Greenhouse Gas Emission from Small Bog Pools in a Boreal Peatland in Newfoundland, Canada.

By

Blessing Ivie Akpoguma

A thesis submitted to School of Graduate Studies

In partial fulfillment of the requirements for the degree of

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Approved:

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Dean of the Graduate School

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Supervisor

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Date

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Dr. Robert Scott

Abstract

Studies on the greenhouse gases (GHG) potential and emissions from peatlands have been studied extensively in recent years due to the increasing atmospheric concentration of GHG and impact on climate change. However, most research estimating GHG emissions and factors regulating these emissions from peatlands are focused on the terrestrial microforms of peatlands. Thus, less is known about the GHG emission potential from peatland pools, which are the aquatic components. I conducted a study in small bog pools during the 2018 growing season to determine the drivers and concentration of CH_4 dissolved in pool surface waters using the headspace method. Also, a five-year growing season (2013, 2014, 2015, 2016 and 2018) static floating chamber was used to quantify the variation in GHG flux from pools across the growing seasons. Results showed that pools are supersaturated with CH_4 ranging in concentration from 2.32 to 180.98 µmol L^{-1}, among the highest concentration reported for small inland waters. The super-saturation observed in these pools may have been influenced by several biological, chemical, and physical factors but were best predicted by a relationship with temperature, vegetation, dissolved organic carbon (DOC), and pool surface area. I also found that CO_2 flux was significantly different across the years ($p < 0.05$) in which pools acted as sources during 2013 and 2018 ($\overline{x}$ = 23.91 and 7.79 mmol m^{-2} d^{-1} respectively) and as sinks in 2014, 2015 and 2016 ($\overline{x}$ = -7.41, -8.98 and -9.04 mmol m^{-2} d^{-1} respectively). In contrast, pools acted mostly as sources of CH_4 to the atmosphere in 2013, 2016 and 2018 and were negligible sinks during 2014 and 2015 ($\overline{x}$ = 0.41, 0.00, -0.01, 0.19 and 0.52 mmol m^{-2} d^{-1} for years 2013 to 2018 respectively). However, flux of CH_4 was not significantly different across the years (P >

0.05). Pools acted mostly as negligible sinks of N_2O flux, which is typical of ombrotrophic peatlands. N_2O flux did not vary among years ($p > 0.05$). Pool depth was found to be the best predictor of CO_2 fluxes, while dissolved organic carbon was found to be the major predictor of CH_4 emission. This study shows that the concentration and emission of GHG from bog pools varies depending on climatic conditions and within pool biogeochemistry, therefore bog pools' GHG emission potential can be influenced in future climate scenarios.

Keywords: Peatlands, Bog pools, Greenhouse gases (GHG), Fluxes, Carbon dioxide (CO_2), Methane (CH_4), Nitrous oxide (N_2O), Dissolved organic carbon (DOC), Total nitrogen (TN), Electrical conductivity (EC), Dissolved oxygen (DO), Hydrogen ion concentration (pH). Vegetation, Sink, Source.

Acknowledgments

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Blessing Ivie Akpoguma.

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List of Abbreviations and Symbols

°C – Degree Celsius

µmol L^{-1} – Micromoles per liter

µmol m^{-2} d^{-1} – Micromoles per square meter per day

µs cm^{-1} – Microsiemens per centimeter

a – Area

ABS – Acrylonitrile butadiene styrene

AIC – Akaike Information Criterion

ANOVA- Analysis of variance

C – Carbon

CH_4 – Methane

cm - Centimeter

CO_2 – Carbon dioxide

DO – Dissolved oxygen

DOC – Dissolved organic carbon

EC – Electrical conductivity

g – Gram

GHG – Greenhouse gas(es)

IPCC – Intergovernmental panel on climate change

km^2 – Square kilometer

m – Meter

m^2 – Square meter

mg L^{-1} – Milligrams per liter

Mha – Million hectare

mm – Millimeter

mmol m^{-2} d^{-1} – Millimoles per square meter per day

N_2O – Nitrous oxide

p - perimeter

pH – Potential of hydrogen (Hydrogen ion concentration)

SE – Standard error

SI – Shape index

Tg – Teragram

VIF – Variance inflation factor

yr^{-1} – Per year

π - Pie

Chapter 1

1.0 Introduction and overview

1.1 Introduction

Peatlands are wetlands that accumulate peat (partially-decomposed organic matter) (Strack, 2008). They store about 450×10^{15} g C which accounts for about one-third of global soil carbon (C) stock and play a significant role in climate regulation (Gorham, 1991; Turunen *et al*., 2002). In their pristine state, peatlands act as C sinks by taking in atmospheric CO_2, and as sources of C by emitting CH_4 into the atmosphere. Peatlands are a low or negligible source of N_2O (Rinne *et al*., 2007; Maljanen *et al*., 2010; Kløve *et al*., 2017). The ability of peatlands to sequester C is due to waterlogged and anoxic soil conditions that is controlled by hydrology, temperature, and vegetation characteristics of the boreal region (Yu *et al*., 2010). Many peatlands are characterized by a microtopographic gradient of hummocks, lawns, hollows, and pools (Rydin and Jeglum, 2006). The distinction among these gradients has been related to differences in water table levels since hummocks, lawns and hollows are raised above the water table making them land surfaces while pools are permanently filled with water (Rydin and Jeglum, 2006, Comas *et al.*, 2011). Consequently, variation in GHG emissions have been reported from the various peatland microforms within a contiguous peatland due to differences in physical and environmental conditions responsible for the microtographic variability (Hamilton *et al*., 1994; Dinsmore *et al*., 2009a; Pelletier *et al*., 2011).

Small bog pools are a common feature in many boreal and temperate peatlands and have been found in all continents except Antarctica (Belyea and Lancaster, 2002; Turner et al.,

2016). Most studies on the control of GHG emission and budget from peatlands are focused on the terrestrial microforms of peatland, with little attention given to peatland pools. Furthermore, available studies on emissions of GHG from peatland pools are based on short-term measurements, which do not capture variation in GHG emissions over long-term changing weather patterns (Hamilton *et al*., 1994; Macrea *et al*., 2004; Pelletier *et al*., 2014). Therefore, GHG emission potential from peatlands pools remains largely uncertain.

1.2 Thesis questions and objectives

This thesis seeks to address these questions:

1) What is the concentration level of CH_4 in bog pools?
2) What are the controlling factors regulating the concentration of CH_4 in pools?
3) What is the growing season flux of GHG (CO_2, CH_4, and N_2O) from bog pools?
4) Do fluxes of GHG vary temporally in peatland pools?

The following specific objectives were formulated to answer these questions:

1) measure the CH_4 concentration in small bog pools (chapter 2),

2) identify local drivers of dissolved CH_4 concentration (chapter 2)

3) quantify and compare the variations in fluxes of CO_2, CH_4, and N_2O from bog pools over five growing seasons in an ombrotrophic peatland (chapter 3).

This study will contribute to the inventory of GHG fluxes from bog pools.

1.3 Thesis outline

This thesis is divided into four chapters, with relevant literature being reviewed within each chapter.

Chapter one provides an introduction and basic overview of current research literature, which includes wetlands, peatlands, bog pools, and greenhouse gas exchange in natural peatlands.

Chapter two and three are the main contribution of this thesis and written in a format suitable for publication in scientific journals. Chapter two presents the result of the concentration of dissolved CH_4 in pools and drivers of its production and concentration. Chapter three presents the results of the multiyear diffusive greenhouse gas flux from the pools and the controlling factors regulating its emission. Although there is an overlap of physicochemical data in the growing season of 2018 in both chapters, chapter two uses data from seven measured pools measured from mid-June to October while chapter three uses data from three pools out of the seven pools in chapter two, and its data included measurements from May. However, chapter two discusses the dissolved CH_4 measured in pools over one growing season (2018) which provides the answer to my thesis questions and objectives (1 and 2), chapter three on the other hand, discusses the temporal variation in diffusive flux of CO_2, CH_4 and N_2O for five growing seasons (2013, 2014, 2015, 2016, 2018) and provides answers to my thesis questions (3 and 4) and objective (3).

Chapter four consists of the summary and conclusion of the significant findings from the research.

1.4 Overview of research

1.4.1 Wetlands

According to Banner and MacKenzie (2000), "Wetlands ecosystems are areas where a water table is at, near or just below the surface and where soil are water-saturated for a sufficient length of time such that excess water and resulting low soil oxygen levels are principal determinants of vegetation and soil development". Due to differences in topography, climate, hydrology, water chemistry, vegetation and other factors including human disturbance the distribution of the extent of wetlands vary widely across the globe (U.S. EPA, 2018). In Canada, wetlands are classified as marsh, swamp, fen, and bog (National Wetlands Working Group, 1997). The classification into these classes is based on physiognomic and dominance type approach (Rydin and Jeglum, 2006). Marshes are characterized by slow-moving water or standing water with submerged, floating-leaved or emergent plant cover while the swamp is forested or thicketed wetland whose water comes from underlying soil or lateral groundwater flow (Rydin and Jeglum, 2006). A fen is a minerotrophic peatland with a water table at or slightly below the surface while bogs are ombrotrophic peatlands with the surface above the surrounding terrain or isolated from laterally moving mineral-rich soil water (Rydin and Jeglum, 2006). Sometimes, peatland landscape may contain areas of both fen and bog (Beadle *et al*., 2015). Therefore, not all wetland areas are peatlands.

1.4.2 Peatlands characteristics

Peat is partially decomposed plant and animal constituents accumulating under anoxic and water-saturated conditions (Rydin and Jeglum, 2006). Therefore, peatlands are ecosystems with peat covered terrain. In Canada, a minimum depth of 40 cm peat is required to be classified peat while in many other countries a minimum depth of 30 cm is required (National Wetlands Working Group, 1997; Joosten and Clarke, 2002). Peatlands are a significant store of the Earth's carbon, storing about 450×10^{15} g C equivalent or about one-third of global soil C stock (Gorham, 1991; Turunen *et al*., 2002). The accumulation of carbon in peatlands is due to the slow decomposition and accretion of partially decomposed biomass (Klove, 2017). They are estimated to cover an area of about 400 Mha which is equivalent to about 3% of the Earth's surface (Strack, 2008; Yu *et al*., 2010; Page *et al*., 2011). About 350 Mha of this distribution, is situated in the Northern hemisphere covering North America and Europe (Strack, 2008). Peatlands cover about 113.6 Mha or 12% of the Canadian land area of which 64% lies in the Boreal Wetland Region and 33% in the Subarctic Wetland Region, giving a total 97% (Tarnocai, 2006; Strack, 2008). The term minerotrophic is used to indicate peatlands that are influenced by mineral soil groundwater while ombrotrophic indicates peatlands which are fed water solely by precipitation (Beadle *et al*., 2015). Ombrotrophic peatlands are characterized by nutrient poor, acidic conditions, and peat depth of more than 40 cm (National Wetlands Working Group, 1997; Rydin and Jeglum, 2006). In many peatlands, a microtopographic gradient of hummocks, lawns, hollows, and pools are formed due to interactions between the underlying terrain, climate, and hydrology (hydromorphology; Glaser, 1992; Rydin and

Jeglum, 2006). Hummocks, hollow and lawns are raised about 5-50 cm above the water table and composed of a variety of vegetation while pools are permanently filled with water with little vegetation within or surrounding their edges (Rydin and Jeglum, 2006). The controlling physical condition dividing peatlands into a microtopographic gradient is based on groundwater table levels (Sjörs, 1948; Rydin and Jeglum, 2006).

1.4.3 Bog pools

Bog pools occur over a variety of climatic conditions and have been found in all continents except Antarctica (Glaser 1998; Belyea and Lancaster, 2002; Turner *et al*., 2016). They are secondary features on peat surfaces resulting from reduced peat accumulation in depressions (Forster and Glaser, 1986; Sjörs, 1990; Comas *et al*., 2011). After initial formation, they are deepened due to changes in vegetation (Sjörs 1990, Rydin and Jeglum, 2006). The interaction of vegetation decomposition and factors such as climate, local hydrology, and topography determines the rate of peat accumulation establishing pool patterning (Belyea and Lancaster, 2002; Beadle *et al*., 2015). As the size of pools increases, they become deeper and elongated in shape (Forster *et al*., 1986). The age of pools determines its location in the peatlands, as younger pools, which are small and shallow, are located at the margins while older pools, which are larger and deep, are located in the center (Belyea and Lancaster, 2002). Bog pools are characterized by low pH, low levels of nutrients and primary productivity but with high levels of dissolved organic matter (Rydin and Jeglum, 2006; Beadle *et al*., 2015).

1.4.4 Greenhouse Gas Exchange (GHG) in Natural Peatlands

Peatlands play a significant role in the balance of GHG. Generally, in their pristine or natural state, peatlands are sinks of CO_2 due to the saturated waterlogged soil condition inhibiting aerobic decomposition and favoring the accumulation of organic soil matter (Dise, 2009; Teh *et al*., 2011). The net sink uptake is estimated to range from -2.5 to -144 g C m^{-2} yr^{-1} (Roulet, 2007; Nilsson *et al*., 2008; Olson *et al*., 2013; Fortuniak *et al*., 2017). The net ecosystem exchange (NEE) of CO_2 uptake is determined by the difference between the process of gross ecosystem photosynthesis (GEP) and ecosystem respiration (ER) (Strack, 2008). Photosynthesis is mostly carried out by plants, while ecosystem respiration includes soil and plant respiration (Strack, 2008).

Conversely, peatlands are natural sources of CH_4 due to the anaerobic soil condition which promote CH_4 production (Strack, 2008). Peatlands are estimated to emit an average of 70 Tg yr^{-1} ranging from 3.7 to 65.7 g C m^{-2} yr^{-1} (Gorham, 1991; Turetsky *et al*., 2008; Moore *et al*., 2011). The net flux of CH_4 emission from peatland is determined by the balance between production, consumption, and transport (Strack, 2008; Lai, 2009). Production of CH_4 is carried out by methanogenic bacteria or methanogens in highly reduced conditions in the saturated zone (Strack, 2008). This is emitted into the atmosphere through either diffusion, ebullition (bubbling), or mass flow or diffusion via vascular plants (Strack, 2008). CH_4 can be oxidized through methanotrophic bacteria when it moves through a reduced zone in peat or the rhizosphere of vascular plants (Stack, 2008). N_2O are low or negligible for natural peatlands and are usually net sinks in many ombrotrophic bogs

(Martikainen *et al*., 1993). The net flux of N_2O is determined by the balance between nitrification and denitrification (Soued *et al*., 2015).

Emission of GHG from waterbodies in peatlands is associated with gas transfer across the water surface to the atmosphere and referred to as 'on-site' emissions using the IPCC terminology (IPCC, 2014). These emissions may include degassing of CO_2, CH_4 and N_2O transported from the peat matrix and gas produced within the waterbody or its underlying sediment as labile organic substrates are metabolized (Evans *et al*., 2016). GHG from waterbodies may also be emitted through diffusive fluxes across the water surface, due to over-saturation of the gas in the water column relative to the atmosphere or through ebullition through the water column (Billet and Moore, 2008; Evans *et al*., 2016).

1.4 Contribution statement

The research site, refinement of objectives and funding for sample collection and analysis were provided by Dr. Jianghua Wu. I formulated the objectives, analyzed data and wrote the first draft of this thesis. Dr. Jianghua Wu reviewed, provided edits, comments and revised this thesis. My committee member, Dr. Robert Scott suggested the statistical tools for analyzing data and data presentation, provided edits and comments to this thesis. Dr. Junwei Luan, Dr. Mei Wang collected the diffusive flux data of GHG for the growing seasons of 2013, 2014 and 2015, Raid Eissa, Asare Gyimah and Maryam Hajheidari collected the diffusive flux data of GHG for the growing season of 2016.

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Chapter 2

2.0 Drivers of methane super-saturation in small bog pools

2.1 Introduction

Methane (CH_4) has 86 times greater global warming potential than CO_2 in a 20-year time horizon (IPCC, 2013). Atmospheric CH_4 concentration increased 150% from 722 ppb to 1803 ppb between 1990s and 2011 following a period of stagnation, since pre-industrial times (IPCC, 2013). While atmospheric CH_4 emission has largely been attributed to anthropogenic human activities, about one-third of its emission are driven by natural sources (Nisbet *et al*., 2014). Wetlands are the most significant natural sources of CH_4, contributing to about 20% of atmospheric CH_4 emissions (Mitra *et al*., 2005b, IPCC 2013; Sabrekov *et al*., 2017). CH_4 emissions from wetlands will likely increase due to climate warming as ecosystem C cycling reacts positively with warmer temperatures, stimulating organic matter breakdown and CH_4 release to the atmosphere (Bridgham *et al*., 2013, Stanley *et al*., 2016).

Peatlands are wetlands with waterlogged, anoxic soils composed of partially decomposed organic matter (Strack, 2008). The rich organic sediments and inputs of labile organic C from root exudates provide suitable conditions for CH_4 production by methanogens (Mitra *et al*., 2005a; Sabrekov *et al*., 2017; Rinne *et al*., 2018). Total CH_4 emissions from peatlands are the balance between production by methanogens in the anaerobic peat layer and consumption or oxidation by methanotrophs in the aerobic peat layer (Rinne *et al*., 2018). The regulatory controls of CH_4 production and consumption have been related to water

table position, temperature, vascular plant activity and substrate quality (Waddington *et al*., 1996; Bellisario *et al*., 1999; Luan and Wu, 2015). However, most of the regulatory control has been studied on terrestrial peatlands microforms, and factors influencing CH_4 flux in peatland pools is not well known.

Small permanent natural pools are a common feature in many boreal and temperate peatlands (Belyea and Lancaster, 2002). Their development occurs over a number of years through differential peat accumulation within a peatland and has been related to several factors such as topography, hydrology, and geology, which cause their variation in shape, area, and depth (Belyea, 2007). However, few studies have been conducted to measure the CH_4 production potential of peatland pools compared to other microforms of peatlands. Conventional thinking is that aerated water and high oxygen concentration of small water bodies is not suitable for CH_4 production (Trimmer *et al*., 2012; Thornton *et al*., 2016). Peatland pools may have also not received much attention due to the difficulty of mapping pools less than 0.1 km^2 invisible to satellites (Lehner, and Döll, 2004; Verpoorter *et al*., 2014).

Small bog pools may have a high potential for CH_4 production due to their intrinsic small water size and water volume, which allows for quicker warming during summer and subsequent elevated CH_4 production since methanogenesis increases with increasing temperature (Yvon-Durocher *et al*., 2014). The increased contact between surface waters and the anoxic bottom sediments of shallower pools helps to reduce CH_4 oxidation, leading to higher CH_4 concentrations in these waters (Juutinen *et al*., 2009; Kankaala *et al*., 2013; Holgerson and Raymond, 2016). Most importantly, peatland pools are underlain with high

organic matter sediments in the form of decomposing peat, which can promote the formation of anoxic conditions facilitating methanogenesis (Zender, 1978; Juutinen *et al*., 2009). Available studies on small peatland pools have reported supersaturated conditions of CH_4 in surface waters (Hamilton *et al*., 1994; Riera *et al*.,1999; Pelletier *et al*., 2014). Due to the high dissolved CH_4 concentration in these waters relative to their atmospheric concentrations, they have been reported to result in evasion of CH_4 from the surface water to the atmosphere (Billet and Moore, 2008; Wanninkhof, 2014; Pelletier *et al*., 2014). However, little is known about the regulatory drivers of CH_4 production such as biogeochemical differences in local conditions at different regions (Saarnio *et al*., 2009; Saunois *et al*., 2016).

The study of small bog pools is especially important in the northern hemisphere due to their relative abundance. For instance, Canada's inland waters (excluding the Great Lakes) are estimated to cover about 884,000 km^2 or 9% of its surface area, and in these estimations contain about 5.4 million small water bodies less than 0.001 km^2 (Butman *et al*., 2018). Small peatland pools with a surface area of less than 1 km^2 are estimated to cover about 77% of the surface area of the Boreal region of Quebec, Canada (Beadle *et al*., 2015). Such small inland waters may contribute significantly to CH_4 production and, since they are widely distributed across the Earth surface, could contribute significantly to the total CH_4 budget when pooled together. The aim of this study is to examine factors responsible for CH_4 production in small bog pools in boreal peatlands. Specifically, our objectives are to 1) measure the CH_4 concentration in small bog pools 2) identify local drivers of dissolved CH_4 concentration.

