Greenhouse gas fluxes from stormwater ponds and urban wetlands in southern Ontario

by

Akshara Withanage

A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Science
in
Geography

Waterloo, Ontario, Canada, 2025

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Urban wetlands and stormwater ponds are an established component of stormwater management integrated with green infrastructure elements. The main aim of these developments is to serve as receptacles for stormwater runoff and mitigate the adverse impact of urbanization on water quality and quantity. While created for stormwater management, urban wetlands and stormwater ponds also provide essential ecosystem services, including sequestration of carbon and preservation of biodiversity while enhancing the aesthetic value of the surrounding environment. Despite these services, these small water bodies accumulate loads of organic matter and nutrients, which undergo different conditions (aerobic/anaerobic) and microbial processes, releasing significant amounts of greenhouse gases (GHGs) such as methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O). Design specification and exposure to aspects of the urban environment may affect the amount of GHGs released. Hence, this study aimed to quantify GHG emissions from 24 distinct stormwater ponds and urban wetlands in the Kitchener-Waterloo region, Southern Ontario, over a seven-month period from May to November and assess the impact of selected environmental, physical and chemical parameters on these GHG emissions. The average daily fluxes across the sampling period were 760 mg CO_2 m^{-2} d^{-1}, 417 mg CH_4 m^{-2} d^{-1}, and 0.23 mg N_2O m^{-2} d^{-1}. Seasonal variation was evident for CO_2 and CH_4 fluxes, whereas N_2O fluxes showed minimal seasonal variation. For CO_2, significant predictors included water temperature, pH, dissolved oxygen (DO), dissolved organic carbon and NO_3^- concentrations, and physical features, including sediment depth, pond depth, catchment area and dredging. Methane emissions were primarily driven by in-situ environmental variables, including water temperature, DO concentration and pH, while chemical and physical factors did not significantly influence CH_4 fluxes. For N_2O,

key drivers included NO_3^- concentration, DO concentration, electrical conductivity and sediment depth. These findings highlight the complex and dynamic role of stormwater management facilities in GHG emissions and the importance of seasonal changes and abiotic factors in shaping emission patterns.

Key words: urban wetlands, storm water ponds, greenhouse gas emissions

Acknowledgements

I would like to express my deepest gratitude to my supervisor Dr. Maria Strack, for her invaluable guidance, patience and encouragement throughout the period of this research. As an international student navigating both academic and personal challenges in a new country, her patience, understanding, and mentorship meant more than words can express. Her belief in my abilities gave me the confidence to persevere and grow both as a researcher and as a person.

I am also grateful to my committee members, Dr. Derek Robinson and Dr. Tonya Delsontro, for their insightful comments and support. My sincere thanks to the Department of Geography and Environmental Management for providing the resources and environment needed to complete this work.

This project would not have been possible without the help and support of many individuals in the lab and in the field. I would like to thank Rayden Laliberte, Dr. Percy Korsah, and Ellie Harrison for the countless hours spent on data collection. Fieldwork would not have been possible without their immense support. I wish to thank all the members in our lab for sharing their ideas, offering help when needed, and listening when I needed to share my thoughts and feelings; it all meant more than words can express.

I am especially thankful to my family whose unwavering support, understanding and encouragement sustained me through the challenges of this journey. A heartfelt thank you to my partner Tharuka Kankanamge, for always being my supporter and for always believing in me.

I acknowledge that my research was conducted on the traditional lands of the Neutral, Anishinaabeg, and Haudenosaunee peoples.

This research is a part of RISE (Residential Development Impact Scorecard for the Environment) project. I am grateful to all the parties involved in this project, particularly the participating cities for their generous support throughout the research. The RISE project was undertaken with the financial support of the Government of Canada's Climate Action and Awareness Fund. Special thanks to City of Kitchener and City of Waterloo for their assistance with site access and background information.

I acknowledge that artificial intelligence tools (Grammarly, ChatGPT version 4o) were used solely for language refinement and for obtaining guidance in generating R codes.

Dedication

I dedicate this work to my loving husband, Tharuka Kankanamge. Thank you for your constant strength, support and love. Your patience through every challenge and your faith in me never wavered. Nothing I have accomplished without your support, comfort and inspiration that you have selflessly provided me throughout this journey.

Table of Contents

Author's Declaration ii
Abstract iii
Acknowledgements v
Dedication vii
List of Figures x
List of Tables xii
Chapter 1 ..... - 1 -
1. Literature Review ..... - 1 -
1.1 Introduction ..... - 1 -
1.2 Stormwater ponds and urban wetlands ..... - 3 -
1.3 Production of GHG in SWP and UW ..... - 7 -
1.3.1 Carbon dioxide (CO_2) ..... - 7 -
1.3.2 Methane (CH_4) ..... - 8 -
1.3.3 Nitrous oxide (N_2O) ..... - 10 -
1.4 Factors influencing GHG emissions in SWP and UW ..... - 11 -
1.4.1 Carbon Dioxide ..... - 11 -
1.4.2 Methane ..... - 13 -
1.4.3 Nitrous oxide ..... - 15 -
1.5 Regional and global emission estimates of GHG emissions ..... - 18 -
1.6 Research Gap ..... - 21 -
Chapter 2 ..... - 24 -
Greenhouse gas dynamics in stormwater ponds and urban wetlands: Quantification and drivers ..... - 24 -
2.1 Introduction ..... - 24 -
2.2 Methods ..... - 28 -
2.2.1. Study sites and experimental design ..... - 28 -
2.2.2 Data collection and instrumentation ..... - 36 -
2.2.3 Statistical Analysis ..... - 41 -
2.3 Results ..... - 44 -
2.3.1 Quantification of GHG fluxes and assessment of temporal variability ..... - 44 -

2.3.2 Effect of in-situ environmental variables on the GHG fluxes ..... - 56 -
2.3.3 Effect of water quality variables on the GHG fluxes ..... - 64 -
2.3.4 Effect of physical variables on GHG fluxes ..... - 65 -
2.4 Discussion ..... - 71 -
2.4.1 Temporal variability and effect of in-situ environmental variables on GHG fluxes ..... - 71 -
2.4.3 Effect of pond water quality on GHG fluxes ..... - 81 -
2.4.4 Effect of physical characteristics of facilities on GHG fluxes ..... - 84 -
2.4.5 Comparison of GHG fluxes from southern Ontario stormwater facilities to other regions ..... - 89 -
2.4.6 Limitations of this study and recommendations ..... - 92 -
2.5 Conclusion ..... - 93 -
Chapter 3 ..... - 96 -
Conclusion ..... - 96 -
3.1 Carbon dioxide fluxes ..... - 96 -
3.2 Methane fluxes ..... - 97 -
3.3 Nitrous oxide fluxes ..... - 98 -
3.4 Future research needs and implications ..... - 100 -
References ..... - 102 -
Appendix ..... - 130 -

List of Figures

Figure 1.1: Diagram of a stormwater pond (top; adapted from **stormwater management plan and swmp design** (omecp,2003) and photos of inlet, main pond and outlet (bottom, from left to right) from selected stormwater ponds in kitchener-waterloo, ontario....- 5 -

Figure 1.2: Diagram of a urban wetland (top; adapted from **stormwater management plan and swmp design** (omecp, 2003) and photos of inlet, main pond and outlet (bottom, from left to right) from selected urban wetlands in kitchener-waterloo, ontario.....- 6 -

Figure 2.1:(a) Location of Kitchener/ Waterloo area in southern Ontario (Canada). (b) locations of the selected study sites within Kitchener-Waterloo, visualized using google earth imagery (© google earth, image © 2025 airbus; accessed july 15,2025).....- 30 -

Figure 2.2: (a)Sampling locations within a facility. (b) depths along the water column .- 35 -

Figure 2.3(a): Floating chambers connected to the portable ghg analyzers, **(b):** floating static chamber deployed alongside the boat. .....- 38 -

Figure 2.4: Heatmap illustrating CO_2 fluxes (g CO_2 m^{-2} day^{-1}) across 24 stormwater ponds over a 7-month sampling period (May–November). .....- 50 -

Figure2.5: Boxplot showing the distribution of CO_2 fluxes (g CO_2 m^{-2} d^{-1}) across different facility types..- 51 -

Figure 2.6: Heatmap illustrating CH_4 fluxes (mg CH_4 m^{-2} d^{-1}) across 24 stormwater ponds over a 7-month sampling period (May–November). .....- 52 -

Figure 2.7: Boxplot showing the distribution of CH_4 fluxes (mg CH_4 m^{-2} d^{-1}) across different facility types..- 53 -

Figure 2.8: Heatmap illustrating N_2O fluxes (µg N_2O m^{-2} d^{-1}) across 24 stormwater ponds over a 7-month sampling period (May–November). .....- 54 -

Figure 2.9: Boxplot showing the distribution of N_2O fluxes (µg N_2O m^{-2} d^{1}) across different facility types..- 55 -

Figure 2.10: Scatterplot depicting the relationship between 4 in-situ environmental variables, and CO_2 flux.. .....- 59 -

Figure 2.11: Scatterplot depicting the relationship between 4 in-situ environmental variables, and CH_4 flux.. .....- 60 -

Figure 2.12: Scatterplot depicting the relationship between 4 in-situ environmental variables, and N_2O flux. .....- 61 -

Figure 2.13: Scatterplot depicting the relationship between water quality variables, and GHG fluxes (CO_2 and N_2O). .....- 65 -

Figure 2.14:Scatter plot showing the effects of catchment area on cumulative CO_2 emissions from stormwater facilities.. .....- 66 -

Figure 2.15: Box plot illustrating the variation in cumulative CO_2 emissions ($g\ m^{-2}$) across stormwater facilities grouped by dredging category.. .....- 67 -

Figure 2.16: Scatter plot showing the relationship between sediment depth (m) and cumulative CO_2 fluxes ($g\ m^{-2}$) at individual sampling locations across 24 stormwater ponds.. .....- 67 -

Figure 2.17: Scatter plot showing the relationship between pond depth (m) and CO_2 fluxes ($g\ m^{-2}day^{-1}$) at individual sampling locations across 24 stormwater ponds.....- 68 -

Figure 2.18: Box plot illustrating the variation in cumulative CH_4 emissions ($g\ m^{-2}$) across ponds grouped by pond type.. .....- 69 -

Figure 2.19: Box plot illustrating the variation in cumulative CH_4 emissions ($g\ m^{-2}$) across ponds grouped by dredging category.. .....- 69 -

Figure 2.20:Scatter plot showing the relationship between sediment depth (m) and cumulative N_2O fluxes ($mg\ m^{-2}$) at individual sampling locations across 24 stormwater ponds.. .....- 70 -

List of Tables

Table 1.1: Average fluxes of methane, carbon dioxide and nitrous oxide from urban water bodies. (d = diffusive flux only; d + e = diffusive plus ebullitive flux. All flux rates are in mg m^{-2} d^{-1}).....- 20 -

Table 2.1: Physical characteristics of 24 stormwater management facilities in kitchener-waterloo area, ON .....- 31 -

Table 2.2: Monthly air temperature and total precipitation during the sampling period (May-November), along long-term averages (1991-2020).....- 33 -

Table 2.3: Sources of data for pond and catchment characteristics.....- 41 -

Table 2.4: Summary of CH4 flux components, including diffusive flux, ebullitive flux, total flux and the relative contribution of ebullition to total flux.....- 47 -

Table 2.5: Summary statistics of environmental variables at different depths across all ponds .....- 56 -

Table 2.6: Results from linear mixed effects models for CO_2, CH_4 and N_2O fluxes using environmental variables measured at various depths.....- 62 -

Table 2.7: Summary statistics of water quality variables across all ponds .....- 64 -

Chapter 1
1. Literature Review

1.1 Introduction

Global warming is one of the most pressing challenges of the 21st century, primarily driven by the increasing concentrations of greenhouse gases (GHGs) in the atmosphere (IPCC, 2023). The projected extent of global warming by the end of the 21st century varies depending on GHG emission scenarios: low GHG emission scenarios (net-zero CO_2 emissions by 2050) are expected to limit warming to 1–1.8 ℃; intermediate emission scenarios (CO_2 emissions remain same until 2050) project warming of approximately 2.1–3.5 ℃; and high emission scenarios (CO_2 emissions roughly doubled by 2050) would lead to an increase exceeding 3.3–5.7 ℃ (IPCC, 2023). Every additional increment in global warming changes the intensity of the extremes in the climate system, including permafrost thawing, loss of glaciers, intensifying global monsoon precipitation, and very wet and dry seasons (IPCC, 2023).

Unsustainable energy use, industrial activities, land use, and land use changes across regions are widely recognized as primary sources of GHGs. In addition, natural and constructed aquatic systems, including lakes, ponds, and other surface waters, have also been identified as globally significant emitters of GHGs (Cole et al., 2007). Those aquatic systems emit carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) as the primary GHG effluxes (Mondal et al., 2022). Annual emissions of CO_2 and CH_4 from global lentic inland waters have been estimated at around 0.3 Pg (1 Pg = 10^{15} g = 1 Gt) and 0.08 Pg, respectively (Raymond et al., 2013). Among them, small water bodies (with area <0.001 km^2) make up only 8.6% of the global lake and pond area, yet they contribute more than

15% of CO_2 and 40% of CH_4 of all diffusive GHG emissions from water bodies (Holgerson & Raymond, 2016). Specifically, constructed aquatic systems, including ponds and urban wetlands, contribute significantly to GHG emissions due to the impact of anthropogenic activities in the catchment, which introduce high nutrient loads and disrupt biogeochemical cycling (Malyan et al., 2022). According to a study in Queensland, Australia, CH_4 flux from artificial water bodies, including farm ponds and urban lakes, is higher than that from larger water bodies in the same region (Grinham et al., 2018).

Constructed aquatic systems, such as stormwater management facilities, are generally included in urban site planning to manage stormwater runoff volume and water quality (Troitsky et al., 2019). The use of conventional stormwater infrastructure (e.g., pipe networks, storage tanks) has shifted towards implementing infrastructure systems comprising blue-green elements such as bioretention filters, stormwater wetlands or wet ponds (Bakhshipour et al., 2019). While this blue-green infrastructure provides numerous environmental and socio-economic benefits, its potential impacts on local GHG dynamics and regional emissions have not yet been quantified (Rovelli et al., 2023). Therefore, recent attention has shifted towards quantifying rates and understanding controls on stormwater pond (SWP) and urban wetland (UW) GHG emissions into the atmosphere to better assess their contribution to urban GHG emissions; this thesis contributes to this goal. Understanding the mechanisms of GHG emissions in small water bodies such as SWP and UW is vital for effective management and mitigation.

1.2 Stormwater ponds and urban wetlands

Stormwater ponds and UW are considered end-of-pipe stormwater management facilities that receive stormwater from a conveyance system (e.g., ditches, sewers) and discharge the water to receiving waters (OMECP, 2003). These ponds and UW play a significant role in the sustainable management of urban landscapes, providing essential ecosystem services such as mitigating flood risk, improving water quality, and providing an additional aesthetic value for the landscape (D'Acunha & Johnson, 2019). Recent data suggested that a wetland or SWP in a residential project can increase property value by 300% (Wong et al., n.d.). Other than preventing storm-related flooding, the most common and widespread use of stormwater management facilities is protecting natural waterways from sediment and human-introduced contaminants carried by stormwater (OMECP, 2003). Therefore, SWP and UW receive many nutrients, organic materials, and sediments deposited on the bottom of the water body.

The main factor for differentiating between the types of stormwater management facilities is the proportions of deep (>0.5 m) and shallow areas (<0.5 m), where a pond has a high percentage of its volume provided in deep water zones while wetlands provide 70% of volume in shallow zones (OMECP, 2003). A comprehensive identification of characteristics and differences between SWP and UW is essential in understanding the GHG-releasing mechanisms.

Stormwater ponds can be defined as small impoundments explicitly designed to manage water flows in developing urban and sub-urban watersheds (Gorsky et al., 2019). These ponds are often designed with characteristics that match the requirements of the urban project, where ponds may vary in depth, embankments, and vegetation (Lusk et al.,

2025; Oertli & Parris, 2019). A SWP consists of three main components (Figure 1.1): an inlet where runoff water enters, an outlet where the runoff exits, and a main body that is often up to 3–8 ft (1–2.5 m) deep, varying based on the volume of runoff collected (Anderson et al., 2000; OMECP, 2003). Stormwater ponds can be divided into two broader classes: dry ponds and wet ponds; wet ponds are designed to have a permanent pool, while dry ponds are designed to be empty during some period (Troitsky et al., 2019). A wet pond has the highest amount of volume provided in deep water zones, and aquatic plants are generally concentrated in the pond's margin due to the water depth, while submerged plants might occur in the open water (OMECP 2003, Wong et al., n.d.). Moreover, wet ponds generally require a drainage area of ≥10 ha. However, a minimum of 5 ha may be sufficient to sustain the permanent pool if supplemented by an additional water source (OMECP, 2003). Additionally, selected natural ponds have been partially engineered into wet ponds to manage stormwater runoff (OMECP, 2003)

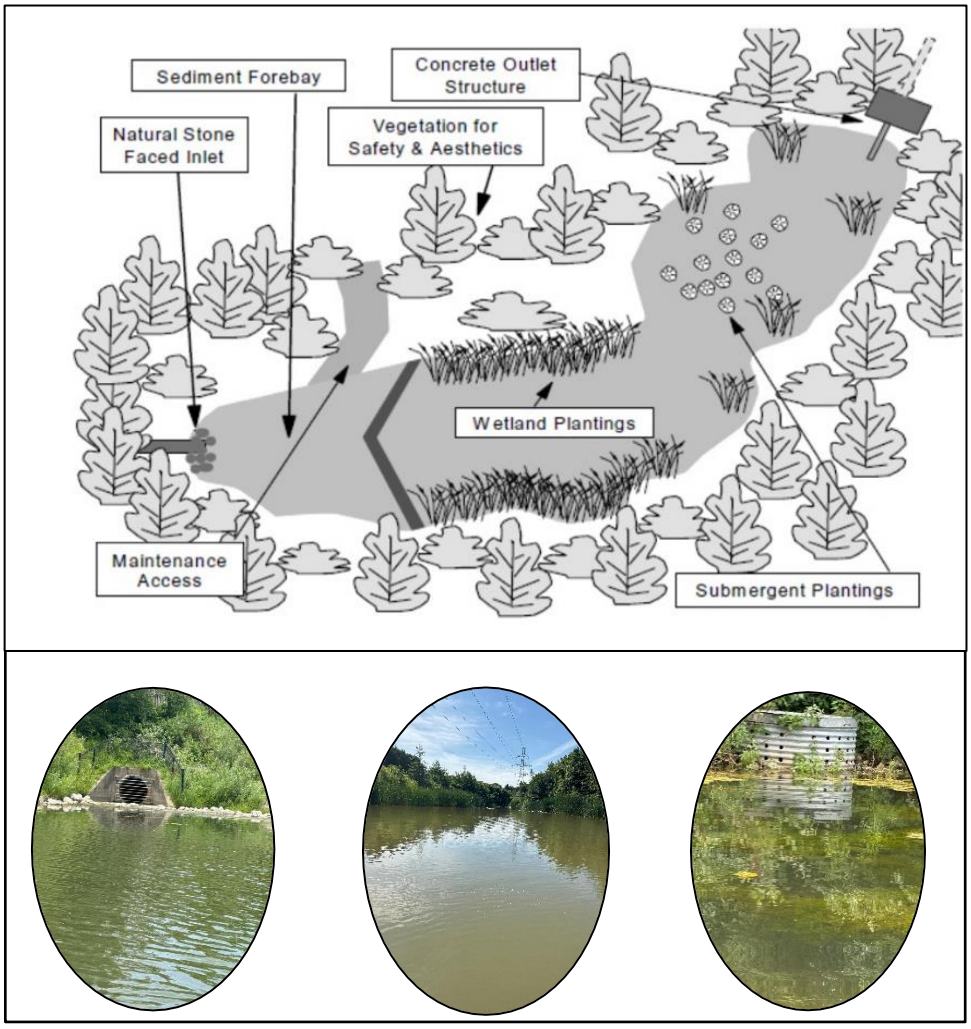


Figure 1.1: Diagram of a stormwater pond (top; Adapted from **Stormwater management plan and SWMP design** (OMECP,2003) and photos of inlet, main pond and outlet (bottom, from left to right) from selected stormwater ponds in Kitchener-Waterloo, Ontario

Urban wetlands are manmade and generally designed to resemble natural marshes, with emergent and submerged vegetation, and are dominated by shallow water zones (normally >70% of the volume) (OMECP, 2003). They are typically dense with vegetation, dominated by emergent aquatic macrophytes (Wong et al., n.d.). Urban wetlands are mainly used for flood control, habitat creation and wastewater treatment (Stefanakis, 2019;S∅vik et al., 2006)). Urban wetlands used for stormwater management require a minimum drainage area to sustain the aquatic vegetation and the permanent pool, with

implementation recommended for drainage areas ≥ 5 ha and preferably 10 ha or more (OMECP, 2003). A constructed wetland consists of deeper inlet and outlet zones, where the deeper areas should be limited to 25% of the total surface area to ensure that most of the wetland supports emergent vegetation (OMECP, 2003). Considering vegetation type, wetlands can be classified as emergent macrophyte wetlands and submerged macrophyte wetlands, where emergent macrophytes are more common (Stefanakis, 2019). Urban wetlands are designed to mimic natural wetland systems with unique biological and physicochemical processes of wetlands removing contaminants while storing large volumes of stormwater runoff (Malaviya & Singh, 2012).

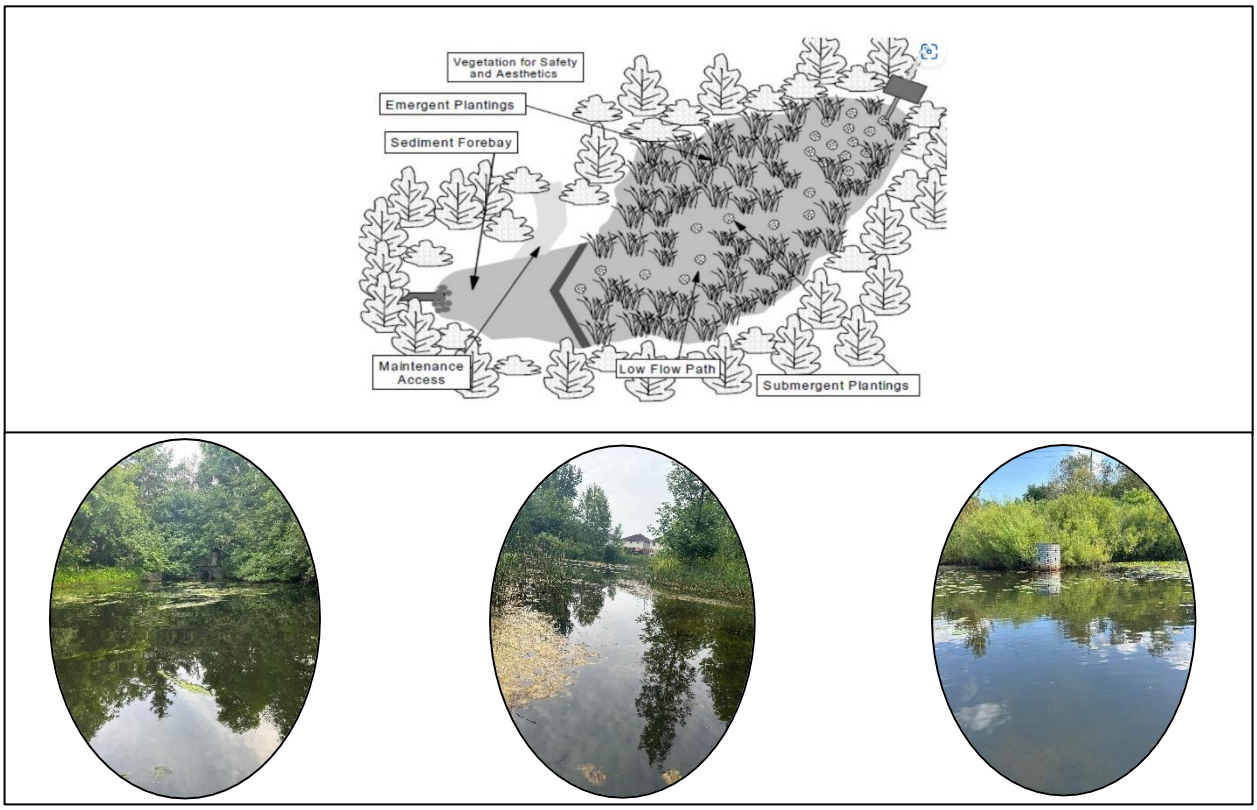


Figure 1.2: Diagram of a urban wetland (top; Adapted from **Stormwater management plan and SWMP design** (OMECP, 2003) and photos of inlet, main pond and outlet (bottom, from left to right) from selected urban wetlands in Kitchener-Waterloo, Ontario

1.3 Production of GHG in SWP and UW

Stormwater ponds and UW serve as a sedimentation pool for organic materials, inorganic contaminants and sediment particles carried by runoff water (Gorsky et al., 2019; Audet et al., 2020; Van Bergen et al., 2019). Furthermore, anthropogenic activities in the catchment contribute to runoff enriched with nutrients (nitrogen, carbon and phosphorous), accumulating in the ponds and significantly influencing water chemistry and carbon dynamics (Malyan et al., 2022). These sedimentation processes and the chemical and biological properties within SWP and UW influence GHG production and emission (Audet et al., 2020; Gorsky et al., 2019; A. Kumar et al., 2019a). When inundated, GHG emissions are driven by the concentration gradient between the water column and the atmosphere, with the concentration of dissolved GHG in the water resulting from the production, consumption and solubility of the gas of interest. Hence, a comprehensive understanding of sources of GHG production and emissions in stormwater ponds and urban wetlands is essential.

1.3.1 Carbon dioxide (CO_2)

Carbon dioxide is one of the most important long-lived GHGs but lacks a specific atmospheric lifetime, as it continuously cycles among the atmosphere, biosphere and oceans, and its removal depends on numerous processes occurring over different time scales (NOAA, 2022c; IPCC, 2007a). The global warming potential (GWP), which quantifies the relative warming effect of a GHG over a specific time period compared to CO2, is 1 for CO2, as CO_2 is the reference gas for GWP (IPCC, 2014).

Autochthonous inputs, such as decaying vegetation and other organisms, and allochthonous inputs in the pond's water inflow contribute organic matter, which is available for microbial degradation (Gorsky et al., 2019). The microbial degradation of this

accumulated organic matter is the primary driver of CO_2 emissions in ponds and wetlands, as the CO_2 is produced through aerobic respiration during the degradation process (McGowan et al., 2016;Van Bergen et al., 2019). Other than that, CO_2 is also a product of anaerobic respiration and a product of CH_4 oxidation by methanotrophs (Vachon et al., 2017; Prairie et al., 2018). CO_2 produced by the above-mentioned processes increases the CO_2 concentration in the water, and excess CO_2 above the saturation limit is released into the atmosphere mainly through diffusion (Holgerson, 2015a). Contrastingly, the sediments could serve as sinks by sequestering carbon, while the presence of algae and submerged plants may offset the release of CO_2 through photosynthesis (Audet et al., 2019). This enhanced productivity can reduce the CO_2 concentration in the water column and potentially lead to a net uptake of CO_2 by the pond, thereby influencing the overall GHG balance (Gorsky et al., 2019; Van Bergen et al., 2019).

1.3.2 Methane (CH_4)

Methane is another important GHG with an atmospheric lifetime of approximately 12.4 years, a GWP of 29 over 100 years, and 82.5 over 20 years (IPCC, 2023). Although the lifetime of CH_4 is short compared to CO_2, CH_4 traps much heat energy and accounts for 30% of global warming (Filonchyk et al., 2024)

Methanogenesis is the final step of the anaerobic decomposition of organic carbon that produces CH_4 (Bastviken et al., 2008). It is a form of anaerobic respiration by methanogens, which belong to the domain Archaea (Lyu et al., 2018). Notably, a large proportion of produced CH4 in anoxic sediments could be oxidized into CO_2 in the oxic sediment and water column by aerobic CH_4 oxidizing methanotrophs (Bastviken et al., 2008).

