

Seasonal Methane Dynamics in Lakes of the Mackenzie River Delta, Western Canadian Arctic

by

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Abstract

Methane (CH_4) dynamics were investigated in lake-waters of the Mackenzie River Delta in 2014 and 2015 to estimate CH_4 emissions and evaluate potential drivers of seasonal CH_4 dynamics. Water-column CH_4 and related variables were measured at end-of-winter and tracked through open-water in up to 43 lakes, plus water-column CH_4 oxidation (MOX) and water-to-atmosphere emissions were measured in 6 lakes. Under-ice CH_4 accumulations were high by end-of-winter, with levels in some lakes greater than 20 years prior. Water-column CH_4 and carbon-quantity are positively related regardless of season, however, relationships between CH_4 and carbon-quality are strikingly different between winter and open-water. CH_4 is inversely related to pH, which, surprisingly, also negatively affects MOX. MOX is highest at ice-out and decreases over open-water. Based on areal-weighted fluxes, Mackenzie Delta lakes emitted 35.79 Gg of CH_4 , with 24% occurring at ice-out, and during open-water 50% and 26% respectively occurring via ebullition and diffusion.

Keywords: methane; methane oxidation; methane emissions; Arctic delta lakes; limnology; biogeochemistry

To Samantha.

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Glossary

λ	Wavelength, expressed in nm throughout thesis
$a(250):a(365)$	Inferred dissolved organic matter molecular weight, where increasing values signify decreasing molecular weight
$a(\lambda)$	Absorbance at the specified wavelength
AIC	Akaike's Information Criterion
AICc	Second order AIC (adjusted for small sample size)
Allochthonous dissolved organic matter	Dissolved organic matter originating from outside the lake
Autochthonous dissolved organic matter	Dissolved organic matter originating from within to the lake
CDOM	Coloured dissolved organic matter
Decadal absorbance	Absorbance at λ divided by cell path length
Diffusion	Movement of gases, and other soluble chemicals, from areas of high concentration to low concentration
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
Ebullition	Bubbling of gases, originating in sediments, through the water column and directly to the atmosphere
Henry's Law of Gases	$C_a = k_H \cdot p$, where C_a is the aqueous concentration of a gas, k_H is the Henry's Law solubility constant for the gas (corrected for water temperature), and p is the partial pressure of the gas
k	Gas transfer coefficient (i.e., piston velocity), used to determine diffusion of gases between atmosphere and water surface
k_{600}	Temperature normalized piston velocity to allow for comparison between gases at different environmental conditions
masl	Metres above sea level
MOX	Methane oxidation
Naperian absorbance	Absorbance at λ multiplied by 2.303 then divided by cell path length
SUVA ₂₅₄	Specific Ultraviolet Absorbance (SUVA) at $\lambda = 254$ nm, where increasing SUVA ₂₅₄ values indicate increasing DOM aromaticity

Chapter 1.

Thesis Overview

1.1. Introduction

Methane (CH_4) is an important component of carbon cycling in the lakes of the Mackenzie River Delta (Figure 1-1). Not only is CH_4 an important greenhouse gas, but it is also an important fuel for food webs in this Arctic ecosystem. The Mackenzie Delta consists of over 45,000 lakes (Emmerton et al. 2007), making it the second largest delta in the circumpolar Arctic. The hydrologic underpinning of Mackenzie Delta lakes has a significant impact on primary productivity in this ecosystem (Squires et al. 2009). During the open-water period, lakes are either continually connected to the river, intermittently connected to the river (during the spring flood), or periodically connected to the river (Figure 1-2) (Mackay 1963, Marsh and Hey 1989). Lakes that are more frequently connected to the river receive greater amounts of suspended sediment, which in turn decreases light availability for photosynthesis (Squires et al. 2002, Squires and Lesack 2003a). Consequently, lakes less frequently connected to the river tend to be the most biologically productive during the open-water period (Squires 2002). Mackenzie Delta lakes can be so productive that most are net carbon dioxide (CO_2) sinks (Tank et al. 2009), whereas lakes globally (Cole et al. 1994) and in Arctic tundra environments (Kling et al. 1991, 1992) tend to be CO_2 sources.

Increases in air temperature are greater in the Arctic than at lower latitudes (ACIA 2005), but the extent to which warming climate affects biogeochemical processes in the Mackenzie Delta is relatively unknown. Climate warming impacts such as increases in ocean water levels and air temperature appear to affect the flooding hydrology (Lesack and Marsh 2007, Lesack et al. 2013) and carbon processing in the Mackenzie Delta (Tank et al. 2009). The majority of lakes in the Mackenzie Delta are affected by thermokarst (melting of permafrost along lake margins or beneath the lake bottom, both of which add permafrost carbon to the lake), so much so that many lakes affected by thermokarst tend to be net CO_2 sources due to these significant inputs of organic matter (Tank et al. 2009, 2011). The CO_2 dynamics in Mackenzie Delta lakes are well understood, however, CH_4 has been previously understudied in this system and the other large delta systems in the circumpolar Arctic. Because increases in CH_4 production tend to coincide with increases in thermokarst (Walter et al. 2007, Sepulveda-Jauregui et al. 2015, Wik et al. 2016), it is essential that careful baselines are established for the CH_4 dynamics of Mackenzie Delta

lakes so that the impact of climate change on carbon cycling in this ecosystem can be more fully understood.

1.2. Research Design

Research 20 years ago found that significant quantities of CH₄ accumulate in Mackenzie Delta lakes under-ice (Pipke 1996), and 10 years ago that open-water CH₄ levels are related to lake productivity (Tank et al. 2009). Generally, a goal of my thesis was to address the hypothesis that the CO₂ absorbed by lakes through in situ photosynthetic production is readily lost as CH₄ (Tank 2009), and that carbon-quality, as affected by the within lake mix (a function of lake closure status) of carbon from photosynthesis, allochthonous DOM, and thermokarst affects the yield of CH₄ in a given lake. Specifically, I endeavoured to address the following questions:

Chapter 2

- Are current levels of under-ice dissolved CH₄ and CO₂ accumulation different than levels observed 20 years ago?
- Does dissolved CH₄ and CO₂ accumulate more in lakes that are greater summertime CO₂ sinks or in lakes known to be impacted by thermokarst?

Chapter 3

- What kind of seasonal variability in CH₄ concentrations occurs during the open-water period, and how are lake closure and CH₄ concentrations related?
- How are seasonal trends in CH₄ concentrations related to dissolved organic matter (DOM)?

Chapter 4

- How is lake closure status related to open-water CH₄ oxidation (MOX) in Mackenzie Delta lakes?
- How is lake closure status related to CH₄ emission from Mackenzie Delta lakes?

