Greenhouse Gas Dynamics in a Freshwater Wetland in Southeastern Ontario: Field Measurements and Laboratory Incubations

By
Calder Jones
Department of Geography
McGill University, Montreal, Quebec
July 2024

A thesis submitted to McGill University
in partial fulfillment of the requirements of the degree of
Master of Science

Abstract

Concentrations of dissolved carbon dioxide (CO_2), dissolved methane (CH_4), and dissolved nitrous oxide (N_2O) were measured in open water areas across a freshwater mineral wetland in the Ottawa Valley. 268 samples were collected on 19 sampling days from September 16th, 2022 to February 5th, 2024. Average dissolved CO_2 ranged from 111 µmol/liter in the spring, to 2548 µmol/liter in mid-winter. Average dissolved CH_4 ranged from 3.33 µmol/liter in the autumn, to 1414 µmol/liter in mid-winter. Average dissolved N_2O concentrations ranged from 0.016 µmol/liter below ambient to 0.036 µmol/liter. CO_2, CH_4, and N_2O accumulated under ice, resulting in high concentrations in winter. Concentrations of CO_2 and CH_4 declined in the autumn and increased from the spring until the end of summer. In late summer, CO_2 and CH_4 concentrations were higher than during the mid-summer despite lower temperatures. These higher gas concentrations coincided with the presence of dense flocks of migrating Canada geese. To further investigate the potential influence of the Canada goose migration and other nutrient sources on greenhouse gas emissions, two laboratory incubations of saturated soils in sealed jars were performed. The first incubation compared a control group with treatment groups of K_2SO_4, KH_2PO_4, KNO_3, and biochar. Each group had five replicates measured 17 times over 141 days for concentrations of CO_2, CH_4, and N_2O. Additions of fertilizers and biochar did not have a large impact on measured gases. The second incubation compared a control group with treatment groups of two different application rates of goose feces and cattle manure. Each group had five replicates measured 20 times over 78 days for concentrations of CO_2, CH_4, and N_2O. Goose feces and cow manure additions led to an increase in peak production of CO_2, CH_4, and N_2O. This research demonstrates the importance of year-round sampling across an entire wetland system and a new understanding of seasonality that includes the influence of nutrient additions from migrating species and local land use.

Résumé:

Les concentrations de dioxyde de carbone dissous (CO_2), de méthane dissous (CH_4) et d’oxyde nitreux dissous (N_2O) ont été mesurées dans des zones d’eau libre à travers une zone humide minérale d'eau douce dans la vallée de l'Outaouais. 268 échantillons ont été prélevés sur 19 jours d’échantillonnage du 16 septembre 2022 au 5 février 2024. La teneur moyenne en CO_2 dissous variait de 111 µmol/litre au printemps à 2 548 µmol/litre au milieu en hiver. La teneur moyenne en CH_4 dissous variait de 3,33 µmol/litre en automne à 1 414 µmol/litre au milieu de l’hiver. Les concentrations moyennes en N_2O dissous variaient de 0,016 µmol/litre sous des concentrations de l'air ambiant à 0,036 µmol/litre. Le CO_2, le CH_4 et le N_2O se sont accumulés sous la glace, ce qui donnait des concentrations élevées en hiver. Les concentrations de CO_2 et de CH_4 ont diminué en automne et ont augmenté du printemps jusqu'à la fin de l'été. À la fin de l'été, les concentrations de CO_2 et de CH_4 étaient plus élevées qu'au milieu de l'été malgré des températures plus basses. Ces concentrations de gaz plus élevées coïncidaient avec la présence de troupeaux denses d'oies canadiennes migratrices. Afin d'étudier plus en détail l'influence potentielle de la migration des oies canadiennes et d'autres sources de nutriments sur les émissions de gaz à effet de serre, deux incubations en laboratoire de sols saturés dans des bocaux hermétiques ont été réalisées. La première incubation a comparé un groupe témoin à des groupes traités de K_2SO_4, KH_2PO_4, KNO_3 et de biochar. Chaque groupe a eu cinq échantillons mesurés 17 fois sur 141 jours pour les concentrations de CO_2, CH_4 et N_2O. Les ajouts d'engrais et de biochar n'ont pas eu d'impact important sur les gaz mesurés. La deuxième incubation a comparé un groupe contrôle à des groupes traités de deux taux d'application différents de matières fécales d'oie et de fumier de bovin. Chaque groupe avait cinq échantillons mesurés 20 fois sur 78 jours pour les concentrations de CO_2, CH_4 et N_2O. Les ajouts d'excréments d'oie et de fumier de vache ont donné une augmentation de la production maximale de CO_2, CH_4 et N_2O. Cette recherche démontre l'importance d'un échantillonnage tout au long de l'année dans l'ensemble d'un système de zones humides, et une nouvelle compréhension de la saisonnalité qui inclut l'influence des ajouts de nutriments provenant des espèces migratrices et de l'utilisation des terres locales.

Acknowledgements

I would like to express my gratitude to my supervisor, Dr. Christian von Sperber. His support and guidance have been invaluable and are always given generously. Additionally, I am grateful for the professional advice, academic opportunities, and financial support he has given me over the years. I would like to thank Ducks Unlimited Canada and Environment and Climate Change Canada: Climate Action and Awareness Fund for funding this research. I would like to thank my co-supervisor, Dr. Tim Moore, for his mentorship, friendship, and knowledge. I also thank Dr. Nigel Roulet for his guidance and expertise. I am grateful to Mike Dalva of the Geography department at McGill University for his immeasurable laboratory and field support as well as his sense of humor and encouragement. I would like to thank Charles Duncan for his enthusiastic and diligent support in the field and laboratory. Likewise, I would like to thank Julie Cagnard for her hard work in the laboratory. I am grateful to Michel La Haye, and Annete and Sylvain Le Page for their donation of their time and knowledge. I would like to thank my family and friends for the endless support throughout my life and specifically my cousin, Sammi Massey, for providing the French translation of my abstract. Lastly, I would like to thank my wife, Claudia, for all the love and encouragement she provides.

Contribution of Authors:

This thesis was written entirely by myself, Calder Jones, with the valued guidance of Dr. Christian Von Sperber and Dr. Tim Moore

Table of Contents

List of Figures

Chapter 1

Chapter 2

Chapter 3

List of Tables

Chapter 1

Chapter 2

Supplementary tables

Chapter 1: Introduction

Wetlands are critical ecosystems in the global carbon cycle with variable characteristics across Canada and the world. Determining which characteristics influence greenhouse gas emissions with more widespread sampling of individual wetlands can increase the understanding of wetland heterogeneity and improve estimates of their role in the carbon cycle. Additionally, year-round sampling is important to capture seasonal variations in temperate climates. This thesis considers the seasonal variations of dissolved greenhouse gases in a wetland in southeastern Ontario. To quantify and understand the factors influencing these seasonal variations, I measured multiple environmental parameters in the field. Additionally, I performed laboratory incubation experiments to monitor how additions of nutrients impact greenhouse gas production. This introductory chapter serves to familiarize the reader with wetlands and the basic processes that control greenhouse gas emissions within wetlands.

Wetlands have the highest carbon density of any terrestrial ecosystem (Kayranli et al., 2010). Wetlands are ecosystems defined by hydrology. According to the United States Environmental Protection Agency, **“**Wetlands are areas where water covers the soil or is present either at or near the surface of the soil all year or for varying periods of time during the year, including during the growing season.” While wetlands make up only 5-8% of the earth’s surface, they contain 30% of the world’s soil carbon (Kayranli et al., 2010). Wetlands are considered a nature-based solution to climate change that could serve as carbon sinks to mitigate global warming (Badiou et al., 2018; Drever et al., 2021). Despite increasing awareness of their importance, wetlands continue to be drained to expand agriculture and infrastructure (Euliss et al., 2006; Drever et al., 2021). Wetland systems are hotspots for the opposing processes of carbon sequestration and greenhouse gas (GHG) production (Badiou et al., 2018). While the accumulation of carbon in wetland sediment is undisputed, wetlands emit GHG, especially large amounts of methane (CH_4) (Z. Zhang et al., 2017). Their role as a net source or sink of GHG depends on age, soil type, hydrology, and chemical composition of sediments and water (Bridgham et al., 2013).

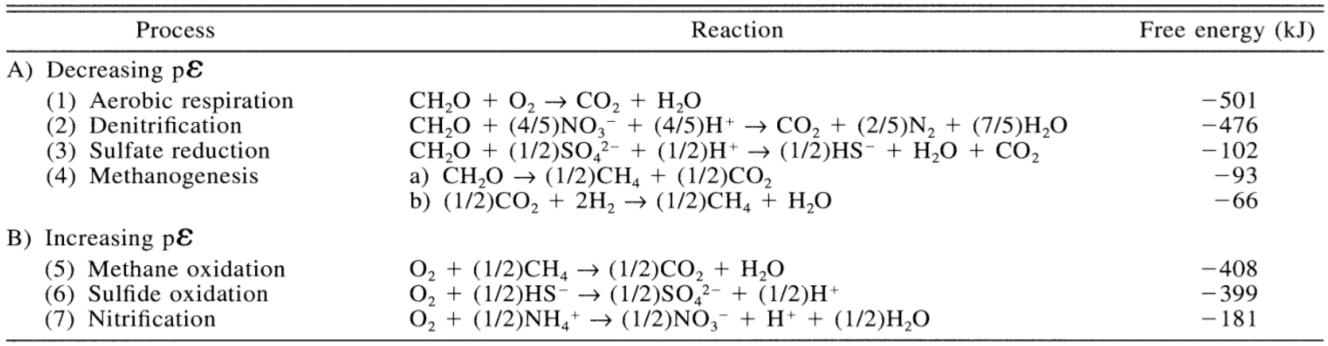
Wetlands provide ideal conditions for the accumulation of carbon due to a high water table. In freshwater mineral wetlands, plants photosynthesize and take up CO_2 from the atmosphere. When plants die, the carbon they have accumulated will persist because waterlogged conditions limit aerobic respiration and slow decomposition (Kayranli et al., 2010). Wetland forms of carbon include dissolved organic carbon (DOC), dissolved inorganic carbon, biomass carbon, particulate organic carbon, microbial biomass carbon, carbonates, and gaseous carbon (e.g. CH_4 and CO_2) (Wynn & Liehr, 2001; Reddy & DeLaune, 2008).

To summarize, wetlands are carbon sinks because of low rates of decomposition. High water tables cause anaerobic conditions which limit microbial respiration. These anaerobic conditions limit CO_2 emissions but lead to the production of CH_4 and nitrous oxide (N_2O) (Kayranli et al., 2010).

1.1: Oxidation-Reduction Reactions

Oxidation-reduction potential (ORP) regulates the chemical reactions occurring in a wetland system. Oxidation-reduction (redox) reactions in wetlands involve microbial populations transferring electrons from one chemical species to another. Throughout these electron transfers, energy stored in carbon compounds is released, fueling the metabolic processes of microbial populations responsible for the reaction. The order of these reactions is determined by the potential energy released (Bridgham et al., 2013). The most productive reactions and their corresponding microbial populations out-compete others until that reaction is no longer possible because of limitations on electron donors, electron acceptors, or substrate. The dominant redox reaction in a system is determined by this order of energy efficiency; therefore, when discussing redox reactions, a measurement known as oxidation reduction potential (ORP) is utilized to quantify the balance between oxidizing and reducing agents.

The most important redox reactions are listed in Table 1.1 (Hedin et al., 1998). When a system's ORP is declining (consuming electron acceptors) the first reaction is aerobic respiration (CO_2 produced). As oxygen (O_2) is consumed through respiration, it is less available as an electron acceptor and denitrification (N_2O produced) takes over. As nitrate (NO_3^-) is consumed, sulfate (SO_4^{2-}) reduction takes over (hydrogen sulfide produced), consuming the electron acceptor SO_4^{2-}. Lastly, CH_4 is produced in a process called methanogenesis (Hedin et al., 1998).



Process	Reaction	Free energy (kJ)
A) Decreasing pε		
(1) Aerobic respiration	$CH_2O + O_2 \rightarrow CO_2 + H_2O$	−501
(2) Denitrification	$CH_2O + (4/5)NO_3^- + (4/5)H^+ \rightarrow CO_2 + (2/5)N_2 + (7/5)H_2O$	−476
(3) Sulfate reduction	$CH_2O + (1/2)SO_4^{2-} + (1/2)H^+ \rightarrow (1/2)HS^- + H_2O + CO_2$	−102
(4) Methanogenesis	a) $CH_2O \rightarrow (1/2)CH_4 + (1/2)CO_2$	−93
	b) $(1/2)CO_2 + 2H_2 \rightarrow (1/2)CH_4 + H_2O$	−66
B) Increasing pε		
(5) Methane oxidation	$O_2 + (1/2)CH_4 \rightarrow (1/2)CO_2 + H_2O$	−408
(6) Sulfide oxidation	$O_2 + (1/2)HS^- \rightarrow (1/2)SO_4^{2-} + (1/2)H^+$	−399
(7) Nitrification	$O_2 + (1/2)NH_4^+ \rightarrow (1/2)NO_3^- + H^+ + (1/2)H_2O$	−181

Table 1.1: Sequence of microbial oxidation-reduction reactions: ordered by free energy yield under decreasing oxidation-reduction potential or reducing conditions (A) and increasing oxidation reduction potential or oxidizing. conditions (B) Reproduced from “Thermodynamic Constraints on Nitrogen Transformations and Other Biogeochemical Processes at Soil-Stream Interfaces.” By Hedin, L. O., von Fischer, J. C., Ostrom, N.E., Kennedy, B. P., Brown, M. G., & Robertson, G. P. (1998). *Ecology*, *79*(2), 684–703.

Wetlands go through these stages as the water table rises and falls, because O_2 diffuses much slower in water compared to air (Yanful, 1993). When sediments are drier, O_2 easily diffuses into soil pores to supply microbial demands. When the soil pores are filled with water, O_2 diffusion slows down to such a degree that O_2 demand surpasses the rate of supply. If these hydrological conditions are sustained, O_2 is depleted and reducing conditions dominate. Different parts of the wetland system may experience different redox conditions concurrently. During periods of flooding, reducing conditions may dominate in the sediment, while precipitation and fresh flood waters oxidize the water column. When the water table drops, exposed sediments undergo oxidizing conditions while the shallower waters may heat up, reducing dissolved O_2. Despite these differences in ORP, emission of GHG is largely dependent on the ORP of sediments. For this reason, water table depth may be the best indicator of CH_4 emissions (Moore & Dalva, 1993). This is because with a higher water table, sediments are more likely anaerobic with ORP falling as O_2 , NO_3^- , and SO_4^{2-} are being depleted. At some point during sustained reducing conditions ORP will favor methanogenesis, producing CH_4.

Methanogens involved in CH_4 production are in competition with SO_4^{2-} reducing microbes, and both processes may occur together simultaneously in sediments with heterogenous ORP (Badiou et al., 2018). Because substrate and electron donor availability determine which reaction will occur, wetlands that are well oxygenated, or rich in NO_3^- and SO_4^{2-} may not produce CH_4. This overview briefly explains why CH_4 emissions are strongly tied to ORP with significant CH_4 emissions occurring only when ORP is below -100 mv (Hou et al., 2000).

1.2: CO_2 Production and Consumption

CO_2 is generated through various natural processes in wetland ecosystems, primarily plant and microbial respiration (Raich & Schlesinger, 1992; Kayranli et al., 2010). Plants and plant roots produce CO_2 through respiration when they oxidize stored carbohydrates to release energy, producing CO_2 and water as end products. Decomposition of organic matter also contributes to CO_2 production in wetlands. As dead plant material and other organic debris decompose, microorganisms break down complex organic molecules, releasing CO_2. Microbial respiration is a major source of CO_2 in wetland soils. Additionally, fermentation produces CO_2 as organic molecules are partially oxidized, with by-products including CO_2 (Kristensen et al., 2008). Various environmental factors such as temperature, soil moisture levels, pH, and the availability of organic matter and nutrients influence CO_2 production in wetlands (Ullah & Moore, 2011). Warmer temperatures accelerate microbial activity and therefore increase CO_2 production rates (Lovelock, 2008). Carbon dioxide is drawn down into wetland systems through photosynthesis. In this process, CO_2 is converted into carbohydrates within the plant. In a wetland, the net CO_2 flux is determined by the balance of respiration (plant and microbial) and photosynthesis. Often, wetlands will be sinks of CO_2 during the day while photosynthesis occurs, and sources of CO_2 at night as respiration continues (Lafleur et al., 1997). Similarly, Seasonal variations in CO_2 flux are driven by solar radiation and by extension temperature (microbial rates), growing season (photosynthesis, plant litter inputs), and ice dynamics (trapped gas, ORP). When plants are photosynthesizing during the growing season, wetlands are net sinks of CO_2. In the early spring, before plant growth, wetlands may be sources of CO_2. Again after senescence in the autumn, wetlands are generally net sources of CO_2 (Lafleur et al., 1997). The CO_2 produced in wetlands enters the atmosphere mainly through diffusive processes at the air-water interface or through wetland vegetation aerenchyma and stomata (Limpert et al., 2020).

1.3: CH_4 Production and Consumption

The CH_4 flux in wetlands is determined mainly by the balance of two microbial processes, methanogenesis and methanotrophy (Mitsch & Gooselink, 2015). Methanogenesis is the process by which microbes breakdown organic matter under anaerobic conditions. In these reduced environments, two main groups of methanogens (the microbes responsible for methanogenesis) generate energy for their metabolisms in two distinct ways (Bridgham et al., 2013). Acetotrophic methanogens rely on acetate as both the electron donor and carbon source of methanogenesis. These methanogens convert acetate into CH_4 and CO_2 under favorable ORP. The other major group of methanogens is the hydrogenotrophic methanogens. These microbes oxidize hydrogen into CH_4 with CO_2 as the electron acceptor (Bridgham et al., 2013; Mitsch & Gooselink, 2015). Methanogens utilize the energy released from the reduction of CO_2 or acetate to fuel their metabolic activities.

The products of fermentation involved in methanogenesis (H_2/CO_2 and acetate) are also utilized by microbial groups with alternate terminal electron acceptors; therefore, methanogenesis does not occur until the reduction of electron acceptors with higher energy potential are depleted. These alternate electron acceptors in order of free energy released are NO_3^-, ferric iron (Fe^{3+}), manganese (Mn^{4+}), and SO_4^{2-} (Bridgham et al., 2013). Therefore, both types of methanogens are limited to environments with sustained reducing conditions in which the depletion of these alternate electron acceptors occurs. This order of reactions explains why there is little CH_4 production in wetlands with high salinity, as there is generally an abundance of alternative electron acceptors such as SO_4^{2-} (Magenheimer et al., 1996; Mitsch & Gooselink, 2015).

Methanotrophy is the process in which CH_4 is oxidized by microorganisms (methanotrophs) to eventually produce CO_2. Methanotrophs sequentially oxidize CH_4 into methanol, formaldehyde, formate, and lastly CO_2 (Whalen, 2005). This process requires O_2 and so occurs in aerobic environments such as surface waters of wetlands.

CH_4 enters the atmosphere via multiple emission pathways, including ebullition, diffusion, and transfer through plant aerenchyma (Bridgham et al., 2013). Few freshwater wetlands are sinks of CH_4 because high water tables and reducing conditions generally lead to methanogenesis producing more CH_4 than is consumed through methanotrophy.

1.4: N_2O Production and Consumption

Nitrous oxide is produced through various processes in wetlands, including nitrification, denitrification, coupled nitrification-denitrification, and nitrifier denitrification. These processes may occur simultaneously in different microenvironments within wetland soils, depending on factors such as ORP, pH, and substrate availability (Wrage et al., 2001). The initial substrate required in nitrification is ammonia or ammonium, while in denitrification it is NO_3^- or nitrite and organic carbon. The abundance of these substrates as well as temperature, pH, and hydrological conditions control the rates of production (Beaulieu et al., 2011).

Nitrification can be subdivided into autotrophic (inorganic carbon energy source) and heterotrophic (organic carbon energy source) nitrification (Wrage et al., 2001). In both processes, either ammonia or ammonium undergo oxidation, leading to the formation of nitrite, which is further oxidized into NO_3^-. During the ammonia/ammonium oxidation and subsequent nitrite oxidation, N_2O is generated as a by-product. Oxygen serves as the electron acceptor in the nitrification process; thus, it predominantly occurs in aerobic environments (Wrage et al., 2001).

Denitrification is a microbial process carried out by denitrifying bacteria in conditions where O_2 is limited or absent. These bacteria use NO_3^- as a terminal electron acceptor instead of O_2 for their metabolic processes. The reduction of NO_3^- to nitrogen gas (N_2) occurs through a series of enzymatic reactions, with several intermediate products, including N_2O (Wrage et al., 2001). A few factors can influence how much of this intermediate N_2O is released into the atmosphere vs. how much goes on to be reduced into N_2. First, lower pH will increase N_2O released as low pH inhibits the activity of N_2O reductase (Wrage et al., 2001). Next, an abundance of NO_3^- in the system may increase N_2O released, as NO_3^- is preferred as an electron acceptor over N_2O (its reduction yields more energy) (Wrage et al., 2001; Beaulieu et al., 2011).

Lastly, if there is more O_2 present in the system, more N_2O will be released, as O_2 inhibits the activity of N_2O reductase more than it inhibits the processes of other enzymes involved in denitrification (Wrage et al., 2001; Beaulieu et al., 2011).

Coupled nitrification-denitrification is not a unique process but is often mentioned in the literature to clarify that the processes of nitrification and denitrification can be tightly linked (Wrage et al., 2001). While nitrification and denitrification require different microbial populations and redox conditions, they can often occur together in the soil matrix. This is because the soil matrix is heterogeneous and there may be soil pores next to each other with a dramatically different ORP. In fact, because these two processes are complimentary (nitrification produces intermediaries and end products that are used as substrate by denitrifying bacteria) N_2O production may be highest where the processes occur in tandem in proximity to one another (Wrage et al., 2001). Therefore, N_2O production may be highest at the interface of the anaerobic and aerobic zones.

Nitrifier denitrification is a unique process in which a single group of microbes transforms ammonia into N_2 (Wrage et al., 2001). This is a separate process from coupled nitrification-denitrification because it does not require the connection between two microbial groups working in two different microenvironments. Nitrifier denitrification is a process carried out by autotrophic nitrifiers that can complete the entire process independently. The conditions that favour this process may be low O_2 and low pH (Wrage et al., 2001).

An overview of the carbon and nitrogen cycles in wetlands is provided in Figure 1.1 and Figure 1.2 from Mitsch & Gooselink (2015). The production and consumption of CO_2, CH_4, and N_2O are only parts of these cycles, but an understanding of the whole system is helpful when discussing GHG dynamics in wetlands. The following chapters will build on this introduction of how GHG are produced in wetlands. Chapter One considers how seasonality and water chemistry influence concentrations of GHG in the field. Chapter Two builds on this, looking at how nutrient additions influence GHG production in laboratory incubations. There are countless factors at play regarding GHG emissions. The two chapters in this thesis aim to unravel some of the most important variables and create a better understanding of these dynamic ecosystems.