Diffusive flux, ebullitive flux, storage flux and plant-mediated transportation are four major pathways of CH_4 emission in the lakes or deep ponds (Bastviken et al., 2008). Among those four pathways, ebullition and diffusion are the primary pathways that emit CH_4 from the pond to the atmosphere (Grinham et al., 2018; Mondal et al., 2022; Gorsky et al., 2019). Diffusive flux occurs when the CH_4 diffuses from the sediment into the water and eventually diffuses into the atmosphere. As soon as the diffused CH_4 enters the oxic layer of the water column, a portion is likely oxidized, and the CH_4 that escapes oxidation reaches the upper mixed layer of the water column and will be emitted (Bogard et al., 2014). Ebullition occurs due to the release of a direct flux of CH_4 in gaseous form (i.e., as bubbles) from sediment to the atmosphere, with the limited impact of oxidation in the water column (Bastviken et al., 2004). If the net CH_4 production exceeds the rate of diffusive transport from the sediment to the water, dissolved CH_4 might become oversaturated in the porewater of the sediment, making CH_4 build up and leading to formation of bubbles that are released (Schmid et al., 2017). Depending on the water chemistry and environmental variables, ebullition contributes 50 to 90% of total CH_4 fluxes, whereas diffusion contributes 10-25% (Grinham et al., 2018; Baron et al., 2022). Storage flux occurs in stratified lakes with an anoxic layer of water where CH_4 can be built up and stored and later be released during lake overturn (Bastviken et al., 2004). As the anoxic layer decreases with the size of the water body, storage flux is less critical in shallow ponds (Branco & Torgersen, 2009). The fourth potential flux component involves plant mediated emissions occurring in littoral zones with emergent vegetation where it depends on CH_4 production and oxidation in the sediments, and vegetation characteristics (Bastviken et al., 2004). However, small ponds are found to be supersaturated with CH_4 due to their shallow nature

and low oxygen and high carbon content; thus, diffusion and ebullition fluxes likely play a larger role in CH_4 emission (Holgerson, 2015).

1.3.3 Nitrous oxide (N_2O)

Nitrous oxide is the third most important GHG emitted from ponds, with a lifetime of 121 years in the atmosphere, a GWP of 273 over 20 years, and 273 over 100 years (IPCC, 2023). Besides the high GWP, it is a more dominant ozone-depleting gas out of all the considered GHGs (Ravishankara et al., 2009).

The N_2O production process is controlled by microbial nitrogen transformation processes in aquatic environments, including denitrification and nitrification in which ammonium (NH_4^+) and nitrates (NO_3^-) are used, and N_2O is released as a by-product (Wang et al., 2023). These processes mainly depend on the availability of dissolved inorganic nitrogen (DIN) and oxygen (Mengis et al., 1997). Nitrification is the aerobic oxidation of NH_4^+ to nitrites (NO_2^-) and NO_3^-. Denitrification is when NO_3^- is reduced to nitrogen (N_2) through anaerobic dissimilatory reduction (Ivens et al., 2011). Nitrous oxide may be produced in both bottom sediments and the water column; hypoxic and anoxic conditions in water and sediments promote denitrification, whereas oxygenated surface water and the surface layer of sediments promote nitrification (Nevison, 2000).

N_2O produced during denitrification or nitrification is emitted dominantly through diffusion (Zheng et al., 2022). Due to the high solubility of N_2O in water, ebullition is not a dominant pathway (Sturm et al., 2014). The N_2O produced in freshwater ponds could diffuse downwards and be consumed by microbes in benthic sediments; therefore, ponds are considered a weak source of N_2O emissions (Yuan et al., 2021).

1.4 Factors influencing GHG emissions in SWP and UW

GHG emissions from SWP and UW are strongly linked to different arrays of factors that shape the dynamics of these aquatic ecosystems. Environmental conditions, water quality, land use practices, seasonal variations, and anthropogenic influences are among the significant factors influencing GHG production and emissions.

1.4.1 Carbon Dioxide

Environmental features such as water temperature, pH, dissolved oxygen, biological activity, nutrient concentrations, and seasonal variations within SWP and UW significantly influence CO_2 production and emissions (Peacock et al., 2019; Gorsky et al., 2019; Holgerson, 2015). Temperature has been widely studied as a potential driver of CO_2 emissions, revealing different patterns that suggest a complex relationship. CO_2 fluxes in ponds are often positively correlated to temperature with the highest reported emissions during summer as warmer temperatures generally accelerate microbial activities, increasing the release of CO_2 (Peacock et al., 2019; Audet et al., 2020). However, CO_2 fluxes can also be negatively correlated to temperature and solar radiation in ponds due to the balance between respiration and photosynthesis (Natchimuthu et al., 2014). During warmer sunny days, CO_2 consumption through photosynthesis is likely higher than CO_2 production through respiration as the daytime fluxes are mostly negative, whereas the ponds emit CO_2 at night and after summer, when organic matter degradation dominates over primary production (Natchimuthu et al., 2014). Furthermore, warmer temperature reduces the solubility of gases in water, so they can easily be released from the water column into the atmosphere (Bauduin et al., 2024; Peacock et al., 2019).

Dissolved oxygen (DO) is the amount of oxygen (O_2) dissolved in the water. Aerobic conditions may lead to the emission of more CO_2 into the atmosphere due to the

acceleration of mineralization processes, which would indicate a positive correlation between CO_2 emissions and DO (Yang et al., 2015). Some studies have identified a negative relationship between CO_2 concentrations and DO, where primary production may have been the cause of the negative relationship as CO_2 is consumed and O_2 is released (Jensen et al., 2022; Audet et al., 2020).

pH negatively correlates with CO_2 emissions (Peacock et al., 2019; Yang et al., 2015; Jensen et al., 2022). An increase in pH may promote the dissociation of CO_2, transforming HCO_3^- into CO_3^{2-}, which negatively affects CO_2 emission (Schrier-Uijl et al., 2011). More specifically, when pH > 8, CO_2 emissions are close to zero, reflecting the influence of the bicarbonate equilibrium on CO_2, where bicarbonate and carbonate dominate dissolved forms over CO_2 (Stets et al., 2017).

Electrical conductivity (EC) measures the ability of the water to conduct electricity, where a high EC indicates the high concentrations of dissolved ions, electrically charged atoms or molecules in the water (Gałczyńska et al., n.d.). Electrical conductivity positively correlates with CO_2 concentrations in small waterbodies (Peacock et al., 2019). A possible reason is that the EC is positively correlated with sulphate (SO_4^{2-}), and sulphate concentration is sometimes positively correlated with dissolved CO_2 concentrations in ponds due to enhanced sulphate reducing bacterial activity that releases CO_2 as a byproduct (Audet et al., 2020; Jensen et al., 2022).

Dissolved organic carbon (DOC), phosphate (PO_4^{3-}), and nitrate (NO_3^-) are important nutrient compounds in the water bodies that drive CO_2 emissions. DOC is a wide range of small organic carbon molecules that can pass through a filter with a pore size 0.45 μm (Sucker & Krause, 2010a). DOC is an energy and carbon source for heterotrophs with

CO_2 fluxes often positively correlated with DOC concentration in ponds (Peacock et al., 2019). Carbon dioxide flux from freshwater systems positively correlates with nitrogen, where nitrate-enriched environments have a visible increase in CO_2 flux due to nitrification and denitrification processes that decompose organic matter and release CO_2 as a byproduct (Malyan et al., 2022, Stadmark & Leonardson, 2007). Other than that, high nutrient contents in water enhance algal growth, and this algal biomass settles in the benthic region of the pond and degrades through biological processes, releasing CO_2 (Malyan et al., 2022).

Seasonal variations such as changes in temperature, precipitation, freeze-thaw cycles and solar radiation play a vital role in CO_2 emissions in SWP and UW by influencing microbial activity, nutrient availability and gas exchange processes (Van Bergen et al., 2019). Sunnier conditions, followed by warmer conditions during spring and summer, accelerate the aquatic primary production, increasing CO_2 uptake (Bauduin et al., 2024). The varying composition and bioavailability of organic bacterial substrates in aquatic sediments also influence the seasonally varying emission patterns of CO_2 (Achtnich et al., 1995). For example, allochthonous organic matter inputs from the watershed typically vary with the seasons, being more substantial in autumn than in spring and summer, with greater input associated with higher CO_2 emissions despite the cooler temperature in the ponds (Bauduin et al., 2024).

1.4.2 Methane

Similar to its effect on CO_2 emissions, temperature also plays a critical role in regulating CH_4 emissions in aquatic systems where air, water and sediment temperatures showed positive correlations with CH_4 fluxes in shallow water bodies (Duc et al., 2010; Xing et al., 2005). Researchers studying UWs in Europe (Estonia, Finland, Norway and

Poland) observed significantly higher emissions during summer than in winter because biological processes respond positively to high temperature within ranges in which the enzymes are stable (S⊘vik et al., 2006). Moreover, the same positive relationship has been observed in some studies based on ponds in Sweden, where CH_4 flux is highest during summer (Peacock et al., 2019; Natchimuthu et al., 2014). Specifically, methanogenesis is highly dependent on temperature, with lower temperatures inhibiting it (van Hulzen et al., 1999). Further, high temperature and solar radiation during the growing season increase the primary production by macrophytes, which provide readily available organic substrates for methanogens (Natchimuthu et al., 2014). However, a decrease in CH_4 emissions can be observed with increased water temperature due to the enhanced activity of methane-oxidizing bacteria as they consume more CH_4 and convert it into CO_2 at higher temperatures (Hao et al., 2021). Moreover, in small water bodies, the ebullition pathway is more strongly influenced by temperature than diffusive CH_4 fluxes, highlighting the effect of temperature in controlling CH_4 emissions (DelSontro et al., 2016).

Dissolved oxygen is another essential factor that negatively affects CH_4 production and emission (Peacock et al., 2019). Anoxic conditions in waterlogged sediments or soil enhance CH_4 production, as methanogenesis is an anoxic process where low DO levels lead to increased CH_4 formation (Audet et al., 2020; Conrad, 2020). Additionally, the activity of methanotrophs, which oxidize CH_4 to CO_2 under oxic conditions, declines under low DO, further increasing CH_4 emissions (Yang et al., 2015).

pH also plays a role in controlling CH_4 emissions. Methane-producing organisms are pH-sensitive and generate CH_4 within a narrow pH range of 6–8. Since the pH of most inland freshwater ponds falls within this range, they provide favorable conditions for CH_4

production (Malyan et al., 2022). Similar to CO_2 emissions, CH_4 emissions are also influenced by nutrient availability in aquatic environments. An increase in DOC would also indicate more organic carbon availability for anaerobic degradation, producing high amounts of CH_4 (Christensen et al., 2003). Methane emissions from ponds show a negative correlation with NO_3^- concentrations and a positive correlation with PO_4^{3-} levels. (Malyan et al., 2022). The negative correlation is because NO_3^- acts as an electron acceptor that inhibits the methanogenesis processes, resulting in lower CH_4 production (Köhn et al., 2021). High PO_4^{3-} in water causes eutrophication, which may enhance the production of more labile organic matter, consumption of DO by decomposition processes, and the CH_4 production by methanogenic organisms (Köhn et al., 2021). Moreover, high SO_4^{2-} levels accelerate the activity of SO_4^{2-} reducing bacteria, suppressing methanogenesis as they both utilize the same carbon source and thereby reducing the production of CH_4 (Webb et al., 2019).

Since methanogenesis occurs in organic matter-rich sediments, seasonal variation of CH_4 production strongly depends on temperature variations and the availability of substrates (Bauduin et al., 2024). Higher CH_4 concentrations are observed during the hottest season, which directly influences the metabolic rates of microbes.

1.4.3 Nitrous oxide

In line with the dynamics observed for CO_2 and CH_4, N_2O production in aquatic systems is also governed by key factors. Among those, temperature plays a significant role. Water temperature strongly correlates with the denitrification pathway, which enhances the N_2O flux (Stadmark & Leonardson, 2007). Higher water temperature speeds up aerobic metabolic pathways, causing a depletion of the DO in water, resulting in more

denitrification (Kumar et al., 2019). Nitrous oxide flux has also been positively correlated with temperature because nitrifying and denitrifying microbial activities depend on the temperature (Saggar et al., 2004; Saleh-Lakha et al., 2009).

Studies of N_2O emissions from urban ponds have observed a complex correlation with water pH, where N_2O emissions increase when pH decreases (Khoiyangbam & Chingangbam, 2022). The highest N_2O flux through denitrification is in the narrow range of pH 7-8, and extreme pH levels suppress microbial activities, which reduces the rate of denitrification and nitrification (Khoiyangbam & Chingangbam, 2022; Tian et al., 2015).

Similar to CO_2 and CH_4 emissions, N_2O emissions are also influenced by nutrient availability in aquatic environments. Nitrates in the water are a primary reactant for the denitrification pathway leading to emission of N_2O into the atmosphere (Marotta et al., 2014). Also, higher SO_4^{2-} concentrations produce sulfide in the water, and this sulfide can inhibit the conversion of N_2O to N_2 gas during denitrification, which increases the N_2O emissions (Audet et al., 2020).

Nitrous oxide is produced due to nitrification and denitrification, which varies seasonally mainly due to temperature, substrate availability, and DO content (Mander et al., 2021). In the autumn, high rates of organic matter degradation and ammonification, along with the decreased ammonium uptake by plants, lead to high ammonium concentrations; this high availability likely promotes N_2O production via nitrification (Soued et al., 2016). Low oxygen levels potentially enhance this process (Rosamond et al., 2012). During spring and summer, ammonium is assimilated by phytoplankton, reducing the substrate available for the nitrification process and causing limits in N_2O production (Bauduin et al., 2024).

Beyond the specific drivers discussed, a range of anthropogenic, hydrology, pond characteristics and infrastructure-related factors have also been broadly recognized as influencing GHG production and emission in stormwater systems (Badiou et al., 2019; Gorsky et al., 2019; Holgerson, 2015). The size of the ponds can play a major role in GHG emissions, with the high perimeter-to-surface area ratio of small urban ponds leading to a greater input of terrestrial organic matter, resulting in higher GHG emissions (Hanson et al., 2007a). Moreover, larger ponds characterized by a deep-water column could allow for oxidation of anaerobically produced CH_4 into CO_2 before being released into the atmosphere (Oswald et al., 2015). However, the shallow depths of small ponds and wetlands reduce the potential for CH_4 oxidation before atmospheric release. This phenomenon makes smaller impoundments typically more concentrated sources of CH_4 emissions (Kifner et al., 2018). However, Audet et al. (2019) identified no significant impact of pond size on dissolved GHG, whereas Holgerson and Raymond. (2016) found that tiny ponds had the highest GHG concentration. Furthermore, emissions are also interconnected with hydrology, where inundation status might influence emission rates (Boon et al., 1997).

Land use is another important factor affecting GHG emissions from small water bodies in different ways. Changes in land cover and imperviousness caused by urbanization alter natural hydrological patterns. Replacing natural vegetation with artificial impermeable surfaces has increased stormwater runoff (Audet et al., 2020), carrying different substrates to SWP and UW, enhancing microbial processes. Agricultural runoff rich in organic material, a considerable amount of nitrogen and phosphorus, and fertilizers cause an accumulation of nutrients in ponds and wetlands, leading to accelerated emissions

(S. A. Jensen et al., 2023b). Human activities such as dredging and infrastructure development can significantly impact on the hydrological and ecological dynamics of SWPs and UWs, ultimately affecting GHG emissions (Oberndorfer et al., 2007). Dredging removes the top layer of the sediment, which is rich in nutrients and organic matter, and thus reduces internal nutrient loading (Wan et al., 2020), thereby also contributing to reduced GHG fluxes (Nijman et al., 2022). Finally, the combined influence of various factors will ultimately shape GHG emission dynamics in stormwater ponds and urban wetlands within urban ecosystems.

1.5 Regional and global emission estimates of GHG emissions

Greenhouse gas emissions exhibit significant regional variability, driven primarily by differences in environmental conditions such as temperature, microbial communities and other ecological conditions. Table 1.1 shows the average CH_4, CO_2 and N_2O fluxes from different urban water bodies in different countries. In summary, most studies have shown that ponds in tropical and sub-tropical regions exhibit comparatively higher GHG fluxes than those in temperate regions. Notably, CO_2 fluxes from temperate ponds have been estimated to vary from 50-750 mg m^{-2} d^{-1}, whereas from subtropical ponds emissions are around 1100-1500 mg m^{-2} d^{-1}, while tropical ponds are estimated to be around 3000 mg m^{-2} d^{-1} (Gorsky et al., 2019; Panneer Selvam et al., 2014). For CH_4 emissions, diffusive fluxes of temperate, subtropical and tropical ponds have been estimated to be 20-30 mg m^{-2} d^{-1}, 120-360 mg m^{-2} d^{-1}, and ~250 mg m^{-2} d^{-1}, respectively (Audet et al., 2020; Peacock et al., 2019; Gorsky et al., 2019; Ollivier et al., 2019; Panneer Selvam et al., 2014). In terms of ebullition flux, temperate ponds show a flux of 150-200 mg m^{-2} d^{-1}, whereas subtropical and tropical ponds have 140 mg m^{-2} d^{-1} and 240 mg m^{-2} d^{-1}, respectively (Ollivier et al., 2019; Panneer Selvam et al., 2014). Regarding N_2O fluxes, temperate ponds range from

uptake to emission with a range of fluxes of -0.25-1.25 mg m^{-2} d^{-1} on average, while subtropical ponds are estimated to emit 0.1-0.13 mg m^{-2} d^{-1} (Gorsky et al., 2019; McPhillips & Walter, 2015; Ollivier et al., 2019b), except one study from China, which estimated N_2O emissions of 0.56 mg m^{-2} d^{-1} (Fan et al., 2022). Multiple studies found ponds with negative fluxes, where 35% of the ponds had negative fluxes, and those fluxes were all close to zero (Audet et al., 2020). Studies on agricultural ponds/lakes in Canada show that 67–80% of the ponds act as N_2O sinks or are in equilibrium with the atmosphere (Webb et al., 2019a; Jensen et al. 2022).

Table 1.1: Average fluxes of methane, carbon dioxide and nitrous oxide from urban water bodies. (D = Diffusive flux only; D + E = Diffusive plus ebullitive flux. All flux rates are in mg $m^{-2}d^{-1}$)

Source of water	Time period of flux measurement	CO_2 (mg $m^{-2}d^{-1}$)	CH_4 (mg $m^{-2}d^{-1}$)		N_2O (mg $m^{-2}d^{-1}$)	Reference
Urban water bodies, Australia	Five months August-December		D+E	129	-	Grinham et al., 2018
Urban ponds, Sweden	Two days in May and June	752	D	30.3	-	Peacock et al., 2019
Urban ponds, Denmark	Four months over 2 years • March • June • August • November	628 ± 795	D	15±70	0.19± 0.363	Audet et al., 2020
Urban pond, Netherlands	12 months	950±40	D E	20 ±100 300±490	-	Van Bergen et al., 2019
Stormwater ponds, USA	Three months June-Aug	1500	D	362	0.101	Gorsky et al., 2019
Ponds, India	Between Jan & April	2953±2817	D E	286 296	-	Panneer Selvam et al., 2014
Stormwater channel, Canada	12 months	4200	D	45.6	0.036	D'Acunha & Johnson, 2019
Stormwater retention basins, Canada	6 months May-Oct	40	D	314	0.042	Badiou et al., 2019
Constructed agricultural reservoirs, Canada	1 month Between June & July	1606	D E	49 224	-0.048	Jensen et al., 2022

1.6 Research Gap

Although GHG emissions from urban aquatic systems have been studied globally, a key gap remains in capturing spatial and temporal variability in emissions. These gaps are primarily due to limited data and scarcity of flux measurements, which have constrained emission estimation of small artificial ponds (Grinham et al., 2018). Furthermore, accounting for different pond types is essential to strengthening regional and global upscaling of pond-based GHG emissions (Grinham et al., 2018).

Moreover, most studies have focused on the quantitative analysis of GHG emissions and identifying the effects of biological activity on emissions. Only a few studies have examined how the degree of CO_2 and CH_4 saturation in small water bodies varies depending on both biological activity and the characteristics of the ponds (Holgerson & Raymond, 2016). In comparison, N_2O, a potent GHG, remains understudied, overlooking the amounts of nitrogen transported to stormwater ponds, which could release N2O into the atmosphere (Audet et al., 2020; D'Acunha & Johnson, 2019).

When considering the national level, there are limited studies on GHG emissions from urban aquatic systems in Canada, with most existing studies primarily focused on agriculture-related water bodies (Jensen et al., 2022; Badiou et al., 2019). Given the importance of stormwater management facilities as blue-green infrastructure for urban development and the scarcity of data on these features in Canada, quantifying GHG emissions from urban water bodies, including SWP and UW, is needed.

A few studies have been completed based on SWP and UW in Ontario focusing on the operation and maintenance of SWP and the use of SWP/UW in wastewater management, highlighting the potential economic and environmental consequences of not

cleaning the ponds (Drake & Guo, 2008). Another group of studies has focused on ecosystem services, including providing habitats, maintaining favorable microclimatic conditions, and biodiversity services (Moore & Hunt, 2012) while other available studies are based on water quality in SWP/UW, focusing on assessing the effectiveness of improving water quality by examining variables such as nutrient levels, sedimentation, and pollutant removal capacity (Marques & Mandrak, 2024; Yang et al., 2023). These indicated that, while other aspects of SWP/UW have been well examined, research on GHG emissions remains limited, indicating a gap in existing literature.

Therefore, understanding the GHG emissions from urban aquatic sources is an emerging requirement for regional GHG emission assessments and addressing climate change, as the number of SWPs and UWs continues to increase and their specific contribution to GHG emissions remains underexplored. As a result, this study aims to quantify the GHG emissions for the ice-free period from 24 selected stormwater ponds and urban wetlands in Southern Ontario and to identify the factors that regulate these emissions. The specific objectives of this study are to: (1) quantify the CO2, CH4, and N2O emissions from SWP and UW and assess the temporal dynamics of these GHG fluxes, (2) assess the effect of environmental variables on GHG fluxes from SWP and UW, (3) assess the effect of water quality (e.g., DOC and dissolved N and P) on GHG fluxes from SWP and UW, and (4) assess the effect of pond and catchment characteristics on GHG flux from SWP and UW. Results from this study will help fill research gaps on GHG emissions in SWP and UW, particularly by quantifying emissions and assessing the physical, chemical, and environmental variables that regulate the emissions. Results can be used to advance urban

GHG reporting and inform land-use planning related to the development of stormwater management infrastructure design that reduces GHG emissions.

Chapter 2
Greenhouse gas dynamics in stormwater ponds and urban wetlands: Quantification and drivers

2.1 Introduction

The proportion of the world's population living in urban areas rose from 30% in 1950 to 54% in 2014 and is projected to reach 66% by 2050 (Bocquier, 2005). This rapid urbanization has driven the expansion of built environments and increased cover of impervious surfaces leading to lower infiltration rates and reduced evaporation. This in turn has intensified the magnitude and frequency of runoff events, accelerating the risk of flooding and reducing water quality (OMCEP, 2003). In order to mitigate urban flooding and improve water quality, stormwater management practices have been designed under municipal and provincial stormwater management initiatives (Pollard, n.d; OMCEP, 2003). Stormwater management practices include lot level and conveyance controls and end-of-pipe controls (OMCEP, 2003). Lot level and conveyance controls involve collecting stormwater at the lot level, suitable for small drainage areas (<2 ha) (OMCEP, 2003). End-of-pipe control involves receiving stormwater, which remains after lot level controls, and ultimately releasing it to receiving water bodies (OMCEP, 2003). Wet ponds, urban wetlands, dry ponds, and infiltration basins are typical end-of-pipe facilities that receive stormwater from the conveyance system. Among those, wet ponds, urban wetlands and dry ponds are predominant due to their high storage volume and effectiveness in improving water quality (OMCEP, 2003). Wet ponds are designed to have a permanent pool, while dry ponds do not have permanent pools as they are designed to be empty between events

(Kolath et al., 2021). Urban wetlands are typically designed to mimic natural marshes with emergent and submerged vegetation and shallower average depths (Troitsky et al., 2019).

Although small artificial water bodies, including stormwater ponds (SWP) and constructed urban wetlands (UW), help to reduce runoff volume and mitigate water quality degradation, they emit greenhouse gases (GHGs), which is a negative impact on the environment (Grinham et al., 2018a). The significant amounts of nutrients and particles transported through stormwater runoff into the SWPs, or UWs affect their water chemistry and carbon dynamics, often providing optimum conditions for GHG production (Peacock et al., 2019; Malyan et al., 2022). Moreover, specific physical properties, such as shallow depths and frequent mixing, cause intense carbon and GHG processing in such small water bodies (Downing, 2010). Autochthonous inputs, such as decaying vegetation and dead organisms, and allochthonous inputs in the pond's water inflow contribute organic matter, which is available for microbial degradation, causing the production and release of GHGs (Gorsky et al., 2019). The most significant GHG effluxes from these SWP and UW are methane (CH_4), carbon dioxide (CO_2), and nitrous oxide (N_2O) (Malyan et al., 2022).

Aerobic and anaerobic decomposition of organic matter produces CO_2, whereas methanogenic archaea produce CH_4 through methanogenesis, consuming organic matter in anoxic conditions (Gorsky et al., 2019; Malyan et al., 2021). In addition, N_2O is generally produced through denitrification in ponds that receive more nitrogen-rich inputs (Kumar et al., 2019), which is common in smaller water bodies near agricultural fields. The emissions of GHGs from these aquatic systems predominantly occur through diffusion from the water surface, where CH_4 is also emitted directly to the atmosphere by ebullition (Audet et al., 2020). However, the degree of saturation of CO_2 and CH_4 in smaller water

bodies varies depending on biological activity and pond characteristics, which affect diffusion rates (Holgerson, 2015; Gorsky et al., 2019). For example, CO_2 produced by decomposition may be used for photosynthesis by algae in the water, offsetting the emissions (Gorsky et al., 2019). Likewise, the anaerobically produced CH_4 can be oxidized into CO_2 with oxygen in the water column before emission by methane-consuming bacteria called methanotrophs (Bastviken et al., 2008).

Greenhouse gas production and emissions from SWP and UW are strongly linked to different factors that shape the dynamics of these aquatic ecosystems. Environmental variables, including temperature (air, water, sediment), dissolved oxygen and pH, control the production and emissions of GHGs in different ways (Birch et al., 2022; Jensen et al., 2022; Peacock et al., 2019). For example, temperature itself shows a positive correlation with the fluxes of all three types of gasses where temperature increases microbial activities, including respiration, methanogenesis, and denitrification, leading to greater production of CO_2, CH_4 and N_2O (Audet et al., 2020; Natchimuthu et al., 2014). Furthermore, increasing temperature reduces the solubility of gases in water, so they can easily be released from the water column into the atmosphere (Bauduin et al., 2024; Peacock et al., 2019). The combined effect of increased production and reduced solubility contribute to elevated fluxes of GHGs. However, the effect of temperature on CO_2 flux is further modulated by solar radiation through its effect on photosynthesis, where primary production by algae and aquatic plants can enhance CO_2 uptake counterbalancing the CO_2 produced by respiration (Audet et al., 2020; Gorsky et al., 2019). Oxygen availability is important where anoxic conditions in waterlogged sediments or soil boost the production of CH_4, whereas oxic conditions may lead to more CO_2 and N_2O emission into the atmosphere (Audet et al.,

2020). Pond features also affect GHG emissions where the shallow depths of ponds and wetlands reduce the potential for CH_4 oxidation before atmospheric release, making smaller impoundments typically more concentrated sources of CH_4 emissions (Kifner et al., 2018). Also, their emissions are interconnected with hydrology, where inundation status might influence emission rates; stagnant or slow-flowing aquatic systems create anoxic conditions, producing more CH_4 (Boon et al., 1997).

