# METHANE DYNAMICS IN SELECTED WETLANDS, RIVERS, AND BAYS OF NEWFOUNDLAND CANADA

by

RACHEL MARIE STEFFEN

(Under the direction of Samantha B. Joye)

#### ABSTRACT

Methane (CH<sub>4</sub>), a potent greenhouse gas, is produced in the sediment and water column of aquatic ecosystems. The release of CH<sub>4</sub> to the atmosphere is partially mitigated by CH<sub>4</sub> oxidizing microorganisms (Ferry & Lessner, 2008; Kiene, 1991; Koo & Rosenzweig, 2021). This work focused on Placentia Bay, the largest bay on the southern coast of the Island of Newfoundland. Placentia Bay is influenced by several marine sources which could introduce CH<sub>4</sub> to coastal Newfoundland. Furthermore, 18% of the landmass of Newfoundland is peatland bogs, which are hotbeds of CH<sub>4</sub> production (Mahdianpari et al., 2020; Pelletier et al., 2007; Rydin & Jeglum, 2010; Wang et al., 2019) . Here, I present dissolved CH<sub>4</sub> concentrations from one peatland and two catchment rivers that flow into the bay, as well as CH<sub>4</sub> concentrations and oxidation rates in the bay. Additionally, nutrient and dissolved organic carbon data provide evidence of the microbial dynamics that may influence CH<sub>4</sub> concentrations. This study provides an initial assessment of CH<sub>4</sub> dynamics within Placentia Bay and its tributaries.

INDEX WORDS:Methane, Methane Oxidation, Placentia Bay, Come by Chance River,Piper's Hole River, Labrador Sea, Peatland

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# DEDICATION

I would like to dedicate this thesis to my two younger sisters who inspire me to never stop asking

"but why?"

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#### CHAPTER 1

#### INTRODUCTION

Methane (CH<sub>4</sub>) is a greenhouse gas that is 28 times more potent than carbon dioxide (CO<sub>2</sub>) over a 100-year timescale (IPCC, 1996). Globally, between 500 and 600 Tg of CH<sub>4</sub> is emitted to the atmosphere each year (Dlugokencky et al., 2011). Given the role of methane in Earth's energy budget, understanding and quantifying CH<sub>4</sub> production and consumption rates and the factors that influence them is important. Canada is warming at twice the average global rate (Bush & Lemmen, 2019). This rapid temperature rise drives increasing rates of CH<sub>4</sub> production (Blake et al., 2015) and the release of stored CH<sub>4</sub> from reservoirs, such as permafrost and CH<sub>4</sub> hydrates (Figure 1; Anisimov, 2007; Dean et al., 2018; Ruppel & Kessler, 2017; N. Shakhova & Semiletov, 2007). Therefore, advancing knowledge of CH<sub>4</sub> dynamics in the arctic and boreal regions of Canada is critical for understanding future climate change. In this study, I investigated the CH<sub>4</sub> dynamics in Placentia Bay, a boreal bay system on the southeastern coast of Newfoundland and Labrador, Canada, which is influenced by the Labrador Sea, the Grand Banks of Newfoundland, the Gulf of St. Lawrence, and run off from boreal peatlands (Figure 2).

The convergence of currents in the Labrador Sea creates a highly dynamic system (Figure 2; Seidenkrantz, 2013; Sicre et al., 2014; Yang et al., 2016). Significant concentrations of CH<sub>4</sub> are introduced into the Labrador Sea via surface currents (Damm et al., 2015; Lamarche-Gagnon et al., 2019). Furthermore, subglacial meltwater from Greenland, containing high CH<sub>4</sub> concentrations ( $\sim 0.3 - 80 \mu$ M), influences the Labrador Sea via the East and West Greenland currents (Dieser et al., 2014; Lamarche-Gagnon et al., 2019). Methane concentrations up to 20

nM were measured in Arctic water flowing south through Baffin Bay via the Labrador Current (Punshon et al., 2014). Subsurface CH<sub>4</sub> hydrates in the extensive gas hydrate stability zone (GHSZ) along the Labrador Shelf could become another source of CH<sub>4</sub> to the Labrador Sea and coastal Canada if warming ocean temperatures mobilize the GHSZ (Majorowicz & Osadetz, 2003; Mosher, 2011; Ruppel & Kessler, 2017). However, these CH<sub>4</sub> sources result in average CH<sub>4</sub> concentrations of 1.5 - 6 nM in transects across the Labrador Sea (Kitidis et al., 2010; Punshon et al., 2014), which is typical of open ocean environments.

The Grand Banks of Newfoundland, located in the southern Labrador Sea, may provide a local source of CH<sub>4</sub> to the waters which influence Newfoundland (Figure 2). The Grand Banks are a series of subsea plateaus which resulted from tectonic rifting ~100 Ma, starting in the Triassic (Macdougall et al., 2020). There are significant hydrocarbon reservoirs stored beneath the sediments of the Grand Banks, and gas seeps along the plateaus are indicated by pockmarks (Fader, 1991; Hemphill, 2015; Hovland, 1992). Hydrocarbon seeps release large quantities of CH<sub>4</sub> gas in almost all cases (Judd, 2004). The advective discharge of CH<sub>4</sub> may prevent effective biological oxidation in the sediments, potentially releasing CH<sub>4</sub> into the water column (Judd et al., 2002; Shakhova et al., 2010). The ability of methane bubbles to remain intact without dissolving relies on the depth and temperature of the water, as well as the composition of the bubble itself (Langenegger et al., 2019). High CH<sub>4</sub> concentrations in the upper water column may result in the transport of CH<sub>4</sub> via the surface currents of the Labrador Sea (Cynar & Yayanos, 1992; Gentz et al., 2014).

To the west of Newfoundland, CH<sub>4</sub> concentrations in the Gulf of St. Lawrence (Figure 2) are as high as 400 nM (Li et al., 2022). On average, methane concentrations increase from the lower estuary (9.8 nM) to the upper estuary (50.3 nM; Li et al., 2022). The main source of CH<sub>4</sub>

to the Gulf of St. Lawrence is ~2,000 hydrocarbon seeps found throughout the region (Lavoie et al., 2010). In addition, there are high CH<sub>4</sub> emissions from St. Lawrence salt marshes, likely contributing CH<sub>4</sub> to the greater estuary (Comer-Warner et al., 2022). The average net flux of CH<sub>4</sub> from the Gulf of St. Lawrence via the Cabot straight is  $1.55 \times 10^6$  mol CH<sub>4</sub> year<sup>-1</sup> (Li et al., 2022). The water, influenced by this CH<sub>4</sub>, then flows around the southern coast of Newfoundland.

Water from the Labrador Sea influenced by the Grand Banks of Newfoundland converges with water from the Gulf of St. Lawrence as it flows into the bays and estuaries along the eastern and southern coast of Newfoundland and Labrador, Canada (Figure 2; Drinkwater, 1996; Seidenkrantz, 2013; Sicre et al., 2014). Based on knowledge from other coastal systems, these coastal areas may be hotspots of CH<sub>4</sub> cycling and atmospheric efflux (Bange, 2006; Borges et al., 2016a; Burgos et al., 2018; Upstill-Goddard & Barnes, 2016). Modeling studies have shown that CH<sub>4</sub> in shallow coastal environments dominate the global ocean CH<sub>4</sub> flux (Weber et al., 2019). Groundwater input and river discharge introduce riverine, and terrestrial CH<sub>4</sub> into coastal receiving waters (Bange, 2006; Middelburg et al., 2002; Rao & Sarma, 2017; Upstill-Goddard & Barnes, 2016). Therefore, understanding the coastal CH<sub>4</sub> dynamics of boreal Canada may reveal the fate of significant CH<sub>4</sub> sources.

Methanogenesis in coastal sediments is driven by high rates of organic matter deposition and subsequent conversion of organic C to CH<sub>4</sub> (Borges et al., 2016a; Clair et al., 1994; Schmale et al., 2010; Weber et al., 2019). Rivers have a growing impact on boreal coastal systems due to higher average temperatures and earlier, warmer springs altering hydrography and hydrology (Gelfan et al., 2017; Reyes & Lougheed, 2015). Throughout the Eurasian pan-arctic, rivers have demonstrated increased spring and winter discharge since 1936 (Shiklomanov et al., 2021). In

shallow coastal environments (< 200 m), the well mixed water column limits  $CH_4$  oxidation throughout the water column (Borges et al., 2016a; Weber et al., 2019). Increasing  $CH_4$  sources and limited consumption may allow more  $CH_4$  to flux to the atmosphere along the boreal coastline of eastern Canada (Weber et al., 2019).

Eighteen percent of Newfoundland landcover is peatland, mainly bogs and fens (Mahdianpari et al., 2020). Peatlands act as a sink for CO<sub>2</sub> but are a source of CH<sub>4</sub> (Lai, 2009; Matthews, 1987; Ortiz-Llorente & Alvarez-Cobelas, 2012). Peatlands contribute ~36 Tg CH<sub>4</sub> yr<sup>-1</sup> (Tg= $10^{12}$ g), which is ~6% of the total CH<sub>4</sub> emitted globally (550–594 Tg CH<sub>4</sub> yr<sup>-1</sup>, Abdalla et al., 2016; Saunois et al., 2019). Wang et al (2018) used an eddy covariance method to measure the CH<sub>4</sub> flux from a peatland in northwest Newfoundland and showed an average annual flux of ~3 g CH<sub>4</sub> m<sup>-2</sup>. However, there was strong seasonal variability due to soil temperature, air temperature, and water table depth. Models consistently demonstrate that increased temperatures increase the amount of CH<sub>4</sub> released from peatlands (Henry et al., 2012; Ortiz-Llorente & Alvarez-Cobelas, 2012; Pelletier et al., 2007). Peatlands also export of dissolved organic carbon (DOC) to groundwater, streams, and rivers and this flux is expected to increase with rising temperatures (Frey & Smith, 2005). Thus, peatlands could have a growing impact on fluxes of the DOC and CH<sub>4</sub> to the streams, rivers, and estuaries of Newfoundland.

To provide current estimates of CH<sub>4</sub> concentrations, oxidation rates and nutrient concentrations, I collected samples across land-sea transects in the Placentia Bay system. I measured CH<sub>4</sub> concentrations and ambient nutrient concentrations in one peatland site, along two rivers (Piper's Hole River and Come by Chance River), at four coastal sites, and at four open bay sites in Placentia Bay. I also measured CH<sub>4</sub> oxidation rates at the four open bay sites. In addition, I collected and analyzed water from six coastal sites in Conception Bay, on the north side of

Newfoundland, to generate comparative data from a nearby system. In this study, I analyzed the upstream versus downstream trends in CH<sub>4</sub> and nutrient concentrations in the rivers. I also examined the CH<sub>4</sub> dynamics within Placentia Bay to assess the impact that river discharge and groundwater input may have on this coastal system.