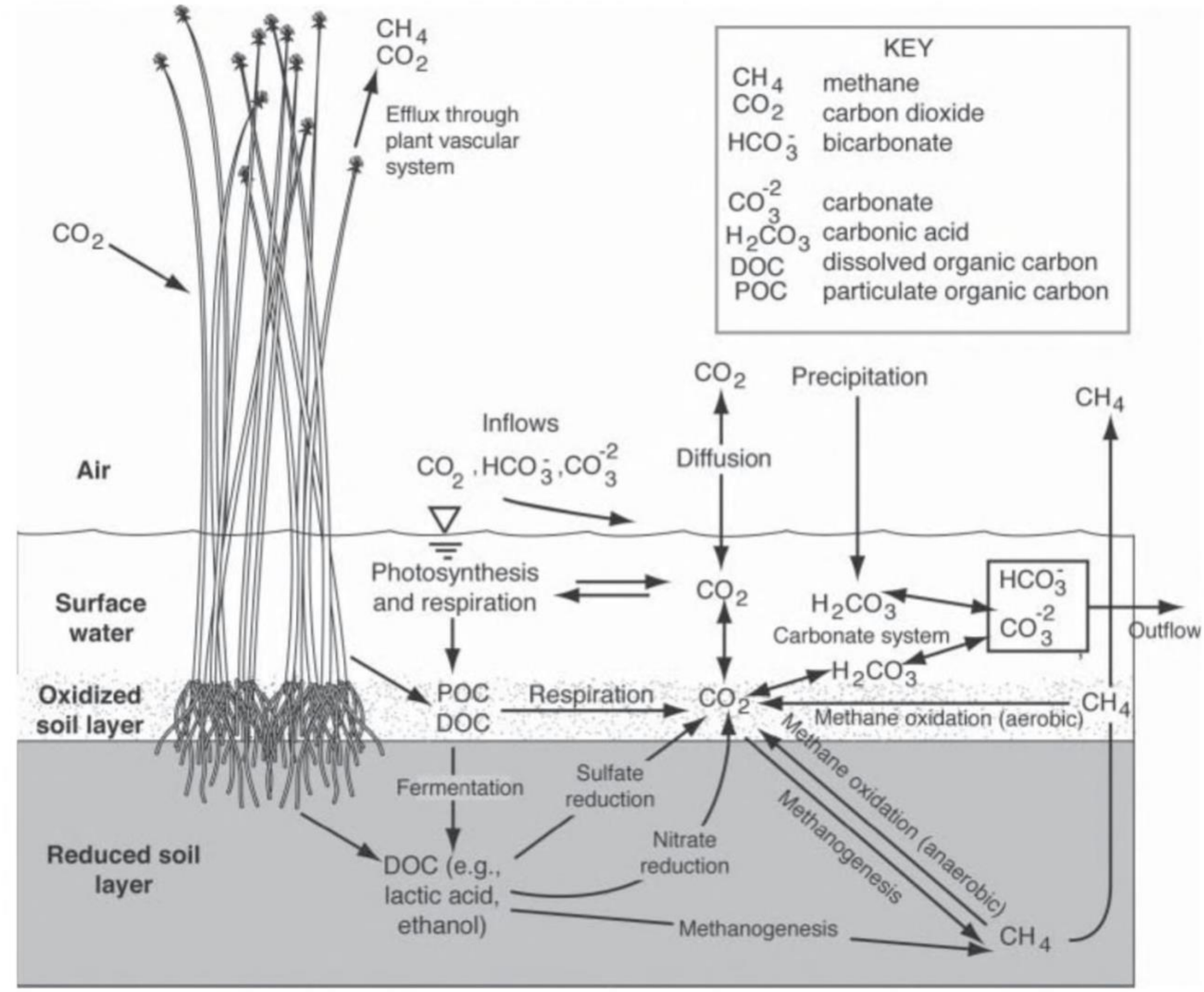


Figure 1.1: Carbon cycle in wetlands: This figure shows the main processes and transport pathways of the carbon cycle in wetlands. Reproduced from Mitsch & Gooselink (2015). *Wetlands* (Fifth edition). John Wiley and Sons, Inc. p. 182

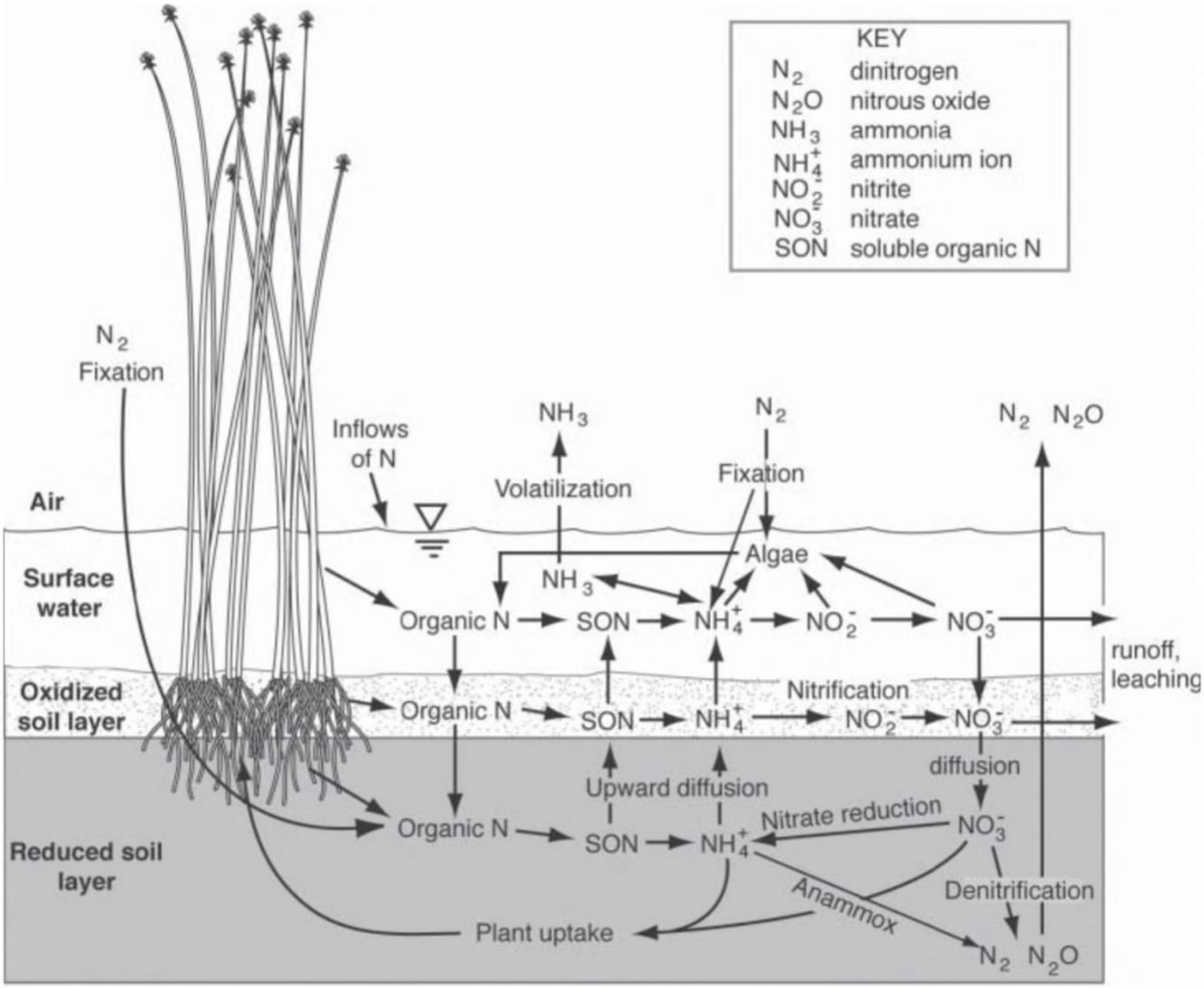


Figure 1.2: Nitrogen cycle in wetlands: This figure shows the main processes and transport pathways of the nitrogen cycle in wetlands. Reproduced from Mitsch & Gooselink (2015). *Wetlands* (Fifth edition). John Wiley and Sons, Inc. p. 196

Chapter 2: Seasonal Variations of Dissolved Greenhouse Gas: Field Measurements

2.1: Objective

This chapter covers field research that analyzes seasonal variations of dissolved GHG within a wetland and explores which factors contribute most to the observed variations. By understanding the factors affecting dissolved GHG within wetlands, restoration efforts can be designed to minimize wetland GHG emissions. Wetland GHG dynamics measured with increased attention to seasonal variations may help reduce errors associated with estimating wetland emissions with growing season sampling bias. I measured concentrations of dissolved CO_2, CH_4, and N_2O and recorded pH, electrical conductivity, dissolved organic carbon (DOC), total dissolved nitrogen (TDN), water temperature, and depth of water. Data was collected over 510 days, and analyzed to determine which factors correlate with dissolved GHG concentrations.

2.2: Introduction

Wetlands have diverse conditions and their role as a net source or sink of GHG is dependent on their history, soil type, hydrology, and other complex factors (Bridgham et al., 2013). In quantifying soil carbon storage and GHG flux for wetlands over time, a judgement can be made on whether a type of wetland in a specific region is a net sink or source of GHG. Regionalized data helps inform land use practices and guide wetland restoration (Pennock et al., 2010).

A greater understanding of wetland heterogeneity is needed to determine the overall impact of wetland conversion and restoration (Bortolotti et al., 2016). This research aims at contributing to the unraveling of the complex controls in wetland GHG production. By focusing on heterogeneity within one wetland, I can unravel some of the complexities influencing emissions. Another benefit of this research may be to inform future wetland restoration efforts to maximize carbon uptake and minimize emissions. By looking at one wetland in detail I may be able to isolate factors of GHG emissions that would be difficult to identify when comparing multiple locations. For example, it may be difficult to conclude that water temperature is a factor determining CH_4 production if the wetlands have different sediments, plant communities, and hydrology.

Influence of Seasonality on Greenhouse Gas Emissions:

This section addresses seasonality as a factor of GHG production in wetlands. Seasonality controls temperature, hydrology, land use patterns, and growing season dynamics. Warmer temperatures impact decomposition due largely to the increased activity of phenol oxidase and increased metabolic activity of microbial populations (Kirwan & Blum, 2011). Decomposition rates roughly double with every 10 ºC warming, therefore, soil carbon pools are strongly tied to temperature, with lower soil organic carbon as average temperatures increase (Rasmussen et al., 1998). In general, GHG fluxes from wetlands increase with warmer summer temperatures and decrease in cooler months (Dalva et al., 2001; J. Zhang et al., 2005).

Carbon Dioxide

Seasonality impacts CO_2 production due to the changes in temperature, water levels, and growing season dynamics. Carbon dioxide flux increases during warmer summer months compared to cooler months (Dalva et al., 2001; J. Zhang et al., 2005). Higher temperatures generally enhance microbial activity, leading to increased rates of organic matter decomposition and respiration, both of which produce CO_2 (Lloyd & Taylor, 1994). In freshwater wetlands, CO_2 is produced in the aerobic layers through respiration and CH_4 oxidation, and in anaerobic layers through decomposition (Limpert et al., 2020). CO_2 is produced under all redox conditions, but aerobic production is generally more significant. Although aerobic CO_2 production occurs in wet soils, CO_2 production is greatest when conditions are not too wet (anaerobic) or too dry (unsuitable for microbial populations) (Strack et al., 2009; Kayranli et al., 2010). For example, studies report higher CO_2 emissions in peat soils when water tables are lower. (Moore & Dalva, 1993; Price & Waddington, 2000; Scanlon & Moore, 2000). The seasonality of CO_2 emissions is closely linked to the biological cycles of plants. During the growing season, warmer temperatures stimulate both plant growth and microbial decomposition. Enhanced plant growth leads to greater CO_2 uptake during photosynthesis, while increased temperatures and increased plant biomass leads to greater plant and root respiration. More microbial activity results in higher CO_2 release from respiration and decomposition. The net effect on CO_2 flux depends on the balance between these processes. During the growing season, photosynthesis is usually a greater carbon sink than the cumulative carbon sources, resulting in a net drawdown of CO_2 (Whiting & Chanton, 2001; Kayranli et al., 2010). In autumn and winter, plant activity diminishes, leading to a decrease in photosynthetic CO_2 uptake. During these colder months, the dominant processes are respiration and decomposition. Dead plant material decomposes, and microbial respiration continues, albeit at a slower rate due to lower temperatures. This may cause a wetland which is a sink of CO_2 in the growing season to become a source in winter as the balance shifts from CO_2 uptake to release (Whiting & Chanton, 2001).

When looking at dissolved CO_2 concentrations in the open water system, these seasonal effects may be less obvious. Despite ecosystem wide sequestration of CO_2, concentrations of dissolved CO_2 will likely be highest in the summer months because, respiration rates and microbial decomposition are highest during the warmest months. Cooler temperatures may lead to a net loss of CO_2 from the system, but the slowing down of decomposition rates and reduction of plant respiration may result in lower concentrations of dissolved CO_2. Ice cover may trap CO_2 produced in the winter, and result in increased concentrations before the thaw in the spring (Kling et al., 1992).

Methane

CH_4 emissions exhibit pronounced seasonality primarily influenced by temperature, water table depth, and organic substrate quality and availability (Panikov et al., 2001; Whiting & Chanton, 2001). Methanogenesis is highly temperature dependent. Warmer temperatures increase the metabolic rates of methanogenic archaea, thereby enhancing CH_4 production (Singh et al., 2000; Yvon-Durocher et al., 2014). Colder temperatures in winter slow rates of methanogenesis (Maljanen et al., 2007). When water table depth is within 10 cm of the surface, temperature is the main limiting factor for CH_4 emissions. When the water table falls below 10 cm from the surface, water table depth is the limiting factor in CH_4 emission (Christensen et al., 2003). Seasonality influences water table through precipitation, evaporation rates, and snowmelt. A higher water table will result in a greater area of potential CH_4 production. When measuring dissolved CH_4 in surface water, changes in water depth or increases in wetland area may not significantly influence dissolved CH_4 concentrations, but rather increase the total emissions from the wetland system. When open water freezes completely in winter, ice cover may limit diffusion of gases into the atmosphere and result in high concentrations of dissolved GHG which are then released during the spring melt (Whalen & Reeburgh, 1988; Moore & Knowles, 1990; Kling et al., 1992; Moore et al., 1994; Phelps et al., 1998).

Nitrous Oxide

Nitrous oxide emissions also exhibit distinct seasonal patterns, predominantly driven by soil temperature and moisture conditions that affect microbial processes (Butterbach-Bahl et al., 2013). Nitrous oxide is produced year-round, but production is greater in warmer temperatures due to increased metabolic activity (Khoiyangbam & Chingangbam, 2022). In autumn and winter, cooler temperatures slow down microbial activity, reducing both nitrification and denitrification rates (Butterbach-Bahl et al., 2013; Hu et al., 2015). Like the other GHG discussed, concentrations of N_2O may increase under ice in the winter.

Seasonal flooding or large precipitation events that cause temporary increases in soil moisture can create mixed ORP favorable for denitrification, potentially leading to episodic N_2O emissions. Nitrous oxide production is often highest in areas with heterogenous ORP that promote coupled nitrification-denitrification processes (Wrage et al., 2001). These conditions are caused by the flooding of previously unsaturated soils. Unflooded soils may contain more NO_3^- than soils which have been exposed to conditions suitable for denitrification. The combination of higher concentrations of NO_3^-, and the heterogenous redox conditions that follow flooding may cause temporary spikes in N_2O production. Agricultural practices such as fertilization or cattle grazing further contribute to N_2O emissions by providing substrates for nitrification and denitrification (Butterbach-Bahl et al., 2013). The land use cycles and seasonal weather will determine the timing of these additions of nitrogen (Chen & Hong, 2011). Autumn fertilization may result in in exports of nutrients over the winter and especially during the spring melt (Irvine et al., 2019). Phosphorus export to the water shed is largely driven by runoff during snow melt and large rain events, while NO_3^- leaching and runoff amounts are influenced by timing of fertilization, especially when large rain events follow application (Irvine et al., 2019). Runoff of nutrients from manure and urine are greater when cattle densities are higher and when cattle spend more time near to a water body (Haynes & Williams, 1993; Nelligan et al., 2021).

Summary

GHG concentrations in wetlands vary seasonally based on temperature, growing season, water levels, and land use in surrounding areas. Higher summer temperatures generally lead to greater production of CO_2, CH_4 and N_2O due to greater metabolic activity of microbes. In winter, cold temperatures slow production, but ice prevents diffusion resulting in a buildup of GHG under ice. Water levels may influence ORP in the sediment and water column as well as the extent of the wetland. Methane fluxes from a wetland will be higher during periods of flooding, with more areas exposed to anoxic conditions. Carbon dioxide emissions will be higher during periods of relative drought when more aerobic respiration occurs. Nitrous oxide emissions may spike shortly after flooding events. The addition of nutrients to the system may alter emission pathways, for example, nitrogen runoff from agricultural fertilizer may increase N_2O emissions. Concentrations of these dissolved gases may not reflect the total emissions from the ecosystem.

Influence of Water Chemistry on Greenhouse Gas Emissions

This section reviews the impacts of water chemistry on GHG emissions. It will focus on variables that are measured in the field. These variables include, pH, electrical conductivity, DOC and TDN.

Carbon Dioxide

CO_2 emissions are limited by alkaline or very acidic soil conditions, and carbon emission will be higher in soils with higher pH (closer to neutral) when soil conditions are otherwise similar (Reth et al., 2005). Most relevant to this research is the relationship between pH and inorganic carbon species (Figure 2.1) (Boyd, 2015). When pH is at 5 or below, CO_2 is the only significant species (Boyd, 2015). With higher pH, bicarbonate becomes more abundant compared to CO_2, until bicarbonate is the only significant species around pH 8.3. With pH higher than 8.3, there is almost no dissolved CO_2. As pH continues to increase the proportion of carbonate increases compared to bicarbonate (Boyd, 2015). pH and inorganic carbon are interdependent, pH increases may decrease dissolved CO_2, but also decreased CO_2 concentrations result in a higher pH (Boyd, 2015). Factors like organic matter decomposition, plant respiration, photosynthesis, ORP, and hydrological inputs drive CO_2 production and consumption, altering pH (Boyd, 2015).

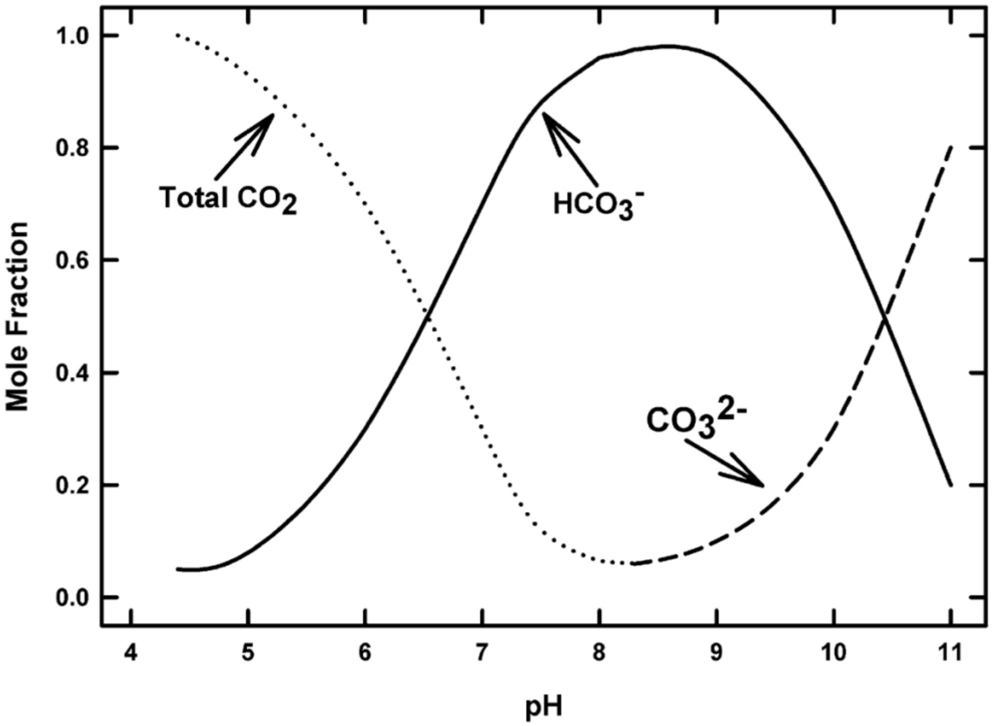


Figure 2.1: Interdependence of pH and the speciation of inorganic carbon. Reproduced from "pH, Carbon Dioxide, and Alkalinity." by Boyd, C. E. (2015). "pH, Carbon Dioxide, and Alkalinity." In *Water Quality: An Introduction* (pp. 153–178). Springer International Publishing.

DOC acts as a substrate for microbial respiration, and greater concentrations of DOC result in greater total CO_2 production (Calleja et al., 2019; Schnecker et al., 2019). High salinity (electrical conductivity) decreased CO_2 emissions due to salt stress in wetland mesocosm experiments (Ardón et al., 2018). However, this study involved freshwater marsh soils exposed to salts and seawater. Other research has found that salinity introduces more terminal electron acceptors, promoting carbon mineralization through SO_4^{2-} reduction with CO_2 as a coproduct (Weston et al., 2006; Loka Bharathi, 2008). Increased electrical conductivity, may also increase the anerobic oxidation of CH_4 and result in higher CO_2 emissions (Soued et al., 2024).

Methane

Methanotrophs and methanogens in wetlands can grow in a pH range of 5 to 9, but prefer a more neutral pH (Z. P. Wang et al., 1993; Kotsyurbenko et al., 2019). Some methanogens in peat soils produce CH_4 in more acidic conditions (Topp & Pattey, 1997). DOC acts as a substrate for methanogens, and is significantly positively correlated with CH_4 emissions in flooded paddy soils (Bertora et al., 2018). Increased DOC is associated with increased CH_4 emission from open water wetlands, but DOC quality is also important (Singh et al., 2000). Electrical conductivity, reflecting the concentration of dissolved ions, can be used to approximate salinity (Soued et al., 2024). Salinity restricts methanogenesis because higher salinity means more ions that serve as alternative terminal electron acceptors (most importantly SO_4^{2-}). These alternative electron acceptors (SO_4^{2-}) are involved in more energy efficient reactions (Soued et al., 2024). As methanogenesis is the least efficient pathway of carbon mineralization, redox dynamics dictate that alternative terminal electron acceptors must be unavailable before methanogenesis occurs. This pattern of decreasing CH_4 emissions with increasing salinity has been shown in research on tidal saline wetlands (Magenheimer et al., 1996).

Nitrous Oxide

N_2O emissions are negatively correlated with soil pH, with increasing N_2O emissions as soil pH decreases (Wrage et al., 2001; Žurovec et al., 2021). DOC may act as a carbon source in the denitrification process. One study found that higher DOC concentrations increased both N_2O production and uptake (Guo et al., 2020). Higher salinity (electrical conductivity) has been found to inhibit nitrification, but shows mixed results on denitrification (Aelion & Warttinger, 2009). Increased concentrations of SO_4^{2-} with increased salinity may result in more SO_4^{2-} reduction and the creation of sulfide. Sulfide inhibits the final steps in denitrification resulting in more emission of N_2O before it is fully reduced (Brunet & Garcia-Gil, 1996). TDN should correlate with increased N_2O by providing substrate for nitrification and denitrification (J. Wang et al., 2015; Bonetti et al., 2022).

Summary

Water chemistry may influence GHG emissions, through variations in pH, DOC, and electrical conductivity. Lower pH may result in greater concentrations of N_2O and CO_2, while higher pH will promote greater production rates of CH_4. DOC may act as a substrate for redox reactions responsible for the production of CO_2, CH_4 and N_2O. Electrical conductivity corresponds with salinity, and may decrease CH_4 concentrations, and increase CO_2 and N_2O concentrations.

2.3: Scope

My research seeks to understand how seasonality and water chemistry affect dissolved GHG concentrations in a freshwater mineral wetland. To answer this question, I measured various biogeochemical parameters in the water column over a period of 510 days. Measurements occurred about every two weeks during the ice-free period and when safety permitted under ice. Besides measuring dissolved CO_2, CH_4, and N_2O, I measured electrical conductivity, pH, DOC, TDN, water temperature, and water depth at each sampling site.

2.4: Hypotheses

I hypothesize that i) warmer temperatures will correlate with greater concentrations of all three measured GHG ii) there will be buildup of all three GHG under ice in winter iii) pH will negatively correlate with concentrations of CO_2 and N_2O iv) higher concentrations of DOC will correlate with greater concentrations of all three GHG v) higher electrical conductivity will correlate with lower CH_4 concentrations and greater CO_2 and N_2O concentrations and vi) greater TDN will correlate with more dissolved N_2O.

2.5: Methods:

Site Description

Samples were taken at Atocas Bay Conservation Site, located in the Ottawa Valley in eastern Ontario (Figure 2.2). Mean annual temperature is 5.3 °C and mean annual precipitation is 1067.7 mm (average 1981-2010 Mirabel International Airport, Environment and Climate Change Canada). The surrounding topsoil is rich in clay (>50%), and slightly acidic or neutral with pH ranging from 5 to 7 (Dong et al., 2024). Soil organic carbon content ranges from 4.6-6.7% (Dong et al., 2024). At roughly 40-50 cm beneath the surface, clay dominates, with nearly 100% clay at depths of 80-100 cm (Figure 2.3). This thick clay layer is a legacy of the Champlain Sea, which deposited marine clay across the St. Lawrence lowlands. The clay layer has a low hydraulic conductivity allowing for many smaller wetlands to remain inundated throughout the year.

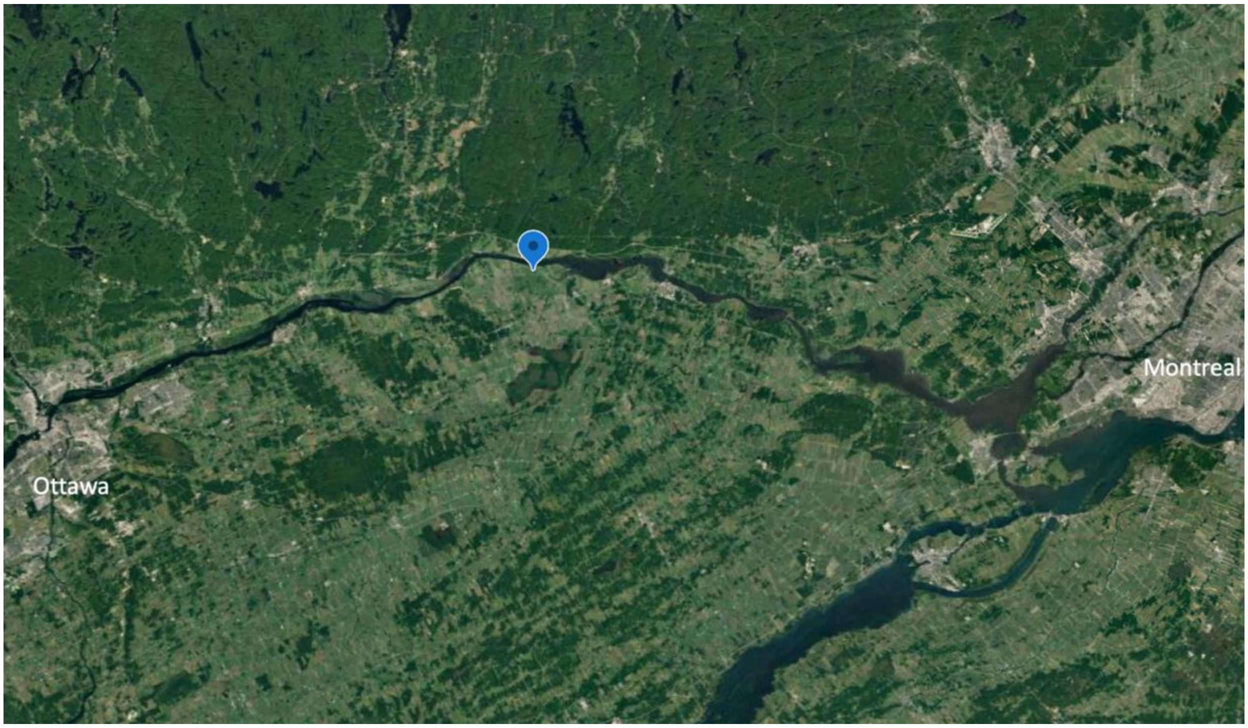


Figure 2.2: Location of Atocas Bay Conservation Site

Figure 2.3: Soil profile dug near wetland site (Ducks Unlimited notation Atocas 188).

Atocas Bay Conservation Site represents a major investment from Ducks Unlimited Canada. Most of the land was purchased in 2000, and with the additional purchases of land in the last 23 years, the property now includes more than 800 hectares of rehabilitated and intact wetland basins and surrounding upland ecosystems. In the 20th century, more than 95 % of the original wetland area had been degraded or lost. Ducks Unlimited has restored more than 300 wetlands at the site, which has contributed to a 24-fold increase in breeding duck populations (Ducks Unlimited, n.d.). Additionally, the surrounding upland on the property is in use for agriculture.

My research focuses on one intact wetland 45°37'29.92"N, 74°50'15.61"W (Figure 2.4). This wetland is located roughly 500 meters south of the Ottawa River and two kilometers west of Atocas Bay. The wetland is oriented north-south, with an inundated area of roughly 8.5 hectares as of September 10th, 2023. The distance is 500 meters from the northern tip to the southern end, and the wetland width is an average of 80 meters from the east bank to the west bank. This wetland serves as an excellent field site for research because of its large variations in morphology. With deep pools on the northern and southern tips, shallow bays, inlets, and outlet streams, there are diverse study areas all accessible by kayak. The wetland is surrounded by pasture for beef production. According to land managers Annette and Sylvain Lepage, about 190 cattle (120 cows/calves, 60 stockers, 10 bulls) graze on roughly 325 hectares of pasture from April to November. The wetland and surrounding area is home to beavers, skunks, muskrats, breeding great blue herons, great egrets, greater and lesser yellow legs, as well as snow geese, mallards, black ducks, blue-winged teals, gadwalls, wood ducks, buffleheads and ring-necked ducks, black terns and short-eared owls, and bobolinks, additionally various insects, fish, leeches, snakes, frogs, and turtles thrive in the wetland (Ducks Unlimited, n.d.).

Figure 2.4: Satellite image of wetland site (Ducks Unlimited notation: Atocas Bay 188). Area of standing water outlined in red. Samples were taken throughout wetland.

