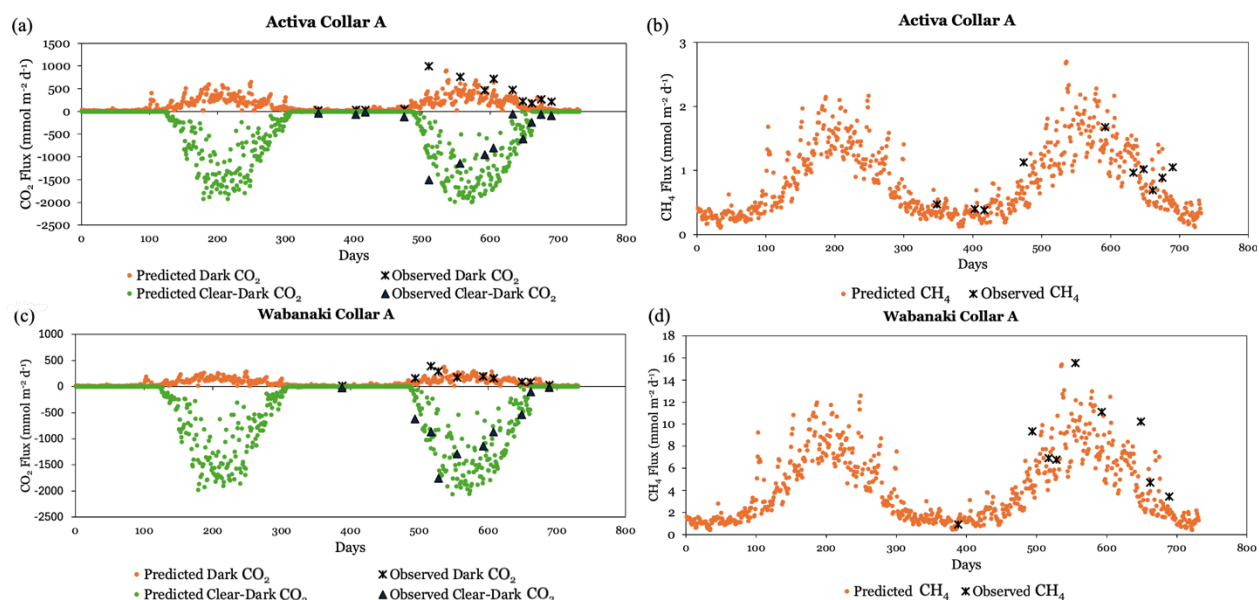


Figure 2-2: Gap-filled time-series of CO₂ and CH₄ fluxes from vegetation collar in location A of two Wabanaki and Activa ponds. Wabanaki collar A was dominated by *Typha sp.* (cattail), while Activa Collar A was dominated by *Salix sp.* (willow). In the CO₂ panels (a and c), predicted dark CO₂ (orange) represents CO₂ release, and predicted clear – dark CO₂ (green) represents CO₂ uptake. Black dots denote observed CO₂ and CH₄ vegetation flux measurements. All panels show daily, gap-filled flux values from January 1st, 2023 (Day 1) to the end of 2024 (Day 731).

2.3.1.2 Carbon vs CO₂-equivalent fluxes

Overall, CH₄ fluxes from vegetation were relatively minor compared to the larger CO₂ fluxes driven by photosynthesis and soil respiration (Figure 2-3a). At Activa, annual per-area vegetation CH₄ emissions was 0.1 mol m⁻² yr⁻¹, whereas Wabanaki exhibited substantially higher CH₄ emissions at 5.2 mol m⁻² yr⁻¹. Dark chamber CO₂ emissions were 33.1 and 38.7 mol m⁻² yr⁻¹ at Activa and Wabanaki, respectively, while clear – dark CO₂ fluxes indicated strong photosynthetic uptake of -175.5 and -184.4 mol m⁻² yr⁻¹. Across all vegetation types, photosynthetic CO₂ uptake far exceeded respiratory CO₂ losses, making the riparian zones net CO₂ sinks. Although Wabanaki showed higher carbon emissions, it also exhibited stronger CO₂ uptake than Activa, resulting in comparable net carbon fluxes between the two ponds (Figure 2-3a). Although CH₄ appeared negligible compared to CO₂ in terms of molar fluxes (Figure 2-3a), it had a much higher climate

impact once the fluxes were converted to CO₂-equivalents (Figure 2-3b). Annual CH₄ emissions corresponded to 1.0 mol CO₂-eq m⁻² yr⁻¹ at Activa and reached 50.9 mol CO₂-eq m⁻² yr⁻¹ at Wabanaki.

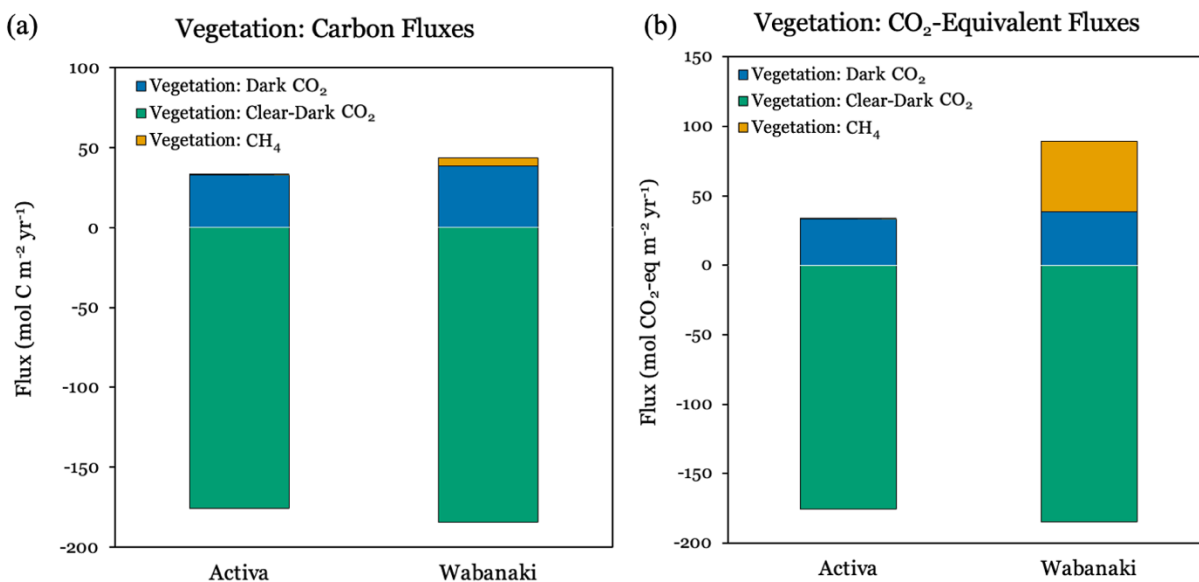


Figure 2-3: Annual vegetation carbon fluxes (a) and CO₂-equivalent fluxes (b) at Activa and Wabanaki ponds. Blue bars represent CO₂ emissions from the dark chamber measurement, orange bars indicate CH₄ emissions, and green bars show CO₂ uptake through clear – dark chamber measurement.

2.3.1.3 Vegetation types and locations

Different vegetation collars contributed differently to CO₂ and CH₄ fluxes, with clear variation between the two pond sites (Figure AI-3). From a climate impact perspective, the carbon GHG emissions at the Activa pond were dominated by CO₂ emissions associated with respiration, whereas at Wabanaki pond, riparian soil CH₄ emissions were the primary contributor to the overall carbon GHG emissions. The annual surface area-normalized average dark CO₂ flux values for the different species at the Activa pond were 20.0 mol m⁻² yr⁻¹ for *Scirpus*, 55.5 mol m⁻² yr⁻¹ for

Nasturtium, and at the Wabanaki pond, they were 25.2 mol m⁻² yr⁻¹ for *Scirpus*, 35.6 mol m⁻² yr⁻¹ for *Phragmites*, and 44.8 mol m⁻² yr⁻¹ for *Typha*. The clear – dark CO₂ showed strong CO₂ uptake across all vegetation types, with the highest uptake by *Typha* at Wabanaki pond (-197.2 mol m⁻² yr⁻¹) and the lowest by *Nasturtium* at Activa pond (-177.1 mol m⁻² yr⁻¹), indicating variability but within a comparable range. In contrast, CH₄ emissions, expressed in CO₂-eq, showed substantial differences (Figure AI-3). At Activa pond, CH₄ emissions were relatively low (0.2 mol CO₂-eq m⁻² yr⁻¹ for *Scirpus* and 2.3 mol CO₂-eq m⁻² yr⁻¹ for *Nasturtium*), while Wabanaki pond showed much higher emissions: 40.0 mol CO₂-eq m⁻² yr⁻¹ for *Typha*, 49.2 mol CO₂-eq m⁻² yr⁻¹ for *Scirpus*, and 57.0 mol CO₂-eq m⁻² yr⁻¹ for *phragmites*.

The same vegetation species acted differently across locations, indicating strong spatial controls on flux dynamics (Figure AI-3). For example, both ponds contain *Scirpus*, which showed similar CO₂ fluxes; however, *Scirpus* at Wabanaki pond emitted nearly 200 times more CH₄ than at Activa pond. Location of vegetations within the pond also influences CO₂ and CH₄ fluxes. At Wabanaki pond, both *Scirpus* and *Typha* were found in the forebay and main basin, but fluxes differ notably between the two zones. Dark CO₂ from *Scirpus* increased from 10.5 mol m⁻² yr⁻¹ in the main basin to 39.8 mol m⁻² yr⁻¹ in the forebay, while *Typha* showed an increase from 26.3 to 63.2 mol m⁻² yr⁻¹. CH₄ emissions (in CO₂-eq) followed a similar pattern: *Scirpus* increased from 34.6 to 63.7 mol CO₂-eq m⁻² yr⁻¹, and *Typha* from 15.0 to 65.0 mol CO₂-eq m⁻² yr⁻¹ (Figure AI-3). Vegetation in the forebay emitted two- to four- times higher CO₂ and CH₄ fluxes than vegetation in the main basin. Clear – dark CO₂ was also higher in the forebay vegetation, with *Typha* showing a 12% increase and *Scirpus* a 15% increase compared to their counterparts in the main basin. In addition, both Wabanaki collars C and D were located in *Phragmites* stands around the main basin; however,

Wabanaki collar C exhibited approximately 4.5 times higher dark CO₂, 21% higher clear – dark CO₂, and twice the CH₄ emission compared to Wabanaki collar D.

Uncertainty in vegetation fluxes was estimated using minimum and maximum vegetation volume corrections. Across all vegetation collars and flux measurements, this approach yielded a mean relative uncertainty of $\pm 2.51\%$, which was applied as the vegetation-volume-related uncertainty on reported fluxes. Uncertainty in LUE-based clear – dark CO₂ (GPP) estimates was quantified using the standard deviation of model residuals between observed and predicted fluxes, with daily uncertainties propagated to annual scales assuming independent errors and expressed as 95% confidence intervals; this resulted in an annual GPP uncertainty of approximately 13-21% of total GPP. Applying the same approach to Arrhenius-based dark CO₂ (ER) and CH₄ estimates yielded annual uncertainties on the order of $\sim 25\%$ for ER and $\sim 30\%$ for CH₄.

2.3.2 Open water fluxes

2.3.2.1 CO₂ and CH₄ seasonal trends

All time-series of open water CO₂ and CH₄ fluxes showed some seasonal trends, although their fluxes were more moderate compared to the vegetation fluxes (Figure AI-4). The independent 30% validation subset confirmed that the models captured most of the variability in daily fluxes (validation $R^2 = 0.91$ for CO₂ and 0.79 for CH₄). For CH₄, the highest fluxes occurred in summer where the ebullitive CH₄ fluxes remained essentially dormant during winter, flatlining near zero (Figure AI-4e). In contrast, diffusive CH₄ flux did not drop to zero in cooler seasons and some small but persistent CH₄ emissions were observed in early spring and late fall when the water temperatures were lower (Figure AI-4f). As a result, the seasonal amplitude of CH₄ diffusion was

smaller. Notably, during peak summer months, diffusive CH₄ flux, while elevated, remained much lower than concurrent ebullitive fluxes. Due to its stochastic nature, ebullitive CH₄ fluxes exhibited highly variable and occasionally extreme values, with the maximum single-day flux exceeding 300 mmol m⁻² d⁻¹ in the forebay of the Wabanaki pond. On days when ebullition occurred, its magnitude far exceeded that of diffusion. For example, in summer, a single ebullition event released a pulse of CH₄ several times greater than the cumulative diffusive flux over the same period. Overall, while diffusive CH₄ flux increased and decreased with water temperature and provided a continuous low-to-moderate CH₄ release year-round with clearer seasonal trends, ebullition derived large, intermittent pulses primarily in summer. Ebullition was therefore the dominant CH₄ emission pathway in these ponds during warmer months. Total CH₄ flux (ebullition + diffusion) was dominated by the ebullitive component, and thus its seasonal pattern closely mirrored that of ebullition (Figure AI-4g). Total CH₄ emissions remained low in winter, increased in late spring, and peaked during summer when ebullition intensifies.

CO₂ fluxes from open water at the Aactiva pond also showed seasonal variation, though less pronounced than CH₄ (Figure AI-4h). In colder months, the water surface acted as a net CO₂ sink, with negative fluxes reducing the total annual CO₂ emissions from Aactiva. In contrast, the Wabanaki forebay exhibited a seasonal trend that was less correlated with temperature and more responsive to precipitation events. Meanwhile, the Wabanaki main basin maintained relatively steady CO₂ fluxes throughout the year.

2.3.2.2 Carbon vs CO₂-equivalent fluxes

Open water CO₂ and CH₄ fluxes varied both between the two ponds and between the forebay and main basin zones (Figure 2-4). Among all gas exchange pathways, ebullitive CH₄ was the

dominant emission at both ponds, contributing the most to total carbon GHG fluxes. Annual area-normalized ebullitive CH₄ emissions were substantially higher in the forebays than in the main basins, especially at Wabanaki pond, where the forebay emitted 26.8 mol m⁻² yr⁻¹ compared to 8.4 mol m⁻² yr⁻¹ in the main basin (Figure 2-4a). At Activa pond, the forebay emitted 18.7 mol m⁻² yr⁻¹, while the main basin emitted 7.6 mol m⁻² yr⁻¹. This indicates that CH₄ ebullition was strongly forebay-dominated in both ponds, with a more pronounced contrast between the forebay and main basin at Wabanaki. Diffusive CH₄ fluxes, while much smaller than ebullition, also followed the same between-basin trends as ebullitive CH₄. Activa's forebay and main basin emitted 1.1 mol m⁻² yr⁻¹ and 0.5 mol m⁻² yr⁻¹, respectively, while Wabanaki's forebay and main basin emitted 3.8 and 0.5 mol m⁻² yr⁻¹, respectively (Figure 2-4a). Diffusive CO₂ flux showed a similar pattern, with higher emissions from the forebay zones than from the main basins. In Wabanaki, the forebay emitted 14.5 mol m⁻² yr⁻¹ and the main basin 7.0 mol m⁻² yr⁻¹ (Figure 2-4a). In contrast, Activa's forebay emitted 3.7 mol m⁻² yr⁻¹, while the main basin showed net CO₂ uptake at -1.8 mol m⁻² yr⁻¹. From a climate impact perspective, after converting CH₄ fluxes into CO₂-equivalents, the contribution of CO₂ becomes negligible, and ebullitive CH₄ emerges as the dominant driver of annual carbon GHG emissions from the open water surface of both ponds (Figure 2-4b).

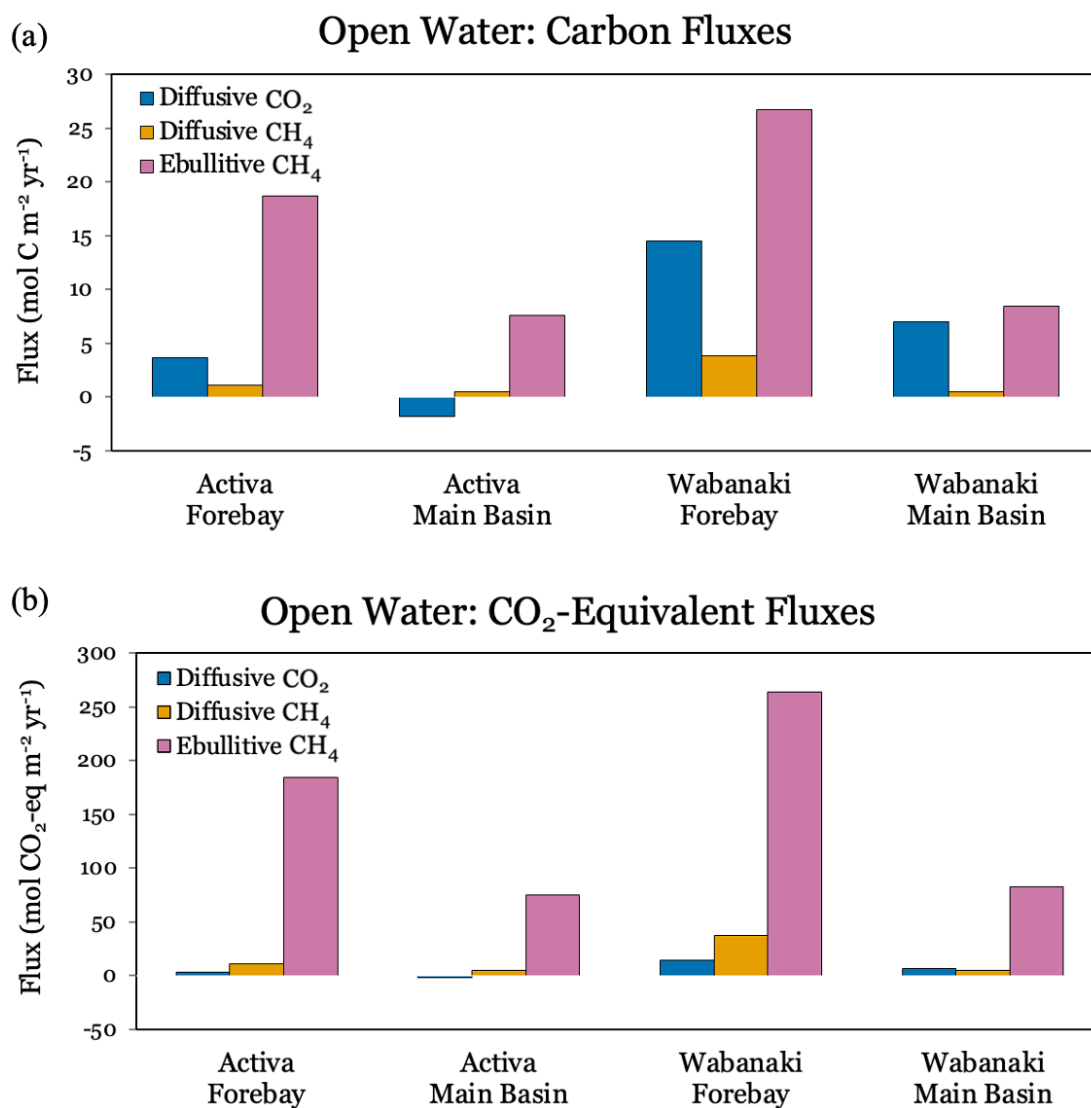


Figure 2-4: Annual open water carbon fluxes (a) and CO₂-equivalent fluxes (b) at Activa and Wabanaki ponds, showing separate values for the forebay and main basin. Blue bars represent diffusive CO₂ fluxes, orange bars indicate diffusive CH₄ emissions, and pink bars show ebullitive CH₄ emissions.