#### **CHAPTER 2**

#### BACKGROUND

Since the initiation of global CH<sub>4</sub> monitoring in 1983, a 17% increase in the average atmospheric mole fraction of CH<sub>4</sub> has occurred (1,630 ppb in 1983 and 1,908 ppb in 2022; Lan et al., 2022). In addition to anthropogenic sources, increased rates of methanogenesis, thawing permafrost, and melting ice sheets, contribute to the global rise in CH<sub>4</sub> (Blake et al., 2015; Lamarche-Gagnon et al., 2019; Philipp et al., 2021; Schuur et al., 2015). Methane hydrate degradation in warming ocean waters may also increase as global temperatures rise (Ruppel & Kessler, 2017). Higher atmospheric CH<sub>4</sub> concentrations accelerate radiative forcing, which causes further warming and, in turn, higher atmospheric CH<sub>4</sub> concentrations, a phenomenon referred to as the CH<sub>4</sub> positive feedback loop (Figure 1; Cui et al., 2015; Walter et al., 2006). Paleoclimate data suggest that previous warming and mass extinction events resulted from rapid increases in atmospheric CH<sub>4</sub> (Brand et al., 2016; Kemp et al., 2005; Pálfy et al., 2002; Shen et al., 2011). Thus, sources and sinks of CH<sub>4</sub> should be identified and monitored in order to understand rapid climate change and develop effective climate mitigation strategies.

#### Methane oxidation

Microbial CH<sub>4</sub> oxidation mitigates the CH<sub>4</sub> flux in both anoxic and oxic environments. Anoxic sediments support the anerobic oxidation of CH<sub>4</sub> (AOM; Knittel & Boetius, 2009; Shen et al., 2019). Anerobic methane oxidation is coupled to the reduction of different electron acceptors including nitrite (NO<sub>2</sub><sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>), iron (Fe-III), and manganese (Mn-IV); (Ettwig et al., 2010, 2016; Haroon et al., 2013; Leu et al., 2020; Vavilin et al., 2021). Due to varied pathways, organisms, and environments that support AOM, the contribution of AOM to global CH<sub>4</sub> consumption is difficult to constrain, but it is assumed to be an extremely significant sink of CH<sub>4</sub> under diffusion-dominated conditions (Conrad, 2009). The CH<sub>4</sub> not consumed by AOM escapes into the water column, where CH<sub>4</sub> can be oxidized aerobically by pelagic methanotrophs (Figure 3).

Aerobic methanotrophic microorganisms are ubiquitous, occurring in ocean and terrestrial sediments, marine and freshwater columns, and even in extreme environments (Murrell, 2010). Methanotrophic bacteria are grouped into four distinct categories: type I, type II, type X, and Verrucomicrobial methanotrophs (Rosenberg et al., 2013; Schmitz et al., 2021). These groups are defined based on mechanism of carbon (C) fixation, arrangement of intracytoplasmic membranes, fatty acid composition of membranes, and ability to fix nitrogen (Cicerone & Oremland, 1988). In general terms, aerobic methane oxidation is the oxidation of  $CH_4$  with oxygen to methanol, formaldehyde, formate, and finally  $CO_2$  (Figure 3, Eq. 1, (Chan et al., 2019). The methane monooxygenase enzyme (MMO) mediates the oxidation of  $CH_4$  to methanol, and it is consistent across methanotrophs of all taxa (Murrell, 2010). There are two forms of MMO, a membrane bound particulate-MMO (pMMO) and a soluble-MMO (sMMO). Iron-containing sMMO enzymes are utilized under conditions of copper deficiency, whereas the pMMO enzyme occurs under copper replete conditions (Ross & Rosenzweig, 2017). The monooxygenase reaction utilizes reducing equivalents from NADH to break the strong C-H bond of CH<sub>4</sub> (Bürgmann, 2011). In this way, aerobic methanotrophs are able to oxidize CH<sub>4</sub> to CO<sub>2</sub>,

but they are not always effective in consuming the  $CH_4$  pool before a substantial fraction reaches the atmosphere (Dean et al., 2018; Y. Li et al., 2020; Walter et al., 2006).

Equation 1.  $CH_4 + 2 O_2 \rightarrow CO_2 + 2H_2O$ 

#### Biotic sources of CH<sub>4</sub> to the marine environment

Methane production is a significant component of the global carbon cycle (Potter, 1997; Saunois et al., 2016). Most CH<sub>4</sub> is produced by methanogenic archaea in anoxic environments. Under SO<sub>4</sub><sup>2-</sup> rich conditions, SO<sub>4</sub><sup>2-</sup> reduction is the dominant metabolism. Thus, the majority of anoxic methanogenesis usually occurs below the sulfate reduction zone under the most reducing conditions in anoxic sediments (D. L. Valentine, 2011). Methanogens produce CH<sub>4</sub> during the terminal metabolism of organic matter. Because methanogenesis is the final step in the decomposition of biomass, sediments having large quantities organic matter, such as coastal systems and estuaries, support higher rates of methanogenesis (Ferry & Lessner, 2008; Weber et al., 2019). Algal blooms triggered by eutrophication can lead to increased dissolved organic matter (DOM) deposition and therefore increased methane production rates (West et al., 2012). Anthropogenic activities and agricultural runoff of nitrogen (N), phosphate (P), and DOM can have a significant impact on CH<sub>4</sub> production rates.

There are three mechanisms of biological CH<sub>4</sub> production: acetoclastic, hydrogenotrophic, and methylotrophic (Ferry & Lessner, 2008; Yin et al., 2019). Acetoclastic methanogenesis occurs in wetlands, lakes, rivers, marine sediments, and the gastrointestinal tracts of animals (White et al., 2000). This pathway involves the fermentation of acetate  $(C_2H_3O_2^-)$  where the methyl group is reduced to CH<sub>4</sub> and the carbonyl group is oxidized to CO<sub>2</sub>

(Ferry & Lessner, 2008; Krause & Treude, 2021). Hydrogenotrophic methanogenesis is considered the most dominant pathway of CH<sub>4</sub> production in freshwater environments including lakes, streams, and bogs (Conrad, 1999). Hydrogenotrophic methanogenesis occurs via a reduction of CO<sub>2</sub> with H<sub>2</sub> (Demirel & Scherer, 2008; Krause & Treude, 2021). As its name suggests, methylotrophic methanogenesis involves the production of CH<sub>4</sub> via the fermentation or reduction of methyl groups (Bräuer et al., 2020; Krause & Treude, 2021). Methylotrophic methanogenesis is observed in the upper sediment layer within the sulfate reduction zone since it is fueled by non-competitive substances (Schorn et al., 2022). Each of these methanogenic pathways generate energy to drive ATP synthase (Al-Mahrouq et al., 1986).

Equation 2  $CH_3COO^- + H^+ \rightarrow CO_2 + CH_4$ 

Equation 3  $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$ 

Equation 4  $4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O$ 

Equation 5  $4CH_3NH_2 + 2H_2O \rightarrow 3CH_4 + CO_2 + 4NH_4^+$ 

Although methanogenesis was thought to be mediated solely by archaea in anoxic environments, extensive evidence of CH<sub>4</sub> production in the aerobic water column exists (Damm et al., 2010; Karl et al., 2008; Keppler et al., 2009). A CH<sub>4</sub> maximum within the oxic mixed layer of the oceanic water column referred to as the "Oceanic Methane Paradox" (Scranton & Farrington, 1977). The original hypothesis was that anoxic microniches, such as the gut tract of zooplankton, were the sources of this pelagic CH<sub>4</sub> maximum (de Angelis & Lee, 1994). However, recent advances showed that CH<sub>4</sub> is produced by nutrient limited phytoplankton (P. Carini et al., 2014; Günthel et al., 2020; Taenzer et al., 2020). Cyanobacteria produce CH<sub>4</sub> under phosphorous (P) limitation, utilizing methylphosphonate as a source of P and producing CH<sub>4</sub> as a byproduct (Günthel et al., 2020; Repeta et al., 2016; Taenzer et al., 2020; Teikari et al., 2018; Q. Wang et al., 2017). In addition, the coccolithophore, *Emiliana huxleyi* produces CH<sub>4</sub> using the methyl group of methionine (Lenhart et al., 2016). Klintzsch et al. (2020) demonstrated that CH<sub>4</sub> production by phytoplankton species was increased with light intensity and duration. Shifts in light availability, nutrient load, or aerobic microbial community dynamics could therefore alter CH<sub>4</sub> oceanic dynamics.

#### Abiotic Sources of CH<sub>4</sub>

The abiotic production of CH<sub>4</sub> also contributes to the global CH<sub>4</sub> pool (Etiope & Lollar, 2013). There are four methods of abiotic CH<sub>4</sub> production: serpentinization, photoproduction, geogenic production and thermogenic production. The process of serpentinization occurs in some tectonically active areas (Hyndman & Peacock, 2003; Klein et al., 2019; Proskurowski et al., 2006). In serpentinization, the hydrolysis of olivine-rich rock creates serpentine. During the Fe<sup>2+</sup> oxidation step of this pathway, H<sub>2</sub> is formed and is available to react with CO<sub>2</sub> to produce CH<sub>4</sub> (Bach et al., 2006). Photoproduction of CH<sub>4</sub> from chromophoric dissolved organic matter (CDOM) in the surface water is another mechanism for production (Li et al., 2020; Zhang & Xie, 2015). The average estimated photoproduction rate in the surface ocean is 64 nmol m<sup>-2</sup> d<sup>-1</sup>, and may increase with increasing global temperatures as more CDOM is transported from terrestrial sources (Larsen et al., 2011; Meier, 2006). Geogenic CH<sub>4</sub> is formed under high temperatures via volcanism and geothermic activity (Daskalopoulou et al., 2019). Thermogenic CH<sub>4</sub> is produced via the thermally activated breakdown of organic matter and occurs over long periods of time (Hunt, 1995). Although much of this CH<sub>4</sub> is oxidized, a portion of CH<sub>4</sub> may be directly emitted

to the atmosphere or contribute to stored  $CH_4$  pools (Elliott et al., 2010; Etiope & Lollar, 2013; Klein et al., 2019).

Permafrost is defined as sediment frozen ( $\leq 0^{\circ}$ C) for more than two years. Although, some areas of permafrost froze as early as the Pleistocene (Rekant et al., 2015). Subsea permafrost was formed during the last glacial maximum. Destabilization of subsea permafrost may increase CO<sub>2</sub> and CH<sub>4</sub> emissions on short (decadal) time scales in response to anthropogenic climate change but estimates of this emission are highly variable and need further refinement (Angelopoulos et al., 2020; Sayedi et al., 2020). Some predict that higher sea levels may stabilize subsea permafrost despite warmer temperatures due to the increased pressure and cooler temperatures found in deeper water (Angelopoulos et al., 2020). There is more than twice as much CH<sub>4</sub> stored in permafrost as there is currently in our atmosphere. Therefore, the emission of CH<sub>4</sub> from permafrost alone could catastrophically alter our climate unless it is effectively consumed (Markon et al., 2012).

Methane hydrates are found in marine sediments along continental slopes and associated with terrestrial permafrost within the GHSZ, regions in which high methane concentrations coincide with low temperature (< 25°C; C. D. Ruppel & Waite, 2020). These frozen latices of water trap CH<sub>4</sub> and can store it over time scales of thousands to tens of thousands of years (Koh et al., 2011). Globally, gas hydrates are estimated to hold ~11,000 Gt C (Kvenvolden, 1988). However, it is unknown how much C is truly stored because of the heterogenous distribution of gas hydrate within the GHSZ (Liu et al., 2021). Warmer ocean temperatures, due to global climate change, are shrinking the GHSZ, and increasing gas hydrate dissociation (Carolyn D. Ruppel & Kessler, 2017).