This wetland and others in the Ottawa Valley are within one of the most critical migration flyways in the world (Figure 2.5) (United States Department of Agriculture Wildlife Services, 2017). From early September to mid-November, Atlantic Population Canada geese migrate through the area flying south from the Ungava peninsula (United States Department of Agriculture Wildlife Services, 2017). The population of Canada geese on the Ungava Peninsula in the summer of 2022 was estimated at 1,316,348, with 163,714 breeding pairs (Maryland Dept of Natural Resources, 2022).

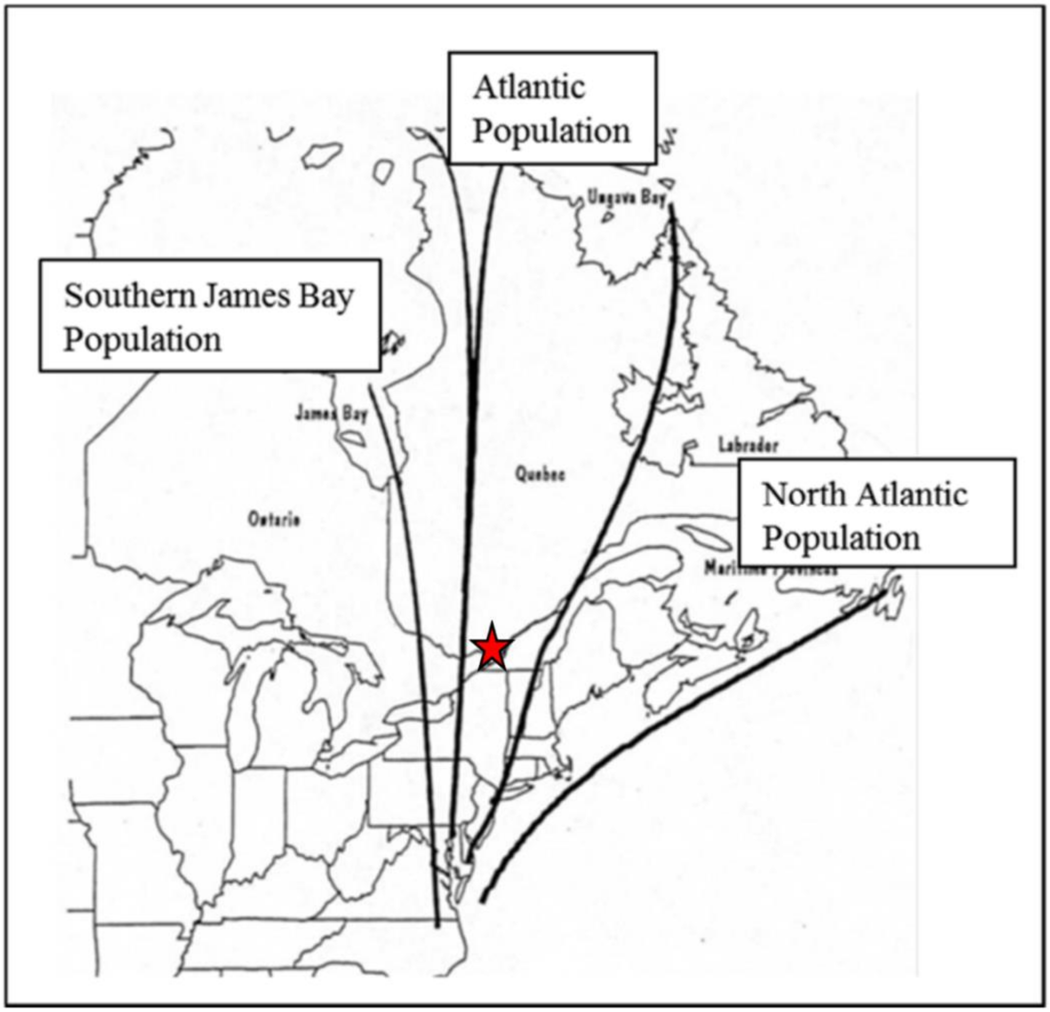


Figure 2.5: Migratory pathways of Canada geese in the Atlantic Flyway. Approximate location of wetland site represented by red star. Figure reproduced from "MANAGING CANADA GOOSE DAMAGE IN THE STATE OF NEW YORK"

After leaving the Ungava Peninsula, Canada geese reach the Ottawa Valley tired and hungry. The Ottawa Valley is the first stop along their route that is rich in forage. Therefore, geese spend time feeding and resting in this region thanks to the abundance of farmland and open water available in the autumn. Much of their behavior depends on the land management and weather in the region. With more corn production and less cattle present in the region, there are more harvested fields for large flocks of geese to land and feed as the birds restore their energy on the residual grains after harvest. Additionally, warming temperatures allow geese to remain for longer, before freezing water and freezing rains force them south. In the spring, geese migrate through the Ottawa Valley from mid-March to mid-April depending on weather conditions. Again, geese may stop to rest in fields or open water before moving further north. These vast flocks of geese rest, forage and defecate in and around the study wetland. Large amounts of feces can be found at the wetland during the migration season. Goose feces introduces labile carbon and nutrients into the wetland, and potentially alters the pH and water chemistry (Mallory et al., 2006). These comments on Canada goose migration are based on field experience and the knowledge of local hunting guide Michel La Hayes (Msc Biology).

Field Observations

During the years 2022 and 2023, I visited the wetland more than 30 times and gained an understanding of notable seasonal dynamics. For example, the wetland was covered with ice by the end of November in both 2022 and 2023. In 2023, the spring melt began in April, with ice breaking up around April 15th. The water level in this wetland is controlled by inflows, evapotranspiration, and an outlet gate in the southeast corner of the basin. Each year during the spring melt, debris and sediment build up around the gate. In 2023, buildup reduced outflow and caused the water level to rise higher than in 2022. From a peak height during the spring melt, water levels slowly but steadily fell through the summer months. In the autumn of 2023, water levels began to rise slightly. Then in late October, the land managers cleared the blocked outlet, causing a 20 cm drop in the water level of the wetland. Over the course of the growing season wetland morphology reveals itself in the distribution of vegetation. What looks like a featureless open water wetland in April becomes more than 80% covered with lily pads by July. Because the lily pads only grow in waters up to about one meter deep, the open water areas can be quickly identified as the deeper areas of the wetland. The boundary areas of the wetland are dominated by *Typha* that can grow to be more than two meters tall.

Sampling and Storage

The sampling sites lie on a north-south transect covering this varied morphology. I collected water samples at the main inlet, main outlet, and roughly 14 locations inbetween. Samples were always taken between the hours of 9:00 am and noon. Upon reaching the desired sampling location, a 60 ml syringe was first flushed with ambient air, then 30 ml of ambient atmosphere was sampled at a height of about one meter above the water surface.

Next, 30 ml of water was sampled 10 cm beneath the water surface. The syringe was sealed under water. Next, water temperature was measured 10 cm below the surface. Lastly, water depth at the sampling location was measured. After sampling, syringes were stored in a bucket filled with water to maintain consistent temperature until the dissolved gas was sampled. When sampling during periods of ice coverage, holes were broken through the ice with steel spikes to provide access to liquid water.

Dissolved gas was sampled by equilibrating water and headspace through vigorous shaking. Samples were shaken for two minutes to ensure the headspace and water were at equilibrium. Then the headspace was transferred into vacuum evacuated exetainers for storage. The water was kept in the syringe and all sample containers were kept in a cooler during transportation until being placed in a fridge. The following day, pH and electrical conductivity were measured with meters, and then water samples were filtered over 40 µm Whatman filters. DOC and TDN were then measured on a Shimadzu TOC-Vcsn analyzer. Gas samples were transferred from vials to a syringe and GHG were measured with a Shimadzu GC-2014 gas chromatograph. Dissolved gas concentrations were determined by the difference in headspace concentration after equilibration compared to ambient atmospheric concentrations.

I performed bidirectional elimination stepwise linear regressions with the software IBM SPSS statistics version 29.0.1.1 (244). These regressions were used to identify the predictors of dissolved CO_2, dissolved CH_4, and dissolved N_2O (dependent variables) using independent variables of temperature, pH, depth, DOC, TDN, and electrical conductivity. At each step, variables were chosen according to their contribution to the models R^2, using significant F-Change to-enter (<= .075), and significant F-Change to remove (>= .15).

2.6: Results

This wetland undergoes substantial changes throughout the year. To illustrate these changes, the measured parameters were averaged for each of the 19 sampling days and a summary is presented in Table 2.1. There were large variations across the wetland on each sampling day as seen in the standard variations. Sampling revealed high variability particularly for CH_4 which sometimes varied by an order of magnitude. Depth also varied significantly within each sampling day. This was to be expected as I intentionally sampled in areas of variable depth. Average surface water temperature ranged from 0 to 26 ºC. Average pH ranged from 6.48 to 7.51. Electrical conductivity ranged from 46 to 237 µs. Dissolved organic carbon, ranged from 7.9 to 18.62 mg/l. Total dissolved nitrogen ranged from 0.38 to 1.79 mg/l. Clear seasonal variations can be identified for the three measured dissolved GHG. Average dissolved CO_2 ranges from 111 µmol/liter in the spring, to 2548 µmol/liter in mid-winter. Average dissolved CH_4 ranged from 3.33 µmol/liter in the autumn, to 1414 µmol/liter in mid-winter. Average dissolved N_2O concentrations were negative on 15 of 19 sampling days, meaning concentrations in the headspace were reduced after equilibration with sampled water. This means that concentrations were lower in water than in the ambient air. Dissolved N_2O ranged from 0.016 µmol/liter below ambient to 0.036 µmol/liter. During 510 days of field research, I sampled during two autumn seasons one summer, one winter, and one spring. For clarity, the reference day is January 1, 2023, and sampling days are measured in days before or after this date. These patterns can be identified in Figure 2.6, 2.7, and 2.8. Other seasonal variables such as ice coverage and goose migration were not quantified but are displayed in Figure 2.9.

Day	#	ice	Temp	Depth	pH	CON	DOC	TDN	µmol CH_4	µmol CO_2	µmol N_2O
-106	9	no	17±0.7	156±123	6.81±0.17	174.7±29	14.1±1.2	1.1±0.13	227.8±68.7	965.8±75.6	-0.009±0.003
-89	13	no	13.7±0.8	202±105	6.48±0.24	152.1±29.4	12.8±1.5	0.88±0.14	18.1±6.3	593±117.4	-0.015±0.013
-70	13	no	9.1±0.4	165±82	7.26±0.05	135.1±16.2	12.1±0.5	0.99±0.19	5.1±4.3	381.2±62.1	0.003±0.004
-39	14	yes	2.9±0.6	166±92	7.33±0.05	173±23.5	12.1±0.5	1.06±0.06	3.8±3.5	185.8±57.1	0.036±0.032
105	14	yes	5.4±1.7	158±106	6.74±0.12	46.4±10	7.9±1.2	0.38±0.13	202.4±71.3	562.1±82.6	-0.002±0.004
119	17	no	11.9±0.2	130±98	7.18±0.05	95.5±5.3	10.3±1	0.49±0.11	8.9±2.7	111.4±24.4	-0.005±0.002
137	18	no	12±0.6	125±85	7.15±0.1	104.8±11.8	12.2±1.4	0.82±0.21	26.1±15.8	138.2±51.7	-0.004±0.002
152	17	no	25±1.6	169±128	7.51±0.24	115.2±9.9	13.2±4.8	0.7±0.24	29.7±37.3	169.4±167.1	-0.001±0.004
180	15	no	21.1±0.4	172±100	6.75±0.05	67.8±13.6	11.2±2.1	0.71±0.12	51.5±65.8	487.8±162.3	-0.007±0.002
194	14	no	21.9±0.6	169±45	6.49±0.1	80±36.9	11.6±1.7	0.56±0.1	117.4±98.2	658.9±206.9	-0.009±0.002
206	16	no	23.5±1	180±101	6.76±0.07	88.8±20.6	12.7±1	0.61±0.08	44.1±24	641.9±132.8	-0.008±0.002
229	16	no	21.9±0.8	184±99	6.81±0.07	84.4±14.1	18.6±7	0.79±0.09	50.6±22.5	660.3±124.1	-0.016±0.002
249	14	no	26.4±1	203±140	6.73±0.19	166.5±10.2	15.3±1.2	1.18±0.38	99.3±46.4	694.2±208.8	-0.01±0.003
265	17	no	16.8±2.1	165±108	6.73±0.1	154.9±28.4	12.5±0.9	0.98±0.13	286.4±94.2	926.2±219.5	-0.009±0.006
289	17	no	11.4±0.7	137±94	7.05±0.11	179.7±31.9	13.8±3.3	1.2±0.26	9.4±6.8	534±124.1	-0.012±0.002
300	17	no	12.3±0.3	156±95	7±0.24	172.6±23.1	12.4±3.6	1.21±0.13	3.3±2.9	342.6±55.8	-0.005±0.001
312	15	no	2.4±0.5	125±91	7.15±0.17	199.8±37.9	11.7±0.9	1.5±0.18	6±10.2	141.8±107.4	-0.003±0.002
325	8	yes	1.6±0.1	126±101	7.42±0.09	178.8±10.3	12.8±0.9	1.79±0.15	9.2±4.6	185.5±23.5	0.002±0.004
403	4	yes	-0.1±0	128±136	6.52±0.13	237.5±6.6	17.2±1	1.18±0.31	1414.5±264.9	2548±379.6	0.031±0.000

Table 2.1: Sampling averages: From left to right: sampling day from January 1st, 2023, number of samples taken, presence of ice, averages, and standard deviation for: temperature (Celsius), Depth (cm), pH, Conductivity (µS), Dissolved organic carbon(mg/L), Total dissolved nitrogen(mg/L), µmol CH_4 / liter, µmol CO_2 / liter, µmol N_2O / liter.

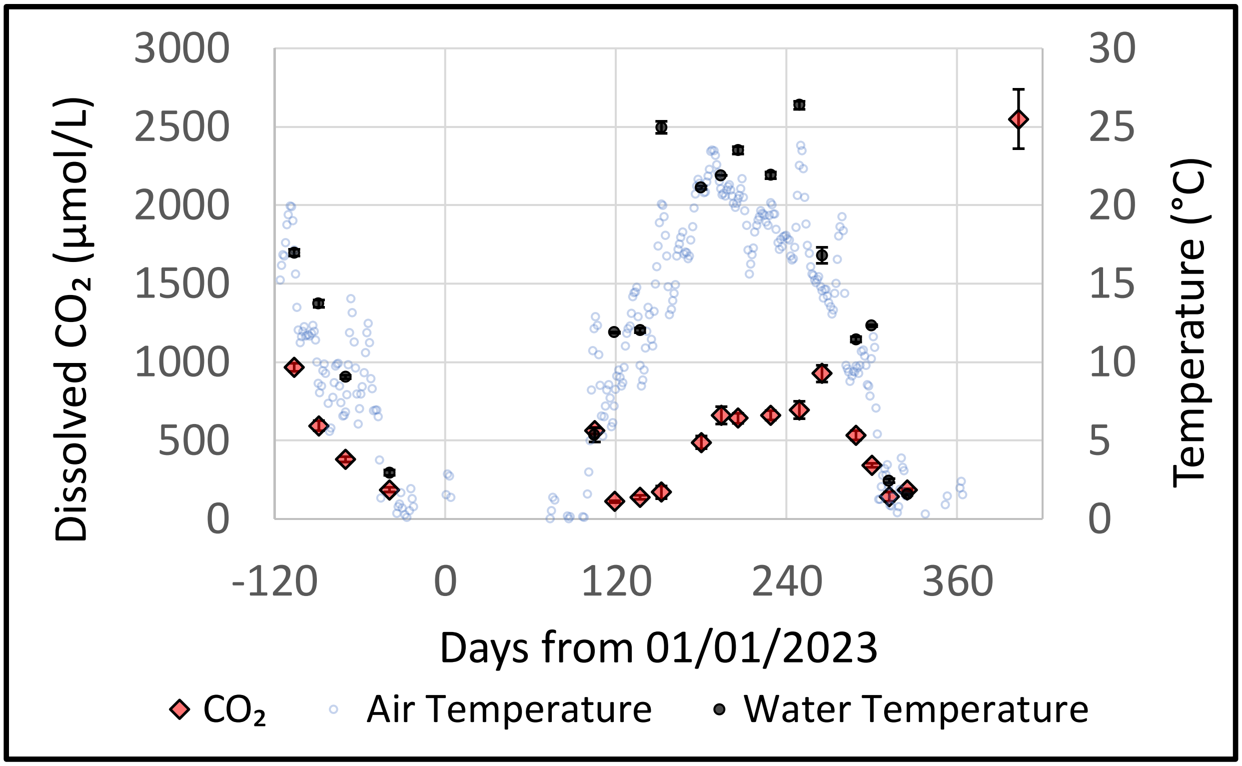
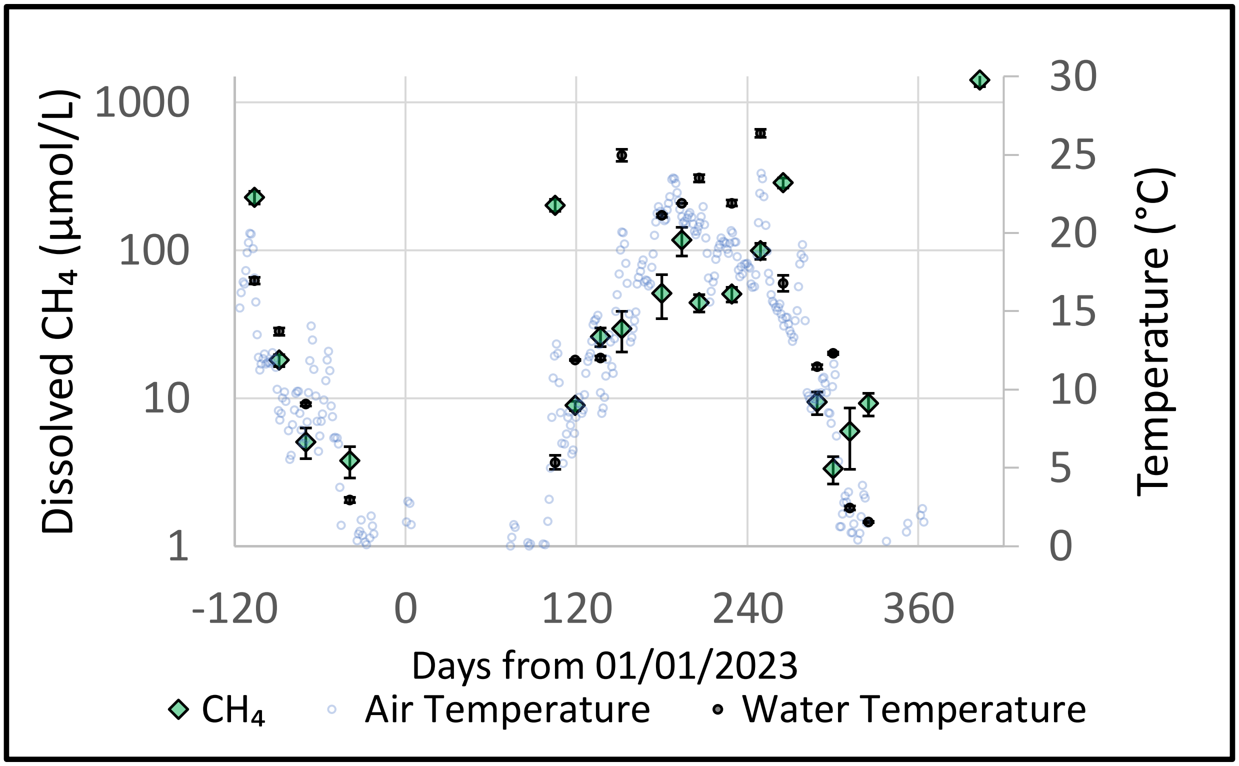


Figure 2.6: Seasonal variation of CO_2 and water temperature in a mineral wetland in Southeastern Ontario. *CO_2* and *Water Temperature* show the average values and standard error of measured dissolved CO_2 and water temperature measured on each sampling day. *Air Temperature* shows the average atmospheric temperature measured at Mirabel airport over the preceding five days.



.

Figure 2.7: Seasonal variation of CH_4 and water temperature in a mineral wetland in Southeastern Ontario. *CH_4* and *Water Temperature* show the average values and standard error of measured dissolved CH_4 and water temperature measured on each sampling day. *Air Temperature* shows the average atmospheric temperature measured at Mirabel airport over the preceding five days.

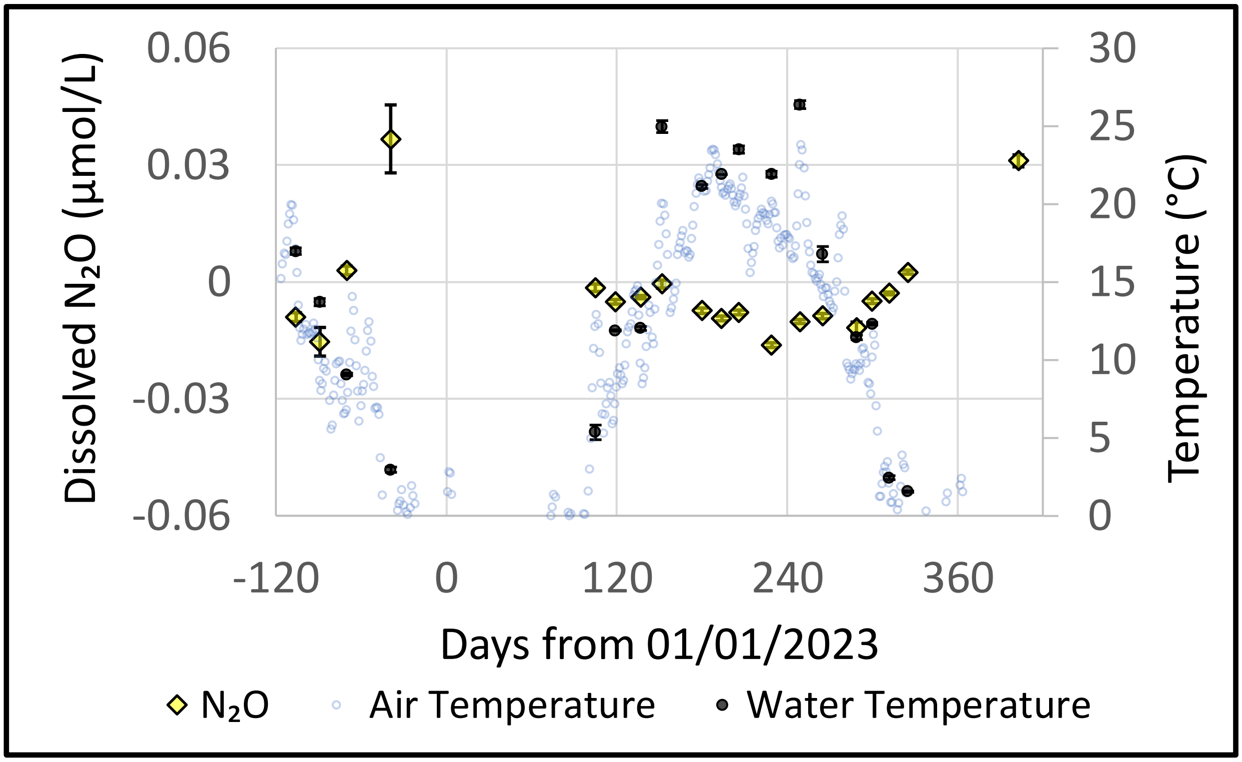


Figure 2.8: Seasonal variation of N_2O and water temperature in a mineral wetland in Southeastern Ontario. *N_2O* and *Water Temperature* show the average values and standard error of measured dissolved N_2O and water temperature measured on each sampling day. *Air Temperature* shows the average atmospheric temperature measured at Mirabel airport over the preceding five days.

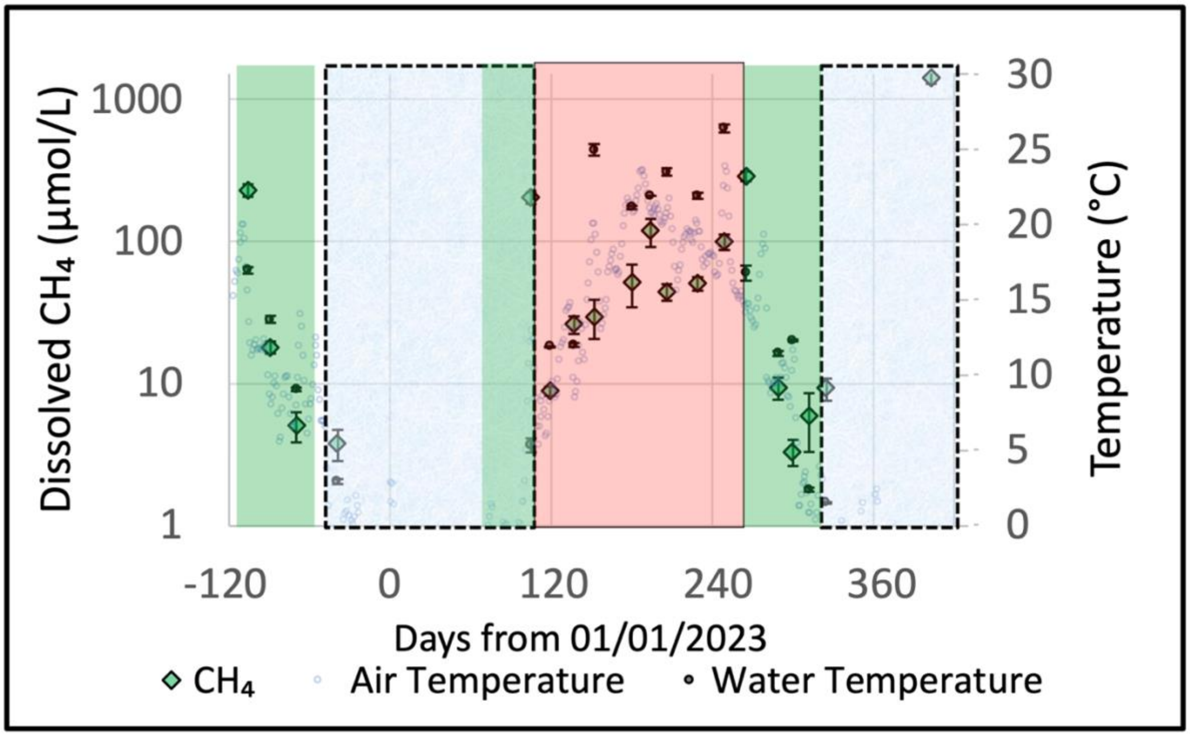


Figure 2.9: Different periods of interest in the wetland, green sections include areas when geese were reported to be in migration, blue areas with dashed outline were times when ice covered the wetland. Red area is the summer. This chart is helpful to distinguish the different data sets used in analysis. NO.ICE includes everything outside the dashed lines, GROWING includes the red area, and GOOSE includes only green areas, outside dashed lines. These colored sections overlay data showing the seasonal variation of CH_4 and water temperature in a mineral wetland in Southeastern Ontario. *CH_4* and *Water Temperature* show the average values and standard error of measured dissolved CH_4 and water temperature measured on each sampling day. *Air Temperature* shows the average atmospheric temperature measured at Mirabel airport over the preceding five days.