2.3.3 Combined and upscaled fluxes

Activa pond had a net annual vegetation carbon flux of $-142.3 \text{ mol m}^{-2} \text{ yr}^{-1}$, while Wabanaki pond had $-140.5 \text{ mol m}^{-2} \text{ yr}^{-1}$ (Figure 2-5a), with riparian zones of both ponds functioning as net carbon GHG sinks. Due to higher CH₄ emissions, the sink strength at Wabanaki pond was largely reduced

once the fluxes were converted to CO₂-eq: the annual CO₂-eq flux was -141.4 mol m⁻² yr⁻¹ at Activa pond and -94.8 mol m⁻² yr⁻¹ at Wabanaki pond (Figure 2-5b). The differing proportions of CH₄ emissions in the total carbon fluxes can mask substantial differences in climate impact.

When combining all three GHG emission pathways from the open water zone, the Wabanaki pond had a net annual carbon flux of 19.1 mol m⁻² yr⁻¹, while the Activa pond emitted slightly less at 12.7 mol m⁻² yr⁻¹ (Figure 2-5a). However, when the fluxes were converted to CO₂-eq, Activa had a slightly higher annual emission flux of 125.6 mol CO₂-eq m⁻² yr⁻¹ compared to 119.6 mol CO₂-eq m⁻² yr⁻¹ at Wabanaki (Figure 2-5b).

Overall, when accounting for surface area, the Activa pond emitted approximately 189.6 kmol of CO₂-eq annually from the open water zone, with 87% attributed to ebullitive CH₄ and the remainder to diffusive CH₄ (Figure 2-5d). In comparison, the Wabanaki pond emitted around 349.9 kmol CO₂-equivalents per year, with 88% as ebullitive CH₄ and less than 3% as CO₂. Meanwhile, the riparian zone of the ponds acted as a GHG sink, with Activa removing 3.6 kmol and Wabanaki removing 132.1 kmol of CO₂-eq annually. Despite this uptake, both ponds remained net carbon GHG sources due to the larger proportion of open water and high CH₄ ebullition from the forebays.

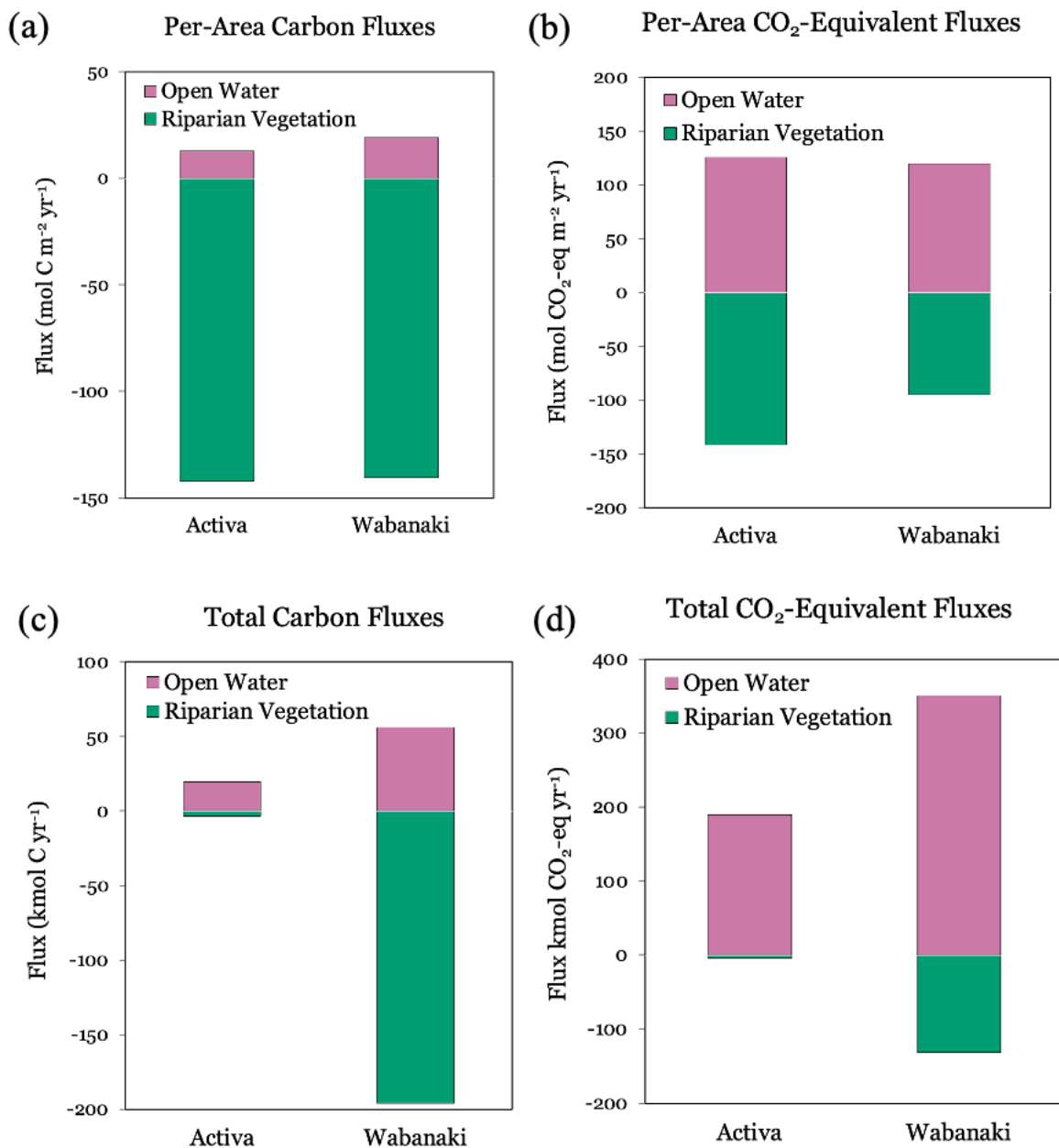


Figure 2-5: Annual combined carbon fluxes (a) and CO₂-equivalent fluxes (b) at Activa and Wabanaki ponds. Pink bars represent overall open water fluxes and green bars indicate overall riparian vegetation uptake.

2.4 Discussion

2.4.1 Vegetation CO₂ and CH₄ flux pathways and environmental controls

2.4.1.1 CO₂ exchanges

The CO₂ flux measured in the dark vegetation chamber captures the dominant respiratory pathways active during the measurement period and thus provides a reasonable field-based estimate of ecosystem respiration (ER). Clear chamber measurements, in contrast, reflect net ecosystem exchange (NEE). Subtracting the dark chamber flux from the clear chamber flux isolates the photosynthetic component of CO₂ exchange, yielding an estimate of gross primary production (GPP) as $GPP = NEE - ER$. Hereinafter, ER, NEE, and GPP are used throughout the discussion.

In our study, the fluxes measured at all collars exhibited distinct seasonal patterns consistent with seasonal changes in vegetation phenology across all the vegetation types (Figures 2-2a and c). The riparian zones of both the Activa and Wabanaki ponds functioned as net sources of CO₂ to the atmosphere throughout the non-growing season, primarily due to the dominance of respiratory processes. As the vegetation developed, the magnitude of daily NEE fluctuations increased, reflecting the growing influence of photosynthetic activity. During the peak of the growing season, enhanced CO₂ uptake by actively photosynthesizing vegetation caused the riparian zones to function as CO₂ sinks (Figures 2-2a and c). These trends align with patterns reported in other wetland studies. Bonneville *et al.* (2008) observed that a cattail (*Typha angustifolia*) marsh operates predominantly as a slight CO₂ source throughout the year, but transitions into a net CO₂ sink during the growing season. In their study, seasonal NEE displayed a pronounced V-shaped pattern during the growing season with the peak negative NEE occurred in July, coinciding with the highest biomass of cattail. Another related study on reed (*Phragmites australis*) wetlands by Han *et al.*, (2013), focusing specifically on the growing season, revealed that daily GPP and ER

were markedly low at the early vegetative stage, with a rapid increase from late May, concurrent with reed growth and the maximum absorption rate and release rate both occurred in July and subsequently, both GPP and ER experienced a sharp decline during the fall. Such findings demonstrate that variations in NEE closely correspond with temperature and vegetation live biomass (Bonneville *et al.*, 2008), consistent with the seasonal progression observed in our riparian flux measurements.

The importance of vegetation live biomass is further illustrated by the comparison between two nearby collars containing the same species but exhibiting different NEE values (Figure AI-3). Both Wabanaki collars C and D were located around the Wabanaki main basin and dominated by *Phragmites*. However, Wabanaki C showed approximately 4.5 times higher ER and 1.21 times higher GPP than Wabanaki D. This discrepancy is primarily attributed to differences in vegetation density and growth: Wabanaki collar C contained 12 large *Phragmites* stems exceeding 3 m in height by August, whereas Wabanaki collar D had only three large stems and six smaller ones, reaching a maximum height of 2.6 m. The greater stem density and height at Wabanaki collar C enhanced photosynthetic capacity and respiratory activity, leading to higher NEE fluxes compared with the adjacent, less dense stand. This finding highlights how vegetation height and density strongly influence carbon exchange even within a single species and under similar local conditions. Meanwhile, broader differences between sites and their surrounding environments can also lead to substantial variation in the magnitude of CO₂ ER and GPP fluxes, largely driven by live biomass. For example, in Han *et al.*, (2013), *Phragmites* exhibited a maximum CO₂ GPP flux of -30 g m⁻² d⁻¹ (-682 mmol m⁻² d⁻¹) and a maximum ER of 18 g m⁻² d⁻¹ (409 mmol m⁻² d⁻¹) in July. In contrast, the *Phragmites* collar in Wabanaki pond showed a peak CO₂ GPP of -2061 mmol m⁻² d⁻¹, with a

peak ER flux of $378 \text{ mmol m}^{-2} \text{ d}^{-1}$. Despite the similar ER fluxes in comparable wetland environments with the same species, the GPP at Wabanaki pond was almost three-times higher. This difference can mainly be explained by the greater maximum height of *Phragmites* at the SWP site ($>3 \text{ m}$) compared to approximately 1.5 m at site reported by Han *et al.*, (2013), though other meteorological factors may also have some influence.

In addition, OC inputs and nutrient availability also lead to differences in CO_2 ER and GPP fluxes. *Scirpus* occurred in the Activa pond, and in both the forebay and main basin of Wabanaki pond, showing the highest ER and GPP at the Wabanaki forebay, followed by Activa, and the lowest fluxes at the Wabanaki main basin (Figure AI-3). Similarly, *Typha* in the Wabanaki forebay exhibited approximately 2.5 times higher ER and 1.12 times higher GPP compared to other locations. These patterns likely reflect greater accumulation of OM and nutrients in the forebay than in the main basin, as well as higher carbon and nutrient inputs at the industrial Wabanaki pond relative to the residential Activa pond. Consequently, for the same vegetation species, CO_2 fluxes measured in the forebay were higher than those in the main basin, and fluxes at Wabanaki exceeded those at Activa.

Although vegetation growth is the dominant control on vegetation CO_2 fluxes, other environmental factors also influence these fluxes. The time series of predicted CO_2 ER and GPP fluxes showed day-to-day fluctuations rather than a smooth increase or decrease following the growth stage (Figures 2-2a and c). Occasionally, low NEE values were observed during the growing season, typically on cloudy days with high soil temperatures, when GPP was suppressed, and ER was elevated. Similar variations driven by light availability and air temperature have been reported in

other studies as well (Zhou *et al.*, 2009; Jimenez *et al.*, 2012). In wetland environments, temperature and light are key environmental drivers that jointly regulate carbon fluxes by affecting both ER and GPP, thereby shaping NEE. The exponential relationship between soil or air temperature and CO₂ ER flux has been widely documented (Hirota *et al.*, 2006; Zhou *et al.*, 2009; Jimenez *et al.*, 2012; Han *et al.*, 2013). This relationship arises from the combined temperature responses of both microbial and plant respiration. Rising temperatures can enhance soil respiration not only through direct effects on enzyme kinetics but also by shifting microbial community composition toward taxa with higher temperature optima, increasing overall metabolic activity (Karhu *et al.*, 2014). Plant respiration exhibits strong temperature sensitivity, with rates of respiratory enzyme activity increasing under warming, though acclimation can moderate long-term responses (Atkin *et al.*, 2005). For example, Hirota *et al.*, (2006) found that soil temperature accounted for approximately 48–88% of the variation in ER emissions. At the same time, temperature and light availability regulate photosynthesis and thus GPP. Zhou *et al.*, (2009) demonstrated that daytime NEE variation in a reed wetland in Northeast China was strongly influenced by the diurnal course of PAR, with daytime NEE becoming more negative (indicating greater CO₂ uptake) as PAR increased. Temperature also constrains ecosystem photosynthesis by influencing the activity of the photosynthetic system. Similarly, Jimenez *et al.*, (2012) reported that light and air temperature were the primary controls on NEE in a short-hydroperiod Florida Everglades marsh. The two studied Wabanaki and Activa ponds were located very close to each other, resulting in similar air temperature and PAR conditions. Consequently, their annual NEE values were also very similar ($-142.3 \text{ mol m}^{-2} \text{ yr}^{-1}$ for Activa and $-145.7 \text{ mol m}^{-2} \text{ yr}^{-1}$ for Wabanaki). These observations underscore the critical role of vegetation in regulating CO₂ levels through the

processes of photosynthesis and respiration. Meanwhile, vegetation CH₄ emission is also a significant carbon GHG emission pathway (see below).

2.4.1.2 Riparian vegetation CH₄ emissions

Temperature plays a crucial role in regulating riparian CH₄ emissions (Bansal *et al.*, 2020; Bodmer *et al.*, 2024; Ge *et al.*, 2024). In this study, we developed site-specific exponential relationships between CH₄ fluxes and measured air temperature for each vegetation collar. This approach integrates temperature-driven variations in CH₄ production and transport. Vegetation can increase OM deposition, providing substrates for methanogens and enhancing CH₄ production in sediments by fostering anoxic conditions, as decaying plant matter contributes to anoxia (Bansal *et al.*, 2020). Production rates have been shown to accelerate under warmer conditions. According to van Winden *et al.* (2012), temperature accelerates microbial metabolism exponentially, often doubling or quadrupling reaction rates per 10°C increase, leading to higher methanogenesis and CH₄ emissions in warmer soils. CH₄ produced in sediments is then transported to the atmosphere through two main pathways: diffusion, which occurs through soil pores and the same internal gas channels that deliver oxygen to roots (Ge *et al.*, 2024), and convective (pressurized) flow through aerenchyma tissues, the dominant and most efficient pathway in emergent macrophytes, often accounting for 70–90% of total CH₄ emissions (Vroom *et al.*, 2022; Knoblauch *et al.*, 2015). The riparian CH₄ emission is strongly influenced by temperature, which accelerates methanogenesis and enhances pressurized flow (van Winden *et al.*, 2012; Konnerup *et al.*, 2011), as well as by external factors such as light, wind, and humidity (Vroom *et al.*, 2022).

In our study, *Phragmites*, *Typha*, and *Scirpus* in the Wabanaki pond exhibited comparable CH₄ emissions within the same pond, with *Phragmites* showing slightly higher fluxes when averaged

across collar locations (Figure AI-3). However, riparian CH₄ fluxes differed dramatically between ponds and zones: for the same *Scirpus* species, Wabanaki displayed nearly 200 times higher annual area-normalized CH₄ emissions than Activa, and nearly twice as high in the forebay compared with the main basin (Figure AI-3). Meanwhile, *Typha* in Wabanaki's forebay exhibited CH₄ emissions approximately four times higher than those in the main basin (Figure AI-3). Similar to CO₂ fluxes, this striking contrast indicates that strong site-level environmental controls, such as OC inputs, nutrient availability, and hydrological conditions, can override species-level similarities. This difference is particularly evident for CH₄ emissions, as CH₄ production depends strongly on sediment OC availability (Bodmer *et al.*, 2024). As an industrial pond, Wabanaki receives significantly greater inputs of OM and nutrients from stormwater runoff than the residential Activa pond. These enriched sediments enhance microbial methanogenesis, providing both the substrate and anoxic conditions favorable for CH₄ production. Consequently, the elevated riparian CH₄ fluxes observed at Wabanaki, especially in the forebay, reflect the combined effects of higher carbon loading, nutrient enrichment, and shallower, warmer conditions that promote sediment CH₄ generation and release.

Globally, large differences in CH₄ fluxes among emergent macrophyte genera have also been reported, with genus identified as a key predictor of flux magnitude (Bodmer *et al.*, 2024). According to Bodmer *et al.*'s review, the three dominant genera found in our ponds follow the trend *Scirpus* > *Phragmites* > *Typha* in median daily CH₄ flux, though with wide variability among studies. Our results, together with these global patterns, suggest that while genus-level differences exist on a large scale, predicting CH₄ emissions solely from vegetation type remains challenging,

as local environmental conditions exert a stronger influence on flux magnitude (Bodmer *et al.*, 2024).

2.4.2 Open water CO₂ and CH₄ flux pathways and environmental controls

In this study, total CH₄ emissions were substantially higher than CO₂ emissions across all pond locations, indicating that CH₄ is the dominant GHG release pathway in SWPs (Figure 2-4). Meanwhile, the time series of total CH₄ emissions closely mirrored the pattern of ebullitive CH₄ fluxes (Figures AI-4e and g), with both on a similar magnitude scale. This alignment shows that ebullition accounts for the majority of total CH₄ emissions, while diffusion contributes only a minor fraction to overall CH₄ release. Similarly, Gorky *et al.* (2019) also observed that CH₄, CO₂, and N₂O accounted for approximately 94%, 6%, and less than 1% of total GHG emissions from small ponds, respectively, with CH₄ emissions primarily occurring through ebullition. This pattern of dominance has been corroborated by various studies (Grinham *et al.*, 2018; Herrero Ortega *et al.*, 2019; van Bergen *et al.*, 2019; Baron *et al.*, 2022). CH₄ in SWPs is produced through methanogenesis, the anaerobic decomposition of OM by methanogenic archaea in oxygen-depleted sediments (Lyu *et al.*, 2018). Because CH₄ has very low solubility in water, about 22 mg L⁻¹ at 25°C (NCBI, 2025), it readily forms bubbles once saturation is reached, leading to ebullition, the dominant emission pathway that can account for 50-90% of total CH₄ fluxes (Malyan *et al.*, 2022). Diffusive CH₄ flux occurs as dissolved gas moves across the air-water interface, while oxidation by methanotrophs can partially convert CH₄ to CO₂ before release. CO₂ originates primarily from microbial mineralization of OC and respiration by algae and aquatic plants, with small, shallow ponds particularly prone to high CO₂ production due to concentrated terrestrial inputs (Holgerson, 2015; Gorsky *et al.*, 2019; Malyan *et al.*, 2022). CO₂ is emitted

mainly through diffusion when supersaturated, though it can also form from CH₄ oxidation. Photosynthesis is the main mechanism for CO₂ consumption during daylight by converting it into OM, but study have shown it may also enhance aerobic CH₄ oxidation, indirectly generating additional CO₂ (Oswald *et al.*, 2015).