Our study lakes consist of the same set of lakes (Table 1-1) where considerable amounts of limnological and biogeochemical studies have been completed. The conceptual frameworks guiding our investigation of CH₄ in Mackenzie Delta lakes are summarized in Figures 1-3 (winter) and 1-4 (open-water).

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1.4. Tables

Table 1-1. Summary of Lakes Investigated in 43 Lake Surveys (LS), the Subset of 6 Lakes From Which Methane Oxidation Was Measured and Where Floating Chambers Were Deployed (6LS), and the Subset of 2 Lakes Where Floating Chambers Were Deployed Throughout Summer 2014 (2LS).

(Following Page)

Lake	Coordinates		Lake Area (ha)	Spring Sill (m)	Winter LS	Early Sum. LS	Mid-Sum. LS	Late Sum. LS	6LS	2LS
	North	West								
L302a	68° 21.012'	133° 47.368'	853.0	1.500	X	X	X	X		
L15a	68° 20.513'	133° 48.437'	437.6	2.177	X	X	X	X		
L4	68° 20.015'	133° 53.978'	330.5	2.363	X	X	X	X		
L129	68° 18.238'	133° 51.145'	37.8	2.363	X	X	X	X	X	X
L85a	68° 18.982'	133° 51.552'	50.6	2.363	X	X	X	X		
L80	68° 19.428'	133° 52.160'	19.3	2.631	X	X	X	X	X	
L501	68° 20.254'	133° 43.529'	126.9	2.631	X	X	X	X		
L148a	68° 16.928'	133° 50.517'	28.4	2.631		X	X	X		
L302b	68° 19.492'	133° 48.707'	18.9	2.631			X	X		
L79a	68° 19.393'	133° 53.078'	34.6	2.631				X		
L107	68° 18.041'	133° 52.404'	16.7	2.990	X	X	X	X		
L272	68° 18.772'	133° 47.680'	27.3	2.990			X	X		
L300	68° 18.900'	133° 49.630'	34.4	2.990	X	X	X	X		
L301a	68° 19.487'	133° 47.755'	36.6	2.990			X	X		
L85b	68° 19.289'	133° 51.747'	1.7	2.990	X	X	X	X		
L58	68° 19.784'	133° 52.049'	13.7	3.389				X		
L87	68° 19.015'	133° 52.460'	3.9	3.389	X	X	X	X	X	
L141	68° 17.878'	133° 50.090'	17.2	3.389	X	X	X	X		
L511	68° 19.763'	133° 43.617'	1.6	3.389	X	X	X	X		
L148b	68° 17.098'	133° 52.062'	94.8	3.389		X	X	X		
L111	68° 17.964'	133° 53.095'	5.3	3.671	X	X	X	X		
L184	68° 17.773'	133° 53.662'	17.7	3.671	X	X	X	X		
L272b	68° 18.747'	133° 46.492'	2.1	3.671			X	X		
L11	68° 20.612'	133° 52.864'	105.4	3.838		X	X	X		
L280	68° 19.248'	133° 50.375'	2.4	3.838	X	X	X	X	X	X
L538	68° 18.568'	133° 45.843'	37.9	3.838	X	X	X	X		
L131	68° 18.065'	133° 51.065'	1.2	4.077	X	X	X	X		
L278	68° 18.706'	133° 50.114'	9.8	4.077	X	X	X	X		
L287	68° 19.145'	133° 46.632'	9.8	4.077	X	X	X	X		
L517	68° 19.377'	133° 43.662'	72.9	4.077		X	X	X		
L148f	68° 16.747'	133° 51.307'	12.4	4.077		X	X	X		
L56	68° 19.394'	133° 50.817'	3.1	4.623	X	X	X	X	X	
L115	68° 18.673'	133° 53.980'	2.3	4.623		X	X	X		
L134	68° 18.218'	133° 48.047'	3.4	4.623	X	X	X	X		
L261	68° 17.922'	133° 47.145'	48.5	4.623			X	X		
L275	68° 18.672'	133° 49.112'	5.9	4.768	X	X	X	X		
L520	68° 18.816'	133° 42.854'	0.2	4.913	X	X	X	X	X	
L522	68° 19.257'	133° 41.518'	22.5	4.913	X	X	X	X		
L143	68° 17.425'	133° 50.205'	2.1	5.169	X	X	X	X		
L181	68° 17.298'	133° 53.688'	0.8	5.169	X	X	X			
L186	68° 18.418'	133° 53.840'	1.0	5.169	X	X	X	X		
L521	68° 19.033'	133° 41.802'	0.1	5.169		X	X	X		
L527a	68° 18.957'	133° 43.530'	8.5	5.169	X	X	X	X		