2.2 Methodology

2.2.1 Study site

The study was conducted at an ombrotrophic peatland located at Robinson's Pasture, 100 km southwest of Corner Brook, Newfoundland, Canada (48° 26′ N, 58° 66′ W). The 30-year climate normal (1981 – 2000) mean daily temperature during the coldest and warmest month is -10.7 °C in February and 20.6 °C in August. The regional climate is classified as oceanic, with annual mean precipitation of 1340.4 mm and mean annual air temperature of 5.0 °C (Environment Canada, 2018). The research site is a peatland complex made up of a discontinued pasture and natural bog. A detailed description of the site was provided by Luan and Wu (2014). My study was restricted to the flat, gently sloping natural peatland portion consisting of hummocks, hollows, lawns, and pools. The pools cover about 10% of the total surface area and range in size from 10 – 200 m^2 with water depth less than 1 m. I chose seven unconnected pools with permanent standing water. Pools were selected to be representative of the range of water depth, pool size, and bottom composition of the site. Pools are fed through precipitation, freeze up entirely during winter, and thaw in spring. The spring thaw causes an elevated water level and temporary connection of pools. The open ice-free period lasts for six to seven months from May/June to October/November depending on the end and start of winter for that given year.

2.2.2 Sampling Design

All measurements were carried out weekly from mid-June to August and biweekly from September to October 2018, except for pool depth and vegetation, which was measured once on the 20th of July, 2018. All measurements were carried out between 9:00 – 15:00h local time. The determination of dissolved methane concentration and local drivers was carried out by collecting water samples from the seven studied pools at 10cm below the water surface. The pools are shallow and well mixed so surface water is representative of the entire depth. Daily air temperature data at the time of sampling and precipitation data for each sampling date was obtained from an eddy covariance tower located at the study site.

2.2.3 Physicochemical Measurements

2.2.3.1 Pool morphology and vegetation

A one-time survey was used to assess pool depth and vegetation cover to determine spatial variability and eliminate variation in water levels caused by precipitation. Pool depths were manually determined by lowering a lightly weighted perforated disk attached to a rope into the pool until its base rests on the surface of the bottom. Seven to ten measurements were made at random locations within each pool depending on its size. Mean pool depth is used in the subsequent analysis.

Surface area and perimeter of each pool were estimated using Google Earth Pro. Shape complexity was determined by calculating shape index (SI) according to: $SI = \frac{p}{2\sqrt{\pi a}}$;

(where 'P' is the pool perimeter (m) and 'a' is the pool area (m^2)).

SI is unit-less and has a range of ≥ 1, in which a circle has a value of 1, with larger values indicating increasing shape complexity (Turner *et al*., 2016; Arsenault *et al*., 2018).

Vegetation cover surrounding and within pools was visually inspected and included both vegetation within the pool (submerged and emergent) and along the pool perimeter. Vegetation cover was estimated using the Braun–Blanquet (1932) method employed in previous studies (e.g. Forster and Glaser, 1986; Turner *et al*., 2016, Arsenault *et al*., 2018) where cover-abundance scale indicated: N = not many individual, 1-10 individuals; T = sparsely present, cover less than 5%; 1 = plentiful, cover less than 5%; 2 = very numerous, cover 5– 25%; 3 = cover 25–50%; 4 = cover 50–75%; 5 = cover more than 75%.

2.2.3.2 Water chemistry

Water temperature, electrical conductivity (EC), dissolved oxygen (DO), and barometric pressure were measured in-situ using an HQ40d multi-parameter meter (Hach Company, Loveland, Colorado, USA). The hydrogen ion concentration (pH) was also measured in-situ using an Oakton EcoTestr pH2 waterproof pH meter. The multi-parameter meter and pH meter were calibrated before the start of data collection.

Dissolved organic carbon (DOC) and total nitrogen (TN) concentration were determined for each pool by collecting water samples 10cm below the surface water using a 60mL syringe. Samples were filtered using a 0.45µm syringe filter to remove particulate matter, acidified, and analyzed using the Shimadzu TOC-LCPH/TN analyzer (Shimadzu Inc., Kyoto, Japan).

2.2.4 Dissolved CH_4 concentration

Dissolved CH_4 gas samples were taken using the headspace method (Dinsmore *et al*., 2009; Turner *et al*., 2016; Arsenault *et al*., 2018). A 60mL syringe was used to directly draw in 40mL pool water from the pool, and then another 60mL syringe was used to draw in ambient atmospheric air of which 20mL was injected into the water sample syringe, and the remaining ambient air was kept aside to calculate ambient concentration. The water sample syringe was subsequently equilibrated at pool temperature by shaking vigorously under water for one minute to shift the dissolved gases from the water phase into the gaseous phase. The equilibrated headspace was then extracted into an empty gas-tight syringe. Headspace samples were analyzed within one week of sample collection using the Bruker GHG gas chromatography (with CH_4 2.52 ppm detection limit). Concentrations of CH_4 in the pool water were calculated from the equilibrated headspace and ambient concentration using Henry's law for headspace concentrations (Hope *et al*., 2001).

2.2.5 Statistical Analysis

To evaluate the gas saturation level of dissolved CH_4 relative to atmospheric concentration, I compared the average monthly CH_4 air concentrations from June to October, 2018 (2.0 ppm) recorded by the Eddy Covariance Tower located at the study site, to the mean dissolved CH_4 concentration measured within the pools. All data were tested for normality using the Shapiro-Wilk test and transformed when necessary to meet the conditions of homogeneity of variance. Differences in concentration of CH_4 among pools were tested

using one-way ANOVA. Significant ANOVA tests were followed with Tukey post-hoc tests.

Simple linear regression and Pearson's correlation analyses were used to examine relationships and correlations among the physiochemical variables and surface dissolved CH_4 concentration. Stepwise linear regression and the Akaike Information Criterion (AIC) (Burnham and Anderson, 2002; Akaike, 2011) were finally applied to select the best model explaining CH_4 concentration in pool water. Stepwise multiple linear regression was built using AIC best subset method. Variables included in the model were determined for collinearity by calculating the variance inflation factor (VIF). Variables with a VIF of ≥ 7 were excluded from the model (Kock and Lynn, 2012). Statistical analysis was done using IBM SPSS 25.0.

2. 3 Results

2.3.1 Site Characteristics

Pools varied in depth and area from 40.0 to 61.0 cm (0.4 – 0.61m) and 27.7 to 165 m^2 (0.0000277 – 0.000165 km^2) respectively. Pool shapes were not very complex, as most were nearly circular (SI=1.13, 1.17, 1.18), linear (SI = 1.94), or convoluted (SI= 2.33) (Table 2.1). Pools had emergent vegetation consisting of *Nuphar variegata* (Yellow Pond-lily) and *Eriocaulon aquaticum* (White Buttons) during the summer months and submerged vegetation consisting of *Utricularia* spp. and algae. The pools were surrounded by sedges, shrubs, *Sphagnum* spp. and grasses all year round. Smaller pools had higher vegetation cover, with pool #2 and #4 having the most abundant cover with vegetation while pool #5 was the least covered with vegetation (Table 2.1).

2.3.2 Seasonal variation and correlation among physicochemical variables

Mean air temperature at the study site ranged from 3.9 to 25.2 °C while the pool water temperature ranged from 6.6 to 25.8 °C throughout the study (Fig. 2.1). Surface water temperature was not significantly different among pools (ANOVA, $F_{(6, 98)} = 0.50$, $p = 0.81$, Table 2.1) but significantly differed across the sampling dates (ANOVA, $F_{(14, 90)} = 203.87$, $P < 0.001$) with the highest mean temperature in August and lowest temperature in October (Fig. 2.1), the onset of winter in Newfoundland. Pool water temperature positively correlated with air temperature and negatively with precipitation (Table 2.3; $p < 0.01$ for both).

DOC concentration ranged from 11.35 to 43.90 mg L^{-1} with a mean of 25.61 ± 0.82 mg L^{-1}. Concentration of DOC was different among pools (ANOVA, $F_{(6, 84)} = 7.79$, $P < 0.001$), with pool #2 having the highest DOC concentration and pool #5 having the lowest concentration (Table 2.1). The concentration of DOC also varied across the sampled dates (ANOVA, $F_{(12, 78)} = 7.48$, $P < 0.001$) with the highest concentration of 43.90 mg L^{-1} recorded in September, and lowest concentration of 11.35 mg L^{-1} recorded in June (Fig. 2.2a). DOC was positively correlated with TN, EC and air temperature and negatively correlated with DO, pH, and precipitation (all p values < 0.05).

The TN concentrations in the measured pools were low with a mean of 0.56 ± 0.02 mg L^{-1} ranging from 0.07 to 1.07 mg L^{-1} (Table 2.1). TN concentration was not different among the pools (ANOVA, $F_{(6, 98)} = 0.26$, $P = 0.95$, Table 2.1) but did vary across the sampling dates (ANOVA, $F_{(14, 90)} = 3.83$, $P < 0.001$, Fig. 2.2b). TN was not correlated with any of the other variable measured (Table 2.3).

DO concentration ranged from 6.63 to 11.41 mg L^{-1} with a mean of 8.97 ± 0.10 mg L^{-1}. Concentration of DO was different across the sampling dates (ANOVA, $F_{(14, 90)} = 41.06$, $P < 0.001$, Fig. 2.2c), with a concentration of 6.63 mg L^{-1} in August and 11.41 mg L^{-1} in October. DO concentration did not vary among the pools (ANOVA, $F_{(6, 98)} = 0.81$, $P = 0.56$, Table 2.1). DO was positively correlated with precipitation and negatively correlated with water and air temperature (Table 2.3; all p values less than < 0.05).

EC ranged from 39.80 to 86.80 µs cm^{-1} with a mean of 51.21 ± 0.89 µs cm^{-1}. Conductivity of pool water varied across the sampled dates, with a conductivity of 39.80 µs cm^{-1} in June

and 86.80 µs cm^{-1} in October (ANOVA, $F_{(14, 90)} = 31.09$, $P < 0.001$, Fig. 2.2d), but did not vary among pools (ANOVA, $F_{(6, 98)} = 2.08$, $P = 0.06$, Table 2.1). EC was positively correlated with DO and vegetation cover and negatively correlated with pH, water and air temperature (Table 2.2; all p values less than < 0.05).

pH ranged from 3.60 to 4.60 with a mean of 4.18 ± 0.02. pH varied across the sampling dates (ANOVA, $F_{(14, 90)} = 22.58$, $P < 0.001$, Fig. 2.2e) but did not vary among the pools (ANOVA, $F_{(6, 98)} = 1.18$, $P = 0.32$, Table 2.1). pH only positively correlated with water and air temperature but did not correlate with any other variable measured (Table 2.3; all p values less < 0.05).

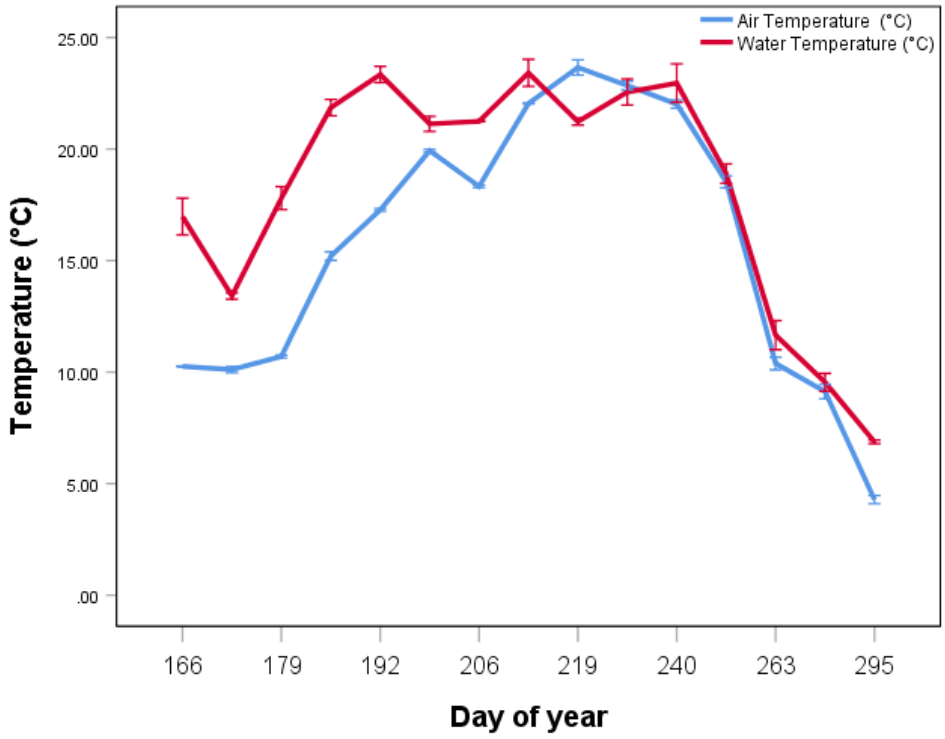

Figure 2.1: Daily mean air and water temperature during the time of sampling. Error bars represent standard errors.

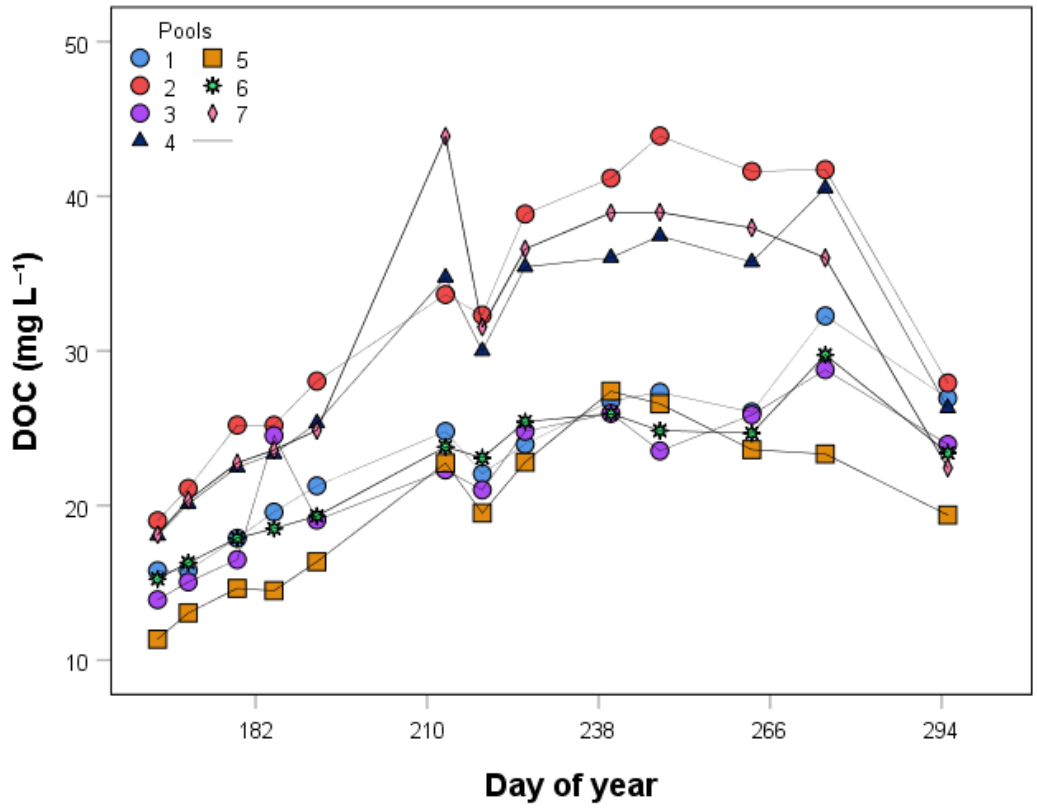

Figure 2.2a: Seasonal variation of dissolved organic carbon (DOC) measured in the seven studied pools over the growing season of 2018.

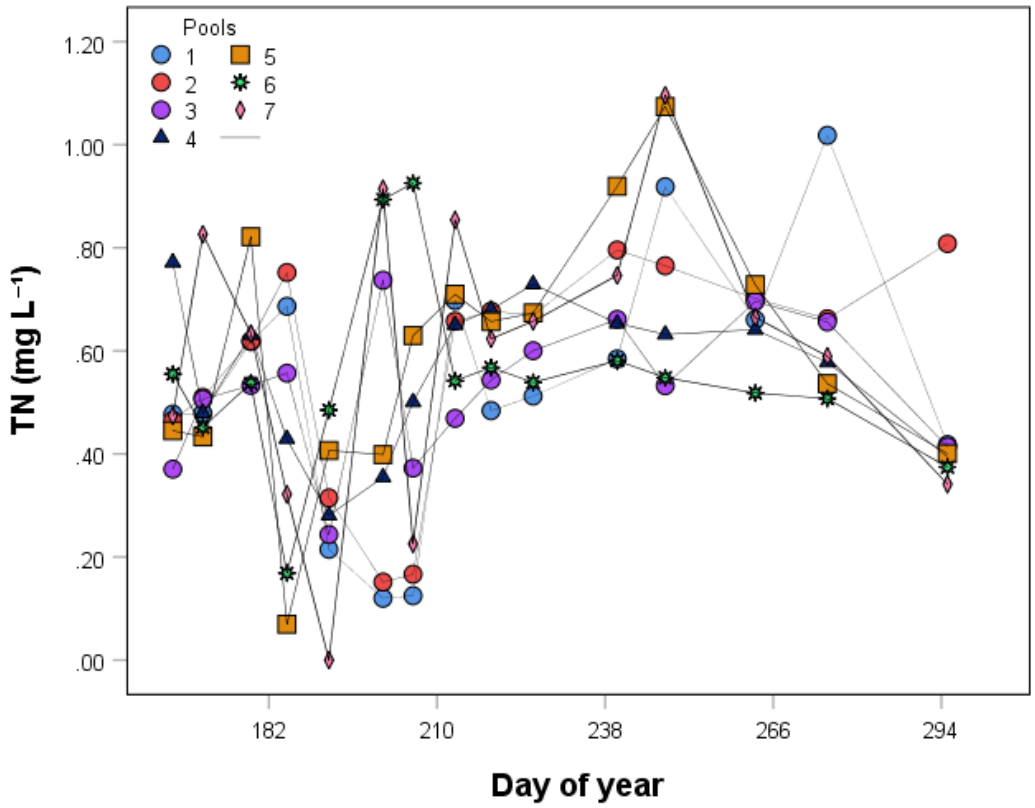

Figure 2.2b: Seasonal variation of total nitrogen (TN) measured in the seven studied pools over the growing season of 2018.

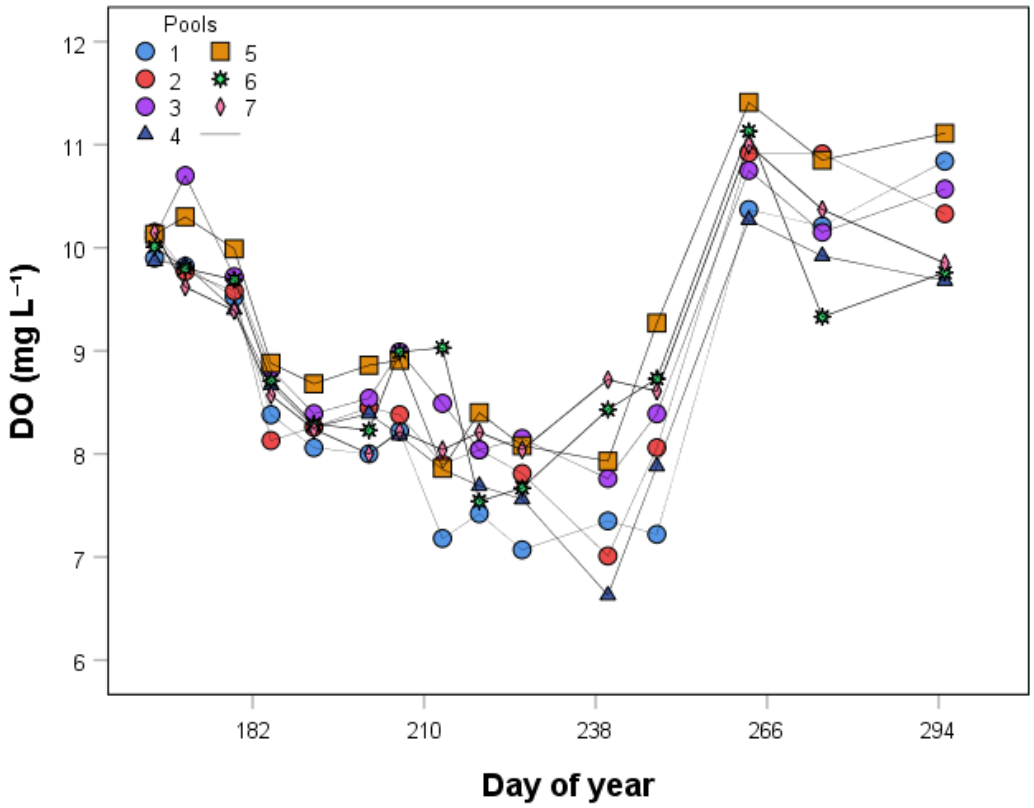

Figure 2.2c: Seasonal variation of dissolved oxygen (DO) measured in the seven studied pools over the growing season of 2018.