CO₂ fluxes and both the ebullitive and diffusive CH₄ emissions were consistently higher in the forebays than in the main basins of both Aactiva and Wabanaki ponds, with the highest rates observed in Wabanaki's forebay (Figure 2-4). This spatial pattern reflects key morphometric and biogeochemical controls. Shallow water depths in the forebays inhibit CH₄ oxidation and reduce hydrostatic pressure, making it easier for gas bubbles to escape. Wabanaki's forebay, with its shallowest average water depth, exhibited markedly higher ebullition than other locations. For context, Wabanaki's forebay averages 38 cm water depth throughout the year, compared to about 133 cm in its main basin, making it much more susceptible to disturbance. Meanwhile, the shallow, small-area forebays are more susceptible to physical disturbance and boundary-layer mixing, which can facilitate CO₂ and CH₄ diffusion. Pond morphology has also been shown to significantly influence GHG emissions in other studies, with both water depth and surface area exhibiting negative correlations with CO₂ and CH₄ fluxes, particularly for CH₄ (Holgerson, 2015; D'Acunha & Johnson, 2019; Gorsky *et al.*, 2019; Peacock *et al.*, 2021). Larger ponds generally have sediments with lower densities of terrestrial OM, which reduces OM mineralization and subsequent CH₄ production (Gorsky *et al.*, 2019). In contrast, small and shallow ponds feature a larger interface between the water column and anoxic sediments and experience reduced CH₄ oxidation during sediment-to-surface transport, both of which enhance CH₄ emissions (Holgerson,

2015). Additionally, greater water depths promote dilution from inflowing water, thereby lowering CH₄ concentrations (Holgerson, 2015).

Another key driver of the observed spatial variability in GHG fluxes is the distribution of OC and nutrient inputs across pond zones. The OC inputs to the SWPs are from two main sources: allochthonous organic carbon, which is transported into the ponds from upstream urban areas, and autochthonous OC, which is generated within the system by plants and algae. The forebay, which directly receives stormwater runoff from the catchment, functions as a primary sedimentation area, leading to the accumulation of OM and nutrients. As a result, the main basin generally receives water with lower OC content and reduced sediment loads. This pattern is even more pronounced in Wabanaki pond, where industrial runoff delivers higher concentrations of both particulate and dissolved OC, enhancing sediment accumulation and fueling microbial processes. Elevated OC and nutrient inputs stimulate microbial respiration and methanogenesis in sediments and are therefore typically associated with elevated CH₄ and CO₂ emissions (Peacock *et al.*, 2021; van Bergen *et al.*, 2019; Holgerson, 2015; Gorsky *et al.*, 2019). This is consistent with our results showing that forebay zones, where OC and nutrient inputs are greatest, exhibited CH₄ and CO₂ fluxes two to three times higher than those measured in the main basins (Figure 2-4).

2.4.3 Overall carbon GHG flux comparisons

In these SWP systems, the dominant GHG emission pathway per unit area was ebullitive CH₄ in CO₂-equivalents (Figure 2-6b). This contrasts with wetland and lake environments, where plant-mediated transport is considered the dominant mechanism for CH₄ release. Vroom *et al.* (2022) highlight that this pathway becomes increasingly important as vegetation matures, whereas

ebullition tends to be more significant in unvegetated areas or during the early growing season when plant biomass is limited (Ge *et al.*, 2024). Dean *et al.* (2018) estimated that plant-mediated transport accounts for approximately 55% to 85% of total CH₄ emissions in peatlands. In lake ecosystems, data from 66 lakes showed that, on a per-area basis, CH₄ emissions from emergent vegetation zones are 6.1 times higher than from open water areas (Kyzivat *et al.*, 2022).

When total carbon GHG fluxes were compared, two contrasting interpretations emerged depending on whether GWP was applied (Figure 2-5). Without GWP conversion, both ponds appeared to function as per-area GHG sinks because strong CO₂ uptake by riparian vegetation outweighed carbon losses from open water (Figure 2-5a). Open water fluxes at the Wabanaki pond, however, were higher than those at Activa pond (19.1 mol m⁻² yr⁻¹ vs. 12.7 mol m⁻² yr⁻¹), driven largely by intense CH₄ ebullition in its shallow, nutrient-rich forebay where conditions favored bubble release. After conversion to CO₂-equivalents, the interpretation changed substantially. Wabanaki's per-area open water emissions became lower than Activa's (119.6 mol CO₂-eq m⁻² yr⁻¹ vs. 125.6 mol CO₂-eq m⁻² yr⁻¹) because its larger, deeper main basin produced far less CH₄ per unit area. However, Wabanaki pond still exhibited a higher net per-area CO₂-eq flux (24.8 mol CO₂-eq m⁻² yr⁻¹) compared to Activa pond, which remained a net sink on a per-area basis (-15.8 mol CO₂-eq m⁻² yr⁻¹; Figure 2-5b). This outcome highlights the importance of riparian vegetation uptake: although Wabanaki pond had greater open water CH₄ emissions, its higher vegetation CH₄ emissions also reduced its overall sink strength relative to Activa pond.

When fluxes were upscaled by pond area, the ponds diverged further. On a molar basis, the Wabanaki pond functioned as a net carbon sink, whereas the Activa pond acted as a net carbon

source (Figure 2-5c). This difference reflects the small riparian zone at Activa pond, which contributed only limited CO₂ uptake, compared with the extensive riparian zone at Wabanaki pond. Thus, even though both ponds had similar per-area vegetation carbon uptake, the contrasting size of their riparian zones resulted in very different whole-pond contributions (Figure 2-5c). After converting to CO₂-equivalents, both ponds became net annual GHG sources, with Activa pond emitting 186 kmol CO₂-eq yr⁻¹ and Wabanaki pond 217.8 kmol CO₂-eq yr⁻¹ (Figure 2-5d).

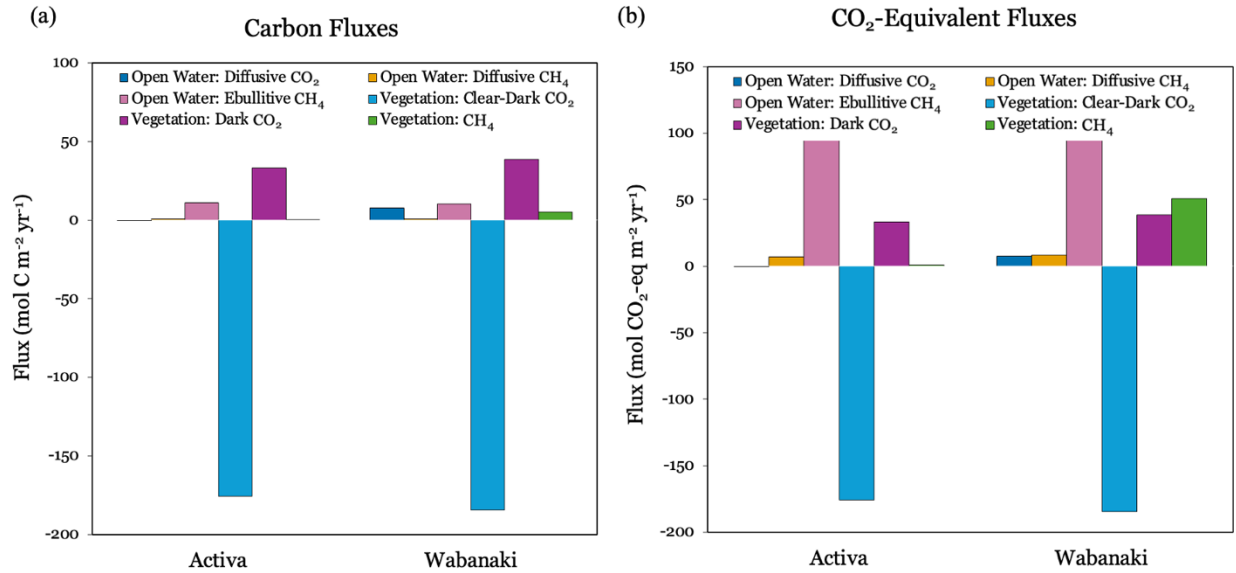


Figure 2-6: Annual carbon fluxes (a) and CO₂-equivalent fluxes (b) at Activa and Wabanaki ponds, separating each flux, including open water diffusive CO₂, open water diffusive CH₄, open water ebullitive CH₄, vegetation CH₄, vegetation dark CO₂, and vegetation clear-dark CO₂. Negative values represent net uptake (sink), while positive values indicate net emissions (source) to the atmosphere.

2.4.4 Uncertainties and limitations

Several limitations and uncertainties should be acknowledged in this study. For the gap-filling of the vegetation GPP flux time series, the use of a constant annual value for light-use efficiency (ϵ_g) introduces uncertainty, as studies have shown that ϵ_g can fluctuate daily in response to changing

environmental conditions (Schwalm *et al.*, 2006). Similarly, GPP estimates assume a P_{scalar} of zero until May, potentially underestimating early-season photosynthetic activity. ER was primarily modeled as a function of temperature, yet other influencing factors, such as soil moisture, substrate availability, and microbial community dynamics, were not fully considered. In particular, soil microbial activity during the non-growing season was overlooked, despite evidence that minor positive NEE values can occur during winter months (Zhou *et al.*, 2009; Han *et al.*, 2013). Meanwhile, because the vegetation chambers reduce wind flow and can increase heat accumulation during measurements, the resulting fluxes may be biased and may not fully represent true, in situ vegetation fluxes. Additionally, vegetation coverage was characterized by areal extent alone, without accounting for differences in plant density, which may affect flux rates. Vegetation CH_4 emissions during the non-growing season are also likely underestimated. For instance, *Phragmites*, although senescent in winter, can still facilitate CH_4 release by acting as a conduit for gas transport through its stems, bypassing the ice-covered water column (Bodmer *et al.*, 2024). Moreover, the embankment contribution on the GHG fluxes were not evaluated, even though Activa pond was surrounded by more woody vegetation than herbaceous emergent plants. Tree-mediated emissions are an emerging area of study with many unknowns and limited empirical data (Vroom *et al.*, 2022).

Similar to the uncertainties associated with vegetation flux estimates, comparable challenges also arise in quantifying open water fluxes. Because the LI-COR analyzer has a relatively low upper detection limit for CH_4 , chambers were removed from the open water surface after each CH_4 concentration spike to allow chamber air to return to ambient levels. During this air-out period, however, diffusive CH_4 continued to be emitted from the water surface but was not captured in the

subsequent chamber deployment. As a result, the diffusive period was underestimated, leading to overestimation of both total and ebullitive CH₄ fluxes. Consequently, the contribution of ebullition (reported as ~88% of open water emissions) and the net GHG fluxes from both ponds are likely overestimated. Together, these factors contribute to uncertainties in the annual carbon budget estimates and highlight the need for more comprehensive year-round flux measurements and refined parameterizations.

2.5 Conclusion

Carbon GHG emissions from open water were dominated by ebullitive CH₄, making the open water zone a net GHG source. Forebays at both ponds consistently showed higher GHG fluxes than the main basins due to higher carbon inputs from contaminated stormwater runoff, greater sedimentation, nutrient enrichment, and more reducing conditions, acting as GHG hotspots in SWPs. Yet, Wabanaki's large, low-emission main basin resulted in lower per-area open water emissions in CO₂-equivalents overall, despite extremely high CH₄ fluxes in its small forebay.

High photosynthetic activity allowed the riparian zone to function as a net CO₂ sink. However, greater OC inputs from the industrial Wabanaki catchment provided more substrate for CH₄ production and emission, especially in the forebay. As a result, higher vegetation CH₄ emissions substantially reduced the sink strength at Wabanaki compared to the residential Activa pond. The size of the riparian zone also plays a critical role. Although Activa had higher per-area vegetation CO₂-eq uptake, its small riparian extent meant that the overall contribution of vegetation uptake was minor relative to total emissions. In summary, both studied residential and industrial SWPs acted as net GHG sources due to substantial CH₄ emissions. Together, these results demonstrate

how land-use-driven differences in carbon inputs not only shape GHG fluxes in both vegetation and open water but also interact with pond morphology to determine the overall climate impact.

Based on this study, GHG emissions from SWPs are tightly linked to biogeochemical controls, including temperature, redox conditions, and OM availability. Elevated OM accumulation, shallow water depth, and persistent anoxia enhance CH₄ production. Accordingly, management practices that influence these biogeochemical conditions, such as periodic sediment dredging to reduce carbon accumulation in the forebay, reducing industrial runoff from surrounding facilities, and removing accumulated industrial material to limit excessive OM inputs, can help constrain CH₄ production. In addition, maintaining or enhancing riparian vegetation cover supports photosynthetic CO₂ uptake and may partially offset open water emissions.

3 Open data of greenhouse gas fluxes and water chemistry from two urban stormwater ponds in Southern Ontario: 2023-2025

3.1 Introduction

Inland waters are critical components of the global carbon cycle, yet small systems such as ponds remain underrepresented in research and global greenhouse gas (GHG) budgets despite evidence of their disproportionate carbon dioxide (CO₂) and methane (CH₄) emissions (Downing *et al.*, 2008; Raymond *et al.*, 2013; Rosentreter *et al.*, 2021). Ponds smaller than 0.001 km², for example, may contribute 15.1% of CO₂ and 40% of diffusive CH₄ emissions from inland waters (Holgerson and Raymond, 2016), and artificial ponds, including urban stormwater ponds (SWPs), have been identified as significant GHG sources, with the smallest exhibiting the highest fluxes (Peacock *et al.*, 2021). Urban SWPs, widely constructed for flood control and water-quality improvement (Gaur *et al.*, 2019; Government of Ontario, 2023), are increasingly recognized not only as climate-change adaptation infrastructure but also as active ecosystems influencing GHG fluxes, nutrient cycling, and pollutant retention (Gorsky *et al.*, 2019; Peacock *et al.*, 2021; Goeckner *et al.*, 2022). Their prevalence is rapidly increasing with urban development and other land-use changes (Grinham *et al.*, 2018). For example, the City of Kitchener (COK) in Ontario, Canada maintains more than 150 stormwater management ponds distributed across diverse catchments (City of Kitchener, 2021), reflecting the scale at which such systems have become integral to urban infrastructure and local hydrologic management. However, despite the widespread implementation of SWPs in urban systems, open accessed peer-reviewed datasets on the emissions of GHGs from the ponds remain scarce.

Globally, initiatives such as the World Meteorological Organization Integrated Global Greenhouse Gas Information System (IG³IS) aim to advance effective practices for quantifying GHG emissions

and removals on decision-relevant scales. In 2025, IG³IS released the *Urban Greenhouse Gas Emission Observation and Monitoring Good Research Practice Guidelines* (WMO, 2025), which are designed to evolve through regular updates that incorporate scientific and technological advancements while clarifying the link between research practices and their policy applications. However, despite the growing sophistication of urban GHG observation networks, current IG³IS and Global Atmosphere Watch (GAW) frameworks primarily emphasize atmospheric monitoring (WMO, 2025). While the framework highlights key components of urban GHG monitoring, it does not account for aquatic features like SWPs (Figure 3-1), which are increasingly recognized as biogeochemical hotspots capable of producing and exchanging CH₄ and CO₂ in response to hydrologic and organic matter (OM) dynamics (Gorsky *et al.*, 2019; Peacock *et al.*, 2021; Goeckner *et al.*, 2022), but remain largely overlooked in most city-scale carbon assessments.

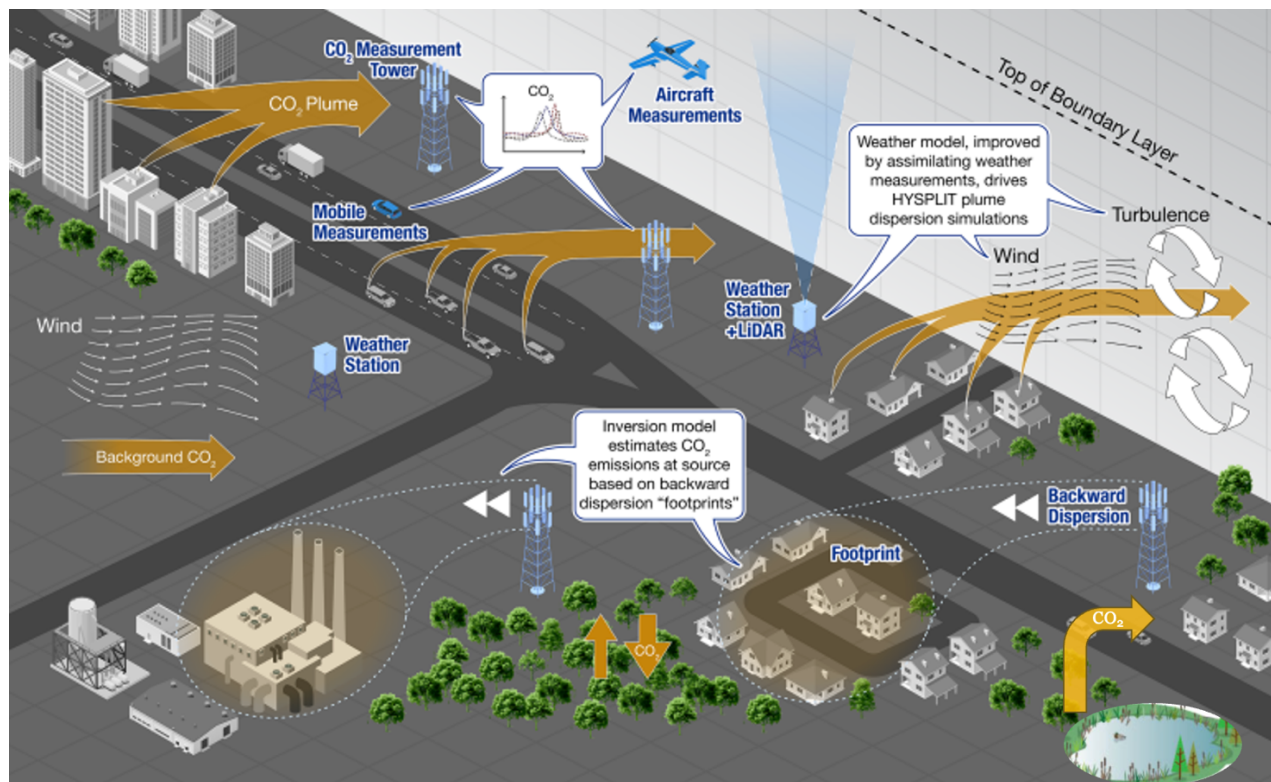


Figure 3-1: Conceptual diagram of an urban GHG observation framework showing the integration of fixed, mobile, and airborne CO₂ measurements with atmospheric dispersion and inversion modelling, with SWPs added to address their omission in the original framework. Image modified from NOAA’s Urban Greenhouse Gas Research (Figure 1 in “New WMO guidelines help cities improve greenhouse gas emission information,” World Meteorological Organization, 2025).

typically omitted or roughly estimated (ICLEI *et al.*, 2021). Routine municipal sampling of gas fluxes, along with key water-chemistry parameters such as dissolved inorganic carbon (DIC), pH, temperature, dissolved oxygen (DO), dissolved organic carbon (DOC), and nutrients, can substantially improve the accuracy, completeness, and actionability of both IPCC- and GPC-aligned inventories. Such datasets enable the development of locally relevant Tier 2-3 emission factors, help explain seasonal and design-driven variability, reduce inventory uncertainty, and support targeted mitigation strategies at the municipal scale.