1.5. Figures

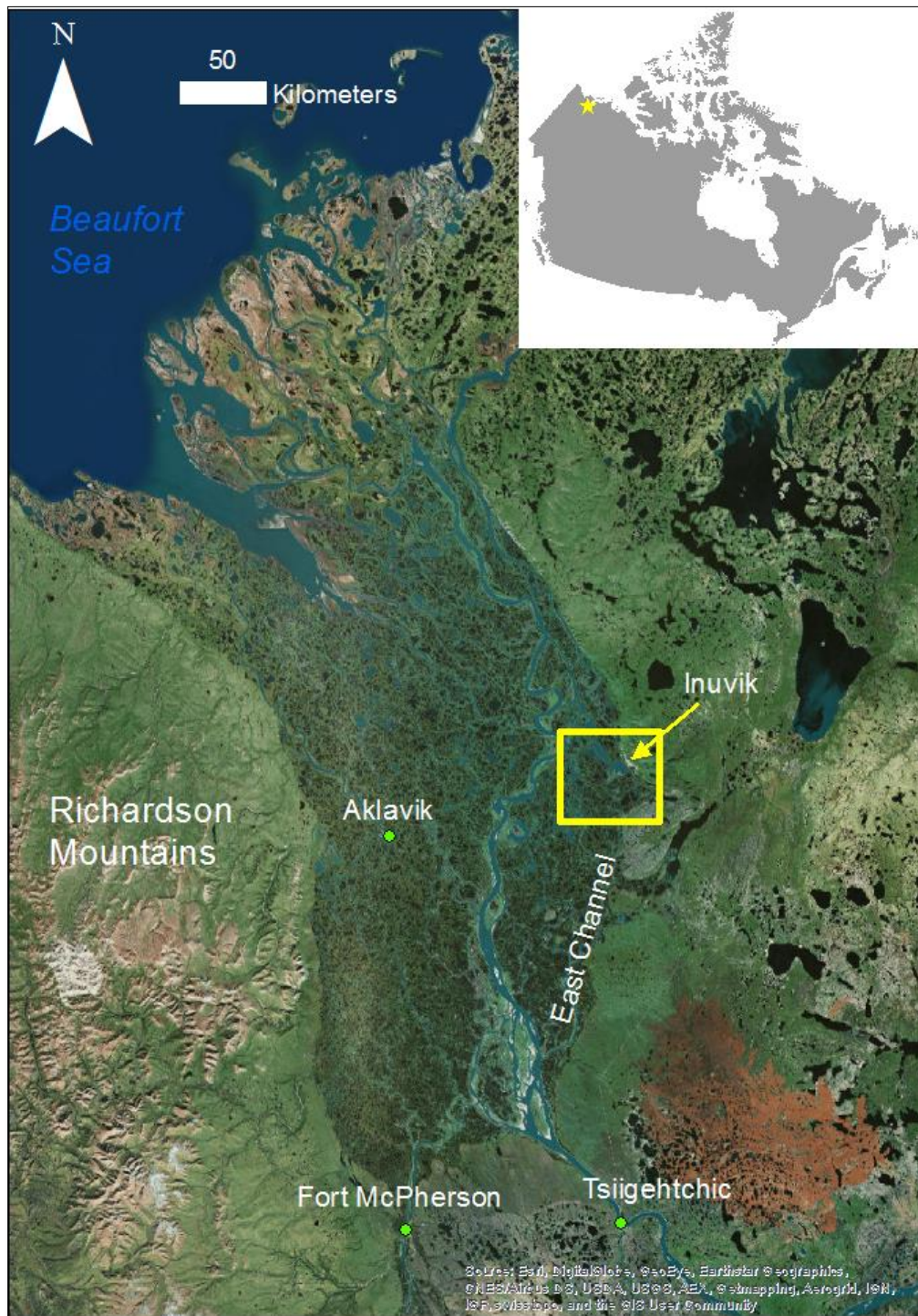


Figure 1-1. Study region (yellow rectangle) within the Mackenzie River Delta (star on inset map).

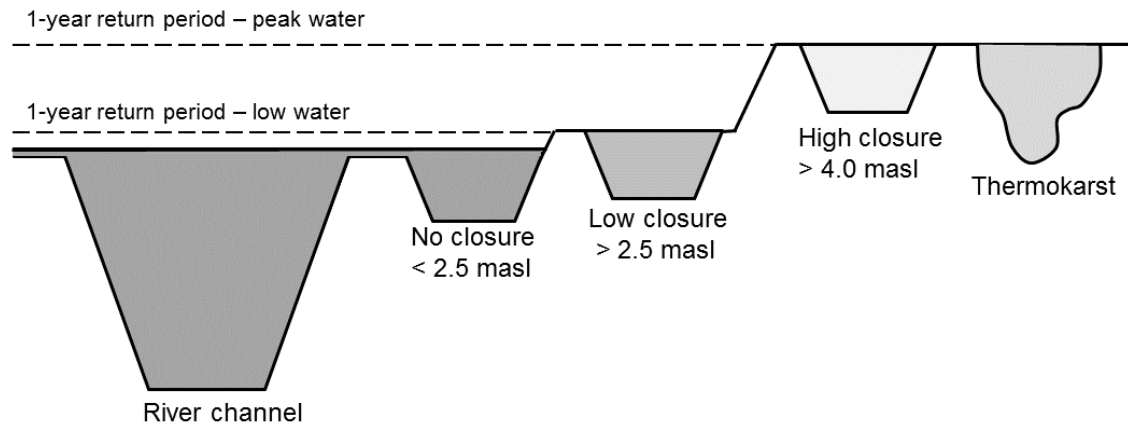


Figure 1-2. Conceptual diagram of Mackenzie Delta lakes.

Modified from Lesack and Marsh (2010) and Tank et al. (2009). Thermokarst lakes are shown as a subset of high closure lakes, both of which are comparatively higher in elevation than low and no closure lakes. As per Mackay (1963) and Marsh and Hey (1989), higher closure lakes are only flooded in intermittent years during peak water levels in the Mackenzie River. Rising river levels during the spring flood allow for annual lake-river connection in low closure lakes, where the connection is broken when river water levels recede in the summer. No closure lakes are connect to the river for the majority of the year.

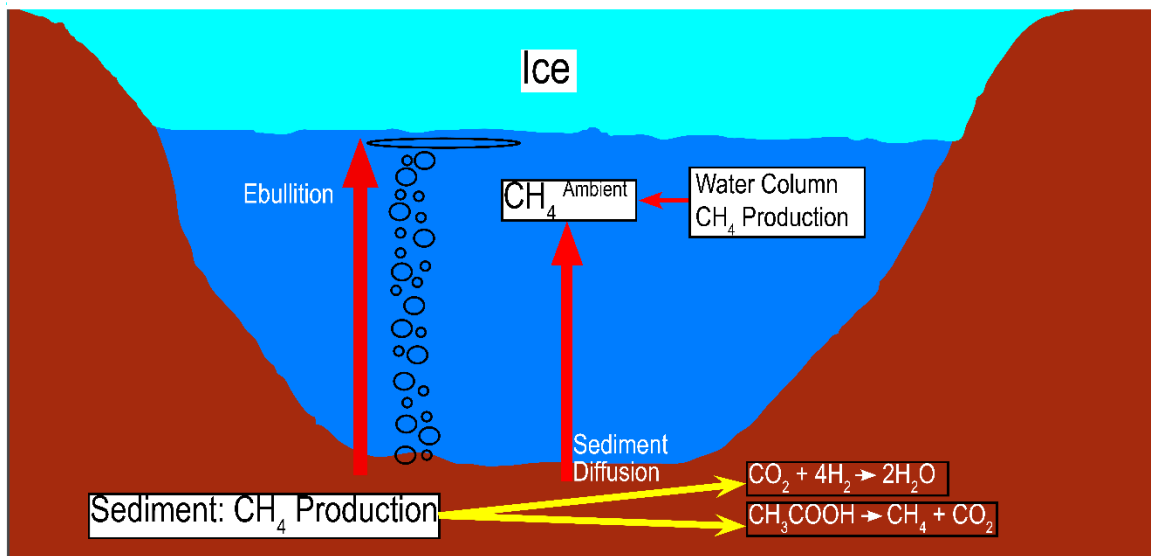


Figure 1-3. Under-ice concept of methane in Mackenzie Delta lakes.