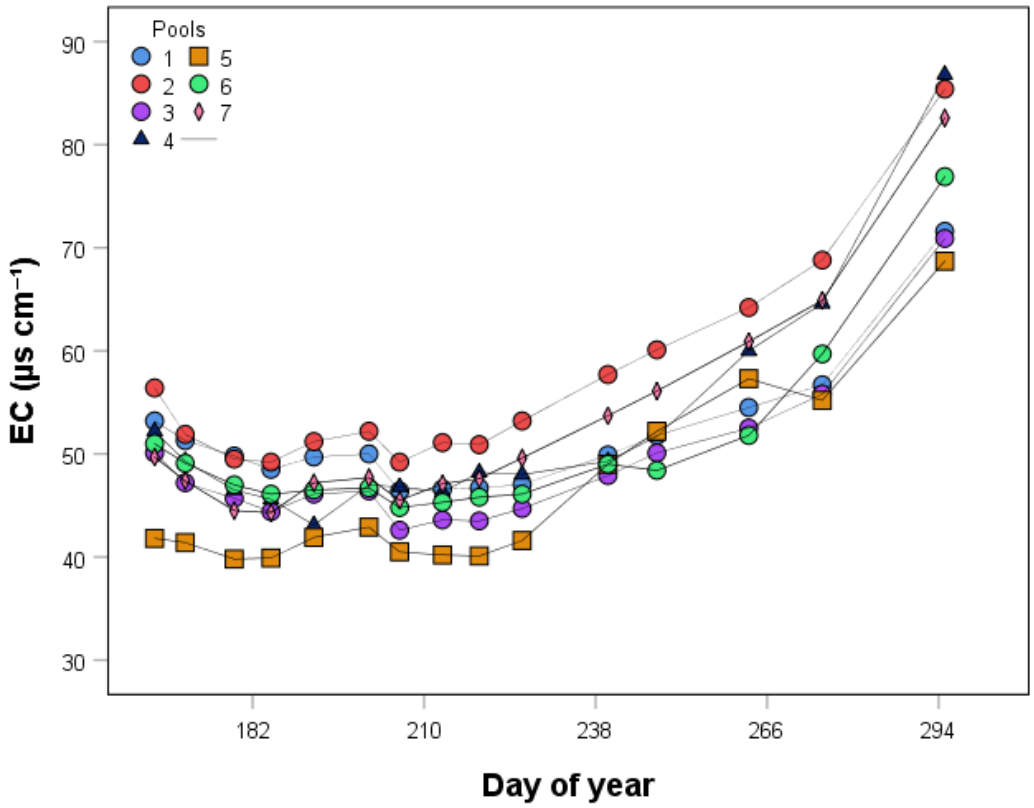

Figure 2.2d: Seasonal variation of electrical conductivity (EC) measured in the seven studied pools over the growing season of 2018.

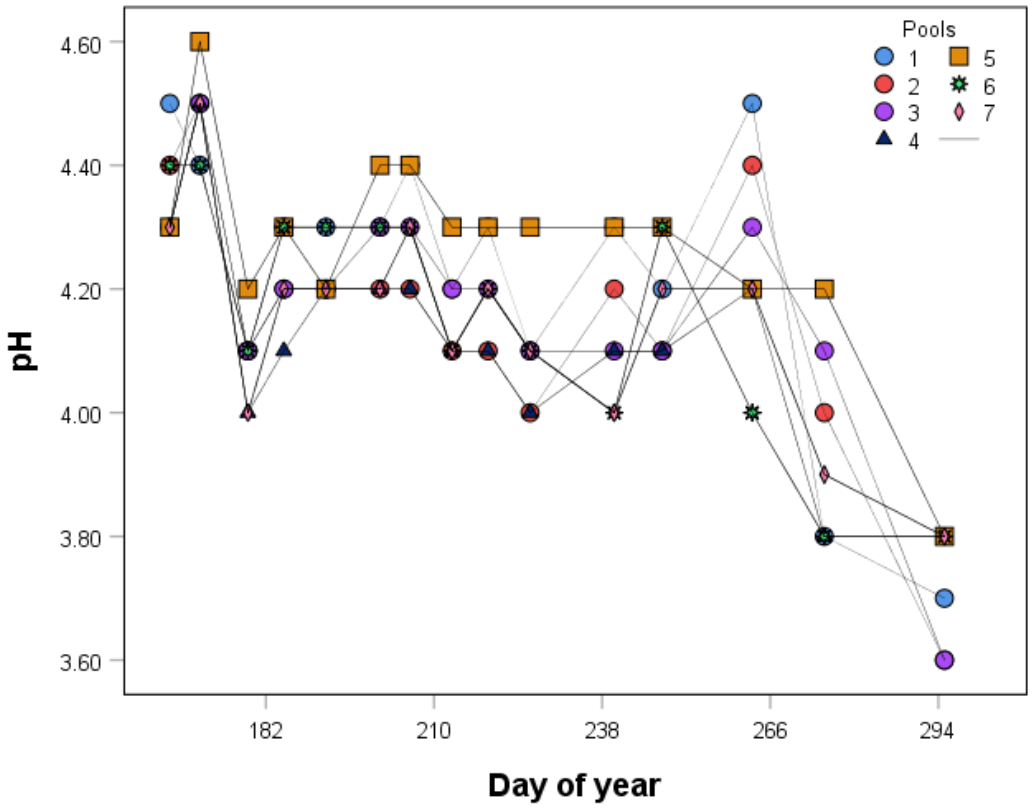

Figure 2.2e: Seasonal variation of the potential of hydrogen (pH) measured in the seven studied pools over the growing season of 2018.

Table 2.1: Physicochemical characteristics of the seven sampled pools during the study period.

	Coordinates	DOC (mg L^{-1})	TN (mg L^{-1})	EC (µs cm^{-1})	DO (mg L^{-1})	pH	Water T. (°C)	Depth (cm)	Area (m^2)	Perimeter (cm)	SI	Vegetation cover
Pool 1	48˚15' 39.03"N, 58˚ 39'45.36"W	23.11 **bcd** (15.78-32.26)	0.53 **a** (0.12-1.02)	51.58 **a** (46.40-71.60)	8.64 **a** (7.07-10.84)	4.23 **a** (3.70-4.50)	17.45 **a** (7.10-23.00)	61	148	48.8	1.13	4
Pool 2	48˚15' 38.32"N, 58˚ 39'44.82"W	32.28 **a** (19.01-43.90)	0.58 **a** (0.15-0.81)	56.73 **a** (49.20-85.40)	8.91 **a** (7.01-10.92)	4.15 **a** (3.60 - 4.50)	16.96 **a** (6.90-22.00)	40	27.7	22	1.18	5
Pool 3	48˚15' 38.33"N, 58˚ 39'44.09"W	21.94 **cd** (13.90-28.78)	0.53 **a** (0.24 - 0.74)	48.77 **a** (42.60-70.90)	9.17 **a** (7.76-10.75)	4.17 **a** (3.60 - 4.50)	17.69 **a** (7.00-23.60)	43	74.7	45.8	1.49	3
Pool 4	48˚15' 37.78"N, 58˚ 39'43.30"W	26.65 **abc** (18.05 - 40.51)	0.56 **a** (0.28 - 0.77)	52.36 **a** (43.10-86.80)	8.67 **a** (6.63-10.27)	4.11 **a** (3.80 - 4.50)	17.64 **a** (6.80-23.10)	43	93.1	50	1.46	5
Pool 5	48˚15' 37.33"N, 58˚ 39'46.78"W	19.63 **d** (11.35 - 27.39)	0.59 **a** (0.07-1.07)	46.17 **a** (39.80-68.70)	9.37 **a** (7.86-11.41)	4.27 **a** (3.80-4.60)	18.95 **a** (7.10-25.00)	42	38.4	25.6	1.17	2
Pool 6	48˚15' 36.14"N, 58˚ 39'48.78"W	22.17 **cd** (15.25-29.74)	0.55 **a** (0.17-0.93)	50.28 **a** (44.80-76.90)	9.02 **a** (7.54-11.13)	4.16 **a** (3.80 - 4.40)	19.03 **a** (6.60-25.30)	58	107	71	1.94	4

Pool 7	48˚15' 37.44"N, 58˚ 39'49.18"W	30.46 **ab** (18.11 - 43.88)	0.59 **a** (0.00 - 1.10)	52.59 **a** (44.30-82.60)	9.00 **a** (8.00-11.00)	4.15 **a** (3.80 - 4.50)	19.62 **a** (6.60-25.80)	45	165	106	2.33	3

Note: Data values are means and range of values given in parenthesis. Common lowercase letter indicate no significant differences ($p > 0.05$) between pools.
Dissolved Organic Carbon (DOC), Total Nitrogen (TN), Electrical Conductivity (EC), Dissolved Oxygen (DO), Water Temperature (Water T.), and Shape Index (SI).

2.3.3 CH_4 concentration

Surface dissolved CH_4 concentration ranged from 2.32 to 180.98 µmol L^{-1} with an overall mean of 39.06 ± 3.92 µmol L^{-1} equal to ~ 437-fold supersaturation. The surface dissolved CH_4 concentration was significantly different across the pools (ANOVA, $F_{(6, 97)} = 8.81$, $p < 0.001$) with smaller pools having the highest concentration compared to pools with larger surface area (Fig. 2.3). Mean monthly CH_4 concentration was significantly different across the sampling dates (ANOVA, $F_{(4, 99)} = 6.35$, $P < 0.001$), with a mean of 13.15 µmol L^{-1} in June, rising to a peak of 50. 95 and 64. 23 µmol L^{-1} in August and September respectively and then declining to 17.96 µmol L^{-1} in October (Fig. 2.4).

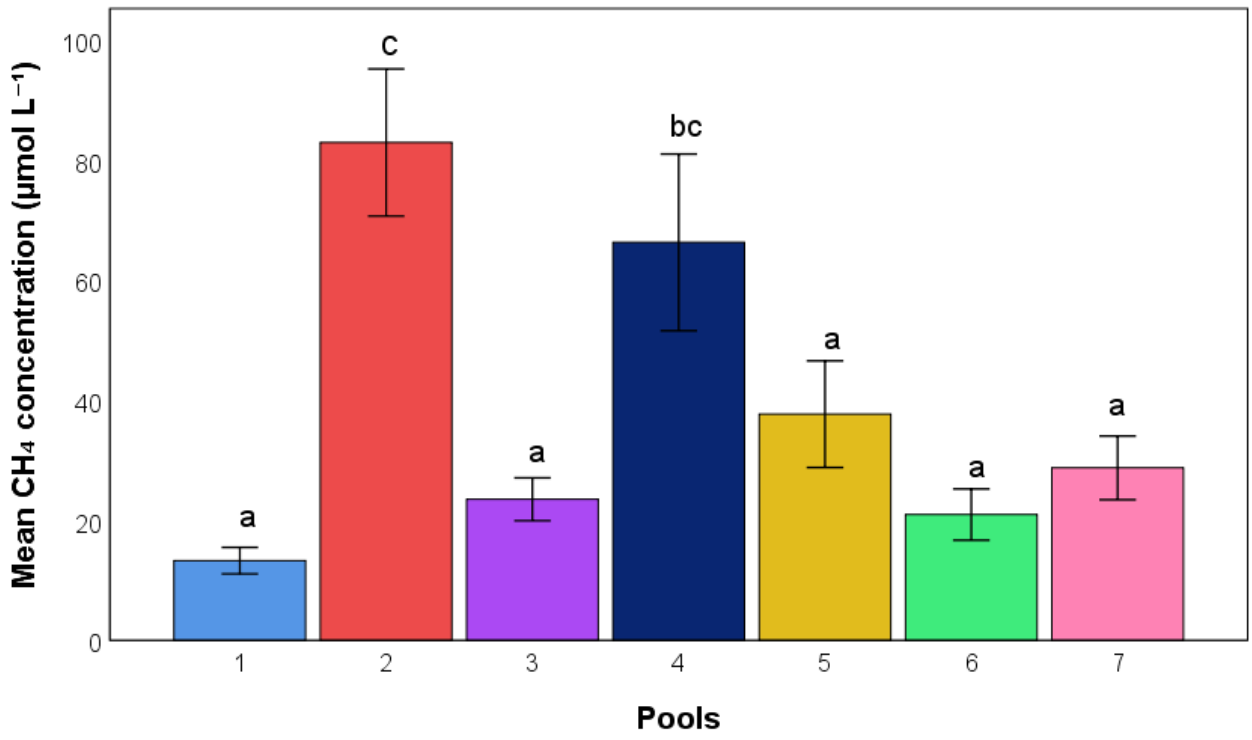

Figure 2.3: Surface water dissolved CH_4 concentration across the pools over the sampled period. Error bars represent standard errors. Different lowercase letters represents significant differences ($p > 0.05$) between pools.

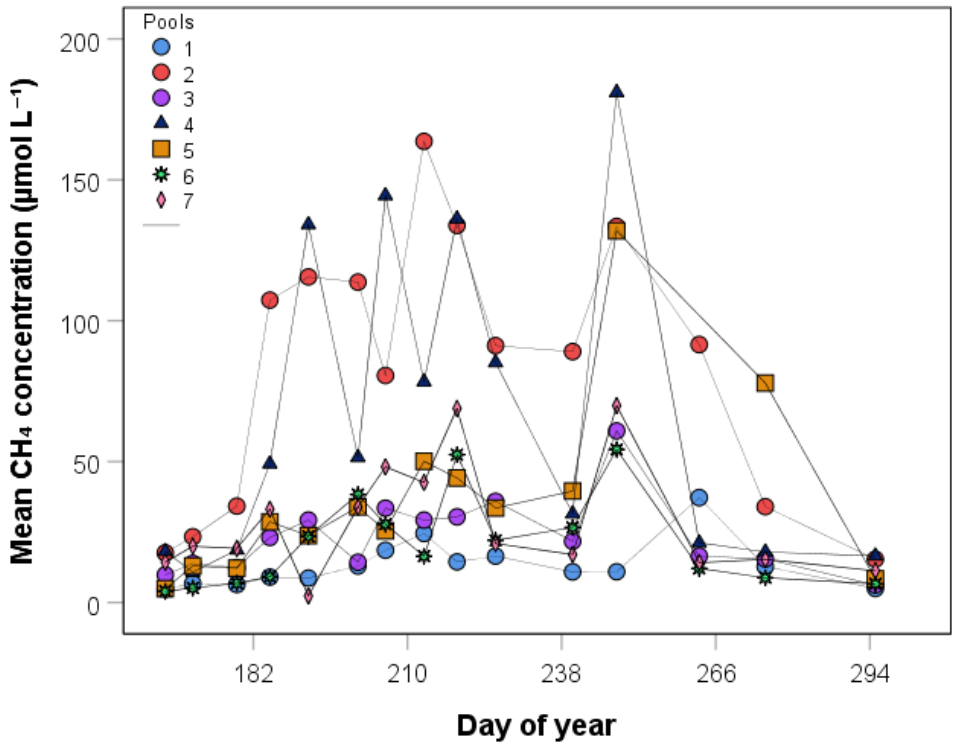

Figure 2.4: Surface water dissolved CH_4 concentration across the sampled months

2.3.4 Physiochemical variables influencing CH_4 concentration

The correlation between CH_4 concentration and physicochemical parameters is reported in Table 2.3. CH_4 concentration had a strong positive correlation with DOC and air temperature ($r = 0.51, 0.53$ respectively) both significant ($p < 0.01$) and weak positive correlation with TN, water temperature and vegetation ($r = 0.24, 0.33, 0.26$ respectively) significant ($p < 0.05$, $p < 0.01$ and $p < 0.01$ respectively). Conversely, it correlated negatively with DO, pool depth, surface area and precipitation ($r = -0.44, -0.41, -0.39, -0.31$ respectively), all significant ($p < 0.01$). However, it did not correlate with EC and pH (Table 2.3). Simple linear regression analysis showed that CH_4 concentration had a stronger relationship with air temperature (Linear regression, $F_{(1, 102)} = 40.68$, $p < 0.001$,

R^2 = 0.29, N= 104) than water temperature (Linear regression, $F_{(1, 102)}$ = 12.70, $p < 0.001$, R^2 = 0.11, N= 104). Water temperature was therefore excluded when building the stepwise linear regression and AIC since it had a weaker relationship with CH_4 concentration and a VIF of ≥ 7. The minimum adequate model based on stepwise linear regression suggests that CH_4 concentration in the pools can be modelled based on air temperature, vegetation cover, DOC and Area (adjusted R^2 = 0.64, Fig. 2.5, Table 2.2.1, 2.2.2, 2.2.3) expressed by the equation:

$$\text{Log}(CH_4) = 1.893 + 0.034 * \log(\text{air temperature}) + 0.259 * \log(\text{vegetation cover}) - 0.012 * \log(\text{DOC}) - 0.002 * \log(\text{area}) \quad \text{--- } \mathbf{Equation\ 1}$$

Table 2.2.1: Parameter Effects on Dissolved CH_4 Concentration in AIC Stepwise Linear Regression Model

Source	Sum of Squares	df	Mean square	F	Sig.	Importance
Corrected model	11.712	5	2.342	38.006	0	
AirTemp_transformed	3.72	1	3.72	60.361	0	0.608
Veg.cover	1.388	2	0.694	11.259	0	0.227
DOC_transformed	0.558	1	0.558	9.047	0.003	0.091
Area_transformed	0.456	1	0.456	7.392	0.008	0.074
Residual	6.04	98	0.062			
Corrected model	17.753	103				

Table 2.2.2: Coefficients of Dissolved CH_4 Concentration in AIC Stepwise Linear Regression Model

					95% Confidence interval		
Model Term	Coefficient	Std.Error	t	Sig.	Lower	Upper	Importance
Intercept	1.893	0.111	17.129	0	1.674	2.112	
AirTemp_transformed	0.034	0.004	7.769	0	0.025	0.042	0.608
Veg.cover_transformed	0.259	0.07	3.699	0	0.12	0.398	0.227
DOC_transformed	0.012	0.004	3.008	0.003	0.004	0.02	0.091
Area_transformed	-0.002	0.001	-2.719	0.008	-0.003	0	0.074

Table 2.2.3: Model Building Summary of Dissolved CH_4 Concentration in AIC Stepwise Linear Regression

		Model									
		1	2	3	4	5	6	7	8	9	10
Information Criterion		-283.11	-282.58	-282.16	-281.88	-281.36	-281.32	-281.31	-281.31	-281.08	-281.90
	Veg.cover_transformation	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	DOC_transformed	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	AirTemp_transformed	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	Area_transformed	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	TN_transformed		✓				✓			✓	✓
Effect	pH_transformed			✓			✓				
	DO_transformed				✓					✓	
	EC_transformed					✓					
	Precipitation_transformed							✓			✓
	Depth_transformed								✓		

Table 2.3: Pearson correlation coefficients of CH_4 concentration and physicochemical variables measured in the seven study pools

	CH_4_log	DOC	TN	EC	DO	pH	Water T.	Air T.	Veg. cover	Area	Depth	Prec.
CH_4_log	1.											
DOC (mg L^{-1})	.51**	1.										
TN (mg L^{-1})	.24*	.46**	1.									
EC (µs cm^{-1})	-.18	.34**	.05	1.								
DO (mg L^{-1})	-.44**	-.22*	-.02	.45**	1.							
pH	.05	-.38**	-.07	-.62**	-.1	1.						
Water T. (°C)	.33**	-.01	-.03	-.77**	-.78**	.34**	1.					
Air T. (°C)	.53**	.27**	.13	-.61**	-.87**	.24*	.86**	1.				
Veg. cover	.26**	.38**	-.03	.27**	-.17	-.17	-.11	-.02	1.			
Area (m^2)	-.39**	.05	-.02	.02	-.1	-.05	.07	.01	-.03	1.		
Depth (cm)	-.41**	-.16	-.05	.02	-.1	.04	.01	-.01	.21*	.55**	1.	
Prec. (mm)	-.31**	-.36**	-.11	.14	.33**	.19	-.40**	-.42**	.	.	.	1.

Note: Significant correlation indicated by: $p < 0.01$, **"**"**, $p < 0.05$, **"*"**

(N = 104 for CH_4, 90 for DOC, 91 for TN and 105 for other variables)

Dissolved organic carbon (DOC), Total nitrogen (TN), Electrical conductivity (EC), Dissolved oxygen (DO), Hydrogen ion concentration (pH), Air Temperature (Air T.), Water Temperature (Water T.) Vegetation cover (Veg. cover) and Precipitation (Prec.).