In Chapter 2, our field measurements and analyses showed that the two urban SWPs, Activa and Wabanaki ponds in the COK, act as net annual sources of GHG, with fluxes modulated by hydrologic variability, OM dynamics, and temperature. Building on these findings, this chapter focuses on data standardization and open dissemination to support reproducible monitoring and municipal-scale GHG assessments. The specific objectives were to: 1) document and share an open-access dataset describing the biogeochemical dynamics and GHG fluxes of two urban SWPs, and 2) provide reproducible methods, and transparent workflows that can support future research on urban carbon cycling and stormwater management practices. The dataset presented in this Chapter follows FAIR (Findable, Accessible, Interoperable, and Reusable) data principles, and includes high-resolution measurements of CO₂ and CH₄ fluxes, dissolved gases, and supporting physicochemical profiles collected between September 2023 and March 2025 in two urban SWPs (Activa and Wabanaki ponds) in the COK, as summarized in Table 3-1. Measurements span both forebay and main basin compartments and include under-ice conditions (January-March 2025), providing rare insights into SWP carbon dynamics across seasons.

Table 3-1: Summary of parameters and sampling periods included in this data chapter.

Parameters	Sampling Period(s)	Field Sampling
Open water CO ₂ and CH ₄ fluxes	2023-09-25 to 2024-11-27	Floating chamber measurements
Vegetation CO ₂ and CH ₄ fluxes	2023-12-14 to 2024-11-19	Vegetation chamber measurements
Dissolved gases (CO ₂ , CH ₄)	2024-04-29 to 2024-11-27 (Ice-free) 2024-01-22 to 2024-03-28 (Under-ice) 2025-01-16 to 2025-03-04 (Under-ice)	Syringe sampling with headspace extraction
Dissolved inorganic carbon and dissolved organic carbon	2023-09-25 to 2024-11-27	Grab and filter surface water samples
Secchi disk depth	2024-05-16 to 2024-11-27	Lowering Secchi disk
Turbidity	2024-05-29 to 2024-11-27	Grab surface water samples
Chlorophyll- <i>a</i>	2024-04-29 to 2024-11-27	Grab surface water samples in brown opaque bottles
Temperature, Dissolved oxygen, Electrical conductivity, pH, Oxidation-reduction potential	2024-04-29 to 2025-03-04 (Surface and near-bottom: Additional mid-water profile started on 2024-09-09)	In situ sonde measurements

3.2 Study area and ponds characteristics

The data were collected from two urban SWPs located in the City of Kitchener (COK), Ontario, Canada: Wabanaki pond (43°24'44"N, 80°26'00"W) and Activa pond (43°24'28"N, 80°30'54"W). Although both ponds serve similar hydrological functions, they differ substantially in catchment land use, morphology, and riparian vegetation (Figure 3-2, Table 3-2). Activa pond, constructed in 2000, functions as a stormwater management wetland that drains a residential subdivision

(catchment area = 33.8 ha; 53% impervious). The Activa pond consists of a forebay (482 m²) and a main basin (1,028 m²), with a permanent pool depth ranging from 0.55 to 1.25 m. It has a permanent pool storage capacity of 935 m³, receives an average annual inflow of 201,850 m³ yr⁻¹, and exhibits a short residence time of approximately 2 days. The annual sediment load is estimated at 85 tonnes. Riparian vegetation is sparse (~26 m²), limited mainly to the central portion of the shoreline and dominated by *Scirpus spp* (bulrush) and *Nasturtium spp.* (watercress), while the remaining perimeter is bordered by trees, restricting aquatic–riparian interaction (Figure 3-2b).

In contrast, Wabanaki pond, constructed in 2011, is a stormwater management wet pond serving an industrial catchment (25.8 ha; 65% impervious) adjacent to a COK operations facility. It has a deeper permanent pool (~1.5 m), a larger open-water area (2,925 m²), and a storage capacity of 4 945 m³. The average annual inflow is 98,667 m³ yr⁻¹, yielding a longer residence time of approximately 21 days and a higher sediment load of 360 t yr⁻¹. The pond layout includes a forebay (294 m²) and a main basin (2,631 m²), with an extensive riparian zone (~1,393 m²) dominated by *Phragmites australis* (common reed), *Typha spp.* (cattails), and *Schoenoplectus spp.* (bulrush). It is supplied by both a main and an overflow inlet, with the outlet situated on the opposite side of the basin (Figure 3-2c).

Together, these two SWPs represent distinct urban land use and hydrological conditions that influence OM inputs, vegetation structure, and ultimately, GHG flux dynamics within stormwater management systems.

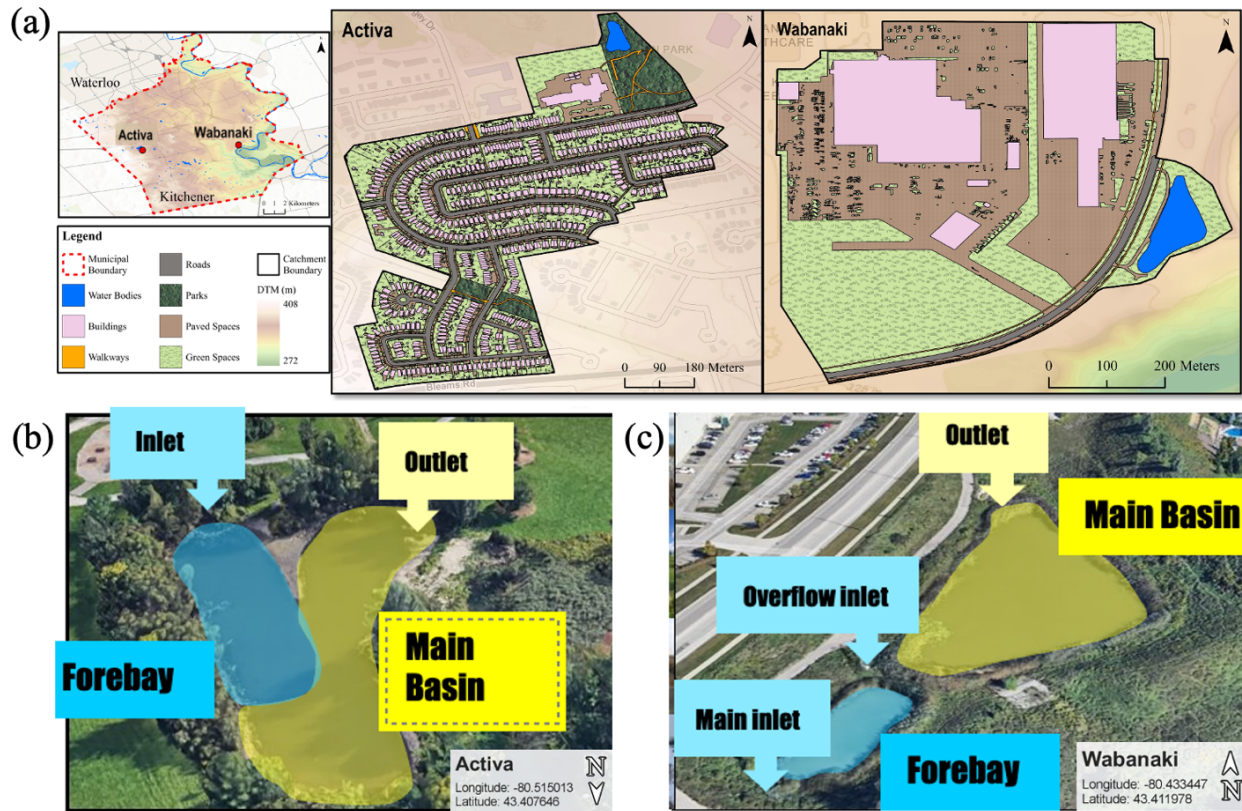


Figure 3-2: Location and layout of the two study sites, Activa and Wabanaki stormwater ponds in the City of Kitchener, Ontario, Canada. (a) Catchment boundaries with surrounding municipal land use. The Activa pond (middle) drains a primarily residential catchment, while the Wabanaki pond (right) drains an industrial catchment. (b) Aerial imagery of the Activa pond showing its two compartments: the forebay (blue) and main basin (yellow), with inlet and outlet locations marked. (c) Aerial imagery of the Wabanaki pond showing the forebay (blue) and main basin (yellow), with main and overflow inlets as well as outlet indicated.

Table 3-2: Key design and hydrological characteristics of Activa and Wabanaki ponds.

	Activa pond	Wabanaki pond
Construction year	2000	2011
Design	Stormwater management wetland	Stormwater management wet pond
Last dredged	2018	N/A
Permanent pool water depth (m)	0.55 to 1.25	1.5
Pond open water surface area (m ²)	1510	2925
Catchment surface area (ha)	33.8	25.8
Catchment imperviousness (%)	53	65
Average annual water inflow (m ³ y ⁻¹)	201,850	98,667
Permanent pool storage capacity (m ³)	935	4945
Average water residence time (days)	2	21
Annual sediment load (t)	85	360

3.3 Field sampling and analytical methods

3.3.1 CO₂ and CH₄ flux measurements (vegetation and open water)

Sampling locations for vegetation flux collars and open water flux transects are provided in Figure 3-3, where yellow markers indicate riparian vegetation collars, and green markers denote open water flux measurement points.

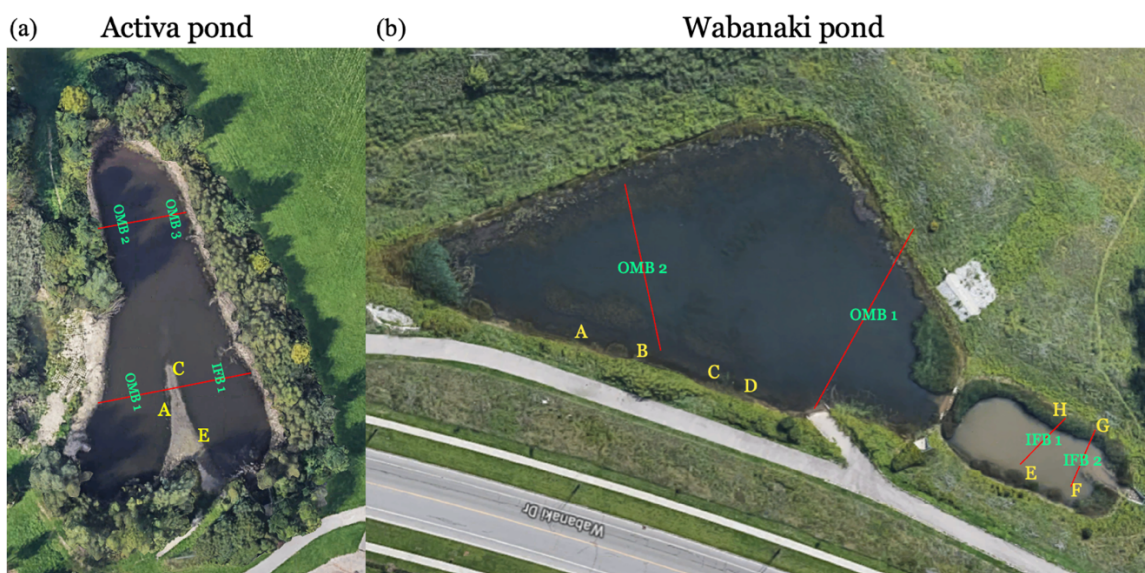


Figure 3-3: Sampling locations for vegetation and open water flux measurements at (a) Activa pond and (b) Wabanaki pond. Yellow letters denote vegetation collar sites, red lines indicate open-water transects, and green labels mark open-water flux sampling locations.

Open water flux data were collected between 2023-09-25 and 2024-11-27 using two different chamber-based approaches. Each chamber covered an area of 0.0531 m^2 and had an effective volume of $14.57 \pm 0.28 \text{ L}$ (mean $\pm$ SD), calculated from the chamber top to the midline of the floating ring. The clear floating chamber was constructed from a clear plastic carboy that had its top cut off and was sealed with a round clear flat piece of plastic. The dark floating chamber was constructed from a black bucket with reflective tape wrapped to minimize heat absorption. From 2023-09-25 to 2023-12-07, fluxes of CO_2 and CH_4 were quantified using a gas chromatography (GC) method. For each flux event, three headspace samples were collected from chambers at 0, 5, and 15 minutes. The collected samples were stored in exetainers and later analyzed for CO_2 and CH_4 using a gas chromatograph (GC, see 3.3.2 for details on GC analysis). These gas samples were analyzed to calculate total CO_2 and CH_4 fluxes, without partitioning diffusive and ebullitive components, and without concurrent in situ environmental measurements. From 2024-04-29 to 2024-11-27, fluxes were measured with a LI-COR system connected directly to the chambers via

tubing. Each floating chamber was mounted on a steel ring attached to buoyant foam (pool noodle) and anchored near the water surface to maintain stability during operation. The chambers were equipped with an internal fan to ensure air circulation and were connected to the LI-7810 infrared gas analyzer (IRGA; LI-COR Biosciences) via paired tubes for continuous measurement of CO₂ and CH₄ concentrations, enabling partitioning of CH₄ into diffusive and ebullitive fluxes. All the measurements were conducted from an inflatable boat, which was stabilized using ropes to minimize disturbance to the chamber and surrounding water. Due to an issue with the LI-COR IRGA, CO₂ and CH₄ concentrations were measured using a Picarro GasScouter™ G4301 analyzer on July 23, July 26 and August 07.

Prior to each deployment, the chambers were aired out to reset CO₂ and CH₄ concentrations to ambient levels. Each deployment continued until a CH₄ ebullition event was detected, characterized by a sharp concentration spike on the LI-COR software interface. Up to six ebullition events were recorded at each sampling location, with maximum three from the clear floating chamber, and the other three from the dark floating chamber to avoid light penetration and eliminate any photosynthesis that may occur from the submerged algae. The resulting fluxes typically exhibited an initial steady diffusive phase, followed by one or more discrete ebullition peaks. From these data, total and component fluxes were computed, where the total CH₄ flux represented the mean flux across the full measurement period, the diffusive CH₄ flux corresponded to the pre-ebullition steady phase, and the ebullitive CH₄ flux was derived as the difference between the total and diffusive components. Similarly, diffusive CO₂ fluxes were calculated from the pre-ebullition portions of the time series, where gas exchange was more stable and undisturbed

by bubble release. The fluxes of CO₂ and CH₄ in both vegetation and floating chambers were calculated using the following equation:

$$F = \frac{S \times V}{mV \times A} \times C \quad (3-1)$$

where F represents the flux in mmol m⁻² d⁻¹; S is the slope obtained from the concentrations of CO₂ and CH₄ measured by LI-COR analyzer over 5 minutes expressed in ppm sec⁻¹; V denotes the chamber volume in L; mV is the molar volume in L mol⁻¹ derived from the Ideal Gas Law (Laugier and Garai, 2007); A is the surface area of the chamber in m²; and C is the conversion factor necessary to convert seconds into days. Positive flux values indicated net emissions of CO₂ and CH₄ to the atmosphere, while negative fluxes represented net uptake by the pond surface.

Figure 3-4 presents the time series in open water total, ebullitive, and diffusive CH₄ fluxes from the open-water zones of Activa and Wabanaki ponds between September 2023 and November 2024 on a biweekly basis. Each panel shows fluxes differentiated by pond and basin type: Activa pond (blue symbols) and Wabanaki pond (orange symbols), with forebay and main basin distinguished by circles and squares, respectively. Due to the use of GC method, total fluxes from 2023-09-25 to 2023-12-07 could not separate into diffusive and ebullitive CH₄. Figure 3-4a illustrates total CH₄ fluxes (mmol m⁻² d⁻¹), showing pronounced temporal variability across both ponds, with several high-emission events (up to >600 mmol m⁻² d⁻¹) occurring primarily in Wabanaki pond during summer and early fall. Figure 3-4b displays ebullitive CH₄ fluxes, revealing strong temporal and spatial variability, with markedly higher emissions in Wabanaki's forebay compared to other sites. Figure 3-4c shows diffusive CH₄ fluxes, which remained relatively low (<50 mmol m⁻² d⁻¹) and stable over time, indicating diffusion as a minor contributor compared to episodic ebullition. For both diffusive and ebullitive CH₄, Wabanaki pond consistently showed

higher emissions than Activa pond, and forebays were higher than main basins. Overall, Wabanaki pond exhibited more frequent and intense CH_4 ebullition than Activa pond, suggesting higher sedimentary CH_4 production and release potential, particularly during warmer months. The clear seasonal clustering indicates that ebullitive fluxes were the dominant driver of total CH_4 emissions in both systems.

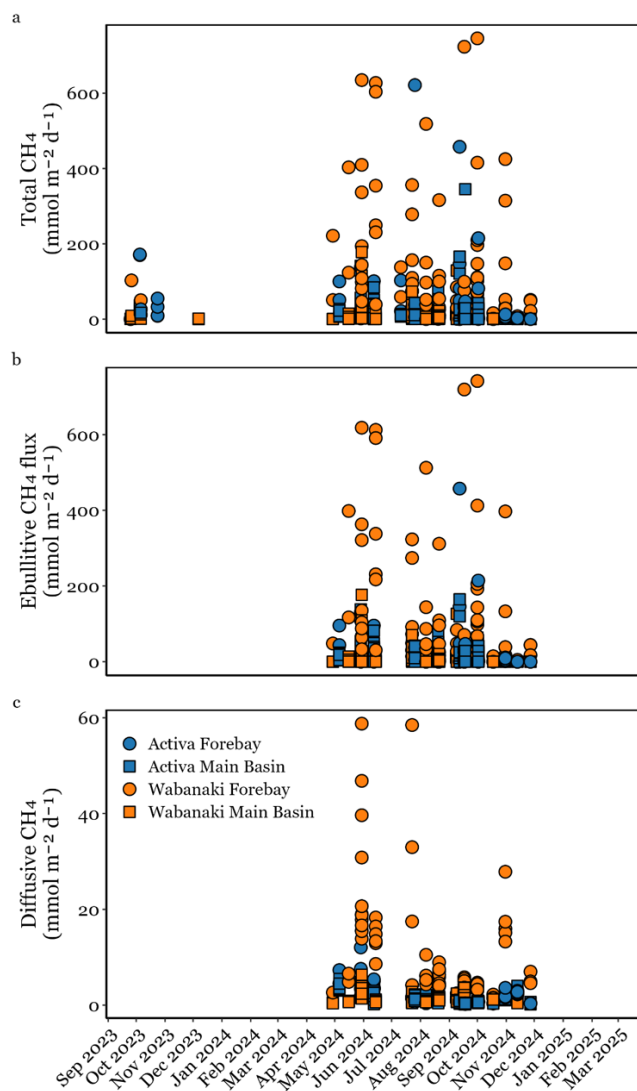


Figure 3-4: Time series in open water total (a), ebullitive (b), and diffusive (c) CH_4 fluxes from the Activa and Wabanaki ponds between September 2023 and November 2024 on a biweekly basis. Each panel shows fluxes differentiated by pond and basin type: Activa pond (blue symbols) and Wabanaki pond (orange symbols), with forebay and main basin distinguished by circles and squares, respectively.