When compared, CO_2 is a long-lived gas in the atmosphere, while CH_4 has a shorter lifespan of nearly ten years due to its tendency to react with labile molecules and OH radicals, and N_2O has a residence time of about 121 years (IPCC, 2014). However, an increase in CH_4 and N_2O could exacerbate global warming as the radiative forcing of CH_4 and N_2O are around 29 and 273 times, respectively, more than that of CO_2 over 100-year time scales (IPCC, 2023). Yet, small water bodies such as ponds and wetlands in urban environments have received minor attention as GHG sources, even though their number and spatial extent are growing due to rapid urbanization (Audet et al., 2020; Van Bergen et al., 2019). Despite the growing number of studies on GHG emissions from small ponds, direct flux measurements are lacking and ebullitive emissions are often excluded, which is especially important for CH_4 emissions (Grinham et al., 2018; Peacock et al., 2019). Despite being a potent GHG, N_2O is also often excluded from most studies (Fan et al., 2022). Moreover, many of the studies focus on either sampling several waterbodies once or sampling one waterbody over some time (Bauduin et al., 2024; Gorsky et al., 2019; Peacock et al., 2019; Van Bergen et al., 2019) limiting our understanding of spatial and temporal variation in emissions. Hence, more comprehensive data is needed to accurately estimate the GHG emissions from small urban waterbodies and identify their drivers to

allow for the inclusion of these GHG emissions in urban GHG estimates and decision-making on urban infrastructure.

Therefore, the objectives of this study were to: (1) quantify the CO_2, CH_4, N_2O emissions from stormwater facilities (SWP and UW) and assess the temporal dynamics of GHG fluxes throughout the ice-free period, (2) assess the effect of environmental variables (e.g., temperature, dissolved oxygen, pH and electrical conductivity) on GHG fluxes from stormwater facilities (SWP and UW), (3) assess the effect of pond water quality (e.g., nutrient and ion concentrations) on GHG fluxes from stormwater facilities (SWP and UW), and (4) assess the effect of stormwater facility physical form (e.g., depth, perimeter) and catchment characteristics on GHG flux. Results from this study will help fill research gaps on GHG emissions from stormwater systems, particularly by quantifying emissions and assessing the physical, chemical and environmental variables which regulate them.

2.2 Methods

2.2.1. Study sites and experimental design

The study was conducted at a series of stormwater management facilities located within Kitchener (43° 25′ 07″N, 80° 28′ 22″W) and Waterloo (43° 28′N, 80° 31′W), southern Ontario, Canada (Figure 2.1). All these facilities receive runoff from urban areas and are distributed across different parts of the region to capture runoff from various land uses. The selected wet pond and wetland stormwater facilities are primarily designed for stormwater management, whereas natural ponds have been partially engineered to manage stormwater runoff (OMECP, 2003). A total of 24 stormwater management facilities were selected representing all the above-mentioned categories (wet ponds (n=13), urban wetlands (n=8), natural wet ponds (n=3)) based on their size, and accessibility, ensuring

diverse representation of stormwater retention systems (Table 2.1). Pond types were categorized based on the classifications provided by the municipalities. All the ponds were located either within the residential or industrial areas of the city, and therefore, their immediate catchments had some degree of urban influence. All the identified facilities were inundated throughout the year. According to the classes defined by Downing et al. (2006), all selected stormwater management facilities fall under the category of very small water bodies (surface area < 0.01 km^2) except for two, which are considered small ponds with surface areas ranging from 0.01 to 0.1 km^2.

Sampling took place over seven ice-free months, from May to November 2024. Each site was sampled once per month during this period. All sampling was conducted during daytime hours, between 08:00 and 17:00. The area has a humid continental climate, with annual precipitation of 695.4 mm and a mean annual temperature of 8.6 °C in 2024. Overall, the year was warm and dry, with intermittent rainfall events. Total precipitation and mean temperatures for the sampled months were shown in Table 2.2, along with the long-term averages based on 1991–2020 data (https://climate.weather.gc.ca for the Kitchener/Waterloo weather station).

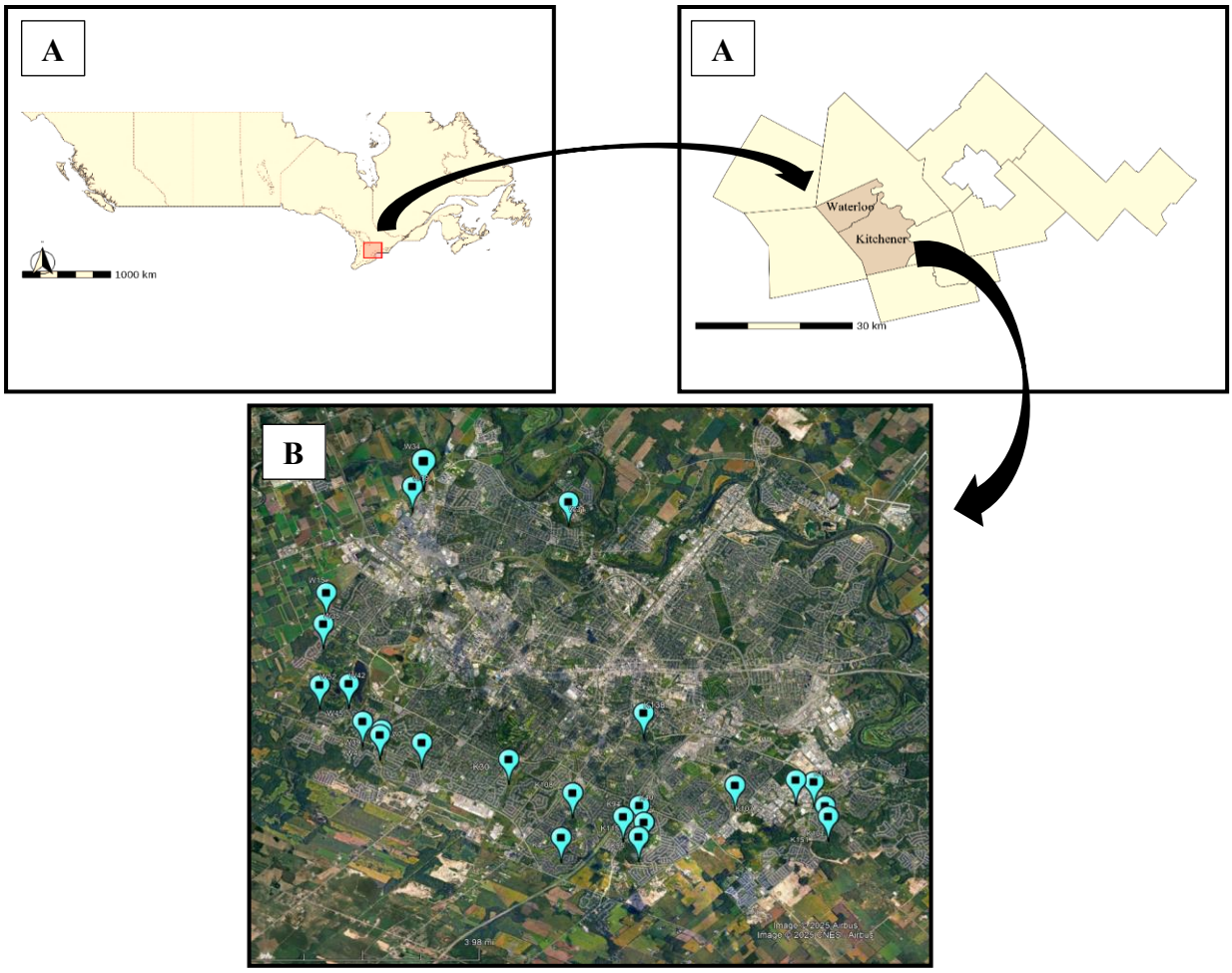


Figure 2.1:(A) Location of Kitchener/ Waterloo area in Southern Ontario (Canada). (B) Locations of the selected study sites within Kitchener-Waterloo, visualized using Google Earth imagery (© Google Earth, image © 2025 Airbus; accessed July 15,2025).

Table 2.1: Physical characteristics of 24 stormwater management facilities in Kitchener-Waterloo area, ON

Region	Facility Number & type	Latitude; longitude	Surface area (km^2)	P:A ratio (km^{-1})	Installation year	Dredged year	Catchment area (ha)
Kitchener	K30 Wet pond	43° 26'15.55"N 80° 32'52.18"W	0.0030	94.1	2013	2013	32.9
	K4 Wet pond	43° 24'48.04"N 80° 32'44.33"W	0.0022	123.8	2010	2023	29.0
	K108 Natural wet pond	43° 25'20.41"N 80° 32'4.36"W	0.0028	81.2	No records	No dredging	2.6
	K40 Urban wetland	43° 24'41.87"N 80° 31'0.51"W	0.0003	237.1	1998	2016	2.5
	K138 Natural wet pond	43° 25'57.64"N 80° 29'58.46"W	0.0235	38.2	No records	No dredging	No records
	K94 Urban wetland	43° 24'39.24"N 80° 31'24.92"W	0.0045	90.0	2002	2024	24.9
	K95 Wet pond	43° 24'25.80"N 80° 31'6.12"W	0.0016	101.2	1999	2018	17.8
	K115 Wet pond	43° 24'16.03"N 80° 31'20.64"W	0.0047	73.4	2008	No dredging	32.4
	K61 Wet pond	43° 23'57.16"N 80° 27'56.49"W	0.0064	69.8	1963	No dredging	48.7
	K151 Natural wet pond	43° 23'12.82"N 80° 27'44.30" W	0.0033	97.4	2010 (retrofitted)	2010	No records
	K100 Wet pond	43° 23'47.90"N 80° 27'38.23"W	0.0038	85.1	2002	2016	25.5
	K107 Wet pond	43° 24'18.33"N 80° 29'5.05"W	0.0037	77.0	2005	2015	41.1
	K101	43° 23'22.98"N	0.0026	137.3	2003	2018	24.5

	Urban wetland	80° 27'41.09"W					
Waterloo	W15 Wet pond	43° 29'52.18"N 80° 34'25.43"W	0.0071	55.6	1995	No dredging	33.7
	W35 Wet pond	43° 29'27.16"N 80° 34'47.91"W	0.0014	132.3	2002	2009	8.0
	W52 Urban wetland	43° 28'37.77"N 80° 35'29.77"W	0.0024	123.2	2002	2017	6.1
	W40 Wet pond	43° 27'33.82"N 80° 34'50.82"W	0.0061	60.1	1998	2008	15
	W45 Urban wetland	43° 27'48.95"N 80° 35'6.16"W	0.0133	40.9	1999	2006	29.4
	W39 Urban wetland	43° 27'30.28"N 80° 34'55.70"W	0.0045	96.1	2002	2017	30.4
	W7 Wet pond	43° 27'6.09"N 80° 34'15.22"W	0.0037	65.6	1990	2018	22.1
	W34 Wet pond	43° 30'57.81"N 80° 31'21.40"W	0.0041	60.4	1998	No dredging	24.9
	W19 Wet pond	43° 30'45.09"N 80° 31'46.47"W	0.0049	76.9	1989	2000	No records
	W31 Urban wetland	43° 29'26.35"N 80° 29'7.71"W	0.0058	74.1	1995	2010	15.4
	W42 Urban wetland	43° 28'26.47"N 80° 34'57.66"W	0.0085	58.1	1998	2023	40.5

Table 2.2: Monthly air temperature and total precipitation during the sampling period (May-November), along long-term averages (1991-2020) (https://climate.weather.gc.ca for the Kitchener/Waterloo weather station)

Month	Max. Temp (°C)		Min. Temp (°C)		Avg. Temp (°C)		Total Precipitation (mm)	
	2024	Long term	2024	Long term	2024	Long term	2024	Long term
May	21.4	19.0	7.8	6.2	14.6	12.6	80.8	80.2
June	24.9	24.1	12.1	11.5	18.5	17.8	78.4	80.5
July	26.9	26.6	13.7	13.7	20.4	20.2	133.0	96.2
August	25.5	25.5	12.4	12.7	19.0	19.1	52.4	67.2
September	23.9	21.6	9.5	8.7	16.7	15.2	21.6	75.2
October	17.1	14.1	2.4	3.4	9.8	8.8	29.8	71.0
November	9.7	6.8	0.9	-1.6	5.3	2.6	44.8	74.9

Sampling was conducted with an inflatable boat in the permanently inundated portion of each facility (Figure 2.3). At each facility, sampling for environmental conditions and GHG fluxes occurred at three distinct locations (Figure 2A): 1) near the inlet to capture conditions influenced by incoming water; 2) in the middle of the permanent pool representing the most stable and least mixed section of the pond; and 3) near the outlet where the water exits the system. The smallest pond included only an inlet and an outlet due to its limited size. Sampling locations were marked using indicators to ensure consistency across the sampling period and we were able to reach the approximately same location at each sampling session, improving the reliability of data. For ponds with multiple

inlets, the most active and easily accessible inlet was selected. The boat was anchored at the designated sampling points before starting the data collection.

To capture the vertical variation along the water column, data was collected at three depths at each location (Figure 2.2B) including 10 cm below the water surface, 50 cm below the surface, and 10 cm above the sediments. These measurements were taken shortly after GHG flux sampling to prevent any disturbance to gas exchange. The YSI probe's cable was manually marked at 10 cm intervals, allowing us to lower the probe to the desired depths by aligning the respective marks with the water surface. For the 10 cm above the sediment measurement, the probe was slowly lowered until it gently touched the sediment and then raised by 10 cm. Efforts were made to minimize disturbance to the sediment, and measurements were recorded only after the probe and water column had stabilized.

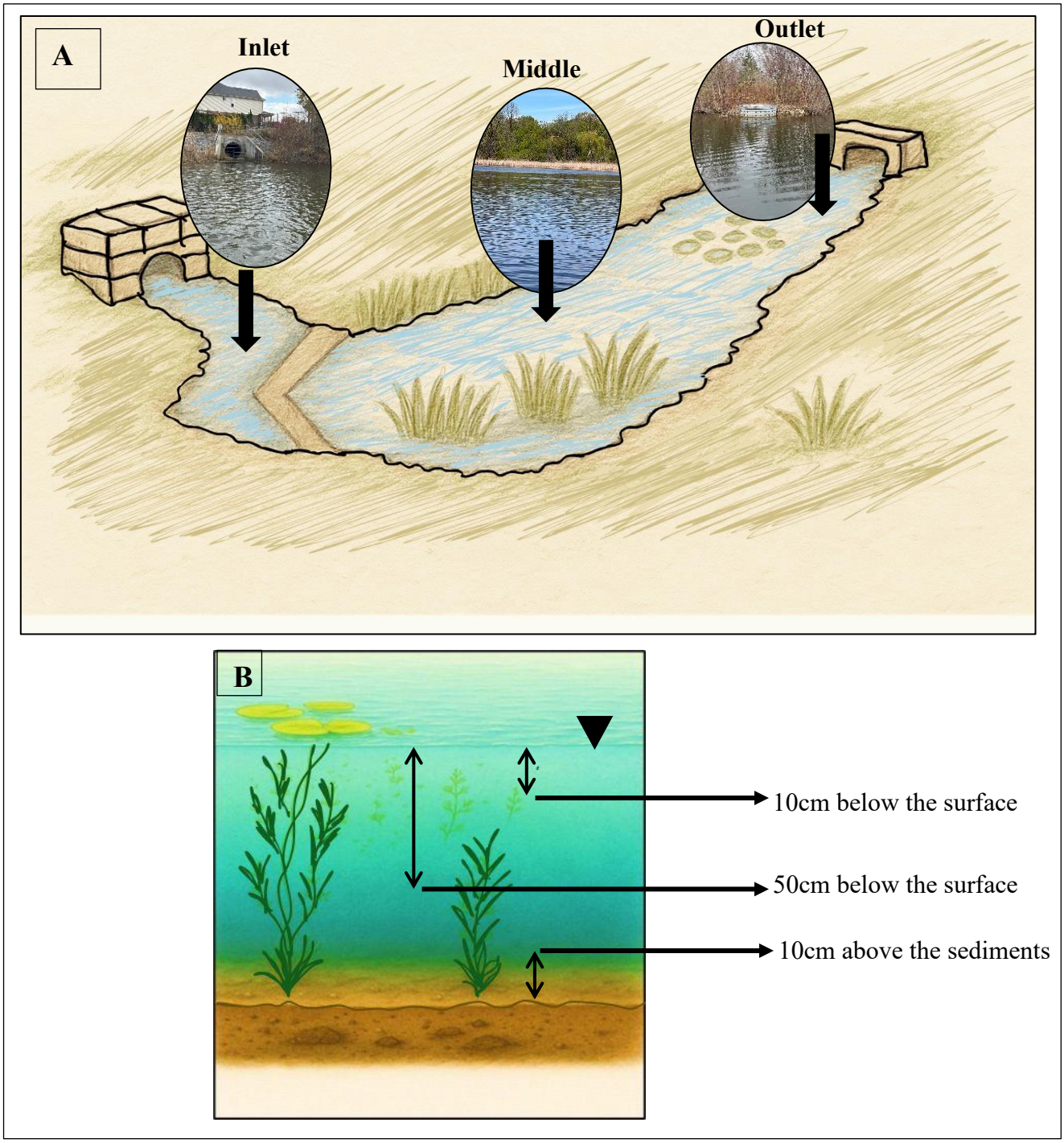


Figure 2.2: (A)Sampling locations within a facility. (B) Depths along the water column

2.2.2 Data collection and instrumentation

2.2.2.1 GHG emissions

A closed floating static chamber (Figure 2.3) was used to measure GHG flux (Gorsky et al., 2019). The static chamber was constructed from an inverted plastic bucket and was equipped with a thermocouple wire and two valves. The thermocouple wire was used to monitor chamber headspace temperature during closure. The valves were used to connect the chamber to a portable GHG analyzer. Two separate greenhouse gas analyzers (LICOR LI7810 for CO_2 and CH_4, LI7820 for N_2O) were used to measure GHG flux. Two separate chambers were used to measure GHG flux: one for CO_2 and CH_4, and the other for N_2O. The floating chambers were attached to the boat by 1 m rope and placed beside the boat, so they floated relatively free during the sampling period (Figure 2.3). After placing the chambers on the water, a 15 second waiting period was given before starting the flux measurements to avoid any disturbances during the chamber deployment. Flux measurements were taken over a 5-minute period. GHG flux measurements were conducted at the three selected sample points (Figure 2.2) for each of the 24 facilities. The start time of the flux was recorded along with the chamber temperature, which was recorded at both the beginning and the end of the flux period. Then, PEDRO - Peatland Equipment Data Re-organizer (Version 1.0.0) [Computer software] (https://github.com/BrianNewton/PEDRO) was used to calculate the linear change in the GHG concentration of interest at each chamber deployment using the collected data. Then this rate of change of GHG concentration over time was used to calculate the flux ($mg/m^2/day$) for each gas as shown in equation 2.1.

When evaluating the linearity of CH_4 flux, ebullition events and diffusion were considered separately. Ebullition events were identified by sudden peaks or sharp

increases in concentration, distinguishing them from the gradual changes associated with diffusion. In such cases, the diffusive fluxes were calculated from the linear changes (slope) before and after the ebullition event. In cases where multiple events occurred, the linear segments between the events were also included. For the ebullitive fluxes, the linear change (slope) during each event was considered and the difference between it and the diffusive slope was calculated to isolate the net contribution of ebullition. Then each ebullitive slope was adjusted for time to reflect its contribution to CH_4 over the total duration of the flux measurement. When multiple ebullition events occurred during a single chamber deployment, each event was analyzed separately using the same procedure. The total ebullitive flux for such an event was then calculated as the sum of all individual event contributions. Total flux, incorporating both diffusive and ebullitive components, was used for further analysis.

Equation (2.1)

$$F_E = \frac{\Delta C}{\Delta t} \times M \times \frac{1}{22.414} \times V \times \frac{1}{A} \times (60 \times 60 \times 24) \times \frac{1}{10^6} \times 10^3$$

Where, FE is the GHG flux (mg m^{-2} d^{-1}), ΔC is the difference in gas concentrations between the beginning and the end of the flux segment (ppb/ppm), Δt is the time interval of the flux (s), V is the temperature corrected volume of the chamber headspace (L), A is the area of the chamber (m^2) and M is for the molar mass of considered gas (CO_2-44 g mol^{-1}, CH_4-16 g mol^{-1}, N_2O-44.01 g mol^{-1}). The conversion factor 60×60×24 is used to convert seconds to days, 10^3 is used to convert g to mg (if needed), 10^6 is used to convert ppm (µmol of considered gas/mol gas) to mol/mol) and

in some cases, 10^9 is used to convert ppb (nmol of considered gas/mol gas) to mol/mol). 22.414 is the molar volume of an ideal gas (L mol^{-1}) at 1 atm pressure and 0 °C.

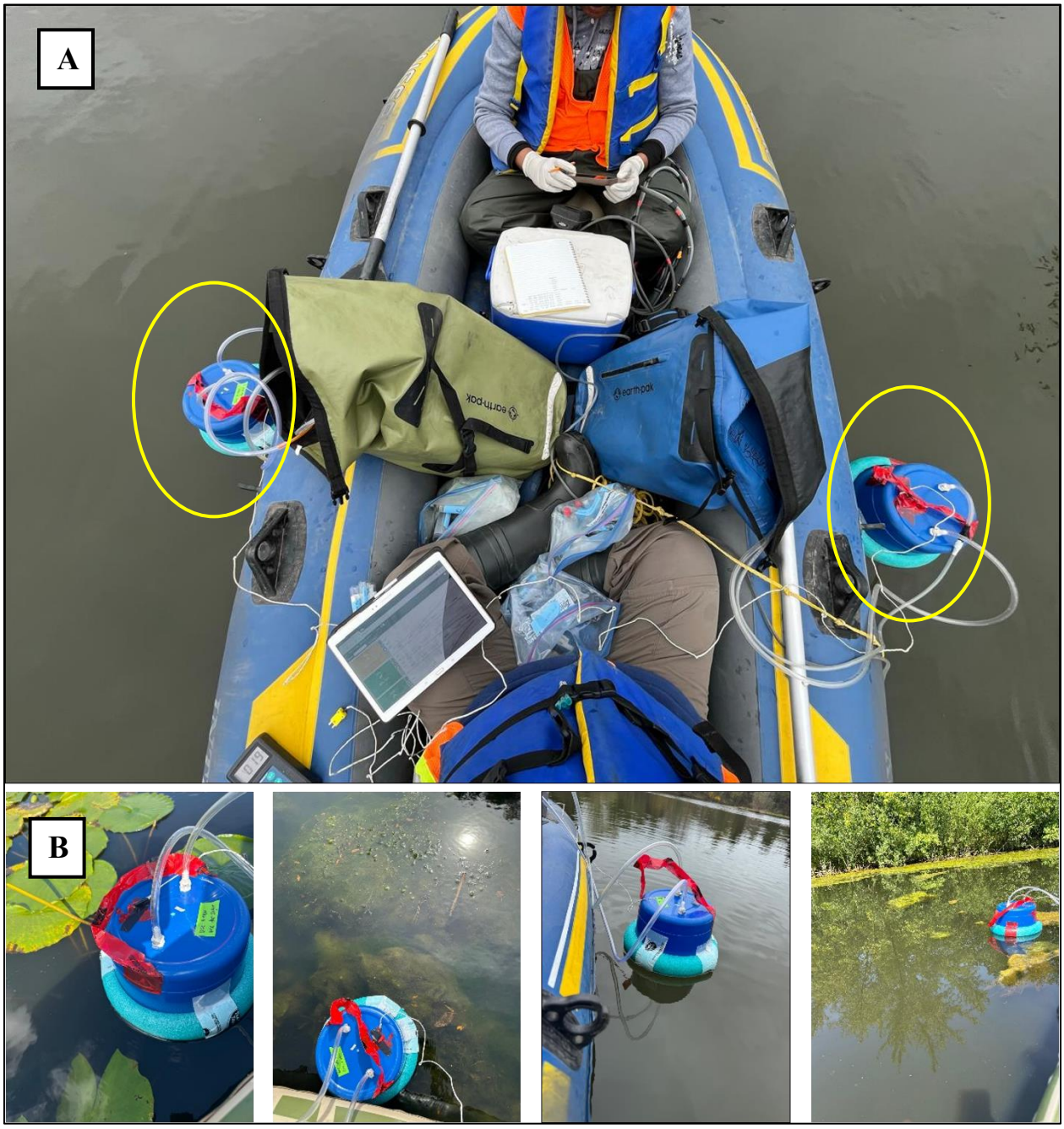


Figure 2.3(A): Floating chambers connected to the portable GHG analyzers, **(B):** Floating static chamber deployed alongside the boat.

2.2.2.2 In-situ environmental variables

Environmental variables, including pH, water temperature, electrical conductivity, and dissolved oxygen percentage (DO%), were measured at the same location as flux measurements just after collecting flux data for each of the 24 ponds. The measurements were taken by inserting a water quality hand-held multimeter (Yellow Springs Instrument; YSI-30) at each flux measurement location at the three depths as illustrated in Figure 2.2B. The sensors were calibrated using relevant standards before starting a monthly sampling round.

2.2.2.3 Water quality

Water samples were collected to measure dissolved ammonium (NH_4^+), dissolved phosphate (PO_4^{3-}), dissolved nitrate (NO_3^-) and dissolved organic carbon (DOC). The pond water samples were collected at the beginning (June) and at the end of the sampling period (October). Water samples were collected from the inlet and outlet (Figure 2.2) of each pond. Acid-washed bottles (120 ml) were primed with pond water prior to sample collection. Then, the samples were directly collected by submerging the bottles 10 cm below the air/water interface. Samples were kept in a cooler and bought back to the lab for further analysis. In the lab, all the samples were pre-treated by filtering using nylon syringe filters. For NO_3^-, the samples were filtered using 0.22 μm filters, while all other samples were filtered through 0.45 μm filters. For DOC, 0.01 M HCL (three drops) was added to 6 ml of samples as a pre-treatment. The samples were then analyzed in the Aqueous Analysis Lab at the University of Waterloo using a Dionex (Thermo Fisher) ICS-5000 capillary ion chromatography system for NO_3^-, automated colorimetric analysis using a Gallery Discrete Analyzer for NH_4^+ and PO_4^{3-}, and a Shimadzu Total Organic Carbon Analyzer for DOC.

2.2.2.4 Assessing physical characteristics of ponds

Physical characteristics of each pond, as shown in Table 2.3, were considered. After flux measurements were completed, pond depth was measured at each location using the graduated rope attached to the YSI probe. This was done while measuring environmental variables. The probe, attached to a graduated rope, was gently lowered into the water until resistance indicated contact with the sediment surface, and the depth was recorded from the graduation at the waterline. Sediment depth was measured using a graduated metal rebar at each sampling location in October. The rebar was pushed into the sediment until resistance was met, and it could not be pushed further. The difference between the surface sediment depth (i.e., water depth) and bottom sediment depth was computed to indicate sediment depth (Holgerson et al., 2024). The surface area and perimeter of the ponds were measured using ArcGIS. All other pond characteristics (Table 2.3) were obtained from the storm water management (SWM) reports provided by the City of Waterloo and City of Kitchener.

Most of the ponds were cleaned (dredged) at a certain point after their initial construction. Based on the year of dredging they were categorized into four groups as follows: 1) Recently Dredged, dredged within the last 2 years, 2) Moderate-aged Dredged, dredged 2-10 years ago, 3) Long-term Dredged, dredged more than 10 years ago and 4) No Dredging, ponds with no dredging record.

Table 2.3: Sources of data for pond and catchment characteristics

Characteristic	Source of data
Pond type (wet pond/ wetland/ natural)	SWM reports
Pond size (surface area and perimeter)	ArcGIS
Water depth (shallow/ deep)	Field measurements
Sediment depth	Field measurements
Sediment disturbance (dredging)	City management
Pond age	SWM reports
Catchment area	SWM reports
Impervious surface area	SWM reports

2.2.3 Statistical Analysis

All data were analyzed using R version 4.3.2 (R Core Team (2023) within RStudio version 2024.12.1 (posit software, PBC)). To assess the temporal dynamics of GHG fluxes, linear mixed models (LMMs) were created with month and pond type as fixed effects and pond ID and Location (Inlet/Middle/Outlet) as the random effect. Then an ANOVA was conducted to evaluate the significance of the fixed effects. The LMMs were created using the function 'lme4' in base R and tested using the Anova output with Type III sum of squares. If statistical significance with a confidence interval of 95% was given to pond type, month or interaction between month and pond type, the 'emmeans' function in the emmeans package (Lenth, 2023) was used with a Tukey adjustment for pairwise comparisons among treatments.