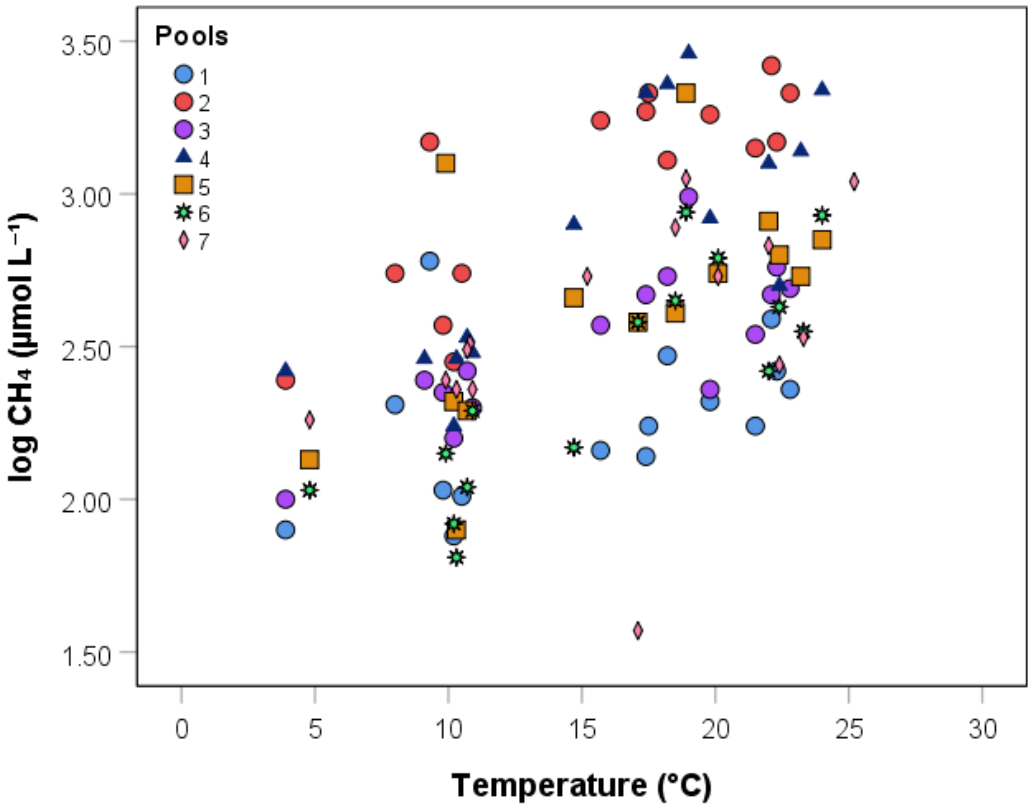

Figure 2.5a: Relationship between dissolved CH_4 concentrations and air temperature across the seven measured pools.

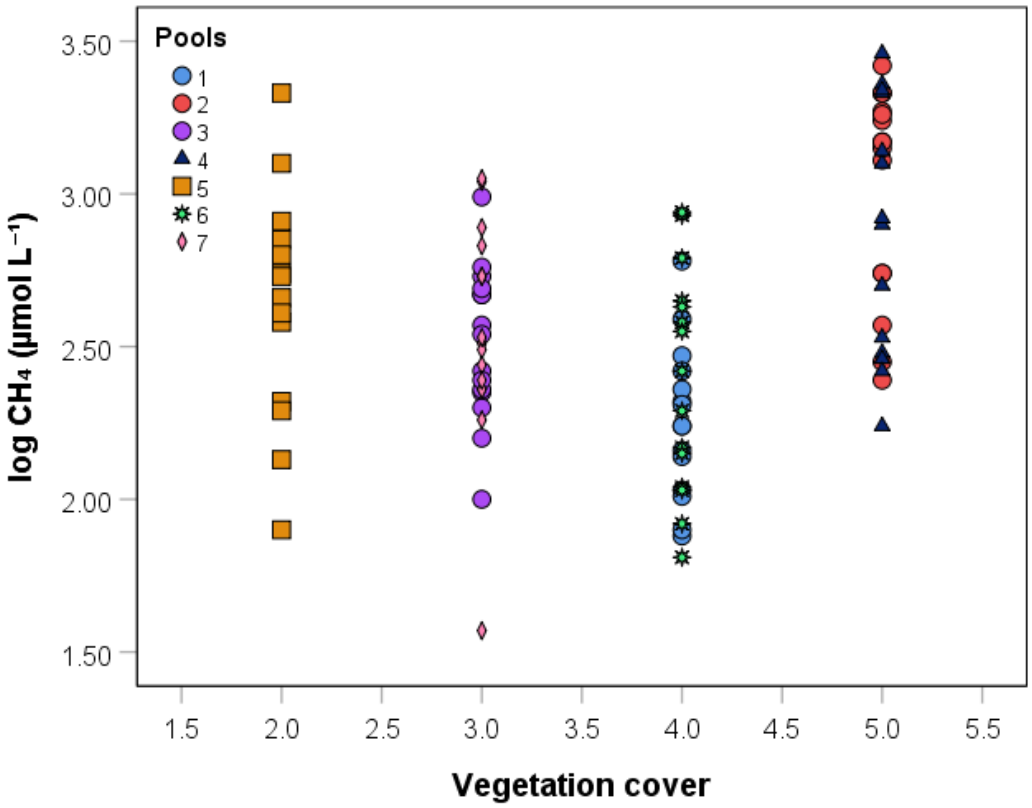

Figure 2.5b: Relationship between dissolved CH_4 concentrations and vegetation across the seven measured pools.

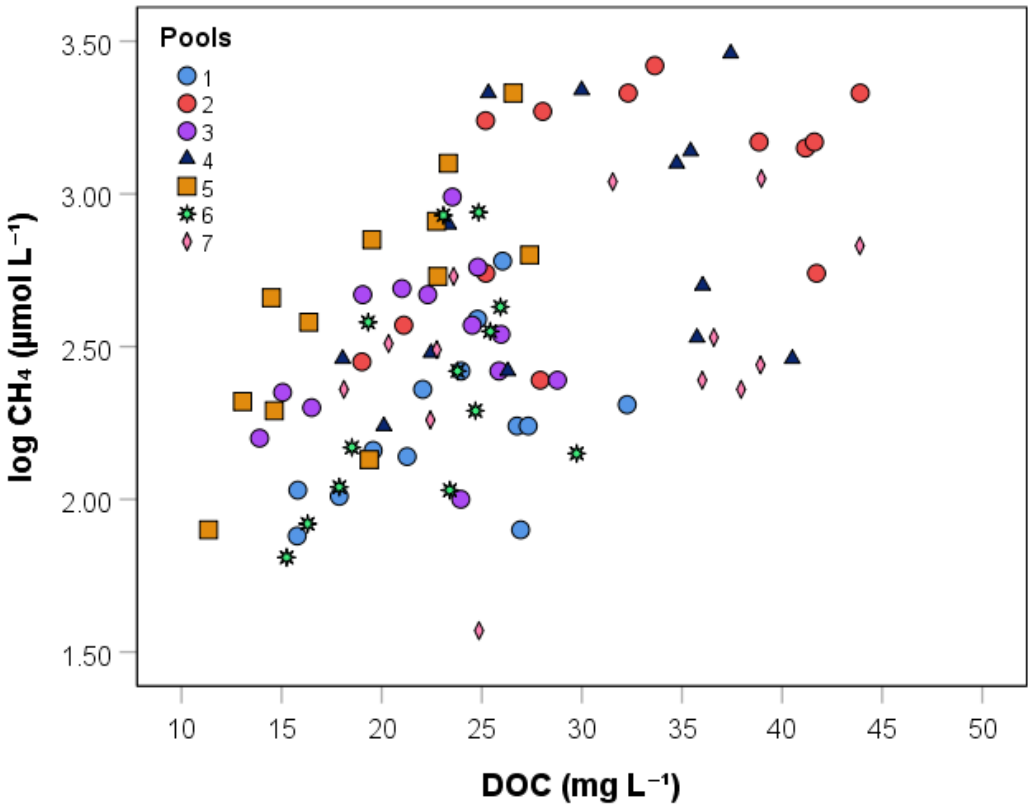

Figure 2.5c: Relationship between dissolved CH_4 concentrations and dissolved organic carbon (DOC) across the seven measured pools.

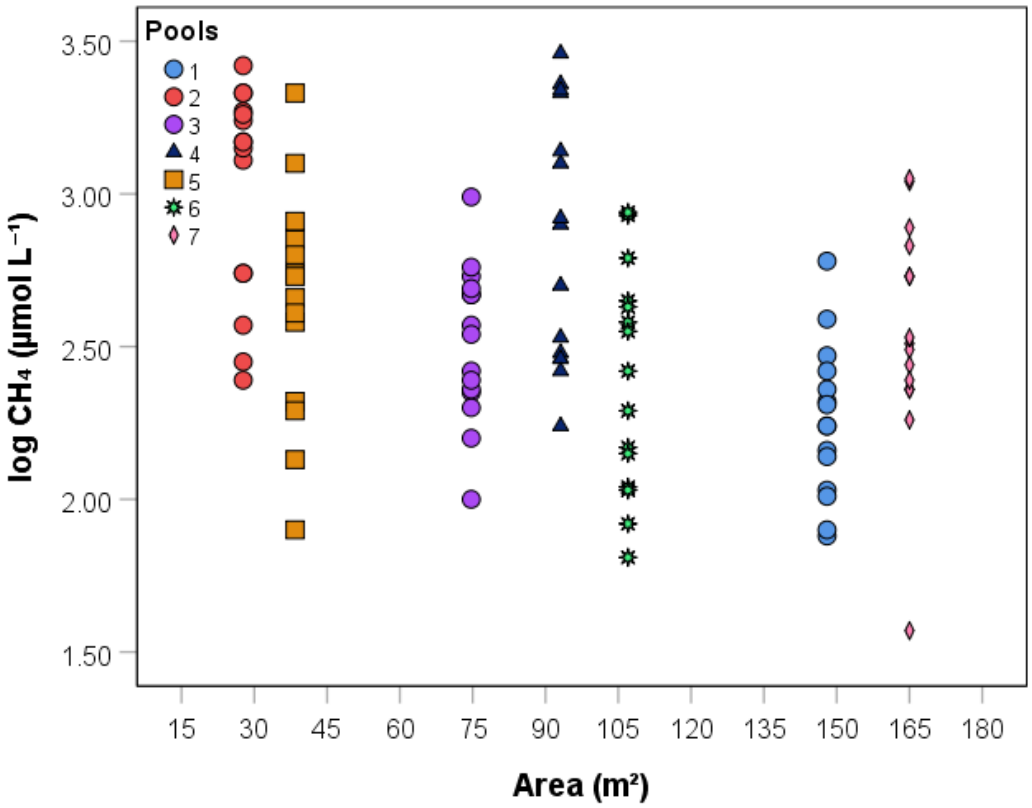

Figure 2.5d: Relationship between dissolved CH_4 concentrations and area across the seven measured pools.

2.4 Discussion

2.4.1 Dissolved CH_4 Concentration in the bog pool

This study shows that small bog pools are super-saturated with dissolved CH_4 and that CH_4 in these pools is influenced by climatic variables, C inputs and pool morphology (Table 2.3, Equation 1, and Figure 2.5). Apart from the major drivers indicated in the model, other parameters significantly correlated with dissolved CH_4 concentration suggesting that biological, physical and chemical factors are connected in the production of CH_4 in aquatic environments. sThe strongest predictor of CH_4 in these pools was temperature followed by vegetation cover, DOC, and pool surface area (Equation 1, Figure 2.5).

The range of dissolved CH_4 concentration at each sampling date and pool (2.32 - 180.96 µmol L^{-1}) were consistently super-saturated (Figure 2.3 and 2.4). The mean concentration of 39.06 µmol L^{-1} was about 482 times above atmospheric concentration. The mean CH_4 concentration found in my study were lower in concentration to that reported from a study conducted in a beaver pond at Mer Bleue peatland (Dinsmore *et al*., 2009), similar to that reported in a study conducted in a forest pond (Holgerson *et al*., 2015) but higher in concentration than those reported in literature from similar peatland pools (Hamilton *et al*., 1994; Riera *et al*., 1999; Repo *et al*., 2007; Pelletier *et al*., 2014) and other small inland water bodies (Barber *et al*., 1988, Kankaala *et al*., 2013, and Shirokova *et al.*, 2013; Table 2.4). The range of surface water dissolved CH_4 concentration in this study is among the highest concentrations reported around the world for small inland water bodies, and this

may be related to the smaller surface area of pools in this study in comparison to other studies (Table 2.4).

Table 2.4: Surface Dissolved CH_4 Concentration from Small Inland Waters

Country	Surface Area (km^2)	Inland water type (No studied)	CH_4 Conc. ($\mu mol\ L^{-1}$)	References
Canada	**0.0000277 - 0.000165**	**Peatland pool (7)**	**39.06 (2.32 - 180.96)**	**This Study**
Canada	-	Beaver pond (1)	93.52 (6.23-230.67)	Dinsmore *et al*. (2009)
Canada	0.00003 - 0.0015	Peatland pool (22)	6.2 (1.6 - 17.9)	Hamilton *et al*. (1994)
Canada	0.00002 - 0.0003	Permafrost pool (9)	1.7 (0.1 - 3.9)	Laurion *et al*. (2010)
Canada	0.00013 - 0.0026	Peatland pool (5)	2.3 (0.5 - 6.7)	Pelletier *et al*. (2014)
Finland	0.0035-0.01	Boreal lake (5)	1.5(0.7-2.6)	Kankaala *et al*. (2013)
Siberia	0.005	Peatland lake (1)	2.6	Repo *et al*. (2007)
Siberia	0.0000025-0.01	Pond (19)	0.8 (0.01-4.09)	Shirokova *et al*. (2013)
UK	0.01	Lake (1)	1.3	Casper *et al*. (2000)
USA	0.005	Pond (1)	2.2	Barber *et al*. (1988)
USA	0.0003 - 0.0008	Forest pond (6)	33.4 (21.0 - 58.9)	Holgerson *et al*. (2015)
USA	0.0054 - 0.0109	Peatland pool (2)	7.1 (3.9 - 10.2)	Riera *et al*. (1999)

2.4.2 Relationship and drivers of dissolved CH_4 concentration in the bog pool

Variation in pool CH_4 was explained mostly by temperature, consistent with previous studies which demonstrated the influence of temperature in CH_4 concentration (Pighini *et al*., 2018, Rasilo *et al*., 2015, Borrel *et al*., 2011). Temperature may be associated with the rate of methanogenesis; increased temperature leads to an increase in methanogenesis (Bastviken, 2010, Guenet *et al*., 2019). Moore and Dalva (1993); reported that a

temperature increases from 10ºC to 23ºC led to 6.6 times more CH_4 production in a laboratory peat column. The dissolved CH_4 concentration in our study followed a temporal trend coinciding with the environmental temperature variation, as it gradually increased from June when the temperature was low to a peak concentration in late July to early September when the temperatures were highest, and dropped sharply in mid-September when the temperature started decreasing (Fig. 2.4). Thus, air temperature was strongly positively correlated to water temperature (Table 2.3, Fig. 2.1). In accordance with studies in lakes, the surface temperature of lakes has been observed to be closely linked with air temperature (Livingstone and Dokulil, 2001). Surface water temperature was removed from the model due to collinearity and because it had a lower significant correlation and linear relationship with CH_4 concentration compared to air temperature. A similar relationship between air and water temperatures with dissolved CH_4 concentration was observed by Cadieux *et al*. (2017) in small arctic lakes. In that study, the air temperature was correlated with the bottom sediment temperature, the location of methanogenesis. Despite the absence of surface water temperature differences across pools in this study (Table 2.1), CH_4 concentration was significantly negatively correlated with depth and DO (Table 2.3), indicating decreased dissolved CH_4 concentration as pool depth increases, due to the gradual increase in anoxic condition in the water column (Huttunen *et al*., 2003). Pelletier *et al*. (2014) observed that the shallowest peatland pool had consistently higher sediment temperatures and also had the highest dissolved CH_4 concentration. A similar negative relationship between CH_4 concentration and depth have also been observed in lakes where dissolved CH_4 is lower at the surface of deepest lakes and higher at the surface

of shallow lakes (Pighini *et al*., 2018, Juutinen *et al*., 2009). This relationship could be explained by faster warming of bottom sediments by the sun leading to an increase in microbial peat degradation and a subsequent higher concentration of CH_4 in the water column of shallow pools and lakes (Thebrath *et al*., 1993, Pighini *et al*., 2018).

The second and third parameter predicting the dissolved surface CH_4 concentration in the model was vegetation cover and DOC concentration. Organic matter can be derived from two sources: autochthonous primary production within pools (plant and algae exudations) and allochthonous organic carbon (decomposition of organic matter from dead plants, peats, sapropel, gyttja, etc.) entering into the water from the surrounding catchment (Whiting and Chanton 1993; Segers, 1998; Mitrovic and Baldwin, 2016; Sabrekov *et al*., 2017). Although bog pools are hydrologically isolated from the surrounding catchment and receive nutrients and water through precipitation and atmospheric deposition of nutrients, temporary connection has been observed between surface water and their adjacent catchments during significant precipitation events and spring runoff (Quinton and Roulet, 1998; Quinton and Marsh, 1999). Such events have been attributed to introducing nutrients and terrestrial organic matter, which support primary production within the pool (Crump *et al*., 2003; Macrea *et al*., 2004). Vegetation was present in our pools with emergent plant growth and submerged algae mats in pool sediment. Pool perimeters were surrounded by macrophytes which had their roots growing within the littoral zones of the pools. Productivity by plants may lead to increased substrate availability in sediments, which may lead to a higher production rate of CH_4 as increased methanogenic biomass has been linked to increased substrate presence (Grant and Roulet 2002; Kettunen, 2003; Sabrekov *et al*.,

2017). Dissolved CH_4 concentration significantly correlated with vegetation cover in my study (Table 2.3). This result is in accordance with studies by Whiting and Chanton 1993 and Mitra *et al*., 2005a who observed a positive correlation between CH_4 production and plant productivity caused by root exudates that provides an additional provision of fresh organic substrates for methanogens (Whiting and Chanton 1993; Mitra *et al*., 2005a). Autochthonous primary production has been associated to driving methanogenesis in lake sediments (Boon and Mitchell, 1995; Schulz and Conrad, 1995) due to more labile algal biomass which can provide a source of organic matter for decomposition. On the other hand, DOC is positively correlated with dissolved CH_4 concentration but was also negatively correlated with precipitation (Table 2.3). However, this is in contrast with other literature, which reported catchment runoff from precipitation events leading to high DOC content within the pool led to increased CH_4 concentration. This relationship suggests that the DOC concentration in our pools were probably obtained from autochthonous derived DOC and microbial decomposition from the underlying peat layer rather than allochthonous organic carbon as is likely the case in the other studies. The corresponding higher dissolved CH_4 concentration and DOC concentration measured in pools having comparatively more vegetation cover (pool #2 and 4), confirms the source of DOC in this study (Table 2.1 and 2.3, Figure 2.5). A similar negative correlation between DOC and precipitation has been observed in small shallow ponds by Holgerson (2015) after a rainfall event, where the depth of the ponds increased, causing a dilution effect for most of its biological and chemical parameters (Holgerson, 2015). In that study, increased precipitation also correlated with decreased DOC, temperature, and increased DO, thus

altering CH_4 production and concentration. The range of DOC concentration in this current study (9.8 – 44.0 mg L^{-1}) is comparable (but higher upper range) to that of other peatland pools (8.64 – 36.91 mg L^{-1}; Arsenault *et al*., 2018, 3.10 – 20.44 mg L^{-1}; Turner *et al*., 2016, 16.7-21.4 mg L^{-1}; Pelletier *et al*., 2014, ~ 25.0 mg L^{-1}; Billett and Moore, 2008); peatland streams (2 – 40 mg L^{-1}; Billett *et al*., 2007, Clark *et al*., 2008; Dinsmore *et al*., 2011) and forest pond 4.9 – 38.4 mg L^{-1} (Holgerson, 2015). The relationship between CH_4 concentration and DOC is consistent with other studies that DOC is an indicator of substrate availability for methanogenesis (Bianchi *et al*., 1996; Garcia *et al*., 2000; Sanches *et al*., 2019).

The TN concentration, which represents nutrient status, showed a positive correlation with CH_4 concentration (Table 2.3), also suggesting that plant and algal productivity could play a role in CH_4 production in pools. TN has been previously linked to influencing primary production and greenhouse gas dynamics in lakes (Rasilo *et al*., 2015; Kortelainen *et al*., 2013; Bergstrom *et al*., 2008). Stimulation of autochthonous production by TN and subsequent decomposition of the organic source would increase CH_4 production in water (Bastviken *et al*., 2004).