Under-ice ambient CH_4 is the accumulation of CH_4 produced in anoxic sediments and the anoxic water column. Sediment CH_4 enters the water column by diffusing through the sediment-water interface. Under-ice water is generally non-mixing, therefore water column CH_4 production may occur with horizontal and vertical heterogeneity. CH_4 ebullition (i.e., bubbles) can occur throughout the winter: approximately 20% of the bubbles are incorporated into newly forming ice, and the remaining 80% dissolve into the water column (Greene et al. 2014).

$$\text{CH}_4^{\text{Sediment Production}} = \text{CH}_4^{\text{Emission}} + \text{CH}_4^{\text{Oxidation}}$$

$$\text{CH}_4^{\text{Emission}} = \text{CH}_4^{\text{Ebullition}} + \text{CH}_4^{\text{Diffusion (water-air)}}$$

$$\Delta\text{CH}_4^{\text{Storage}} = \text{CH}_4^{\text{Gains}} - \text{CH}_4^{\text{Losses}}$$

$$\text{CH}_4^{\text{Gains}} = \text{CH}_4^{\text{Sediment Diffusion}}$$

$$\text{CH}_4^{\text{Losses}} = \text{CH}_4^{\text{Diffusion (water-air)}} + \text{CH}_4^{\text{Oxidation}}$$

$$\text{CH}_4^{\text{Sediment Diffusion}} = \Delta\text{CH}_4^{\text{Storage}} + \text{CH}_4^{\text{Diffusion (water-air)}} + \text{CH}_4^{\text{Oxidation}}$$

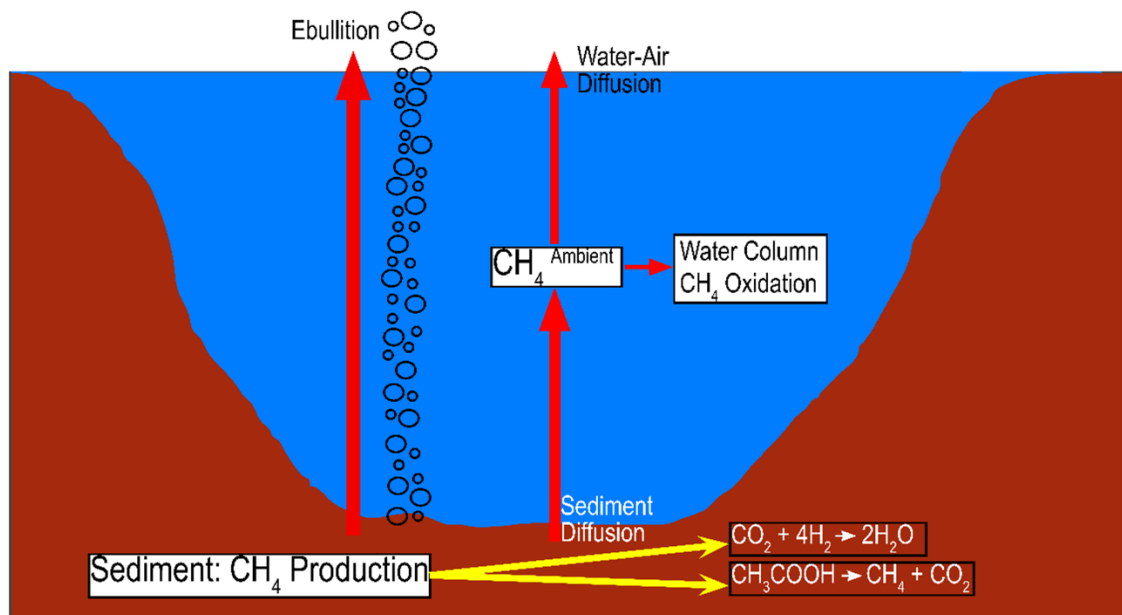


Figure 1-4. Open-water concept of methane in Mackenzie Delta lakes.

Emission of CH_4 occurs through ebullition (bubbles), diffusion, and vegetation in open-water conditions. In mixed lakes that are well aerated, such as expected in lakes in the Mackenzie Delta, Northwest Territories, methanogenesis occurs in anoxic sediments. CH_4 through vegetation (not annotated in figure) is beyond the scope of this study, so was not measured. CH_4 produced in sediments that becomes ebullition escapes oxidation. CH_4 diffusion from the water to the atmosphere is the balance of dissolved CH_4 produced in the sediments and that which escapes oxidation at the sediment-water interface and in the water column. Consequently, diffusion of CH_4 from the sediment into the water column (i.e., $\text{CH}_4^{\text{Gains}}$) can be determined as the balance between the change in storage of water column dissolved CH_4 and losses of CH_4 from the water column (i.e., $\text{CH}_4^{\text{Losses}}$, which consists of water column CH_4 oxidation and diffusion of CH_4 from the water column to the atmosphere).

Chapter 2.

Under-Ice Methane Accumulation in Mackenzie Delta Lakes

2.1. Introduction

The Mackenzie Delta is a dynamic hydrologic system located in the western Canadian Arctic (Figure 2-1). With over 45,000 shallow lakes (mean depth 1.5 m) it is the second largest river delta system (by surface area) draining into the Arctic Ocean (Emmerton et al. 2007). Global climate changes such as rise in sea level and decline in effects of river-ice breakup (i.e., decrease in lake-river connection times in higher elevation lakes) are expected to greatly impact the Delta and other Arctic floodplains (ACIA 2005, Lesack and Marsh 2007). The Mackenzie Delta experiences ice cover 7-8 months each year, and the open-water season takes place from June-October (Emmerton et al. 2007). Mackenzie Delta lakes are surrounded by permafrost, which prevents input of water from subsurface and groundwater flows, and have small catchments that limit input from precipitation (Marsh 1991). The spring flood is the dominant hydrologic event in the Delta. Meltwater from warm southern reaches of the Mackenzie River flow north to the ice-covered Delta causing water levels to rise very quickly and flooding to occur (Mackay 1963, Marsh and Hey 1989). Not all lakes receive the same influx of water because Mackenzie Delta lakes occur at different elevations, and this difference of elevation between a lake and the Mackenzie River limits the influx of floodwater (i.e., river connectivity) (Mackay 1963, Emmerton et al. 2007, Lesack and Marsh 2010).

2.1.1. Delta Hydrology as a Driver of Primary Production

Three general types of lakes have emerged along the elevation gradient in the Mackenzie Delta: no closure lakes (lowest elevation), low closure lakes, and high closure lakes (Figure 1-2) (Mackay 1963, Marsh and Hey 1989). No closure lakes are continually connected to the river, low closure lakes are annually connected to the river during flooding, and high closure lakes are connected to the river in intermittent years (Mackay 1963, Marsh and Hey 1989, Emmerton et al. 2007). Lake connectivity is a function of lake elevation, where connectivity decreases as elevation increases (Marsh and Hey 1989). Lakes affected by thermokarst (i.e., ice-rich soils that thaw and collapse) are prominent in the Mackenzie Delta due to warming air temperatures, resulting in the thawing and slumping of ice-rich permafrost along lake margins (Kokelj and Burn 2005, Burn and Kokelj

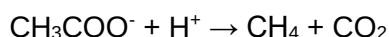
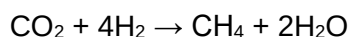
2009). Thermokarst effects tend to be more prominent around high closure lakes than low and no closure lakes (Tank 2009).