For the environmental variables (pH, EC, DO, water temperature), data was separated by measured depths, and a Spearman correlation matrix was used to identify variables significantly correlated with the emissions. Significantly correlated variables at each depth were selected for each gas type. Then, LMMs were created for each depth using the variables significantly correlated to the GHG of interest, with the pond ID and location included as random effect. Separate models were used for each depth to avoid having highly correlated variables in the same model and to evaluate how conditions at each measured depth affected GHG fluxes.

To assess the impact of water quality variables on fluxes, linear models (LMs) were initially run including all measured variables as fixed effects. The response variable was GHG flux measured at two distinct time points, which corresponded to the timing of water quality sampling, allowing for direct pairing of flux and water chemistry data. Based on the significance levels from this initial model, a second set of models was constructed using only the variables that showed a significant effect and by dropping variables that had negligible effects on model fit. For that Akaike's information criterion (AIC) was used to identify the best model (Gorsky et al., 2024). The LMs were created using the function ‘lm’ in base R.

To assess the effect of pond characteristics, cumulative fluxes were calculated for each pond by averaging monthly fluxes over 7 months and multiplying by the total number of days across the sampling period (196 days). These cumulative flux values were used to examine the significant effects of pond size (perimeter: area ratio), pond type, pond age, catchment area, impervious surface area and dredging date on fluxes. The effect of all these variables were assessed using separate LMs followed by model selection based on AIC

(Gorsky et al., 2024). To assess the impact of sediment depth, a separate cumulative flux calculation was done for each location within each pond, and LMs were conducted. To determine the effect of pond depth, LMMs were run with the random effects set as pond ID and location.

2.3 Results

2.3.1 Quantification of GHG fluxes and assessment of temporal variability

2.3.1.1 Fluxes of CO_2

Across all facilities and sampling months, CO_2 fluxes ranged from -11.21 to 14.67 g CO_2 m^{-2} d^{-1} with a mean value of 0.76 ± 2.68 g CO_2 m^{-2} d^{-1}. Both positive and negative fluxes were observed. The maximum flux was recorded in August at the inlet of a wet pond and the minimum in July at the outlet of an urban wetland (Figure 2.4). Over the seven-month sampling periods, the mean CO_2 fluxes were highest in natural SWP, followed by wetlands and wet ponds. The LMM model revealed a significant main effect of the month ($F_{6, 454.08}$ =10.08, $p<0.001$) and a significant interaction between month and facility type ($F_{12, 454.07}$ = 3.71, $p<0.01$), indicating the temporal pattern of CO_2 emissions differed between facility types (Figure 2.5). Random intercept variances for Pond ID (site number) and sampling location were 2.34 and 0, respectively, indicating moderate spatial variability across sites. The natural stormwater ponds had CO_2 fluxes ranging from -2.66 to 11.6 g CO_2 m^{-2} d^{-1}, with a mean of 2.07 g CO_2 m^{-2} d^{-1} across the sampling period, where the highest fluxes were recorded in November and the lowest in July. Similarly, the wet ponds exhibited fluxes from -11.2 to 14.7 g CO_2 m^{-2} d^{-1} (mean: 0.5 g CO_2 m^{-2} d^{-1}), with peak fluxes in November and the lowest in July. In both the facility types, CO_2 fluxes generally declined towards July, followed by a sharp increase in August, a drop in September and then a gradual rise towards November. The wetlands had measured CO_2 fluxes ranging from -10.60 to 9.12 g CO_2 m^{-2} d^{-1}, with a mean of 0.69 g CO_2 m^{-2} d^{-1} across the 7 months, with the peak fluxes in November and lowest in May. Those wetlands showed a steady increase in fluxes until August, experienced a sharp decline during September and October, and then showed an increase again in November (Figure 2.5).

Cumulative CO_2 fluxes across the facilities ranged from -229 g CO_2 m^{-2} to 945 g m^{-2}, with a mean flux of 148 g CO_2 m^{-2}. Out of 24 facilities, 15 (62.5%) were net emitters of CO_2, while the remaining 9 (37.5%) facilities showed a net uptake of CO_2.

2.3.1.2 Fluxes of CH_4

Across all ponds and sampling months, CH_4 fluxes ranged from 0.12 to 9068.54 mg CH_4 m^{-2} d^{-1} with a mean value of 416.41 ± 971.84 mg CH_4 m^{-2} d^{-1}. The maximum flux was recorded in July at the outlet of a wet pond and the minimum in November at the inlet of a wet pond (Figure 2.6). The LMM model revealed a significant main effect of the month ($F_{6,401.48} = 5.76$, $p < 0.05$) and a non-significant main effect of facility type ($F_{2,68.48} = 3.08$, $p > 0.05$). Interaction between month and facility type was also not significant ($F_{12,407.16} = 4,01$, $p > 0.05$), suggesting that the temporal variations in CH_4 emissions were consistent across all facility types (Figure 2.7). Random intercept variances for Pond ID (site number) and sampling location were 64392 and 3505, respectively, indicating high spatial variability across sites and moderate within a site.

The natural stormwater ponds showed fluxes ranging from 1.09 to 6192 mg CH_4 m^{-2} $d^{-1}$with a mean of 323 mg CH_4 m^{-2} d^{-1} through the sampling period. The wet ponds exhibited fluxes from 0.12 to 9069 mg CH_4 m^{-2} d^{-1} with a mean of 453 mg CH_4 m^{-2} d^{-1}, whereas the wetlands showed fluxes from 2.11 to 4978 mg CH_4 m^{-2} d^{-1} with a mean of 391 mg CH_4 m^{-2} d^{-1}. The trend of CH_4 emissions appeared relatively consistent across facility types, with fluxes increasing until July, followed by a gradual decline through October and a sudden rise in November. However, deviations were observed in wet ponds with a sudden drop in mean flux in June and sudden increase in mean flux in September compared to the other two systems (Figure 2.7).

Methane was released from stormwater facilities via diffusion and ebullition, with ebullition playing a substantial role in overall CH_4 emissions. During the sampling period, we captured ebullition events in about 35% of flux measurements and observed more frequent ebullition events during warmer months. The contribution of ebullition flux to total flux varied among ponds, ranging from 43% to 92% (Table 2.4). On average, ebullitive fluxes were three times higher than diffusive fluxes, accounting for approximately 68% of the total CH_4 released across all ponds (Table 2.4).

Cumulative CH_4 fluxes from each pond ranged from 22 to 272 g CH_4 m^{-2}, with a mean flux of 79.9 g CH_4 m^{-2}. All the 24 facilities were net emitters of CH_4.

Table 2.4: Summary of CH_4 flux components, including diffusive flux, ebullitive flux, total flux and the relative contribution of ebullition to total flux

Facility Number	Diffusive flux (mg CH_4 $m^{-2}d^{-1}$)	Ebullitive flux (mg CH_4 $m^{-2}d^{-1}$)	Total flux (mg CH_4 $m^{-2}d^{-1}$)	% of ebullition
K30	459	3761	4220	89
K4	375	2761	3136	88
K108	753	664	1417	47
K40	1551	1177	2728	43
K138	365	1920	2285	84
K94	421	608	1029	59
K95	182	854	1036	82
K115	560	1004	1564	64
K61	336	496	832	60
K151	42	391	433	90
K100	481	1008	1489	68
K107	213	2521	2734	92
K101	3614	6280	9894	63
W15	572	2011	2583	78
W35	2082	1980	4062	49
W52	1009	1041	2050	51
W40	521	1143	1664	69
W45	1325	1914	3239	59
W39	1809	3158	4967	64

W7	544	1111	1655	67
W34	2929	3940	6869	57
W19	904	2476	3380	73
W31	264	1984	2248	88
W42	313	643	956	67
Average	901	1869	2770	68

2.3.1.3 Fluxes of N_2O

Across all ponds and sampling months, N_2O fluxes ranged from -1454 to 7913 µg N_2O m^{-2} d^{-1} with a mean value of 241.98 ± 762.34 µg N_2O m^{-2} d^{-1}. The maximum flux was recorded in September in the middle of a wet pond and the minimum in November at the outlet of a wet pond (Figure 2.8). Seasonal average fluxes indicated emission of N_2O with all three types of facilities showing occasional uptake during certain periods. Nitrous oxide fluxes did have significant temporal variation over the seven-month sampling period with a significant main effect of the month ($F_{6, 433.19} = 2.74$, $p=0.01$; Figure 2.9). Despite these patterns, the LMM indicated there was no significant main effect of pond type ($F_{2, 21.10} =0.192$, $p>0.05$) or interaction between month and pond type ($F_{12, 433.21} = 1.04$, $p>0.05$). Random intercept variances for Pond ID (site number) and sampling location were 301819 and 0.004, respectively, indicating high spatial variability across sites but little within pond variation (Figure 2.8).

The natural stormwater ponds had N_2O fluxes ranging from -388 to 1650 µg N_2O m^{-2} d^{-1}, with a mean of 50.9 µg N_2O m^{-2} d^{-1} across the sampling period. The wet ponds exhibited fluxes from -1454 to 6867 µg N_2O m^{-2} d^{-1} with a mean of 251 µg N_2O m^{-2} d^{-1},

whereas the wetlands showed fluxes from -541 to 7913 μg N_2O m^{-2} d^{-1} with a mean of 299 μg N_2O m^{-2} d^{-1}. Wet ponds and wetlands recorded the highest fluxes in May and the lowest in October and November, respectively. In contrast, natural SWPs showed the highest flux during July and lowest in May. Further, these fluxes only exhibited minor fluctuations among the months, with an overall gradual decrease from May to November (Figure 2.9).

Cumulative N_2O fluxes across all facilities ranged from -25.4 to 309 mg N_2O m^{-2}, with a mean flux of 44 mg N_2O m^{-2}. Out of 24 facilities, 15 (62.5%) were net emitters of N_2O, while the remaining 9 (37.5%) facilities showed a negative flux of N_2O, with the consumption levels exceeding their emissions.

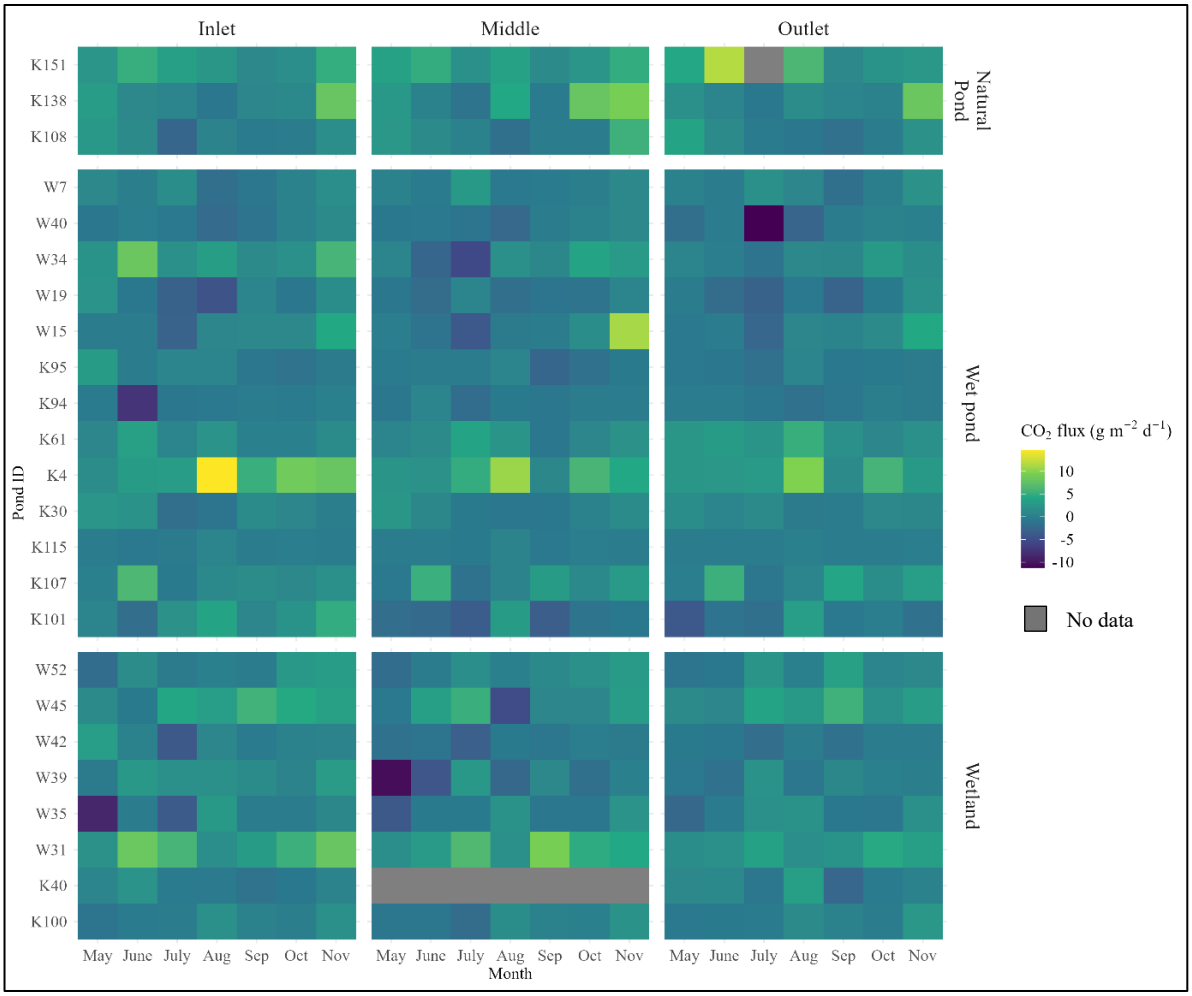


Figure 2.4: Heatmap illustrating CO_2 fluxes (g CO_2 m^{-2} day^{-1}) across 24 stormwater ponds over a 7-month sampling period (May–November). Rows represent individual ponds, while columns represent sampling months. Color intensity reflects the magnitude of gas flux, with warmer colors indicating higher emission levels**.**

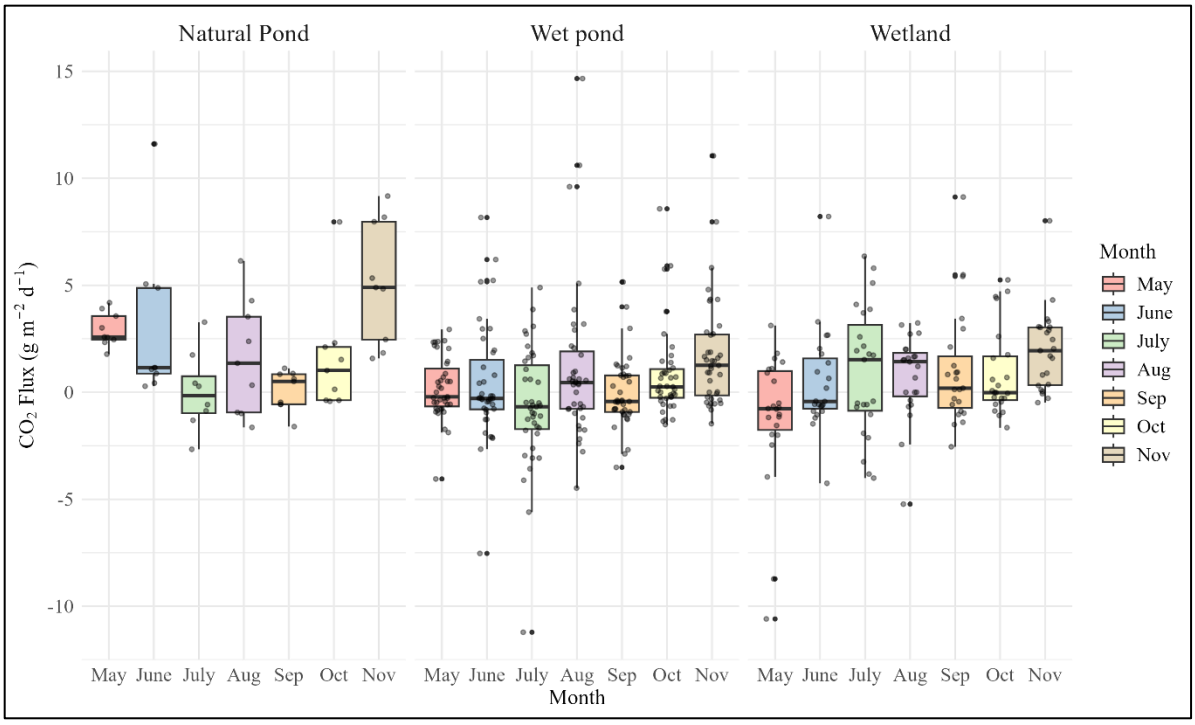


Figure 2.5: Boxplot showing the distribution of CO_2 fluxes (g CO_2 m^{-2} d^{-1}) across different facility types. Each box represents the interquartile range (IQR) of flux values for a given facility, with the median shown as a horizontal line. Whiskers indicate variability outside the upper and lower quartiles, and individual points represent outliers.

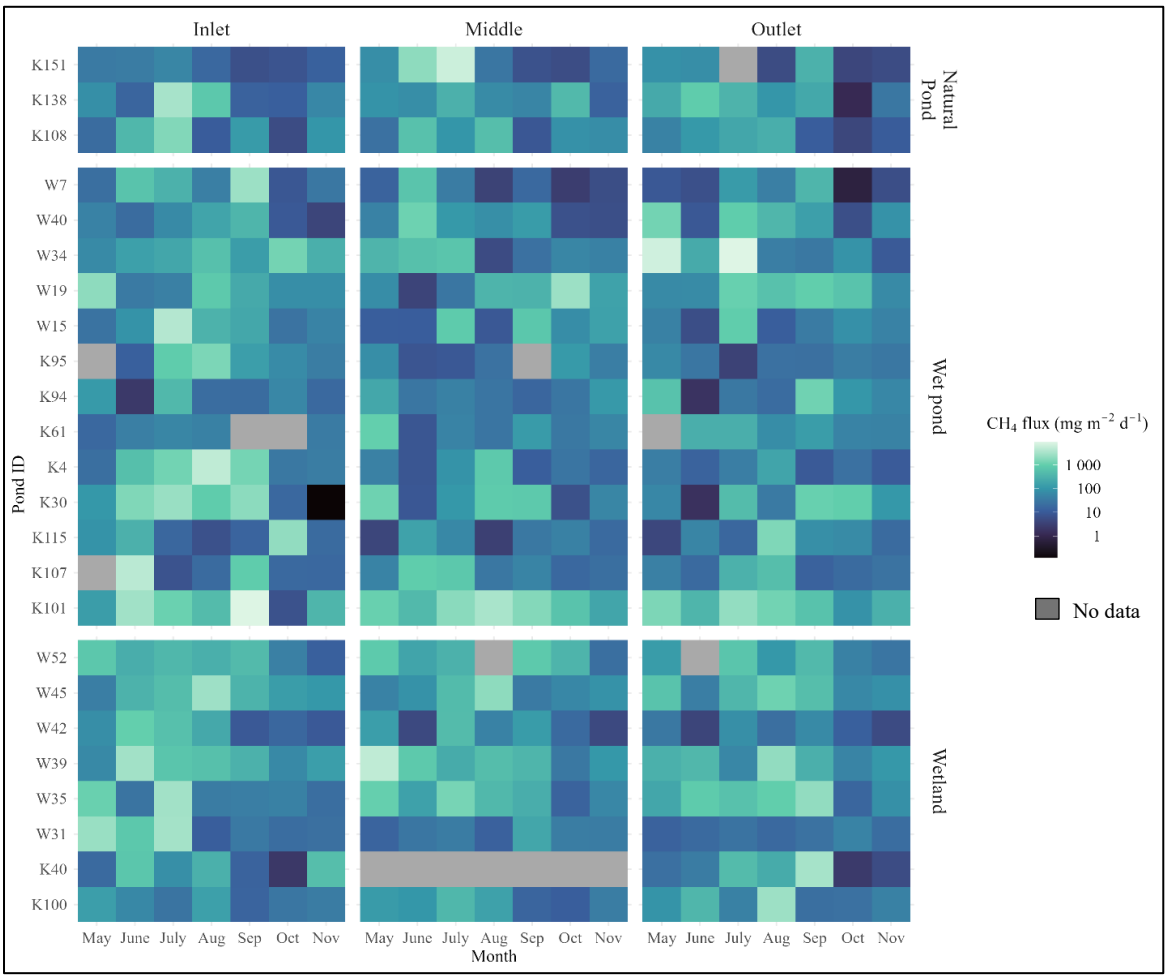


Figure 2.6: Heatmap illustrating CH_4 fluxes (mg CH_4 m^{-2} d^{-1}) across 24 stormwater ponds over a 7-month sampling period (May–November). Rows represent individual ponds, while columns represent sampling months. Color intensity reflects the magnitude of gas flux, with warmer colors indicating higher emission levels.

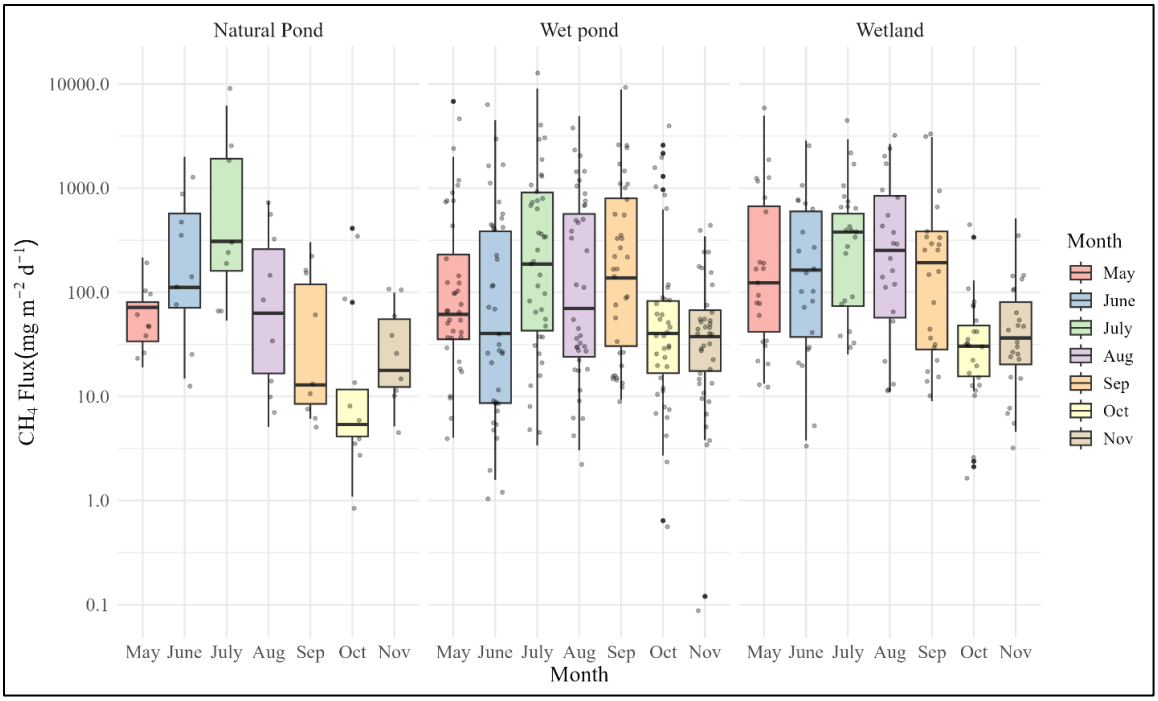


Figure 2.7: Boxplot showing the distribution of CH_4 fluxes (mg CH_4 m^{-2} d^{-1}) across different facility types. Each box represents the interquartile range (IQR) of flux values for a given facility, with the median shown as a horizontal line. Whiskers indicate variability outside the upper and lower quartiles, and individual points represent outliers.

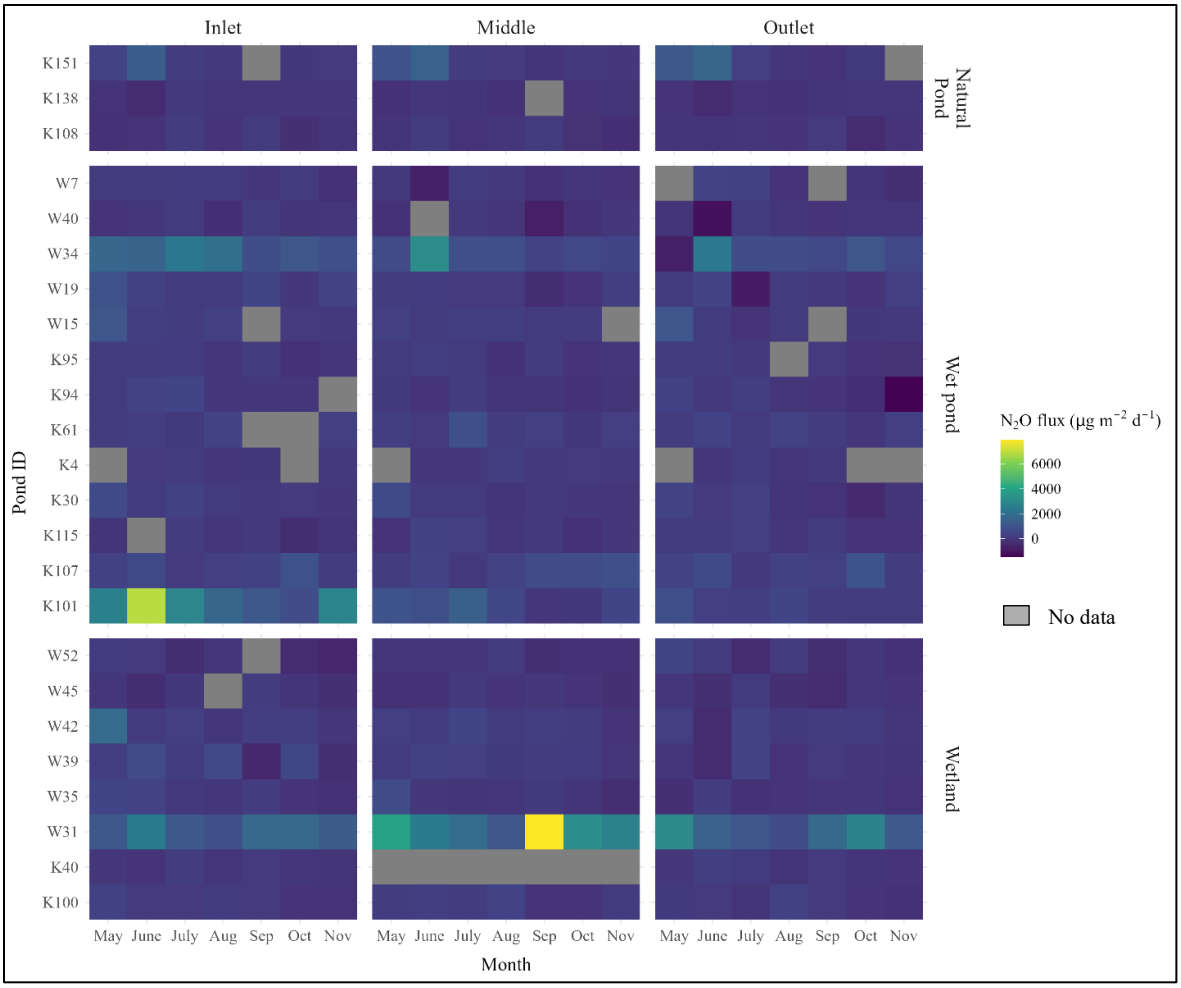


Figure 2.8*:* Heatmap illustrating N_2O fluxes (µg N_2O m^{-2} d^{-1}) across 24 stormwater ponds over a 7-month sampling period (May–November). Rows represent individual ponds, while columns represent sampling months. Color intensity reflects the magnitude of gas flux, with warmer colors indicating higher emission levels.