Pool surface area is a weaker predictor in our model and is negatively correlated with dissolved CH_4 concentration (Table 2.3). This indicates that an increase in the surface area likely leads to a decrease in concentration, as observed in Fig. 2.4. Surface area, however, did not influence other variables but positively correlated with depth, indicating that an increase in the area may lead to an increase in pool depth (Table 2.3). This correlation between area and depth has been observed in other boreal waters (Juutinen *et al*., 2013;

Kankaala *et al*., 2013 Pighini *et al*., 2018). These studies also found a similar negative relationship between water body area and CH_4 concentration. The relative depth to area ratio may influence the level of dissolved concentration of CH_4 in water, as small and shallow pools are more compact and have more water in contact with the anoxic peat sediment. Thus, frequent wind forced mixing experienced by the shallow waters allows CH_4 produced in pool sediments to get to the pool surface before methane oxidation, permitting higher dissolved CH_4 concentration in the pool (Bastviken *et al*., 2004; Kankaala *et al*., 2013; Holgerson *et al*., 2015). A comprehensive study of 427 lakes and ponds ranging in size from 2.5 m^2 to 674 km^2 by Holgerson and Raymond (2016) reported higher CH_4 concentration from smaller ponds than larger sized lakes due to their shallower waters, high sediment and edge to water ratio and frequent wind mixing.

The drivers of CH_4 concentration established in this study are related to some of the factors described by other studies; Forster and Glaser (1986) postulated that warm temperatures and high oxygen in shallower water pools enhanced peat degradation in the bottom sediment which increased CH_4 concentration in water. Hamilton *et al*. (1994) was of the same opinion but proposed that the degradation of peat in pool bottom is introduced and maintained by nitrogen-fixing cyanobacteria, whereas Wang *et al*. (2017) stated that the oversaturation of CH_4 experienced in lakes water with high oxygen concentration was produced by phototrophs and oxygen tolerant methanogens. However, most studies have attributed surface area and depth to be a major factor in CH_4 production (Bastviken *et al*., 2008; Juutinen *et al*., 2009; Kankaala *et al*., 2013 Holgerson and Raymond, 2016) which is consistent with this study.

2.5 Conclusion

This study shows that surface waters of small peatland pools are super-saturated with the surface dissolved CH_4 concentration and are therefore "hot-spots" for CH_4 emissions. The dissolved CH_4 concentration was significantly related to several internal and external characteristics but was mainly driven by temperature, vegetation, dissolved organic carbon, and pool surface area. These results suggest that CH_4 production in small peatlands pools is not dependent upon a single parameter. The prediction of temperature as the most important factor leading to increased dissolved CH_4 concentration measured in pools in our study is not surprising, as higher temperature levels have been known to drive methanogenesis.The small pool size and depth also facilitated faster warming experienced in the pool sediment. This relationship, therefore, shows that small peatland pools are sensitive to climate conditions. Further research in inland water types especially in small bog pools, will help provide a comprehensive knowledge of local drivers of CH_4 from aquatic environments and their impact in CH_4 concentration in future climate scenarios.

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Chapter 3

3.0 Multi-year Greenhouse Gas Flux from Small Bog Pools in a Boreal Peatland in Newfoundland

3.1 Introduction

Carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) are three greenhouse gases (GHG) with high radiative forcing and global warming potential (IPCC, 2013). These three gases accounts for up to 80% of the total radiative forcing from well-mixed GHG (Ciais *et al*., 2013). Atmospheric concentrations of these gases have also exceeded pre-industrial levels (pre 1750) of 391 ppm, 1803 ppb, and 324 ppb by 40%, 150%, and 20 % respectively in 2011 (IPCC, 2013). The net emissions of these gases into the atmosphere result from the changing balance between anthropogenic emissions and changes in natural processes that has caused a switch from net removal or sink from the atmosphere to net release or source (Cias *et al*., 2013). Thus, the study of concentrations and pathways of emissions of these GHG has gained significant attention in recent times due to their recent surge in the atmosphere and contribution to climate change (IPCC, 2013).

Peatlands cover approximately 3% of the Earth's surface but store about one-third of the total soil carbon (Gorham, 1991; Strack, 2008). Generally, undisturbed peatlands are sinks for CO_2, sources of methane CH_4 and low or negligible sources of N_2O (Rinne *et al*., 2007, Maljanen *et al*., 2010, Kløve *et al*., 2017). The flux of CO_2 is controlled by the balance between absorption of CO_2 for photosynthesis by surface vegetation and release of CO_2 through autotrophic and heterotrophic respiration (Pelletier *et al*., 2014). Similarly, CH_4 flux is determined by the balance between production by methanogenic bacteria in

anaerobic sediment and consumption by methanotrophs in aerobic peat sediment (Rinnie *et al*., 2018). The balance between nitrification and denitrification processes determines N_2O flux (Maljanen *et al*., 2010). GHG emissions in peatlands are regulated by natural ecosystem processes. However, GHG emissions have been reported to vary within the same peatland due to environmental conditions and differences in microtopography: hummocks, hollows, lawns and pools (Waddington and Roulet *et al*., 1996; Dinsmore *et al.*, 2009b, Trudeau *et al.*, 2013).

Natural water pools are a common feature of many peatlands (Glaser, 1998; Turner et al., 2016). Until recently, peatland pools were not considered important in GHG studies, as most research on peatlands was biased towards the terrestrial microforms of peatland i.e. the hummocks, hollows, and lawns (Bubier *et al.*, 1995; Pelletier *et al*., 2011). A comprehensive study of GHG from whole peatland microforms at Hudson Bay Lowlands (HBL), Canada, by Hamilton *et al.* (1994) revealed that peatland pools, covering only 8-12% of the HBL area, accounted for 30% of the total CH_4 flux to the atmosphere. The net CO_2 flux from the pool was similar in scale but opposite in direction to the magnitude of fluxes from the land microforms (Hamilton *et al*., 1994). This indicates that the GHG emission potential of peatland pools is more important than previously thought. Similar results were also reported in other peatland catchments (Huttunen *et al*., 2002; Billet *et al*., 2004; Dinsmore *et al*., 2009a).

In the last decade, research on emissions of GHG at scales ranging from aquatic microforms of peatlands to the total GHG budget from peatlands has been increasing (McEnroe *et al*., 2009; Pelletier *et al*., 2014; Burger *et al*., 2016). Most previous studies

estimating flux of GHG from peatland pools have been based on short-term (one or two growing seasons) seasonal measurements, which do not capture GHG emission over long-term changing weather patterns. Furthermore, most studies are focused on measurement of single GHG gases (CO_2, CH_4 or N_2O) or pairs of C (CO_2 and CH_4) (Macrea *et al*., 2004; Pelletier *et al*., 2014, Burger *et al*., 2016). Consequently, there is still much uncertainty in the magnitude of GHG from peatland aquatic microforms (Billet *et al*., 2010). An understanding of the variations in GHG emissions over a temporal period (over three growing seasons) is essential, as the estimation of atmospheric GHG has been recommended to be the quickest method of observing efforts towards mitigating climate change (Fletcher and Schaefer, 2019).

Peatland pools may be susceptible to the effects of climate change (Strack, 2008). Water bodies can act either as sinks or sources of GHG depending on the balance between primary production and respiration which are sensitive to temperature and precipitation (Sobek *et al*., 2005; Cole *et al*., 2007). For instance, increase or decrease in precipitation changes the inputs of organic matter and nutrients from the catchment into the water body, which can influence primary production, aquatic respiration and substrate availability and ultimately C emissions (Schallenberg and Burns, 1997; Kosten *et al*., 2010). Therefore, anticipated climate change scenarios such as increased Earth temperature and rainfall are likely to impact peatland GHG emissions (Dinsmore *et al*., 2009a).

The overall aim of this study is, therefore, to emphasize the role of small peatland pools in GHG emissions and contribute to the inventory of data of GHG fluxes from bog pools. The

specific objective of this study is to quantify and compare the variations in fluxes of CO_2, CH_4, and N_2O from pools over five growing seasons in an ombrotrophic peatland.

3.2 Methodology

3.2.1 Study site, Pool Descriptions and Climate

This study was carried out at the same site, described in chapter 2 of this thesis. However, only three pools #1, 2, and 3 described in chapter 2 are analyzed in this chapter because only these pools have been sampled since the growing season of 2013, 2014, 2015 and 2016.

3.2.2 Gas Measurements

Fluxes of CO_2, CH_4 and N_2O representing diffusive fluxes were measured at three pools in the growing seasons of 2013, 2014, 2015, 2016 and 2018. Measurements were conducted biweekly in the growing seasons of 2013, 2014, 2015, 2016, while measurements were obtained weekly from May to August and biweekly from September to October in the growing season of 2018. All measurements were carried out between 9:00 – 15:00 local time. Diffusive flux measurement across the water-air interface was measured with floating static chambers (50 cm height and 26.3 cm diameter, Huttunen *et al*., 2002). To ensure that the chambers were held in position and floating when placed in the water, four Acrylonitrile Butadiene Styrene (ABS) pipes with supporting frames were permanently inserted into the pools two weeks before the start of measurements in May 2013. The static floating chamber method was chosen because a drifting chamber may likely disrupt the aqueous boundary layer contolling gas exchange (Kremer *et al*., 2003). However, static floating chambers

have been noted to possibly lead to underestimation of flux due to the wind breaking effect of the chamber walls but this effect is minimal in lentic water bodies e.g lakes, pools (Duchemin *et al*., 1999; Kremer *et al*., 2003). Flux measurements were made by lowering the chamber at least 5 to 10 cm beneath the pool surface in between the ABS pipes (Fig.3.1). An airtight syringe of 60 mL was used to draw four gas samples from the chamber headspace every 10 minutes over 30 minutes (0, 10, 20, and 30). Before sampling, the sampling tube was flushed with chamber air three times. Air samples were stored temporarily in the syringe and analyzed within a week after collection using a Bruker GHG gas chromatography equipped with flame ionization detector (FID) to analyze the CH_4, thermal conductivity detector (TCD) for CO_2 and electron capture detector (ECD) for N_2O. All fluxes were adjusted for field sampling temperature, headspace volume, and chamber area (Holland *et al*., 1999). The slope of the gas concentration change over the sampling period was estimated using linear regression, and the flux was calculated using:

$F = (dC/dt) \times V/A$ (where F is the individual gas flux (CH_4, CO_2, or N_2O), V is the volume of the chamber, A is the chamber cover area, and dC/dt is the rate of concentration change). Normalized root mean square error (NRMSE) was used to screen the samples, and fluxes were accepted if NRMSE < 0.01 (Minke *et al*., 2016, Gong *et al.*, 2018 and 2019).

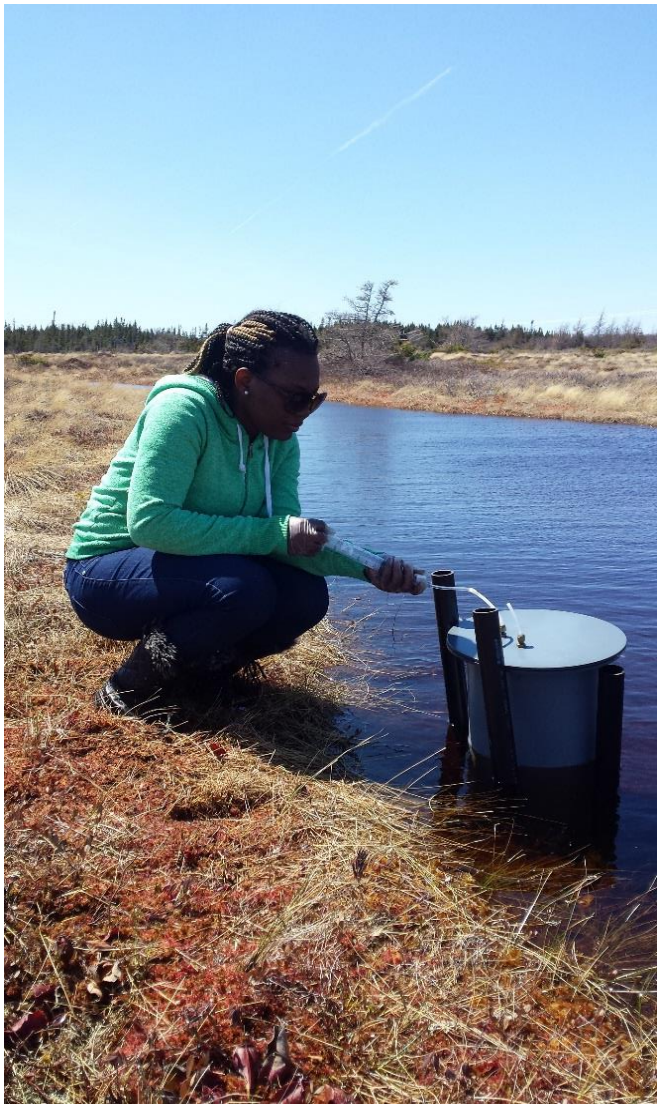

Figure 3.1: Collection of GHG samples from pool using the static floating chamber method

3.2.3 Physicochemical measurements sampling design

Physicochemical parameters were measured simultaneously with the diffusive flux weekly from May to August and biweekly from September to October, in the growing season of 2018. To evaluate the drivers of CO_2, CH_4, and N_2O fluxes, long-term mean monthly air temperature and precipitation data for the study period of 2013, 2014, 2015, 2016 and 2018

and 30-year (1981 – 2010) climate normal were obtained from the closest weather station in Stephenville, ~ 50 km away from our study area. (Environment Canada, 2018).

3.2.3.1 Pool morphology and vegetation

Pool depth, surface area, perimeter, shape index, and vegetation cover were determined at the same date and procedure described in chapter 2 of this thesis.

3.2.3.2 Water chemistry

Dissolved organic carbon (DOC), total nitrogen (TN), water temperature, electrical conductivity (EC), dissolved oxygen (DO), and barometric pressure were measured in-situ weekly from May to August and biweekly from September to October using the same procedure described in chapter 2 of this thesis.

3.2.4 Statistical Analysis

Data were tested for normality using the Shapiro-Wilk tests and transformed when necessary to meet the conditions of homogeneity of variance. Differences in fluxes of CO_2, CH_4, and N_2O among the five growing seasons were tested using one-way ANOVA. Significant ANOVA tests were followed with Tukey post-hoc tests. Simple linear regression and Pearson's correlation analysis were used to examine relationships and correlations among the physiochemical variables and GHG flux. Stepwise linear regression and the Akaike Information Criterion (AIC) (Burnham and Anderson, 2002; Akaike, 2011) were finally applied to select the best model explaining gas fluxes. Stepwise multiple linear regression was built using AIC best subset. Variables included in the model were

determined for collinearity by calculating the variance inflation factor (VIF) and excluding any variable with a VIF of ≥ 18 (Kock and Lynn, 2012). Statistical analysis was done using IBM SPSS 25.0 statistical software.

3.3 Results

3.3.1 Climatic conditions during the study period

The mean monthly air temperature generally varied from 11.4 °C to 13.6 °C in the study period (Table 3.1). Air temperature during the study period was within range of the long-term climate average of 12.2 °C except for the growing season of 2014 with a higher mean temperature of 13.6 °C and a lower mean temperature of 11.4 °C in the growing season of 2018 (Table 3.1). Peak air temperature was measured during July and August, which are the primary summer months in Newfoundland while lower air temperatures were recorded in May and October, which represented the end and beginning of winter (Fig. 3.2a). Cumulative precipitation for the growing season months was 815.8 mm in 2013, 469.6 mm in 2014, 658.0 mm in 2015, 734.8 mm in 2016 and 740 mm in 2018 (Table 3.1), compared to the long-term average of 704.8 mm. The lower than normal 30-year average precipitation of the growing seasons of 2014, 2015, and 2016 indicate drier conditions compared to growing seasons of 2013 and 2018 (Fig. 3.2b).

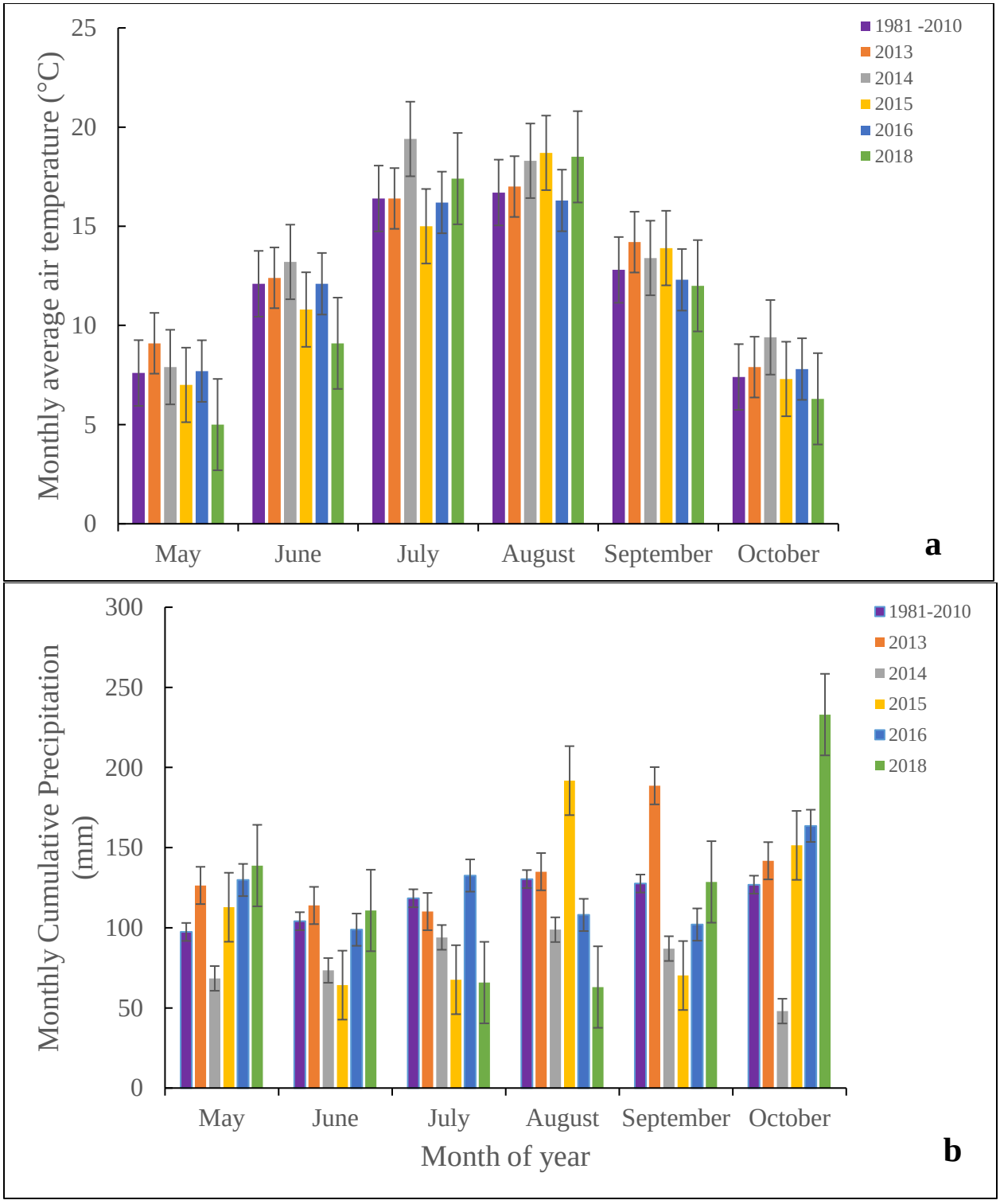

Figure 3.2: Climate data for the study area in 2013, 2014, 2015, 2016, and 2018 compared to 30-year climate normal (1981-2010). Error bars represent standard errors.

Table 3.1: Average cumulative monthly precipitation and mean monthly air temperature during the five years' study period and 30-years climate normal (1981 -2010).