At first glance, concentrations appear to vary seasonally mainly based on water temperature (Figures 2.6 and 2.7). As temperatures decrease in the autumn of 2022, so do concentrations of gases. In the spring and into the late summer of 2023, the concentrations rise as the water temperature increases. Then concentrations decline again in the autumn of 2023. However, when analyzing all the data collected, it became clear that water temperature was not a strong predictor of dissolved GHG over the entire data set (data set "ALL"). For example, in these regressions (Supplementary Tables S.1, S.2, S.3) water temperature was not a significant predictor of dissolved CO_2, explaining only 2.7% of the variation of dissolved CH_4, and just 6.2% of dissolved N_2O. Additionally, water temperature had a negative correlation with CH_4

and N_2O. This counter-intuitive finding can be attributed to the accumulation of gas concentrations under ice in winter. The winter sampling on day 403 (February 2024) had the highest measured concentrations of CO_2 and CH_4 due to the length of time under continuous ice coverage. Also, dissolved concentrations of N_2O were only above ambient on four days, three of which had ice coverage. On day 105 (April 2023), sampling occurred as thick ice was breaking up. Despite sampling after ice was broken up, there was still significantly more CO_2 and CH_4 than measured on the previous and following sampling days. As I captured after the moment of ice break up, one can hypothesize that if I had sampled a week or two earlier, before the breakup of ice permitted the diffusion of gases, concentrations would have been even higher, similar to levels measured on sampling day 403. Even a few days under ice led to accumulation of gases, such as on day 312 when there was a slight increase in concentrations of all three gases when compared to the previous sampling days. Ice coverage increases concentrations on day 312, despite the trend of decreasing concentrations with decreasing temperatures in the autumn. Cold water temperatures and high concentrations of gases under ice resulted in negative correlations between water temperature and concentrations of gases.

Ice coverage led to the accumulation of GHG in this wetland. For this reason, the data collected on days with ice coverage was marked and excluded from the next round of regressions (Data set “NO.ICE”). For this round of regressions (Supplementary Tables S.4, S.5, S.6) water temperature was a significant predictor of all three measured GHG concentrations. Water temperature was positively correlated with concentrations of all three dissolved gases, and explained 10.1% of the variation in dissolved CO_2, 6.2% of the variation of dissolved CH_4, and only 1.6% of the variation of dissolved N_2O. Perhaps there is more to the seasonal variation than just water temperature because gas concentrations on various sampling days fall above or below the expected trend based on their water temperature. For example, on day 265, surface water temperatures were lower than the previous sampling day, but there were much higher CH_4 and CO_2 concentrations. Likewise, on day 156 water temperatures were roughly four degrees higher than the following sampling day, but concentrations of CH_4 and CO_2 were far lower. pH was a stronger predictor of dissolved gases, explaining 47.3% of the variation in dissolved CO_2(negative correlation), 17.1% of the variation of dissolved CH_4 (negative correlation), and 12% of variation of dissolved N_2O. Electrical conductivity was also a predictor of all three gases, explaining 4.5% of variation in dissolved CO_2, 2.6% of the variation of dissolved CH_4, and 1.7% of variation of dissolved N_2O (negative correlation). Lastly, TDN was positively correlated with N_2O, and explained 2.5% of variation.

Another seasonal variable potentially influencing concentrations is the feces deposited during Canada goose migration. Large flocks were observed on the days in the autumn on which I recorded the highest measured GHG (excluding winter sampling). To investigate the potential influence of goose feces, the days excluding ice sampling were broken into two data sets. First, regressions were performed on data that was sampled when no goose migration was occurring at the wetland (these samples were all taken during the growing season). Second, regressions were performed only on data sampled during goose migration season. These data sets are referred to as “GROWING” and “GOOSE” respectively. For “GROWING”, regressions (Supplementary Tables S.7, S.8, S.9) revealed that water temperature was only a significant predictor for dissolved CO_2, explaining 12.8% of variation. pH was a strong predictor of all three gases, explaining 65.8% of the variation of dissolved CO_2 (negative correlation), 29.3% of the variation of dissolved CH_4 (negative correlation), and 45.8% of variation of dissolved N_2O. Electrical conductivity was positively correlated with CO_2 and CH_4 and explained 2.4% and 12.7% of variation respectively. Lastly, DOC was positively correlated with dissolved CO_2 and N_2O, explaining 1.5% and 8.3% of variation respectively.

The pattern of pH being the most important predictor of dissolved CO_2 and CH_4 reversed in “GOOSE” regressions (Supplementary Tables S.10, S.11, S12). Water temperature explained 57.2% of the variation of dissolved CO_2, 36.6% of dissolved CH_4 variation, and 3.2% of the variation of dissolved N_2O (negative correlation). Electrical conductivity explained 5% of the variation of CO_2 and 7.7% of N_2O variation. pH was weakly negatively correlated with CO_2 explaining 2.4% of variation, and positively correlated with N_2O explaining 11.8% of variation. TDN accounted for 2.1% of the variation of dissolved CH_4.

To briefly summarize, stepwise linear regressions were performed on four data sets: “ALL”, “NO.ICE”, “GROWING”, and “GOOSE”. All steps of the model are presented in the model summaries along with predictor variables, R, R^2 , adjusted R^2, STD of estimate, R^2 change, F-

Change, degrees of freedom, and significant F-Change (Supplementary Tables 1-12). The regression models explained the highest proportion of variance for dissolved CO_2, CH_4, and N_2O in the "GROWING" data set. pH was the most important predictor for dissolved CO_2, CH_4 except in the "GOOSE" data set. Depth was not a predictor of gas concentrations in any regression models.

2.7: Discussion

I hypothesized that i) warmer water temperatures would correlate with greater concentrations of all three measured GHG ii) there would be buildup of all three GHG under ice in winter iii) pH would negatively correlate with concentrations of CO_2 and N_2O iv) higher concentrations of DOC would correlate with greater concentrations of all three GHG v) higher electrical conductivity would correlate with lower CH_4 concentrations and greater CO_2 and N_2O concentrations and vi) greater TDN would correlate with more dissolved N_2O.

My hypotheses were partly supported. When samples taken under ice coverage were excluded, water temperature correlated with concentrations of CO_2 and CH_4. This finding supports my first hypothesis. Temperature was the most important predictor of CO_2 and CH_4 only during the goose migration periods. Temperature was a weak predictor of N_2O, sometimes showing negative correlations. This finding does not support my first hypothesis.

There is clear evidence that ice coverage resulted in buildup of gases, in support of my second hypothesis. Firstly, looking at Figures 2.6 and 2.7, one can see the outliers which occur under ice. In the analysis, negative correlations between water temperature and concentrations were found in the ALL data sets. This was caused by outliers of high concentrations in cold water under ice. When ice samplings were excluded, water temperature (when a predictor) was a positively correlated with concentrations of the gases (except N_2O GOOSE data set).

The pH was very strongly negatively correlated with CO_2 concentrations in support of my third hypotheses. The pH was less important as a predictor of CO_2 concentrations during the goose migration. The pH was weakly positively correlated with N_2O concentrations, a finding contrary to my third hypothesis. This may be because pH does not necessarily alter the rates of

N_2O production, but rather how much N_2O is reduced into N_2. Additionally, pH was negatively correlated with CH_4, which was an unexpected finding.

DOC was only a weak predictor of concentrations; however, it did appear as a predictor for each gas in one or more data set. When it was a predictor, DOC was positively correlated with concentrations of gases. This finding that DOC was a predictor for each gas in some data sets agrees with my fourth hypothesis, but there is only very weak evidence for this relationship.

Electrical conductivity was a predictor of CH_4 in all data sets except GOOSE, however, it was positively correlated. This disagrees with my fifth hypothesis. Electrical conductivity was a predictor of CO_2 in all data sets and was always positively correlated with concentrations of CO_2, agreeing with my fifth hypothesis. Electrical conductivity showed mixed results on N_2O. It was only a predictor in NO.ICE and GOOSE. In NO.ICE it was negatively correlated, while in GOOSE it was positively correlated. This finding is inconclusive but is contrary to my hypothesis that electrical conductivity increases would correlate with increased N_2O concentrations.

TDN only appeared as a predictor for N_2O concentrations in the NO.ICE data set. Additionally, it was a weak predictor. This is very weak evidence to support my sixth hypothesis. TDN also appeared as a weak predictor for CO_2 in one data, and for CH_4 in two data sets, with inconsistent relationships. The impacts TDN may have been overshadowed by the more important variables in this system. The relationship between increased N loading and increased N_2O emission is well documented (Murray & Knowles, 2003; J. Wang et al., 2015) .

The fact that water temperature was only the primary predictor during the goose migration demonstrates the importance of breaking up the data by seasons. It is also a counter intuitive result. When looking at Figures 2.6 and 2.7, it seems clear that there is a relationship between water temperature and concentrations of CO_2 and CH_4. Clearly ice coverage threw off this relationship, as ALL showed a small negative correlation with water temperature and concentrations. Even in NO.ICE, water temperature is still relatively unimportant compared to pH. While data were still being collected, it seemed clear that temperature was going to be the master variable. Only once the regressions were performed did I see the influence was less important than expected. This led to questions about the relationship between temperature, pH, and dissolved gas.

Past studies have demonstrated the inverse relationship between pH and dissolved CO_2 (Boyd, 2015). This inverse relationship became clear in the regression analysis. Figure 2.10 shows seasonal variations of pH and dissolved CO_2 with sampling days 105 and 403 removed due to months of ice coverage. The general pattern in Figure 2.10 is that when CO_2 concentrations are higher, pH is lower and when CO_2 decreases, pH increases. While this does not demonstrate causality, there is an inverse relationship. There is also a strong negative correlation between water temperature and pH when the same outliers are removed (Figure 2.11). The measurement of pH can be significantly impacted by the temperature of water during measurement (Westcott, 2012). This is not a problem in my study, because water samples were stored overnight in fridges, and sampled the following day. Therefore, all water samples were at the same temperature when measured, regardless of their temperature at the time of sampling. When Figures 2.10 and 2.11 are put together, a potential explanation arises for the seasonal variations of pH and its inverse relationship with both CO_2 and water temperature.

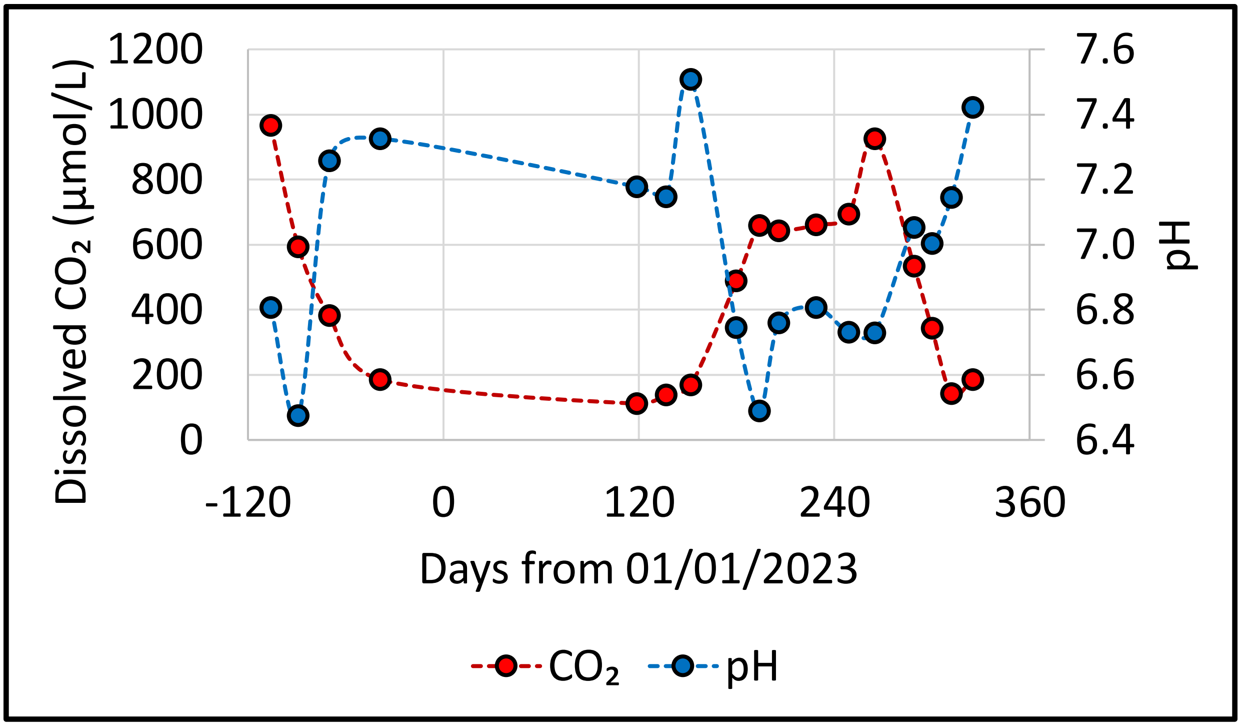


Figure 2.10: Seasonal variations of dissolved CO_2 and pH. Inverse relationship between pH and dissolved CO_2. Each marker on the graph is an average for one sampling day. Days 105 and 403 (removed from graph) were sampled after months of ice coverage.

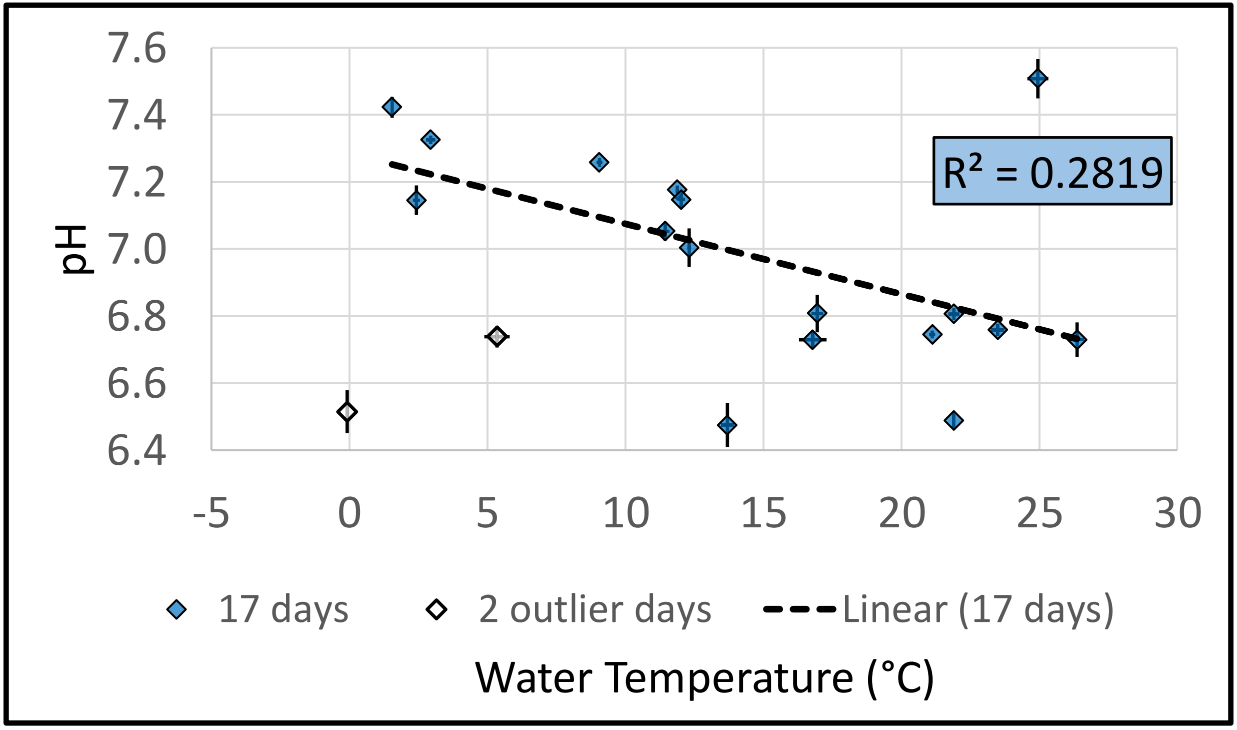


Figure 2.11: Relationship between water temperature and pH. Each diamond shows average and standard error for one sampling day. Days 105 and 403 (2 outlier days) were sampled after months of ice coverage.

The relationship between water temperature and pH (Figure 2.11) may be a legacy of the relationship between temperature and dissolved CO_2. As sediment temperatures increase in the spring and summer, rates of decomposition and microbial respiration rise. This increases CO_2 production, resulting in more dissolved CO_2. The rise in dissolved CO_2 decreases pH in the water column (Figure 2.10). pH can be thought of as a legacy of CO_2 production which in turn is controlled by sediment temperatures. Because CO_2 production occurs predominantly in the sediment, measures of temperature at the water surface are not accurately representing the temperature of the CO_2 source area. pH, which is closely linked with dissolved CO_2, becomes a better predictor of sediment temperature than the surface water temperature measurements. This not only explains the strong relationships between pH and CO_2, but also pH as a strong predictor of CH_4 concentrations. Because pH is so closely tied to CO_2 production and CO_2 production tied to sediment temperatures, CH_4 appears to be controlled by pH. In reality, pH changes reflect the changes in sediment temperature. As sediment temperatures rise, CH_4 production increases as pH happens to decrease due to increased dissolved CO_2. This inverse relationship between temperature and pH has been recorded in other wetlands, however evidence of a relationship between pH and CO_2 or CH_4 production was not identified (Singh et al., 2000). One study found that pH decreased in wetlands during the growing season, but did not identify CO_2 production as the cause (Gehant, 2015). Other potential causes for pH variation include precipitation events or deposition of nitrogen or sulphur oxides (Psenner, 1994)

This separation of surface water temperature and sediment temperature also explains some of the outliers identified in the seasonal sampling. On day 152 (June 1, 2023), concentrations of dissolved CH_4 and CO_2 are low despite high surface water temperatures. The high water temperature follows a series of hot spring days. Although the surface has warmed up, sediments are still cool and production of GHG is low. The lag between surface and sediment temperature can be thought of in terms of seasonal temperatures. Although June 20th is the longest day of the year, it is rarely the hottest. Air temperatures continue to rise until late July. Water temperatures take even longer to catch up; the Great Lakes reach their warmest temperatures in August (National Data Bouy Center NOAA, n.d.). The sediments in this wetland may continue to warm up into the late summer.

Days -106 and days 265 (September 16th, 2022, and September 22nd, 2023), show very high concentrations of dissolved CO_2 and CH_4, but surface water temperatures are lower than summer averages. It is possible that despite cooler air and surface water temperatures, sediments are still warm and therefore capable of high rates of production. The combination of warm sediment and additions of labile carbon and nutrients from goose feces and senescing vegetation may provide the perfect conditions for CO_2 and CH_4 production.

By removing days under ice and days when sediment temperatures may be most different to water temperature (-106,105,152, 265, 403) there is a clear relationship between average concentration of CO_2 or CH_4 and average water temperature on each sampling day (Figure 2.12, Figure 2.13). There is certainly a positive correlation between temperature and dissolved GHG, but measuring the surface water temperature may not be the best way to unveil that relationship. Measurements should focus on source areas of GHG production rather than the most accessible measurement location. Although sampling water temperature at the surface is far more feasible, it may not be useful as a predictor of GHG production. Water temperature and other variables including dissolved O_2, pH, and suspended solids measured in a wetland all showed large changes over only 30 cm of depth (Boeckman & Bidwell, 2007).

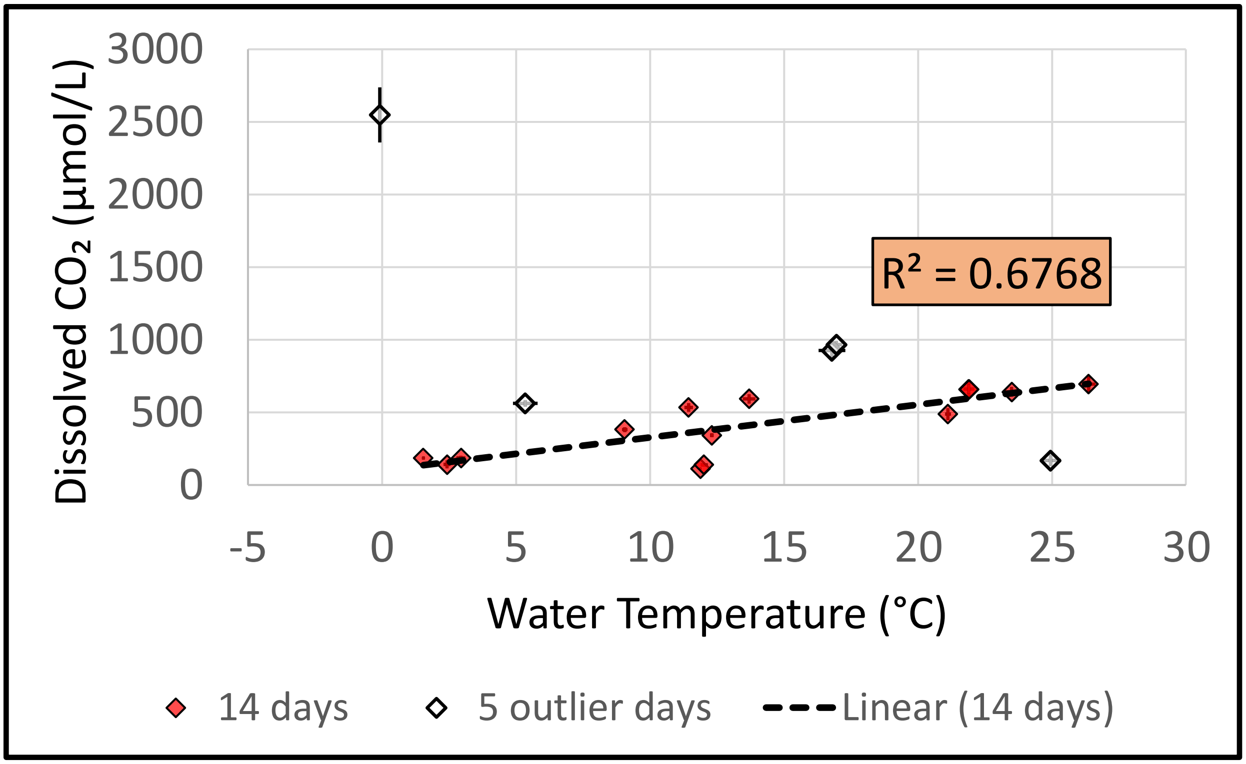


Figure 2.12: Relationship between water temperature and dissolved CO_2. Each diamond shows average and standard error for one sampling day. five outlier days: -106,105,152, 265, 403. Days 105 and 403 were sampled after months of ice coverage. Days -106, and 265 had outlier gas concentrations, also sampled during GOOSE season. Day 152 was a very hot day, in early June. All these days had gas concentrations that did not "fit" the pattern based on temperature, potentially due to large differences between surface water temperature and sediment temperature.

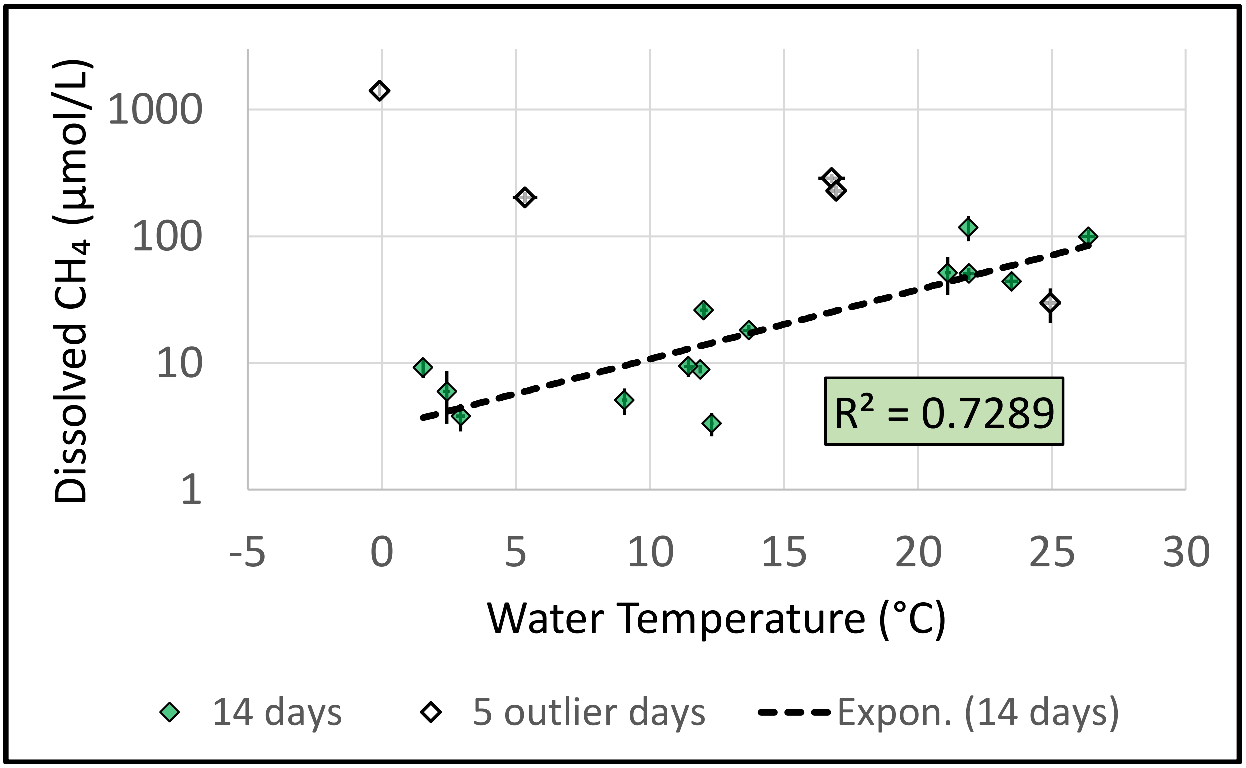


Figure 2.13: Relationship between water temperature and dissolved CH_4 . Each diamond shows average and standard error for one sampling day. five outlier days: -106,105,152, 265, 403. Days 105 and 403 were sampled after months of ice coverage. Days -106, and 265 had outlier gas concentrations, also sampled during GOOSE season. Day 152 was a very hot day, in early June. All these days had gas concentrations that did not "fit" the pattern based on temperature, potentially due to large differences between surface water temperature and sediment temperature.