Ice sheets serve as a significant C reservoir, but as the ice begins to melt this C is being released into subglacial rivers in the form of CH<sub>4</sub> (Wadham et al., 2019). In 2015, a CONTROS HydroC CH<sub>4</sub> sensor was deployed in the proglacial river of Leverett Glacier in southwest Greenland. The average CH<sub>4</sub> concentration near the ice margin (< 2 km) of this river was 271 nM (Lamarche-Gagnon et al., 2019). Methane concentrations from the runoff of the Russel Glacier, also on the western margin of the Greenland ice sheet, were as high as 83  $\mu$ M (Dieser et al., 2014). In comparison, CH<sub>4</sub> concentrations in the open ocean as well as along continental shelves usually ranges from 5 – 20 nM (Borges et al., 2016b; Gentz et al., 2014; Schmale et al., 2010; Shakhova et al., 2010). There is no clear estimate of CH<sub>4</sub> flux from the Greenland icesheet and there are no quantified rates of CH<sub>4</sub> oxidation in this region (Christiansen et al., 2021; Dessandier et al., 2021; Lamarche-Gagnon et al., 2019). Still, it is likely that meltwater is an important methane source to associated receiving waters.

Stable isotope data suggests that the CH<sub>4</sub> released from melting ice sheets is biologically produced (Dieser et al., 2014). However, it is unclear if this CH<sub>4</sub> is old and has been stored under the ice sheet in the GHSZ, or if the CH<sub>4</sub> is being produced currently within the sediments under the ice sheet (Christiansen et al., 2021; Lamarche-Gagnon et al., 2019; Portnov et al., 2016). Anoxic conditions and a plethora of organic C sources under ice sheets could provide ideal conditions for methanogenesis (Dieser et al., 2014; Stibal et al., 2012). Most likely, both of these sources contribute to the CH<sub>4</sub> released from ice sheets (Lamarche-Gagnon et al., 2019). Although, there is evidence of sustained CH<sub>4</sub> oxidation, Greenland ice sheet meltwater is considered a source of CH<sub>4</sub> to the atmosphere due to the supersaturation of the meltwater (Christiansen et al., 2021; Dieser et al., 2014). In addition to the Greenland ice sheet, the Antarctic ice sheet and glaciers across the globe may act as significant sources of  $CH_4$  to the atmosphere (Hopcroft et al., 2017; Wadham et al., 2019).

#### Wetland Methane Dynamics

Wetlands cover 4-9% of the Earth's surface, storing vast quantities of C and accounting for 60-80% of global CH<sub>4</sub> emissions (Kirschke et al., 2013; Matthews, 1987). Anoxic wetland soils slow the process of decomposition leading to the accumulation of organic matter and C sequestration (Vepraskas et al., 1999). However, these conditions are also favorable for methanogenesis which occurs in wetlands via the acetoclastic and hydrogenotrophic pathways (Söllinger & Urich, 2019). Timescales are an important consideration when discussing the C emission versus uptake by wetlands. Over decadal timescales a wetland may release more C (in the form of CH<sub>4</sub>) than it stores. But over centuries, the absorption of CO<sub>2</sub> likely outweighs CH<sub>4</sub> production resulting in a net C sink (Whiting et al., 2016). It is also important to take geographic location into consideration. Wetlands in polar regions emit a higher ratio of CH<sub>4</sub> emission to CO<sub>2</sub> fixation than more temperate and tropical wetlands, due to lower annual plant productivity in northern latitudes (Whiting et al., 2016). Higher annual temperatures increase the amount of CH<sub>4</sub> released from wetlands (Pelletier et al., 2007; Z. Zhang et al., 2017). Thus, CH<sub>4</sub> emissions from wetland systems across a variety of geographic locations must be monitored.

Vascular plants contribute to both CH<sub>4</sub> production, oxidation, and efflux in wetland systems. Low molecular C compounds released by plant roots provide substrates that fuel high rates of rhizosphere methanogenesis (Bhullar et al., 2013; Joabsson et al., 1999). Vascular plants can also provide the oxygen required for CH<sub>4</sub> oxidation (Öquist & Svensson, 2002). The balance

of these processes depends on the specific microbial and physical attributes of the wetland system. Higher rates of photosynthesis provide more C substrate for methanogenesis in the rhizosphere (Joabsson et al., 1999). However, plant growth rate is positively correlated to the suppression of methanogenesis due to the net rhizosphere oxidation effect that occurs during rapid growth periods (Agethen et al., 2018). Plant species is the greatest predictor of CH<sub>4</sub> emission because the diffusion rate of CH<sub>4</sub> into the root aerenchyma is dependent on the species (Schimel, 1995). Diffusion of CH<sub>4</sub> via vascular plants provides a route for CH<sub>4</sub> efflux that bypasses the oxic sediment layer (Joabsson et al., 1999). Therefore, CH<sub>4</sub> emission via vascular plants may be a significant mode of CH<sub>4</sub> release to the atmosphere.

Peatlands are classified as cold anoxic wetlands that accumulate layers of partially decayed organic matter and plant material; they are found in boreal climates (Gore, 1983). Less than three percent of the Earth's land area is considered peatland, but peatland soils contain about one third of global soil C (Rydin & Jeglum, 2010). Northern peatlands are responsible for 12% of global CH<sub>4</sub> emissions (Gorham, 1991; Wuebbles & Hayhoe, 2002). Peatlands have high rates of DOC export to groundwater, rivers, streams, and estuaries. In three peatlands of central North America, the average DOC export was 8-40 g m<sup>-2</sup> yr<sup>-1</sup>. In boreal regions of Atlantic Canada, increased precipitation could increase this export (Clair et al., 1994; Urban et al., 1989). In addition to DOC, peatlands may be transporting CH<sub>4</sub>, DOM, particulate organic matter (POM), and nutrients into the rivers and streams they flow in to (LAI, 2009; Mattsson et al., 2005; Richardson et al., 2020). In this study, we sampled one such peatland environment and gauge its influence on CH<sub>4</sub> concentrations in the river it influences.

#### **Riverine Methane Dynamics**

Globally, rivers are considered a CH<sub>4</sub> source to the coastal ocean and atmosphere because many rivers contain CH<sub>4</sub> concentrations that exceed those expected from equilibrium with the atmosphere (Shakhova et al., 2014; Xiao et al., 2017). These high CH<sub>4</sub> concentrations are mostly the result of methanogenesis in the riverbed and adjacent wetlands (Stanley et al., 2016). However, exchange with groundwater via the hyporheic zone may also impact riverine CH<sub>4</sub> concentrations. Known as the "liver of the river", the hyporheic zone regulates the exchange of both nutrients and gases, including CH<sub>4</sub>. The net volume flux depends on the flow and hydrography of the river and on groundwater input (Anthony et al., 2012). Isotopic data has demonstrated a varied degree of influence of these CH<sub>4</sub> sources in different river systems, dependent on the surrounding terrestrial system, flow rate, time of year, and temperature (Sansone et al., 1999).

The emission of riverine CH<sub>4</sub> to the atmosphere depends on the hydrology of the river. Turbulence, bubble formation, and wind stress. Wind stress increases gas exchange and thus increases the amount of CH<sub>4</sub> emitted. Therefore, in calm flat rivers, less CH<sub>4</sub> is emitted to the atmosphere than those with intense rapids (de Angelis & Lilley, 1987). In this study, I sampled river sites that experienced turbulence and were subjected to strong winds, as well as sites that were calm and shielded from the wind by vegetation. Below I discuss these physical aspects and how they could have affected the CH<sub>4</sub> dynamics and exchange at specific sites.

#### Newfoundland Canada and Placentia Bay

Newfoundland is an island off the eastern coast of Canada which protrudes into the Labrador Sea and is the southern portion of the Newfoundland and Labrador province. The Labrador Current flows around the southern portion of Newfoundland over the Grand Banks of Newfoundland (Pickart et al., 1999). This current collides with water from the Gulf of St. Lawrence along the southern coast of Newfoundland. Therefore, there are several bodies of water and sources of nutrients and CH<sub>4</sub> acting on the southern coast of Newfoundland creating a highly dynamic environment.

In Newfoundland, volcanism, glacial erosion, tectonic forces, continental drift, and the most northern extension of the Appalachian Mountains formed a rugged coastline consisting of several major bays (Grant, 1989; Waldron et al., 2011). The largest of these bays is Placentia Bay (Figure 2, 4). In addition to marine impacts on the bay, Placentia Bay is also influenced by catchment rivers. The two sampled in this study were Piper's Hole River and Come by Chance River. These catchment rivers are supplied by the drainage of the surrounding peatlands and streams, and they then flow into the bays of Newfoundland (Figure 4; Catto et al., 1999). Newfoundland's expansive network of boreal peatlands, streams, and rivers is similar those found in the rest of eastern Canada. The northern portion of the Labrador and Newfoundland province also contains a vast area of peatlands which drain into catchment rivers and run into the coastal regions (Engstrom, 2018; Gagnon-Poiré et al., 2021; Way et al., 2018). The influence of multiple marine water sources as well as the extreme wind stress and contribution of peatland runoff, present an opportunity to use Placentia Bay as a model system for other subarctic bays in Labrador and Newfoundland.

#### **CHAPTER 3**

#### **METHODS**

Sites in two rivers (Come by Chance River and Piper's Hole River) and two bays (Placentia Bay and Conception Bay) in Newfoundland, Canada, were sampled to determine concentrations of CH<sub>4</sub>, DOC, and dissolved nutrients (Figure 4). Sites the Come by Chance River and Piper's Hole River were sampled in November of 2020 as well as May and June of 2021. Coastal Conception Bay and Placentia Bay sites were sampled in June of 2021. In September of 2021, water from four open bay in Placentia Bay were sampled. Samples were analyzed for CH<sub>4</sub>, dissolved nutrients, and dissolved organic carbon (DOC). Samples collected in May and June of 2021 were also analyzed for silicate (Si), and urea. Samples collected in September of 2021 were analyzed for methane oxidation rates.

#### Sample Collection

All samples for  $CH_4$  concentration and  $CH_4$  oxidation rates were collected headspace free in 1 L PETG bottles according to the methods presented in Rogener et al. (2020). For surface samples, the PETG bottles were fully submerged and capped headspace and bubble free. For samples from 2 m or deeper, samples were collected using a 10 L Niskin bottle fitted with silica tubing for over-filling PETG bottles and capping them headspace free. An EXO2 Multiparameter Sonde was used to document water temperature, salinity, conductivity, depth, turbidity, chlorophyll *a* (Chl. *a*), and dissolved oxygen (DO) content at each site and depth.

In November 2020, six bottles from each river site along Piper's Hole River (PHR1, PHR2, and PHR3) and one in Come by Chance River (CBC1) were collected and shipped to UGA (Figure 4). In September of 2021, sample water in three 1 L PETG bottles and three 250 mL PETG bottles from 2-3 depths at four stations in Placentia Bay (stations 4, 6, 7, and 10) were collected and shipped to UGA. A fishing vessel was used to reach the open bay stations, and a 10 L Niskin bottle was used to collect water from depth. Three of the PETG bottles were designated for measuring nutrient concentrations and methane oxidation rates. The other three were designated for CH<sub>4</sub> concentration measurements. These samples were shipped back to the University of Georgia (UGA) at *in situ* temperature in coolers and processed within 10 days of collection.