Figure 3-5 shows the time series in diffusive CO₂ fluxes from the open water zones of Aactiva pond and Wabanaki pond between September 2023 and November 2024. In both ponds, CO₂ fluxes varied seasonally, with generally higher emissions observed during the summer months (May-September) compared to spring and fall. Aactiva pond displayed moderate positive fluxes (up to ~300 mmol m⁻² d⁻¹) in summer, indicating net CO₂ release, while occasional negative values (below 0 mmol m⁻² d⁻¹) suggested short periods of CO₂ uptake. Wabanaki pond exhibited a broader range of fluxes and greater variability, particularly in the forebay. Overall, CO₂ fluxes were consistently higher and more variable in forebays than in main basins.

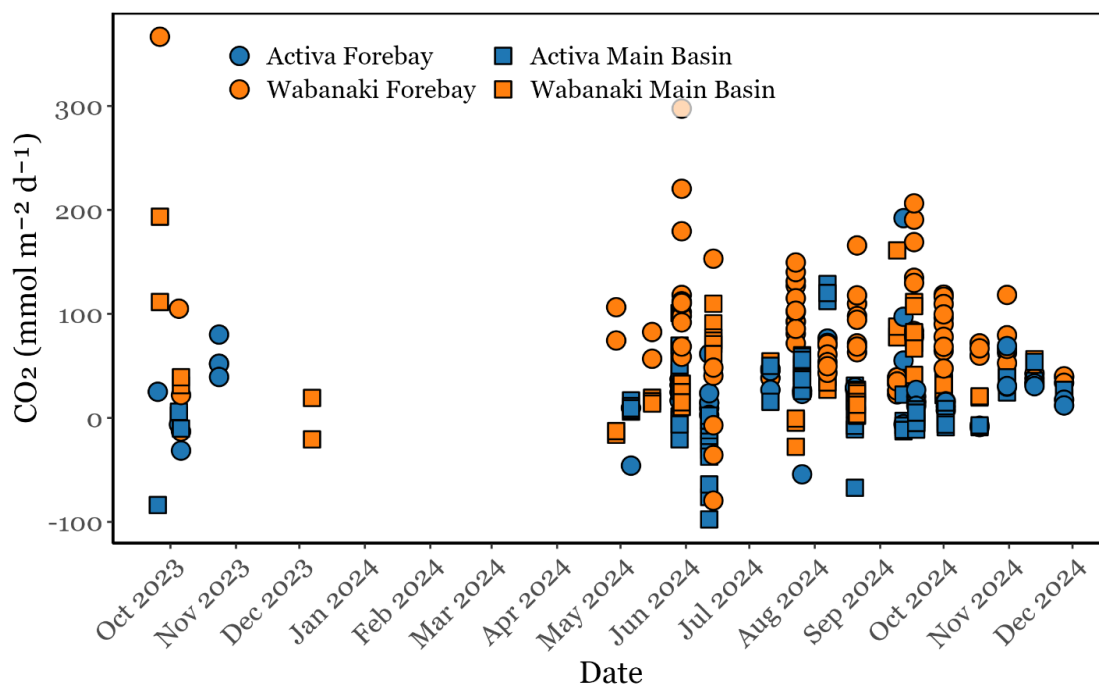


Figure 3-5: Time series in diffusive CO₂ fluxes from the open water zones of Aactiva and Wabanaki ponds between September 2023 and November 2024 on a biweekly basis, differentiated by pond and basin type: Aactiva pond (blue symbols) and Wabanaki pond (orange symbols), with forebay and main basin distinguished by circles and squares, respectively.

Because the flux measurement technique is designed to capture transient ebullition events, multiple data points collected at the same location within a short period (*e.g.*, within half an hour) can exhibit considerable variability (Figures 3-4 and 3-5). Such fluctuations are largely influenced by environmental factors, including wind, water column disturbance, or occasional movement by small aquatic animals within the ponds. The forebays of both SWPs are smaller and shallower than their respective main basins, making them more sensitive to these physical disturbances and consequently exhibiting a wider range of flux values.

Vegetation fluxes were measured using a closed-chamber technique analogous to that used for open water fluxes. Steel vegetation collars (60 cm × 60 cm) were installed in the sediment and sealed with sealant to prevent leakage. Depending on water level fluctuations, collars were occasionally submerged below or exposed above the water surface. Collars were positioned to represent the dominant plant communities at each pond (Figure 3-3). At Activa pond, collars were placed within patches of *Salix spp.* (willow; Activa-A), *Scirpus spp.* (bulrush; Activa-C), and *Nasturtium spp.* (watercress; Activa-E), reflecting the limited riparian vegetation among tree-dominated shorelines. Wabanaki Pond, in contrast, supported a broader distribution of emergent macrophytes, with collars established in stands of *Typha spp.* (cattail; Wabanaki-A and Wabanaki-F), *Scirpus spp.* (bulrush; Wabanaki-B and Wabanaki-E), and *Phragmites australis* (common reed; Wabanaki-C, -D, and -G). These configurations illustrate the contrast between the sparse, patchy vegetation at Activa and the dense emergent cover at Wabanaki, which provides a stronger interface for carbon and GHG exchange. Each vegetation chamber was constructed from clear acrylic panels, consisting of a 60 cm × 60 cm × 60 cm base and a 60 cm × 60 cm × 30 cm top section (total volume = 324 L, surface area = 0.36 m²), with internal fans to ensure air mixing.

Chambers were connected via tubing to the same LI-COR system. After each clear chamber measurement, the chamber was briefly removed to allow gas concentrations to return to ambient levels, then replaced with a dark chamber wrapped in aluminum tape to exclude light and measure ecosystem respiration. This procedure separated net ecosystem exchange (photosynthesis – respiration) from respiration alone, enabling estimates of gross primary production.

During deployment, water was added around seals between the chamber sections and the collar to ensure airtight closure. Each flux measurement lasted approximately 5 min, with fluxes calculated using the chamber's effective volume, determined as the total chamber volume minus estimated vegetation volume. For ground collars, collar height above ground was added to the effective volume; for submerged collars, the height above the water surface was subtracted. Continuous water level was logged at each pond, and Photosynthetically Active Radiation (PAR) was measured above the chambers using an Apogee MQ-500 sensor. Air temperature inside and outside the chambers was recorded using HOBO MX2201 temperature loggers at the end of each flux period.

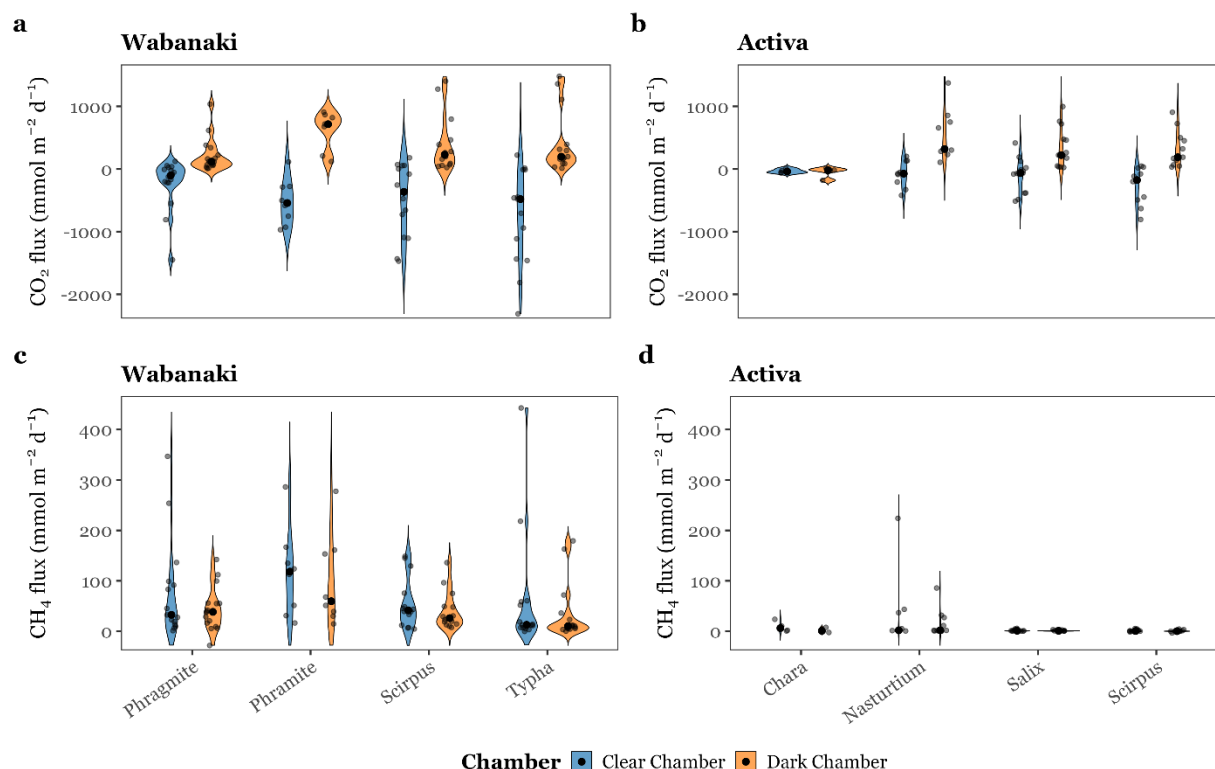


Figure 3-6: Distribution of daily CO₂ and CH₄ fluxes (mmol m⁻² d⁻¹) across vegetation types in Wabanaki and Activa ponds, measured under Clear (blue) and Dark (orange) chamber conditions. Violin plots illustrate the spread and density of flux observations for each vegetation type, with black points showing medians and semi-transparent dots representing individual measurements.

At Wabanaki pond (Figures 3-6 a and c), both CO₂ and CH₄ fluxes exhibited variability among species. Under clear chambers (representing net ecosystem exchange), *Phragmites*, *Scirpus*, and *Typha* showed strong CO₂ uptake (negative fluxes) associated with photosynthetic activity, whereas dark chamber measurements (representing ecosystem respiration) indicated consistent CO₂ release. CH₄ emissions were substantially higher in Wabanaki compared to Activa, with large variations. At Activa pond (Figures 3-6b and d), both CO₂ and CH₄ fluxes were generally lower and less variable. Clear-chamber CO₂ fluxes indicated moderate photosynthetic uptake, while dark chamber values were relatively uniform across species. CH₄ fluxes at Activa remained near detection limits for all vegetation types, reflecting lower sediment organic content and reduced

methanogenic activity. Overall, these patterns highlight the stronger photosynthetic activity and CH₄ emissions in the OC-rich Wabanaki pond, compared to the sparse and small riparian vegetation of Activa pond. A detailed comparison between open-water and vegetation fluxes, forebay-main basin differences, and Activa and Wabanaki pond CO₂ and CH₄ dynamics was presented in Chapter 2.

3.3.2 Dissolved gas (CO₂ and CH₄)

Each gas flux measurement also involved collecting dissolved gas samples from both the forebay and the main basin of the Wabanaki and Activa ponds. The concentrations of dissolved CO₂ and CH₄ were measured using the headspace equilibrium technique, employing a method similar to that described by D'Acunha and Johnson (2019). Approximately 15 mL of water sample from each pond was collected in a 50 mL syringe, both at the inlet forebay and the outlet main basin. This sample was then mixed with field air. Following vigorous shaking for 2-3 minutes to achieve equilibrium, the headspace gas was extracted into a smaller syringe via a three-way stopcock and a hydrophobic filter and then injected into an exetainer using a 25-gauge needle. The temperature of the equilibrated water was recorded immediately after this process. The headspace gas and field air samples were then transported to the laboratory and analyzed using a Shimadzu Gas Chromatograph (Model GC-2014) equipped with a flame ionization detector and methanizer (for CO₂ and CH₄), electron capture detector (for N₂O) and thermal conductivity detector (for O₂). The GC was calibrated using four standards with CO₂ concentrations ranging from 60 to 883 ppm and CH₄ concentrations from 5 to 4970 ppm.

The total moles of CO₂ and CH₄ in the original pond water sample (n_{sam}) were calculated by adding the moles in the headspace (n_{HS}) to the moles in the water (n_w) after reaching equilibrium and then subtracting the moles in the field air (n_{gas}). To determine n_{HS} , the concentration of gas in the headspace from GC analysis in ppm is first converted to partial pressure using Dalton's Law. Then, the Ideal Gas Law was applied to calculate moles, incorporating the headspace volume, pressure, and temperature in the appropriate units. For n_w , Henry's Law using values for CO₂ and CH₄ from Sander (2015) was used, whereby the headspace's partial pressure multiplied by Henry's Law constant equals the concentration of gas in the water. This constant is derived from the water temperature post-equilibrium. n_{gas} was calculated similarly to n_{HS} , by converting ppm readings to partial pressure and then to moles with the Ideal Gas Law. Finally, n_{sam} was converted to a concentration based on the water sample's volume.

Dissolved gas samples were also collected during two distinct winter campaigns and throughout the 2024 ice-free season. During 2024-01-22 to 2024-03-28 and 2025-01-16 to 2025-03-04, winter sampling was conducted beneath the ice cover. Ice holes were drilled at each sampling site, and water samples were collected immediately for dissolved gas analysis to minimize atmospheric exchange. From 2024-04-29 to 2024-11-27, dissolved gas samples were collected regularly during open water conditions in conjunction with flux measurements. Duplicate or triplicate samples (in winter when no flux measurement) were collected from each location. Data points shown in Figure 3-7 are the average.

Across both ponds, dissolved CH₄ concentrations remained low during the ice-free period, typically below ~30 $\mu\text{mol L}^{-1}$ (Figure 3-7). In contrast, dissolved CO₂ showed higher variability,

with elevated values during summer, often exceeding $300 \mu\text{mol L}^{-1}$, reflecting enhanced biological activity and warmer water temperatures. In contrast, winter conditions, including ice cover, led to pronounced accumulation of dissolved gases, especially in the forebays. Axta showed the strongest buildup, with CO_2 exceeding $1500 \mu\text{mol L}^{-1}$ and CH_4 surpassing $300 \mu\text{mol L}^{-1}$, while Wabanaki displayed similar but smaller increases (Figure 3-7). These patterns illustrate a consistent seasonal signal: dissolved gas buildup is markedly higher in winter, when reduced mixing, ice cover, and lower oxygen conditions restrict gas exchange with the atmosphere and allow CO_2 and CH_4 produced in sediments to accumulate in the water column. Once the ponds transition into spring, concentrations decline as ice melts, mixing resumes, and gas exchange increases (Figure 3-7).

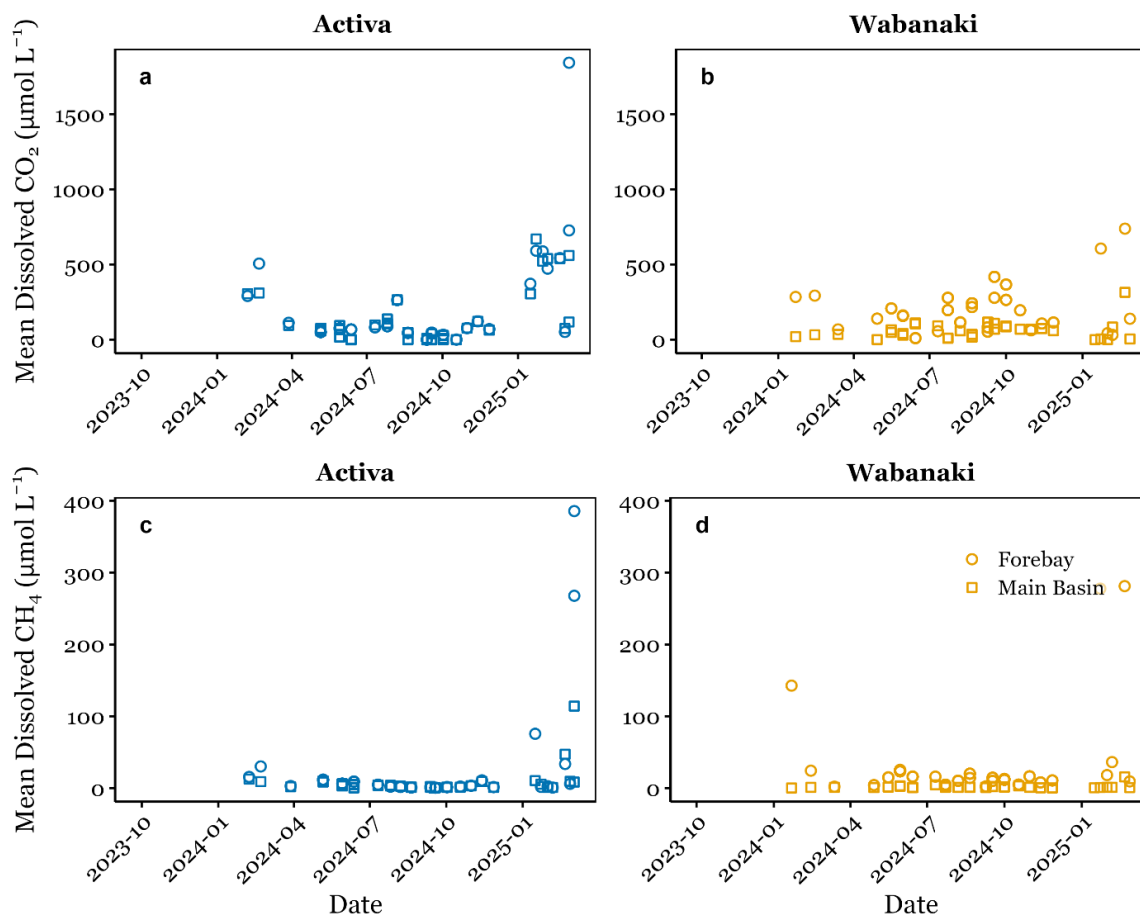


Figure 3-7: Temporal variation in mean dissolved CO₂ and CH₄ concentrations (μmol L⁻¹) across Activa and Wabanaki ponds from 2023-2025. Panels (a, b) show CO₂ and panels (c, d) show CH₄. Hollow circles represent the forebay and hollow squares represent the main basin.

3.3.3 Dissolved inorganic carbon and dissolved organic carbon

Pond surface water samples were also collected from the forebay and main basin along with each flux measurement, filtered through a 0.45 μm pore size membrane filter (polypropylene syringe filters, VWR), and analyzed to quantify dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC). DOC concentrations in filtered water samples acidified to pH <3 using 1M HCl were measured using a total organic carbon analyzer (Shimadzu TOC-LCPH/CPN, MDL 6 μmol L⁻¹). Non-acidified samples were analyzed for DIC (MDL 3 μmol L⁻¹) using the same analyzer.

DIC and DOC were analyzed throughout the full study period. Samples were collected consistently from both ponds to provide baseline information on carbon pools across all seasons. Activa pond exhibited a wide range of DIC values, including several high pulses ($>40 \text{ mg L}^{-1}$), indicating episodic inputs or periods of intensified mineralization (Figure 3-8). DOC in Activa also fluctuated but generally remained below $\sim 15 \text{ mg L}^{-1}$. In contrast, Wabanaki maintained consistently higher and more variable concentrations of both DIC and DOC across all seasons. Within Wabanaki, concentrations were typically higher in the forebay than in the main basin, reflecting stronger sedimentation and carbon processing near the inlet. In Activa, differences between forebay and main basin were less pronounced because the two basins are hydraulically connected, resulting in a more uniform dissolved-carbon distribution.