The explanation for water temperature becoming the best predictor of CO_2 and CH_4 in the autumn (GOOSE) data set may be related to this separation between sediment and surface temperatures. Perhaps the decline in air and water temperature in the autumn coincides with a turnover of the stratified water column, mixing the surface waters with the lower levels. This results in more homogenous temperatures across a depth profile and measurements at the surface actually reflect the temperatures in the sediments. This mixing may also explain the large outliers during the autumn goose migration (-106, 265). As lower-level waters closer to the source of production have higher concentrations of gases which are then mixed with the surface waters, resulting in higher measured concentrations after the turnover. This is speculation and future research may want to focus on the role of depth and water column turnover on wetland GHG emissions. Like first hypothesized, these outliers may be connected to goose feces or senescence and the halting of photosynthesis.

As discussed, a better way to measure temperature would have been to probe sediments at each sampling location. When trying to determine how temperature influences production one should focus on sediments as they are the source of most GHG production.

The summer season or GROWING had only two days where average water temperatures were below 20 ºC. Additionally, there were three days with temperatures between 21 and 22 ºC. The lack of a wide variation in water temperatures may have limited the efficacy of water temperature as a predictor. Although I began sampling everyday between 8:45 and 9:15 in the morning, slight differences in timing may have caused some unidentified errors. From the opposite perspective, only sampling in the mornings may result in a sampling bias by not capturing diurnal variations. Future research could focus on diurnal variations especially in shallow areas of wetlands where temperatures may change more rapidly.

Additional unmeasured influences on this wetland system may include runoff of agricultural fertilizers from surrounding fields, or runoff of cow manure into the wetland. Rainfall in the spring may wash recently applied fertilizers from the catchment into the wetland. During the summer and autumn, grazing cattle may deposit manure that could be washed into the wetland. Additions of plant litter after senescence in the autumn may provide additional substrate for decomposition. In deeper areas of the wetland, there may be a fall turnover, bringing higher concentrations of dissolved gases from close to the sediment to the surface.

2.8: Conclusion

This field research identifies seasonal trends in dissolved gas concentrations in the study wetland. The wide variation across the wetland within each sampling day demonstrates the importance of sampling in many different areas within a wetland rather than one single spot. By sampling from all around the wetland, I reduced the chances of outlier measurements throwing off the daily averages. Sampling even more locations within the wetlands would have improved my estimates of average dissolved gas. Although I sampled the wetland on 19 days, more frequent sampling would have improved the results and clarified seasonal patterns. This research demonstrated the importance of winter sampling. A particular focus on increased frequency of sampling during the changing of seasons may have resolved some of the outstanding questions and helped identify the causes of outliers.

This research demonstrated a relationship between pH and dissolved GHG concentrations. While this was expected for CO_2, the correlation of pH and CH_4 led to further questions. I hypothesize that the correlations of pH with CH_4 are ultimately related to the relationship between temperature and dissolved CO_2. As temperatures increase, CO_2 production increases, leading to more dissolved CO_2 and therefore a lower pH. The rise in temperature that increases CO_2 production also increases CH_4 production. The reason there is not a stronger correlation between temperature and dissolved CO_2 and CH_4 is because measurements of surface water temperature may not represent the temperature in the areas of production. pH change is indirectly caused by changes in temperature in the areas of production and is a better predictor of CH_4 than surface water temperature.

Water temperature was only the main predictor of GHG concentrations when I isolated the sampling days during goose migration (autumn). Perhaps during the autumn, mixing of the water column caused by the fall turnover results in measurements of surface temperatures that are more representative of areas of GHG production. This mixing could explain why surface water temperature is only the best predictor in autumn/during the goose migration. The shift from pH being the main predictor in NO.ICE, and GROWING, to water temperature being the most important predictor in GOOSE, demonstrates that different variables are more important during different “seasons”. The goose migration or autumn season seems to be unique compared to the other times of year, and field researchers in this region may consider taking migration into consideration when sampling.

Another potential area of further research is on the relationship between temperature, dissolved CO_2, pH, and dissolved CH_4. A laboratory incubation could control temperature in otherwise identical flooded treatments, measuring dissolved carbon dioxide concentrations and pH as the incubations goes on. This experiment might reveal a positive correlation between dissolved carbon dioxide and temperature, and potentially a negative correlation between temperature and pH. This idea could be extended in a larger scale experiment in which large soil columns are flooded and controlled for temperature, measuring pH, dissolved methane, and dissolved carbon dioxide. Larger soil columns would allow for the development of anaerobic and aerobic zones with methane and carbon dioxide production. In this experimental design, relationships between temperature, methane production and pH could potentially be revealed.

High frequency and widespread sampling led to a deeper understanding of the wetland and a consideration of the immeasurable variables of the field. During time spent in the field, I witnessed a large scale ebullition event. Rather than a few bubbles, the wetland seemed to boil with gas bubbles breaking the surface around my kayak. Despite being in the right place at the right time to capture this phenomenon, I did not have the proper equipment to quantify this event. I was not in the field often enough to know if this was a regular or rare event. Future research could attempt to quantify the impact of large scale ebullition events on net emissions.

The presence of outliers during goose migration, and the differences made clear during analysis led to more questions about the influence of goose feces on GHG emissions. Additionally, other potential influences such as fertilizer and manure runoff warrant further investigation. These unmeasured variables and their potential impacts led to the second chapter of this thesis. A more controlled laboratory experiment may elucidate the impact of goose feces, manure, and fertilizer runoff on wetland GHG emissions.

Chapter 3: Greenhouse Gas Emissions from Saturated Soils after the Addition of Mineral Fertilizers, Manure and Goose Feces

3.1: Objective:

Wetland soils are subject to additions of nutrients derived from agricultural manure, fertilizers, and goose feces. To determine the effect of these additions on the production of CO_2, CH_4 and N_2O from a wetland soil sample, I conducted laboratory incubations under aerobic to anaerobic conditions over 141 days.

3.2: Introduction

Wetlands continue to be drained for agriculture, while other remaining wetlands are exposed to nutrient runoff from nearby agricultural production (Euliss et al., 2006). Nutrients come from applied fertilizers as well as animal manure which can run off or leach into surrounding wetlands (Kato et al., 2009; J. Li et al., 2021).Additionally, waterfowl may add nutrients in certain waterbodies (Manny et al., 1975; Unckless & Makarewicz, 2007; Mariash et al. 2019) Excess nutrient inputs may affect the carbon balance of wetlands by increasing net primary productivity, altering plant communities, changing emission pathways by altering the composition of microbial populations, providing substrates for GHG producing redox reactions, and by causing eutrophication events which can tip a productive aquatic carbon sink into a source (Verhoeven et al., 2006; Sánchez-Carrillo et al., 2011). Lastly, changing plant species may transport gases differently due to their morphology, resulting in more or less oxygenated sediment, or more rapidly releasing gases produced in sediments via aerenchyma (Keller et al., 2006). Therefore, changing the nutrient status in a wetland may alter the flux of GHG from a wetland.

Nutrient Impacts on Carbon Dioxide Emissions

The impact of phosphorus on CO_2 emissions from wetlands is dependent on the length of the study and the type of wetland (Keller et al., 2006). Research on peat soils found no significant impact of phosphorus fertilization on CO_2 emissions (Aerts & Toet, 1997). A phosphorus and potassium addition had no significant impact on CO_2 during a multi-year fertilization in a bog (Juutinen et al., 2018). In an anaerobic incubation of wetland soils sampled in the Everglades, phosphorus additions did not impact CO_2 flux (Medvedeff et al., 2014). Yet, In the short term (days/weeks), phosphorus additions may stimulate soil respiration by increasing microbial populations that are phosphorus limited (Lund et al., 2009; Johnston et al., 2019; Wu et al., 2022).

When looking at the impact of nitrogen on CO_2, emissions are increased with higher NO_3^- concentrations likely due to greater respiration and decomposition (Mwagona et al., 2019). Additionally, nitrogen additions were found to significantly increase ecosystem respiration when applied with phosphorus and potassium (Juutinen et al., 2018). Nitrogen inputs may increase the decomposability of organic matter through vegetation changes (Lund et al., 2009; Juutinen et al., 2018). Nitrogen additions also may stimulate microbial respiration by promoting the growth of nitrogen limited microbial populations (Gunnarsson et al., 2008). In a field experiment, medium and high application of ammonium nitrate significantly increased ecosystem respiration, while low applications had no significant impact (Song et al., 2013). The most relevant finding is from a wetland mesocosm experiment, in which CO_2 flux was increased by 30% in inundated soils after the addition of a liquid nitrogen fertilizer (Total N = 12.5%, comprised of ammonium = 5%, N organic = 1.1%, N as urea = 4.8%, N as NO_3^- = 1.6%) (Bonetti et al., 2022). Additionally, nitrogen may increase the ratio of CO_2/CH_4 emitted by increasing the chances of anaerobic CH_4 oxidation (the by-product is CO_2) (Mwagona et al., 2019). Sulfur, like nitrogen, may increase the ratio of CO_2/CH_4 emitted by promoting the anaerobic oxidation of CH_4 (Timmers et al., 2016; L. Li et al., 2019; Soued et al., 2024).

Nutrient Impacts on Methane Emissions

Research by Song et al. (2012) suggests that long-term phosphorus loading reduces CH_4 emissions under various application rates; however, other research found no effect of phosphorus additions on CH_4 emissions (Keller et al., 2005). Adding to the debate is the finding that a phosphorus addition caused a short-term increase in CH_4 emissions in peat soil (Aerts & Toet, 1997). A possible explanation for reduced CH_4 production following long-term phosphorus enrichment may be reduced root exudation, which provides some of the organic substrate for CH_4 production, resulting in decreased microbial activity of methanogens (Le Mer & Roger, 2001). In an anaerobic incubation of soils collected from agricultural wetland drainage ditches, phosphorus additions alone had no impact on CH_4 production (Kim et al., 2015). Contrary to this finding is that in an anaerobic incubation of wetland soils from the Everglades, phosphorus addition increased CH_4 production (Medvedeff et al., 2014). To summarize, it is unclear how phosphorus additions impact CH_4 flux from wetlands (Song et al., 2012).

Findings on the impact of nitrogen fertilization on wetland CH_4 emissions are contradictory, and mechanisms have yet to be explained (Bodelier, 2011). The type of nitrogen added may alter the outcome and outcomes vary significantly between natural wetlands and rice paddies (Bodelier, 2011; Juutinen et al., 2018). Methane emissions may be lower in NO_3^- rich environments because NO_3^- reduction yields more energy than methanogenesis, leading to NO_3^- reducing organisms outcompeting methanogens for carbon substrates (Gao et al., 2014). Increased denitrification with NO_3^- addition can also lead to intermediates of denitrification that are toxic to methanogens (NO_2^-, NO, N_2O) (Bodelier, 2011). Additionally, NO_3^- may decrease CH_4 emission due to increased anoxic CH_4 oxidation (Ettwig et al., 2010; Mwagona et al., 2019). Methane may be oxidized in anoxic conditions with NO_3^- acting as an electron acceptor (Kim et al., 2015). However, increased nitrogen in the form of ammonium has increased CH_4 emission, likely due to the inhibition of methanotrophs, slowing rates of CH_4 oxidation (L. Liu & Greaver, 2009; Juutinen et al., 2018). One study of inundated mesocosms of wetland soils found that the addition of a liquid nitrogen fertilizer (Total N = 12.5%, comprised of ammonium = 5%, N organic = 1.1%, N as urea = 4.8%, N as NO_3^- = 1.6%) increased CH_4 flux by 90% when compared to an inundated control (Bonetti et al., 2022). Lastly, four different application rates of ammonium nitrate had no impact on CH_4 emissions during a five year experiment in a wetland (Song et al., 2013).

It has been shown that increased salinity decreases CH_4 emissions likely due to SO_4^{2-} inhibiting methanogenesis (Magenheimer et al., 1996). This is due to SO_4^{2-} reducing bacteria competing with methanogens as well as driving the anaerobic oxidation of CH_4 (Gauci et al., 2004; L. Li et al., 2019; Soued et al., 2024). Large-scale field studies in rice paddies have shown that adding SO_4^{2-} in the form of gypsum can reduce CH_4 emissions by up to 72% at heavy application rates (Gauci et al., 2004).

Nutrient Impacts on Nitrous Oxide Emissions

Y. Zhang et al. (2019) found that phosphorus additions had no effect on N_2O emissions from a high altitude wetland, and Wang et al. (2014) and Zheng et al. (2016) found that that phosphorus addition had no impact on N_2O emissions in forest soils. N_2O emissions are increased with greater NO_3^- concentrations (J. Wang et al., 2015; Mwagona et al., 2019). Ammonium nitrate additions increased N_2O emissions in an alpine wetland (Gao et al., 2014). Additionally, ammonium rich fertilizer increases N_2O. In a mesocosm experiment, the addition of a liquid nitrogen fertilizer (Total N = 12.5%, comprised of ammonium = 5%, N organic = 1.1%, N as urea = 4.8%, N as NO_3^- = 1.6%) increased N_2O fluxes 15 fold when compared to the control (Bonetti et al., 2022). Greater concentrations of NO_3^- lead to greater N_2O/N_2 in the soil matrix and more efflux of N_2O (Wrage et al., 2001; Kim et al., 2015). It is important to note that impacts of nitrogen addition on N_2O may depend on initial wetland stoichiometry (Song et al., 2013).

3.3: Scope

I performed two separate laboratory incubations of wetland soils under saturated conditions in sealed jars starting with ambient atmosphere in headspace. The first was an incubation using common cropland fertilizers (K_2SO_4, KH_2PO_4, KNO_3) with biochar included as a stable carbon addition. The second was an incubation using different rates of cattle manure and goose feces, representing additions of nitrogen, phosphorus, sulphur, and labile carbon. I analyzed the headspace of these jars nearly 20 times over a period of 140 days to determine how nutrients additions affect GHG production rates.

3.4: Hypotheses

To date, it is not clear how nutrient additions affect GHG emissions of wetland soils. I hypothesize that i) the CO_2 production increases with additions of KNO_3, biochar, or fecal matter, ii) the CH_4 production increases with additions of biochar, or fecal matter, and decreases with additions of KNO_3 or $K_2SO_4^{2-}$, and iii) N_2O production increases with additions of NO_3^- or fecal matter.

3.5: Methods

Sample Collection

Soil samples were collected from the from the top 10 cm of the riparian zone of the wetland mentioned in chapter 2. These riparian areas are occasionally flooded during the spring melt. I collected a bulk sample, by digging a trench and then digging into the soil profile from the side to collect the upper 10 cm of soil (Figure 2.3). The samples were placed on ice in a cooler immediately after sampling and transferred to a 4 ºC fridge. Samples were broken up by hand to aid in the removal of large roots, worms, rocks, and large plant litter. The sorted soil was then homogenized and stored in plastic Ziploc gallon bags in the fridge until incubations began.

Experimental Design

The first incubation (agricultural nutrient application) included four treatment groups and one control. Each group had five replicates for a total of 25 incubation jars. The four treatments were potassium sulfate (K_2SO_4), potassium dihydrogen phosphate (KH_2PO_4), and potassium nitrate (KNO_3), as well as a biochar addition. I applied the three nutrients at a rate of 12 kg/ha, estimating the bulk density of the topsoil as 15000 kg/ha. For a sample of 50 g, 0.4 mg of fertilizer was added (0.0008% by weight). The biochar was added at a rate of 10000 kg/ha or 333 mg per 50 g soil (0.6666% by weight).

To begin the incubations, 50 g of homogenized soil was transferred to clean 250 ml mason jars. The nutrients were dissolved in pond water collected from the wetland to ensure they were completely and homogeneously incorporated into the soil matrix. Next, 50 ml of either treated or untreated pond water was added to each soil. As soon as the water was incorporated, the lids were sealed, leaving 190 ml of headspace. This headspace was immediately sampled to establish the initial conditions. Each time I sampled, I removed 10 ml of gas through a sealed stopcock in the lid of the mason jar and replaced it with 10 ml of pure N_2 (99.999%). I sampled 17 times over 141 days with sampling occurring more often in the earlier stages of the incubation to capture the rapid changes anticipated at the beginning of the experiment.

The second incubation (fecal nutrients) involved the application of manure and goose feces to the incubation jars. The application rate of goose feces was determined based on previous studies, with special attention given to rates applied by a previous incubation experiment that applied waterfowl feces to soil based on camera trap observations and published defecation rates for birds (Hahn et al., 2008; Winton & Richardson, 2016). Winton & Richardson (2016) used two application rates in their experimental design, a 0.1% and a 0.3% addition by weight as well as a control with no feces. In my incubation, I included a 0.3% as well as a 3% fresh fecal matter addition by weight. The logic behind the 3% application rate is to help determine what occurs at a hyper local scale when geese defecate in a wetland. The average weight of each dropping of goose feces collected was roughly 15 g. Therefore, each soil column in the 3% goose feces treatment receiving 1.5 g of fresh fecal matter is the equivalent 1/10th of a dropping, and a 0.3% addition represented 1/100th of a dropping.

Manure was applied at the same rates as goose feces but was dry unlike the fresh goose feces addition. The homogenized soil was weighed and deposited in 250ml mason jars and treatments were applied. Fecal additions were dropped on top of the soil to simulate the natural deposition of feces. The soil was then inundated with 50 ml of pond water collected from the wetland, sealed, and sampled as soon as possible to establish initial conditions. Jars were incubated at 23 ºC and sampled 20 times over 78 days. Measurements were performed more often in the beginning to capture the periods of interest for the production of N_2O. This chapter does not include statistical analysis but rather a description of the data.

Nutrient Content of Fecal Additions

Nutrient content of Canada goose feces has been sourced from various studies. Ayers et al. (2010) measured nutrient content in fresh feces at 24.2 mg nitrogen, and 4 mg phosphorus per g dry mass. Manny et al. (1975) found that the average nutrient content in Canada goose feces was 759 mg carbon, 44 mg nitrogen and 13.4 mg phosphorus per g dry mass. Unckless & Makarewicz (2007) determined that there was 1.69 mg phosphorus and 10.53 mg nitrogen per g dry mass (based on 80%) moisture of fresh droppings. Mariash et al. (2019) determined the nutrient composition of Canada goose droppings as 446 mg carbon, 40 mg nitrogen, and 4 mg phosphorus per g dry mass. Lastly, Kear (1963) measured wild geese feces to have a nutrient content of 22 mg nitrogen, and 10 mg of phosphorus per g dry weight. With such wide variation in nutrient measurements, there is clearly an influence of diet. The average of sourced studies is 602 mg carbon (n=2 std=156.5) 28.15 mg nitrogen (n=5, std=12.29) and 6.6 mg phosphorus (n=5 std=4.36) per g dry weight.

According to the literature, the average dry weight of a goose dropping is 3.5 g, and the average dropping is 21% solids (Dessborn et al., 2016). So according to the literature review on nutrient content of goose feces, the 3% treatment added 0.285 g of dry matter representing 172 mg carbon, 8 mg of nitrogen, and 1.9 mg of phosphorus per replicate. The 0.3% treatment added 17.2 g of carbon, 0.8 mg of nitrogen, and 0.19 mg of phosphorus per replicate.

For manure nutrient composition, the nutrient content of organically raised cow manure is reported. The results for the nutrient composition of less than three month old organic farm yard manure as found by Shepherd et al. (2002) are 380 mg carbon, 20.2 mg nitrogen, and 3.6 mg phosphorus per g dry matter. The similarity between waterfowl feces and cow manure has been discussed (Kear, 1963).

The manure was added dry; therefore, the 3% treatment added 1.5 g dry mass representing 570 mg carbon, 30 mg nitrogen, and 5.4 mg phosphorus per replicate. The 0.3% treatment added, 57 g carbon, 3 mg nitrogen, and 0.54 mg of phosphorus per replicate.

Sampling and Measurement

CO_2, CH_4, and N_2O in headspace samples were analyzed with a Gas-Chromatograph (Shimadzu-GC-2014). On each day, standards were analyzed before the samples to calibrate the measurements. To convert ppm measurements into gas production per g of soil per day, I used the ideal gas law, assuming constant temperature (incubation temperature 23 ºC) constant pressure (standard atmospheric) and constant headspace volume (190 mL). I corrected the measurements for the removal of gases due to headspace sampling. This was done by adding the number of moles of each gas removed due to the previous sampling to the next measurement. And lastly, I normalized the production for each sampling day by dividing the production since the last sampling by the number of days between samplings.

3.6: Results

Nutrient Incubation

Across all treatments in the nutrient incubation the production and concentrations of the three measured GHG were similar in timing and magnitude (Figure 3.1). The control, the 0.0008% applications of K_2SO_4, KH_2PO_4, KNO_3, and the 0.6666% application of biochar all had peaks and declines occurring in unison and with similar magnitude for all three measured gases. The GHG concentrations in the headspace of the incubation jars were measured with high temporal resolution during the first 60 days. I sampled one last time on day 141 of the incubation.

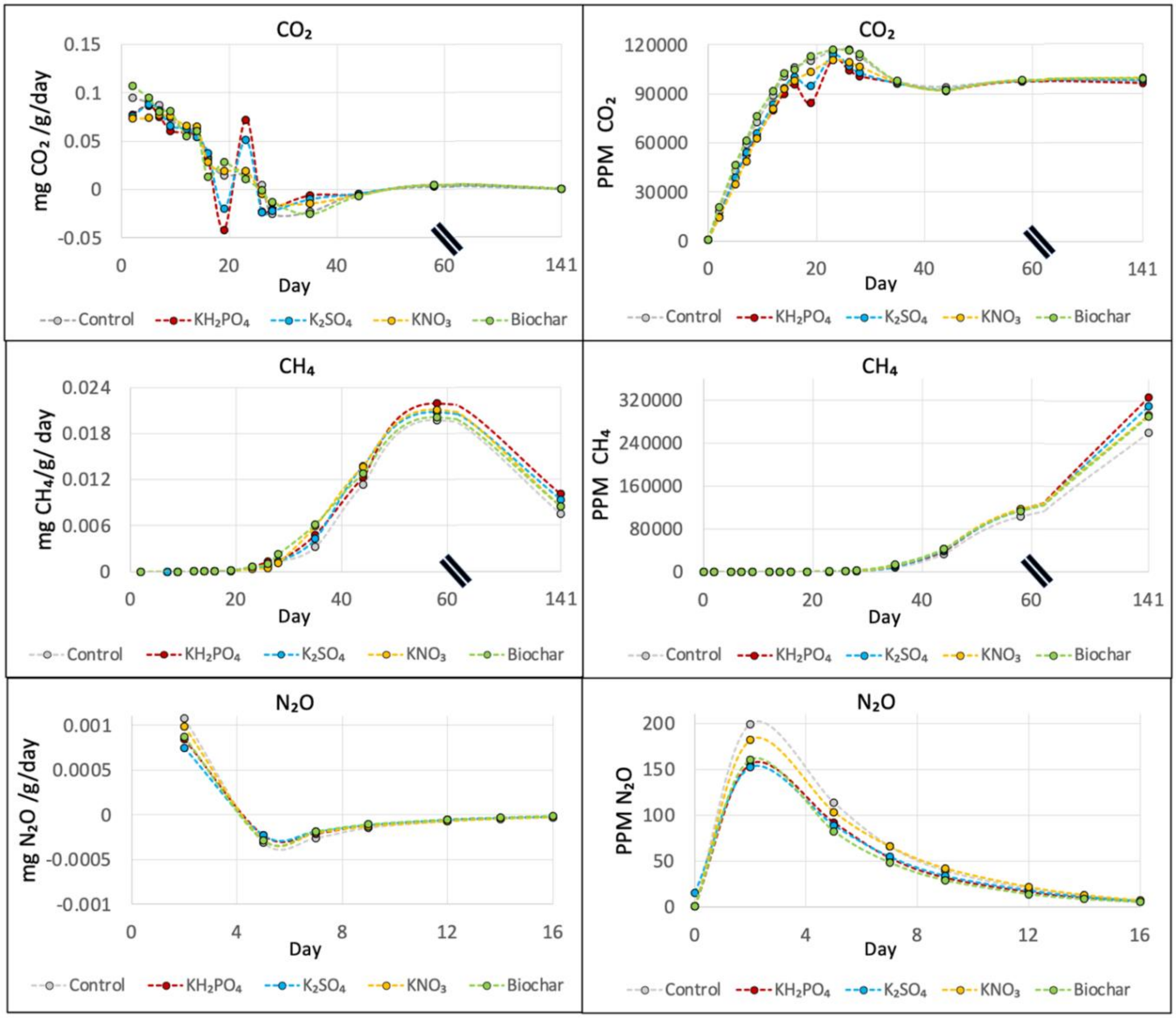


Figure 3.1: Nutrient incubation GHG production and concentrations: These six charts show averages of each treatment group for measured gases on each sampling day (0-141) in the "nutrient addition incubation". From top to bottom the charts show data for CO_2, CH_4, and N_2O. Charts on the left side show the daily fluxes in mg gas per g soil per day. Charts on the right-side show concentrations of gas in parts per million (PPM). (X-Axis scale change at 60 days).

Carbon Dioxide

In the nutrient addition incubation, all five treatment groups measured roughly the same concentrations of CO_2 throughout the incubations. On most days, the biochar treatment showed the highest concentrations of CO_2 followed closely by the control group. The three nutrient additions of K_2SO_4, KH_2PO_4, and KNO_3 all had slightly lower concentrations of CO_2

compared to the control and biochar addition. On day 19 of the incubation, there was a dip in the CO_2 concentrations of the K_2SO_4 and KH_2PO_4 treatments. Despite these decreases, both treatment groups rebound and by the following sampling day again showed similar concentrations to the other treatments. The aberration of these two treatments on days 19 and 23 may be the result of an unidentified sampling or measurement error. To summarize, in the nutrient incubation concentrations of CO_2 began near ambient atmospheric levels and increased for the first 26 days, peaking between 117180 ppm in the control and 110726 ppm in the KH_2PO_4 treatment. After peaking, they declined over the next 20 days until stabilizing at about 97000 ppm for the remainder of the incubation period.

Methane

All five treatments measured roughly the same concentrations of CH_4 on each measurement day. Therefore, the calculated production rates were also similar between the five treatments during the incubation period. As the incubation continued, larger differences in concentrations appeared. For example, 141 days after the incubation began, CH_4 concentrations were highest in the KH_2PO_4, treatment at 326499 ppm, and lowest in the control at 259705 ppm. It is possible that continuing the high frequency sampling for a longer period than 60 days would reveal significant differences between the nutrient treatment groups and the control.