In May and June 2021, I collected six 1 L PETG bottles from Come by Chance River, Piper's Hole River, and coastal sites along Placentia Bay and Conception Bay (Figure 4). In addition to collecting six bottles for measuring CH<sub>4</sub> concentration and CH<sub>4</sub> oxidation, samples for measuring dissolved nutrients were collected by passing the sample through a 150 µm nitex mesh into a 5 L bottle. The sample bottles were stored in coolers on ice and were transported back to Memorial University of Newfoundland (MUN) within 8 hours of collection. Nutrient samples were filtered immediately upon return, and 1 L PETGs were stored in cold rooms within 4°C of *in situ* temperature until processing (1-3 days).

#### Nutrient Samples

The sieved nutrient samples processed at MUN were filtered through sterile GF-75 filters  $(0.3 \ \mu m)$  using a vacuum filtration rig within 8 hours of sampling. Filtration volumes ranged

from 50-200 mL depending on turbidity. The filters and filtrate were stored frozen. The filtrate was then used to quantify concentrations of  $PO_4^{3^-}$ , nitrate ( $NO_3^-$ ), nitrite ( $NO_2^-$ ), and urea using a Lachat QuickChem 8500 autoanalyzer according to the methods in (Parsons et al., 1984). Ammonium ( $NH_4^+$ ) concentrations in the filtrate were measured using the salicylate method presented in Bower & Holm-Hansen (1980).

Nutrient samples processed at UGA were processed using different methods than those used at MUN. To collect a subsample for DOC and nutrient analysis, water was filtered through a sample-rinsed 0.2  $\mu$ m Target<sup>®</sup> filter into an acid-washed 60 mL HDPE bottle. Five mL of this filtered sample water was transferred to a 15 mL Falcon tube containing 0.5 mL phenol for immediate analysis of ammonium (NH<sub>4</sub><sup>+</sup>). The rest of the filtered sample was stored frozen for subsequent quantification of dissolved organic carbon (DOC), total dissolved nitrogen (TDN), phosphate (PO<sub>4</sub><sup>3-</sup>), total dissolved phosphorous (TDP), nitrate + nitrite (NO<sub>x</sub>), and nitrate (NO<sub>3</sub><sup>-</sup>).

DOC and TDN were measured using a Shimadzu TOC-V<sub>CPH</sub> analyzer coupled to a Shimadzu Instruments TN unit. The DOC standard curve was generated with ACS reagent grade potassium hydrogen phthalate (detection limit of 0.3  $\mu$ M, (Suzuki, 1993)). The TDN standard curve was generated with ACS reagent grade glycine (detection limit of 0.4  $\mu$ M; Suzuki, 1993). The molybdate blue colorimetric method was used to measure PO<sub>4</sub><sup>3-</sup> (detection limit of 160 nM; Strickland & Parsons, 1972) on a Shimadzu spectrophotometer model UV-1601. Solutions of ASC reagent grade potassium orthophosphate were used to create a standard curve. TDP samples were prepared according to the methods in (Solórzano & Sharp, 1980). First, 0.1 mL MgSO<sub>4</sub> was added to a 5 mL samples and then the samples were heated at 90 °C so they could evaporate. The evaporated samples were then combusted at 500 °C overnight. Then 1.5 mL of 38% hydrochloric acid (HCl) was added, and the vials were allowed to sit at 80 °C for 2 hours. Finally, the samples were brought back up in ultra-purified water and again heated at 80 °C for 1 hr. The molybdate blue colorimetric method was then used to determine concentration (Strickland & Parsons, 1972). Standard solutions made with ASC reagent grade potassium orthophosphate were subjected to the same treatments to generate a standard curve.

The phenol hypochlorite method was used to measure  $NH_4^+$  concentration. Absorbances were determined using the Shimadzu spectrophotometer model UV-1601. ACS grade ammonium chloride was used to generate a standard curve (detection limit of 100 nM, Solórzano, 1969). Nitrite concentrations were determined using the sulfanilamide and N-(1-naphthyl) ethylenediamine colorimetric method (Grasshoff et al., 1983; Parsons et al., 1984). ACS grade NaNO<sub>2</sub> reagent solutions were used to create a standard curve (detection limit of 50 nM). A chemiluminescence method was used to measure NO<sub>x</sub> concentrations using an Antek 7050 nitric oxide detector. Samples were reduced to nitric oxide using acidic vanadium III (detection limit of 150 nM, Braman & Hendrix, 1989). I ran two sub-samples and averaged their peaks for each sample. A standard curve for  $NO_3^-$  was made using ACS reagent solution of KNO<sub>3</sub>. Nitrate concentration was determined by subtracting the  $NO_2^-$  concentration from the total  $NO_x$  concentration.

#### Methane Concentrations

The remaining three 1 L PETG bottles were used to measure CH<sub>4</sub> concentration using a sonication/vacuum gas extraction method (Lammers & Suess, 1994; Schmitt et al., 1991). The gas was extracted from 500 mL of sample water and then stored in 20 mL brine vials, where brine was displaced with the extracted gas sample (Blount & Price, 1982). The volume of gas

recovered was recorded. A 0.25 mL gaseous subsample was analyzed using a gas chromatograph (GC; model 8610C, SRI<sup>®</sup> Torrance, California). The GC contained a HP-PLOT AI2O3S column (19095P-S25E) and a flame ionization detector. Sample concentrations were determined using a standard curve generated from certified gas mixtures (Airgas Specialty Gases). Standard curves run while at MUN were developed by injecting different volumes (100  $\mu$ L, 250  $\mu$ L, and 500  $\mu$ L) of a 50 ppm CH<sub>4</sub> standard (Praxair Specialty Gases). In the case of samples sent back to UGA, varying injection volumes (100  $\mu$ L, 250  $\mu$ L, and 500  $\mu$ L) of a 100 ppm CH<sub>4</sub> standard were used to create a standard curve (Airgas Specialty Gases).

#### **Predicted Equilibrium Concentrations of Methane**

I used the CH<sub>4</sub> concentrations I measured and the most recently reported atmospheric mole fraction of CH<sub>4</sub> (1,908 ppb; Dlugokencky, 2022) to calculate the CH<sub>4</sub> concentration predicted from equilibrium with atmospheric CH<sub>4</sub> in the surface water at every site (Table 1). According to Henry's law, the solubility of a gas is dependent on the salinity and temperature of the solution as well as the partial pressure of the gas. Therefore, the concentration of a dissolved gas at atmospheric equilibrium (C\*) is equal to the partial pressure of the gas (P) multiplied by the Bunsen coefficient ( $\alpha$ ), which takes into account the temperature and salinity of the water (Eq. 6; Wiesenburg & Guinasso, 1979; Yamamoto et al., 1976). To calculate  $\alpha$ , I used the equation presented in (Wiesenburg & Guinasso, 1979) (Eq. 7), where S‰ is the salinity of the water, and T is the temperature in Kelvin of the water. A<sub>i</sub> and B<sub>i</sub> are constants determined specifically for the solubility of CH<sub>4</sub> (Wiesenburg & Guinasso, 1979). I then divided the measured concentration of CH<sub>4</sub> at each site ([CH<sub>4</sub>]<sub>m</sub>) by the calculated CH<sub>4</sub> concentration of the

water at atmospheric equilibrium ( $[CH_4]_{eq}$ ), which equals the percent atmospheric equilibrium of the surface water at each site (% atm eq.; Eq. 8).

Equation 6  $C^* = \alpha \times P$ Equation 7  $\ln(\alpha) = A_1 + A_2(100 / T) + A_3 \ln(T/100) + S_{\infty}^{\infty} [B_1 + B_2(T / 100) + B_3(T / 100)^2]$ Equation 8 % atm eq. =  $[CH_4]_m / [CH_4]_{eq} * 100$ 

#### <sup>3</sup>*H*-*CH*<sup>4</sup> Isotope Methane Oxidation Rate

I determined rates of CH<sub>4</sub> oxidation using tritiated CH<sub>4</sub> (<sup>3</sup>H-CH<sub>4</sub>; Eq. 9) for samples collected in November 2020 and September 2021 that were shipped to UGA. This method was published previously (Carini et al., 2005; Crespo-Medina et al., 2014). I used silica tubing and an open-bore 60 mL syringe to distribute sample water into 16 mL Hungate tubes. I capped the Hungate tubes headspace free using Labco® septum and screw caps. I amended triplicate samples from each site/depth (plus killed controls) with a trace amount of <sup>3</sup>H-CH<sub>4</sub> (~20,000 Bq). Killed samples were spiked with 37% formaldehyde (1.6 mL) before tracer addition. Equation 9 <sup>3</sup>H-CH<sub>4</sub> + 2O<sub>2</sub>  $\rightarrow$  CO<sub>2</sub> + 2 <sup>3</sup>H-H<sub>2</sub>O

All samples were incubated within 4 °C of *in-situ* temperature. River samples collected in November 2020 were incubated at 4 °C for 50.4 hours, and bay samples collected in September 2021 were incubated at 12 °C for 37 hours. The Hungate tubes were subsampled to quantify initial tracer counts by transferring 100  $\mu$ L of <sup>3</sup>H-CH<sub>4</sub>-amended sample to 1 mL glass vial filled with scintillation cocktail and capping the vial headspace free. Radioactivity was quantified using a Perkin Elmer Tri-Carb 2910 TR liquid scintillation counter. The remaining sample was then transferred to a 20 mL scintillation vial amended with 2 mL of 37% formaldehyde to halt biological activity. A purging manifold passed a hydrated N<sub>2</sub> gas stream through each sample to remove residual <sup>3</sup>H-CH<sub>4</sub>. Samples were purged for at least 1 hour. Once purged, 5 mL of killed sample was added to a 20 mL scintillation vial and scintillation fluid was added to fill the vial. Later, samples were counted on the scintillation counter. The counts from the scintillation counter are first blank corrected by subtracting the average blank count (scintillation fluid only) from the initial and final counts of the samples. The counts from the killed samples are then subtracted from the blank corrected counts, and the result is divided by the blank corrected initial count. This provides an alpha value. Dividing alpha by the number of days the sample was incubated results in *k* (d<sup>-1</sup>), a fractional turnover rate constant. The CH<sub>4</sub> oxidation rate was then determined by multiplying *k* by the [CH<sub>4</sub>] for that site and depth (Eq. 10, 11).

Equation 10 k = (activity of oxidation product/total initial activity) / time

Equation 11  $MOx = k[CH_4]$ 

#### <sup>13</sup>C-CH<sub>4</sub> Methane Oxidation Rates

For water samples collected in May and June of 2021, a  ${}^{13}$ C-CH<sub>4</sub> isotope tracer method was used to estimate methane oxidation rates based on the methods presented in previous studies (Oswald et al., 2015; Saarela et al., 2020; Uhlig & Loose, 2017). Water from 1 L PETG bottles was distributed into 36 mL serum vials using a large sterile open-bore plastic syringe and silica tubing. At the start of the incubation, the vials were injected with 1.2 mL of saturated  ${}^{13}$ C-CH<sub>4</sub> solution. Triplicate amended samples, an amended killed sample, and an unlabeled sample (no  ${}^{13}$ C addition, only water) were included for each time point. Time-one and time-two bottles were placed in a dark incubator within 4 °C of *in-situ* temperature. Time-zero samples were collected by pulling 5 mL of aqueous sample from the 36 mL vial and injecting it into an 11- or 15-mL serum vial purged with nitrogen. The smaller serum vials were used, so subsamples could be more easily shipped back to UGA for analysis. The subsamples were killed with 100  $\mu$ L saturated zinc chloride solution (ZnCl<sub>2</sub>). After allowing the ZnCl<sub>2</sub> to take effect for 24 hours, the samples were preserved by adding 250  $\mu$ L of 8 M base. I used mock samples with Come by Chance River water to see how much 8 M base was required to reach a pH of ~8. Time-one and time-two samples were subsampled and preserved in the same manner.