	Precipitation (mm)						Temperature (°C)					
Period	Normal	2013	2014	2015	2016	2018	Normal	2013	2014	2015	2016	2018
May	97.4	126.4	68.4	112.8	129.8	138.8	7.6	9.1	7.9	7.0	7.7	5.0
June	104.1	113.9	73.4	64.2	98.8	110.8	12.1	12.4	13.2	10.8	12.1	9.1
July	118.4	110.1	94.0	67.6	132.6	65.8	16.4	16.4	19.4	15.0	16.2	17.4
August	130.4	135.0	98.8	191.8	108.0	63.0	16.7	17.0	18.3	18.7	16.3	18.5
September	127.6	188.6	87.0	70.2	102.0	128.6	12.8	14.2	13.4	13.9	12.3	12.0
October	126.9	141.8	48.0	151.4	163.6	233.0	7.4	7.9	9.4	7.3	7.8	6.3
Sum	**704.8**	**815.8**	**469.6**	**658.0**	**734.8**	**740.0**	73.0	77.0	81.6	72.7	72.4	68.3
Mean	117.5	136.0	78.3	109.7	122.5	123.3	**12.2**	**12.8**	**13.6**	**12.1**	**12.1**	**11.4**
SEM	5.6	11.6	7.7	21.5	10.1	25.4	1.7	1.5	1.9	1.9	1.6	2.3

Note: SEM indicates standard error of mean

3.3.2 Pool Characteristics

Measured pools were small and shallow, with an average depth of 48 cm and a surface area of 83.47 m^2 (Table 3.2). Vegetation was present in each pool and consisted of emergent plants: *Nuphar variegata* (Yellow Pond-lily) and *Eriocaulon aquaticum* (White Buttons) which emerged during the summer months, and submerged vegetation consisting of *Utricularia* spp. and algae. Sedges, shrubs, Sphagnum spp., and grasses also surrounded pool perimeters all year round. Surface area of pool correlated positively with pool depth ($r = 0.86$, $p < 0.01$, Table 3.3) and negatively with vegetation cover ($r^2 = -0.39$, $p < 0.01$, Table 3.3).

3.3.3 Seasonal variation and correlation among physicochemical variables

Daily air temperature and water temperature at sampling time ranged from 2.0 °C to 21.8 °C and 5.7 °C to 23.7 °C, respectively. Air and water temperature increased steadily through the growing season, starting with a low temperature of 2.0°C in May rising to a peak temperature in July and decreasing in mid-September (Fig. 3.3a and b). Water temperature significantly differed across the growing season of 2018 (ANOVA, $F_{(5, 54)} = 90.24$, $p < 0.001$) and correlating strongly with air temperature ($r = 0.94$; $p < 0.01$) (Table 3.3).

Pools had a DOC mean concentration of 23.78 ± 1.23 mg L^{-1} and differed across the growing season (ANOVA, $F_{(5, 48)} = 15.76$, $p < 0.001$), ranging from 10.3 to 43.9 mg/L (Table 3.2, Fig. 3.3c). DOC positively correlated with TN ($r = 0.68$) at a significance of ($p < 0.01$), moderately positive with vegetation cover ($r = 0.44$; $p < 0.01$) and negatively with DO and pH ($r = -0.42$, -0.46 respectively; both at $p < 0.01$). DOC however had a significant positive weak correlation with EC ($r = 0.33$, $p < 0.05$), water temperature ($r = 0.29$, $p < 0.05$) and air temperature ($r = 0.37$, $p < 0.01$) and negative weak correlation with area ($r = -0.35$; $p < 0.01$) (Table 3.3).

TN concentration differed across the growing season (ANOVA, $F_{(5, 53)} = 10.35$, $p < 0.001$) ranging from 0.12 to 1.02 mg L^{-1} with a mean of 0.55 ± 0.03 mg L^{-1} (Table 3.2, Fig. 3.3d). Concentration of TN correlated negatively with pH ($r = -0.32$, $p < 0.05$).

Pools DO ranged from 7.01 to 12.39 mg L^{-1} with a mean 8.91 ± 0.18 mg L^{-1} (Table 3.2, Fig. 3.3e), differing significantly across the growing season (ANOVA, $F_{(5, 54)} = 39.09$,

$p < 0.001$). A strong negative correlation between DO with both air and water temperature ($r = -0.90$ and -0.90 respectively; $p < 0.01$) were observed from Pearson's correlation (Table 3.3).

Mean pools EC was 52.36 ± 1.25 µs cm^{-1} with a range of 42.60 to 85.40 µs cm^{-1} (Table 3.2, Fig. 3.3f), varying significantly across the growing season (ANOVA, $F_{(5, 54)} = 14.42$, $p < 0.001$). It correlated strongly negatively with water temperature ($r = -0.61$; $p < 0.01$) and moderately negative with air temperature and pH ($r^2 = -0.57, -0.43$ respectively; $p < 0.01$). Positive correlation was observed between DO and vegetation cover ($r = 0.40, 0.45$; $p < 0.01$) (Table 3.3).

Pools were acidic with a mean pH of 4.18 ± 0.03, ranging from 3.60 to 5.00 (Table 3.2, Fig. 3.3g). It varied significantly across the growing season (ANOVA, $F_{(5, 54)} = 14.30$, $p < 0.001$), but did not correlate significantly with any measured variable (Table 3.3).

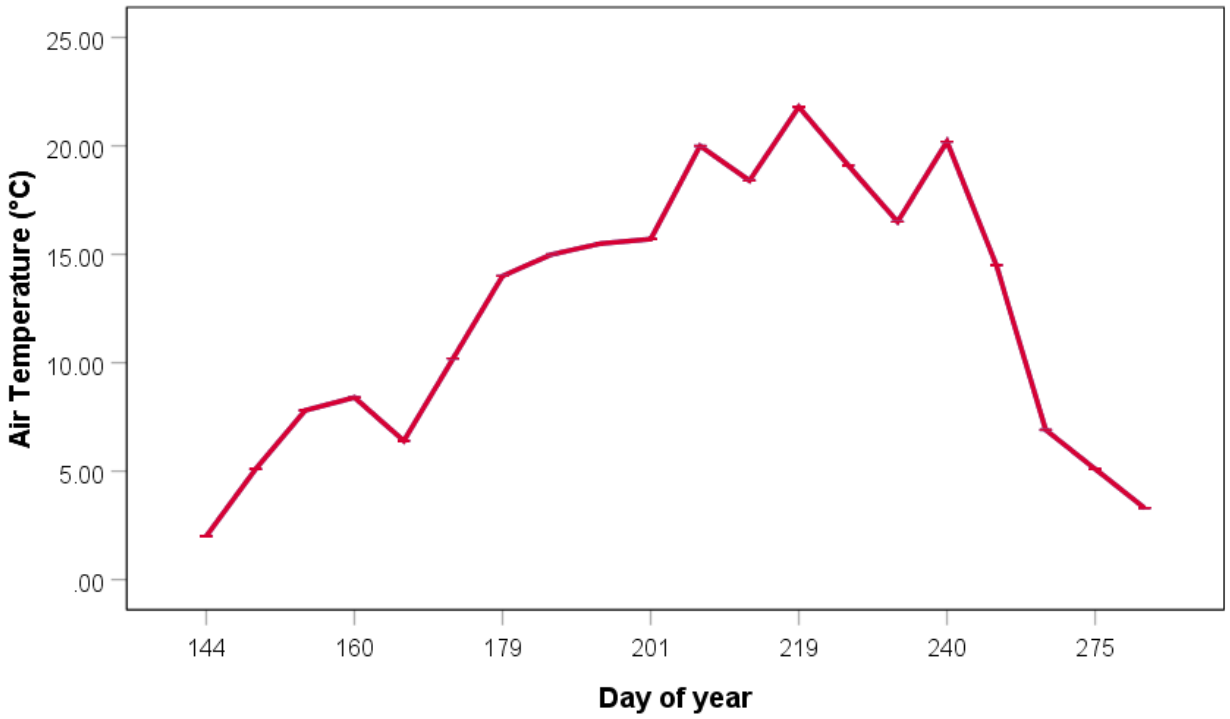

Figure 3.3a: Seasonal variation of air temperature across the sampled pools in the growing season of 2018. Error bars represent standard errors (SE).

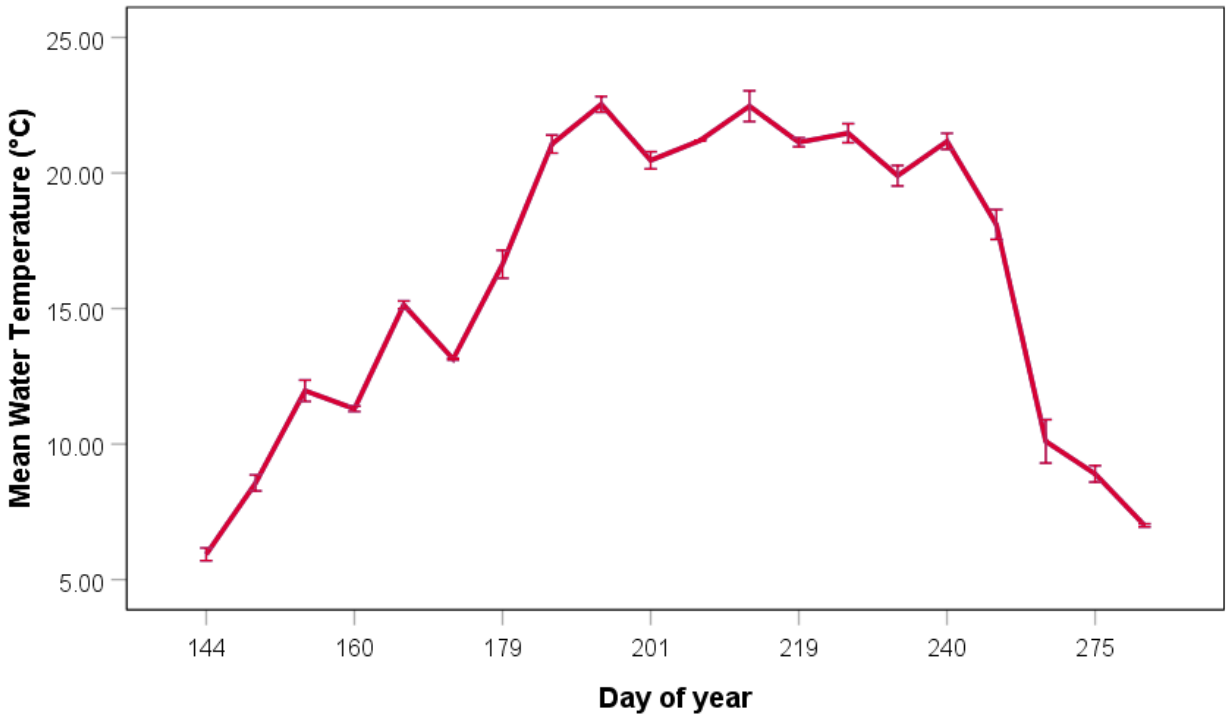

Figure 3.3b: Seasonal variation of water temperature across the sampled pools in the growing season of 2018. Error bars represent standard errors (SE).

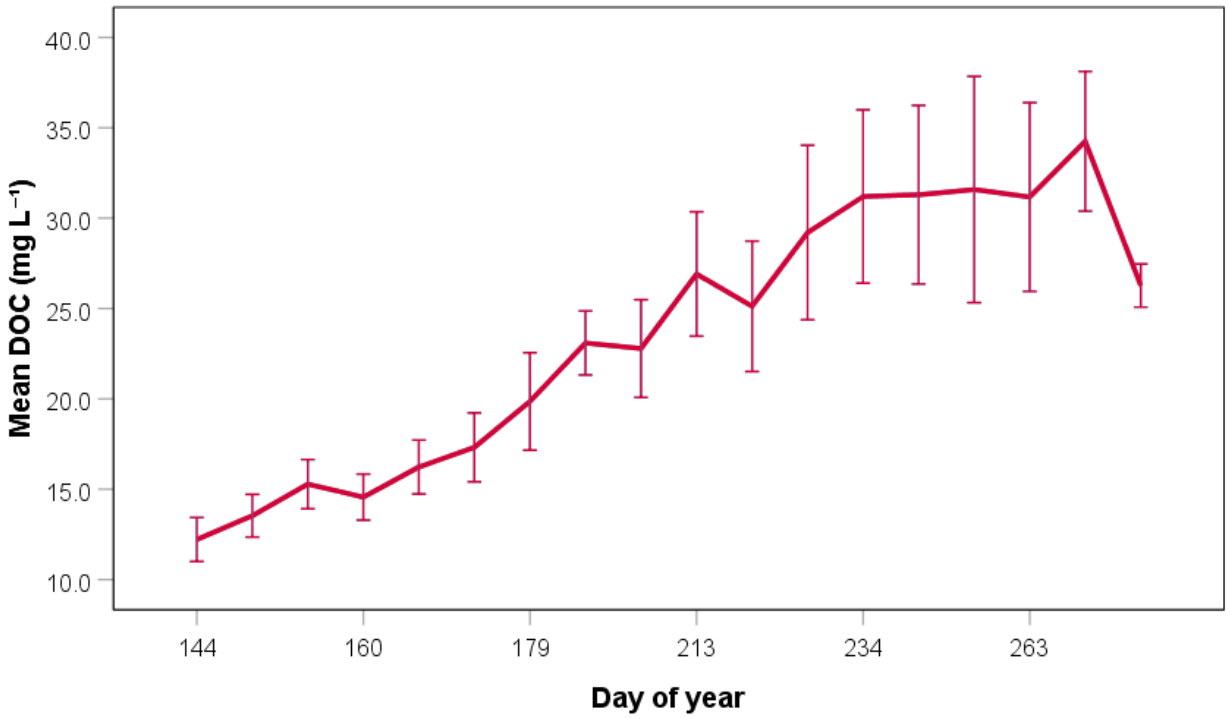

Figure 3.3c: Seasonal variation of dissolved organic carbon (DOC) across the sampled pools in the growing season of 2018. Error bars represent standard errors (SE).

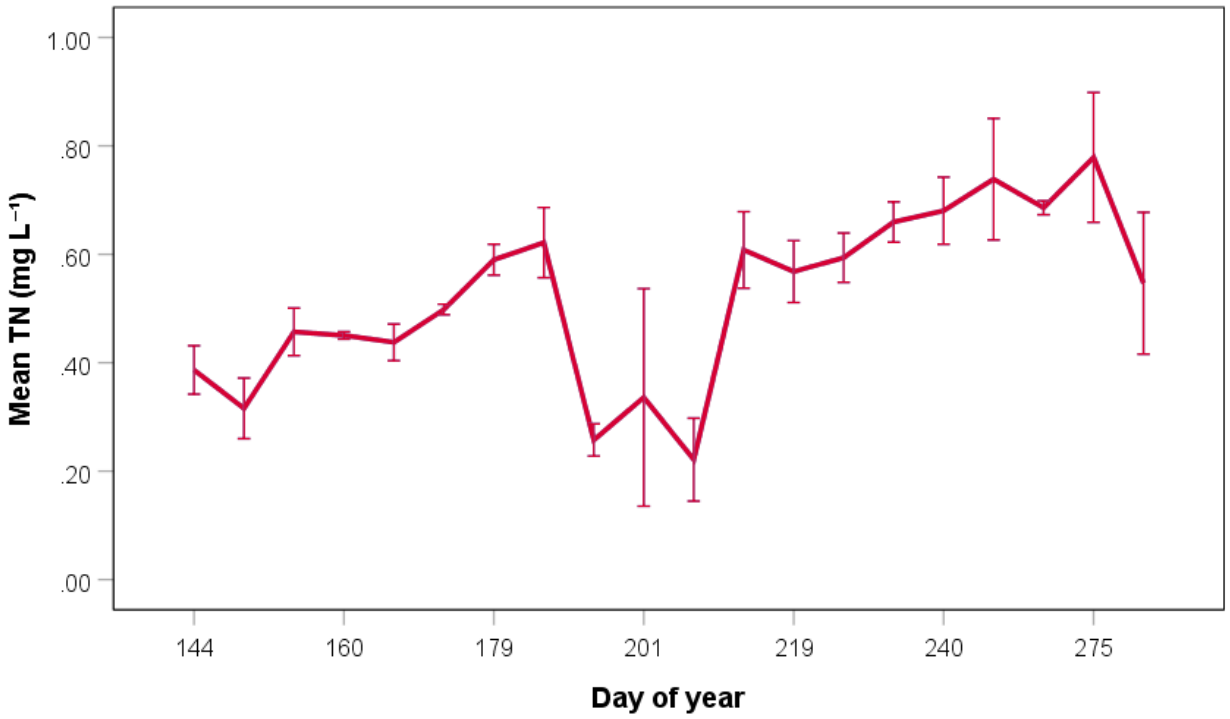

Figure 3.3d: Seasonal variation of total nitrogen (TN) across the sampled pools in the growing season of 2018. Error bars represent standard errors (SE).

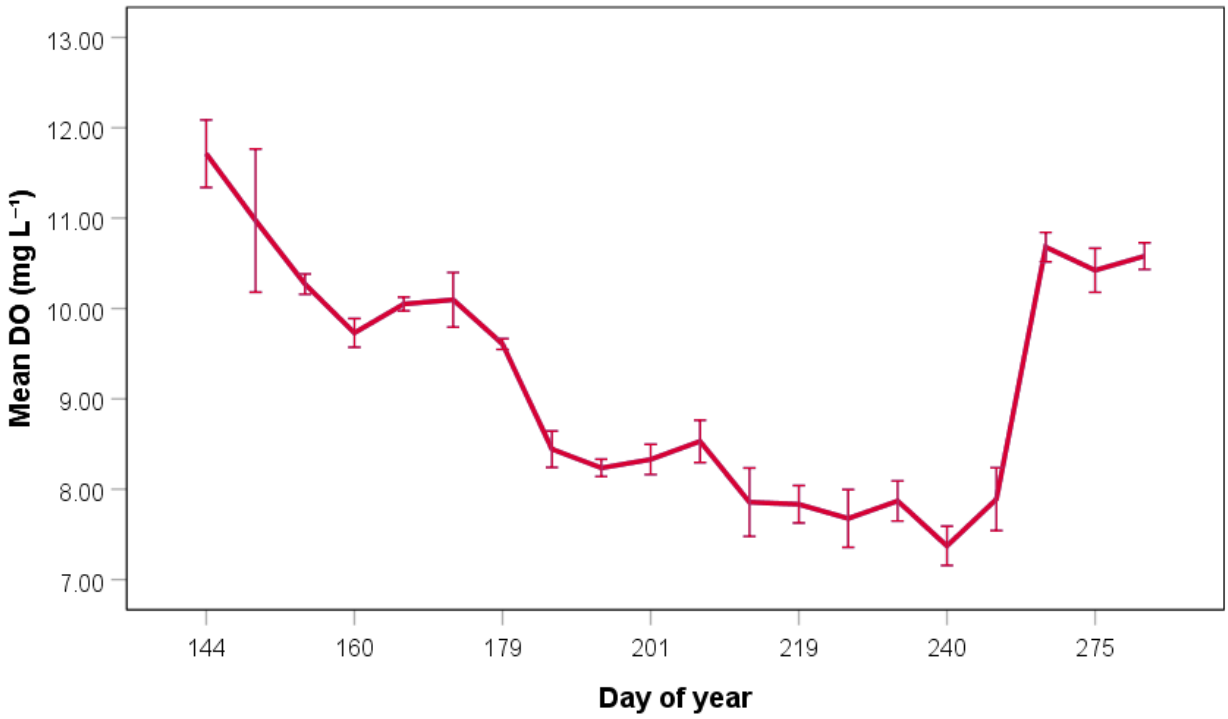

Figure 3.3e: Seasonal variation of dissolved oxygen (DO) across the sampled pools in the growing season of 2018. Error bars represent standard errors (SE).

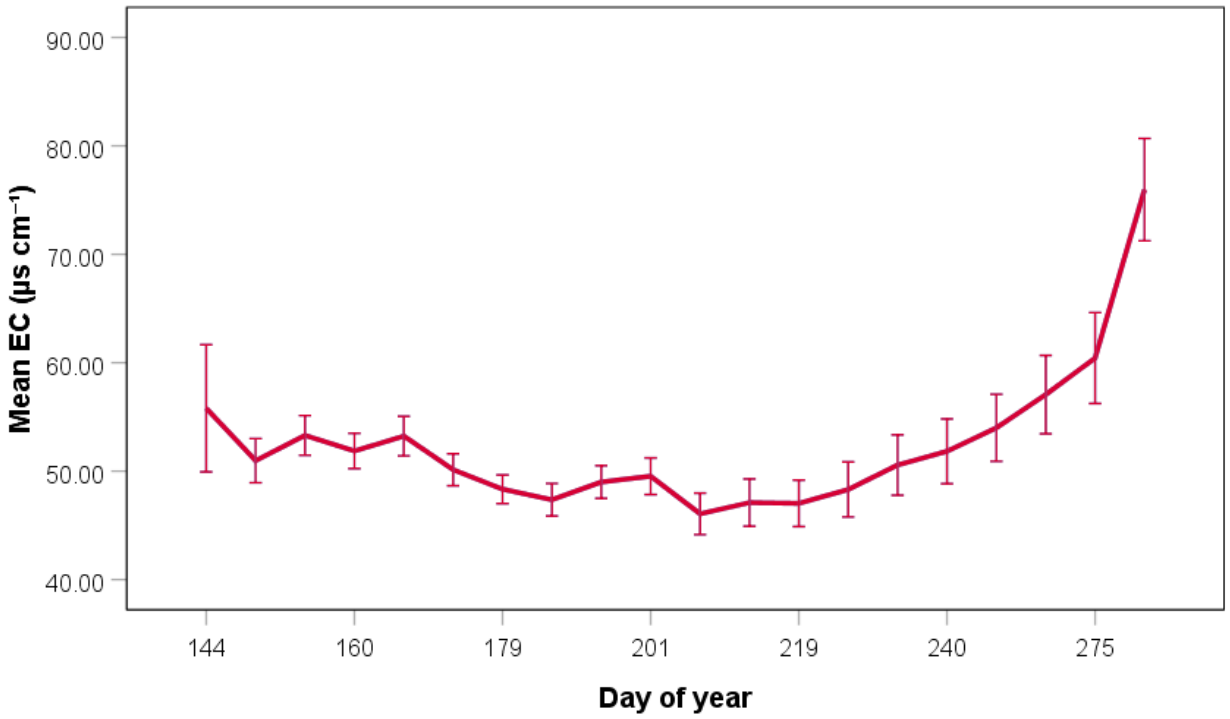

Figure 3.3f: Seasonal variation of electrical conductivity (EC) across the sampled pools in the growing season of 2018. Error bars represent standard errors (SE).