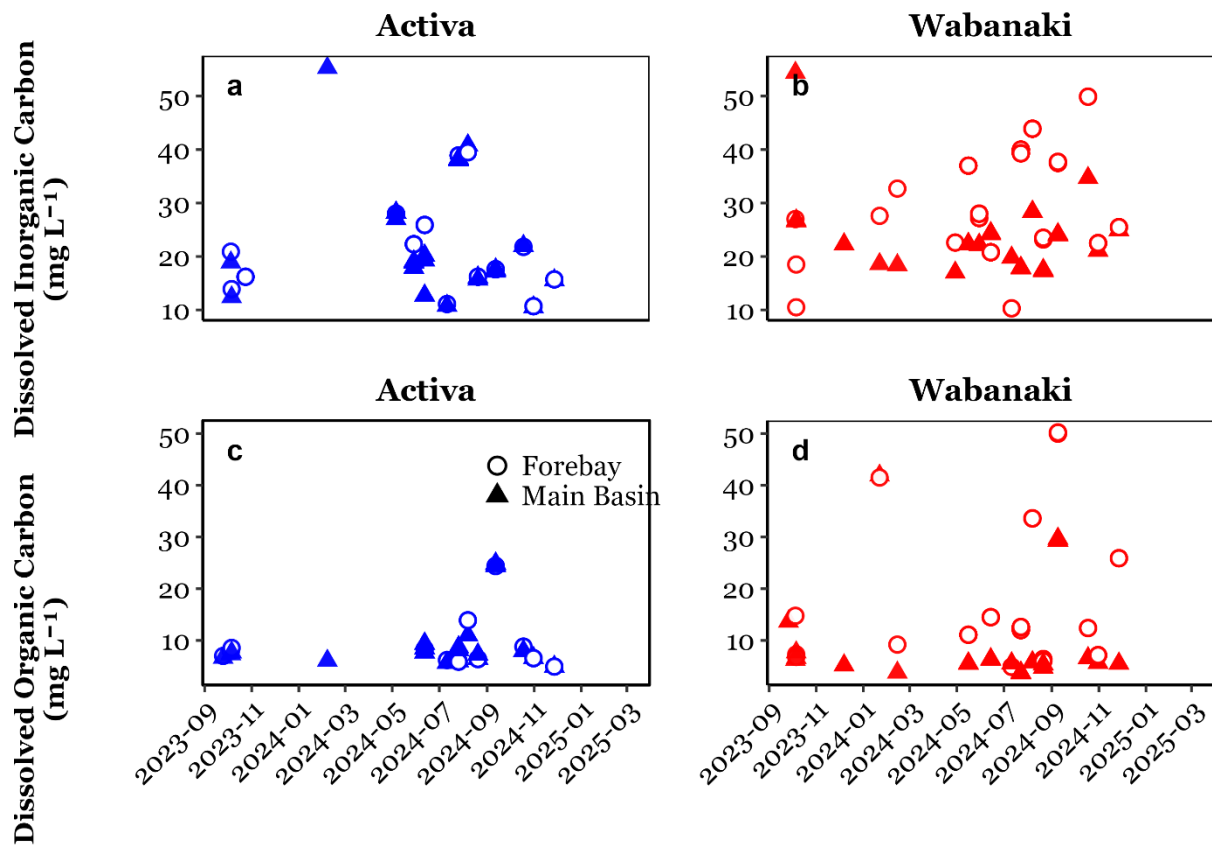


Figure 3-8: Temporal variation in dissolved carbon concentrations in Activa and Wabanaki ponds. Panels a–b shows dissolved inorganic carbon (DIC, mg L⁻¹) and panels c–d show dissolved organic carbon (DOC, mg L⁻¹) measured in the Activa (left) and Wabanaki (right) ponds from October 2023 to November 2024. Hollow circles represent the forebay and solid triangles represent the main basin.

3.3.4 Secchi disk depth and turbidity

To assess water clarity and light penetration, Secchi disk depth and turbidity were measured at both the forebay and main basin of the Wabanaki and Activa ponds. These parameters were selected to provide complementary indicators of optical water quality, with Secchi disk depth reflecting transparency to the human eye and turbidity quantifying suspended particles that scatter light. Secchi disk measurements were taken using a standard 20 cm black-and-white disk attached

to a rope. The disk was lowered into the water column until it just disappeared from view (descending depth) and then raised until it reappeared (ascending depth). The depths were measured by a measuring tape. The Secchi disk depth is the average of descending and ascending depths. Turbidity was measured using a portable turbidity meter. Prior to use, the meter was calibrated with Milli-Q water (0 NTU) and three standard solutions (10, 100, and 1000 NTU). Surface grab samples were collected from each site and transported to land for measurement. Before analysis, each sample was shaken to homogenize suspended material, and the turbidity vial was rinsed three times with the sample water to minimize contamination. Turbidity measurements were then recorded in triplicate for each location, and the mean value was reported in NTU.

Secchi disk transparency was monitored between 2024-05-16 and 2024-11-27 (Figure 3-9a). Activa pond showed similar Secchi depths in its forebay and main basin, indicating generally uniform water clarity across the pond, though the forebay displayed a wider range, reflecting greater variability driven by inflow conditions. In contrast, Wabanaki exhibited pronounced spatial differences: its forebay had much lower Secchi depths (reduced clarity), while the main basin is considerably clearer. This pattern reflects Wabanaki's separated forebay design, which traps sediments and particulates before water enters the larger, deeper main basin.

Turbidity samples were collected between 2024-05-29 and 2024-11-27 (Figure 3-9b). Turbidity values were low and comparable between forebay and main basin in Activa, consistent with its more hydraulically connected structure. Wabanaki, however, showed much higher turbidity in the forebay than in the main basin, including several extreme outliers. This pattern indicated stronger sediment and particulate loading at the Wabanaki forebay, likely due to industrial stormwater

inputs, while the main basin maintains lower turbidity due to settling and larger volume. The turbidity results were consistent with the average Secchi disk depths.

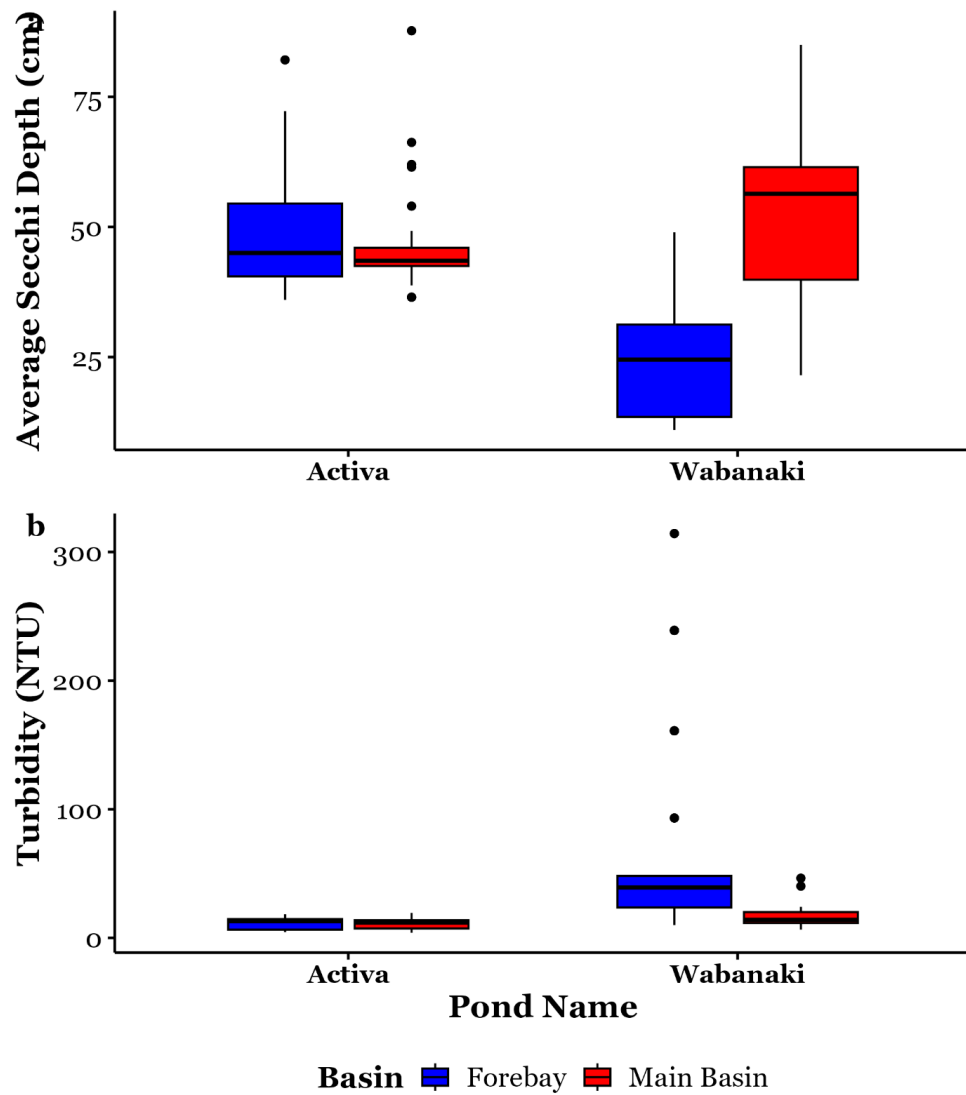


Figure 3-9: Average Secchi disk depth (a) and turbidity (b) in the forebay (blue) and main basin (red) of Aactiva and Wabanaki ponds.

3.3.5 *Chlorophyll-a*

Surface water samples were collected from both the forebay and main basin of the Wabanaki and Activa ponds using brown opaque grab bottles, following a chlorophyll-*a* (Chl-*a*) sampling protocol based on EPA Method 445.0 (Arar & Collins, 1997). Bottles were pre-rinsed with pond water before filling, and samples were kept cold and dark until filtration within 24 h. Depending on season, 100-200 mL of water were filtered in duplicate through 47 mm Whatman GF/F glass-fiber filters under low vacuum pressure and minimal lighting to concentrate phytoplankton pigments. Filters were wrapped in aluminum foil, frozen at -20°C, and later cut into small pieces under low light. Pigments were extracted in 90% acetone by grinding the filter material into a slurry, which was transferred to centrifuge tubes and rinsed with additional acetone to ensure complete pigment recovery. Extracts were capped, shaken, and stored in the dark at 4°C for two hours with intermittent shaking, then centrifuged at 1000 g for 5 min to separate clarified supernatant. A 3 mL aliquot of supernatant was pipetted into a quartz cuvette, and fluorescence was measured using a fluorometer regularly calibrated with prepared Chl-*a* standards. Fluorescence readings (in RFU) were converted to Chl-*a* concentrations ($\mu\text{g L}^{-1}$).

Chlorophyll-*a* concentrations were measured between 2024-04-29 and 2024-11-27. Wabanaki pond showed a much stronger spatial contrast in Chl-*a* concentrations than Activa pond (Figure 3-10). In Activa, forebay and main basin values overlapped substantially, with similar medians and ranges, indicating relatively uniform algal biomass across the pond. In Wabanaki, however, the forebay exhibited markedly higher and more variable Chl-*a* concentrations, including several extreme peaks, while the main basin remained consistently low. This pattern reflects higher

nutrient and particulate loading into Wabanaki's forebay and effective settling and dilution in its larger, deeper main basin.

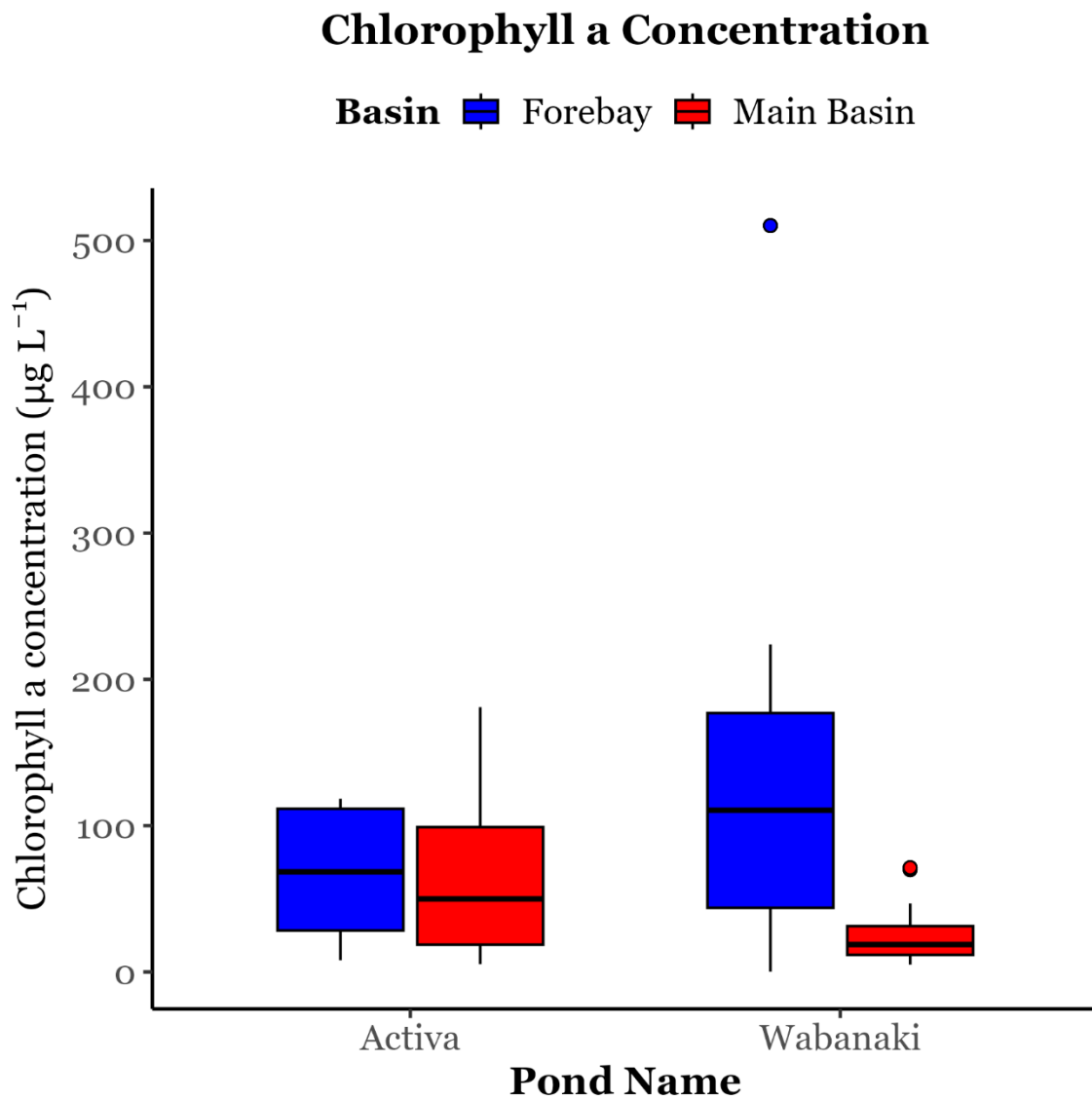


Figure 3-10: Chlorophyll-*a* concentration (µg L⁻¹) in forebay and main basins of the Activa (blue) and Wabanaki ponds (red).

3.3.6 temperature, pH, electrical conductivity, dissolved oxygen, and oxidation-reduction potential

At both the forebay and main basin of Aactiva and Wabanaki ponds, the water chemistry parameters were measured using a handheld YSI multiparameter sonde (Yellow Springs Instruments, USA), which provided data on water temperature, pH, electrical conductivity (EC), dissolved oxygen (DO), and oxidation-reduction potential (ORP). Each parameter provides insights into the environmental conditions affecting open water fluxes. Prior to each sampling day, the YSI probe was calibrated following the manufacturer's standard procedures. The pH sensor was calibrated using two buffer standards (pH 7.00 and pH 10.00) to bracket the expected range of pond water pH. The EC probe was calibrated using a 1,413 $\mu\text{S cm}^{-1}$ specific conductivity standard. The ORP probe was calibrated using a 225 mV standard solution to ensure accurate redox potential readings. All standard solutions were prepared in the laboratory and transported to the field for on-site calibration. DO was calibrated daily using the 100% air-saturation method. For this procedure, a small volume of water was added to the protective cap of the DO probe, which was then loosely sealed to maintain a humid air space. The probe was left to equilibrate for 5–10 minutes until a stable reading corresponding to 100% air saturation was obtained. All calibrations were verified by cross-checking with field standards prior to deployment, and measurements were performed immediately after calibration to minimize drift. Measurements were made at both the surface water and near-bottom depths from 2024-04-29 to 2025-03-04. Beginning on 2024-09-09, an additional mid-water measurement was included, resulting in three-point vertical profiles (surface, mid-depth, and near-bottom) for the remainder of the dataset.

3.4 Application: carbon flux and water chemistry correlations

After collecting water-column measurements during each field visit, the resulting physicochemical data enable direct examination of how SWPs' biogeochemistry influences GHG exchanges. Correlation analyses are good examples to provide an interpretive link between the water conditions and the carbon fluxes measured using chambers. Figure AII-1 demonstrates how CO₂, total CH₄, diffusive CH₄, and ebullitive CH₄ fluxes vary with DOC and DIC concentrations across both Wabanaki and Activa ponds. CO₂ fluxes tended to increase with higher DOC and DIC concentrations in both ponds. In contrast, CH₄ fluxes were generally elevated at moderate DOC and DIC levels, while extremely high DOC concentrations were often associated with reduced CH₄ emissions. Figure AII-2 expands this interpretation by linking dissolved CO₂ and CH₄ concentrations to surface-water pH and temperature. Dissolved gases decline as pH increases, reflecting reduced CO₂ availability under higher alkalinity and the shift toward bicarbonate/carbonate forms. Temperature increases are associated with lower dissolved-gas concentrations because of reduced solubility, but simultaneously higher emission rates due to enhanced biogeochemical production and gas release mechanisms. These patterns demonstrate how routine water-chemistry measurements collected with each flux measurement help explain daily and seasonal shifts in dissolved carbon pools.

3.5 Recommended practices for municipal-scale urban SWP GHG monitoring

Building on the ponds-specific sampling and data collection methods described in this Chapter as well as based on research limitations and experience gained during this study, this section situates the Activa and Wabanaki pond datasets within the broader context of urban GHG monitoring frameworks. This study aligns field protocols and data workflows with the Integrated Global

Greenhouse Gas Information System (IG³IS) and related international guidance, extending their application by incorporating SWPs as active and measurable sources and sinks of GHGs within the urban landscape. Through field-based investigations and the application of FAIR-aligned data workflows, the dataset and methods of measurements and analyses presented in this Chapter demonstrate how systematic, reproducible sampling of SWPs can improve the completeness and comparability of urban GHG assessments. The following recommendations translate empirical findings and field experience into actionable guidance that municipalities can adopt to support routine, evidence-based monitoring and routine sampling.

Define monitoring objectives and decision linkages: Develop a monitoring plan that connects sampling goals to operational or policy decisions as cities are expected to report their GHG emissions. Objectives may include compliance tracking, optimization of pond retrofits, or annual GHG reporting. Define measurable outcomes (*e.g.*, CH₄/CO₂ seasonal flux ranges, sediment thresholds for dredging, vegetation-cover limits) following municipal criteria.