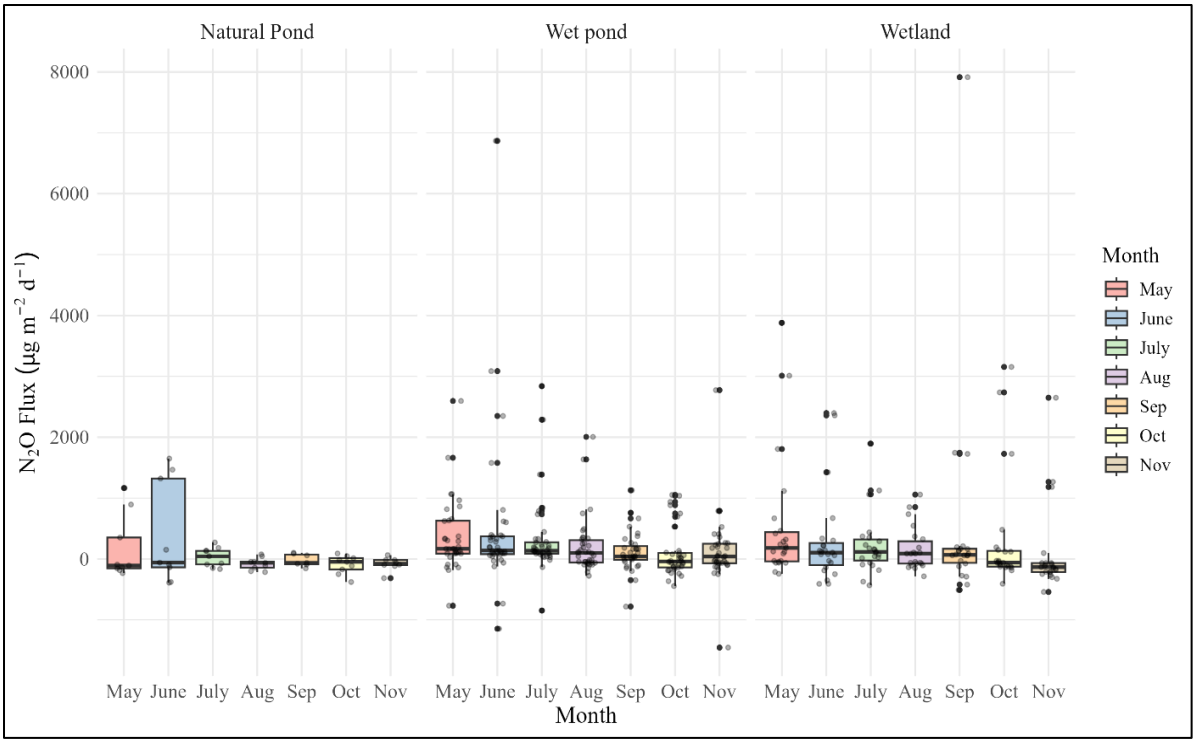


Figure 2.9: Boxplot showing the distribution of N_2O fluxes (µg N_2O m^{-2} d^{1}) across different facility types. Each box represents the interquartile range (IQR) of flux values for a given facility, with the median shown as a horizontal line. Whiskers indicate variability outside the upper and lower quartiles, and individual points represent outliers.

2.3.2 Effect of in-situ environmental variables on the GHG fluxes

Summary statistics for the measured in-situ environmental variables across all ponds and sampling depths are presented in Table 2.5. The environmental conditions exhibited considerable variability across the ponds and sampling depths. Dissolved oxygen values exceeding 25 mg/L were excluded from the analysis, as such values are likely to result from instrumental errors or extreme supersaturation events that are not representative of typical pond conditions.

Table 2.5: Summary statistics of environmental variables at different depths across all ponds

Parameter	Depth	Min. value	Max. value	Mean. value
Temperature (°C)	10cm*	5.2	29.9	18.6
	50cm*	5.0	28.8	17.8
	10cm_as*	4.9	28	16.9
DO (mg/L)	10cm	0.02	22.1	9.34
	50cm	0.51	19.0	8.49
	10cm_as	0.01	20.5	6.68
pH	10cm	6.30	10.17	8.41
	50cm	6.50	9.82	8.22
	10cm_as	6.12	9.99	8.00
EC (µS/cm)	10cm	100.5	4702.0	793.5
	50cm	100.0	4821.0	844.5
	10cm_as	101.9	4794.0	841.9

*"10cm" refers to 10 cm below the water surface, "50cm" refers to 50 cm below the surface, and "10cm_as" refers to 10 cm above the sediment layer

2.3.2.1 Environmental controls on CO_2 flux

The spearman correlation matrix showed that CO_2 flux had a significant negative correlation with pH and temperature at all three depths. A significant negative correlation was observed with DO at 10 cm and 50 cm below the water surface. Electrical conductivity 10 cm above the sediments positively correlated with CO_2 fluxes (Appendix, Table A2). We also observed collinearity between predictor variables.

Linear mixed models' results indicated the temperature and pH at all three depths significantly negatively affected CO_2 flux ($p<0.05$). Dissolved oxygen at 10 cm and 50 cm below the surface negatively affected CO_2 flux, whereas EC at 10 cm above sediments showed no significant effect on CO_2 flux ($p>0.05$) (Figure 2.10; Table 2.6).

2.3.2.1 Environmental controls on CH_4 flux

Methane fluxes were positively correlated with the temperature at three depths and negatively correlated with pH at 10 cm above the sediments, DO at 50 cm below the surface and 10 cm above the sediments (Appendix, Table A2). No significant correlation was observed between CH_4 fluxes and EC.

According to the LMM results, the temperature at all three depths showed a significant positive effect on CH_4 flux, whereas DO at 50 cm below the surface negatively affected CH_4 flux ($p<0.05$). However, there was no significant effect of DO at 10 cm above the sediments on CH_4 flux. The pH 10 cm above the sediments showed a significant negative effect (Figure 2.11; Table 2.6).

2.3.2.1 Fluxes of N_2O

Nitrous oxide fluxes were positively correlated with the temperature and EC at all three measurement depths and negatively correlated with DO at 10 cm below the surface and 10 cm above the sediment (Appendix, Table A2). No significant correlation was observed with pH.

Linear mixed models indicated that DO at 10 cm below the surface and 10 cm above the sediment significantly positively affected N_2O flux ($p<0.05$). Conductivity at all three depths had a significant positive effect on N_2O flux ($p<0.05$), whereas the temperature at all three depths had no significant impact on N_2O flux ($p>0.05$) (Figure 2.12; Table 2.6).

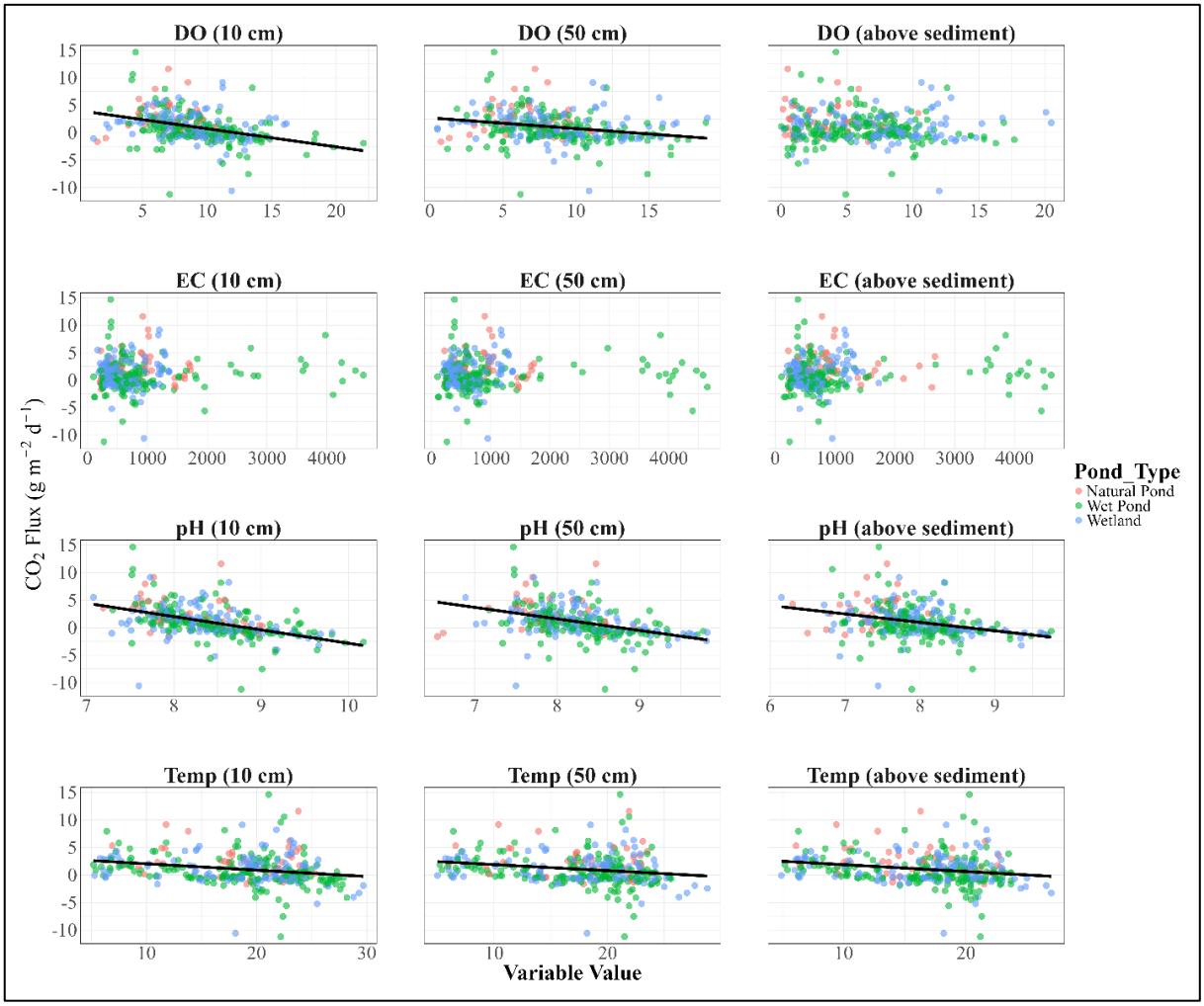


Figure 2.10: Scatterplot depicting the relationship between 4 in-situ environmental variables, and CO_2 flux. The x-axis represents variable values, and the y-axis represents CO_2 flux (g m^{-2} day^{-1}). Each subplot represents a different in-situ environment parameter measured at one of three depths. DO = Dissolved oxygen (mg/L), EC = Electrical Conductivity (µS/cm), Temp = Temperature (°C); 10 = 10cm below the surface, 50 = 50cm below the surface, above sediments = 10 cm above the sediments.

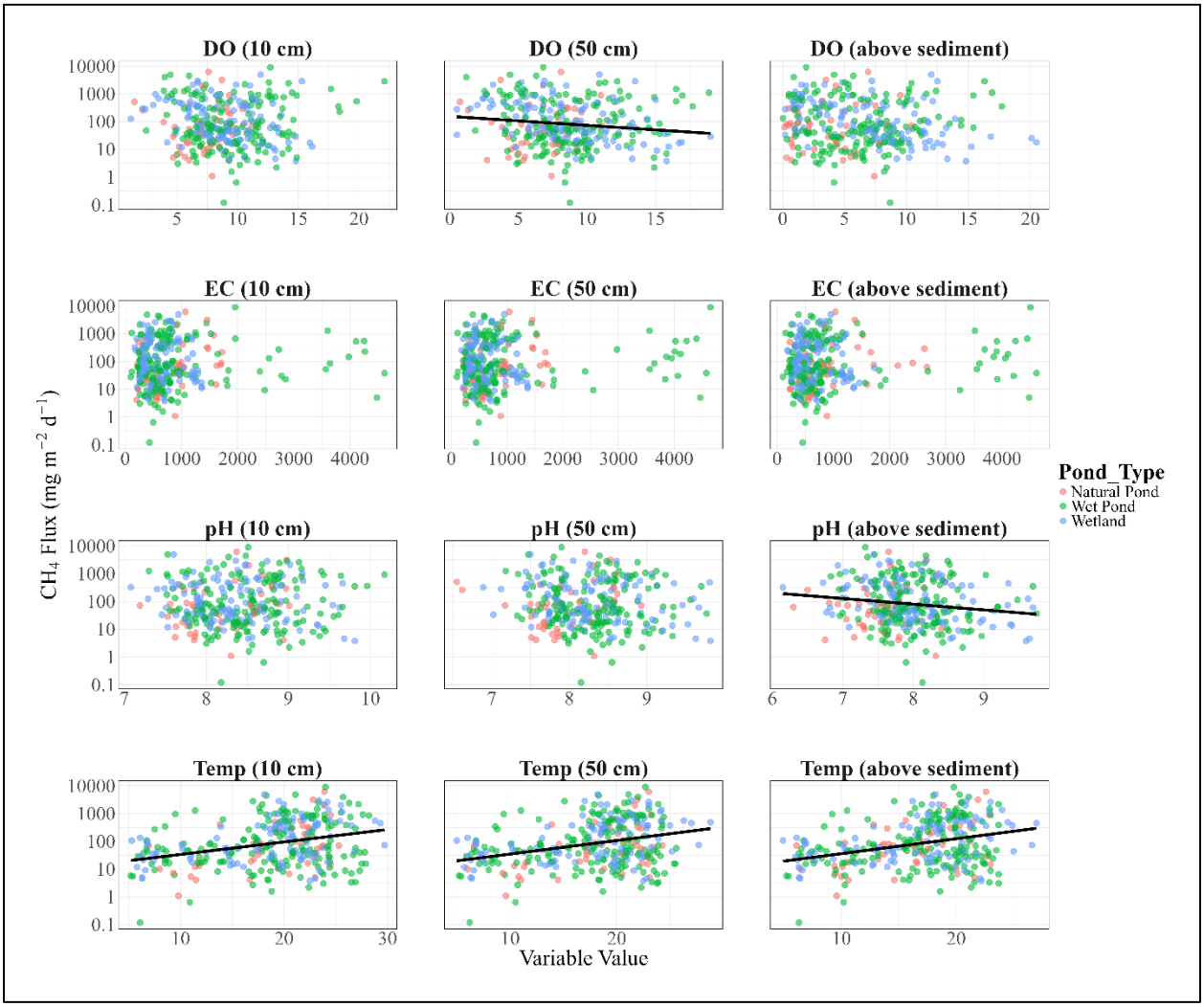


Figure 2.11: Scatterplot depicting the relationship between 4 in-situ environmental variables, and CH_4 flux. The x-axis represents parameter values, and the y-axis represents CH_4 flux (mg m^{-2} day^{-1}). Each subplot represents a different in-situ environment parameter measured at one of three depths. DO = Dissolved oxygen (mg/L), EC = Electrical Conductivity (µS/cm), Temp = Temperature (°C); 10 = 10cm below the surface, 50 = 50cm below the surface, above sediment = 10 cm above the sediments

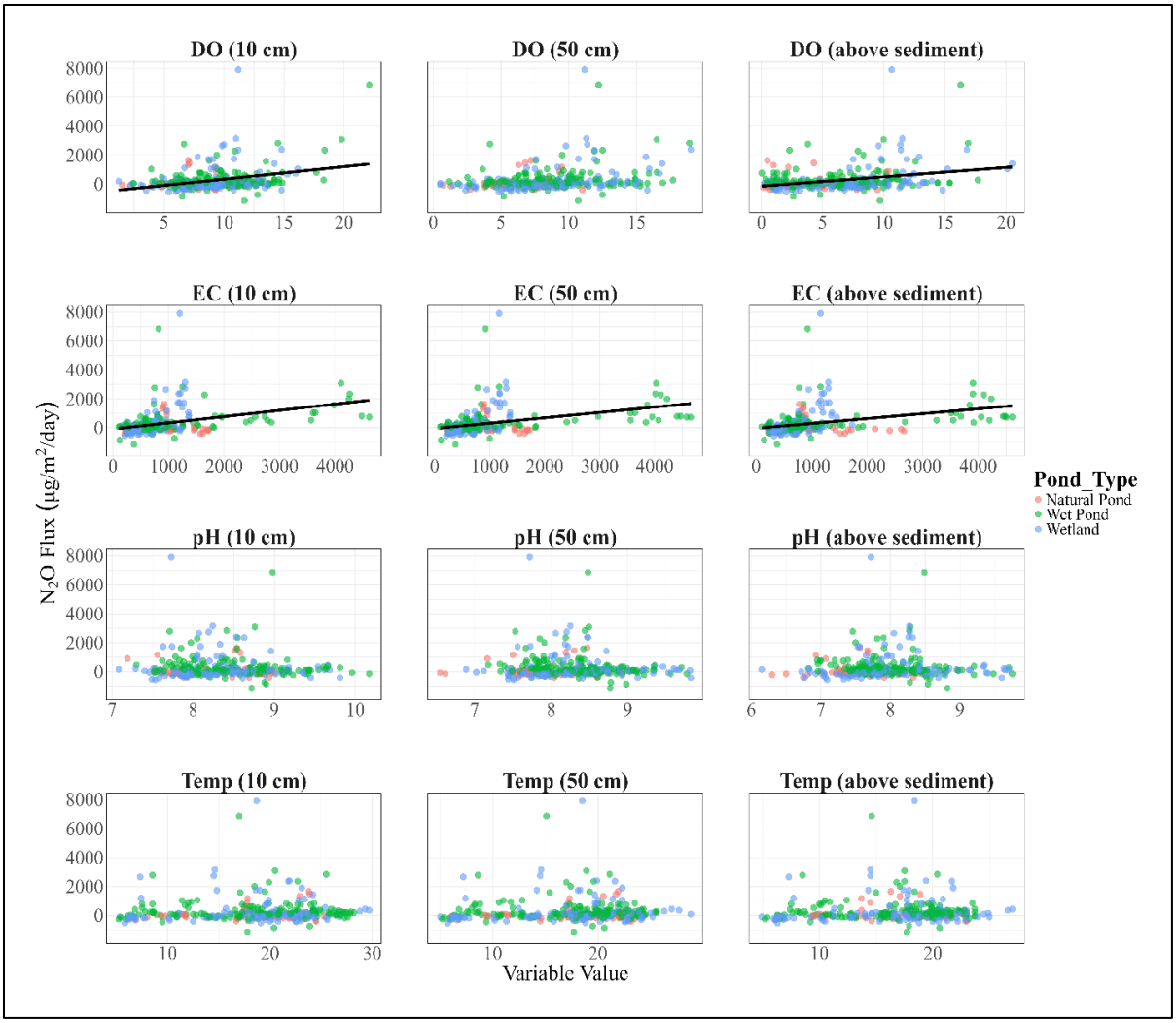


Figure 2.12: Scatterplot depicting the relationship between 4 in-situ environmental variables, and N_2O flux. The x-axis represents parameter values, and the y-axis represents N_2O flux (µg m^{-2} day^{-1}). Each subplot represents a different in-situ environment parameter measured at one of three depths. DO = Dissolved oxygen (mg/L), EC = Electrical Conductivity (µS/cm), T = Temperature (°C); 10 = 10cm below the surface, 50 = 50cm below the surface, above sediment = 10 cm above the sediments

Table 2.6: Results from linear mixed effects models for CO_2, CH_4 and N_2O fluxes using environmental variables measured at various depths.

Model	Response variables	Depth	Fixed effects		R^2M^a	R^2C^a
			Variable	Estimate		
1	CO_2 (g m^{-2} d^{-1})	10 cm	Intercept	0.95	0.16	0.48
			Temp	-0.24		
			DO	-0.66		
			pH	-0.50		
2	CO_2 (g m^{-2} d^{-1})	50 cm	Intercept	0.94	0.11	0.45
			Temp	-0.39		
			DO	-0.46		
			pH	-0.45		
3	CO_2 (g m^{-2} d^{-1})	10 cm above sediments	Intercept	0.95	0.08	0.45
			Temp	-0.42		
			EC	-0.55		
			pH	-0.55		
4	CH_4 (mg m^{-2} d^{-1})	10 cm	Intercept	1.93	0.12	0.27
			Temp	0.28		
5	CH_4 (mg m^{-2} d^{-1})	50 cm	Intercept	1.93	0.15	0.29
			Temp	0.30		
			DO	-0.14		
6	CH_4 (mg m^{-2} d^{-1})		Intercept	1.93	0.14	0.25

		10 cm above sediments	Temp	0.28		
			DO	-0.01		
			pH	-0.12		
7	N_2O (µg m^{-2} d^{-1})	10 cm	Intercept	265.73	0.10	0.57
			Temp	11.07		
			DO	92.30		
			EC	166.6		
8	N_2O (µg m^{-2} d^{-1})	50 cm	Intercept	267.61	0.11	0.59
			Temp	3.32		
			DO	12.79		
			EC	260.13		
9	N_2O (µg m^{-2} d^{-1})	10 cm above sediments	Intercept	262.90	0.10	0.56
			Temp	24.51		
			DO	85.21		
			EC	194.88		

a. Marginal (M; fixed effects only) and conditional (C; fixed and random effects) R^2 values from specified linear mixed effects models. Temp= Temperature, DO= Dissolved Oxygen, EC= Electrical conductivity. 10 cm= 10cm below the surface, 50 cm = 50cm below the surface.

2.3.3 Effect of water quality variables on the GHG fluxes

Summary statistics for the measured water quality variables, including DOC, NO_3^-, PO_4^{3-}, NH_4^+ and SO_4^{2-} are presented in Table 2.7. These variables exhibited considerable variability across the ponds and sometimes among sampling locations.

Table 2.7: Summary statistics of water quality variables across all ponds

Nutrient	Min:	Max:	Mean	SD (±)
DOC* (mg/L)	2.0	13.7	6.8	2.2
PO_4^{3-}* (µg/L)	5.6	57.3	10.1	7.7
NH_4^+* (µg/L)	13.9	675.0	84.1	120.9
NO_3^-* (mg/L)	0.01	20.7	1.8	4.0
SO_4^{2-}* (mg/L)	0.79	87.6	16.4	13.9

*"DOC" refers to Dissolved Organic Carbon, "PO_4^{3-}" refers to Phosphate anions, "NH_4^+" refers to Ammonium ions, "NO_3^-" refers to Nitrate anions and "SO_4^{2-}" refers to Sulphate anions.

According to the models, DOC concentration had a significant negative effect ($p<0.05$) on CO_2 flux, whereas the NO_3^- concentrations showed a significant positive effect ($p<0.05$) on CO_2 flux (Figure 2.13). In contrast, NH_4^+, NO_3^- and SO_4^{2-} concentrations had no significant effect on the CO_2 flux(Appendix, Figure A1). Nitrate concentration showed a significant positive correlation with N_2O flux (Figure 2.13) when none of the other variables showed a significant effect on N_2O flux (Appendix, Figure A3). No variable showed a significant effect on CH_4 emissions in the models (Appendix, Figure A2).

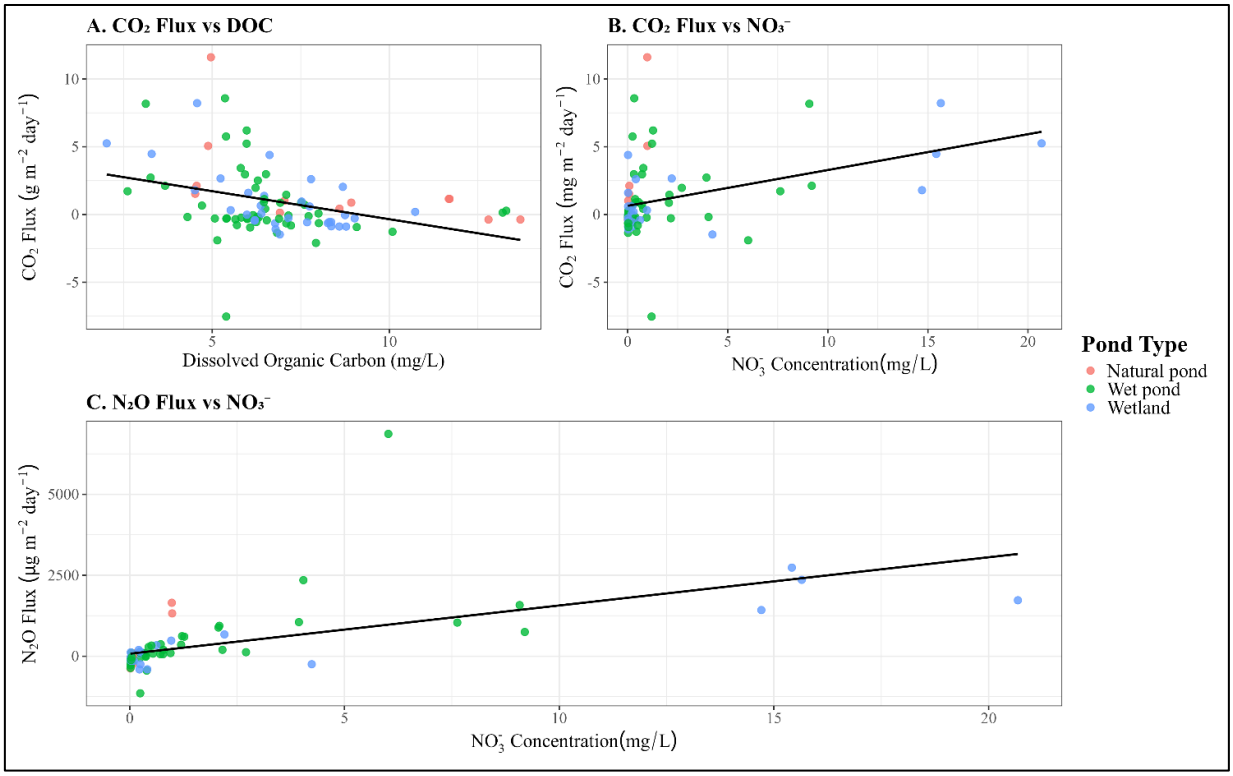


Figure 2.13: Scatterplot depicting the relationship between water quality variables, and GHG fluxes (CO_2 and N_2O). The x-axis represents concentration of the relevant variable, and the y-axis represents CO_2 flux (g m^2 day^{-1}) or N_2O (µg m^2 day^{-1}). Each subplot represents a different variable that showed a statistically significant relationship ($p<0.05$) with GHG fluxes.

2.3.4 Effect of physical variables on GHG fluxes

Physical pond characteristics exhibited considerable variability across the ponds. Pond ages ranged from 12–62 years, and the perimeter: area ratio (P:A ratio) was high in most of the facilities, indicating that they have irregular or elongated shapes. Pond depth varied within each pond and among the different ponds over the 7-month period. Inlet depths ranged from 0.1–2.4 m, while middle and outlet depths ranged from 0.2–3.8 m and 0.2–4.0 m, respectively. Sediment thickness also varied, ranging from 0.2–1 m at the inlet, 0.1–1.2 m at the middle, and 0.1–1.2 m at the outlet.

2.3.4.1 Fluxes of CO_2

According to the models, pond depth had a significant positive effect on the CO_2 fluxes ($p<0.05$), while the sediment depth showed a marginally significant positive effect ($p=0.05$) (Figures 2.16 & 2.17). The dredging category itself also had a significant effect on CO_2 flux, with the highest fluxes observed in non-dredged ponds and the lowest in recently dredged ponds (Figure 2.15). Catchment area had a significant positive effect on CO_2 fluxes (Figure 2.14). Other physical parameters, including pond age, P:A ratio and impervious surface area, did not significantly explain variation in CO_2 fluxes among facilities.