Once back on UGA's campus, the <sup>13</sup>C-CH<sub>4</sub> oxidation samples were acidified with 150  $\mu$ L of 18 M sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) to drive the <sup>13</sup>C-CO<sub>2</sub> into the headspace. In order to test the effectiveness of acidification, I made mock samples with leftover river water. I spiked them with ultra-purified water (in place of the CH<sub>4</sub> solution) and then added 1.2 mL of NaOH. I then added the 150  $\mu$ L of 18 M H<sub>2</sub>SO<sub>4</sub> and let them sit for 48 hours. After 48 hours, I measured the pH and found that the mock samples all had a pH  $\leq$  2. I allowed the acidified samples to sit for at least 48 hours before withdrawing 2.5 mL of the headspace and analyzing it on the Picarro G2201-i Cavity Ring Down Spectrometer (CRDS) analyzer. Purged CH<sub>4</sub> free brine was used to displace the headspace sample. All headspace samples were run twice on the CRDS and once on the SRI GC-FID to check for consistent CH<sub>4</sub> concentrations.

#### <sup>13</sup>C-CH<sub>4</sub> Oxidation Rate Calculations

To calculate potential turnover rates from the  ${}^{13}$ C-CH<sub>4</sub> stable isotope data, I attempted to calculate the change in concentration of  ${}^{13}$ C-CO<sub>2</sub> over time. The CRDS provided  ${}^{13}$ C-CO<sub>2</sub> concentrations in units of parts per million (ppm). I corrected for the dilution of the injection

chamber by dividing the injection volume in liters ( $V_{inj}$ ) by the injection chamber volume in liters (0.02 L) and multiplying that value by the measured mole fraction of <sup>13</sup>C-CO<sub>2</sub> in ppm ( $P_m$ ; Eq. 12). This resulted in the mole fraction of <sup>13</sup>C-CO<sub>2</sub> in ppm of the injected headspace ( $P_{HS}$ ). Using the Ideal Gas Law, I converted the mole fraction of <sup>13</sup>C-CO<sub>2</sub> in ppm to moles. In the injected volume ( $n_{inj}$  Eq. 13, R = 0.0821 liter atm/mol·K, T = 293 K). Then, I multiplied the number of moles injected by the fraction of the injected volume to the headspace volume ( $V_{HS}$ ) to get the total number of moles of <sup>13</sup>C-CO<sub>2</sub> in the headspace ( $n_{HS}$ , Eq. 14). Assuming that all the <sup>13</sup>C-CO<sub>2</sub> was in the headspace, I divided the number of moles in the headspace by the aqueous sample volume ( $V_{aq}$ , in liters, Eq. 15). This provided the molar concentration of <sup>13</sup>C-CO<sub>2</sub> in the initial sample ([<sup>13</sup>C-CO<sub>2</sub>]<sub>sample</sub>). I then subtracted the molar concentration of <sup>13</sup>C-CO<sub>2</sub> in the initial sample ([<sup>13</sup>C-CO<sub>2</sub>]<sub>TO</sub>) from the molar concentration of <sup>13</sup>C-CO<sub>2</sub> in the later time point samples ([<sup>13</sup>C-CO<sub>2</sub>]<sub>Tf</sub>) and divided this value by the incubation time in days ( $d_{inc}$ , Eq. 16). The final result should be the potential rate of product accumulation in units of moles per liter per day.

- Equation 12  $(0.02 \text{ L} / \text{V}_{inj}) * P_m = P_{inj}$
- Equation 13  $n_{inj} = (P_{inj} * V_{inj}) / RT$
- Equation 14  $n_{HS} = n_{inj} * (V_{inj} / V_{HS})$
- Equation 15  $[^{13}C-CO_2]_{sample} = n_{HS} / V_{aq}$
- Equation 16  $[^{13}C-CO_2]_{Tf} [^{13}C-CO_2]_{T0} / d_{inc}$

#### **Statistics**

I conducted the statistical analysis using the dyplr package in the R programing software (Wickham et al., 2022). I used a one-way analysis of variance test in R to compare the difference in means among, sites, depths, and time points for the various data sets. In some cases, I used

Tukey's Honest Significant Difference test to determine which differences between groups were significant. In addition, I used principal component analysis to justify the different groupings among sites and sampling time periods.
#### CHAPTER 4

#### RESULTS

#### **Defining Regions and Sampling Periods**

I conducted a principal component analysis of all CH<sub>4</sub> and nutrient data across all sites and depths over the entire sampling period (Figure 5). Principal component one accounts for 30% of the variation in the data and principal component two explains 28% of the variation. Together, they account for 58% of the variation in all data across all sites. The main drivers of principal component one are the day and year the sample was collected as well as NO<sub>2</sub><sup>-</sup> concentration. The main drivers of principal component two are  $HPO_4^{2-}$  and  $CH_4$  concentrations. Based on the PCA analysis of all sites and depths across all sampling periods, there are 6 clearly defined site groups which are used throughout the rest of this paper to compare region dynamics. The groups are defined as rivers 2020, rivers 2021, coast 2020, coast 2021, and open bay. The coast values include measurements from saline river sites as well as dock sites along the coast (< 30 m from the shoreline). All sites sampled in Conception Bay are coastal sites and grouped with the Placentia Bay coastal sites in the PCA plot. Thus, the Conception Bay sites are directly compared to the coastal sites of Placentia Bay. These groupings are utilized throughout the duration of this paper to describe and compare the trends in CH<sub>4</sub> and nutrients throughout the various regions and time periods of sampling more easily and accurately.

## Methane Concentrations

Methane was highest in the peatland (n = 1), lower throughout the river sites (n = 13), and lowest along the coast (n = 10) and in the open bay (n = 11). The average CH<sub>4</sub> concentration at the Peatland site was 21  $\mu$ M and exceeded the atmospheric equilibrium of CH<sub>4</sub> (3.2 nM) by a substantial margin (Figure 6, Table 1). The concentration of CH<sub>4</sub> ranged from 3 to 62 nM across the main stem river sites in May and June of 2021 with an average of 31 nM. Samples collected in the wider portion of the river,  $\sim 100 - 200$  m downstream of the peatland and thus more heavily influenced by the peatland, had a higher average CH<sub>4</sub> concentration of 151 nM. Along the coast, CH<sub>4</sub> ranged from 0 to 9 nM, and had an average of 4 nM. However, one site near the mouth of the bay which had a concentration of 50 nM. In the open bay, CH<sub>4</sub> concentrations remained consistent throughout the water column in September. There was not a significant difference in the concentration of CH<sub>4</sub> between depths at stations 4 (F(2,6) = 0.032, p = 0.968), 6 (F(2, 4) = 0.42, p = 0.683), 7 (F(2, 4) = 0.555, p = 0.613), or 10 (F(1,2) = 1.8, p = 0.312). There was also no significant difference in the  $CH_4$  concentrations among different sites (F(3, 23) = 1.293, p = 0.3). Thus, throughout the water column across all sites the CH<sub>4</sub> concentration remained the same from the deep water to the surface. The average CH<sub>4</sub> across all open bay sites was 5 nM, which is lower than the river sites and comparable to the concentrations measured along the coast. Overall, CH<sub>4</sub> decreased as the water flowed downstream, and was thus leaving the system.

In November 2020, samples shipped to the University of Georgia were analyzed for  $CH_4$  (Sup. Table). the concentration of  $CH_4$  across river sites (n = 2) ranged from 30 to 79 nM and had an average of 59 nM. Whereas coastal sites in November 2020 (n = 3) had  $CH_4$  concentrations ranging from 0 to 89 nM with an average of 30 nM. Variation among  $CH_4$ 

replicates was greater in November than in May or June, but the results of a one-way ANOVA indicate that there was significantly higher CH4 concentrations measured in May and June than in November. Unfortunately, peatland and open bay data was not collected in November.

## Methane Oxidation Rates

Extremely high CH<sub>4</sub> turnover rates were measured across all sites and depths of the open bay sites in Placentia Bay (0.2-0.5 d<sup>-1</sup>; Table 2, Figure 7). This results in turnover times of 2-7 days. Methane oxidation rates ranged from 0.7 to 4 nmol/L/d with an average of 2 nmol/L/d. One-way analysis of variance tests revealed that there was no significant difference among turnover rates (F(3, 29) = 1, p = 0.3) as well as CH<sub>4</sub> oxidation rates (F(3, 29) = 5, p = 0.7) measured across all sites and depths in September 2021. Methane oxidation and turnover rates were unable to be measured in the peatland, rivers, or coastal sites.

## Profile Data

An EXO2 Multiparameter Sonde was used to collect profile data at the open bay sites (Figure 8). According to the temperature profiles at station 4 there was a mixed depth layer of ~40 m, at station 6 there was a mixed depth layer of ~50 m, at station 7 there was a mixed depth layer of ~25 meters, and at station 10 there was a mixed depth layer of ~20 m. The pH at all sites remained at ~8 – 8.5 throughout the water column. Salinity remained at ~34 PSU at every site throughout the water column. There was a chl. *a* max. at ~20m for all sites. At stations 4, 6,

and 7 there was a peak in DOC at the chl. a max. (82 - 88  $\mu$ M; Figure X). The profiles demonstrated a stratified water column.

#### Placentia Bay Nutrients

When compared to the Redfield ratio, the peatland and river sites along the coast of Placentia Bay were P-limited, while the bay sites were N-limited. This was reflected by the concentration of TDN and PO<sub>4</sub><sup>3-</sup> measured in May and June of 2021 (Figure 9). Total dissolved nitrogen was highest at the peatland site (20  $\mu$ M), decreased throughout the main stem of the rivers (12  $\mu$ M), and was lowest along the coast (7  $\mu$ M). There was no significant difference in NO<sub>3</sub><sup>-</sup> (F(2, 68) = 0.4, p = 0.7) among peatland, river, and coastal sites. However, there was more NO<sub>2</sub><sup>-</sup> in the peatland (0.1  $\mu$ M) and river (0.05  $\mu$ M) than in the coastal (0.2  $\mu$ M) or bay (0  $\mu$ M) sites. Phosphate concentrations in the Bay, on the other hand, were higher in the coastal (0.2  $\mu$ M) and open bay (0.5  $\mu$ M) than in the peatland (0.04  $\mu$ M) or river (0.03  $\mu$ M; F(3, 91) = 26 , p < 0.001 ). Both DOC and urea were highest in the peatland and decreased at the river sites. There was 1  $\mu$ M urea measured in the peatland and only 0.5  $\mu$ M urea measured in the river. The average concentration of DOC was 918  $\mu$ M in the peatland and only 542  $\mu$ M in the river. These nutrients reflect the physical and biological processes occurring throughout the system.

I compared nutrients of river and coastal sites between November 2020 and May and June of 2021 (Figure 10). During both sampling periods the TDN was higher at river sites than the coastal sites, but the samples collected in November had higher TDN than the samples collected in May or June. This was also the case for DOC, which was also highest in the river samples collected in November. The sources of nitrogen also appeared to differ between seasons.

In May and June  $NO_2^-$  and  $NH_4^+$  were higher in both the rivers and at the coastal sites. Nitrate was higher in November than in May or June at both the river and the coastal sites. Phosphate was higher in November for both river and coastal sites. Extensive sampling over a broader time period is required to understand the full extent of these seasonal trends.