Apply tiered spatial and temporal sampling design: Collect samples at inlet/forebay/main basin/outlet locations of each pond to capture hydraulic and biogeochemical gradients. Use a mixed temporal design: biweekly baseflow sampling (ice-free seasons for flux measurements) supplemented by event-based sampling (*e.g.*, ≥ 15 – 25 mm or first flush after ≥ 72 h dry weather; and under-ice dissolved gas and water chemistry data collection).

Quantify GHG fluxes with simple, defensible methods and quantify different flux pathways: Use standardized floating and vegetation chambers coupled to an infrared gas analyzer (*e.g.*, LI-7810) to measure diffusive and ebullitive fluxes under both clear and dark conditions. Floating chambers are the accepted, cost-effective approach for ponds; automated/low-cost chamber

designs now exist if higher temporal resolution is needed. Add bubble traps or chamber protocols that capture ebullitive bursts and annotate windy vs. calm conditions.

Measure the right core parameters, paired water and sediment: Profile temperature, DO, ORP, EC, and pH using calibrated YSI probes (surface and bottom). Complement with turbidity, Secchi depth, chlorophyll-*a*, DOC, and DIC analyses to assess productivity and organic-matter availability. These indicators are essential to explain spatial CH₄ and CO₂ variability between forebays and main basins. These directly influence CH₄ and CO₂ production and exchange and are consistent with Canadian water-quality protocols.

Couple dissolved gas and sediment measurements: Collect dissolved CH₄ and CO₂ samples from surface and sub-surface layers and analyze sediment organic carbon (%OM/LOI) and redox proxies to link sedimentary processes to gas exchange. These variables constrain methanogenesis and oxidation dynamics.

Deploy continuous environmental sensors: Install level, temperature, DO, and PAR loggers to quantify diel and seasonal drivers of gas exchange. Continuous data enable the identification of storm-driven emission spikes and stratification events that cannot be captured by periodic manual sampling.

Link hydrology to GHG dynamics: Integrate rainfall, inflow, and outflow records with flux data to normalize emissions by discharge or residence time. This hydrologic linkage clarifies how runoff and detention influence organic-carbon delivery and subsequent GHG production.

Track and manage vegetation cover: Monitor emergent and floating vegetation coverage (*e.g.*, duckweed, Typha, Phragmites) through field mapping or drone imagery. This information supports the upscaling of the vegetation zone fluxes and supports adaptive management actions such as selective harvesting or shading to maintain aerobic conditions.

Ensure QA/QC, data archiving, and transparency: Calibrate field instruments before each campaign. Apply field blanks, duplicates, and metadata standards. Archive water-chemistry and flux datasets on open platforms (*e.g.*, DataStream) with accompanying metadata for long-term municipal reference.

These recommendations highlight the need for structured, transparent, and scalable monitoring and sampling approaches that recognize the dual role of stormwater ponds as both water management infrastructure and active components of the urban carbon cycle. By extending the IG³IS principles to include aquatic systems and integrating hydrologic, chemical, and flux observations within FAIR data frameworks, municipalities can generate evidence-based insights that inform both water and climate policy. Collectively, these recommendations offer a foundation for developing standardized, city-scale monitoring networks and for advancing the inclusion of stormwater ponds within future iterations of IG³IS and GAW best-practice guidance.

4 Conclusion

4.1 Summary of key findings

This thesis examined greenhouse gas (GHG) fluxes from urban stormwater ponds (SWPs) to understand their role in urban carbon cycling and inform future design and management strategies. Chapter 2 quantified carbon dioxide (CO₂) and methane (CH₄) fluxes from riparian vegetation and open water zones across two contrasting SWPs: Activa (residential) and Wabanaki (industrial) ponds (Table 4-1), to determine their net carbon-based GHG balance, spatial variability between forebay and main basin zones, and the influence of pond design and land use on GHG dynamics. Chapter 3 complemented this analysis by developing and sharing a standardized, open-access dataset encompassing all fluxes, dissolved gases, and supporting physicochemical parameters collected between September 2023 and March 2025, following FAIR (Findable, Accessible, Interoperable, and Reusable) data principles to enable reproducible and scalable municipal GHG monitoring.

Vegetation fluxes exhibited strong seasonal patterns with CO₂ emissions, CO₂ uptake, and CH₄ release were all elevated during the warmer months, peaked in July, and reached their lowest levels in winter. While the riparian zones at both ponds functioned as net GHG sinks due to high photosynthetic activity, CH₄ emissions, given its stronger climate warming potential, can substantially reduce their overall sink strength. Wabanaki pond, an organic carbon (OC) rich industrial pond, exhibited higher per-area CH₄ emissions in the forebay for the same vegetation species, resulting in amplified CH₄ release compared to Activa pond. Consequently, the per-area CO₂-equivalent flux from the riparian zones was -141.4 mol m⁻² yr⁻¹ at Activa pond and only -94.8 mol m⁻² yr⁻¹ at Wabanaki pond. When scaled by area, differences in riparian zone extent emerged

as a critical determinant of the sink strength of the two ponds. Wabanaki, with its extensive riparian vegetation, removed $132.1 \text{ kmol yr}^{-1}$ of CO_2 -equivalents annually, whereas Activa, with a much smaller riparian zone, only removed 3.6 kmol yr^{-1} .

The open water zones were GHG sources at both ponds, dominated by CH_4 ebullition which accounted for roughly 88% of total CO_2 -equivalent emissions from the open water surface. Forebays exhibited markedly higher emissions than main basins due to higher OC inputs, shallower depths, and anoxic sediment, acting as GHG hotspot from the SWPs. Despite Wabanaki's higher open water carbon flux ($19.1 \text{ mol m}^{-2} \text{ yr}^{-1}$ vs. $12.7 \text{ mol m}^{-2} \text{ yr}^{-1}$ in Activa), its larger and deeper main basin moderated overall CO_2 -equivalent emissions ($119.6 \text{ mol m}^{-2} \text{ yr}^{-1}$ vs. $125.6 \text{ mol m}^{-2} \text{ yr}^{-1}$). This indicated that industrial ponds with high OC loading were more prone to CH_4 dominance, while deeper basins reduce emissions by limiting sediment-water interactions.

At the whole-pond scale, Wabanaki operated as a net molar carbon sink, while Activa remained a net carbon source due to Activa's much smaller riparian zone, which provided only limited CO_2 uptake compared with the extensive vegetated margins at Wabanaki. Although their per-area vegetation carbon uptake was similar, the difference in riparian extent produced markedly different whole-pond carbon balances. From a climate impact perspective, however, both ponds were net GHG sources acted as net GHG sources due to high CH_4 emissions, with annual totals emissions of approximately $186 \text{ kmol CO}_2\text{-eq}$ for Activa and $217.8 \text{ kmol CO}_2\text{-eq}$ for Wabanaki.

Table 4-1: Annual carbon and CO₂-equivalent fluxes for Activa and Wabanaki ponds, reported as per-area (mol m⁻² yr⁻¹) and total fluxes (kmol yr⁻¹).

Pond	Zone	Carbon Flux (mol m ⁻² yr ⁻¹)	CO₂-eq Flux (mol m ⁻² yr ⁻¹)	Total Carbon Flux (kmol yr ⁻¹)	Total CO₂-eq Flux (kmol yr ⁻¹)
Activa	Riparian vegetation	-142.3	-141.4	-3.7	-3.6
	Open water	12.7	125.6	19.2	189.6
	Whole pond	-129.6	-15.8	15.5	186
Wabanaki	Riparian vegetation	-140.5	-94.8	-195.8	-132.1
	Open water	19.1	119.6	55.9	349.9
	Whole pond	121.4	24.8	-139.9	217.8

This study demonstrates that the net carbon-based GHG balance and their climate impact of urban stormwater ponds is shaped by the interplay between land-use-driven carbon inputs, pond morphology, and extent of riparian vegetation when evaluating the climate impacts of urban stormwater systems.

Our findings suggest that SWP management should prioritize the reduction of CH₄ emissions. This could include periodic sediment dredging to reduce carbon accumulation in the forebay, reducing industrial runoff from surrounding facilities, and removing accumulated industrial material to limit excessive OM inputs, can help constrain CH₄ production. In addition, preserving or expanding riparian vegetation can strengthen photosynthetic CO₂ uptake, helping to counterbalance emissions and lower the overall GHG impact of urban stormwater ponds.

4.2 Recommendations for future research

Several limitations and sources of uncertainty in Chapter 2 must be considered when interpreting the annual carbon-based GHG fluxes. First, the use of a constant annual light-use efficiency (ϵ_g) introduces uncertainty, as ϵ_g is known to vary with short-term environmental conditions (Schwalm *et al.*, 2006). Likewise, assuming a P_{scalar} of zero prior to May may underestimate early-season photosynthetic activity. Ecosystem respiration (ER) was modeled primarily as a function of air temperature, yet other key drivers, such as soil moisture, substrate availability, and microbial community dynamics, were not incorporated. This is particularly relevant for the non-growing season, when soil microbial activity can generate small but non-negligible CO₂ fluxes (Zhou *et al.*, 2009; Han *et al.*, 2013). In addition, vegetation structure was characterized only by areal extent, and the live biomass was estimated based on height and stem counts, limiting the precision of vegetation-related flux estimates. Vegetation CH₄ emissions during the non-growing season are also likely underestimated. It was suggested that winter emissions may be more substantial than assumed. For example, senescent *Phragmites australis* can continue to vent CH₄ through standing stems, bypassing the water column and ice cover (Bodmer *et al.*, 2024). Future work should incorporate dynamic ϵ_g values, improved phenology and density metrics for vegetation, winter flux measurements across all pathways (including tree stems), and expanded modeling of ER beyond temperature alone. In addition, direct measurements that separate plant-mediated CH₄ transport from CH₄ emitted by riparian soils, such as stem chambers, vegetation removal experiments, or paired bare-soil collars, would provide clearer insight into the relative contributions of specific vegetation types within the riparian zone. Such partitioning would help clarify how different plant species influence overall GHG dynamics and improve our ability to assess and model vegetation-specific impacts on stormwater pond carbon budgets. Such

refinements would strengthen the accuracy of riparian vegetation fluxes in constructed urban ponds and support more robust assessments of their climate impacts. Incorporating embankment fluxes would help produce a more complete carbon-based GHG budget for these stormwater ponds.

Regarding the open water fluxes, ebullitive CH₄ was estimated indirectly from total CH₄ emissions and diffusive CH₄ fluxes. Direct measurements, such as using bubble traps, would allow for method comparison and better quantify the contribution of ebullition. Additionally, tree-mediated CH₄ emissions were not assessed, even though Aactiva pond has extensive woody vegetation along the embankment. Tree emissions are increasingly recognized as a potentially important but poorly quantified pathway with little empirical data available (Vroom *et al.*, 2022). Together, these limitations introduce uncertainty into the annual GHG budgets and highlight the need for more comprehensive, year-round measurements.

Although the present dataset in the Chapter 3 includes key parameters for assessing biogeochemical dynamics and GHG dynamics in urban SWPs, such as CO₂ and CH₄ fluxes, dissolved gas concentrations, and core physicochemical variables, future monitoring could be expanded to include additional biogeochemical indicators. For example, measurements of nutrient levels (total phosphorus, total nitrogen, and their dissolved inorganic forms such as NH₄⁺ and NO₃⁻) would improve understanding of nutrient-carbon interactions driving microbial respiration and methanogenesis. Similarly, incorporating sediment chemistry (*e.g.*, OC content, redox potential, and porewater CH₄/ CO₂) would help quantify sediment-water coupling processes influencing gas fluxes. Seasonal characterization of chlorophyll-*a*, dissolved organic matter quality, and isotopic signatures could further refine source attribution of carbon cycling within these systems. Longer-

term continuous monitoring using automated sensors for dissolved oxygen, temperature, and water level would also enhance temporal resolution and facilitate integration with atmospheric GHG modeling. Collectively, such additions would strengthen process-based understanding and enable development of locally parameterized emission factors for municipal and regional GHG inventories.

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Appendix I: Supplementary Materials for Chapter 2

Gap-filling of open water CO₂ and CH₄ fluxes using imputation method

The original time series of daily CO₂ and CH₄ fluxes (F_{CO_2} and F_{CH_4}) contained substantial gaps due to inability to measure fluxes at the daily scale. To derive continuous daily records suitable for estimating seasonal and annual budgets, we reconstructed missing values using a regression-based multiple imputation approach driven by external meteorological variables.

For each calendar day $t = 1, \dots, T$, we defined:

$F_{\text{CO}_2,t}$: daily CO₂ flux ($\text{mmol m}^{-2} \text{ d}^{-1}$)

$F_{\text{CH}_4,t}$: daily CH₄ flux ($\text{mmol m}^{-2} \text{ d}^{-1}$)

P_t : precipitation accumulated over the preceding 6 h (mm)

T_t : mean daily air temperature (°C)

U_t : mean daily wind speed (m s^{-1})

PAR_t : mean daily photosynthetically active radiation (e.g. $\mu\text{mol m}^{-2} \text{ s}^{-1}$)

Fluxes were kept in their original units ($\text{mmol m}^{-2} \text{ d}^{-1}$), while the predictors were recorded in their respective physical units (mm, °C, m s^{-1} , and $\mu\text{mol m}^{-2} \text{ s}^{-1}$). Because these variables have very different magnitudes and units, we standardized the predictors before model fitting to improve numerical stability and comparability of regression coefficients.

For each predictor $x_{k,t} \in \{P_t, T_t, U_t, \text{PAR}_t\}$, we calculated:

$$x_{k,t}^* = \frac{x_{k,t} - \mu_k}{\sigma_k}$$

where μ_k and σ_k are the mean and standard deviation of predictor k , computed over all days for which both fluxes and predictors were available. Note that only the predictors were standardized; all reported and imputed fluxes remained in $\text{mmol m}^{-2} \text{d}^{-1}$.

Calibration and evaluation of the flux-driver relationships:

We assumed that missing fluxes are missing at random (MAR) once conditioned on the meteorological drivers. For each gas $g \in \{\text{CO}_2, \text{CH}_4\}$, we first extracted the subset of days with observed flux $F_{g,t}$ and complete predictor information. This set was randomly divided into a training subset (70% of the days) used to fit the model and an independent validation subset (30% of the days) used to assess predictive performance.

For the training data, we specified a linear model of the form:

$$F_{g,t} = \beta_{g,0} + \beta_{g,1}P_t + \beta_{g,2}T_t + \beta_{g,3}U_t + \beta_{g,4}\text{PAR}_t + \varepsilon_{g,t}$$

where $\varepsilon_{g,t} \sim \mathcal{N}(0, \sigma_g^2)$.

In vector-matrix notation, letting $\mathbf{y}_g$ be the vector of observed fluxes for gas g in the training subset (length n_g), and $\mathbf{X}$ the corresponding $n_g \times 5$ design matrix consisting of a column of ones and the four standardized predictors, we have:

$$\mathbf{y}_g = \mathbf{X}\beta_g + \varepsilon_g,$$

with parameter vector $\beta_g = (\beta_{g,0}, \dots, \beta_{g,4})^\top$ and residuals $\varepsilon_g \sim \mathcal{N}(0, \sigma_g^2 \mathbf{I})$.

The regression coefficients $\hat{\beta}_g$ and residual variance $\hat{\sigma}_g^2$ were obtained by ordinary least squares.

For any day with known predictors, the model prediction is:

$$\hat{F}_{g,t} = \hat{\beta}_{g,0} + \hat{\beta}_{g,1} P_t^* + \hat{\beta}_{g,2} T_t^* + \hat{\beta}_{g,3} U_t^* + \hat{\beta}_{g,4} PAR_t^*$$

Model performance was quantified on the independent 30% validation subset. We computed the root mean square error (RMSE) and the coefficient of determination (R^2) as:

$$RMSE_g = \sqrt{\frac{1}{n_g^{val}} \sum_{t=1}^{n_g^{val}} (F_{g,t}^{val} - \hat{F}_{g,t}^{val})^2}$$

$$R_g^2 = 1 - \frac{\sum_{t=1}^{n_g^{val}} (F_{g,t}^{val} - \hat{F}_{g,t}^{val})^2}{\sum_{t=1}^{n_g^{val}} (F_{g,t}^{val} - \bar{F}_g^{val})^2}$$

where $F_{g,t}^{val}$ and $\hat{F}_{g,t}^{val}$ denote observed and predicted fluxes in the validation subset, and $\bar{F}_g^{val}$ is the mean observed validation flux for gas g . The models reproduced the day-to-day variation in fluxes well, with $R^2 = 0.91$ for CO_2 and $R^2 = 0.79$ for CH_4 on the validation data.

Multiple imputation of missing daily fluxes:

To fill the gaps while retaining an explicit representation of uncertainty, we used multiple imputation. For each gas separately, we generated m complete realizations of the daily time series ($m=30$; this is the number of imputed datasets in multiple imputation).

For any day t where predictors were available but the flux $F_{g,t}$ was missing, we first evaluated the regression prediction $\hat{F}_{g,t}$ using the fitted model. Then, for each imputed data set $j = 1, \dots, m$, we sampled a residual from the estimated error distribution:

$$\varepsilon_{g,t}^{(j)} \sim \mathcal{N}(0, \hat{\sigma}_g^2)$$

and constructed an imputed value

$$F_{g,t}^{(j)} = \hat{F}_{g,t} + \varepsilon_{g,t}^{(j)}$$

Thus, every missing flux value is replaced by a set of m plausible realizations driven by the meteorological state on that day and the empirically constrained residual variability. For days on which flux measurements were available, we kept the observations unchanged:

$$F_{g,t}^{(j)} = F_{g,t} \quad \forall j$$

This yields m complete daily time series for CO₂ and m for CH₄, each internally consistent with the measured predictors and preserving the observed fluxes.

Combining imputed data sets for derived quantities:

Many quantities of interest (e.g. annual totals, seasonal means) can be expressed as scalar functions Q of the full time series. For each imputed data set j , we computed $\hat{Q}^{(j)}$. The final point estimate was taken as the arithmetic mean across imputations:

$$\bar{Q} = \frac{1}{m} \sum_{j=1}^m \hat{Q}^{(j)}$$

We decomposed the variability in $\hat{Q}^{(j)}$ into within- and between-imputation components. $U^{(j)}$ denote the variance of $\hat{Q}^{(j)}$. The within-imputation variance is:

$$\bar{U} = \frac{1}{m} \sum_{j=1}^m U^{(j)}$$

and the between-imputation variance is:

$$B = \frac{1}{m-1} \sum_{j=1}^m (\hat{Q}^{(j)} - \bar{Q})^2$$

The total variance associated with $\bar{Q}$ is then:

$$T = \bar{U} + \left(1 + \frac{1}{m}\right) B$$

Approximate 95% confidence intervals for Q were obtained as:

$$\bar{Q} \pm t_{v,0.975} \sqrt{T}$$

where $t_{v,0.975}$ is the 97.5th percentile of the Student's t distribution with v degrees of freedom (computed using standard multiple-imputation formulas).