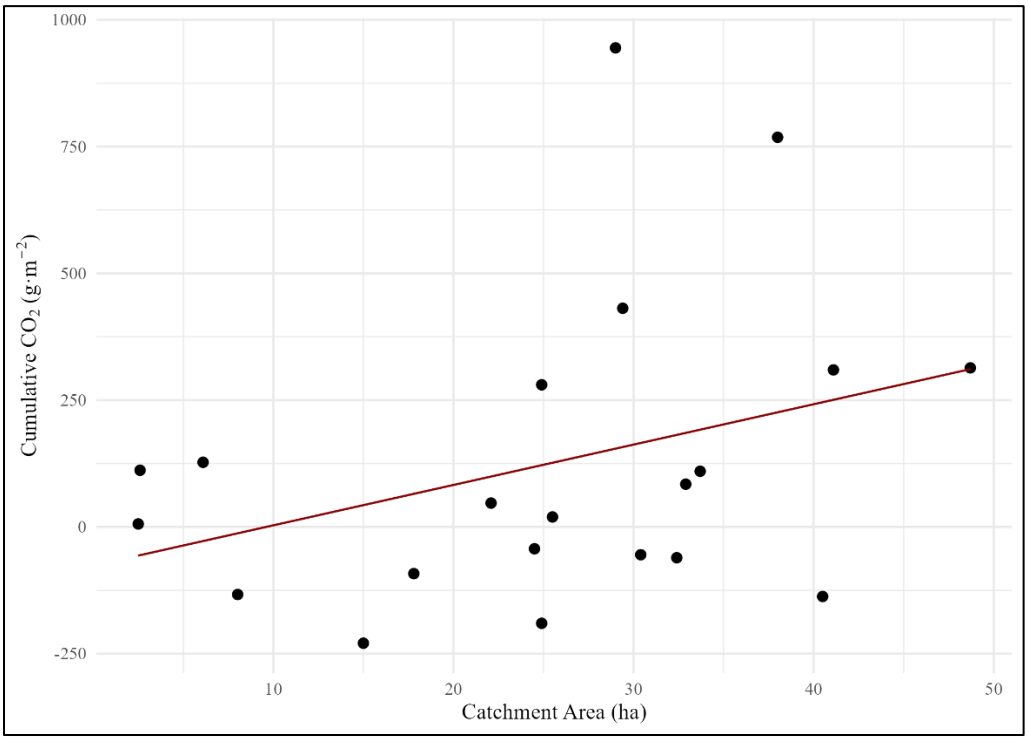


Figure 2.14: Scatter plot showing the effects of catchment area on cumulative CO_2 emissions from stormwater facilities. Each point represents a facility, with the x-axis showing catchment area (ha). The y-axis showing cumulative CO_2 flux (g m^{-2}) over the sampling period. Trend lines illustrate how the relationship between the variables and CO_2 emissions.

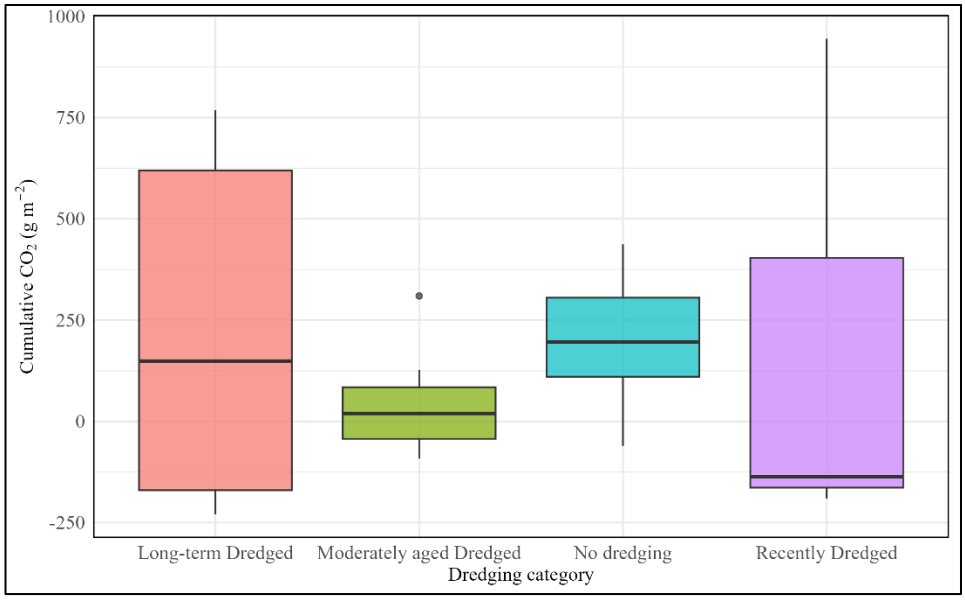


Figure 2.15: Box plot illustrating the variation in cumulative CO_2 emissions (g m^{-2}) across stormwater facilities grouped by dredging category. Each box represents the distribution of total CO_2 fluxes for facilities within each dredging group.

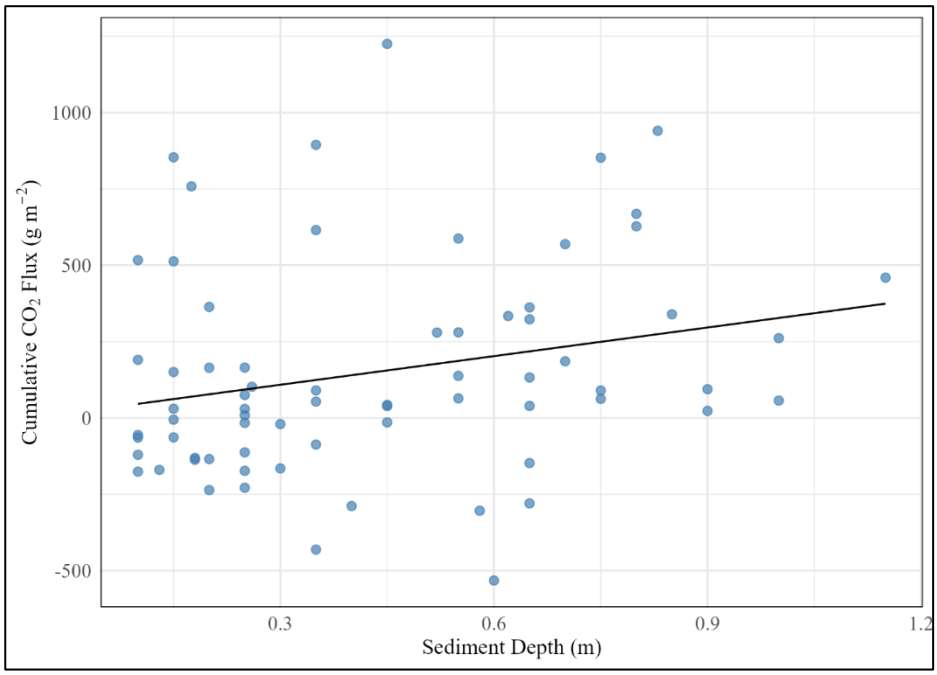


Figure 2.16: Scatter plot showing the relationship between sediment depth (m) and cumulative CO_2 fluxes (g m^{-2}) at individual sampling locations across 24 stormwater ponds. Each point represents a unique location (e.g., inlet, middle, or outlet) within a pond.

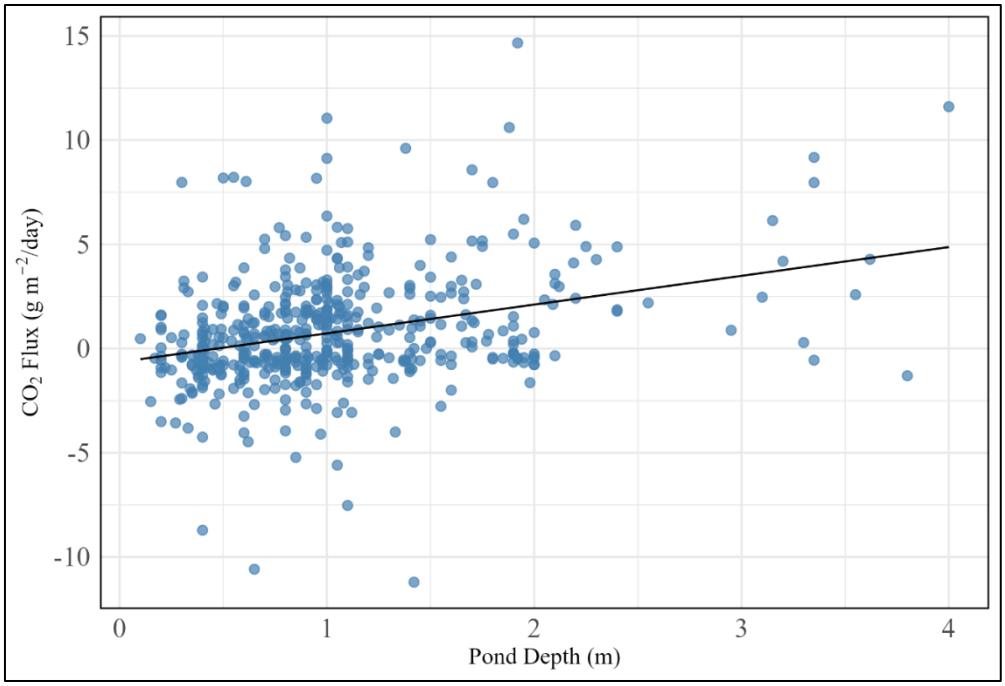


Figure 2.17: Scatter plot showing the relationship between pond depth (m) and CO_2 fluxes (g $m^{-2}day^{-1}$) at individual sampling locations across 24 stormwater ponds. Each point represents a unique location (e.g., inlet, middle, or outlet) within a pond.

2.3.4.2 Fluxes of CH_4

According to the models, the sediment and pond depths did not significantly affect the CH_4 fluxes. Moreover, the other physical parameters, including pond age, pond type, dredging status, impervious surface area and P:A ratio, did not significantly affect CH_4 fluxes. Despite the lack of statistically significant effects, there was a general pattern of higher CH_4 emissions from wet ponds and wetlands compared to natural ponds (Figure 2.18) and lower emissions from ponds that had been recently dredged or had no dredging recorded (Figure 2.19)

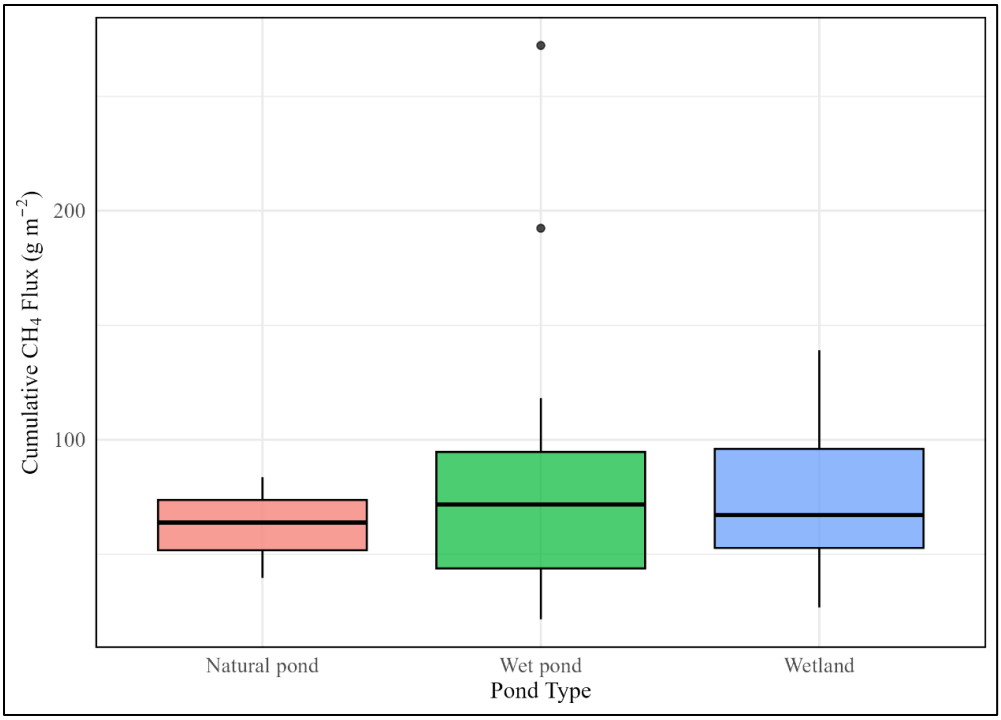


Figure 2.18: Box plot illustrating the variation in cumulative CH_4 emissions (g m^{-2}) across ponds grouped by pond type. Each box represents the distribution of total CH_4 fluxes for ponds within each pond type.

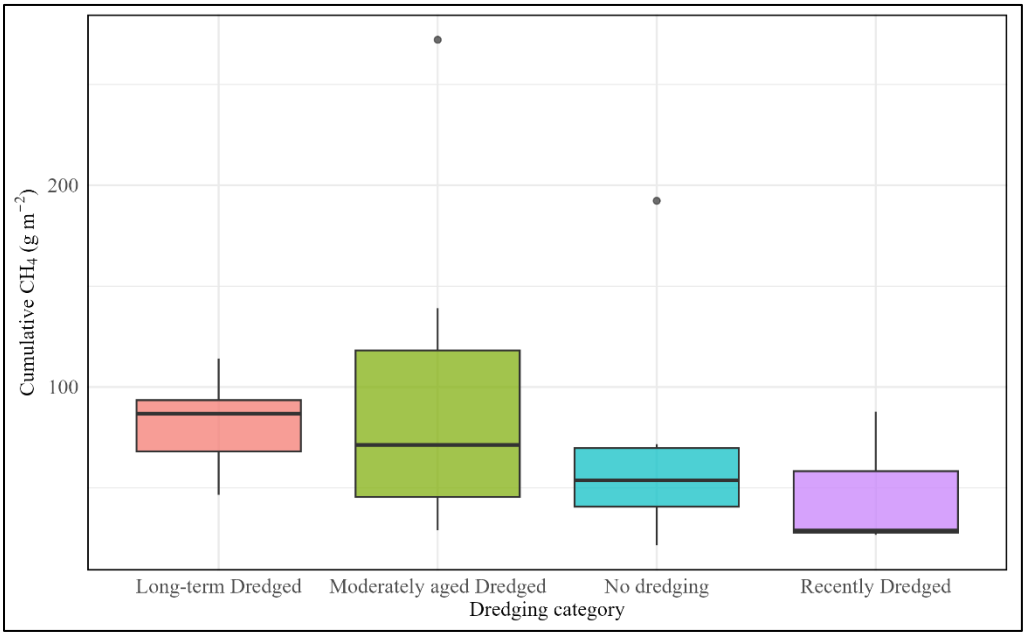


Figure 2.19: Box plot illustrating the variation in cumulative CH_4 emissions (g m^{-2}) across ponds grouped by dredging category. Each box represents the distribution of total CH_4 fluxes for ponds within each dredging group.

2.3.4.1 Fluxes of N_2O

According to the models, the sediment depth had a significant positive effect on the N_2O fluxes ($p<0.05$) (Figure 2.20), while pond depth showed no significant effect on N_2O fluxes. Further, the physical parameters including pond age, pond type, dredging status, catchment area, impervious surface area and P:A ratio, did not show any significant effect on N_2O emissions.

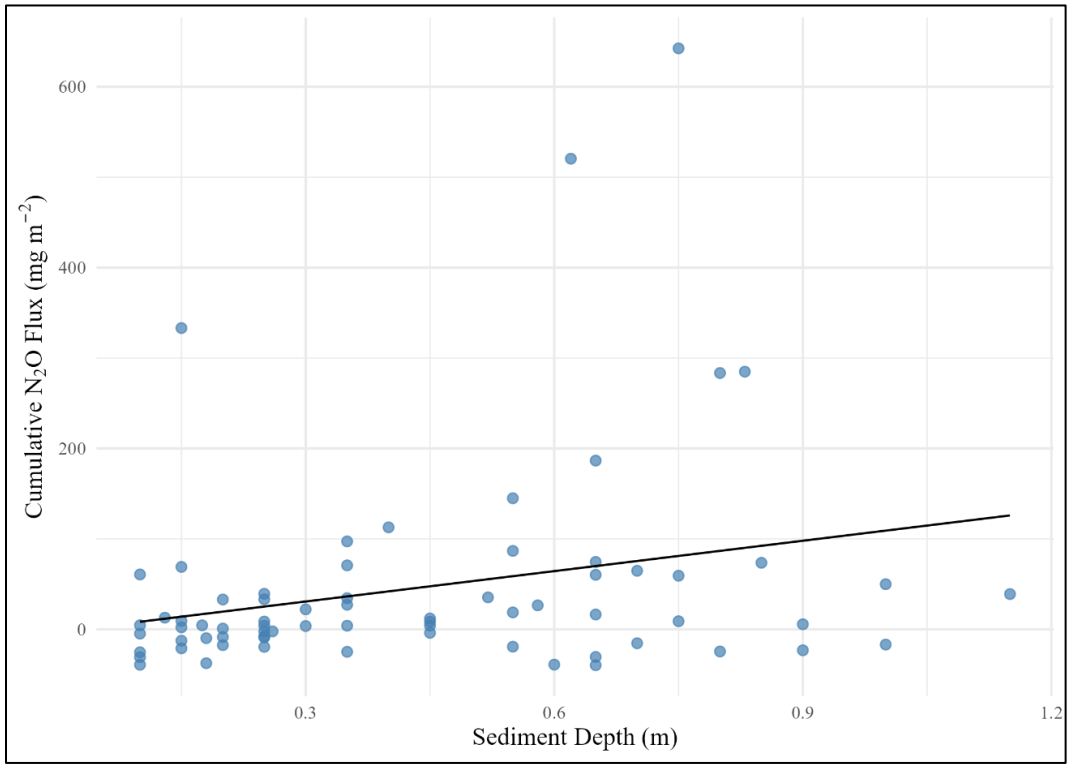


Figure 2. 20: Scatter plot showing the relationship between sediment depth (m) and cumulative N_2O fluxes (mg m^{-2}) at individual sampling locations across 24 stormwater ponds. Each point represents a unique location (e.g., inlet, middle, or outlet) within a pond.

2.4 Discussion

2.4.1 Temporal variability and effect of in-situ environmental variables on GHG fluxes

Temporal dynamics of GHG emissions are particularly important in temperate climates due to seasonal shifts in temperature, biological activity, and hydrology, which can alter gas production and release processes (Holgerson, 2015). Capturing this temporal variation is needed for accurate seasonal and annual GHG emission estimates. Hence, the first key objective of the present study was to assess the temporal variability of GHG fluxes (CO_2, CH_4, N_2O) from stormwater management facilities over seven months from late spring (May) through late autumn (November). Linked to this temporal variability, the GHG production and emissions are mainly driven by in-situ environmental conditions within the water column (Van Bergen et al., 2019). Therefore, the second key objective of this study was to determine the in-situ environmental drivers that affect GHG fluxes (CO_2, CH_4, N_2O) in stormwater facilities. For that, the effect of water temperature, DO, pH, and EC were assessed at three selected depths along the water column.

2.4.1.1 Carbon dioxide fluxes

Carbon dioxide fluxes from the stormwater facilities in this study exhibited significant temporal variability, with clear seasonal patterns that were influenced by the facility type (Figure 2.5). These patterns appear to be modulated by the behavior of measured environmental variables including water temperature, DO concentration and pH.

During warmer months, elevated temperatures accelerate microbial respiration in both the water column and sediments leading to elevated CO_2 production and emissions (Cole et al., 1994). However, this period also coincides with high sunlight intensity, which enhances autotrophic processes including photosynthesis by the algal and aquatic

vegetation community. This enhanced productivity may temporarily offset CO_2 produced through respiration, reducing emissions in the warmer months (Gorsky et al., 2019). This mechanism likely explains the lower CO_2 fluxes during summer in both natural SWPs and wet ponds of this study. Similar trends have been reported from urban ponds elsewhere with CO_2 fluxes decreasing in summer due to increased photosynthetic activity (Bauduin et al., 2024; Davidson et al., 2015). The significant negative relationship observed between CO_2 fluxes and water temperature at all three depths further supports this pattern, suggesting that higher temperatures coincided with increased primary production, which may have suppressed net CO_2 emissions despite enhanced microbial activity. In particular, UW in this study maintained moderate to elevated CO_2 emissions during summer, despite experiencing similar environmental conditions. This may be attributed to the high abundance of rooted submerged and emergent macrophytes, which oxygenate the sediment and release labile carbon via root exudates, along with the greater availability of organic matter, potentially promoting degradation processes and the release of CO_2 (Audet et al., 2020; Badiou et al., 2019b).

The productivity driving temporal patterns of CO_2 flux was further supported by the observed negative relationship with DO at 10 cm and 50 cm below the surface. The top and middle layers in the water column are most likely to have high photosynthesis rates due to light availability, which uptakes CO_2 and releases oxygen reflecting the balance between photosynthesis and respiration (Bauduin et al., 2024; Borges et al., 2015). Thus, oxygen rich conditions symbolize net autotrophy and reduction in net CO_2 emissions, especially in productive systems (Cole et al., 2007a). Many studies have also found a similar negative correlation between DO and concentration of CO_2 in aquatic systems

(Balmer & Downing, 2011; Cole et al., 2007; Holgerson, 2015; Kankaala et al., 2013). On the other hand this negative relationship might be linked with respiration rates where high ecosystem respiration produces CO_2 while consuming DO as observed in urban ponds by Holgerson (2015).

At the beginning of the autumn (September) CO_2 fluxes were low as the water temperatures were still warm, and a good amount of sunlight was available to draw down produced CO_2 through photosynthesis by primary producers. The further temperature drop and reduced sunlight intensity into October and November caused senescence of primary producers which led to a large amount of potentially degradable autochthonous organic matter (Bartosiewicz et al., 2021) aligning with the higher CO_2 emissions observed (Figure 2.5). This organic matter may cause higher CO_2 fluxes accelerated by high respiration rates and low photosynthetic uptakes (Bartosiewicz et al., 2021). Moreover, the input of allochthonous organic matter to ponds increases in the autumn with litterfall from surrounding trees and with runoff due to higher precipitation (Bauduin et al., 2024; Sørensen et al., 1980). This trend is consistent with the findings of Bauduin et al. (2024), who reported lower CO_2 concentrations in summer followed by an increase during the autumn.

Finally, pH demonstrated a significant negative relationship with CO_2 fluxes across all three depths, indicating low pH conditions were associated with higher CO_2 fluxes. This effect can be largely caused by the pH dependent speciation of dissolved inorganic carbon in the water column. When CO_2 dissolves in water it forms carbonic acid (H_2CO_3), which then dissociates into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) (Gorsky et al., 2019). At lower pH values, a greater fraction of dissolved inorganic carbon remains in the form of

free CO_2 which is capable of escaping to the atmosphere. As pH increases, CO_2 is highly dissociated into HCO_3^- and CO_3^{2-} ions, reducing CO_2 fluxes (Duarte et al., 2008). The pH of the stormwater facilities studied ranges from 6.12 to 10.17 which might accelerate the dissociation of CO_2 resulting in low CO_2 fluxes.

Ultimately, seasonal variability in CO_2 fluxes depends on the shift between periods dominated by ecosystem heterotrophy (ecosystem respiration) and periods characterized by more autotrophic (photosynthetic) conditions (Bauduin et al., 2024) followed with complex interactions among environmental drivers such as temperature, DO concentration and pH.

2.4.1.2 Methane fluxes

Methane emissions from stormwater facilities in this study exhibited temporal variability with clear seasonal pattern across all facility types (Figure 2.7). Peak emissions generally occurred during the summer months (June and July) followed by a decline towards the autumn (September to November). This seasonal pattern is consistent with the observations from other studies in temperate urban wetlands and ponds (Audet et al., 2020; McPhillips & Walter, 2015; Morin et al., 2022). These seasonal patterns corresponded with the variation in measured environmental variables including water temperature, DO concentration and pH.

Elevated CH_4 emissions observed during the warmer months can be attributed to enhanced methanogenesis in sediments or bottom waters, as methanogenic microorganisms exhibit temperature sensitive metabolic rates, with CH_4 production increasing significantly under warmer conditions (Conrad, 1996; Westermann, 1993). A significant positive relationship between CH_4 and water temperature at all three depths in

this study confirms this dependency, consistent with previous research in urban ponds (Peacock et al., 2019; Rabaey & Cotner, 2024; Van Bergen et al., 2019). Furthermore, Rabaey & Cotner (2024) observed high sediment and water temperatures in summer compared to the other seasons highlighting that methanogenesis is accelerated during summer. Methanogenesis rates can increase up to four times with every 10 ℃ increases in temperature in aquatic systems (Bastviken et al., 2008). Moreover, it has been observed that the increase of CH_4 oxidation with increasing temperature is much lower than increase in CH_4 production and release from sediment, resulting in a high CH_4 emission during summer (Van Bergen et al., 2019). Further, increasing temperature decreases gas solubility, facilitating the release of CH_4 from sediment to the atmosphere (Turetsky et al., 2014). Even small shallow ponds can be strongly stratified during the summer with high temperature (Holgerson et al., 2022), which leads to anoxic bottom conditions, resulting in elevated CH_4 accumulation by limiting CH_4 oxidation (Bastviken et al., 2008). This accumulation can cause high emissions through diffusion as the ponds are shallow, or can be release as pulses of higher CH_4 during summer mixing events (Holgerson et al., 2022; Rabaey & Cotner, 2024).

When considering the major CH_4 transport methods, ebullition is often the dominant and frequent pathway of CH_4 emissions in shallow waters (<5m) (Chanton, 2005), where ebullition accounted for 30% to 95% of flux (Grinham et al., 2018b; Natchimuthu et al., 2014a; Repo et al., 2007; Van Bergen et al., 2019). This is further confirmed by the findings of this study, where the highest proportion of CH_4 emissions (68%) occurred through ebullition. When temperature rises, the solubility of gases decreases making CH_4 produced in the sediment less likely to stay dissolved in porewater

resulting in release as gas bubbles increasing the CH_4 fluxes (Bastviken et al., 2008; Bauduin et al., 2024; Chanton, 2005). Hence, ebullition is strongly influenced by temperature (DelSontro et al., 2016) with highest ebullition rates observed during the summer and contributing to high CH_4 fluxes during warmer months in stormwater ponds (Rabaey & Cotner, 2024).

Dissolved oxygen is negatively correlated with CH_4 concentrations as anoxic sediments or waters are required for methanogenesis (Bastviken et al., 2004; Kankaala et al., 2013). Accordingly, our study showed a negative relationship between CH_4 fluxes and DO at 50 cm below the surface. This negative relationship specifically at 50 cm below the water column may be due to CH_4 oxidation with the presence of oxygen in the water column (Bastviken et al., 2004). When oxygen penetrates deeper to the water column, it can inhibit methanogenic activity and promote methanotrophic process, which oxidize CH_4 into CO_2 prior to emission to the atmosphere (Bastviken et al., 2008; Oswald et al., 2015a).

The decline in CH_4 fluxes during the autumn months corresponds to the temperature reduction where lower temperatures reduce microbial activity and may reduce production. During the autumn, greater wind mixing causes reoxygenation of the water column facilitating the methanotrophic activities in the previously stratified layers (Bastviken et al., 2004). Corresponding to that, a high proportion of CH_4 oxidation in autumn and winter has been observed in an urban pond resulting in low emissions (Van Bergen et al., 2019). However, slight increase of CH_4 fluxes in late autumn (November) despite cooler temperatures (Figure 2.7) may be due to the availability of fresh organic substrates through the senescence of aquatic vegetation and litter inputs causing temporary stimulation of CH_4 production (Grasset et al., 2018).

The most favorable pH range for methanogenesis is around 6.2-7.5 where methanogenesis still occurs at pH >7.5 to 9 starting a slight decline in activity of some methanogenic archaea depending on the species (Borrel et al., 2011; Kotsyurbenko et al., 2004). In our study, a negative effect was observed between CH_4 fluxes and pH measured 10 cm above the sediment. This relationship may reflect the influence of high pH on microbial community composition and enzymatic activity involved in methanogenesis. Previous studies have shown that slightly acidic to neutral pH conditions are optimal for methanogenic archaea (Kotsyurbenko et al., 2004) and deviations from this range can suppress their metabolic efficiency which caused lower CH_4 fluxes with increasing pH.