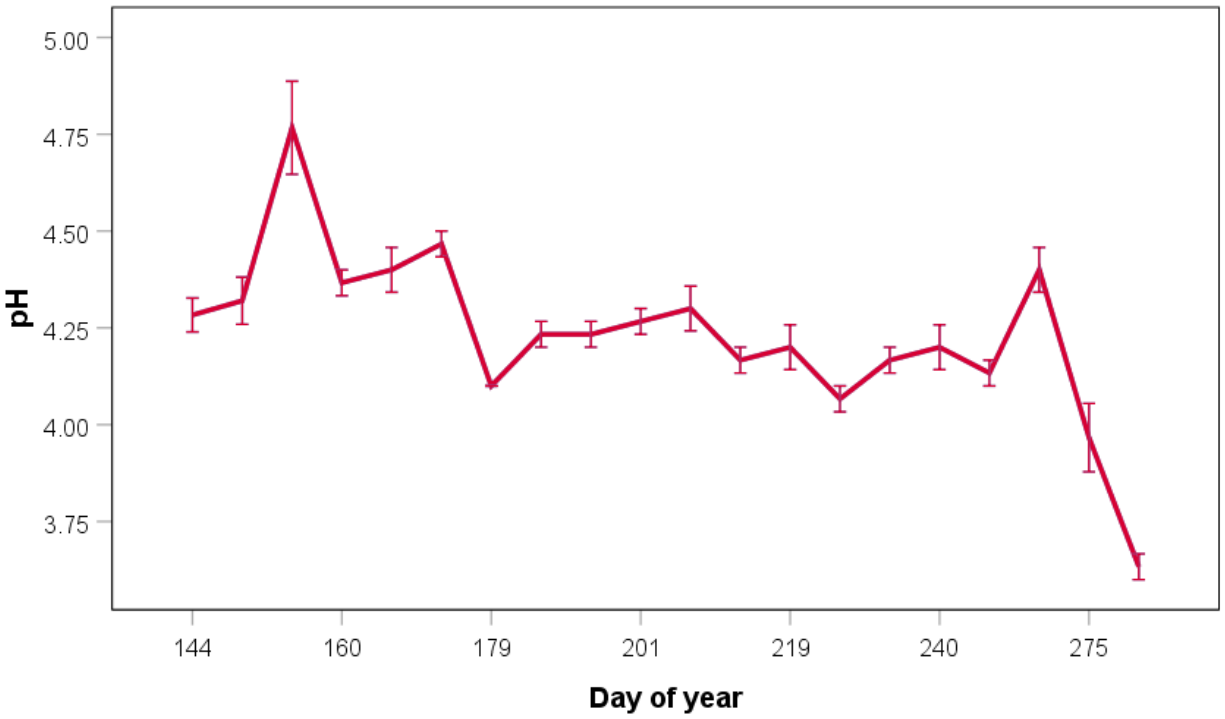

Figure 3.3g: Seasonal variation of the potential of hydrogen (pH) across the sampled pools in the growing season of 2018. Error bars represent standard errors (SE).

Table 3.2: Summary of physicochemical properties of pools measured in the growing season of 2018 (N = 54 for DOC, 59 for TN and 60 for other variables)

Pool property	Mean ± Standard Error (Minimum - Maximum)
DOC (mg L^{-1})	23.78 ± 1.23 (10.23 - 43.9)
TN (mg L^{-1})	0.55 ± 0.03 (0.12 - 1.02)
DO (mg L^{-1})	8.91 ± 0.18 (7.01 - 12.39)
EC (µs cm^{-1})	52.36 ± 1.25 (42.60 - 85.40)
pH	4.18 ± 0.03 (3.60 - 5.00)
Water T. (°C)	17.37 ± 0.78 (5.70 - 23.60)
Veg. Cover	4.00 ± 0.12 (3 -5)
Area (m^2)	83.47 ± 7.46 (27.7 - 148.0)
Depth (cm)	48.00 ± 1.39 (40 - 61)

Note: Dissolved Organic Carbon (DOC), Total Nitrogen (TN), Dissolved Oxygen (DO), Electrical Conductivity (EC), potential of hydrogen (pH), Water Temperature (Water T.), and Vegetation cover (Veg. cover)

Table 3.3: Pearson's correlation (r) coefficients between fluxes of (CO_2, CH_4, and N_2O) and physicochemical variables measured in the three study pools in the growing season of 2018 (N= 54 for CO2, 49 for CH4, 54 for DOC, 59 for TN and 60 for other variables)

	CO_2	CH_4	N_2O	DOC	TN	EC	DO	pH	Water T.	Air T.	Prec.	Area	Depth	Veg. C.
CO_2 (mmol m^{-2} d^{-1})	1.													
CH_4 (mmol m^{-2} d^{-1})	-.11	1.												
N_2O (µmol m^{-2} d^{-1})	.12	-.07	1.											
DOC (mg L^{-1})	.05	.41**	.04	1.										
TN (mg L^{-1})	.04	.28	-.01	.68**	1.									
EC (µs cm^{-1})	-.09	.13	.1	.33*	.23	1.								
DO (mg L^{-1})	-.17	-.19	.15	-.42**	-.15	.40**	1.							
pH	-.05	.01	.01	-.46**	-.32*	-.43**	.12	1.						
Water T. (°C)	.2	.08	-.11	.29*	-.01	-.61**	-.90**	.	1.					
Air T. (°C)	.16	.06	-.11	.37**	.06	-.57**	-.90**	-.05	.94**	1.				
Precipitation	.03	.01	.22	-.23	-.04	.12	.2	.05	-.24	-.18	1.			
Area (m^2)	-.01	-.04	.	-.35**	-.09	-.22	-.15	.16	.03	.	.	1.		
Depth (cm)	-.13	.14	.06	-.14	-.05	.01	-.19	.15	.01	.	.	.86**	1.	
Vegetation cover	-.22	.34*	.11	.44**	.1	.45**	-.06	-.05	-.05	.	.	-.39**	.13	1.

Note: Significant correlation indicated by: $p < 0.01$, **"**"**, $p < 0.05$, **"*"**

Dissolved Organic Carbon (DOC), Total Nitrogen (TN), Electrical Conductivity (EC), Dissolved Oxygen (DO), Water Temperature (Water T.), Air Temperature (Air T.) and Precipitation (Prec.).

3.3.4 CO_2, CH_4 and N_2O Dynamics

Fluxes of CO_2, CH_4, and N_2O across the growing seasons of 2013, 2014, 2015, 2016, and 2018 are presented in Fig. 3.4, 3.5, 3.6 and Table 3.6. Negative fluxes indicate uptake or absorption (sink) from the atmosphere into the pool while positive fluxes indicate release or gas emission (source) into the atmosphere. Generally, GHG flux varied widely between uptake and release, and no systematic pattern of flux could be deduced across the growing seasons. However, only CO_2 flux was observed to vary temporarily over the study period while flux of CH_4 and N_2O were similar over the study period.

3.3.4.1 CO_2 flux

Daily flux of CO_2 ranged widely from -39.80 to 71.79 mmol m^{-2} d^{-1} with a mean of 23.91 ± 13.90 mmol m^{-2} d^{-1} in 2013, acting as a mean source of CO_2 into the atmosphere. In 2014, pools acted as a sink of CO_2 with a mean of -7.41 ± 6.46 mmol m^{-2} d^{-1}, ranging from -41.89 to 12.76 mmol m^{-2} d^{-1}. Pools also acted as mean sinks in 2015 with a mean of 8.98 ± 7.07 mmol m^{-2} d^{-1} and in 2016 with a mean of -9.04 ± 8.05 mmol m^{-2} d^{-1}, ranging from -50.65 to 51.61 mmol m^{-2} d^{-1}, and -65.70 to 43.61 mmol m^{-2} d^{-1} respectively. However, it acted as mean source in 2018 with a mean of 7.79 ± 2.21 mmol m^{-2} d^{-1}, ranging from -21.09 to 52.37 mmol m^{-2} d^{-1}. Overall, yearly growing season CO_2 fluxes ranged from - 65.70 to 71.79 mmol m^{-2} d^{-1} with a mean of 2.39 ± 2.45 mmol m^{-2} d^{-1} (Table 3.6). Nevertheless, no seasonal variation in daily mean CO_2 fluxes was observed across sampling dates and among pools (ANOVA, $F_{(2, 98)} = 0.57$, $p = 0.57$) but flux varied significantly across the growing seasons (ANOVA, $F_{(4, 96)} = 4.59$, $P = 0.002$; Fig. 3.4). Pearson's correlation

between physiochemical variables and CO_2 fluxes in the growing season of 2018 showed no significant correlations (Table 3.3), but analysis of stepwise linear regression suggested that CO_2 flux is best predicted by pool depth, DO and vegetation cover (adjusted $R^2 = 0.07$; Table 3.4.1, 3.4.2, 3.4.3).

$CO_2 = 28.01 + 10.12 * \log(\text{depth}) - 2.54 * \log(\text{DO}) + 0.00 * \log(\text{Veg. cover})$ ------ **Equation 1**

Table 3.4.1: Parameter Effects on CO_2 Flux in AIC Stepwise Linear Regression Model

Source	Sum of Squares	df	Mean square	F	Sig.	Importance
Corrected model	1,531.57	2	765.783	3.126	0.052	
Depth_transformed	1,149.26	1	1,149.26	4.691	0.035	0.636
DO_transformed	656.837	1	656.837	2.681	0.108	0.364
Veg.cover_transformed	.	0	.	.	.	0
Residual	12,494.23	51	244.985			
Corrected Total	14,025.80	53				

Table 3.4.2: Coefficients of CO_2 Flux in AIC Stepwise Linear Regression Model

Model Term	Coefficient	Std. Error	t	Sig.	95% Confidence interval		Importance
					Lower	Upper	
Intercept	28.013	14.25	1.966	0.055	-0.595	56.62	
Depth_transformed	10.117	4.671	2.166	0.035	0.74	19.494	0.636
DO_transformed	-2.544	1.554	-1.637	0.108	-5.664	0.575	0.364
Veg.cover_transformed	0[a]						0

Note: [a] – This coefficient is set to zero because it is redundant

Table 3.4.3: Model Building Summary of CO_2 Flux in AIC Stepwise Linear Regression

		Model									
		1	2	3	4	5	6	7	8	9	10
	Information Criterion	300.458	300.458	301.145	301.145	301.942	301.942	302.051	302.051	302.233	302.233
Effects	Depth_transformed	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	Veg.cover_transformed	✓		✓		✓		✓		✓	
	DO_transformed	✓	✓			✓	✓				
	AirTemp_transformed			✓	✓					✓	✓
	EC_transformed					✓	✓			✓	✓
	DOC_transformed							✓	✓		

Note: A checkmark means the effects is in the model

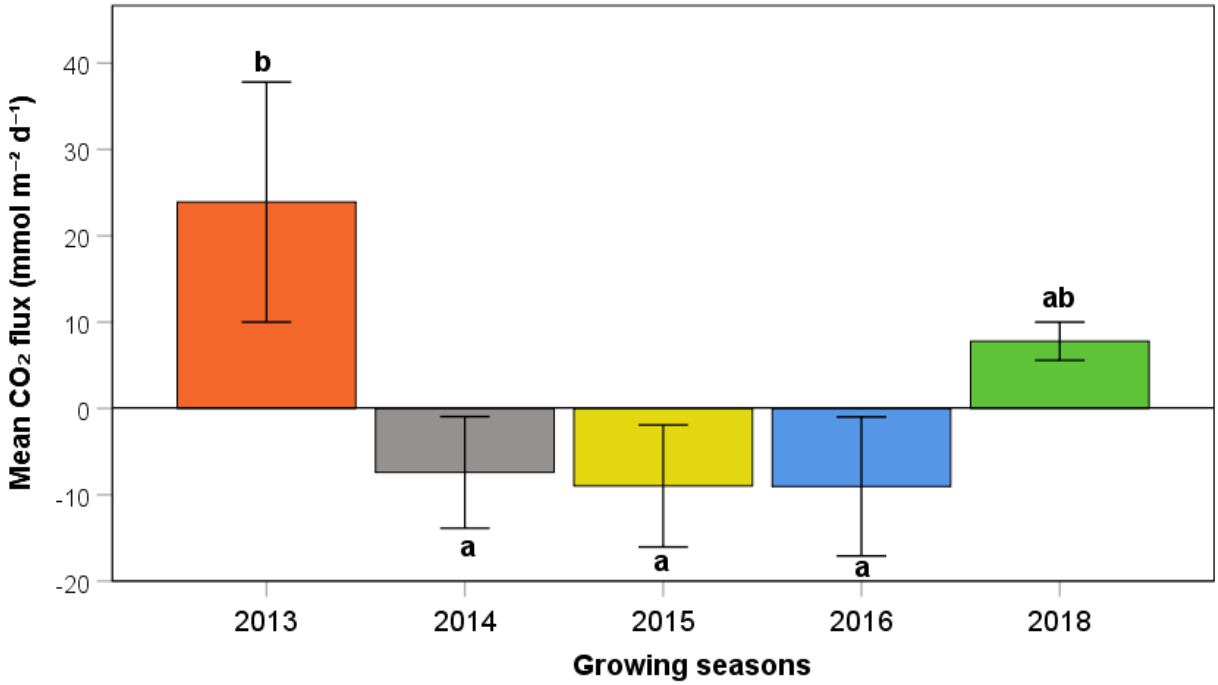

Figure 3.4: Mean CO_2 flux across the growing season of 2013, 2014, 2015, 2016 and 2018. Error bars and letters represent standard errors (SE) and significant differences ($p < 0.05$) between the growing seasons.

3.3.4.2 CH_4 flux

Average fluxes of CH_4 did not vary across the growing seasons (ANOVA, $F_{(4, 99)} = 1.70$, $p = 0.156$; Fig. 3.5), but were significantly different among pools (ANOVA, $F_{(2, 101)} = 4.27$, $p = 0.02$). Fluxes of CH_4 ranged from -0.19 to 2.66 mmol m^{-2} d^{-1} in 2013, -0.19 to 0.38 mmol m^{-2} d^{-1} in 2014, -2.28 to 1.52 mmol m^{-2} d^{-1} in 2015, -0.38 to 1.14 mmol m^{-2} d^{-1} in 2016 and -2.09 to 2.97 mmol m^{-2} d^{-1} in 2018 (Table 3.6). Overall, mean yearly growing season flux ranged from -2.8 to 2.97 mmol m^{-2} d^{-1} with a mean of 0.32 ± 0.09 mmol m^{-2} d^{-1}. Pools acted as sources in three growing seasons with a mean 0.41 ± 0.23 mmol m^{-2} d^{-1} in 2013, with a mean of 0.19 ± 0.08 mmol m^{-2} d^{-1} in 2016 and a mean of 0.52 ± 0.15 mmol

m^{-2} d^{-1} in 2018. Conversely, pools were mean sinks in 2014 and 2015 with mean fluxes of -0.001 ± 0.06 mmol m^{-2} d^{-1} and -0.01 ± 0.21 mmol m^{-2} d^{-1} respectively.

Pearson's correlation between CH_4 fluxes and physicochemical variables in the 2018 growing season showed significantly positively correlation between CH_4 flux with DOC ($r = 41$, $p < 0.01$) and vegetation cover ($r = 0.34$, $p < 0.05$) (Table 3.3). Stepwise multiple linear regression suggested that DOC, depth, EC and air temperature and vegetation cover best predicted CH_4 fluxes (adjusted $R^2 = 0.22$; Table 3.5.1, 3.5.2 and 3.5.3).

$CH_4 = 5.01 + 0.08 * \log(DOC) - 0.92 * \log(Depth) - 0.098 * \log(EC)$

$- 0.084 * \log(\text{air temperature}) + 0.00 * \log(\text{vegetation cover})$ ---- **Equation 2**

Table 3.5.1: Parameter Effects on CH_4 Flux in AIC Stepwise Linear Regression Model

Source	Sum of Squares	df	Mean square	F	Sig.	Importance
Corrected model	15.046	4	3.762	4.401	0.004	
DOC_transformed	8.733	1	8.733	10.218	0.003	0.391
Depth_transformed	5.917	1	5.917	6.923	0.01	0.265
EC_transformed	4.241	1	4.241	4.962	0.03	0.190
AirTemp_transformed	3.449	1	3.449	4.036	0.051	0.154
Veg.cover_transformed	.	0	.	.	.	0
Residual	37.605	44	0.855			
Corrected Total	52.651	48				

Table 3.5.2: Coefficients of CH_4 Flux in AIC Stepwise Linear Regression Model

					95% Confidence interval		
Model Term	Coefficient	Std.Error	t	Sig.	Lower	Upper	Importance
Intercept	5.005	2.373	2.109	0.041	0.223	9.786	
DOC_transformed	0.084	0.026	3.197	0.003	0.031	0.138	0.391
Depth_transformed	-0.921	0.350	-2.631	0.012	-1.627	-0.216	0.265
EC_transformed	-0.098	0.044	-2.228	0.031	-0.186	-0.009	0.190
AirTemp_transformed	-0.084	0.042	-2.009	0.051	-0.169	0	0.154
Veg.cover_transformed	0[a]						0

Note: [a] – This coefficient is set to zero because it is redundant

Table 3.5.3: Model Building Summary of CH_4 Flux in AIC Stepwise Linear Regression

		Model									
		1	2	3	4	5	6	7	8	9	10
	Information Criterion	-1.574	-1.574	-1.35	-1.35	-1.334	-1.334	-1.22	-1.22	-1.143	-1.143
	Depth_transformed	✓	✓			✓	✓			✓	✓
	Veg.cover_transformed	✓		✓		✓		✓		✓	
	EC_transformed	✓	✓								
Effects	AirTemp_transformed	✓	✓					✓	✓		
	DOC_transformed	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	pH_transformed			✓	✓	✓	✓	✓	✓		
	DO_transformed							✓	✓		

Note: A checkmark means the effects is in the model

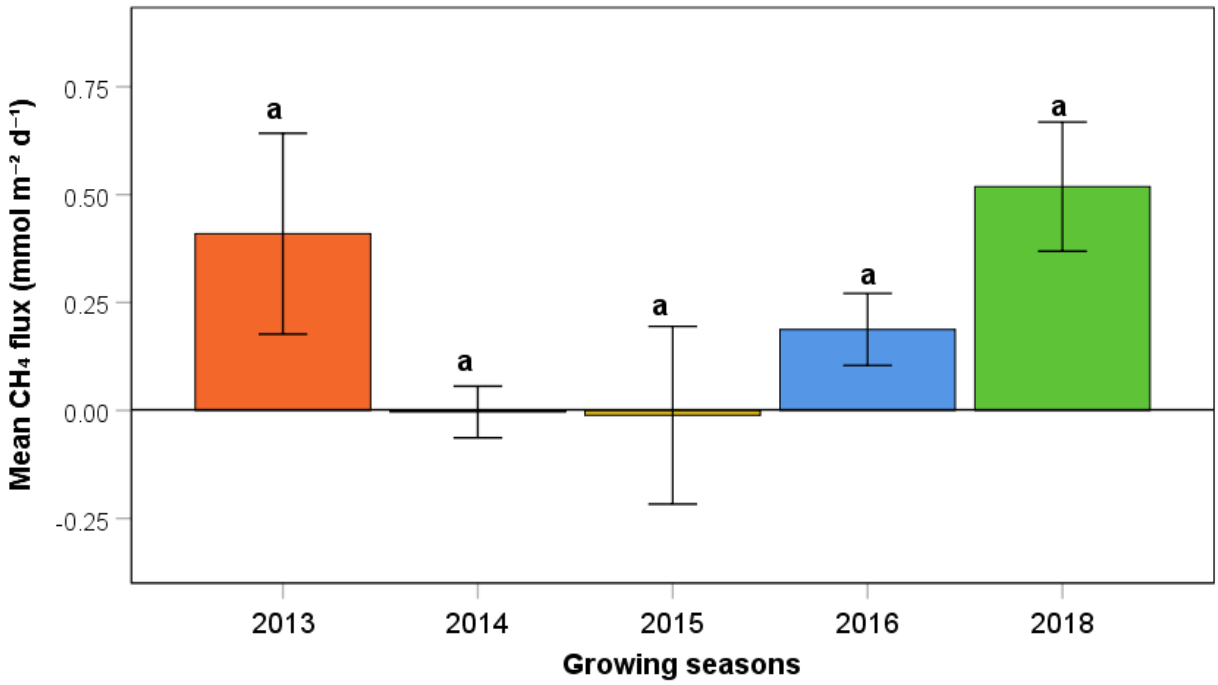

Figure 3.5: Mean CH_4 flux across the growing season of 2013, 2014, 2015, 2016 and 2018. Error bars and letters represent standard errors (SE) and significant differences ($p < 0.05$) between the growing seasons.