The hydrologic underpinning of Mackenzie Delta lakes results in a striking biogeochemical gradient, where lakes that are less frequently connected to the river are more productive and exert unusual gas balances compared to lakes with greater river connectivity. The Mackenzie River carries a high sediment load by the time it reaches the Mackenzie Delta, and during the spring flood sediment is input to the lakes, which decreases water transparency and constrains within lake primary production. Dense mats of submerged macrophytes (e.g., *Potamogeton richardsonii*) are found in Mackenzie Delta lakes (Squires et al. 2002), which are so productive during the long days in the Arctic summer that the lakes tend to be net carbon dioxide (CO₂) sinks (Tank et al. 2009). During the winter, however, the lakes become ideal habitats for methanogenesis (Figure 1-3) (Pipke 1996).

2.1.2. Methane

Methane (CH₄) is a greenhouse gas present in the atmosphere at lesser quantities than carbon dioxide (CO₂), but has a global warming potential (GWP) that is 34 times larger when compared over a 100 year time scale (Myhre et al. 2013). Approximately 25% of atmospheric CH₄ concentration is anthropogenic, while the remaining 75% is produced naturally due to microbial processes (69%) and chemical production from plant material (6%) (Conrad 2009). Lakes are a large source of atmospheric CH₄, emitting 71.6 teragrams (Tg) per year (yr⁻¹) across the planet (Bastviken et al. 2011), where approximately 16.5 Tg is estimated to be emitted by lakes north of 50° latitude (Wik et al. 2016).

CH₄ is produced by Archaea through methanogenesis at the endpoint of organic matter decomposition. Methanogenesis is regulated by substrate availability (e.g., hydrogen (H₂), CO₂, formate (HCOO⁻), acetate (CH₃COO⁻), and methyl compounds), reduction-oxidation (redox) potential, and temperature (Capone and Kiene 1988, Scandella et al. 2011, Chaudhary et al. 2013). The two primary pathways for methanogenesis are the reduction of CO₂ and acetic acid:



where CO_2 reduction is considered the primary methanogenic process. Microbial decomposition of dissolved organic matter (DOM) is the critical process behind methanogenesis (Bertilsson et al. 2013), which occurs in anoxic areas of sediment and water column where redox potential is lowest and pH is high (Michmerhuizen et al. 1996, Segers 1998, Bastviken et al. 2004). Once oxygen (O_2) is depleted, alternate electron acceptors (e.g., nitrate (NO_3^-), manganese (IV) (Mn^{4+}), iron (III) (Fe^{3+}), and sulphate (SO_4^{2-})) are used for organic matter decomposition until sufficiently consumed to allow for CO_2 reduction. Lakes may experience anoxia during prolonged periods of ice cover and yield high levels of under-ice CH_4 and CO_2 accumulation. Addition of organic substrate by thermokarst activity (melting of permafrost) into Arctic lakes due to rising temperatures may result in enhanced levels of methanogenesis (Walter et al. 2006, Walter Anthony et al. 2010, Martinez-Cruz et al. 2015, Sepulveda-Jauregui et al. 2015).

2.1.3. Dissolved Organic Matter

Differential flooding results in a substantial gradient in sources of DOM between Mackenzie Delta lakes. DOM consists of organic molecules derived from decomposing plant and animal material, and is a critical component of the carbon cycle (Lennon et al. 2006, Kritzberg et al. 2006, Tranvik et al. 2009). DOM in aquatic environments is an important substrate for microbial communities, which can mineralize carbon (produce CH_4 or CO_2) or transfer it to higher trophic levels through zooplankton grazing (Bastviken et al. 2003, 2008, Jones and Grey 2011, Sanseverino et al. 2012). As such, microbial communities provide an alternative energy source in food webs to photoautotrophic organisms. DOM is either autochthonous (produced within lake) or allochthonous (terrestrially derived). Autochthonous DOM molecules are less complex than allochthonous DOM (mostly humic and fulvic acids), therefore autochthonous DOM is a more labile substrate (easier to consume) for microbial communities (Kritzberg et al. 2006, Mann et al. 2012). DOM can be measured quantitatively as dissolved organic carbon (DOC) or qualitatively as chromophoric (i.e., coloured) DOM (CDOM). The Mackenzie

River and snowmelt supply lakes with a pulse of allochthonous DOM during the spring flood (Gareis 2007, Tank et al. 2011). Lakes that remain connected to the river are periodically flushed during the ice-free season, which reduces DOC concentration while maintaining turbidity, whereas higher elevation lakes are more likely to retain floodwater DOC and be more transparent because of lower suspended sediment loading (Squires et al. 2009, Tank et al. 2011).

Three sources dominate the supply of DOM in Mackenzie Delta lakes: the Mackenzie River and snowmelt (allochthonous), macrophytes (autochthonous), and thermokarst activity (allochthonous). Macrophyte density and productivity tends to increase with elevation, where high-closure lakes tend to be macrophyte-rich relative to low- and no-closure lakes (Squires et al. 2009). Although macrophyte production is quite high in macrophyte-rich lakes, the elevated concentration of DOC in these lakes may be attributable to its hydrologic isolation and evaporation rather than contribution of macrophyte DOM per se (Tank et al. 2011). Furthermore, primary production by macrophytes is rapid in mid- and late summer, and these lakes tend to act as a sink for CO₂ (Tank et al. 2009). In contrast, thermokarst-affected lakes receive input of terrestrial DOC from thawing and collapse of permafrost along lake margins (Tank et al. 2011) and are net sources of atmospheric CO₂ (Tank et al. 2009). Permafrost is considered a terrestrial C sink, but thawing exposes soil C to degradation and bacterial respiration in lakes (Lennon et al. 2006). Consequently, elevated DOC concentrations in thermokarst-affected lakes are primarily a result of input of soil C from permafrost (Tank et al. 2011).

2.1.4. Objectives

Research 20 years ago has shown that a significant amount of CH₄ accumulates in Delta lakes under-ice during the winter, where lakes least connected to the river tend to accumulate the most CH₄ (Pipke 1996). The objectives of our research were to address the following gaps in our understanding of CH₄ cycling in Mackenzie Delta lakes:

Question 1: Does dissolved CH₄ and CO₂ accumulate more in lakes that are greater summertime CO₂ sinks or in lakes known to be impacted by thermokarst?