### Comparing Conception Bay to Placentia Bay

According to the PCA, coastal Placentia Bay sites grouped with the Conception Bay sites (Figure 11). All Conception Bay sites were considered coastal (< 30 m from shore), so this grouping is logical. Both bays were sampled in May and June of 2021. Thus, I compared the CH<sub>4</sub> and nutrients between the coastal sites of Conception Bay and Placentia Bay measured in May and June of 2021 (Figure 12). There were no significant difference in NO<sub>3</sub><sup>-</sup> (F(1, 42) = 21, p < 0.001), NH<sub>4</sub><sup>+</sup> (F(1, 39) = 0.5, p = 0.5), PO<sub>4</sub><sup>3-</sup> (F(1, 49) = 1, p = 0.3), or CH<sub>4</sub> (F(1, 41)=0.1, p = 0.7) between the two bays. However, concentrations of urea (F(1, 29) = 42, p < 0.001), silicate (F(1, 49) = 16, p < 0.001), and NO<sub>2</sub><sup>-</sup> (F(1, 32) = 382, p < 0.001) were higher in Conception Bay than in Placentia Bay. These results can be used to justify comparisons and generalizations across these boreal systems.

#### CHAPTER 5

#### DISCUSSION

The nutrient and CH<sub>4</sub> concentrations measured across marine and freshwater transects in the boreal system of Placentia Bay can be used to infer the movement and processes controlling these concentrations throughout the system. The results of this study provide evidence of the physical and biological controls on CH<sub>4</sub> concentration. They also act as a baseline for this area, from which future studies can utilize these data as a comparison. It is important to understand the dynamics of this potent greenhouse gas throughout various boreal systems to anticipate any potential shifts in these dynamics due to higher temperatures, earlier springs, or eutrophication.

### Peatland

Peatlands are a recognized source of CH<sub>4</sub> to the atmosphere, and the peatland site sampled in this study was not an exception (Abdalla et al., 2016; Lai, 2009; Pelletier et al., 2007; Trudeau et al., 2013). The peatland site had an average CH<sub>4</sub> concentration of 21  $\mu$ M, which is two orders of magnitude greater than the closest downstream site (157 nM, Sup. Table) and was well over that expected from equilibrium with atmospheric CH<sub>4</sub> (3.2 nM, Table 1). However, the CH<sub>4</sub> concentration in this peatland falls within the concentration ranges measured in other boreal peatland systems. A study of dissolved CH<sub>4</sub> in the surface water of a peatland in Québec, Canada demonstrated concentrations of 1 – 450  $\mu$ M (Strack & Waddington, 2008). The main source of CH<sub>4</sub> in boreal peatland systems was anaerobic methanogenesis in sediments; this was probably fueled by high loads of organic C and anoxic conditions (Bräuer et al., 2020; Daulat & Clymo, 1998; Le Mer & Roger, 2001; Pelletier et al., 2007). Thus, the majority of CH<sub>4</sub> at this boreal peatland site was likely the result of anaerobic methanogens. The peatlands of Newfoundland, and other boreal systems, drain into catchment rivers such as Come by Chance River and Piper's Hole River. However, a decrease in the CH<sub>4</sub> concentration a few hundred meters downstream indicates that this CH<sub>4</sub> was significantly diluted, was released to the atmosphere, or was consumed.

I did not measure CH<sub>4</sub> emission into the atmosphere at the peatland site, but multiple studies have found a strong correlation between wind speed and gas flux transfer velocity from estuaries which lacked substantial tree coverage (de Angelis & Lilley, 1987; Jähne et al., 1987; Upstill-Goddard, 2006; Wanninkhof, 1992). Newfoundland experiences the highest wind speeds in Canada (Khan & Iqbal, 2004). Thus, CH<sub>4</sub> in the peatland sampled here may have been emitted to the atmosphere, in part, due to immense wind stress (Barber et al., 1988; Sebacher et al., 1983). This assumption was supported by the efflux rate (~3 g CH<sub>4</sub> m<sup>-2</sup> yr<sup>-1</sup>) measured at a peatland site in northwest Newfoundland by Wang et al., 2018, which was less than the emission rate measured in a peatland in the Hudson Bay Lowlands (HBL) (8.44g CH<sub>4</sub> m<sup>-2</sup> yr<sup>-1</sup>), but still presented a significant source of CH<sub>4</sub> to the atmosphere. However, there was substantial spatial and temporal heterogeneity in CH<sub>4</sub> emissions across northern peatlands (LAI, 2009). Thus, the extent peatlands across Newfoundland impact the CH<sub>4</sub> concentrations in the atmosphere, catchment rivers, and groundwater systems may vary.

In addition to emission at the water-atmosphere interface, high concentrations of  $CH_4$  can diffuse through the vasculature of peatland plants, bypassing the oxic sediment layer, where  $CH_4$  oxidation can occur and providing a direct conduit to the atmosphere (Joabsson et al., 1999). The

vegetation at the peatland site was comprised mostly of water horsetail (*Equisetum fluviatile*). In a previous study, diffusion rates of CH<sub>4</sub> from water horsetail in a boreal lake were as high as 813 mg m<sup>-2</sup> day<sup>-1</sup> in the summer, a rate that depends on the dissolved concentration of CH<sub>4</sub> (Hyvönen et al., 1998). Schimel, 1995 found that plant species was the greatest predictor of CH<sub>4</sub> transpiration from vascular plants when controlling for pore fluid CH<sub>4</sub> concentrations. The CH<sub>4</sub> flux from water horsetail was less than the diffusion rates found in other peatland plant species such as *Typha latifolia* (0.94 g CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup>; Alm et al., 1995; Yavitt & Knapp, 1998) and *Phragmites australis* (4.8 ± 6.0 g CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup>; Alm et al., 1995; Yavitt & Knapp, 1998), but nevertheless the abundance of water horsetail suggests that some portion of CH<sub>4</sub> could be transported from the sediment to the atmosphere via these vascular plants (Alm et al., 1995; Yavitt & Knapp, 1998).

The decrease in CH<sub>4</sub> from the peatland to the river sites likely also results from dilution and possibly some consumption. The river sites, closest to the peatland, were deeper (~2 m, ~1.5 m) than the water overlying the shallow peat ( $\leq 0.5$  m). Thus, as the peat water drained into the pond the concentrations of CH<sub>4</sub> were probably diluted due to the additional sources of water to the pond, such as streams and precipitation. For a significant portion of the CH<sub>4</sub> in the peatland to be consumed, CH<sub>4</sub> oxidation rates at the pond sites would have to be extremely high. As stated previously, the <sup>13</sup>C-CH<sub>4</sub> oxidation rate experiments attempted during the spring sampling period did not produce reliable results. Thus, additional measurements of CH<sub>4</sub> oxidation rates in these river and peatland environments are required to constrain the role of aerobic CH<sub>4</sub> oxidation in the CH<sub>4</sub> dynamics of the peatlands of Newfoundland. Based on results from other systems (Abdalla et al., 2016; Bräuer et al., 2020; Trudeau et al., 2013; M. Wang et al., 2018, 2019), the fate of the CH<sub>4</sub> present at CBC-Marsh was likely emission to the atmosphere via diffusive flux at the surface of the water and via plant vasculature. However, dilution via other water sources and consumption in the water column of the pond and the surface water of the marsh likely also play a role in the reduced concentrations of  $CH_4$  measured in the Come by Chance River compared to the peatland which drains into it (Stanley et al., 2016).

## **River and Coastal Sites**

The two catchment rivers sampled for this study, the Come by Chance River and Piper's Hole River, have decreasing concentrations of CH<sub>4</sub> from the freshwater sites to saline sites in May and June (Figure 5, 10). The sources of CH<sub>4</sub> to the river were most likely diluted CH<sub>4</sub> draining from the peatlands, biological production of CH<sub>4</sub> in the sediment of the riverbed, or diffusion from groundwater CH<sub>4</sub> via the hyporheic zones of the rivers (Stanley et al., 2016). The decrease in CH<sub>4</sub> as the water moves downstream was explained by dilution into a larger body of water, efflux into the atmosphere due to turbulence, and consumption of CH<sub>4</sub> via methanotrophic bacteria in the water column of the river(Sansone et al., 1999). Based on the trends observed here, there was no evidence that drainage of the peatlands via river discharge significantly impacts the CH<sub>4</sub> pool of the bay at large or even the coastal zones of Placentia Bay.

The average nutrient concentrations in the rivers and along the coast of Placentia Bay indicate the capacity of terrestrial run-off to influence the rivers versus the coastal areas (Figure 9). Concentrations of DOC, urea, and TDN all decrease from the peatland to the river to the coastal sites. Terrestrial runoff is a major source of DOC, urea, and N (Bruhn et al., 2021; Khoo et al., 2022; Sutula et al., 2021), and this runoff is diluted in the deeper bodies of water. Khoo et al. (2022) demonstrated that there was increased flocculation of dissolved C with increasing

salinity in the Come by Chance River and Piper's Hole River, the same locations discussed in this study. Thus, there was a high probability that DOC decreased as salinity increased due to the much of the dissolved fraction of carbon becoming particulate material. This could have an impact on CH<sub>4</sub> production as deposition of particulate matter fuels rates of decomposition and thus methanogenesis (Ferry & Lessner, 2008). However, this was not reflected in the data gathered here, since CH<sub>4</sub> concentrations decreased with increasing salinity. It is possible that this pattern resulted from efficient oxidation in the sediment or water column. Thus, the interaction between terrestrial run off and microbial dynamics, as they pertain to CH<sub>4</sub> metabolism, requires further investigation.

In contrast to TDN and DOC, PO<sub>4</sub> was higher at the coastal sites than in the river or peatland. The main source of N to the rivers and coastal areas was organic N due to the lack of inorganic N despite the high TDN concentrations measured at these sites. Previous studies have demonstrated that a large percentage of organic N was actually bioavailable to phytoplankton species (Bronk et al., 2007). Thus, the increase in PO<sub>4</sub> was likely not due to N limitation based on refiled ratio (Redfield, 1960). The increase in PO<sub>4</sub> could be due to an increase in zooplankton grazing from the rivers to the coastal area. It could also be due to additional freshwater sources carrying terrestrial  $PO_4^{3-}$  from urban and agricultural areas into the bay.

#### **Open Bay Samples**

Seasonal stratification plays a role in the nutrient and CH<sub>4</sub> dynamics in Placentia Bay. The mixing of Placentia Bay occurs due to the Labrador Current as well as strong winds. In the summer, wind from the southeast leads to an upwelling zone along the western coast of Placentia

Bay. The upwelling drives cyclonic flow through the rest of the bay (Ma et al., 2012). However, heat flux in the spring and summer results in a more stratified water column. In the fall, as the surface temperature cools, the bay becomes less stratified, and the mixed layer deepens. (Ma et al., 2012). Temperature and salinity profiles from the September sampling period indicated that the water column was still stratified from summer warming (Figure 8). This stratified water column was at odds with the CH<sub>4</sub> concentrations, which were consistent across sites and depths (Figure 7).