Nitrous Oxide

Looking at the N_2O data for the nutrient incubations, there was no production after day 16, as the concentrations reached zero and remained so for the rest of the incubation. The N_2O concentrations in the treatments peaked on day 2, after which the concentrations declined until reaching zero. The peaks vary, with the control having the highest peak at 200 ppm, KNO_3 peaking at 180 ppm and the remaining treatments peaking at 150 ppm. From these peaks, all treatments declined at roughly the same rate, although the KNO_3 treatment declined slightly slower than the control group.

Fecal Incubation

Beginning with a summary of the fecal incubation, Figure 3.2 illustrates that the control treatment and the fecal addition treatments (3% goose feces, 0.3% goose feces, 3% manure, 0.3% manure) had different production rates and peak concentrations for all three measured GHG. Despite these differences, there were similarities in the overall patterns. Similarities included the decline of CO_2 production from day 0 onwards, the delay in CH_4 production with the increase starting around day 20, and the N_2O peak and decline to 0 ppm around day 20. The GHG concentrations in the headspace of the incubation jars were measured 20 times over 78 days.

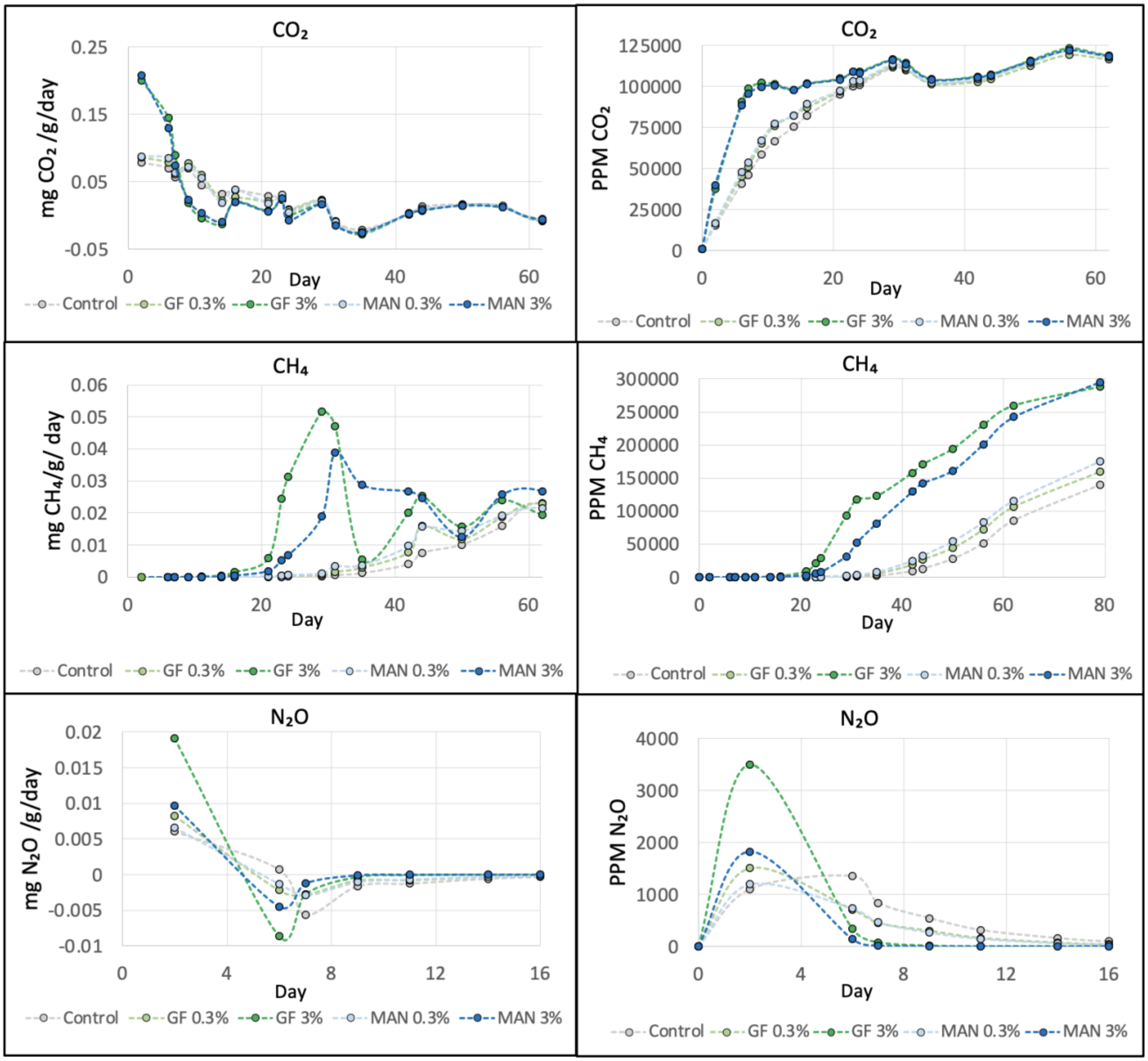


Figure 3.2: Fecal incubation GHG production and concentrations: These six charts show averages of each treatment group for measured gases on each sampling day (0-78) in the “Fecal addition incubation”. From top to bottom the charts show data for CO_2, CH_4, and N_2O. Charts on the left side show the daily fluxes in mg gas per g soil per day. Charts on the right-side show concentrations of gas in PPM.

Carbon Dioxide

Looking at CO_2, there was an evident difference between the fecal addition treatments and the control. Throughout the incubation, 0.3% fecal additions treatment (manure and goose feces) had similar concentrations of CO_2 with higher initial production than the control.

Likewise, the 3% fecal addition treatments had similar concentrations during the incubations. Both the 3% goose feces and the 3% manure treatments started off with much higher CO_2 production than the control. These high initial production rates led to rapidly increasing concentrations, but production for the 3% treatments dropped to near 0 mg CO_2 per g soil per day by the 11th day of the incubation. The control and 0.3% treatment CO_2 production rates declined more gradually, reaching 0 mg CO_2 per g soil per day by the 24th day of the incubation. Despite the different timing and magnitude of the CO_2 production, concentrations of the control and 0.3% fecal additions ended up at the same levels as the 3% treatments by the 30th day of the incubation. To summarize, the 3% treatments started with very high production rates that quickly dropped to near 0, while the control and the 0.3% treatments had lower initial production, but steadily declined over the first 25 days. All treatments reached a plateau in CO_2 concentrations between 100000 ppm and 125000 ppm and fluctuated slightly for the remainder of the incubation.

Methane

There were noticeable differences in CH_4 concentrations between all of the treatments in the fecal addition incubation. Again, the CH_4 concentrations in the 3% treatments were more similar to each other than they were to their respective lower application rates of the same treatment type. On day 16, CH_4 concentrations began to quickly increase in the 3% goose feces and 3% manure treatments. Production rates rose rapidly over the next 15 days, peaking on day 31, and then declining for most of the remaining incubation period. The 3% goose feces addition underwent more rapid increases in concentrations between day 16 and 31 compared to the 3% manure treatment, resulting in higher overall concentrations until day 78 when the 3% manure treatment concentration surpassed the 3% goose feces concentrations of CH_4. The 0.3% treatments of goose feces and manure also had greater CH_4 concentrations when compared to the control. Besides slightly higher concentrations, the 0.3% additions followed the same pattern as the control, with production increases beginning around day 24, and the peak production occurring on day 62. In summary, the 3% goose feces addition had the most rapid increases in concentrations closely followed by the 3% manure. These increases occurred earlier than in the control treatment, but production declined after peaking at day 31. The control and 0.3% treatments had a slower start, but production continued to increase until day 62. These differences in timing resulted in the 3% goose feces treatment having a concentration of CH_4 360 times higher than the control on day 23. The 3% manure treatment had a concentration of CH_4 96 times greater than the control on day 23. By day 78 of the incubation, the 3% manure and goose feces treatments had only twice the concentrations of CH_4 compared to the control.

Nitrous Oxide

The 3% treatments had a large impact on peak N_2O concentrations. The 3% goose feces treatment exceeded the limit of detection on day two (>3500ppm), and then decreased rapidly to 0 ppm by day 7. Likewise, the 3% manure treatment peaked at 1800 ppm and declined dramatically after day 2. The N_2O concentrations peaked sooner in the fecal addition treatments than in the control. The control did not peak until day six while the treatments peaked on day two. The 0.3% treatment of goose feces also had a higher peak than the control but declined much more gradually than the 3% goose feces addition. The 0.3% manure treatment had a lower measured peak than the control but declined more rapidly than the control. To summarize, the goose feces had a greater impact on peak N_2O concentrations than the manure treatments at the same application levels. The higher the peak concentration of N_2O, the more quickly the decline occurred. And lastly, the fecal additions caused the peak to occur sooner in the incubation when compared to the control.

Differences between Incubations

When comparing the controls of both sets of incubations, there were obvious differences (Figure 3.3). First, CO_2 concentrations increased more rapidly in the nutrient incubation, reaching a peak and then declining slightly. The fecal incubation control also peaked and declined, but the peak occurred later in the incubation, and after declining for 10 days, CO_2 again began to rise. The CO_2 in the fecal incubation control reached a level higher than the first peak before declining again. In summary, the fecal incubation had two peaks, and the first peak occurred later than in the nutrient incubation that had only one peak. CH_4 concentrations were similar in both controls, but CH_4 increased sooner in the nutrient incubation. The differences between incubations were most dramatic for N_2O concentrations. The nutrient incubation control had a peak on day two of 199 ppm, while the fecal incubation control had a peak on day six of 1348 ppm.

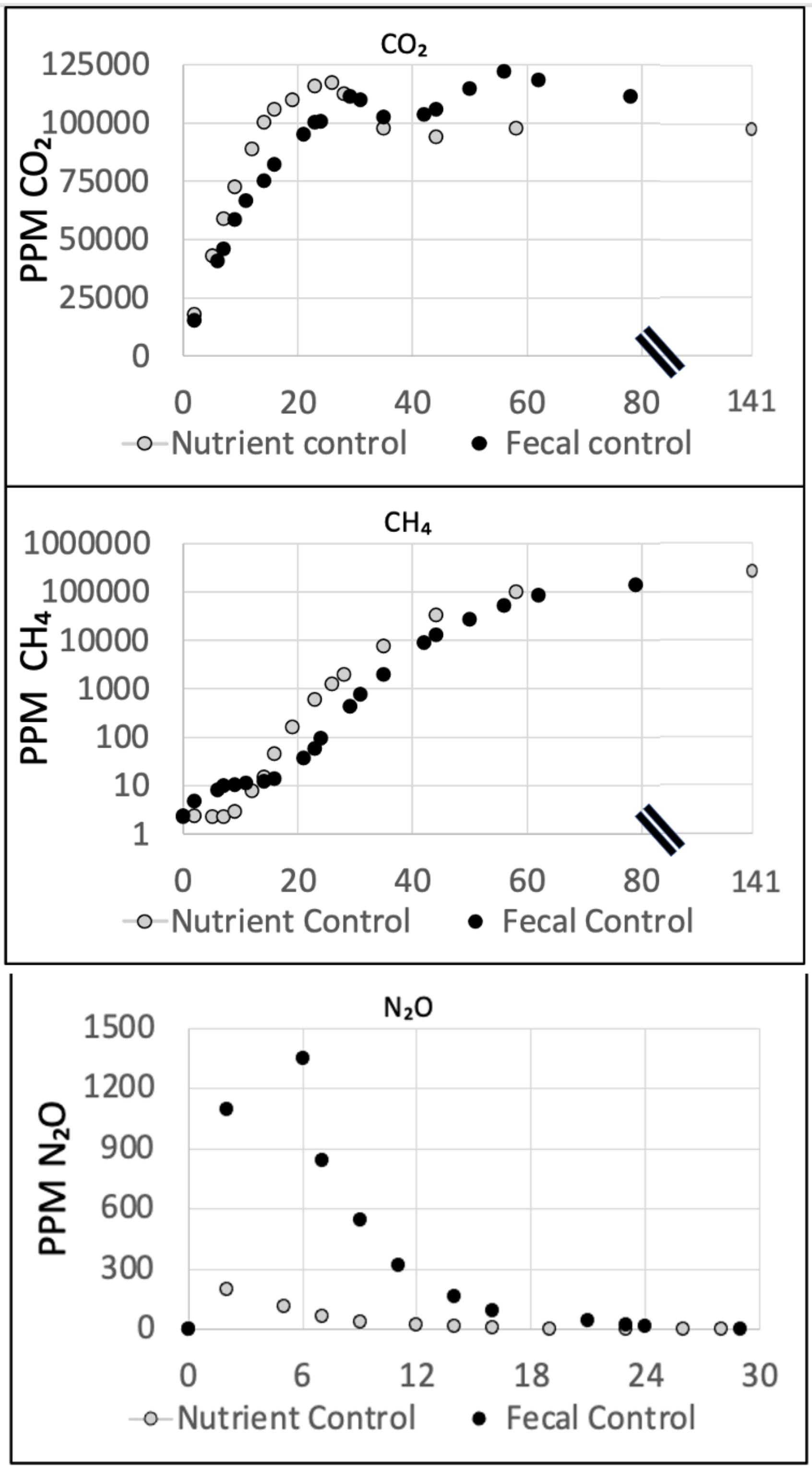


Figure 3.3: Comparison of incubation controls: These three charts show averages of each control group for measured gases on each sampling day (0-141) for both sets of incubations. From top to bottom the charts show concentrations of gas in parts per million for CO_2, CH_4, and N_2O. The nutrient incubation began 148 days after sampling, while the fecal incubation began 255 days after sampling. (Note the scale of the x-Axis changes at day 80)

3.7: Discussion

Nutrient Incubation

The small addition of common agricultural fertilizers had a minimal impact on the GHG production from incubated soils. Although the differences were slight, the biochar addition had the highest peak production and highest concentration of CO_2. This may be due to increased organic carbon which supports my hypothesis that CO_2 would be increased with the addition of biochar. Additions of K_2SO_4, KH_2PO_4, KNO_3 resulted in slightly lower peak CO_2 concentrations compared to the control. This finding does not support my hypothesis that CO_2 would increase with the addition of KNO_3.

The KH_2PO_4 addition had the highest peak production and the highest concentrations of CH_4 by the end of the incubation period. Biochar additions also increased CH_4 concentrations when compared to the control, potential evidence of the positive influence of biochar on CH_4 emission I predicted in my hypothesis. However, I hypothesized that KNO_3 or K_2SO_4 additions would have a negative effect on CH_4 concentrations, but both treatments had greater concentrations of CH_4 than the control at the end of the incubation.

N_2O emissions reached the highest production rates and the highest concentrations in the control group. This result is an unexpected finding and does not support my hypothesis that KNO_3 addition would increase concentrations of N_2O. However, the KNO_3 addition had the second highest production rates and concentrations.

The agricultural nutrient incubations represented low field application rates relative to those common in agriculture. Additionally this application rate is not accounting for the accumulation of nutrients after runoff into a wetland. Depending on the size of the drainage basin, even low application rates could lead to much higher amounts of these nutrients in wetland soils, with larger surrounding fertilized areas resulting in more accumulation of nutrients in the wetland system. This incubation represents the “best case scenario” and determined that under light loading of agricultural fertilizers, there was not a major change in the GHG production in a laboratory setting. Future incubations could increase the application rate under similar conditions to determine if the accumulation of nutrients in a wetland due to runoff might influence GHG results more substantially.

Fecal Incubation

The fecal incubations revealed a positive relationship between fecal additions and maximum daily GHG production in an anaerobic laboratory incubation of riparian wetland soil. The highest production for CO_2 was in the 3% manure treatment, followed by the 3% goose feces addition. The 0.3% additions also showed higher production rates and peak concentrations of CO_2 than the control. This finding supported my hypothesis that fecal matter would increase CO_2 production. It is important to note however, that by the end of the incubation all treatments and the control contained roughly the same concentrations of CO_2 despite differences in the first half of the incubation.

The increase in CO_2 production may be due to the addition of labile carbon and nutrients present in the feces; however, it is difficult to isolate the effects of the carbon and nutrients from one another. It is important to note that the manure addition represented roughly 3.3 times the carbon, 3.75 times the nitrogen, and 2.8 times the phosphorus of the goose feces addition, but the 3% goose feces treatment was within 5% of this peak production and recorded the highest peak concentration, as well as the highest local peaks. This suggests that there was more to the increase in CO_2 than just labile carbon and nutrients, and that microbes or soil pH changes from the goose feces addition may have played a role in altering CO_2 production. Another explanation could be the elements present in goose feces or cow manure that have not been considered.

For CH_4, the highest production rate and highest concentration on every day except the final sampling was recorded in the 3% goose feces treatment followed by the 3% manure. The 0.3% fecal additions also had higher CH_4 production rates than the control. These findings support my hypothesis that fecal matter will increase CH_4 production.

Again, the goose feces had a large impact despite its high water content, with only about 0.285 g of dry mass containing approximately 172 mg carbon, 8 mg nitrogen, and 1.9 mg phosphorus compared to the manure which is 1.5 g dry mass containing approximately 570 mg carbon, 30 mg nitrogen, and 5.4 mg phosphorus. One explanation is that the goose feces was higher in ammonia and ammonium compounds which may have inhibited CH_4 oxidation. A goose feces application in water was found to significantly increase ammonia while NO_3^- concentrations were unaffected (Purcell, 1999). On the other hand, manure treatment as a larger source of SO_4^{2-} or NO_3^- could explain why CH_4 production rates were generally lower when compared to the 3% goose feces treatment despite greater additions of carbon. For the 0.3% additions, the manure treatment had a greater impact on concentrations CH_4 than the 0.3% addition of goose feces. This was a contradictory finding as the 3% additions showed the goose feces having a greater impact on CH_4 concentrations than manure.

The highest calculated production rate and highest peak concentrations for N_2O were recorded in the 3% goose feces treatment. This finding agreed with my hypothesis that fecal matter additions would increase N_2O. The mechanism behind this increase was unclear considering that more nitrogen was added in the manure additions than in the goose feces additions. Differences between fecal additions may be due to the types of nitrogen present in goose feces vs. manure. Again, there may be an undetermined influence of microbial populations or pH change due to the fecal additions.

After a statistical analysis, I found no significant increase in any of the measured GHG for the total incubation period for either of the 0.3% fecal additions. This agreed with the findings of Winton & Richardson (2016) who found no statistically significant impact of a 0.3% addition of goose feces on GHG fluxes. For both 3% fecal additions, a brief statistical analysis revealed significant increase in CH_4 concentrations at the final sampling day.

Another comparison can be made between the biochar addition and the fecal additions. Both treatments introduced carbon to the wetland soils in comparable amounts (goose feces 3%: 172 mg, Manure 3%: 380mg, biochar: 333mg), but the fecal additions had a far greater influence on the GHG production rates than the biochar addition. This may be because of the carbon in biochar was more recalcitrant and carbon additions from feces are more labile.

I included a 3% goose feces addition as a simulation of the hyper local effect of goose droppings on GHG emissions. This is relevant due to the density of flocks in some areas and the amount of feces produced daily by these flocks. Depending on the total area of interest, density of birds, and residence time of these flocks, the high peak production rates of CH_4, carbon, dioxide, and N_2O may influence the estimate of total gas flux. This could apply to a wetland that hosts large migratory or resident goose populations during certain times of the year. For example, researchers should be aware of the possible influence of goose feces when looking at wetland GHG emissions or collecting soil samples when geese are moving though or living in the area of interest. These findings may also be of interest to the managers of locations where flocks of geese congregate year-round, including city parks, golf courses, stormwater retention ponds, and airports.

Similarities between Incubations

The frequency of measurement demonstrated patterns and relationships in the dominant emission pathways that would have been missed with less frequent measurements. For example, while I did not have an independent metric of ORP, Figure 3.4 illustrates the switch from aerobic decomposition (CO_2 production) to anaerobic decomposition (CH_4 production) as O_2 was depleted in the closed system. Oxygen depletion was the result of respiration, removal of O_2 through headspace sampling, and dilution of remaining O_2 through replacement with N_2. The high frequency of measurement also revealed dynamic changes in the N_2O concentrations that would be missed with less frequent samplings.

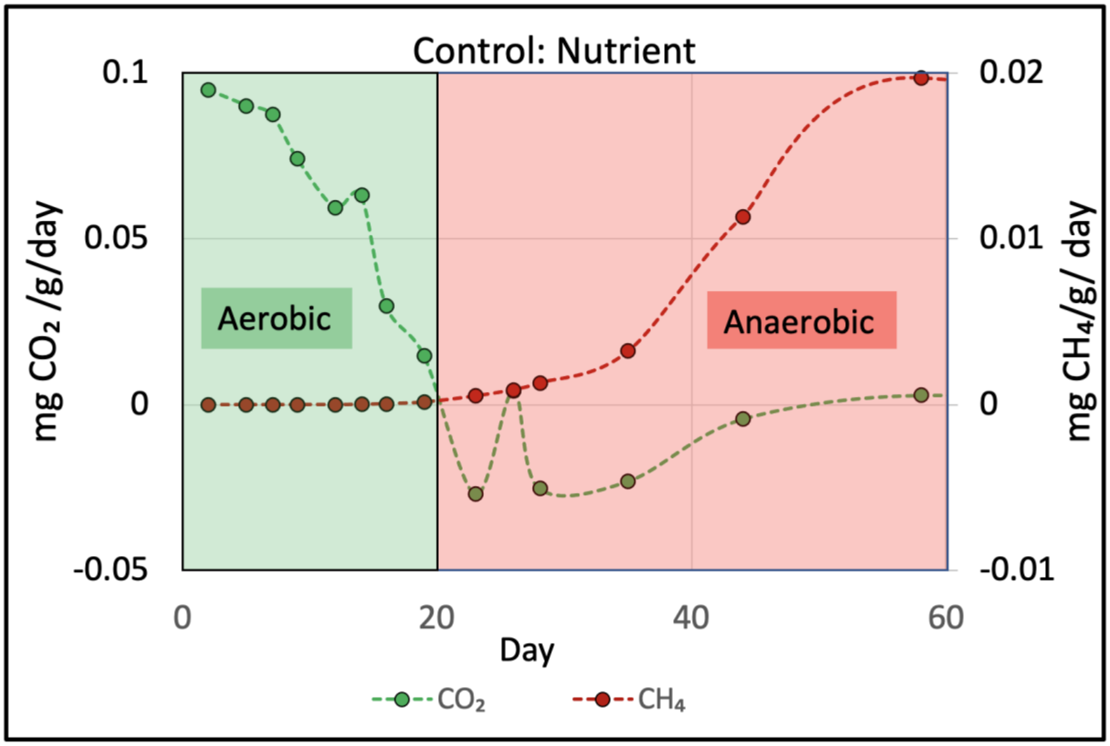


Figure 3.4: Anaerobic vs aerobic production in mg gas per g soil per day of CO_2 and CH_4 in the control treatment of the nutrient incubation on each sampling day (0-58). The switch from primarily aerobic decomposition to primarily anaerobic decomposition can be identified around day 20.

Carbon Dioxide

The overall pattern for CO_2 concentrations can be explained by O_2 availability. Early on, it can be assumed that there was plentiful O_2 both dissolved and in the headspace. This provided the necessary electron acceptor for aerobic respiration. The breakdown of organic matter through microbial respiration continued albeit at a slower rate until O_2 depletion (Inglett et al., 2005). This gradual decline in O_2 explains the steady decline in CO_2 production until microbial respiration stopped due to a lack of O_2.

Once the system was anaerobic, the small increases in CO_2 concentrations may have been the result of the anaerobic production of CO_2. Anaerobic CO_2 production occurs when organic matter is broken down via fermentation into smaller molecules which are then oxidized into CO_2 during the microbial reduction of NO_3^-, Fe^{3+}, manganese (Mn^{4+}), and SO_4^{2-} (Kristensen et al., 2008; Y. Liu et al., 2021). The small decreases in CO_2 concentrations may have been the result of methanogens using CO_2 as their carbon source.

Methane

The CH_4 production was evidence of the consumption of the more energetic electron acceptors (Bridgham et al., 2013). During the first 20 days of the incubation, methanogenesis was minimal although concentrations did increase by small amounts in the first 20 days. This may have occurred due to heterogenous redox conditions in the soil matrix (Hedin et al., 1998). Some micropores may have had less alternative electron donors, and therefore lower ORP. In these pores, methanogenesis began sooner resulting in small increases in CH_4 concentrations. As the incubation progressed, more of these pores became sites that suit methanogens, leading to the steady increase in CH_4 until nearly the entire soil matrix was in a fully reduced state, leading to high CH_4 production rates.

Nitrous Oxide

One consistent finding from both incubations was the rapid increase in N_2O production and the subsequent consumption of this gas by day 20. This dynamic may have been the result of changing ORP in the incubation jars. Bouwman (1998) demonstrated the interplay between nitrification and denitrification based on water-filled pore space. N_2O production is at a maximum when there are heterogeneous redox conditions, with both nitrification and denitrification occurring simultaneously (Wrage et al., 2001). When nitrification ceased because of O_2 depletion, the denitrification process reduced the NO_3^- into N_2O and eventually N_2.

Applications of pond water exceeded the soils' field capacity and resulted in standing water in incubation jars. Despite this saturation, the first few days still represented mixed redox conditions. Headspace and water would have been initially oxygenated, but O_2 was being consumed through respiration and the nitrification process in which ammonia was oxidized with NO_3^- as the product. The nitrification process created N_2O as a by-product.

Denitrification began in the soil matrix in areas where O_2 was depleted, and reduced NO_3^- into N_2, with N_2O as an intermediary. The amount of N_2O that is fully reduced into N_2 decreases with a higher abundance of NO_3^- and greater O_2 concentrations (Wrage et al., 2001). During these first few days of mixed redox conditions, there was an abundance of NO_3^- due to the nitrification process and some O_2 was still present in the system. These dynamics may explain the early spike in N_2O.

As O_2 became fully depleted in the system, nitrification ceased, ending the production of NO_3^-. Nitrate continued to be consumed by denitrification, eventually resulting in the depletion if NO_3^-. With both O_2 and NO_3^- depleted, denitrifying bacteria reduced the remaining N_2O, resulting in the reduction of N_2O concentrations until concentrations reached zero ppm. These sequential processes explain the pattern I observed, with an early spike of N_2O and the eventual reduction to 0 ppm.

Differences between Incubations

There were some noticeable differences between the controls of the two incubations. Despite identical experimental designs, differences in the timing and magnitude of concentration increases were easily observed . One explanation would be the change in microbial populations due to different storage times before the beginning of the incubations (Stotzky et al., 1962; Stenberg et al., 1998; Meyer et al., 2019).

The nutrient incubation began 148 days after collection. The fecal incubation began 255 days after sampling. All soils were stored at 3 ºC in sealed Ziplock bags until the incubations began. Ziplock bags may have reduced gas exchange which could impact microbial populations (Stotzky et al., 1962).