Other than all these factors, storm events in urban ponds can introduce organic carbon from the catchment, stimulate microbial activity or alternatively suppress the emission through dilution and oxygenated events causing different fluctuation patterns which do not align with seasonal temperature patterns, highlighting the short-term hydrological influences (Peacock et al., 2019). Moreover, methanogenic activity may be suppressed by other anerobic pathways such as sulphate or nitrate reduction accelerated by high temperatures (S. Jensen et al., 2022). Given the monthly sampling regime in the present study, we were unlikely to capture these specific effects, but they may contribute to variation among the study sites.

2.4.1.3 Nitrous Oxide Fluxes

Nitrous oxide emissions from lakes and ponds show seasonal variation mainly as a function of oxygen content, dissolved inorganic nitrogen availability and temperature (Mander et al., 2021; Myrstener et al., 2016). Hence, most studies based on urban ponds and urban wetlands have reported higher N_2O fluxes during autumn compared to the

summer (Bauduin et al., 2024; Mander et al., 2021) . However, our study observed a general declining trend from May through November (Figure 2.9) with some minor fluctuation among months. This decreasing flux pattern may be related to reduced availability of nitrogen substrates, particularly NO_3^-/NH_4^+, essential for nitrification and denitrification processes. Early in the growing season (May and June), mineral nitrogen availability can be elevated due to spring runoff carrying residual fertilizers or organic matter from urban landscapes that facilitates nitrification or denitrification. However, with time, plants and microbes can assimilate the NO_3^-/NH_4^+, reducing the substrate availability for the processes (Badiou et al., 2019a) which is supported by the observed decrease in NO_3^- concentration from the beginning to the end of sampling (Appendix, Table A.1). Moreover, increasing water temperatures over the summer may shift redox conditions and microbial communities in a way that favors complete denitrification, lowering the net N_2O emissions (Murray et al., 2015). Minor fluctuations among the fluxes throughout the period are likely the result of storm events, water column mixing, and shifts in oxygen availability, which can temporarily affect the redox gradient and shift the balance between nitrification and denitrification, causing sharp but quick changes in N_2O dynamics in stormwater facilities (Mander et al., 2021). However, a slight increase of N_2O in wet ponds in November compared to October may align with the high heterotrophic degradation of organic matter and ammonification, with lower plant uptake of NH_4^+ and low DO conditions (Rosamond et al., 2012; Soued et al., 2016). These temporal dynamics and N_2O fluxes can be further explained by the effects of in-situ environmental variables such as DO and EC measured in the water column.

The yield of N_2O production from both nitrification and denitrification depends on oxygen levels (Mander et al., 2021). Nitrification is an aerobic process that produces N_2O as a byproduct, whereas denitrification is a process that occurs under limited oxygen or anaerobic conditions, where N_2O is produced as an intermediate product of the process. Therefore, DO concentration can either increase or decrease N_2O flux depending on how complete the processes are. Higher temperatures enhance metabolic activity, which depletes the DO of the water and sediments, creating an anoxic environment, resulting in higher rates of denitrification (Kumar et al., 2019; Marotta et al., 2014). Moreover, the oxic zones favor N_2O production via nitrification, especially when oxygen is present at moderate levels, sufficient to support microbial oxidation but potentially limiting complete conversion to NO_3^-, thereby allowing N_2O to accumulate (Beaulieu et al., 2011; Wrage et al., 2001). Our results showed a positive correlation between N_2O flux and DO, suggesting that nitrification may be a dominant pathway contributing to N_2O emissions in these systems (Nevison, 2000).

The positive relationship with the EC at all three depths suggests a strong connection between N_2O and ionic content in stormwater facilities. This significant effect possibly reflects the elevated nutrient, or pollutant loads that facilities receive through urban runoff. Higher EC often correlates with increased concentrations of NO_3^-, NH_4^+, SO_4^{2-}, and other dissolved ions, which can fuel both nitrification and denitrification (Racchetti et al., 2017; Wang et al., 2023). The positive effect of EC on N_2O flux may be due to the anthropogenic nutrient enrichment, which has been shown to increase microbial nitrogen cycling and associate N_2O production within shallow waters (Audet et al., 2024).

As mentioned above, N_2O fluxes in lakes and ponds vary with the water temperature (Mander et al., 2021; Myrstener et al., 2016). Water temperature negatively correlates with N_2O flux, where low temperature inhibits the complete denitrification, releasing high amounts of N_2O (Bauduin et al., 2024). However, we observed no significant relationship between water temperature and N_2O, indicating that temperature was not the primary driver of N_2O fluxes in these systems and its impact on N_2O production may be minimal when other limiting factors such as substrate availability and DO are dominant (Audet et al., 2024).

We observed no significant effect of pH on N_2O flux, similar to results from Hao et al. (2021). Although pH can influence microbial enzyme activity and redox potential, its effect on N_2O emissions is often weaker than direct controls like substrate availability and DO (Mazur & Fulweiler, 2023).

Overall, N_2O fluxes from stormwater facilities in our study include both positive and negative, where the net N_2O flux depends on the balance between production and consumption of N2O (Yuan et al., 2021). Positive N_2O fluxes are typically associated with incomplete denitrification under limited oxygen levels to anoxic conditions or with nitrification under oxic conditions (Ivens et al., 2011; Nevison, 2000). In contrast, negative fluxes indicate that N_2O is being consumed, possibly as an intermediate in the denitrification process, when reduction of N_2O to N_2 gas (Yuan et al., 2021). Moreover, denitrifiers will potentially be stimulated to use dissolved N_2O for their growth when NO_3^- availability is limited in pond sediment and anoxic portions of the water column (Blicher-Mathiesen & Hoffmann, 1999; Clough et al., 2007), resulting in net N_2O consumption (Schlesinger, 2013).

2.4.3 Effect of pond water quality on GHG fluxes

Chemical variables including DOC, NH_4^+, PO_4^{3-}, NO_3^- and SO_4^{2-} play a fundamental role mediating the production of GHGs in aquatic ecosystems (Holgerson, 2015; Peacock et al., 2019). These compounds serve as energy sources or electron acceptors in microbial processes like aerobic respiration, methanogenesis, nitrification and denitrification influencing CO_2, CH_4 and N_2O dynamics (Burgin & Hamilton, 2007; Holgerson, 2015). In urban stormwater facilities, which often receive nutrient-rich runoff, water quality can vary widely and exert both direct and indirect effects on GHG fluxes (Mander et al., 2021; Novotny, 1999; Scherer et al., 1995; Van Bergen et al., 2019). Hence, another key objective of this study was to determine the chemical variables that affect GHG fluxes (CO_2, CH_4, N_2O) in stormwater facilities.

Dissolved organic carbon provides a substrate for microbial processes that generate all three major GHGs. It supports both aerobic and anaerobic respiration, contributing to CO_2 production, provides carbon for methanogenesis, which produces CH_4, and serves as an electron donor, contributing to denitrification (Malyan et al., 2022; Bertolet et al., 2019). According to our results, DOC concentration had a significant effect only on CO_2 fluxes, with no significant effect on CH_4 or N_2O fluxes. Interestingly, DOC concentration was negatively correlated to CO_2 fluxes, which contrasts with the commonly reported positive relationship in lakes and pond systems (Jonsson et al., 2003; Kelly et al., 2001; Raymond et al., 2013). The observed negative relationship may result from greater photosynthetic activity, which offsets CO_2 produced by respiration and lowers emissions, while also producing fresh photosynthates that increase DOC. Alternatively, in small ponds where depth is limited, CO_2 emissions are primarily driven by sediment respiration, whereas in larger ponds or lakes, microbial processing of DOC in the water column tends to dominant

(Holgerson, 2015). Therefore, in shallow systems like stormwater facilities, the large amount of terrestrial carbon settling at the bottom may drive high respiration rates, leading to high CO_2 (Holgerson, 2015), while surface water DOC concentrations may not reflect these underlying processes, potentially explaining the unexpected negative effect. In this study the DOC was measured only in the upper layer of the water column, which may not fully capture the contribution of deeper organic carbon sources near the sediment-water interface where microbial activity is often more intense. This may be the same reason for having non-significant effect on CH_4, where a study done based on constructed wetlands has reported a strong positive correlation between DOC and CH_4 fluxes when they measured DOC at multiple depths down to the sediment interface where methanogenesis actively occurs (West et al., 2012).

Consistent with previous studies, NO_3^- concentrations were positively associated with CO_2 and N_2O fluxes (Audet et al., 2020; Bauduin et al., 2024), but showed no apparent relationship with CH_4. The observed positive correlations may reflect heterotrophic denitrification, where NO_3^- serves as an electron acceptor, driving the oxidation of organic matter (releasing CO_2) and producing N_2O as a byproduct (Burgin and Hamilton, 2007; Beaulieu et al., 2011). Also, higher concentrations of nitrogen stimulate nitrification, thus leading to consumption of DO, resulting in increased CO_2 production (Peacock et al., 2019). On the other hand, high nitrogen concentration in the water enhances algal growth, and this algal biomass settles down in the benthic region of the pond and degrades through the biological processes, resulting in high CO_2 production and emissions (Webb et al., 2019). High NO_3^- concentrations in the water column thus provide the substrate necessary

for increased CO_2 and N_2O production, particularly under fluctuating oxygen conditions, a common scenario in urban ponds (Wrage et al, 2001).

No significant relationship was observed between GHG fluxes and SO_4^{2-} concentration. In contrast to our observations, SO_4^{2-} concentration has been reported to have varying effects on CO_2 emissions in freshwater systems. Some studies have shown minimal influence on CO_2 emissions in shallow eutrophic lakes, suggesting that sulfate-driven anaerobic respiration may be limited under certain conditions (Liikanen, 2002) while Audet et al. (2020) reported SO_4^{2-} as a key factor influencing CO_2 fluxes because sulfate can enhance emissions by supporting sulfate-reducing bacteria, which oxidize organic matter and produce CO_2 under anoxic conditions. Moreover, some studies have shown a negative relationship between CH_4 emissions and SO_4^{2-} concentration, as sulfate-reducing bacteria can inhibit methanogenesis under anoxic conditions (Baron et al., 2022; Audet et al., 2020a). Not only that, some studies have shown that the sulfide produced through the reduction of SO_4^{2-} can inhibit the conversion of N_2O to N_2, suggesting that SO_4^{2-} concentrations may also influence N_2O levels (Audet et al., 2020a; Sørensen et al., 1980). As with DOC, our study focused only on near-surface water column SO_4^{2-} concentrations and thus likely underrepresented sulphate-reducing bacterial activity in deeper anoxic sediments.

In our study, NH_4^+ and PO_4^{3-} concentration showed no significant relationship with fluxes of any of the three studied GHGs. Similarly, previous research on constructed wetlands found that DOC was a strong predictor of CO_2 flux, whereas inorganic nutrients such as NH_4^+ and PO_4^{3-} had no significant influence (Wang et al. 2016). However, a positive relationship between NH_4^+ and N_2O fluxes has been identified under certain

conditions. For example, Singh et al.(2021)observed elevated N_2O fluxes in response to NH_4^+ enrichment via nitrification in shallow urban ponds. The lack of such relationships in this study suggests that N_2O production in these systems may instead be driven by NO_3^- availability rather than NH_4^+ oxidation.

This limited response to nutrient inputs may further be explained by the fact that, under nutrient-saturated conditions, primary production and microbial metabolism are often regulated by factors such as light, temperature and substrate quality, thereby reducing the impact of additional nutrient inputs (Kadlec & Wallace, 2009; D'Angelo & Reddy, 1999). Moreover, water nutrient concentrations vary substantially over time due to the dynamic nature of stormwater inputs, where storm events introduce and flush large volumes of water, altering water chemistry (Pollard, n.d.). Because of this high variability of nutrient concentration in stormwater ponds, sediment nutrient concentrations could be a more stable and reliable indicator of overall nutrient status.

2.4.4 Effect of physical characteristics of facilities on GHG fluxes

Stormwater facilities vary in design, structure and management history which can influence their capacity to produce and emit GHGs (Gorsky et al., 2019; Holgerson et al., 2024; Peacock et al., 2019). Understanding these physical and management controls could help to design stormwater management wetlands and ponds with lower GHG emissions. According to Holgerson (2015), the degree of saturation of CO_2 and CH_4 in small water bodies depends on biological characteristics and pond characteristics. Physical parameters such as pond depth and sediment depth determine the extent of stratification, thermal buffering and redox conditions that regulate microbial processes such as respiration, methanogenesis and denitrification (Søndergaard et al., 2023). Additionally, the age of the

pond, time since last dredging and catchment area size can shape biogeochemical dynamics by affecting allochthonous organic matter inputs, nutrient loads and sediment accumulation (Khan & Ansari, 2005; Van Bergen et al., 2019). Small ponds having a high P:A ratio and shallow depths indicate higher load of terrestrial carbon relative to water volume which can provide substrates for microbial respiration influencing GHG fluxes (Holgerson & Raymond, 2016). Thus, the key objective of this part was to determine the physical parameters that drive GHG fluxes (CO_2, CH_4, N_2O) in stormwater facilities

In contrast to the findings of Grinham et al. (2018) who reported differences in GHG emissions between facility types, the present study observed no such differences in consistent with the results of Peacock et al. (2019). This may be because the anthropogenic influence local to each pond overrides any effect on the pond's physicality or function (Audet et al., 2020b).

We observed a significant positive effect of sediment depth on CO_2 and N_2O flux because the production of these gases is particularly active in sediments enriched with organic matter and nitrogen loading (Beaulieu et al., 2011). Thick organic rich sediment layers often support higher microbial activity, increasing the sediment respiration depending upon the aeration (Lang et al., 2025) where, CO_2 can be a product of both anaerobic and aerobic mineralization of organic matter in sediments (Gorsky et al., 2019). Further, deeper sediments often promote the formation of sub-oxic and anoxic zones within the benthic layer, which are favorable for nitrogen transformation processes such as nitrification and denitrification. In addition, in shallow, well-mixed ponds, sediment respiration can affect the entire water column by increasing CO_2 concentrations (Holgerson & Raymond, 2016). Moreover, the rooted macrophytes oxygenate the sediment which

might promote degradation processes and the release of CO_2 (Audet et al., 2020) where most of the studied ponds had a considerable amount of macrophytes. Additionally, the presence of contaminants such as copper (Cu) and lead (Pb) in sediments can inhibit the final step of denitrification, the reduction of N_2O to dinitrogen (N_2) leading to greater N_2O accumulation and release (Blaszczak et al., 2018). Despite all these factors, differences in the community composition and abundance of microbial denitrifiers in pond sediments can also alter the composition of the final gaseous N products released to the atmosphere (Wallenstein et al., 2006).

Out of the three GHGs, CO_2 and CH_4 fluxes are known to be affected by pond depth. Previous studies have reported that pond depth is generally positively associated with CO_2 fluxes, while showing a negative relationship with CH_4 fluxes (Bastviken et al., 2004; DelSontro et al., 2016; Gorsky et al., 2019). Deeper water columns allow some labile organic matter to oxidize aerobically in the water column which can release CO_2 (Gorsky et al., 2019). Besides that, deeper water columns may enhance CH_4 oxidation into CO_2 during its upward diffusion through oxygenated layers, increasing CO_2 concentrations and decreasing CH_4 concentration (Bastviken et al., 2008; Holgerson & Raymond, 2016). Further, ebullition is strongly influenced by water column depth, where the limited depth in shallow water bodies reduces the opportunity for CH_4 oxidation, allowing a greater proportion of bubbles transported directly from sediments to the atmosphere (Ostrovsky et al., 2008), contributing to total CH_4 emissions (Bastviken et al., 2004; DelSontro et al., 2011). This is particularly evident in small and shallow systems (2-4 m deep), which emit more CH_4 due to increased sediment water interface with anoxic conditions and less opportunity for CH_4 oxidation (DelSontro et al., 2016; Holgerson, 2015). Accordingly, CO_2

fluxes showed a positive relationship with pond depth (Figure 2.18), while no significant effect of facility depth on CH_4 fluxes was observed. This may be because CH_4 fluxes are more strongly driven by internal biogeochemical processes than by physical parameters (Audet et al., 2020b; Gorsky et al., 2019). Moreover, the dominance of ebullition driven CH_4 emissions (68%) across ponds irrespective of their facility features, may have masked any potential relationship.

Dredging is a standard eco-engineering technology that permanently removes contaminated sediments from aquatic systems (Song et al., 2023). Hence, the impacts of dredging are centered around nutrients, organic matter content, and biological communities (Yan & Li, 2023). By removing the nutrient and organic-rich sediment, dredging reduces internal nutrient loading (Wan et al., 2020), which can, in turn, lower GHG fluxes (Nijman et al., 2022). Dredging can temporarily suppress nutrient cycling by disrupting microbial communities and removing active sediment layers (Song et al., 2023). This effect of dredging was clearly observed in CO_2 fluxes, with average fluxes highest in non-dredged facilities and lowest in recently dredged facilities (Figure 2.15). However, our study did not observe any direct effect of dredging on CH_4 and N_2O fluxes.

Sønderup et al. (2016) found that nutrient retention was highest in ponds less than 5 years old, whereas ponds older than 10 years retained little to no nutrients. This higher nutrient retention in younger ponds may enhance the biological activity, leading to increased GHG fluxes. However, no effect of pond age was observed on CO_2, N_2O and CH_4 fluxes in our study.

A significant positive effect of catchment area was observed only with CO_2 flux. This positive effect suggests that large and heterogeneous catchments typically contribute

more runoff and organic loading (Yang & Lusk, 2018), which can enhance microbial activity and CO_2 production in stormwater facilities. This nutrient and organic matter loading has also been shown also to drive CH_4 emissions by providing substrates for methanogenesis (Gorsky et al., 2019), but we did not observe any effect on CH_4 fluxes. Blaszczak et al. (2018), found no clear relationship between the proportion of urban land cover and the nutrient and contaminant concentrations in the stormwater pond sediments, suggesting no more specific conditions in the catchment over may be needed to explain variation in CH_4 flux.

Moreover, facilities with a low P: A ratio, which are typically more compact and circular in shape, may experience reduced edge effects, which can influence macrophyte cover and sediment oxygenation, potentially altering GHG production (Audet et al., 2020b). Further, the high P:A ratio of small urban ponds increases the relative length of shoreline resulting in high levels of allochthonous organic materials, which may play an important role in GHG production (Hanson et al., 2007). P:A ratio may also affect redox stratification and hydrologic retention, but this effect can be masked in systems dominated by external nutrient loads and rapid mixing (Audet et al., 2020b; Gorsky et al., 2019). However, the influence of pond size on GHG emissions remains controversial, with some studies reporting a significant effect (Holgerson and Raymond, 2016) while others have found no clear relationship (Peacock et al. 2019). In line with these mixed findings, our study did not detect a significant effect of the P:A ratio on GHG fluxes.

Altogether, our results suggest that CO_2 fluxes are regulated by a combination of sediment maturity, facility features and disturbance history. The lack of observed effects on CH_4 and N_2O may be due to overlapping ranges across ponds, frequent hydrologic

retention time and sediment-water interaction with unmeasured factors such as sediment quality or vegetation structure. Moreover, site-specific localized anthropogenic influences can override any effect of pond physical form (Audet et al., 2020b)

2.4.5 Comparison of GHG fluxes from southern Ontario stormwater facilities to other regions

Greenhouse gas emissions from stormwater facilities in our study were dominated by CO_2 and CH_4 fluxes, with little N_2O detected, as observed by studies in other regions (Audet et al., 2020b; Gorsky et al., 2019; Van Bergen et al., 2019).

The average CO_2 flux in our study was 760 mg CO_2 m^{-2} d^{-1}, which falls within the range reported for similar urban systems. Reported values include average CO_2 flux of 950 mg CO_2 m^{-2} d^{-1} from an urban pond in Netherlands (Van Bergen et al., 2019), and 752 mg CO_2 m^{-2} d^{-1} from urban ponds in Sweden (Peacock et al., 2019). In contrast, considerably higher fluxes have been observed in other stormwater management systems, such as 4100 mg CO_2 m^{-2} d^{-1} from stormwater channels in Canada (D'Acunha & Johnson, 2019) and 1500 mg CO_2 m^{-2} d^{-1} of CO_2 from stormwater ponds in Virginia, USA (Audet et al., 2020b). At the lower end, constructed wetlands and stormwater retention basins in Canada emit 40 mg CO_2 m^{-2} d^{-1} on average (Badiou et al., 2019a). Compared with these studies, our results are neither among the highest nor the lowest. Among all 24 sites, 37.5% of our sites showed net negative CO_2 flux, suggesting greater CO_2 uptake than respiration during the sampling period, while 62.5% were net emitters, a pattern consistent with prior studies (Gorsky et al., 2019; Lazar et al., 2014; Van Bergen et al., 2019). It is important to consider that our daytime-only sampling may underestimate daily emissions, as nighttime emissions may offset the uptake during the day because CO_2 concentrations will likely follow a diel cycle (Maberly, 1996).

According to our study, all the temperate stormwater management facilities acted as sources of CH_4 emissions throughout the sampling seasons, which aligns with most previous studies on urban aquatic systems (Bastviken et al., 2004; Grinham et al., 2018; Peacock et al., 2019; Van Bergen et al., 2019). The average CH_4 emissions in our study was 417 mg CH_4 m^{-2} d^{-1}, including both the ebullition and diffusion pathways. These rates are slightly higher than those reported in some prior studies. For example, two studies on urban ponds in Sweden and the Netherlands observed 160 and 120 mg CH_4 m^{-2} d^{-1}, respectively, including both diffusion and ebullition fluxes (Natchimuthu et al., 2014; Van Bergen et al., 2019). Further, CH_4 diffusion fluxes of 314 to 362 mg CH_4 m^{-2} d^{-1} were observed in urban wetlands and stormwater retention basins in Canada (Badiou et al., 2019) and stormwater ponds in the USA (Audet et al., 2020b), respectively.

In our study, N_2O fluxes contributed minimally to the overall GHG flux, consistent with the findings of Blaszczak et al. (2018), who concluded that urban stormwater facilities are unlikely to be significant sources of atmospheric N_2O. However, the average N_2O flux observed in our study, 0.23 mg N_2O m^{-2} d^{-1}, was slightly higher than those reported in previous studies. For instance, stormwater ponds in Virginia, USA, had an average flux of 0.1 mg N_2O m^{-2} d^{-1} (Audet et al., 2020b), while urban stormwater basins in Canada emitted 0.042 mg N_2O m^{-2} d^{-1} (Badiou et al., 2019). Among the 24 facilities we examined, 62.5% were net emitters of N_2O, whereas the remaining 37.5% of facilities showed negative fluxes of N_2O, indicating N_2O consumption exceeded their emissions.

Over the 7-month period, the average cumulative CO_2 emission per facility was 148 g m^{-2} (range: -229 to 945 g m^{-2}), CH_4 was 80 g m^{-2} (range: 22 to 272 g m^{-2}), and N_2O was 0.044 g m^{-2} (range: -0.025 to 0.309 g m^{-2}). Using 100-year global warming potential

(GWP) for each of the measured gases, the average total GWP per facility was 2400 g CO_2-eq m^{-2} (range: 380 to 8643 g CO_2-eq m^{-2}), with CH_4 contributing approximately 93% of the average total GWP. The average total GWP in this study is slightly higher than reported values for a riparian marsh wetland in Ohio. In that system, the open water areas emitted 2089 g CO_2-eq m^{-2}, and vegetated areas emitted 1407 g CO_2-eq m^{-2} during a similar period (Nag et al., 2017). These results suggest that stormwater facilities can emit GHG at comparable or even higher levels than natural wetlands. Furthermore, a study done based on CO_2 and CH_4 fluxes from four temperate ponds including three stormwater ponds and one natural forested pond (5m < maximum depth, <5 ha surface area) in Minnesota, USA reported annual emissions ranging from 1800 – 2600 g CO_2-eq m^{-2} (Rabaey & Cotner, 2024). Although their estimates span a full year, our shorter duration total (196 days) falls near the upper end of their range. It is important to note that the exclusion of N_2O in their study may led to lower reported totals.

According to the available statistics, the City of Waterloo has 103 stormwater management facilities, collectively covering a total area of 67 ha. Based on the average total GWP of 2400 g CO_2-eq m^{-2}, all these facilities are estimated to emit approximately 1617 Mg CO_2-eq (1.6 kt CO_2-eq) over the sampling period. The city of Kitchener has stormwater management facilities collectively covering a total area of 883 ha. These facilities are estimated to emit approximately 21,186 Mg CO_2-eq (21 kt CO_2-eq) over the sampling period.

2.4.6 Limitations of this study and recommendations

Our synoptic study demonstrates that the GHG emissions from stormwater management facilities are driven, in part by seasonal changes, in-situ environmental factors, water quality and physical properties of the facilities. However, the controls on GHG emissions from storm water facilities are not straightforward; much of the variation remained unexplained, suggesting that further drivers remain to be identified.

Including the site as a random effect significantly improved the models for GHG fluxes, highlighting the importance of site-specific variation. Hence, accounting for the site-specific variables will be further helpful to capture the variation in emissions within the ponds in future studies.

Unidentified drivers such as pond sediment properties, hydrology including groundwater, vegetation within and around the ponds, and associated microbial communities could relate to GHG fluxes. Submerged macrophytes have complex effects on GHG dynamics (Badiou et al., 2019a; Bastviken et al., 2023). As most of our studied facilities had noticeable amount of submerged vegetation, a vegetation survey and/or biomass sampling of submerged vegetation including chlorophyll measurements could have helped identify the impact of submerged vegetation on GHG cycling. The surrounding land cover of studied stormwater facilities is highly varied, with some facilities located in the center of green space, while some were connected to forested lands. Hence, investigation into the vegetation cover adjacent to the ponds could help to determine more drivers of GHG fluxes because differences in land use and cover influences aquatic ecosystem characteristics including nutrient levels and organic matter quantity and quality (Mitrovic & Baldwin, 2016; Vaughan et al., 2017).

Moreover, this study did not include any biodiversity measures as an explanatory factor for GHG emissions; however, there are several organisms, such as methanogenic archaea, methane-oxidizing bacteria, sulfate-reducing bacteria or nitrifying bacteria, related to production pathways of the GHG emissions studied. Thus, a further analysis including the abundance and diversity of related organisms is strongly suggested to be able to further analyze the emissions and understand the major drivers.

Finally, this study did not capture the winter and early spring fluxes. Although emissions from storm water facilities are probably low during the winter, their sum of emissions during winter and spring melt may account for an important portion of annual emissions (Denfeld et al., 2018). Therefore, our cumulative emissions represent some underestimate of annual emissions and future studies should aim to include year-round flux measurements.

2.5 Conclusion

This study investigated the GHG emissions from stormwater management facilities in Southern Ontario, along with the in-situ environmental, water quality and physical factors that influence these emissions. It was observed that stormwater management facilities were important sources of GHGs, especially CH_4 and CO_2 emissions. The mean daily fluxes were 760 mg CO_2 m^{-2} d^{-1}, 417 mg CH_4 m^{-2} d^{-1}, and 0.23 mg N_2O m^{-2} d^{-1}. All measured ponds were net emitters of CH_4 while 62.5% of them were net emitters of CO_2 and N_2O and the remaining 37.5% acted as sinks for these gases. Mean CO_2 and CH_4 fluxes were all similar to previous studies; however, the mean N_2O flux was slightly higher than reported for similar systems. Clear seasonal variations were observed for CO_2 and CH_4 fluxes, whereas N_2O fluxes varied minimally throughout the season. Carbon dioxide fluxes

were low in summer months compared to other seasons where CH_4 emissions observed higher in summer than late spring and autumn. Nitrous oxide fluxes gradually declined throughout the sampling period.

The results revealed the main drivers and their effects on the GHG fluxes. Water temperature, pH, DO, and DOC concentrations were negatively associated with CO_2 fluxes, indicating warm, more oxygenated and optimum pH levels may suppress CO_2 release. In contrast, higher NO_3^- concentration were associated with higher CO_2 flux. Moreover, facilities with deep sediment layers, greater pond depth, larger catchment areas, and younger ages tended to exhibit higher CO_2 fluxes. For CH_4, in-situ variables were the main drivers of emissions, where higher temperatures accelerate the emissions while higher DO and pH lower the emissions. However, the water quality and physical variables measured in this study did not significantly explain variation in CH_4 emissions. Finally, higher NO_3^- concentration, elevated DO and EC, and deeper sediment depth were each associated with increased N_2O fluxes.