Throughout the water column, there was consistent CH<sub>4</sub>, despite extremely high turnover rates of CH<sub>4</sub>. A source of CH<sub>4</sub> input into the system is required to keep up with these high rates of methanotrophy and allow the rapid cycling of the CH<sub>4</sub> pool. High CH<sub>4</sub> production in the sediments of the bay is the first logical source of CH<sub>4</sub> to consider. However, the concentration of CH<sub>4</sub> should decrease at shallower depths in the water column if that were the only source. While production in the sediment almost definitely contributes to the overall CH<sub>4</sub> pool in the bay, there must be an additional source impacting the whole water column. Groundwater and river discharge into Placentia Bay present an opportunity for CH<sub>4</sub> transport from freshwater and terrestrial sources that could fuel high turnover rates. However, based on the riverine and coastal CH<sub>4</sub> concentrations in Placentia Bay, at least in May and June. Therefore, it is possible that groundwater acts as a significant source of CH<sub>4</sub> to Placentia Bay.

Significant CH<sub>4</sub> flux from groundwater has been measured in both the North Pacific (35  $\pm$  27 mg m<sup>-1</sup>d<sup>-1</sup>) and Arctic Ocean (4.1  $\pm$  0.6 – 11.8  $\pm$  3.9 mg m<sup>-1</sup>d<sup>-1</sup>; Lecher et al., 2016). Increases in tidal amplitude drive the flushing of groundwater (Wilson & Morris, 2012), but the estuaries of Placentia Bay are considered microtidal experiencing daily tides of only 2 m (Catto

et al., 1999). However, due to the strong winds acting on Placentia Bay, wind driven changes in water level are probably common and can lead to both higher and lower water levels, as seen in other bays globally (Lin et al., 2017; K. Valentine & Mariotti, 2019; Zhong et al., 2008). These changes in water level could lead to pulses of groundwater discharge into the bay, but currently there are no studies assessing this in Placentia Bay. The temperature and salinity profiles from the four open water sites in Placentia Bay do not indicate that fresh water from rivers had a significant impact on the main stem of the bay, but most groundwater intrusions are actually salty (Moore & Joye, 2021), making groundwater inputs possible and likely in this region.

In the surface water of all four open bay sites,  $CH_4$  concentrations (3.0 – 4.7 nM) exceed atmospheric equilibrium (2.4 – 2.5 nM; Figure 7; Table 1). The high winds of this region may work to strip  $CH_4$  from the surface water (Wanninkhof, 1992). Thus, in September, the diffusive flux of  $CH_4$  from the surface water of Placentia Bay could be significant, due to wind stress acting on surface  $CH_4$  concentrations that are above atmospheric equilibrium (Barber et al., 1988; Sebacher et al., 1983).

#### Conception Bay versus Placentia Bay

I compared the coastal sites of Placentia Bay to those in Conception Bay, a boreal bay on the opposite side of Newfoundland, to determine how the measurements compare across boreal systems. The water in Conception Bay is heavily influenced by the Labrador current which derives its water from the Labrador Shelf. In addition, the coastal area around Conception Bay is more heavily populated than Placentia Bay and includes urban areas as well as agricultural land. Conception Bay also receives icebergs annually from the Labrador Sea which can contribute to

the overall nutrients, microorganisms, and freshwater input into the bay (Marson et al., 2021; Smith et al., 2007). Placentia Bay is located on the southern side of Newfoundland and is thus influenced by the hydrocarbon seeps along the Grand Banks of Newfoundland and water from the Gulf of St. Lawrence. Placentia Bay does not receive any icebergs, and its coastal areas are not as populated as Conception Bay. However, both of these bays are influenced by discharge from the catchment rivers that drain the peatlands covering a large portion of Newfoundland. Due to the varied influences in these two bays, their comparison provides evidence of the controls on the local CH<sub>4</sub> dynamics across systems.

Methane,  $NO_3^-$ ,  $NH_4^+$ , and  $PO_4^{3-}$  concentrations were not significantly different between bays (Figure 11). Both coastal systems also appear to be N-limited when compared to the Redfield ratio (Redfield, 1934, 1960). This implies that the microbial dynamics may be similar between the two bays, and that the local boreal system may have greater control over the CH<sub>4</sub> and nutrient dynamics in the bays than the greater marine sources of water flowing into them. This could provide support for generalizing the CH<sub>4</sub> dynamics in the Placentia Bay system across other boreal bays.

Overall, the two bays were very similar, but the greater urbanization of Conception Bay was apparent in nutrient measurements. Runoff from the coast of Conception Bay was most likely responsible for the higher Si, urea, and NO<sub>2</sub><sup>-</sup> compared to Placentia Bay. The higher concentrations of both urea and NO<sub>2</sub><sup>-</sup> could be the result of human produced sewage or livestock and fertilizers. The higher silicate could be the result of fewer diatoms populating the microbial community in Conception Bay. Future studies are needed to elucidate the full extent of urban run-off and its impacts on Conception Bay.

Nutrient and CH<sub>4</sub> data across multiple coastal sites in Conception Bay and Placentia Bay demonstrate similar concentrations and trends (Figure 11). Despite the more urban coastal area surrounding Conception Bay there was no significant difference between CH<sub>4</sub> concentrations and most nutrient concentrations. The observed patterns of CH<sub>4</sub> dynamics in Placentia Bay may be transferable to other boreal bay systems. Boreal ecosystems act as significant reservoirs of C boreal carbon. They are highly susceptible to climate change due to arctic amplification in northern latitudes (Gorham, 1991; Jonsson et al., 2007; Stralberg et al., 2020). Therefore, Placentia Bay could potentially act as a model system for other boreal coastal systems across the world. The data presented here can act as a baseline for future studies on C and CH<sub>4</sub> dynamics in this region.

Understanding current CH<sub>4</sub> dynamics is vital for constraining the global CH<sub>4</sub> budget and how that budget may shift as temperatures, currents, and weather patterns change due to global climate change. Further sampling in the open water of Conception Bay and in the tributaries of Conception Bay would further elucidate an accurate comparison of these two systems over time. However, based on the summer data presented here, Placentia Bay could provide a framework for what may occur in other boreal regions that are rapidly changing due to earlier springs and warmer summers.

#### Seasonal Differences

Differences in nutrient concentrations between November 2020 and June and May 2021 show seasonal shifts in the nutrient dynamics of the Come by Chance River and Piper's Hole River (Figure 10). There was an apparent shift in the source of N at both river sites and coastal

sites between November and May and June. In November the more abundant source of N was NO<sub>2</sub> while in May and June it was NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>. This could be due to the grazing of zooplankton that occurs in the spring in boreal systems. Sloppy feeding and fecal excretion via zooplankton recycle NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> into the water (Attayde & Hansson, 1999; Saba et al., 2011). In addition, runoff and atmospheric pollution from nearby agricultural sources may be contributing a significant amount of NO<sub>3</sub><sup>-</sup> in the spring after NO<sub>3</sub><sup>-</sup>-rich fertilizer is applied to the soil (Khan & Mohammad, 2014). This change in nutrient concentrations could result in the overall shift of the microbial community between these two seasons. This was also demonstrated in the difference in CH<sub>4</sub> between seasons. In November there was much greater variability among the CH<sub>4</sub> measured at different sites, so although the maximum CH<sub>4</sub> was greatest in November, the average CH<sub>4</sub> measured across all sites measured in both seasons was higher in May and June.

### Approach and Challenges

The optimal approach for measuring CH<sub>4</sub> oxidation rates is to use a radiotracer because radiotracer methods have a much lower detection limit (Carini et al., 2005; Crespo-Medina et al., 2014). During the May and June sampling period, I was working at MUN, and did not have access to their radioisotope laboratory. I instead tried to implement a stable isotope tracer method using <sup>13</sup>C-CO<sub>2</sub>, similar to those presented in (Oswald et al., 2015; Saarela et al., 2020; Uhlig & Loose, 2017). Unfortunately, the variability in the <sup>13</sup>C-CH<sub>4</sub> oxidation method did not result in any reliable rate measurements. The variability in the <sup>13</sup>C-CO<sub>2</sub> measurements far exceeded the precision required to determine accurate rates. Higher <sup>13</sup>C-CO<sub>2</sub> concentrations in longer incubations would have provided more robust data. Higher concentrations may have been achieved via the addition of higher initial  $^{13}$ C-CH<sup>4</sup> concentrations. For this experiment, I calculated the amount of  $^{13}$ C-CH<sub>4</sub> saturated water to add to the samples to achieve a final concentration of 50  $\mu$ M. However, the measured final concentration of CH<sub>4</sub> for most samples was 13-20  $\mu$ M CH<sub>4</sub>. This mismatch may have resulted from 1) a mistake in the CH<sub>4</sub> addition, 2) a mistake in the calculation, or 3) failure to equilibrate the spiked solution for long enough. The loss in  $^{13}$ C-CH<sub>4</sub> from the solution could have occurred due to degassing during the transition step before I injected the solution into the incubation vial. Bubbles emerged in the incubation vials which indicates degassing during the incubation, possibly due to air entering through the grey rubber septa when the CH<sub>4</sub> was injected. If a large portion of the  $^{13}$ C-CH<sub>4</sub> came out of solution and into this bubble, there would be a reduced amount of labeled substrate for oxidation. Further refinement of this method is required to produce accurate rate measurements in future experiments.

I failed to adequately prepare for these experiments. I did not test the methods in a way that would allow me to fine tune the procedures or optimize the volume of  $^{13}$ C-CH<sub>4</sub> that needed to be added. These methods work well under some conditions, as shown in previous studies (Oswald et al., 2015; Saarela et al., 2020; Uhlig & Loose, 2017), but I was unable to use them successfully. For future experiments, I suggest killing the sample in the 36 mL incubation vial and removing 5 ml of headspace from that vial rather than subsampling 5 mL into a smaller vial to be killed. This will provide a higher mole fraction of  $^{13}$ C-CO<sub>2</sub> in the headspace once the sample is acidified, producing a larger signal. In addition, this removes a transfer step in which gas could be lost from solution. Final  $^{13}$ C-CO<sub>2</sub> concentrations also rely on the CH<sub>4</sub> oxidation rate of the microbial community in the sample. Thus, estimated CH<sub>4</sub> oxidation rates should be taken

into consideration when deciding the concentration of  ${}^{13}$ C-CH<sub>4</sub> to add and the incubation length. Additionally, I recommend testing the assumption that acidification of the killed sample results in all of the  ${}^{13}$ C-CO<sub>2</sub> transferring from the aqueous sample into the headspace. Unfortunately, I did not give myself sufficient time to perform the proper assessments, or optimizations of this method. More time, thought, and testing is needed to produce an accurate method which results in potential rates within a reasonable margin of error.

## Next Steps

Further measurements are required to constrain the contribution of Newfoundland peatbogs to atmospheric, groundwater, and river water CH<sub>4</sub>. More CH<sub>4</sub> concentration and flux measurements in additional peatlands across Newfoundland are needed to determine if there is heterogeneity among peatbogs in Newfoundland, if so, what factors control it, and what proportion of CH<sub>4</sub> is able to reach the atmosphere (LAI, 2009). Chamber experiments, in which CH<sub>4</sub> emissions are measured in areas of vegetated and unvegetated peatland, would further constrain the role of the water horsetail and other common vegetation to Newfoundland on CH<sub>4</sub> emission from peatbogs in this region (Li et al., 2021). Methane oxidation in the shallow water column as well as in the sediment would provide rates of consumption within the peatbog system. These steps will help elucidate the effects that peatlands have on CH<sub>4</sub> in aquatic systems and the coastal systems they influence.