Unfortunately, I have no microbial data, but the differences between the control groups was likely due to changes in microbial populations during the extended storage time. For example, reduced O_2 availability in sealed Ziploc bags may have decreased microbial respiration rates, and reduced the population of microbes that thrive in oxic conditions (Meyer et al., 2019). A study on microbial changes during cold storage found that populations of all organisms except actinomycetes decreased in topsoil, while in deeper soil, denitrifying bacteria and fungi increased (Stotzky et al., 1962).

Minor differences in timing of CO_2 increases may be attributable to changes of microbial activity during the storage period, leading to slower respiration rates in the fecal incubation control. One study on the impact of different storage times and temperatures found that after seven weeks of storage at 4ºC, soil respiration rates of sieved soil decreased from 3.38 ± 1.62 µgCO_2 h^{-1} g^{-1} soil to 2.57 ± 1.15 62 µgCO_2 h^{-1} g^{-1} (Meyer et al., 2019). This slowing down of respiration may explain the delayed increase in CO_2 concentrations found in the fecal incubation control.

Decreases in microbial populations may also explain the differences in CH_4 increases between controls. Another mechanism for differences in CH_4 concentrations could be the slowing down of respiration due to less microbial activity. This could result in delayed CH_4 increase, as O_2 is consumed slower, leading to methanogenesis starting later.

Another potential explanation for the delayed increase in CO_2 and CH_4 in the fecal incubation could be that the most labile carbon pools are more likely to be consumed by respiration during storage. When the incubations begin, CO_2 is produced at a slower rate because the carbon left behind is slightly more complex and resistant to respiration. Again, this could slow down the rates of respiration, therefore delaying CH_4 increases as O_2 is consumed more slowly.

The large differences in N_2O concentrations may be due to some change in microbial populations due to extended storage time and slightly reduced O_2. These conditions may have led to less nitrifying bacteria present and the success and growth of denitrifying populations (Stotzky et al., 1962). When the fecal incubation began, slower nitrification rates caused the peak to occur later, and the presence of more denitrifying bacteria early in the incubation caused more of the N_2O to escape the system before being reduced to nitrogen as O_2 availability slowed the rate of N_2O reduction while having no effect on the speed of other denitrifying reductions. One study determined that special attention should be placed on the microbial changes occurring during storage when examining nitrogen transformations (Stotzky et al., 1962).

Another explanation is that longer storage time led to more nitrification, and an accumulation of NO_3^-. When the incubation began and conditions became less oxic, denitrifying bacteria produced more N_2O and more of it escaped to the headspace as an abundance of NO_3^- increased the amount of N_2O that escapes the soil matrix before being reduced to N_2.

3.8: Conclusion

The addition of agricultural nutrients did not affect GHG as I had hypothesized. For example, there was no evidence to support my hypothesis that KNO_3 addition would increase concentrations of N_2O or CO_2. Additionally, I hypothesized that KNO_3 or K_2SO_4 additions would have a negative effect on CH_4 concentrations, but both treatments had greater concentrations of CH_4 than the control at the end of the incubation. There was a small increase in CO_2 and CH_4 concentrations after the addition of biochar as I hypothesized; however, the differences were not very substantial. In fact, none of the additions of agricultural nutrients and biochar had a major effect on production of CO_2, CH_4, and N_2O. Only small differences in concentrations were identified, and future research should investigate the potential influence of these substances under higher application rates.

The addition of nutrients in the form of goose feces and cattle manure led to large increases in production of CO_2, CH_4, and N_2O, confirming my hypothesis. Production increases were greater when application rates were higher. Peak production of CO_2 was similar in both fecal treatments. Goose feces additions led to greater peak production of CH_4 and N_2O than manure additions.

The conditions of the incubation design led to dynamic redox conditions. While ORP was not measured, redox conditions can be inferred based on gas production. Starting with ambient atmosphere in the headspace, respiration and aerobic process dominated (high CO_2 production). This was followed by a period of heterogenous redox conditions, where CO_2 production declined, and N_2O production occurred through nitrification and denitrification processes. Lastly, sustained reducing conditions led to methanogenesis and the reduction of N_2O. The data from these laboratory incubations may not be applicable or comparable to field measurements due to the entirely closed system within the mason jars. A real system would include the diffusion of O_2 into the soil, and the transfer of GHG out of the system.

The addition of goose feces and cattle manure are not perfectly comparable as the goose feces was wet and fresh, while the manure was dried out in the sun. This meant the goose feces was introducing more water to the system in addition to the dry matter. Also, the goose feces additions added less dry matter than the manure. It would be revealing to compare the GHG production rates from incubations in which fresh goose feces and dry goose feces are added. Another potential future study could test fresh goose feces for exact nutrient concentrations, and then apply inorganic nutrients in exact amounts to mirror the nutrients present in the feces. Either of these experiments could reveal influences of microbial populations present in feces. Future biological research in wetlands that host large goose migrations should attempt to better quantify the impact of fecal deposition.

Chapter 4: Conclusion

The goal of this research was to understand the seasonal variations of dissolved GHG and the factors influencing these variations in a wetland located at the Atocas Bay Conservation Site. I measured dissolved GHG and multiple water parameters over 510 days with 19 sampling days. These sampling days were spaced out over multiple years and seasons. On each sampling day I sought to represent the variation within the entire wetland. This strategy of taking many samples throughout the wetland was justified by field measurements. Some sampling days saw CH_4 concentrations vary by an order of magnitude. By measuring across the wetland, I reduced the bias of my sampling. This thesis contributes to the growing number of wetland GHG data sets and demonstrates the importance of year-round sampling, especially in temperate environments.

I hypothesized that greenhouse gas concentrations would be positively correlated with water temperature. This was confirmed for CO_2 and CH_4 in my analysis, but the correlation was generally weaker than expected. I propose that this correlation may have been stronger if I had measured sediment temperature rather than surface water temperature. Next, I hypothesized that GHG would accumulate under ice cover which was confirmed by my measurements and analysis and can be attributed to ice sealing the air/water interface and preventing the diffusion of gases. Third, I hypothesized that pH would be negatively correlated with concentrations of CO_2 and N_2O. pH had a strong negative correlation with CO_2 likely due to the acidification caused by dissolved CO_2. pH showed a weak positive correlation with N_2O, rejecting the second half of this hypothesis. Next, I hypothesized that DOC would be positively correlated with concentrations of all three gases because increases in DOC would provide more substrate for redox reactions that produce CO_2, CH_4, N_2O. This correlation was occasionally found in my analysis, but it was a weak relationship. I hypothesized that electrical conductivity would correlate with lower CH_4 concentrations and greater CO_2 and N_2O concentrations. This hypothesis can be rejected due to the mixed results and very weak relationships in the analysis. Lastly, I hypothesized that TDN would positively correlate with dissolved N_2O. This relationship was only found for one of the data sets and was a very weak correlation.

One unexpected finding was that dissolved concentrations of N_2O were only above ambient on four days, which could mean that this wetland is generally a sink of N_2O. Additionally, I found a negative correlation between CH_4 and pH. This was also unexpected, but I propose that the relationship with pH was a legacy of the impact of temperature on CO_2 and CH_4 production. Increasing temperatures resulted in greater concentrations of CO_2, lowering pH in the water column. Increasing temperatures also resulted in increased concentrations of CH_4. These processes occur simultaneously, so pH was negatively correlated with CH_4. Future research could control the temperature of multiple incubations while measuring pH and concentrations of CO_2 and CH_4. This could reveal the causality of the relationship between pH and CH_4. A final unexpected finding was that concentrations of dissolved CO_2 and CH_4 were higher in the end of September than in mid-summer even after temperatures began to drop. I propose that this could be due to the fall turnover, with mixing bringing deeper waters with high concentrations to the surface. Another potential explanation is that Canada goose migration resulted in nutrient additions from fecal deposition. To examine the influence of goose migration on the seasonal variation of dissolved greenhouse gas, I performed two laboratory incubation experiments.

These laboratory incubation experiments involved the addition of common agricultural fertilizers, biochar, cattle manure, and Canada goose feces. The two incubations had identical experimental designs to allow for comparisons; however, extended storage time before the second incubation resulted in different GHG production in the two control groups. The incubations affirmed my hypothesis that goose feces and manure would increase GHG production. This finding could be important to researchers working in ecosystems that host large populations of migrating birds and for those located in close proximity to cattle farming sites. Future research should schedule field sampling to capture periods of migration. More research on the influence of bird migration may better define the influence of bird feces on wetland GHG dynamics.

My hypotheses regarding the impact of agricultural nutrients and biochar were partly confirmed and partly rejected; however, there was only weak evidence as discussed in the conclusion of Chapter 3. A future experiment could add different amounts of each nutrient, looking at how gas production changes with each increase of nutrients added. This same framework could be applied to the goose feces incubations to better define the amount of increase in gas production that can be expected based on how much feces is added. Potentially, these findings could be tied to bird counts at a wetland and field sampling to determine whether observed increases of GHG concentrations in the fall are attributable to fecal deposition during goose migration.

Appendix

Supplementary Tables

Model Summary[e]

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics				
					R Square Change	F Change	df1	df2	Sig. F Change
1	.637[a]	.405	.403	297.78	.405	179.193	1	263	<.001
2	.705[b]	.497	.493	274.45	.091	47.610	1	262	<.001
3	.723[c]	.523	.518	267.63	.027	14.524	1	261	<.001
4	.734[d]	.538	.531	263.82	.015	8.586	1	260	.004

a. Predictors: (Constant), pH

b. Predictors: (Constant), pH, electrical conductivity

c. Predictors: (Constant), pH, electrical conductivity, DOC

d. Predictors: (Constant), pH, electrical conductivity, DOC, TDN

e. Dependent Variable: CO2.ALL

Table S.1: Stepwise linear regression model summary for ALL data, dissolved CO_2

Model Summary[f]

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics				
					R Square Change	F Change	df1	df2	Sig. F Change
1	.372[a]	.139	.135	178.36	.139	42.357	1	263	<.001
2	.449[b]	.202	.196	172.04	.063	20.685	1	262	<.001
3	.478[c]	.229	.220	169.41	.027	9.213	1	261	.003
4	.496[d]	.246	.234	167.89	.017	5.751	1	260	.017
5	.521[e]	.272	.257	165.30	.026	9.200	1	259	.003

a. Predictors: (Constant), pH

b. Predictors: (Constant), pH, electrical conductivity

c. Predictors: (Constant), pH, electrical conductivity, temperature

d. Predictors: (Constant), pH, electrical conductivity, temperature, TDN

e. Predictors: (Constant), pH, electrical conductivity, temperature, TDN, DOC

f. Dependent Variable: CH4.ALL

Table S.2: Stepwise linear regression model summary for ALL data, dissolved CH_4

Model Summary[c]

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics				
					R Square Change	F Change	df1	df2	Sig. F Change
1	.249[a]	.062	.058	.0374	.062	17.381	1	263	<.001
2	.280[b]	.078	.071	.0371	.016	4.674	1	262	.032

a. Predictors: (Constant), temperature

b. Predictors: (Constant), temperature, pH

c. Dependent Variable: N2O.ALL

Table S.3: Stepwise linear regression model summary for ALL data, dissolved N_2O

Model Summary[e]

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics				
					R Square Change	F Change	df1	df2	Sig. F Change
1	.687[a]	.473	.470	215.14	.473	199.819	1	223	<.001
2	.720[b]	.518	.514	206.16	.045	20.850	1	222	<.001
3	.787[c]	.619	.614	183.60	.101	58.903	1	221	<.001
4	.792[d]	.627	.620	182.27	.007	4.233	1	220	.041

a. Predictors: (Constant), pH

b. Predictors: (Constant), pH, electrical conductivity

c. Predictors: (Constant), pH, electrical conductivity, temperature

d. Predictors: (Constant), pH, electrical conductivity, temperature, DOC

e. Dependent Variable: CO2.NO.ICE

Table S.4: Stepwise linear regression model summary for NO.ICE data, dissolved CO_2

Model Summary[d]

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics				
					R Square Change	F Change	df1	df2	Sig. F Change
1	.413[a]	.171	.167	84.40	.171	45.893	1	223	<.001
2	.443[b]	.197	.189	83.25	.026	7.182	1	222	.008
3	.508[c]	.258	.248	80.17	.062	18.413	1	221	<.001

a. Predictors: (Constant), pH

b. Predictors: (Constant), pH, electrical conductivity

c. Predictors: (Constant), pH, electrical conductivity, temperature

d. Dependent Variable: CH4.NO.ICE

Table S.5: Stepwise linear regression model summary for NO.ICE data, dissolved CH_4

Model Summary[e]

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics				
					R Square Change	F Change	df1	df2	Sig. F Change
1	.346[a]	.120	.116	.0134	.120	30.414	1	223	<.001
2	.369[b]	.136	.129	.0133	.016	4.227	1	222	.041
3	.391[c]	.153	.142	.0132	.017	4.328	1	221	.039
4	.422[d]	.178	.163	.0130	.025	6.795	1	220	.010

a. Predictors: (Constant), pH

b. Predictors: (Constant), pH, temperature

c. Predictors: (Constant), pH, temperature, electrical conductivity

d. Predictors: (Constant), pH, temperature, electrical conductivity, TDN

e. Dependent Variable: N2O.NO.ICE

Table S.6: Stepwise linear regression model summary for NO.ICE data, dissolved N_2O

Model Summary[e]

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics				
					R Square Change	F Change	df1	df2	Sig. F Change
1	.811[a]	.658	.655	167.13	.658	236.316	1	123	<.001
2	.886[b]	.786	.782	132.83	.128	72.726	1	122	<.001
3	.900[c]	.810	.805	125.61	.024	15.426	1	121	<.001
4	.908[d]	.824	.818	121.22	.015	9.923	1	120	.002

a. Predictors: (Constant), pH

b. Predictors: (Constant), pH, temperature

c. Predictors: (Constant), pH, temperature, conductivity

d. Predictors: (Constant), pH, temperature, conductivity, DOC

e. Dependent Variable: CO2.GROWING

Table S.7: Stepwise linear regression model summary for GROWING data, dissolved CO_2

Model Summary[c]

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics				
					R Square Change	F Change	df1	df2	Sig. F Change
1	.542[a]	.293	.288	47.78	.293	51.044	1	123	<.001
2	.648[b]	.421	.411	43.44	.127	26.786	1	122	<.001

a. Predictors: (Constant), pH

b. Predictors: (Constant), pH, electrical conductivity

c. Dependent Variable: CH4.GROWING

Table S.8: Stepwise linear regression model summary for GROWING data, dissolved CH_4

Model Summary[c]

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics				
					R Square Change	F Change	df1	df2	Sig. F Change
1	.677[a]	.458	.454	.0038	.458	103.999	1	123	<.001
2	.736[b]	.541	.534	.0035	.083	22.081	1	122	<.001

a. Predictors: (Constant), pH

b. Predictors: (Constant), pH, DOC

c. N2O.GROWING

Table S.9: Stepwise linear regression model summary for GROWING data, dissolved N_2O

Model Summary[d]

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics				
					R Square Change	F Change	df1	df2	Sig. F Change
1	.756[a]	.572	.567	197.11	.572	130.776	1	98	<.001
2	.789[b]	.622	.614	186.16	.050	12.873	1	97	<.001
3	.803[c]	.645	.634	181.18	.024	6.404	1	96	.013

a. Predictors: (Constant), temperature

b. Predictors: (Constant), temperature, electrical conductivity

c. Predictors: (Constant), temperature, electrical conductivity, pH

d. Dependent Variable: CO2.GOOSE

Table S.10: Stepwise linear regression model summary for GOOSE data, dissolved CO_2

Model Summary[c]

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics				
					R Square Change	F Change	df1	df2	Sig. F Change
1	.605[a]	.366	.360	98.03	.366	56.587	1	98	<.001
2	.623[b]	.388	.375	96.85	.021	3.405	1	97	.068

a. Predictors: (Constant), temperature

b. Predictors: (Constant), temperature, TDN

c. Dependent Variable: CH4.GOOSE

Table S.11: Stepwise linear regression model summary for GOOSE data, dissolved CH_4

Model Summary^d

					Change Statistics				
Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	R Square Change	F Change	df1	df2	Sig. F Change
1	.343^a	.118	.109	.0193	.118	13.054	1	98	<.001
2	.441^b	.194	.178	.0185	.077	9.250	1	97	.003
3	.475^c	.226	.202	.0182	.032	3.928	1	96	.050

a. Predictors: (Constant), pH

b. Predictors: (Constant), pH, electrical conductivity

c. Predictors: (Constant), pH, electrical conductivity, temperature

d. N2O.GOOSE

Table S.12: Stepwise linear regression model summary for GOOSE data, dissolved N_2O

References Cited

Aelion, C. M., & Warttinger, U. (2009). Low sulfide concentrations affect nitrate transformations in freshwater and saline coastal retention pond sediments. *Soil Biology and Biochemistry*, *41*(4), 735–741. https://doi.org/10.1016/j.soilbio.2009.01.015

Aerts, R., & Toet, S. (1997). Nutritional controls on carbon dioxide and methane emission from Carex-dominated peat soils. *Soil Biology and Biochemistry*, *29*(11), 1683–1690. https://doi.org/10.1016/S0038-0717(97)00073-4

Ardón, M., Helton, A. M., & Bernhardt, E. S. (2018). Salinity effects on greenhouse gas emissions from wetland soils are contingent upon hydrologic setting: A microcosm experiment. *Biogeochemistry*, *140*(2), 217–232. https://doi.org/10.1007/s10533-018-0486-2

Ayers, C. R., DePerno, C. S., Moorman, C. E., & Yelverton, F. H. (2010). Canada Goose Weed Dispersal and Nutrient Loading in Turfgrass Systems. *Applied Turfgrass Science*, *7*(1), 1–6. https://doi.org/10.1094/ATS-2010-0212-02-RS

Badiou, P., Page, B., & Akinremi, W. (2018). Phosphorus Retention in Intact and Drained Prairie Wetland Basins: Implications for Nutrient Export. *Journal of Environmental Quality*, *47*(4), 902–913. https://doi.org/10.2134/jeq2017.08.0336

Beaulieu, J. J., Tank, J. L., Hamilton, S. K., Wollheim, W. M., Hall, R. O., Mulholland, P. J., Peterson, B. J., Ashkenas, L. R., Cooper, L. W., Dahm, C. N., Dodds, W. K., Grimm, N. B., Johnson, S. L., McDowell, W. H., Poole, G. C., Valett, H. M., Arango, C. P., Bernot, M. J., Burgin, A. J., … Thomas, S. M. (2011). Nitrous oxide emission from denitrification in stream and river networks. *Proceedings of the National Academy of Sciences*, *108*(1), 214–219. https://doi.org/10.1073/pnas.1011464108

Bertora, C., Cucu, M. A., Lerda, C., Peyron, M., Bardi, L., Gorra, R., Sacco, D., Celi, L., & Said-Pullicino, D. (2018). Dissolved organic carbon cycling, methane emissions and related microbial populations in temperate rice paddies with contrasting straw and water management. *Agriculture, Ecosystems & Environment*, *265*, 292–306. https://doi.org/10.1016/j.agee.2018.06.004

Bodelier, P. L. (2011). Interactions between nitrogenous fertilizers and methane cycling in wetland and upland soils. *Current Opinion in Environmental Sustainability*, *3*(5), 379–388. https://doi.org/10.1016/j.cosust.2011.06.002

Boeckman, C., & Bidwell, J. (2007). *Spatial and Seasonal Variability in the Water Quality Characteristics of an Ephemeral Wetland*.

Bonetti, G., Limpert, K. E., Brodersen, K. E., Trevathan-Tackett, S. M., Carnell, P. E., & Macreadie, P. I. (2022). The combined effect of short-term hydrological and N-fertilization manipulation of wetlands on CO2, CH4, and N2O emissions. *Environmental Pollution*, *294*, 118637. https://doi.org/10.1016/j.envpol.2021.118637

Bortolotti, L. E., St. Louis, V. L., Vinebrooke, R. D., & Wolfe, A. P. (2016). Net Ecosystem Production and Carbon Greenhouse Gas Fluxes in Three Prairie Wetlands. *Ecosystems*, *19*(3), 411–425. https://doi.org/10.1007/s10021-015-9942-1

Bouwman, A. (1998). Environmental science Nitrogen oxides and tropical agriculture. *Nature*, *392*, 866–867. https://doi.org/10.1038/31809

Boyd, C. E. (2015). pH, Carbon Dioxide, and Alkalinity. In C. E. Boyd (Ed.), *Water Quality: An Introduction* (pp. 153–178). Springer International Publishing. https://doi.org/10.1007/978-3-319-17446-4_8

Bridgham, S. D., Cadillo-Quiroz, H., Keller, J. K., & Zhuang, Q. (2013). Methane emissions from wetlands: Biogeochemical, microbial, and modeling perspectives from local to global scales. *Global Change Biology*, *19*(5), 1325–1346. https://doi.org/10.1111/gcb.12131

Brunet, R. C., & Garcia-Gil, L. J. (1996). Sulfide-induced dissimilatory nitrate reduction to ammonia in anaerobic freshwater sediments. *FEMS Microbiology Ecology*, *21*(2), 131–138. https://doi.org/10.1016/0168-6496(96)00051-7

Butterbach-Bahl, K., Baggs, E. M., Dannenmann, M., Kiese, R., & Zechmeister-Boltenstern, S. (2013). Nitrous oxide emissions from soils: How well do we understand the processes and their controls? *Philosophical Transactions of the Royal Society B: Biological Sciences*, *368*(1621), 20130122. https://doi.org/10.1098/rstb.2013.0122

Calleja, M. L., Al-Otaibi, N., & Morán, X. A. G. (2019). Dissolved organic carbon contribution to oxygen respiration in the central Red Sea. *Scientific Reports*, *9*(1), 4690. https://doi.org/10.1038/s41598-019-40753-w

Chen, N., & Hong, H. (2011). Nitrogen export by surface runoff from a small agricultural watershed in southeast China: Seasonal pattern and primary mechanism. *Biogeochemistry*, *106*(3), 311–321. https://doi.org/10.1007/s10533-010-9514-6

Christensen, T. R., Ekberg, A., Strom, L., Mastepanov, M., Oquist, M., Svensson, B., Nykänen, H., Martikainen, P., & Óskarsson, H. (2003). Factors controlling large scale variations in methane emissions from wetlands. *Geophysical Research Letters*, *30*, 1414–1419. https://doi.org/10.1029/2002GL016848

Dalva, M., Moore, T. R., Arp, P., & Clair, T. A. (2001). Methane and soil and plant community respiration from wetlands, Kejimkujik National Park, Nova Scotia: Measurements, predictions, and climatic change. *Journal of Geophysical Research: Atmospheres*, *106*(D3), 2955–2962. https://doi.org/10.1029/2000JD900500

Dessborn, L., Hessel, R., & Elmberg, J. (2016). Geese as vectors of nitrogen and phosphorus to freshwater systems. *Inland Waters*, *6*, 111–122. https://doi.org/10.5268/IW-6.1.897

Dong, D., Badiou, P., Moore, T., & Sperber, C. (2024). Litter decomposition and nutrient dynamics of four macrophytes in intact, restored, and constructed freshwater marshes of Canada. *Restoration Ecology*, *32*. https://doi.org/10.1111/rec.14135

Drever, C. R., Cook-Patton, S. C., Akhter, F., Badiou, P. H., Chmura, G. L., Davidson, S. J., Desjardins, R. L., Dyk, A., Fargione, J. E., Fellows, M., Filewod, B., Hessing-Lewis, M., Jayasundara, S., Keeton, W. S., Kroeger, T., Lark, T. J., Le, E., Leavitt, S. M., LeClerc, M.-E., … Kurz, W. A. (2021). Natural climate solutions for Canada. *Science Advances*, *7*(23), eabd6034. https://doi.org/10.1126/sciadv.abd6034

Ducks Unlimited. (n.d.). *The Atocas Bay Conservation Project: Ducks Unlimited*. Retrieved January 10, 2023, from Https://Www.Ducks.Org/, www.ducks.org/conservation/conservation-projects/the-atocas-bay-conservation-project

Environment and Climate Change Canada. (n.d.). *Montreal Mirabel Intl A*. Retrieved June 6, 2024, from https://climate.weather.gc.ca/climate_data/hourly_data_e.html?hlyRange=2012-09-13%7C2024-08-05&dlyRange=2018-10-30%7C2024-08-05&mlyRange=%7C&StationID=49608&Prov=QC&urlExtension=_e.html&searchType=stnProx&optLimit=specDate&Month=9&Day=13&StartYear=1840&EndYear=2019&Year=2012&selRowPerPage=25&Line=0&txtRadius=25&optProxType=navLink&txtLatDecDeg=45.666666666667&txtLongDecDeg=-74.033333333333&timeframe=1.