3.3.4.3 N_2O flux

Flux of N_2O did not vary across the growing seasons (ANOVA, $F_{(4, 108)} = 0.56$, $p = 0.69$; Fig. 3.6) and among pools (ANOVA, $F_{(2, 110)} = 2.31$, $p = 0.10$). Overall, it has a mean flux of -2.77 ± 3.98 µmol m^{-2} d^{-1} ranging from -133.37 to 114.28 µmol m^{-2} d^{-1} (Table 3.6). Pools acted as sinks of N_2O in three growing season of 2013, 2016 and 2018 with a means of -3.92 ± 4.09 µmol m^{-2} d^{-1} (-38.17 to 19.09 µmol m^{-2} d^{-1}), -2.49 ± 14.29 µmol m^{-2} d^{-1} (-133.37 to 76.11 µmol m^{-2} d^{-1}) and mean of -7.51 ± 5.09 µmol m^{-2} d^{-1} (-99.06 to 95.20 µmol m^{-2} d^{-1}) respectively. Conversely, pools acted as mean sources in the growing season of 2014 and 2015 with a mean 3.96 ± 4.22 µmol m^{-2} d^{-1} (-13.41 - 38.17 µmol m^{-2} d^{-1}) and 9.63 ± 18.17 µmol m^{-2} d^{-1} (-133.37 - 114.28 µmol m^{-2} d^{-1}) respectively.

N_2O fluxes did not significantly correlate with any physicochemical parameters and were not best predicted by any variable when applied in the stepwise multiple linear regression model.

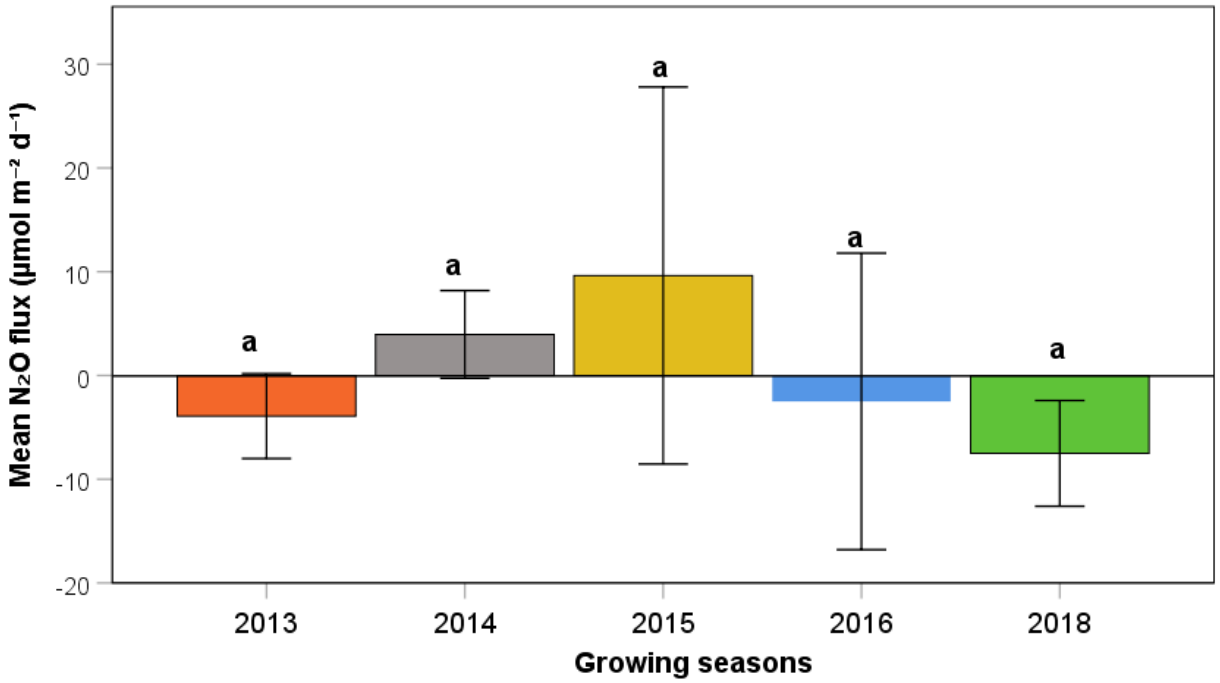

Figure 3.6: Mean N_2O flux across the growing season of 2013, 2014, 2015, 2016 and 2018. Error bars and letters represent standard errors (SE) and significant differences ($p < 0.05$) between the growing seasons.

Table 3.6: Mean (±Standard Error) and range of CO_2, CH_4 and N_2O fluxes during the growing seasons of 2013, 2014, 2015, 2016 and 2018 (N = 101 for CO_2, 104 for CH_4, 113 for N_2O, take note for differences in unit)

	CO_2 (mmol m^{-2} d^{-1})	CH_4 (mmol m^{-2} d^{-1})	N_2O (µmol m^{-2} d^{-1})
2013	23.91 ± 13.90 (-39.80 - 71.79)	0.41 ± 0.23 (-0.19 - 2.66)	-3.92 ± 4.09 (-38.17 - 19.09)
2014	-7.41 ± 6.46 (-41.89 - 12.76)	-0.00 ± 0.06 (-0.19 - 0.38)	3.96 ± 4.22 (-13.41 - 38.17)
2015	-8.98 ± 7.07 (-50.65 - 51.61)	-0.01 ± 0.21 (-2.28 - 1.52)	9.63 ± 18.17 (-133.37 - 114.28)
2016	-9.04 ± 8.05 (-65.70 - 43.61)	0.19 ± 0.08 (-0.38 - 1.14)	-2.49 ± 14.29 (-133.37 - 76.11)
2018	7.79 ± 2.21 (-21.09 - 52.37)	0.52 ± 0.15 (-2.09 - 2.97)	-7.51 ± 5.09 (-99.06 - 95.20)

3.4 Discussion

3.4.1 CO_2 flux

The range of CO_2 fluxes from this study varied widely from an influx of -65 mmol m^{-2} d^{-1} to efflux of 71.79 mmol m^{-2} d^{-1} with an average evasion value of 2.39 mmol m^{-2} d^{-1}. CO_2 fluxes in this study were lower in range than the CO_2 fluxes of 3.18 to 377.19 mmol m^{-2} d^{-1} reported from open water pools in a peatland in Quebec, Canada (Pelletier *et al*., 2014) and highly organic peatland open water pool in Hudson Bay Lowland, Canada with a range of 84.07 to 249.94 mmol m^{-2} d^{-1} (Hamilton *et al*., 1994). The variability of fluxes from influx to evasion observed in this study is consistent with reported fluxes from other inland waters. Kling *et al*. (1991) reported instantaneous fluxes of -5.5 to 59.8 mmol m^{-2} d^{-1} in a study of lakes in Alaska. Invasion of CO_2 into the lake from the atmosphere was recorded in that study due to the photosynthetic need of algae for production after fertilization experiment. Laurion *et al*. (2010) also recorded atmospheric influx of CO_2 in the range of -20.5 to 114.4 mmol m^{-2} d^{-1} to support the photosynthetic demands of benthic microbial mats in arctic ponds in Nunavik, Canada. Similarly, a flux range of -8.9 to 161.1 mmol m^{-2} d^{-1} was also reported from a reservoir in Germany also attributed to primary production (Halbedel and Koschorreck, 2013). The uptake of CO_2 by high primary productive inland waters have also been observed by (Hanson *et al*., 2004; Cole *et al*., 2007, Downing *et al*., 2008, Tranvik *et al*., 2009). In this study, analysis of stepwise linear regression predicted vegetation to be one of the important predictors of CO_2 flux in the pools in the growing season of 2018. Thus, the invasion of CO_2 into pools in our study may be related to an

influx of CO_2 to support photosynthesis activities of macrophytes highly visible in our studied pools.

Atmospheric exchange of CO_2 across the water-air interface varied significantly among the different growing seasons (Table 3.6, Fig. 3.4). The switch of CO_2 emission between sink and source has also been observed in peatland pools, lakes and reservoirs (Kling *et al*., 1992, Macrea *et al*., 2004, Tranvik *et al*., 2009). Inter-annual CO_2 flux variability observed in other previous studies has been linked to variation in precipitation and summer conditions (Rantakari and Kortelainen, 2005; Halbedel and Koschorreck, 2013, Knoll *et al*., 2013). In a comprehensive six-year study by Fontes *et al*. (2015), higher levels of CO_2 in lake surface water were related to rainfall. Precipitation events have been observed to increase dissolved inorganic carbon (DIC) inputs into water (Macrea *et al*., 2004; Raymond and Oh, 2007) and have been suggested to be positively related to CO_2 evasion in Boreal lakes (Einola *et al*., 2011). Rantakari and Kortelainen (2005) demonstrated that the annual CO_2 emission followed the open water season precipitation while Kelly *et al*. (2001) also found that the year-to-year variability in the partial pressure in 11 boreal lakes was linked to changes in the weather pattern. Kortelainen *et al*. (2006) observed higher CO_2 emission during years with the highest precipitation in small boreal lakes while Waddington and Roulet (1996) attributed reduced evasion from peatland pools to be related to revegetation of pools as they dry up due to no precipitation. A study by Macrea *et al*. (2004) reported that instantaneous fluxes of -49.7 to 1490 mmol m^{-2} d^{-1} in peatland open water pools in the subarctic region of Manitoba, Canada. The varied fluxes of CO_2 in that study were attributed to hydrological connection with the peatland catchment after precipitation

events. Evasion of CO_2 was observed to occur after input of DIC during summer storms while the invasion of CO_2 into pools occurred to support photosynthetic demand of aquatic plants due to lack of precipitation to cause hydrological connection of pools.

Knoll *et al*. (2013) observed that both reservoirs in their study were CO_2 sinks during dry summers and sources during wet summers. Although CO_2 flux did not significantly correlate with precipitation in our study, comparison of the yearly growing season long-term precipitation data shows that the CO_2 flux of growing season 2013 with considerably higher total precipitation and low temperature was significantly different from the other growing seasons with lower precipitation and higher temperature (Fig.3.2 and Fig. 3.4). The dryer growing seasons of 2014, 2015 and 2016 acted as sinks of CO_2 in contrast with the wetter growing season of 2013 and 2018 which, acted as sources of CO_2. Therefore, the variability of CO_2 fluxes among the different growing seasons may be related to the differences in precipitation. Interestingly, shallow pools have been observed to have higher biological activities during the summer period, due to water dry-up from evaporation, which enables revegetation of macrophytes in the littoral and perimeters of pools, increasing CO_2 concentration (Waddington and Roulet, 1996). Thus, the shallow depth of pools in this study (Table 3.1) may have also contributed to the gas exchange recorded. Although the R^2 of the adjusted minimum adequate model was low, the influence of pools depth as a regulator of CO_2 fluxes in this study was confirmed in the stepwise linear regression (equation 1). The low R^2 value suggests that other explanatory variables such as chlorophyll a, or photosynthetic active radiation (PAR) not measured in this study may be required to establish a more robust linear model for CO_2.

3.4.2 CH_4 flux

The mean fluxes of CH_4 across the different growing seasons were not significantly different among each other (Table 3.6, Fig. 3.5). Pools acted as mean sources in 2013, 2016 and 2018 and sink in 2014 and 2015. Variation in CH_4 emissions in peatlands has been linked to changes in temperature and precipitation (Walter *et al.*, 2001; Sanches *et al*., 2019). This may be due to the influx of DOC during precipitation events or temporary connection of pools with peatland catchment increased substrate availability for methanogenesis and ultimately evasion of CH_4 into the atmosphere (West *et al*., 2012; Camino-Serrano *et al*., 2014; Sabrekov *et al*., 2017). Increased frequency of passing low pressures and rainstorms may also enable the transport of CH_4 from pool sediments to the atmosphere, reducing the time for oxidation (Natchimuthu *et al.*, 2014). Precipitation and temperature may have influenced the mean fluxes of CH_4 in this study, as pools were sources in the wetter growing season and sinks in the drier season (Fig 3.2 and 3.5).

CH_4 fluxes in this study were low, with an overall mean of 0.32 ± 0.09 mmol m^{-2} d^{-1} and range of -2.8 to 2.97 mmol m^{-2} d^{-1}. Fluxes were lower but within range of CH_4 fluxes from a subtropical lake in India with a flux range of -3.1 to 194.7 mmol m^{-2} d^{-1} (Mallick and Dutta, 2009), in a beaver pond in Canada with a range of -0.25 to 17.24 mmol m^{-2} d^{-1} (Roulet *et al*., 1997), lakes in Alaska with a range of 0.08 to 1.02 mmol m^{-2} d^{-1} (Kling *et al*., 1992) and a permafrost thaw pond in Quebec, Canada with a range of 0.03 to 5.62 mmol m^{-2} d^{-1} (Laurion *et al*., 2010). Fluxes were, however, lower in range to fluxes reported in peatland open water pools in Canada, with a flux range of 0 to 184.54 mmol m^{-2} d^{-1}

(McEnroe *et al*., 2009), with a range of 6.86 to 11.22 mmol m^{-2} d^{-1} (Hamilton *et al*., 1994) and 0.06 to 116.58 mmol m^{-2} d^{-1} (Pelletier *et al*., 2014).

Emission of methane to the atmosphere has been reported to occur through a combination of plant-mediated transport through emergent aquatic plants, ebullition through bubble flux from sediments and diffusive flux (Bastviken *et al*., 2004, Pelletier *et al*., 2014). Ebullition and plant-mediated transport are the major pathways of CH_4 emissions (Bastviken *et al*., 2004, 2011). Ebullition is considered the most important contributor to emissions in surface water and has been reported to be larger than diffusive fluxes in shallow pools (Bastviken *et al*., 2004, Juutinen *et al*., 2009). Consequently, the fluxes of CH_4 reported in this study are likely underestimated because ebullition flux and plant-mediated transport were not captured. It is interesting to note that higher fluxes reported from pools in Canada by Hamilton *et al*. (1994), McEnroe *et al*. (2009) and Pelletier *et al*. (2014) were measured from open water pools containing very little vegetation or devoid of vegetation.

Despite the significant input of other drivers, DOC was predicted to be the most important driver of CH_4 flux in the 2018 growing season in this study. Also, a significant positive correlation was observed between CH_4 flux and DOC emphasizing their relationship (Table 3.3). The positive relationship between DOC and CH_4 flux has been reported in other studies, where DOC indicated substrate availability for methanogenesis increasing CH_4 concentration and flux (Bianchi *et al*., 1996, Garcia *et al*., 2000, Sanches *et al*., 2019). DOC can be derived from autochthonous sources (plant and algae exudations) and allochthonous sources (terrestrial organic matter) which can both be utilized by methanogens for methanogenesis (Casper, 1992, West *et al*., 2012). The positive

correlation between DOC and vegetation in this study suggests that DOC concentration was sourced more from autochthonous production.

3.4.3 N_2O flux

Pools in this study acted as mean net sinks of N_2O. The low flux range reported in this study is similar in range to other inland waters in the Boreal region (Huttenen *et al*., 2003; Hendzel *et al*., 2005; Soued *et al*., 2015). The low flux recorded in this study could be attributed to the low nutrient availability in ombrotrophic peatlands, as ponds receive their nutrients solely from precipitation events. Hence, small natural boreal pools are not important sources of atmospheric N_2O (Huttenen *et al*., 2002; Soued *et al*., 2015). Soued *et al*. (2015) observed that lakes acted as sinks when pH was less than 6.27 and DOC were more than 7.49 mg L^{-1} due to the limitation of nitrification by pH thus, supplying NO_3 for denitrification which reduces N_2O production. In our study, pools were acidic with a pH range of 3.60 to 5.00 and DOC range of 10.3 to 43.9 mg L^{-1}, which may suggest the possible invasion of N_2O recorded in this study.

3.5 Conclusion

To the best of our knowledge, this is the first comprehensive five year temporal study of GHG: CO_2, CH_4 and N_2O fluxes from peatland pools in Newfoundland, Canada. The fluxes of GHG were dynamic over the study period, switching between uptake and release over the growing seasons. However, no systematic pattern of gas exchange with the atmosphere was observed seasonally. This study demonstrated that small peatland pools could be net sinks and sources of CO_2 and CH_4 to the atmosphere depending on the weather pattern, pool morphology and within pool biogeochemical processes. Consequently, small peatland pools would either act as sinks of CO_2 and CH_4 in a drier climate or sources of CO_2 and CH_4 in a wetter climate. The net emission of GHG from our study pools would, therefore, depend on future weather changes.

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Chapter 4

4.0 Summary and Conclusion

The overall aim of my research was to highlight the significance of the research of bog pools in peatland studies and its inclusion in greenhouse gas budget from peatlands to ensure accurate budgeting of greenhouse gas levels in the atmosphere. Specifically, the purpose of this thesis was to measure the concentration of dissolved methane in bog pools, identify the local drivers of methane concentration and estimate and compare the variation of fluxes of GHG from bog pools.

In chapter 2, I found that pools in our study had dissolved CH_4 concentrations ranging from 2.32 to 180.98 µmol/L. This was found to be among the highest range of dissolved CH_4 concentration reported from small inland waters around the world, showing that small bog pools are "hot-spots" for methane production. It is interesting to note that concentration increase and decrease of CH_4 in the pools coincided with temperature increase and decrease, respectively. Higher concentration was found in mid-July to early September, which is the typical summer months in Newfoundland, Canada. Also, concentrations were lower in June and October when air temperatures are lower. The influence of temperature on the concentration levels of the pool was supported by the stepwise linear model, which predicted air temperature to be the most important predictor of CH_4 concentration in the pool. This was similar to other studies (Pighini *et al*., 2018, Rasilo *et al*., 2015). This was not surprising as temperature has been reported to affect methanogenesis, where an increase in temperature leads to a rise in methanogenesis and subsequent increase in the CH_4 levels. However, the influence of temperature in determining CH_4 concentration in

my studied pools shows that bog pools are sensitive to climatic conditions. Also, the influence of within pool factors such as vegetation, DOC, and surface area shows that these intrinsic characteristics of bog pools have a particular effect in aiding CH_4 production.

In chapter 3, the estimate and variation of GHG fluxes over the five-year growing seasons were determined. The temporal pattern of CH_4 and N_2O were similar across the years, while only fluxes of CO_2 were different. Also, there was no systematic pattern of emissions of GHG as pools alternated between acting as sinks and sources, and no pattern of emission could be established seasonally. However, I found that the mean growing season fluxes of CO_2 and CH_4 were influenced by the prevailing weather conditions of that growing season, where pools acted as CO_2 and CH_4 sources to the atmosphere in a wetter growing season and net sinks in a drier growing season.

Overall, this study has shown that bog pools have natural intrinsic features aiding CH_4 production, and the emission of CO_2 and CH_4 varies depending on climate and within pool biogeochemistry. Thus, bog pools may be affected in future climate scenarios.

4.1 Future work

This study improves the knowledge of GHG in peatlands and contributes to a better understanding of the role of bog pools in peatlands GHG flux budget. However, based on my finding that the fluxes are rather variable, future work should focus on continuous measurements of GHG from peatlands pools at different regional locations, as well as comparing inter-annual variations. This would help to link unusual emission patterns to the prevalent climatic conditions and physicochemical drivers.

Also, in the estimation of CH_4 flux from pools, future work should consider a more comprehensive methodology involving diffusive flux measurements, in addition to ebullition, and plant-mediated flux measurements to ensure accurate assessment and budgeting.

4.2 References

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