Our results highlight that stormwater facilities act as sources of GHGs to the atmosphere throughout the whole study period. With the continued global expansion of urban areas, the number of stormwater facilities will continue to increase (Peacock et al., 2019; Seto et al., 2011), suggesting their cumulative contribution to regional carbon budgets may be significant. Therefore, small engineered aquatic systems must be included in climate mitigation and urban land use planning strategies. We also observed that the in-situ environmental variables, including water temperature, influence GHG fluxes from stormwater facilities, which may intensify under future climate warming scenarios. Hence, adopting adaptive design and maintenance strategies to minimize emissions from urban

stormwater infrastructures will be important. And, managing those infrastructures through proper maintenance and dredging at regular intervals is required, as the sediment accumulation in stormwater facilities can affect GHG fluxes.

Chapter 3
Conclusion

This synoptic study was conducted with the main objectives to quantify GHG fluxes from stormwater management facilities in Southern Ontario and to identify the key in-situ environmental, water quality and physical factors that explain variation in these fluxes. Specifically, the study focused on CO_2, CH_4 and N_2O fluxes measured over a seven-month period (May to November) across 24 stormwater management facilities and addressed research questions related to their temporal variations and the influence of different variables. The study aimed to: (1) quantify the CO_2, CH_4, and N_2O emissions from stormwater facilities (SWP and UW) and assess the temporal dynamics of GHG fluxes, (2) assess the effect of environmental variables (e.g., temperature, dissolved oxygen, pH and electrical conductivity) on GHG fluxes (3) assess the effect of pond water quality (e.g., nutrient and ion concentrations) on GHG fluxes, and (4) assess the effect of pond physical form (e.g., depth, perimeter) and catchment characteristics on GHG flux. In the following sections, the main findings are summarized for each gas separately and how those insights advance our understanding of the role of urban stormwater management facilities (UW and SWP) in regulating GHG emissions.

3.1 Carbon dioxide fluxes

Carbon dioxide fluxes from the studied stormwater ponds exhibited clear temporal variation, decreasing from late spring into the summer and then increasing again toward the autumn. However, UW deviated from this pattern, with elevated CO2 fluxes in summer, suggesting the temporal pattern may vary depending on pond type. This interaction suggests that differences in design, hydrology, substrate availability or biotic factors may

influence seasonal CO_2 gas exchange. On average, ponds emitted 760 mg CO_2 m^{-2} d^{-1}, with 62.5% functioning as net sources and 37.5% acting as sinks. Several in-situ environmental, chemical and physical variables significantly influenced CO_2 fluxes. Temperature and pH measured at all three depths in the water column were negatively correlated with fluxes, while DO concentration showed a significant negative effect at 10 cm and 50 cm below the surface. Among the measured chemical variables, DOC and NO_3^- concentrations showed significant effect on CO_2 fluxes. DOC concentrations were negatively associated while NO_3^- concentration was positively associated with CO_2 fluxes, likely reflecting enhanced microbial activity. Among physical features, pond depth, sediment depth and catchment area had positive impact, whereas pond age was negatively associated with CO_2 fluxes. The significant impact of dredging indicates that such physical disturbances can significantly alter carbon dynamics in stormwater facilities. These findings highlight the complex interactions between temporal conditions, vertical water column properties and pond scale characteristics shaping CO_2 dynamic across different stormwater facility types.

3.2 Methane fluxes

All 24 storm water facilities were net emitters of CH_4 throughout the sampling period. Methane fluxes from stormwater facilities showed strong temporal variation, increasing from late spring to summer and decreasing towards autumn. This trend reflects the strong temperature dependence of CH_4 production through microbial methanogenesis, which is typically enhanced under warmer, low oxygen conditions (Audet et al., 2020)**.** This significant seasonal effect was observed across all pond types, though the magnitude of emissions and the timing of seasonal peaks varied slightly among them, indicating a potential influence of site-specific characteristics. In-situ environmental variables particularly temperature DO, and pH were the significant drivers of CH_4 fluxes in this

study. Temperature across all three depths showed a strong positive relationship with CH_4 emissions, while pH at 10 cm above the sediments and DO concentration at 50 cm below the surface were negatively associated with aligning with anaerobic conditions favoring CH_4 production. In contrast to CO_2, pond water quality and physical characteristics, such as nutrient concentrations and sediment depth, pond depth, catchment area did not significantly influence CH_4 fluxes. These findings suggest that CH_4 emissions in stormwater ponds are largely controlled by environmental conditions within the water column, rather than structural pond attributes.

3.3 Nitrous oxide fluxes

Nitrous oxide fluxes from the studied facilities were low compared to the other two GHGs and showed minimal seasonal variation compared to them. Mean daily fluxes were 0.23 mg N_2O m^{-2} d^{-1} across the sampling period, with 62.5% of the ponds acting as net sources and the remaining 37.5% functioning as sinks. Although the overall fluxes declined slightly over time, no clear seasonal pattern was evident. Nitrate concentration was one of the most significant predictors that showed a positive relationship with N2O fluxes, likely due to its role in microbial nitrification and denitrification processes (Van Bergen et al., 2019). Moreover, DO concentration at 10 cm below the surface and 10 cm above sediment and EC at all three depths and sediment depth also positively influenced N_2O emissions. Unlike CO_2 and CH_4, N_2O fluxes did not respond to variations in temperature or pH, and physical characteristics such as pond depth, pond age, P:A ratio or catchment area. These findings suggest that N_2O production in stormwater management facilities is more tightly linked to nutrient availability and redox sensitive conditions near sediments and less to seasonal or structural factors.

While this study provides comprehensive understanding of GHG emissions from stormwater management facilities and the variables influencing them, the findings should be interpreted considering certain limitations. The results and interpretations of this study must be considered within the context of error and uncertainty, which can propagate through the work at each stage, from conceptualization, methodology, data collection, and analysis. The analysis was based on data collected over a single sampling period within a year, and although key environmental variables were measured at multiple depths, some underlying processes particularly microbial activity and sediment interactions could not be directly assessed. Despite these constraints, the observed variability across gas types, seasons and pond types emphasizes the complexity of biogeochemical functioning in urban stormwater management systems and highlights the importance of continued investigation into their roles as both sources and sinks of GHGs. This research is a part of the RISE (Residential Development Impact Scorecard for the Environment) project, which aims to develop a simple, dynamic GHG and carbon scorecard to complement green building standards of residential developments. As a part of this initiative, this research provides critical data on GHG emissions from urban stormwater facilities, helping fill a major gap in urban carbon accounting. The findings demonstrate that these stormwater facilities are sources of GHGs under the influence of various environmental conditions, water quality variables, and physical factors. Hence, when designing new stormwater facilities and managing existing ones, it should be a priority to consider the significant drivers of GHG emissions and proactively mitigate them. Finally, these findings can be directly applied in the RISE Scorecard to identify stormwater features associated with lower emissions and effective mitigation measures.

3.4 Future research needs and implications

The findings of this study highlight the complex and dynamic nature of GHG fluxes in stormwater management facilities but also point to several areas where further research is needed for further understanding and improve the accuracy of emission assessments. First, long-term data on GHG emissions from stormwater facilities is essential to better understand how fluxes vary across seasons, years and climatic conditions. This study captured a single open-water season, which limits the ability to separate consistent seasonal trends from interannual variability. Multi-year datasets are needed to assess the influence of climate variation, storm events and hydrological extremes on CO_2, CH_4 and N_2O emissions.

Second, further research is required to directly quantify microbial processes and sediment dynamics that drive GHG production and consumption in these systems. While this study inferred microbial activity based on in-situ parameters such as temperature, DO concentration and nutrient concentrations, measurements of sediment chemistry, redox potential and microbial community structure would allow for a more mechanistic understanding of GHG cycling. Future studies should also consider measuring pore water gas concentrations and microbial enzyme activity to better link surface fluxes with underlying biogeochemical pathways.

Moreover, future research should explore the influence of hydrological and biogeochemical factors that we did not include in this study, such as water retention time, inflow volume and quality, and the carbon and nutrient content of incoming runoff. Assessing how inflow characteristics and hydrologic connectivity affect internal pond

processes could help to improve understanding of the external drivers that regulate GHG fluxes in urban stormwater systems.

At the applied level, these findings are important in upscaling approaches for GHG emission estimates. For instance, extrapolating emissions based on stormwater facility area can support regional GHG emission reporting. The results of this study clearly illustrate that stormwater management facilities are active biogeochemical systems whose behavior can vary with season and environmental conditions. Hence, developing predictive models that link fluxes to environmental drivers will be helpful in predicting future fluxes with a changing climate. Such approaches will allow municipalities to compare these emissions with other urban sources, such as landfills and transportation.

The study identifies opportunities to mitigate the emissions. When designing or retrofitting, developers can incorporate the features that reduce GHG production and emissions, such as deeper ponds with large oxic zones to suppress CH_4 by enhancing oxidation. For the existing facilities, effective management practices, including periodic dredging to reduce organic matter and nutrient accumulation, reducing nutrient inputs from catchments, and strategically planting vegetation, can be beneficial. Other than that, proper aeration methods can be introduced to increase oxygen availability. Incorporating such strategies into design guidelines could support broader climate objectives, including progress toward net-zero emissions.

As urbanization continues and climate patterns shift, the role of stormwater management facilities in carbon and nitrogen cycling may become increasingly important. Their role as potential sources and sinks of GHGs mean they cannot be overlooked in broader efforts to quantify and manage urban emissions.

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Appendix

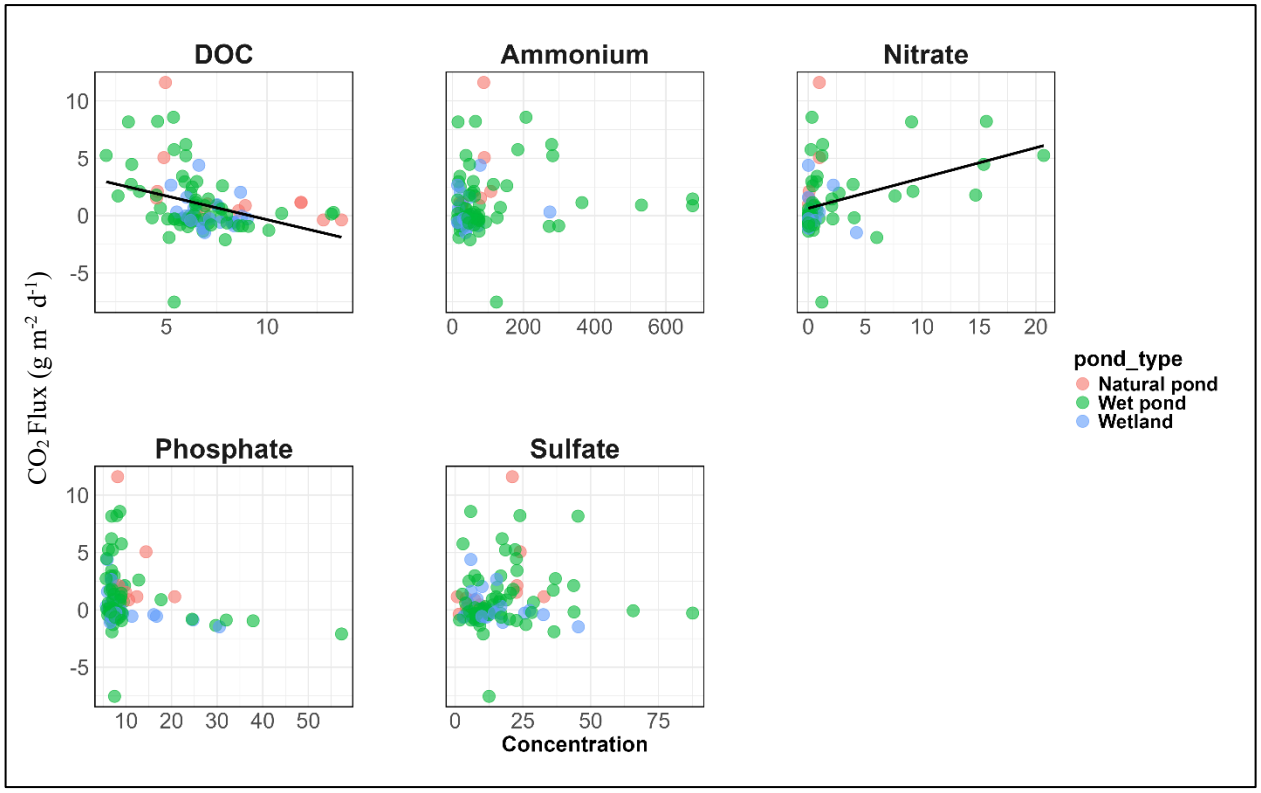


Figure A1: Scatterplot depicting the relationship between chemical variables and CO_2 flux. The x-axis represents concentration of the relevant variable, and the y-axis represents CO_2 flux (g m^2 day^{-1}). Each subplot represents a different in-situ environment parameter measured at one of three depths. DOC = Dissolved Organic Carbon (mg/L), Nitrate /Sulphate (mg/L), Phosphate/Ammonium (µg/L).

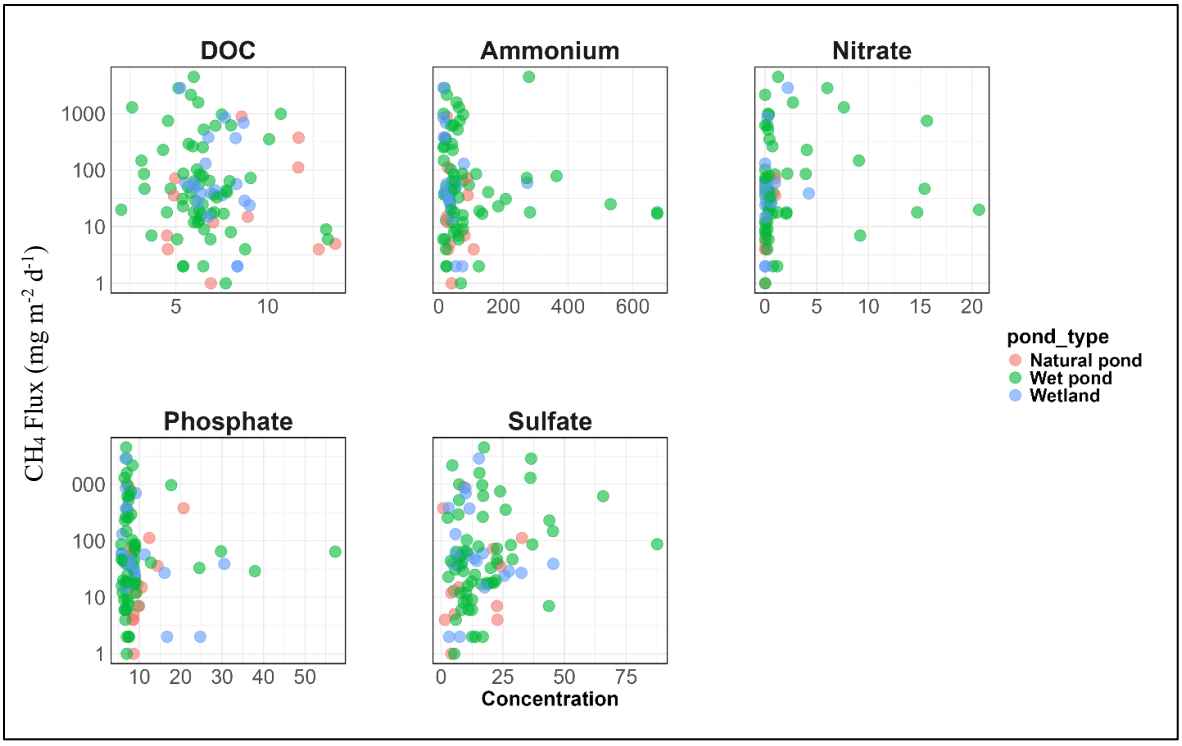


Figure A2: Scatterplot depicting the relationship between chemical variables, and CH_4 flux. The x-axis represents concentration of the relevant variable, and the y-axis represents CH4 flux (mg m^2 day^{-1}). DOC = Dissolved Organic Carbon (mg/L), Nitrate /Sulphate (mg/L), Phosphate/Ammonium (µg/L).

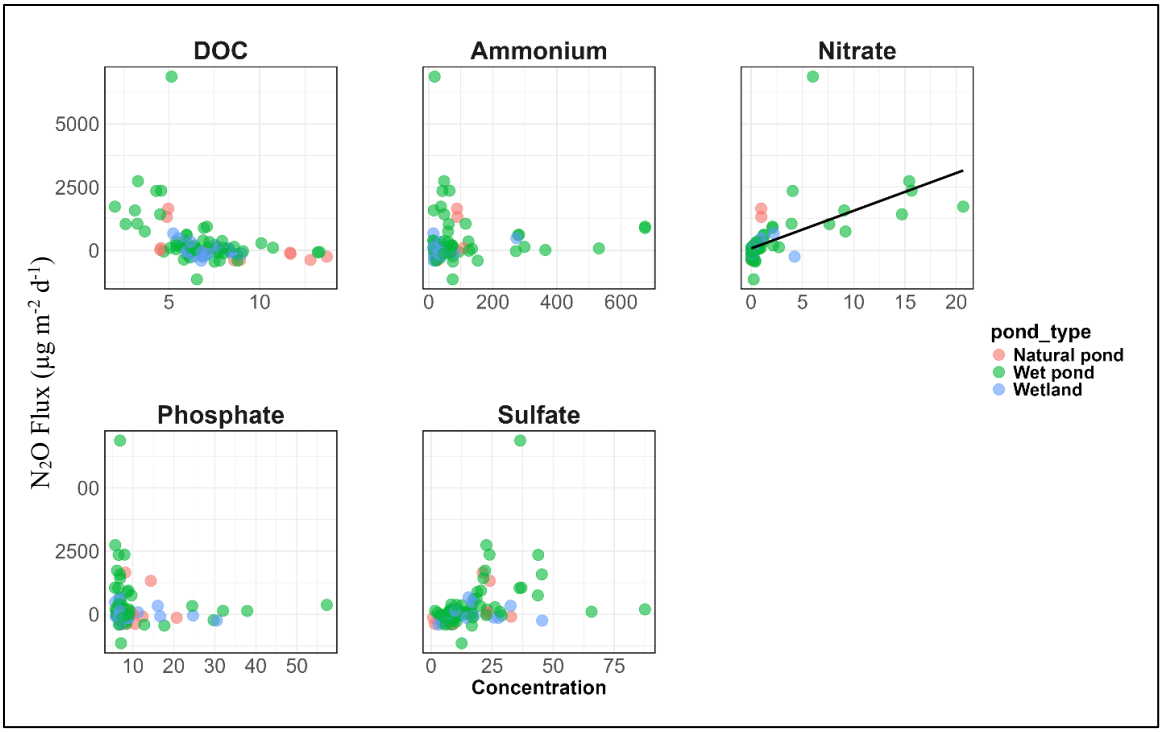


Figure A3: Scatterplot depicting the relationship between chemical variables, and N_2O flux. The x-axis represents concentration of the relevant variable, and the y-axis represents N_2O flux (µg m^2 day^{-1}). DOC = Dissolved Organic Carbon (mg/L), Nitrate /Sulphate (mg/L), Phosphate/Ammonium (µg/L).

Table A1: Concentrations of measured water quality variables in this study

Pond ID	Location	Month	DOC (mg/L)	NH_4^+ (µg/L)	PO_4^{3-} (µg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)
K30	Inlet	June	6.224	55.2	7.01	2.708	15.529
K30	Outlet	June	6.496	24	7.49	0.777	13.89
K30	Inlet	October	7.61	135	9.44	0.7128	16.28
K30	Outlet	October	7.51	75.6	17.7	0.3955	16.66
K4	Inlet	June	6.517	58.9	7.41	0.316	7.233
K4	Outlet	June	6.288	22.5	6.91	na	5.108
K4	Inlet	October	5.36	207	8.64	0.3319	5.74
K4	Outlet	October	5.39	184	8.99	0.2479	2.9
K108	Inlet	June	11.7	21.1	20.7	na	0.791
K108	Outlet	June	11.68	28	12.4	na	32.76
K108	Inlet	October	13.7	33.4	8.6	0.07	5.38
K108	Outlet	October	12.8	29.2	8.53	0.0147	1.501
K138	Inlet	June	8.925	25.5	10.6	na	7.163
K138	Outlet	June	8.593	24.9	7.46	na	9.179
K138	Inlet	October	7.04	28.4	9.08	0.0315	4.073
K138	Outlet	October	6.91	40.1	8.61	0.0344	4.11
K40	Inlet	June	8.689	22.3	9.13	na	9.941
K40	Outlet	June	7.524	21.9	7.84	na	8.082
K40	Inlet	October	8.36	73	24.7	0.0221	7.5

K40	Outlet	October	8.36	52	16.7	0.0446	3.16
K94	Inlet	June	5.395	124	7.49	1.197	12.521
K94	Outlet	June	5.397	23.5	6.98	na	16.87
K94	Inlet	October	6.24	93.4	7.25	0.065	7.96
K94	Outlet	October	6.15	37.4	8.25	0.0211	10.38
K95	Inlet	June	5.988	74	9.26	0.23	10.068
K95	Outlet	June	6.071	32.4	37.9	na	8.935
K95	Inlet	October	6.83	75.1	29.7	0.0248	9.1
K95	Outlet	October	7.09	17	8.51	0.0187	6.62
K115	Inlet	June	5.697	40.9	8.05	na	6.982
K115	Outlet	June	5.654	23.1	8.12	na	7.454
K115	Inlet	October	5.82	25.2	8.33	0.0181	4.5
K115	Outlet	October	6	40.6	8.63	0.0646	6.04
K61	Inlet	June	5.805	21.3	6.83	0.785	22.833
K61	Outlet	June	5.925	17.5	6.75	0.722	16.846
K61	Inlet	October	4.81	26.8	9.82	0.1733	26.8
K61	Outlet	October	4.71	35.2	8.76	0.2437	28.9
K100	Inlet	June	8.303	24.1	11.3	0.227	10.938
K100	Outlet	June	8.264	18.3	6.79	na	11.467
K100	Inlet	October	8.75	33.7	8.84	0.0986	27.48
K100	Outlet	October	9.02	36.4	8.95	0.0457	25.63

K101	Inlet	June	5.144	18.6	6.9	6.022	36.483
K101	Outlet	June	10.09	21.8	7.16	0.438	26.125
K101	Inlet	October	3.67	60.6	9.7	9.199	43.73
K101	Outlet	October	6.31	47.1	8.55	0.9496	28.25
K151	Inlet	June	4.885	89.9	14.4	0.988	24.006
K151	Outlet	June	4.962	88.3	8.17	0.98	21.104
K151	Inlet	October	4.52	79.4	9.93	0.0704	22.6
K151	Outlet	October	4.56	108	8.39	0.0871	22.8
K107	Inlet	June	5.974	279	6.82	1.271	17.353
K107	Outlet	June	5.971	282	7.05	1.218	18.584
K107	Inlet	October	6.92	675	8.66	2.066	18.9
K107	Outlet	October	7.09	675	8.95	2.0866	20.4
W39	Inlet	June	5.235	14.8	6.7	2.205	15.316
W39	Outlet	June	6.908	37.1	30.5	4.238	45.468
W39	Inlet	October	5.52	274	5.68	0.9662	16.9
W39	Outlet	October	5.98	53	6.04	0.0228	13.2
W40	Inlet	June	6.272	126	6.8	0.375	12.351
W40	Outlet	June	6.541	74.9	7.14	0.244	12.489
W40	Inlet	October	13.2	54.6	6.35	0.0405	10.4
W40	Outlet	October	13.3	62	6.57	0.0337	11.1
W45	Inlet	June	6.775	16.1	6.89	na	3.005

W45	Outlet	June	6.371	16.9	6.73	0.247	4.678
W45	Inlet	October	6.62	78	5.89	0.0216	5.8
W45	Outlet	October	6.02	49.7	5.93	0.0243	5.9
W7	Inlet	June	7.152	39.1	7.11	0.249	65.697
W7	Outlet	June	6.887	13.9	6.46	na	8.228
W7	Inlet	October	8	47	7.38	0.0401	9.1
W7	Outlet	October	7.72	68.6	6.97	0.0227	5.3
W42	Inlet	June	10.73	15.6	7.03	0.301	7.267
W42	Outlet	June	8.781	22.3	6.65	0.227	5.928
W42	Inlet	October	6.39	74	5.78	0.2095	10.8
W42	Outlet	October	6.19	43.2	5.99	0.0246	7.7
W52	Inlet	June	6.467	15.1	7.35	na	2.649
W52	Outlet	June	8.59	299	32	na	1.624
W52	Inlet	October	7.79	153	12.8	0.4093	8.4
W52	Outlet	October	7.75	39.3	6.12	0.0253	3.9
W15	Inlet	June	5.411	73	9.03	2.159	87.62
W15	Outlet	June	5.074	20.3	6.99	0.349	12.483
W15	Inlet	October	6.46	531.2	7.15	0.5418	13.7
W15	Outlet	October	6.47	364.1	8.88	0.3749	15.1
W35	Inlet	June	6.206	36.3	16.1	0.622	32.548
W35	Outlet	June	7.678	14.7	6.77	0.236	9.843

W35	Inlet	October	7.15	31	7.79	0.0237	14.4
W35	Outlet	October	6.79	41.3	6.54	0.0332	17.6
W34	Inlet	June	3.124	16.1	6.87	9.079	45.338
W34	Outlet	June	4.301	43	6.57	4.043	43.884
W34	Inlet	October	2.61	62.6	6.49	7.6265	36.2
W34	Outlet	October	3.26	115.4	5.65	3.94	37
W19	Inlet	June	7.224	61.4	24.5	0.507	20.081
W19	Outlet	June	7.929	49.7	57.3	na	10.368
W19	Inlet	October	9.08	272.2	9.02	0.047	22.6
W19	Outlet	October	8.01	46.3	7.58	0.0313	17
W31	Inlet	June	4.573	65	7.97	15.648	23.916
W31	Outlet	June	4.512	48.4	6.91	14.707	21.417
W31	Inlet	October	2.02	38.3	6.14	20.6815	22.1
W31	Outlet	October	3.29	48.3	5.73	15.4177	22.6

Table A2: Spearman correlation coefficient among in-situ environmental variables.

	CH4	CO2	DO_10	DO_50	DO_as	EC_10	EC_50	EC_as	N2O	pH_10	pH_50	pH_as	T_10	T_50	T_as
CH4	1	-0.06299	-0.06752	-0.1502	-0.1303	0.066516	0.075164	0.079214	0.044852	0.019215	-0.04262	-0.14013	0.282256	0.263465	0.269425
CO2		1	-0.45712	-0.32699	-0.10682	0.071959	0.084239	0.115012	0.154145	-0.58983	-0.54414	-0.40335	-0.29904	-0.26076	-0.27239
DO_10			1	0.841659	0.506787	0.426117	0.410656	0.387168	0.270903	0.520977	0.461531	0.345743	0.19355	0.1091	0.07944
DO_50				1	0.673873	0.425735	0.395998	0.366627	0.289906	0.377966	0.479688	0.425067	0.059489	0.031648	-0.00747
DO_as					1	0.215827	0.201677	0.137253	0.263975	0.192168	0.325015	0.614392	-0.20434	-0.1978	-0.09502
EC_10						1	0.981401	0.940859	0.495745	0.007023	0.024573	-0.03511	0.22224	0.203561	0.139735
EC_50							1	0.956592	0.498338	-0.00808	-0.01614	-0.06055	0.222184	0.197357	0.141693
EC_as								1	0.492019	-0.0142	-0.02978	-0.13337	0.23539	0.213277	0.127636
N2O									1	-0.00175	0.017791	0.046809	0.162426	0.147962	0.143444
pH_10										1	0.871417	0.624307	0.375592	0.292853	0.263243
pH_50											1	0.758434	0.275633	0.250987	0.209451
pH_as												1	-0.03605	-0.04556	0.049814
T_10													1	0.952587	0.871152
T_50														1	0.915351
T_as															1