Hypothesis: Past measurements indicate that the majority of Mackenzie Delta lakes are net CO₂ absorbers because of intense production by submerged macrophytes, whereas lakes affected by thermokarst tend to continually emit CO₂. Lakes affected by thermokarst are expected to contain more CH₄ and CO₂ than other lakes. Thermokarst lakes are expected to have more CO₂ from bacterial remineralization of less labile DOM, thus fuelling more CH₄ production.

Question 2: How do current levels of under-ice dissolved CH₄ and CO₂ accumulation compare to levels observed 20 years ago?

Hypothesis: Current under-ice levels of CH₄ accumulation in Mackenzie Delta lakes are higher than what was observed 20 years ago. Thermokarst affects most of these lakes to some degree due to warming air temperatures over the past 20 years, where we expect lakes with a higher degree of thermokarst activity along their margins to experience a more significant amount of CH₄ accumulation than in lakes where thermokarst is less prominent.

2.2. Methods

2.2.1. Preparation of Sampling Bottles

Samples for dissolved CH₄ and CO₂ were collected in 160 mL Wheaton serum bottles capped with butyl rubber stoppers that we prepared similarly as others (Hesslein et al. 1991, Hamilton et al. 1994, Pipke 1996, Matthews et al. 2003). We determined empty bottle and stopper mass, added 8.9 g KCl as preservative (to inhibit microbial activity), flushed bottles with zero carbon air (200-500 mL min⁻¹ for 2 min) to remove ambient room CH₄ and CO₂, evacuated bottles (to approximately 27 in Hg for 2 min), and backfilled with 10 mL of zero carbon air to create headspace.

Samples for DOC and CDOM were collected in acid washed 1 L bottles (10% HCl and rinsed 6x with distilled deionized (DDI) water. Samples for chlorophyll *a* and TSS were collected in 1 L bottles that were rinsed 6x with DDI water.

2.2.2. Field Sampling

Since the biogeochemistry and limnology of the subset of Mackenzie Delta lakes investigated by Tank (2009) is better understood than those investigated by Pipke (1996), we sampled the subset of the former. Under-ice sampling took place in 29 randomly selected lakes (Table 2-1, Figure 2-1) of varying sill elevations, split over 2 consecutive days in early May 2014. Lake water was sampled through ice holes, approximately 30 cm in diameter and drilled with an ice auger, using Nalgene tubing connected to a battery powered submersible bilge pump. Tubing was flushed for a minimum 2 min prior to sample collection. When the water column was less than 1 m deep, dissolved gas samples were collected in duplicate at the middle of the water column. If the water column was greater than 1 m, one dissolved gas sample was taken within 0.3 m of sediment-water interface, and another within 0.3 m of the water-ice interface. Dissolved gas samples were collected by submerging serum bottles in a bottom filling container attached to the pump apparatus (open-water gas samples were obtained by gently filling a bucket while lying flat on helicopter floats), then piercing the bottle septum with a hypodermic needle. The needle was carefully removed when water stopped flowing into the bottle (i.e., pressure was equilibrated between the bottle and water), and serum bottles were kept submerged for 5-10 seconds to allow the stopper to reseal. Once the stopper resealed we swirled the bottles to dissolve the KCl. Samples for DOC, CDOM, chlorophyll *a*, and TSS were collected by pumping lake water directly into the prepared 1 L bottles. In situ water temperature, water conductivity, atmospheric pressure, and water depth, and ice thickness and snow depth were measured.

2.2.3. Laboratory Analysis

Headspace gas concentrations were measured by gas chromatography at the Western Arctic Research Centre (Inuvik, Northwest Territories, Canada) using a gas chromatograph (GC; Carle 100 AGC, Ametek Chandler Engineering, Broken Arrow, Oklahoma, USA). The GC was fitted with molecular sieve (packed) 80/100 and Hayesep A 60/80 columns maintained at 70°C, and helium was used as the carrier gas (30 mL min⁻¹). The GC was equipped with a flame ionization detector (FID; using zero carbon hydrogen and air as detector gases) and thermal conductance detector (TCD) to allow

simultaneous measurement of CH₄ and CO₂. Certified gas standards (CH₄: 100 – 250,000 ppm, and CO₂: 5,000 – 300,000) from Scott Specialty Gases (Air Liquide, Plumsteadville, Pennsylvania, USA) were used to calibrate the GC. Serum bottles were placed in a room-temperature (measured with a Hg thermometer) water bath at least two hours prior to analysis, and were shaken vigorously by hand for 30 seconds to ensure equilibration immediately before sampling headspace. Gas samples and standards were never kept in the gastight syringe (VICI Precision Sampling, Baton Rouge, Louisiana, USA) for longer than five seconds before injection (250 µL) into the GC. Standard gases and samples were always injected in duplicate, where only runs producing peak area within 5% were accepted for calibration and sample analysis. DIC was determined by injecting serum bottles with 0.2 mL of H₃PO₄ (85%) so that all CO₃²⁻ and HCO₃⁻ could be measured as CO₂ with the GC.

Water samples for CDOM and DOC were vacuum filtered with 0.22 µm pore size Millipore GPWP filters. Filtered samples were stored in acid washed (10% HCl) bottles refrigerated at 4°C until analysis. DOM spectral qualities were analyzed in Inuvik by performing absorbance scans (wavelength (λ): 250 to 750 nm at 1.0 nm intervals) with a Thermo Fisher Scientific Genesys 10S UV-Vis Spectrophotometer and a 0.05 m quartz glass cell. Samples for DOC were analyzed as non-purgeable organic carbon with a Shimadzu TOC-V (Shimadzu Corporation, Kyoto, Japan). Samples for chlorophyll a were filtered onto Whatman GF/C filters, which were immediately frozen until fluorometric analysis. Samples for TSS were filtered onto ashed and pre-weighed GF/C filters that were reweighed once reaching constant dry weight.

2.2.4. Calculations and Data Acquisition

Dissolved gas concentrations were determined following Henry's Law of gases and accounting for KCl using the Bunsen solubility coefficient for CH₄ (Yamamoto et al. 1976) and Henry's Law constant for CO₂ (Weiss 1974). We corrected for temperature and pressure differences between sampling and analysis, as well as H₃PO₄ addition for DIC samples. Where under-ice gas samples were obtained at two separate depths, reported gas concentrations are the average of the two samples. We used dissolved CO₂ and DIC

concentrations to calculate pH, HCO_3^- , and CO_3^{2-} using respective carbonate equilibrium coefficients (Millero 1995, Stumm and Morgan 1996).