Quality checks of the imputed fluxes:

We evaluated the plausibility of the gap-filled fluxes in several ways:

1. Predictive performance: The independent 30% validation subset confirmed that the models captured most of the variability in daily fluxes (validation $R^2 = 0.91$ for CO_2 and 0.79 for CH_4), with RMSE values small relative to the observed spread.
2. Distributional consistency: Distributions of imputed values (considering only days originally missing) were compared with the distributions of observed values to ensure similar ranges and shapes, avoiding artificial inflation of extremes.

3. Temporal coherence: The reconstructed time series were visually inspected to verify that imputed segments followed the seasonal patterns and did not introduce abrupt, nonphysical jumps at the edges of gaps.

4. Sensitivity to the number of imputations: Increasing m beyond 30 did not materially change annual or seasonal budget estimates, and between-imputation variance remained modest compared to within-imputation variance, indicating that the chosen number of imputations was sufficient.

(a) Vegetation collar

(b) Clear chamber with extension

(c) Dark chamber with reflective tape



Figure AI-1: Field setup for vegetation flux measurements. (a) Installed vegetation collar enclosing the vegetation. (b) Clear chamber with an extension used for tall vegetation. (c) Dark chamber wrapped with reflective tape to suppress photosynthesis and minimize heat buildup.



Figure AI-2: Clear and dark floating chamber setup for open water flux measurements. Chambers were deployed from an inflatable boat and anchored during each measurement.

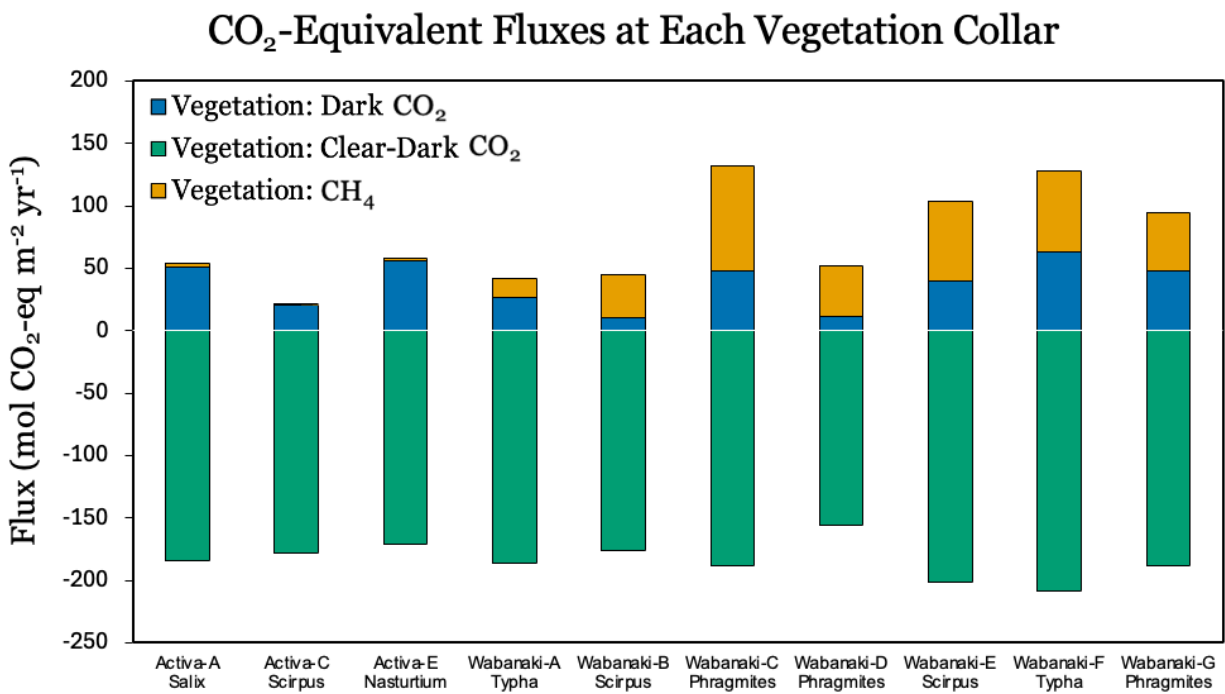


Figure AI-3: Annual CO₂-equivalent fluxes at each vegetation collar of Aactiva and Wabanaki ponds.

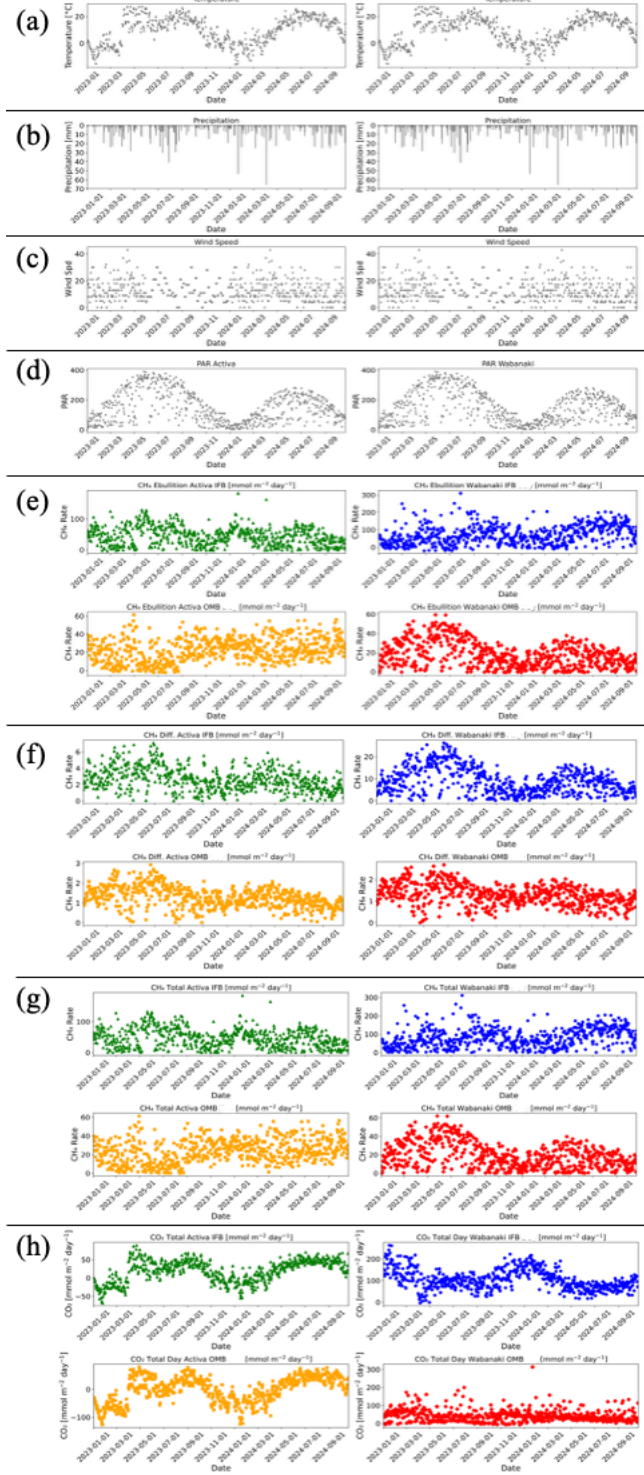


Figure AI-4: Time series of temperature (a), precipitation (b), wind speed (c), and PAR (d) data at the Activa and Wabanaki ponds, along with the corresponding gap-filled time series of ebullitive CH₄ (e), diffusive CH₄ (f), total CH₄ (g), and CO₂ fluxes (h) from outlet main basin (OMB) and inlet forebay (IFB) of two ponds.

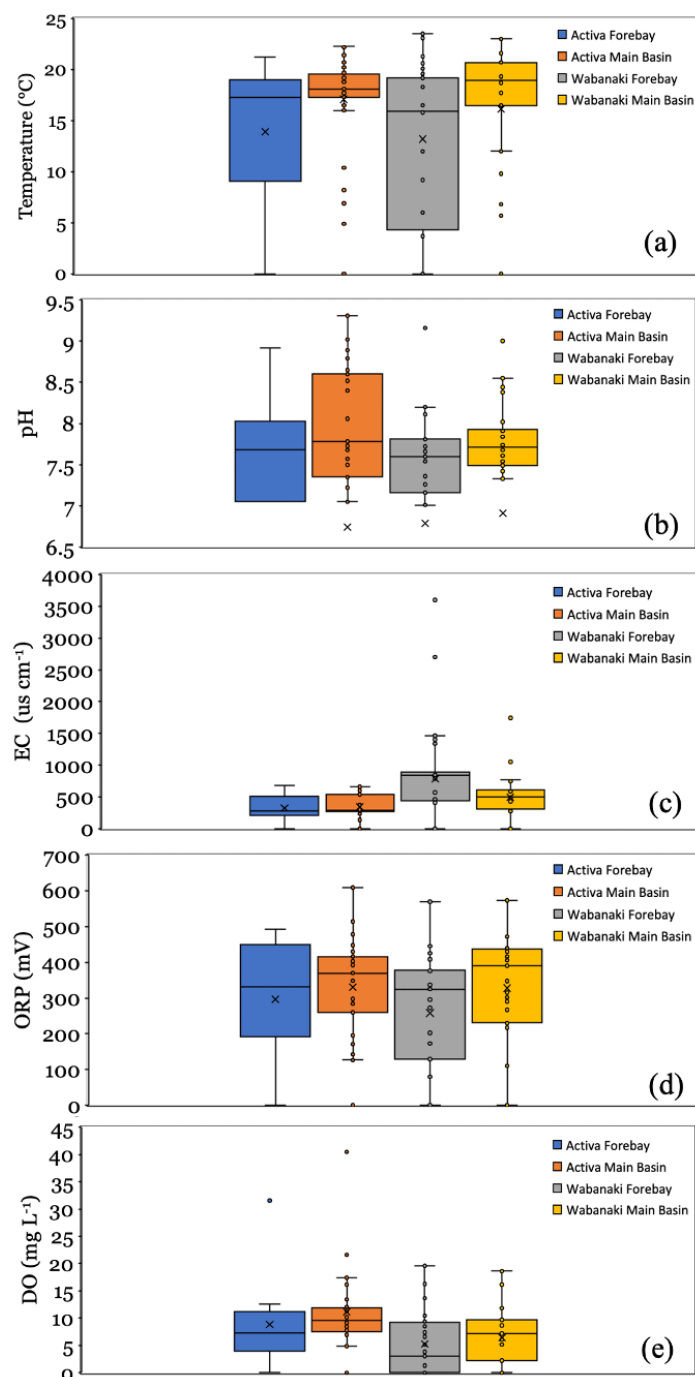


Figure AI-5: Box plots showing the range of water temperature (a), pH (b), specific electrical conductivity (EC) (c), oxidation-reduction potential (ORP) (d), and dissolved oxygen (DO) (e) from the water column in the Activa and Wabanaki ponds. pH was measured from the surface water, while all other parameters were measured near the bottom of the water column, just above the sediment. The blue box represents the Activa forebay, the orange box represents the Activa main basin, the grey box represents the Wabanaki forebay, and the yellow box represents the Wabanaki main basin.

Appendix II: Supplementary Materials for Chapter 3

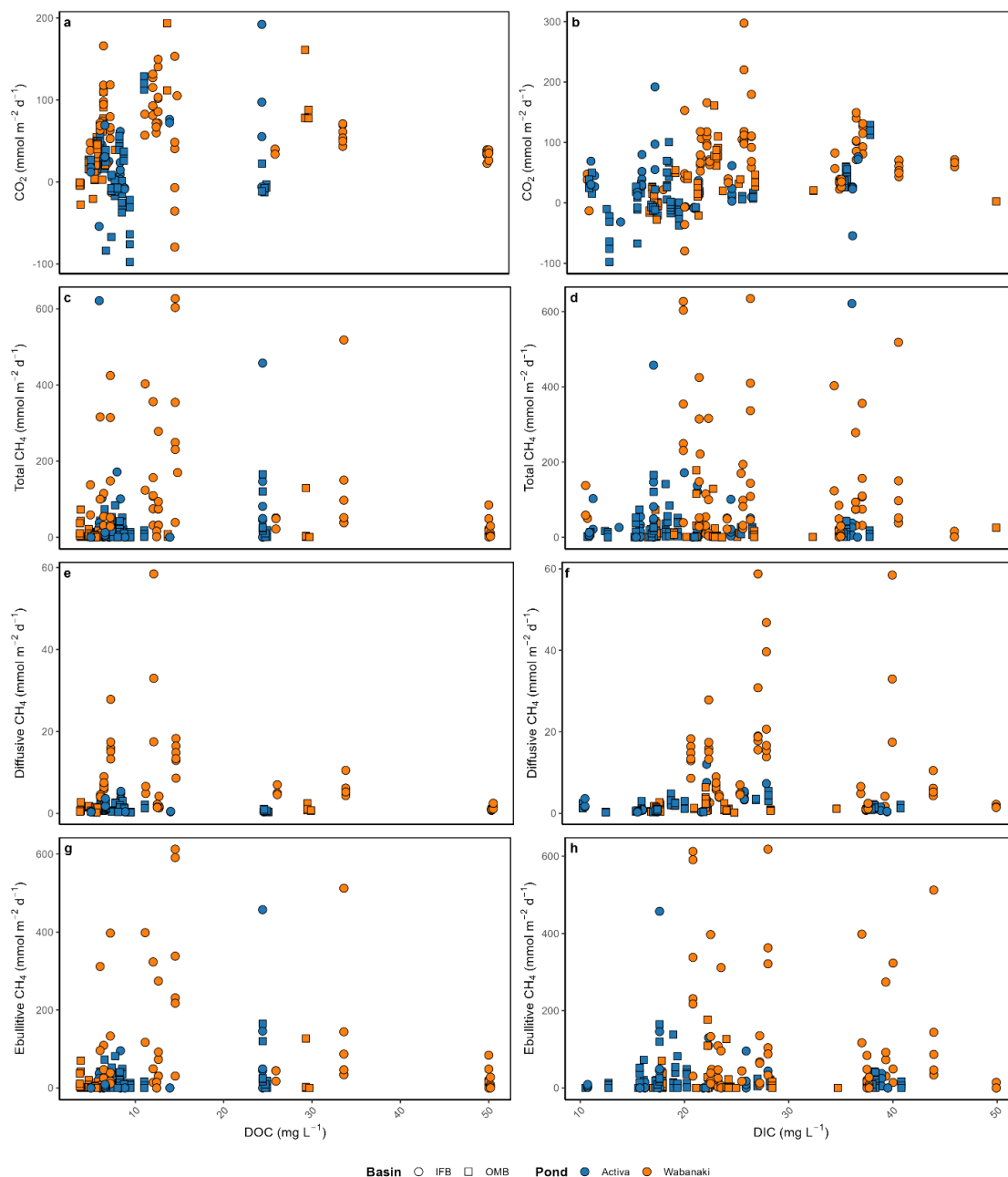


Figure AII-1: Relationships between carbon fluxes and dissolved organic and inorganic carbon (DOC and DIC, mg L^{-1}) concentrations in the Wabanaki and Activa ponds. Panels a, c, e, g show fluxes versus DOC and panels b, d, f, h show fluxes versus DIC. Flux variables include CO₂ (a-b), total CH₄ (c-d), diffusive CH₄ (e-f), and ebullitive CH₄ (g-h), expressed in $\text{mmol m}^{-2} \text{d}^{-1}$. Points represent individual sampling events in Activa (blue) and Wabanaki (orange) ponds, with inlet basins (IFB) shown as circles and main basins (OMB) as squares.

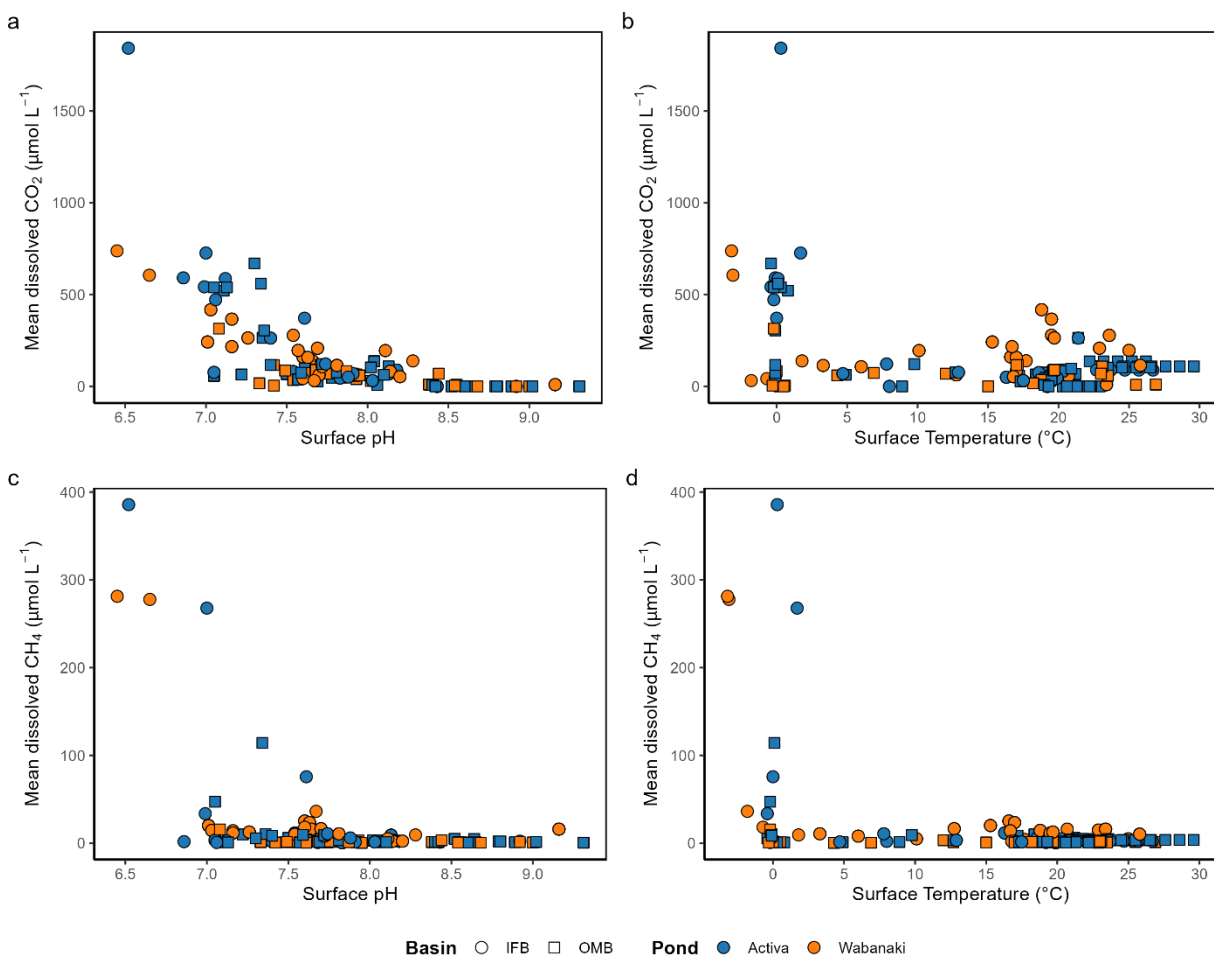


Figure AII-2: Mean dissolved CO₂ and CH₄ concentrations in relation to surface water pH and temperature in Wabanaki and Activa ponds.