Ettwig, K. F., Butler, M. K., Le Paslier, D., Pelletier, E., Mangenot, S., Kuypers, M. M. M., Schreiber, F., Dutilh, B. E., Zedelius, J., de Beer, D., Gloerich, J., Wessels, H. J. C. T., van Alen, T., Luesken, F., Wu, M. L., van de Pas-Schoonen, K. T., Op den Camp, H. J. M., Janssen-Megens, E. M., Francoijs, K.-J., … Strous, M. (2010). Nitrite-driven anaerobic methane oxidation by oxygenic bacteria. *Nature*, *464*(7288), 543–548. https://doi.org/10.1038/nature08883

Euliss, N. H., Gleason, R. A., Olness, A., McDougal, R. L., Murkin, H. R., Robarts, R. D., Bourbonniere, R. A., & Warner, B. G. (2006). North American prairie wetlands are important nonforested land-based carbon storage sites. *Science of The Total Environment*, *361*(1), 179–188. https://doi.org/10.1016/j.scitotenv.2005.06.007

Gao, Y., Chen, H., & Zeng, X. (2014). Effects of nitrogen and sulfur deposition on CH4 and N2O fluxes in high-altitude peatland soil under different water tables in the Tibetan Plateau. *Soil Science and Plant Nutrition*, *60*(3), 404–410. https://doi.org/10.1080/00380768.2014.893812

Gauci, V., Matthews, E., Dise, N., Walter, B., Koch, D., Granberg, G., & Vile, M. (2004). Sulfur pollution suppression of the wetland methane source in the 20th and 21st centuries. *Proceedings of the National Academy of Sciences*, *101*(34), 12583–12587. https://doi.org/10.1073/pnas.0404412101

Gehant, P. A. (2015). *Seasonal trends in permanent and ephemeral wetland water chemistry*. https://minds.wisconsin.edu/handle/1793/77549

Gunnarsson, U., Boresjö Bronge, L., Rydin, H., & Ohlson, M. (2008). Near-zero recent carbon accumulation in a bog with high nitrogen deposition in SW Sweden. *Global Change Biology*, *14*(9), 2152–2165. https://doi.org/10.1111/j.1365-2486.2008.01638.x

Guo, B., Zheng, X., Yu, J., Ding, H., Pan, B., Luo, S., & Zhang, Y. (2020). Dissolved organic carbon enhances both soil N2O production and uptake. *Global Ecology and Conservation*, *24*, e01264. https://doi.org/10.1016/j.gecco.2020.e01264

Hahn, S., Bauer, S., & Klaassen, M. (2008). Quantification of allochthonous nutrient input into freshwater bodies by herbivorous waterbirds. *Freshwater Biology*, *53*(1), 181–193. https://doi.org/10.1111/j.1365-2427.2007.01881.x

Haynes, R. J., & Williams, P. H. (1993). Nutrient Cycling and Soil Fertility in the Grazed Pasture Ecosystem. In D. L. Sparks (Ed.), *Advances in Agronomy* (Vol. 49, pp. 119–199). Academic Press. https://doi.org/10.1016/S0065-2113(08)60794-4

Hedin, L. O., von Fischer, J. C., Ostrom, N. E., Kennedy, B. P., Brown, M. G., & Robertson, G. P. (1998). Thermodynamic Constraints on Nitrogen Transformations and Other Biogeochemical Processes at Soil-Stream Interfaces. *Ecology*, *79*(2), 684–703. https://doi.org/10.2307/176963

Hou, A. X., Chen, G. X., Wang, Z. P., Van Cleemput, O., & Patrick Jr., W. H. (2000). Methane and Nitrous Oxide Emissions from a Rice Field in Relation to Soil Redox and Microbiological Processes. *Soil Science Society of America Journal*, *64*(6), 2180–2186. https://doi.org/10.2136/sssaj2000.6462180x

Hu, H.-W., Chen, D., & He, J.-Z. (2015). Microbial regulation of terrestrial nitrous oxide formation: Understanding the biological pathways for prediction of emission rates. *FEMS Microbiology Reviews*, *39*(5), 729–749. https://doi.org/10.1093/femsre/fuv021

Inglett, P., Reddy, K., & Corstanje, R. (2005). Anaerobic soils. *Encyclopedia of Soils in the Environment*, 72–78. https://doi.org/10.1016/B0-12-348530-4/00178-8

Irvine, C., Macrae, M., Morison, M., & Petrone, R. (2019). Seasonal nutrient export dynamics in a mixed land use subwatershed of the Grand River, Ontario, Canada. *Journal of Great Lakes Research*, *45*(6), 1171–1181. https://doi.org/10.1016/j.jglr.2019.10.005

Johnston, E. R., Kim, M., Hatt, J. K., Phillips, J. R., Yao, Q., Song, Y., Hazen, T. C., Mayes, M. A., & Konstantinidis, K. T. (2019). Phosphate addition increases tropical forest soil respiration primarily by deconstraining microbial population growth. *Soil Biology and Biochemistry*, *130*, 43–54. https://doi.org/10.1016/j.soilbio.2018.11.026

Juutinen, S., Moore, T. R., Bubier, J. L., Arnkil, S., Humphreys, E., Marincak, B., Roy, C., & Larmola, T. (2018). Long-term nutrient addition increased CH4 emission from a bog through direct and indirect effects. *Scientific Reports*, *8*(1), Article 1. https://doi.org/10.1038/s41598-018-22210-2

Kato, T., Kuroda, H., & Nakasone, H. (2009). Runoff characteristics of nutrients from an agricultural watershed with intensive livestock production. *Journal of Hydrology*, *368*(1), 79–87. https://doi.org/10.1016/j.jhydrol.2009.01.028

Kayranli, B., Scholz, M., Mustafa, A., & Hedmark, Å. (2010). Carbon Storage and Fluxes within Freshwater Wetlands: A Critical Review. *Wetlands*, *30*(1), 111–124. https://doi.org/10.1007/s13157-009-0003-4

Kear, J. (1963). The agricultural importance of wild goose droppings. *Wildfowl*, *14*(14), Article 14.

Keller, J. K., Bauers, A. K., Bridgham, S. D., Kellogg, L. E., & Iversen, C. M. (2006). Nutrient control of microbial carbon cycling along an ombrotrophic-minerotrophic peatland gradient. *Journal of Geophysical Research: Biogeosciences*, *111*(G3). https://doi.org/10.1029/2005JG000152

Keller, J. K., Bridgham, S. D., Chapin, C. T., & Iversen, C. M. (2005). Limited effects of six years of fertilization on carbon mineralization dynamics in a Minnesota fen. *Soil Biology and Biochemistry*, *37*(6), 1197–1204. https://doi.org/10.1016/j.soilbio.2004.11.018

Khoiyangbam, R. S., & Chingangbam, S. S. (2022). Assessing seasonal variation of diffusive nitrous oxide emission from freshwater wetland in Keibul Lamjao National Park, Manipur Northeast India. *Atmospheric Environment: X*, *13*, 100147. https://doi.org/10.1016/j.aeaoa.2022.100147

Kim, S. Y., Veraart, A. J., Meima-Franke, M., & Bodelier, P. L. E. (2015). Combined effects of carbon, nitrogen and phosphorus on CH4 production and denitrification in wetland sediments. *Geoderma*, *259–260*, 354–361. https://doi.org/10.1016/j.geoderma.2015.03.015

Kirwan, M. L., & Blum, L. K. (2011). Enhanced decomposition offsets enhanced productivity and soil carbon accumulation in coastal wetlands responding to climate change. *Biogeosciences*, *8*(4), 987–993. https://doi.org/10.5194/bg-8-987-2011

Kling, G. W., Kipphut, G. W., & Miller, M. C. (1992). The flux of CO2 and CH4 from lakes and rivers in arctic Alaska. *Hydrobiologia*, *240*(1), 23–36. https://doi.org/10.1007/BF00013449

Kotsyurbenko, O. R., Glagolev, M. V., Merkel, A. Y., Sabrekov, A. F., & Terentieva, I. E. (2019). Methanogenesis in Soils, Wetlands, and Peat. In A. J. M. Stams & D. Z. Sousa (Eds.), *Biogenesis of Hydrocarbons* (pp. 211–228). Springer International Publishing. https://doi.org/10.1007/978-3-319-78108-2_9

Kristensen, E., Bouillon, S., Dittmar, T., & Marchand, C. (2008). Organic carbon dynamics in mangrove ecosystems: A review. *Aquatic Botany*, *89*(2), 201–219. https://doi.org/10.1016/j.aquabot.2007.12.005

Lafleur, P. M., McCaughey, J. H., Joiner, D. W., Bartlett, P. A., & Jelinski, D. E. (1997). Seasonal trends in energy, water, and carbon dioxide fluxes at a northern boreal wetland. *Journal of Geophysical Research: Atmospheres*, *102*(D24), 29009–29020. https://doi.org/10.1029/96JD03326

Le Mer, J., & Roger, P. (2001). Production, oxidation, emission and consumption of methane by soils: A review. *European Journal of Soil Biology*, *37*(1), 25–50. https://doi.org/10.1016/S1164-5563(01)01067-6

Li, J., Zheng, B., Chen, X., Li, Z., Xia, Q., Wang, H., Yang, Y., Zhou, Y., & Yang, H. (2021). The Use of Constructed Wetland for Mitigating Nitrogen and Phosphorus from Agricultural Runoff: A Review. *Water*, *13*(4), Article 4. https://doi.org/10.3390/w13040476

Li, L., Xue, S., & Xi, J. (2019). Anaerobic oxidation of methane coupled to sulfate reduction: Consortium characteristics and application in co-removal of H2S and methane. *Journal of Environmental Sciences*, *76*, 238–248. https://doi.org/10.1016/j.jes.2018.05.006

Limpert, K. E., Carnell, P. E., Trevathan-Tackett, S. M., & Macreadie, P. I. (2020). Reducing Emissions From Degraded Floodplain Wetlands. *Frontiers in Environmental Science*, *8*. https://doi.org/10.3389/fenvs.2020.00008

Liu, L., & Greaver, T. L. (2009). A review of nitrogen enrichment effects on three biogenic GHGs: The CO2 sink may be largely offset by stimulated N2O and CH4 emission. *Ecology Letters*, *12*(10), 1103–1117. https://doi.org/10.1111/j.1461-0248.2009.01351.x

Liu, Y., Yang, J., Ning, K., Wang, A., Wang, Q., Wang, X., Wang, S., Lv, Z., Zhao, Y., & Yu, J. (2021). Temperature sensitivity of anaerobic CO2 production in soils of *Phragmites australis* marshes with distinct hydrological characteristics in the Yellow River estuary. *Ecological Indicators*, *124*, 107409. https://doi.org/10.1016/j.ecolind.2021.107409

Lloyd, J., & Taylor, J. A. (1994). On the Temperature Dependence of Soil Respiration. *Functional Ecology*, *8*(3), 315–323. https://doi.org/10.2307/2389824

Loka Bharathi, P. A. (2008). Sulfur Cycle. In S. E. Jørgensen & B. D. Fath (Eds.), *Encyclopedia of Ecology* (pp. 3424–3431). Academic Press. https://doi.org/10.1016/B978-008045405-4.00761-8

Lovelock, C. E. (2008). Soil Respiration and Belowground Carbon Allocation in Mangrove Forests. *Ecosystems*, *11*(2), 342–354. https://doi.org/10.1007/s10021-008-9125-4

Lund, M., Christensen, T. R., Mastepanov, M., Lindroth, A., & Ström, L. (2009). Effects of N and P fertilization on the greenhouse gas exchange in two northern peatlands with contrasting N deposition rates. *Biogeosciences*, *6*(10), 2135–2144. https://doi.org/10.5194/bg-6-2135-2009

Magenheimer, J. F., Moore, T. R., Chmura, G. L., & Daoust, R. J. (1996). Methane and carbon dioxide flux from a macrotidal salt marsh, Bay of Fundy, New Brunswick. *Estuaries*, *19*(1), 139–145. https://doi.org/10.2307/1352658

Maljanen, M., Kohonen, A.-R., VirkajaäRvi, P., & Martikainen, P. J. (2007). Fluxes and production of N2O, CO2 and CH4 in boreal agricultural soil during winter as affected by snow cover. *Tellus B: Chemical and Physical Meteorology*, *59*(5), 853–859. https://doi.org/10.1111/j.1600-0889.2007.00304.x

Mallory, M., Fontaine, A., Smith, P., Robertson, M., & Gilchrist, H. (2006). Water chemistry of ponds on Southampton Island, Nunavut, Canada: Effects of habitat and ornithogenic inputs. *Archiv Für Hydrobiologie*, *166*, 411–432. https://doi.org/10.1127/0003-9136/2006/0166-0411

Manny, B. A., Wetzel, R. G., & Johnson, W. C. (1975). Annual contribution of carbon, nitrogen and phosphorus by migrant Canada geese to a hardwater lake. *SIL Proceedings, 1922-2010*, *19*(2), 949–951. https://doi.org/10.1080/03680770.1974.11896143

Mariash, H. L., Rautio, M., Mallory, M., & Smith, P. A. (2019). Experimental tests of water chemistry response to ornithological eutrophication: Biological implications in Arctic freshwaters. *Biogeosciences*, *16*(23), 4719–4730. https://doi.org/10.5194/bg-16-4719-2019

Maryland Dept of Natural Resources. (2022). *A Breeding Pair Survey of Canada Geese In Northern Quebec—2022*. https://dnr.maryland.gov/wildlife/Documents/AP-Survey-report-2022.pdf

Medvedeff, C. A., Inglett, K. S., & Inglett, P. W. (2014). Evaluation of direct and indirect phosphorus limitation of methanogenic pathways in a calcareous subtropical wetland soil. *Soil Biology and Biochemistry*, *69*, 343–345. https://doi.org/10.1016/j.soilbio.2013.11.018

Meyer, N., Welp, G., & Amelung, W. (2019). Effect of sieving and sample storage on soil respiration and its temperature sensitivity (Q10) in mineral soils from Germany. *Biology and Fertility of Soils*, *55*(8), 825–832. https://doi.org/10.1007/s00374-019-01374-7

Mitsch, W. J., & Gooselink, J. G. (2015). *Wetlands* (Fifth edition). John Wiley and Sons, Inc.

Moore, T., & Knowles, R. (1990). Methane emissions from fen, bog and swamp peatlands in Quebec. *Biogeochemistry*, *11*, 45–61. https://doi.org/10.1007/BF00000851

Moore, T. R., & Dalva, M. (1993). The influence of temperature and water table position on carbon dioxide and methane emissions from laboratory columns of peatland soils. *Journal of Soil Science*, *44*(4), 651–664. https://doi.org/10.1111/j.1365-2389.1993.tb02330.x

Moore, T. R., Heyes, A., & Roulet, N. T. (1994). Methane emissions from wetlands, southern Hudson Bay lowland. *Journal of Geophysical Research: Atmospheres*, *99*(D1), 1455–1467. https://doi.org/10.1029/93JD02457

Murray, R. E., & Knowles, R. (2003). Production of NO and N2O in the presence and absence of C2H2 by soil slurries and batch cultures of denitrifying bacteria. *Soil Biology and Biochemistry*, *35*(8), 1115–1122. https://doi.org/10.1016/S0038-0717(03)00163-9

Mwagona, P. C., Yao, Y., Yuanqi, S., & Yu, H. (2019). Greenhouse gas emissions from intact riparian wetland soil columns continuously loaded with nitrate solution: A laboratory microcosm study. *Environmental Science and Pollution Research*, *26*(32), 33702–33714. https://doi.org/10.1007/s11356-019-06406-1

National Data Bouy Center NOAA. (n.d.). *Station 45012 (LLNR 2655)—EAST Lake Ontario—20NM North Northeast of Rochester, NY*. https://www.ndbc.noaa.gov/view_climplot.php?station=45012&meas=st

Nelligan, C., Sorichetti, R. J., Yousif, M., Thomas, J. L., Wellen, C. C., Parsons, C. T., & Mohamed, M. N. (2021). Then and now: Revisiting nutrient export in agricultural watersheds within southern Ontario’s lower Great Lakes basin. *Journal of Great Lakes Research*, *47*(6), 1689–1701. https://doi.org/10.1016/j.jglr.2021.08.010

Panikov, N. S., Dedysh, S. N., Kolesnikov, O. M., Mardini, A. I., & Sizova, M. V. (2001). Metabolic and Environmental Control on Methane Emission from Soils: Mechanistic Studies of Mesotrophic Fen in West Siberia. *Water, Air and Soil Pollution: Focus*, *1*(5), 415–428. https://doi.org/10.1023/A:1013153927194

Pennock, D., Yates, T., Bedard-Haughn, A., Phipps, K., Farrell, R., & McDougal, R. (2010). Landscape controls on N2O and CH4 emissions from freshwater mineral soil wetlands of the Canadian Prairie Pothole region. *Geoderma*, *155*(3–4), 308–319. https://doi.org/10.1016/j.geoderma.2009.12.015

Phelps, A. R., Peterson, K. M., & Jeffries, M. O. (1998). Methane efflux from high-latitude lakes during spring ice melt. *Journal of Geophysical Research: Atmospheres*, *103*(D22), 29029–29036. https://doi.org/10.1029/98JD00044

Price, J. S., & Waddington, J. M. (2000). Advances in Canadian wetland hydrology an biogeochemistry. *Hydrological Processes*, *14*(9), 1579–1589. https://doi.org/10.1002/1099-1085(20000630)14:9<1579::AID-HYP76>3.0.CO;2-#

Psenner, R. (1994). Environmental impacts on freshwaters: Acidification as a global problem. *Science of The Total Environment*, *143*(1), 53–61. https://doi.org/10.1016/0048-9697(94)90532-0

Purcell, S. L. (1999). *The significance of waterfowl feces as a source of nutrients to algae in a prairie wetland*. http://hdl.handle.net/1993/7326

Raich, J. W., & Schlesinger, W. H. (1992). The global carbon dioxide flux in soil respiration and its relationship to vegetation and climate. *Tellus B*, *44*(2), 81–99. https://doi.org/10.1034/j.1600-0889.1992.t01-1-00001.x

Rasmussen, P. E., Albrecht, S. L., & Smiley, R. W. (1998). Soil C and N changes under tillage and cropping systems in semi-arid Pacific Northwest agriculture. *Soil and Tillage Research*, *47*(3), 197–205. https://doi.org/10.1016/S0167-1987(98)00106-8

Reddy, K. R., & DeLaune, R. D. (2008). Carbon. In *Biogeochemistry of Wetlands*. CRC Press.

Reth, S., Reichstein, M., & Falge, E. (2005). The effect of soil water content, soil temperature, soil pH-value and the root mass on soil CO2efflux – A modified model. *Plant and Soil*, *268*(1), 21–33. https://doi.org/10.1007/s11104-005-0175-5

Sánchez-Carrillo, S., Angeler, D. G., Álvarez-Cobelas, M., & Sánchez-Andrés, R. (2011). Freshwater Wetland Eutrophication. In A. A. Ansari, S. Singh Gill, G. R. Lanza, & W. Rast (Eds.), *Eutrophication: Causes, consequences and control* (pp. 195–210). Springer Netherlands. https://doi.org/10.1007/978-90-481-9625-8_9

Scanlon, D., & Moore, T. (2000). CARBON DIOXIDE PRODUCTION FROM PEATLAND SOIL PROFILES: THE INFLUENCE OF TEMPERATURE, OXIC/ANOXIC CONDITIONS AND SUBSTRATE. *Soil Science*, *165*(2), 153–160.

Schnecker, J., Bowles, T., Hobbie, E. A., Smith, R. G., & Grandy, A. S. (2019). Substrate quality and concentration control decomposition and microbial strategies in a model soil system. *Biogeochemistry*, *144*(1), 47–59. https://doi.org/10.1007/s10533-019-00571-8

Shepherd, M., Philipps, L., Jackson, L., & Bhogal, A. (2002). The Nutrient Content of Cattle Manures from Organic Holdings in England. *Biological Agriculture & Horticulture*, *20*(3), 229–242. https://doi.org/10.1080/01448765.2002.9754967

Singh, S. N., Kulshreshtha, K., & Agnihotri, S. (2000). Seasonal dynamics of methane emission from wetlands. *Chemosphere - Global Change Science*, *2*(1), 39–46. https://doi.org/10.1016/S1465-9972(99)00046-X

Song, C., Wang, L., Tian, H., Liu, D., Lu, C., Xu, X., Zhang, L., Yang, G., & Wan, Z. (2013). Effect of continued nitrogen enrichment on greenhouse gas emissions from a wetland ecosystem in the Sanjiang Plain, Northeast China: A 5 year nitrogen addition experiment. *Journal of Geophysical Research: Biogeosciences*, *118*(2), 741–751. https://doi.org/10.1002/jgrg.20063

Song, C., Yang, G., Liu, D., & Mao, R. (2012). Phosphorus availability as a primary constraint on methane emission from a freshwater wetland. *Atmospheric Environment*, *59*, 202–206. https://doi.org/10.1016/j.atmosenv.2012.06.003

Soued, C., Bogard, M. J., Finlay, K., Bortolotti, L. E., Leavitt, P. R., Badiou, P., Knox, S. H., Jensen, S., Mueller, P., Lee, S. C., Ng, D., Wissel, B., Chan, C. N., Page, B., & Kowal, P. (2024). Salinity causes widespread restriction of methane emissions from small inland waters. *Nature Communications*, *15*(1), 717. https://doi.org/10.1038/s41467-024-44715-3

Stenberg, B., Johansson, M., Pell, M., Sjödahl-Svensson, K., Stenström, J., & Torstensson, L. (1998). Microbial biomass and activities in soil as affected by frozen and cold storage. *Soil Biology and Biochemistry*, *30*(3), 393–402. https://doi.org/10.1016/S0038-0717(97)00125-9

Stotzky, G., Goos, R. D., & Timonin, M. I. (1962). Microbial changes occurring in soil as a result of storage. *Plant and Soil*, *16*(1), 1–18. https://doi.org/10.1007/BF01378154

Strack, M., Waddington, J. M., Lucchese, M. C., & Cagampan, J. P. (2009). Moisture controls on CO $_2$ exchange in a *Sphagnum* -dominated peatland: Results from an extreme drought field experiment. *Ecohydrology*, *2*(4), 454–461. https://doi.org/10.1002/eco.68

Timmers, P. H., Suarez-Zuluaga, D. A., van Rossem, M., Diender, M., Stams, A. J., & Plugge, C. M. (2016). Anaerobic oxidation of methane associated with sulfate reduction in a natural freshwater gas source. *The ISME Journal*, *10*(6), 1400–1412. https://doi.org/10.1038/ismej.2015.213

Topp, E., & Pattey, E. (1997). Soils as sources and sinks for atmospheric methane. *Canadian Journal of Soil Science*, *77*(2), 167–177. https://doi.org/10.4141/S96-107

Ullah, S., & Moore, T. R. (2011). Biogeochemical controls on methane, nitrous oxide, and carbon dioxide fluxes from deciduous forest soils in eastern Canada. *Journal of Geophysical Research: Biogeosciences*, *116*(G3). https://doi.org/10.1029/2010JG001525

Unckless, R. L., & Makarewicz, J. C. (2007). The impact of nutrient loading from Canada Geese (Branta canadensis) on water quality, a mesocosm approach. *Hydrobiologia*, *586*(1), 393–401. https://doi.org/10.1007/s10750-007-0712-8

United States Department of Agriculture Wildlife Services. (2017). *Managing Canada Goose Damage in the State of New York*. https://www.aphis.usda.gov/sites/default/files/ny-2017-canada-goose-damage-mgt-ea.pdf

Verhoeven, J., Arheimer, B., Yin, C., & Hefting, M. (2006). Regional and global concerns over wetlands and water quality. *Trends in Ecology & Evolution*, *21*(2), 96–103. https://doi.org/10.1016/j.tree.2005.11.015

Wang, F., Li, J., Wang, X., Zhang, W., Zou, B., Neher, D. A., & Li, Z. (2014). Nitrogen and phosphorus addition impact soil N2O emission in a secondary tropical forest of South China. *Scientific Reports*, *4*(1), 5615. https://doi.org/10.1038/srep05615

Wang, J., Chen, N., Yan, W., Wang, B., & Yang, L. (2015). Effect of dissolved oxygen and nitrogen on emission of N2O from rivers in China. *Atmospheric Environment*, *103*, 347–356. https://doi.org/10.1016/j.atmosenv.2014.12.054

Wang, Z. P., DeLaune, R. D., Patrick Jr., W. H., & Masscheleyn, P. H. (1993). Soil Redox and pH Effects on Methane Production in a Flooded Rice Soil. *Soil Science Society of America Journal*, *57*(2), 382–385. https://doi.org/10.2136/sssaj1993.03615995005700020016x

Westcott, C. (2012). *Ph Measurements*. Elsevier.

Weston, N. B., Dixon, R. E., & Joye, S. B. (2006). Ramifications of increased salinity in tidal freshwater sediments: Geochemistry and microbial pathways of organic matter mineralization. *Journal of Geophysical Research: Biogeosciences*, *111*(G1). https://doi.org/10.1029/2005JG000071

Whalen, S. C. (2005). Biogeochemistry of Methane Exchange between Natural Wetlands and the Atmosphere. *Environmental Engineering Science*, *22*(1), 73–94. https://doi.org/10.1089/ees.2005.22.73

Whalen, S. C., & Reeburgh, W. S. (1988). A methane flux time series for tundra environments. *Global Biogeochemical Cycles*, *2*(4), 399–409. https://doi.org/10.1029/GB002i004p00399

Whiting, G. J., & Chanton, J. P. (2001). Greenhouse carbon balance of wetlands: Methane emission versus carbon sequestration. *Tellus B*, *53*(5), 521–528. https://doi.org/10.1034/j.1600-0889.2001.530501.x

Winton, R., & Richardson, C. (2016). Top-down control of methane emission and nitrogen cycling by waterfowl. *Ecology*, *98*. https://doi.org/10.1002/ecy.1640

Wrage, N., Velthof, G. L., van Beusichem, M. L., & Oenema, O. (2001). Role of nitrifier denitrification in the production of nitrous oxide. *Soil Biology and Biochemistry*, *33*(12), 1723–1732. https://doi.org/10.1016/S0038-0717(01)00096-7

Wu, W., Wang, F., Xia, A., Zhang, Z., Wang, Z., Wang, K., Dong, J., Li, T., Wu, Y., Che, R., Li, L., Niu, S., Hao, Y., Wang, Y., & Cui, X. (2022). Meta-analysis of the impacts of phosphorus addition on soil microbes. *Agriculture, Ecosystems & Environment*, *340*, 108180. https://doi.org/10.1016/j.agee.2022.108180

Wynn, T. M., & Liehr, S. K. (2001). Development of a constructed subsurface-flow wetland simulation model. *Ecological Engineering*, *16*(4), 519–536. https://doi.org/10.1016/S0925-8574(00)00115-4

Yanful, E. K. (1993). Oxygen Diffusion through Soil Covers on Sulphidic Mine Tailings. *Journal of Geotechnical Engineering*, *119*(8), 1207–1228. https://doi.org/10.1061/(ASCE)0733-9410(1993)119:8(1207)

Yvon-Durocher, G., Allen, A. P., Bastviken, D., Conrad, R., Gudasz, C., St-Pierre, A., Thanh-Duc, N., & del Giorgio, P. A. (2014). Methane fluxes show consistent temperature dependence across microbial to ecosystem scales. *Nature*, *507*(7493), 488–491. https://doi.org/10.1038/nature13164

Zhang, J., Song, C., & Yang, W. (2005). Cold season CH4, CO2 and N2O fluxes from freshwater marshes in northeast China. *Chemosphere*, *59*(11), 1703–1705. https://doi.org/10.1016/j.chemosphere.2004.11.051

Zhang, Y., Wang, C., & Li, Y. (2019). Contrasting effects of nitrogen and phosphorus additions on soil nitrous oxide fluxes and enzyme activities in an alpine wetland of the Tibetan Plateau. *PLoS ONE*, *14*(5), e0216244. https://doi.org/10.1371/journal.pone.0216244

Zhang, Z., Zimmermann, N. E., Stenke, A., Li, X., Hodson, E. L., Zhu, G., Huang, C., & Poulter, B. (2017). Emerging role of wetland methane emissions in driving 21st century climate change. *Proceedings of the National Academy of Sciences*, *114*(36), 9647–9652. https://doi.org/10.1073/pnas.1618765114

Zheng, M., Zhang, T., Liu, L., Zhu, W., Zhang, W., & Mo, J. (2016). Effects of nitrogen and phosphorus additions on nitrous oxide emission in a nitrogen-rich and two nitrogen-limited tropical forests. *Biogeosciences*, *13*(11), 3503–3517. https://doi.org/10.5194/bg-13-3503-2016

Žurovec, O., Wall, D. P., Brennan, F. P., Krol, D. J., Forrestal, P. J., & Richards, K. G. (2021). Increasing soil pH reduces fertiliser derived N2O emissions in intensively managed temperate grassland. *Agriculture, Ecosystems & Environment*, *311*, 107319. https://doi.org/10.1016/j.agee.2021.107319