DOM quality is typically characterized by estimating molecular weight and aromaticity (i.e., humic content) from DOM spectral characteristics. We calculated the ratio between the absorbance at $\lambda = 250$ nm to $\lambda = 365$ nm [$a(250):a(365)$] to use as a proxy of DOM molecular weight (Strome and Miller 1978). An increasing $a(250):a(365)$ indicates decreasing molecular weight, and therefore increasing DOM quality. In order to determine DOM aromaticity, we normalized DOC concentrations to decadal absorbances (i.e., $a(\lambda)$ divided by cell path length) at $\lambda = 254$ nm to determine specific ultraviolet absorbance (SUVA_{254}), where increasing SUVA_{254} indicates increasing aromaticity and greater humic acid content (Weishaar et al. 2003). To explore potential DOM outliers, we also modeled DOM spectral slope (S):

$$a(\lambda) = a(\lambda_0)e^{S(\lambda_0 - \lambda)},$$

where $a(\lambda)$ is the naperian absorbance (i.e., $a(\lambda)$ multiplied by 2.303 then divided by cell path length) and λ_0 is a model reference point (we used $\lambda = 330$ nm). We modeled S at two different λ ranges: 275 – 295 nm (i.e., $S_{275-295}$) and 350 – 400 nm (i.e., $S_{350-400}$), and took the ratio of $S_{275-295}$ to $S_{350-400}$ to calculate S ratio (S_R), where increasing S_R indicates lower DOM molecular weight (Helms et al. 2008). CDOM was determined as naperian absorbance at $\lambda = 350$ nm. All spectral absorbances were corrected for scatter by subtracting the average absorbance from 701-750 nm from absorbances measured between 250-700 nm.

Submerged macrophyte density (g m^{-2}) and organic matter content (%) were obtained from Squires et al. (2002).

2.2.5. Statistics

Due to unbalanced design, a Type III two factor analysis of variance (ANOVA) was used to analyze differences between 1994 and 2014 levels of CH_4 , CO_2 , and DIC, respectively, in high, low, and no closure lakes. Year (levels: 1994 and 2014) and closure class (high, low, and no) were used as factors. We followed the two factor ANOVA with

pairwise comparisons of least-squares means. We used a one factor ANOVA to compare thermokarst-affected lakes to high, low, and no closure lakes, also followed with pairwise comparisons of least-squares means. Tukey-adjusted *P*-values are reported for all pairwise comparisons.

We also used Akaike Information Criterion (AIC) to assess every possible combination of CH₄ predictor variables in multiple regression. AIC is a log-likelihood method involving the comparison of models by determining how likely each model (among those models specified in the comparison) is to be the best model in predicting the response variable (Burnham and Anderson 2002). Given that our ratio of sample size to models assessed was <40, we computed second order AIC (AICc) weights to determine which combinations were best at explaining dissolved CH₄ (Burnham and Anderson 2002). After pre-screening data, variables not exhibiting a significant correlation with CH₄ were excluded from the analysis (Tank et al. 2009). We calculated ΔAICc (difference from model with lowest AIC) for each model, and retained models with $\Delta\text{AICc} < 4$ and a variance inflation factor <10 for computation of model-averaged regression coefficients and relative importance of predictor variables (Burnham and Anderson 2002).

All models in ANOVA and simple regression analyses were assessed for residual normality and homoscedasticity, and variables were Box-Cox transformed when necessary to satisfy model assumptions. The Box-Cox procedure uses the log-likelihood function to estimate the best transformation to normality within the family of power transformations (Sokal and Rohlf 1995). Box-Cox transformations were also applied in all regression, and AIC, analyses. We report adjusted r^2 for all relationships. Data analyses were performed in RStudio, version 3.2.5 (RStudio Team 2016).

2.3. Results

2.3.1. Gas Accumulation over the Hydrological Gradient

Primary production in Mackenzie Delta lakes is rooted in the underpinning hydrologic cycle, where lakes with higher spring sill elevations are less frequently recharged with turbid water from the Mackenzie River during spring ice-out.

Consequently, light becomes a limiting factor in primary production and macrophyte density tends to increase with sill elevation. Both under-ice CH₄ ($r^2 = 0.43$, $P < 0.001$; Figure 2-2A) and CO₂ ($r^2 = 0.30$, $P < 0.01$; Figure 2-2B) significantly increased with spring sill elevation. CH₄ and CO₂ in thermokarst-affected lakes, which have previously exhibited unusual CO₂ levels during the summer season (Tank et al 2009), did not exhibit unusual levels (compared to other lakes) during the under-ice period (Figures 2-2A and 2-2B). For 2014 measurements, grouping of lakes into high, low, or no closure classes in the following analyses was based on differences in sill elevation (see Figures 2-2A and 2-2B) as in previous studies (e.g., Lesack et al. 2010). Measurements of CH₄ and CO₂ from individual lakes are given in Table 2-1.

2.3.2. Comparison of Under-ice Gas Accumulations

Our CH₄, CO₂, and DIC results are based on the same methods as in Pipke (1996) and can be compared directly to those results from 1994. Important to interpreting these comparisons is that Pipke's full data set was based on a cross-Delta transect of 81 lakes, broken down into 3 clusters of 27 lakes located within the western, middle, and eastern side (i.e., Inuvik region) of the central Mackenzie Delta. Pipke's analysis detected a modest increase in under-ice CH₄ from west to east across the Delta, whereas CO₂ and DIC were greatest in the central Delta, so the full results from her cross-Delta lake set may not be completely comparable to our present study lakes located within the Inuvik region. Pipke's eastern lake cluster overlaps with our present study lakes, though not fully, and thus it may also not be completely comparable to our present study lakes.

Methane

Current mean CH₄ concentrations within the Inuvik region of the Delta were 684, 428, and 34 μM in high, low, and no closure lakes, respectively. These are in the range measured by Pipke (1996), where cross-Delta CH₄ means were 477, 315, and 165 μM in high, low, and no closure lakes, respectively, and within the subset of Inuvik region lakes were 718, 230, and 216 μM in high, low, and no closure lakes, respectively (Figure 2-3). In comparing the 1994 cross-Delta CH₄ means with our 2014 means for the Inuvik region, differences between years (1994 vs 2014) are not significant based on two factor ANOVA ($P = 0.48$), nor was there a significant interaction between Year and Closure class ($P =$

0.20), however, there was a significant difference among Closure classes ($P < 0.001$). If the ANOVA comparison is restricted to the Inuvik region lakes of Pipke (1996), the results are similar: differences in mean CH_4 between years (1994 vs 2014) are not significantly different ($P = 0.91$), nor was there a significant interaction between Year and Closure class ($P = 0.15$). Table 2-2 summarizes pairwise comparisons between Years and Closure classes. Compared to Pipke's (1996) cross-Delta survey, current mean CH_4 levels are higher in high and low closure lakes and lower in no closure lakes (Figure 2-3). For lakes in the Inuvik region only, mean CH_4 concentrations were slightly lower in high closure lakes, higher in low closure lakes, and lower in no closure lakes in 2014 than in 1994 (Figure 2-3). In 1994, CH_4 in high closure lakes of the Inuvik region were significantly higher than in low ($P = 0.02$) and no ($P = 0.004$) closure lakes, whereas 2014 CH_4 levels in high closure lakes are no longer different from low closure lakes ($P = 0.55$), but are still significantly higher than no closure lakes ($P < 0.001$; Table 2-3). The 2014 CH_4 levels in low closure lakes are significantly higher than in no closure lakes ($P = 0.04$), whereas in 1994 there was no significant difference between low and no closure lakes in the Inuvik region ($P = 0.99$).