Seasonal trends across the entire system of Placentia Bay and its tributaries would be better elucidated with frequent sampling over the course of several years. These seasonal changes across transects of fresh to saline water could better constrain the impact of river

discharge in Placentia Bay and how this impact could be changing seasonally and over time as global temperatures increase.

Future studies should strive to further unveil the microbial dynamics and transfer of CH<sub>4</sub> across regions of the system. A better understanding of microbial dynamics could be provided via molecular genomic data. Microbial community dynamics are the key to the balance between production and consumption of CH<sub>4</sub> throughout the entire system. In addition, to know how much CH<sub>4</sub> is produced in groundwater sediments or is leached into the groundwater from peatlands, sampling of groundwater is required. Stable isotope measurements of Placentia Bay water can also be used to determine the origin of the CH<sub>4</sub> fueling the high turnover rates in the bay. Methane oxidation rates throughout the water column of the rivers and peatlands would provide evidence of how much CH<sub>4</sub> is consumed. Methane production rates in the sediment of the peatlands, rivers, and bay would account for how much CH<sub>4</sub> is produced locally versus what was contributed from upstream or groundwater sources. Comparison of the data presented here with data from analogous systems could allow this and future findings of Placentia Bay to be assumed across boreal bay systems.

#### CHAPTER 6

#### CONCLUSION

Overall, this study provides an initial assessment of CH<sub>4</sub> concentrations and CH<sub>4</sub> oxidation rates in boreal bay systems. The peatbog measured here demonstrated a high dissolved CH<sub>4</sub> concentration which dissipated quickly as the water moved downstream into the Come by Chance River. Methane concentrations continued to decrease from the river to the coastal areas and into the open bay. High CH<sub>4</sub> turnover rates coupled with consistent CH<sub>4</sub> concentrations throughout the entire water column within Placentia Bay indicate a significant source of CH<sub>4</sub> fueling the high turnover rates. The source of this CH<sub>4</sub> is most likely groundwater discharge. Further research is required to identify key controls on CH<sub>4</sub> dynamics and to account for potential seasonal changes in these dynamics.

Boreal systems around the world present regions of significant C cycling that are currently subjected to rapid climate change (Greene et al., 2008; Stralberg et al., 2020). The consequences of warming on C cycling in these regions, especially C in the form of CH<sub>4</sub>, are extremely pertinent to global climate trends. This study demonstrates a baseline of CH<sub>4</sub> dynamics in boreal systems, for future research to be compared in order to better predict global climate models and develop proper mitigation strategies.

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# **APPENDICES**

## TABLES

Table 1: **Saturation of CH<sub>4</sub> compared to concentration atmospheric equilibrium.** The temperature (Temp K) and salinity (‰) were used to calculate the Bunsen coefficients (α) based on the equation and constants presented in (Wiesenburg & Guinasso, 1979). The equilibrium CH<sub>4</sub> concentration was calculated based on the equation in (Wiesenburg & Guinasso, 1979) and (Yamamoto et al., 1976). Bolded values indicate that saturation exceeds 100%.

September 2021									
Placenita Bay									
Site	Event	Depth (m)	Temp (°C)	Temp (K)	Salinity (‰)	α	Equilibrium [CH <sub>4</sub> ] (nM)	Sample [CH <sub>4</sub> ] (nM)	% Saturation
4	Boat	1.5	15	288	35	0.0307	2.5	4.7	191
6	Boat	1.5	16	289	34	0.0303	2.4	3.7	153
7	Boat	1.5	16	289	34	0.0303	2.4	3.9	158
10	Boat	1.5	15	288	35	0.0307	2.5	3.0	121
May-June 2021									
Come by Chance R	iver and Pi	per's Hole Rive	er						
Site	Event	Depth (m)	Temp (°C)	Temp (K)	Salinity (‰)	α	Equilibrium [CH <sub>4</sub> ] (nM)	Sample [CH <sub>4</sub> ] (nM)	% Saturation
PBSouth	9	2	8	281	35	0.0364	3.0	50	1647
Fox Harbor	9	2	11	285	35	0.0332	2.7	9	314
Arnolds Cove	5	2	8	281	0	0.0457	3.8	4	110
CBC-Delta	10	1.5	8	281	35	0.0363	3.0	0	0
CBC2	7	0	10	283	34	0.0345	2.8	5	181
CBC2	5	0	7	281	34	0.0368	3.0	6	202
CBC1-East	5	0	9	282	0	0.0441	3.6	38	1055
CBC1-East	7	0	16	289	0	0.0381	3.1	32	1050
CBC1-East	8	0	14	287	0	0.0395	3.2	38	1182
CBC1-East	9	0	17	290	0	0.0368	3.0	31	1060
CBC1-Mid	8	0	14	287	0	0.0395	3.2	43	1343
CBC0-East	7	0	15	288	0	0.0385	3.1	20	631
CBC0-East	8	0	18	291	0	0.0359	2.9	24	835
CBC0-Mid	8	0	16	290	0	0.0373	3.0	36	1202
CBC0-West	8	0	17	291	0	0.0366	2.9	23	774
CBC-Pond	7	0	15	288	0	0.0389	3.1	62	1981
CBC-Pond	8	0	16	289	0	0.0376	3.0	148	4889
CBC-Midpond	8	0	16	289	0	0.0374	3.0	157	5207
CBC-Marsh	8	0	14	287	0	0.0394	3.2	20628	646820
PHR1	6	0	10	283	0	0.0430	3.5	5	142
PHR2	6	0	8	281	25	0.0388	3.2	3	87
PHR3	6	2	6	279	32	0.0383	3.2	3	85
Conception Bay									
Site	Event	Depth (m)	Temp (°C)	Temp (K)	Salinity (‰)	α	Equilibrium [CH4] (nM)	Sample [CH <sub>4</sub> ] (nM)	% Saturation
PC-1	2	5	13	286	5	0.0395	3.2	2	69
PC-2	2	25	9	282	25	0.0356	2.9	5	163
CB-1	3	32	8	281	32	0.0368	3.0	0	0
CB-2	3	34	9	282	34	0.0363	3.0	10	327
CB-3	3	25	12	285	25	0.0340	2.8	8	285
CB-4	3	26.5	11	284	27	0.0373	3.1	4	120
November 2020									
Come by Chance R	iver and Pi	per's Hole Rive	er						
Site	Event	Depth (m)	Temp (°C)	Temp (K)	Salinity (‰)	α	Equilibrium [CH <sub>4</sub> ] (nM)	Sample [CH₄] (nM)	% Saturation
PHR1	NA	0	2	275	0	0.0541	4.6	61	1334
PHR2	NA	0	2	275	25	0.0437	3.7	0	0
PHR3	NA	2	2	275	32	0.0431	3.6	119	3271
CBC1-East	NA	0	2	275	0	0.0541	4.6	79	1727
Table 2: **Methane oxidation rates and turnover rates** at three sites along Piper's Hole River (PHR1, PHR2, PHR3), at one site in the Come by Chance River (CBC1), and at the four open bay stations in Placentia Bay (4, 6, 7, 10). Water from the river sites was collected in November 2020, and water from the open bay sites was collected and processed in September 2021.

Placentia Bay - September 2021									
Station	Depth	[CH <sub>4</sub> ] (nM)	MOx Rate (nM $d^{-1}$ )	Turnover rate (d <sup>-1</sup> ) Turnover time (d)					
4	1.5	4.7	2.4	0.5	2.0				
4	35	4.8	1.8	0.4	2.7				
4	69	4.9	0.7	0.2	6.6				
6	1.25	3.7	0.8	0.2	4.7				
6	25	12.2	5.3	0.3	2.3				
6	50	4.6	1.4	0.2	3.2				
7	1.5	3.9	1.3	0.2	3.1				
7	35	5.1	1.7	0.3	3.0				
7	69	5.8	1.8	0.2	3.2				
10	1.5	3.0	0.9	0.2	3.3				
10	69	4.7	1.9	0.4	2.4				
Pipers Hole River and Come by Chance River - November 2020									
Station	Depth	[CH₄] (nM)	MOx Rate (nM d <sup>-1</sup> )	Turnover rate (d <sup>-1</sup> ) Turnover time (d)					

Station	Depth	[CH <sub>4</sub> ] (nM)	MOx Rate (nM d <sup>-</sup> )	Turnover rate (d <sup>-</sup> )	Turnover time (d)
PHR1	0	61	0.34	0.0055	179
PHR2	2	0	BDL	BDL	NA
PHR3	2	119	0.10	0.0009	1144
PHR3	7	30	BDL	BDL	NA
CBC1	0	79	0.45	0.0056	177

## FIGURES



Figure 1: Schematic demonstrating the mechanisms of the CH<sub>4</sub> feedback loop. The items in the yellow circle produce or release more CH<sub>4</sub> under warmer conditions. Before the CH4 is emitted to the atmosphere it has the opportunity to be oxidized by methanotrophic organisms. Any CH<sub>4</sub> not oxidized is released to the atmosphere where it caused further radiative forcing (the greenhouse effect) that drives global warming inducing further CH<sub>4</sub> production and release. Adapted from Dean et al., 2018.



Figure 2: The Island of Newfoundland and the surface currents in the surrounding waters.

Placentia Bay and Conception Bay are highlighted in red.



Figure 3: Aerobic methane oxidation metabolism. Adapted from Bürgmann, 2011.



Figure 4: **Map of Placentia Bay and Conception Bay study sites.** Color indicates the type of site according to the legend. Piper's Hole River (PHR) sites are magnified above the map. Come by Chance River (CBC) sites are magnified to the right. Boat sites were visited via fishing vessel.



Figure 5: **Results of a principal component analysis among all sites sampled in the Placentia Bay system in 2020 and 2021.** Color indicates location of site, and size indicates methane concentration.



Figure 6: Nutrient concentrations across the Placentia Bay system. Includes data from May and June 2021. Area classifications include peatland, river, coast, and bay and were determined via principal component analysis. The label "n.d." indicates that no data was collected for that analyte in that defined area.



Figure 7: **Methane concentrations across the Placentia Bay system.** Areas defined by principal component analysis. Methane concentration is displayed on a logarithmic scale.



Figure 8: Methane concentrations and oxidation rates (MOx) at four open bay sites in Placentia Bay sampled in September 2021. The measurements are presented at every sampled depth in the water column and averaged across sites.



Figure 9: Comparing the concentration of nutrients and methane between seasons in two tributaries of Placentia Bay. Samples were collected and measured in November 2020 (n = 2 (river), n = 3 (coast)) and May and June of 2021 (n = 13 (river), 10 (coast)). Color indicates time of year water was sampled (red = May and June of 2021, blue = November 2020).



Figure 10: **Depth profiles from the four open water stations in Placentia Bay** (stations 10, 7, 6, and 4). Blue indicates salinity (PSU), red indicates temperature (°C), green indicates Chlorophyll *a* (Chl. *a*,  $\mu$ g/L), and orange indicates pH. Measurements were taken using an Exo profiler on September 22<sup>nd</sup> (St. 10 and 7) and September 23<sup>rd</sup>, 2021 (St. 6 and 4). This data is still provisional as it has not undergone the proper quality assurance checks.



Figure 11: Comparing concentrations of methane and nutrients in Placentia Bay (n = 10) to Conception Bay (n = 6). All sites included in these averages are considered coastal sites based on the results of the principal component analysis.

## SUPPLEMENTAL INFORMATION

Sup. Table: Methane and nutrient values from all sites sampled in this study. Two or three replicate bottles were sampled at each site.