Carbon Dioxide

Based on two factor ANOVA using Pipke's (1996) cross-Delta measurements, mean CO_2 levels between 1994 and 2014 are not significantly different ($P = 0.42$), differences between closure classes are significantly different ($P = 0.0014$), and there is no significant interaction in mean CO_2 between year and closure class ($P = 0.43$). Similarly, there is no significant difference between years ($P = 0.34$), difference in closure class is significant ($P = 0.0010$), and there is no significant interaction between year and closure class ($P = 0.78$) using Pipke's (1996) Inuvik region CO_2 measurements.

The 2014 mean CO_2 level in high closure lakes (815 μM) are higher, but not statistically different than Pipke's (1996) cross-Delta (740 μM) and Inuvik region measurements (750 μM ; Figure 2-3). Low closure lakes during 2014 have mean CO_2 levels lower than the 1994 cross-Delta measurements (704 μM in 1994), but if the comparison is restricted to Inuvik region lakes, 2014 levels (654 μM) may be trending upwards relative to 1994 (619 μM ; Figure 2-3). In no closure lakes, 2014 mean CO_2 levels (299 μM) are lower than in the 1994 cross-Delta measurements (493 μM), but are higher

compared to the Inuvik region subset from 1994 (279 μM ; Figure 2-3). When the comparison is restricted to only the Inuvik region lakes from 1994, 2014 high closure lakes had significantly higher CO_2 than in 1994 no closure lakes ($P = 0.001$), and 2014 low closure lakes had significantly higher CO_2 than 1994 no closure lakes ($P = 0.01$; Table 2-2). Looking at the 2014 results only, CO_2 levels in high closure lakes are not significantly different from low closure lakes ($P = 0.89$), but are trending towards being significantly higher than in no closure lakes ($P = 0.06$), and no closure lakes are not significantly different from low closure lakes ($P = 0.34$; Table 2-3).

Dissolved Inorganic Carbon

Temporal changes are more apparent in DIC, where 2014 levels are trending lower compared to 1994 (Figure 2-3). Based on two factor ANOVA using Pipke's (1996) cross-Delta measurements, mean DIC levels between 1994 and 2014 are significantly different ($P < 0.001$), differences between closure classes are nearing significance ($P = 0.082$), and no significant interaction between year and closure class was found ($P = 0.35$). Post hoc comparison across years using Pipke's cross-Delta measurements shows that DIC is significantly lower in 2014 than 1994 ($P < 0.001$). Using Pipke's (1996) Inuvik region DIC measurements, 2014 concentrations are significantly lower than in 1994 ($P = 0.011$), difference in closure class is significant ($P = 0.005$), and there is no significant interaction between year and closure class ($P = 0.90$).

In 2014, mean DIC was 3902, 3661, and 2720 μM in high, low, and no closure lakes, respectively. In 1994, DIC means of the cross-Delta lake set (4586, 5105, and 4370 μM) were higher than in 2014, and the 1994 Inuvik region means (5089, 4818, and 3315 μM) were also higher. The 2014 levels of DIC in high closure lakes are not significantly different than high closure lakes in the 1994 cross-Delta lakes ($P = 0.64$) and in the 1994 subset from the Inuvik region ($P = 0.35$; Table 2-2). The 2014 DIC levels in low closure lakes are significantly lower than in low closure lakes from the 1994 cross-Delta set ($P = 0.04$), but not significantly different from the 1994 subset of Inuvik region low closure lakes ($P = 0.42$). The 2014 DIC levels in no closure lakes are trending towards being significantly lower than no closure lakes from the 1994 cross-Delta set ($P = 0.08$), but they are not significantly different than the 1994 subset of Inuvik region no closure lakes ($P = 0.93$). In 2014, as well as 1994 cross-Delta and Inuvik region lakes, no statistically

significant differences existed between high/low, high/no, and low/no closure lakes (Table 2-3).

Thermokarst Lakes

Most lakes in the Mackenzie Delta are affected by thermokarst to some degree, and it is more common among lakes of higher sill elevation. During the summer, thermokarst-affected Delta lakes tend to emit CO₂ rather than absorb CO₂ due to allochthonous input of carbon (Tank et al. 2009) and may be considerable sources of CH₄ (Walter et al. 2006). Following a significant one factor (i.e., lake type) ANOVA of under-ice CH₄ ($P = 0.002$), post hoc comparisons show mean CH₄ in thermokarst-affected Delta lakes is the same as in high closure lakes, and higher than in low and no closure lakes, however, these differences are not significantly different except in the case (tested at $\alpha = 0.05$) of no closure lakes (Figure 2-4). Similarly, one factor ANOVA of CO₂ indicated a significant difference between lake types ($P < 0.05$), and post hoc comparisons show that CO₂ in thermokarst lakes is not significantly different than in high or low closure lakes, but is significantly higher than no closure lakes (tested at $\alpha = 0.05$; Figure 2-4). One factor ANOVA of DIC indicated that there is no significant difference in DIC between the lake types ($P = 0.33$; Figure 2-4).

Given that thermokarst lakes are appreciably deeper (mean depth ~2.0 m) than other Mackenzie Delta lakes (1.5 m) (Tank 2009), CH₄, CO₂, and DIC content per unit area of lake was also compared, respectively, among the lake classes with one factor ANOVA. One factor ANOVAs for CH₄, CO₂, and DIC found significant differences between lake types ($P < 0.001$). Post hoc comparisons showed that CH₄ per unit area was greater in thermokarst lakes than in the primary lake classes, and was significantly higher (tested at $\alpha = 0.05$) than in low and no closure lakes, but was not significantly different from high closure lakes (Figure 2-4). Similarly, CO₂ and DIC, respectively, per unit area in thermokarst lakes was equivalent to high closure lakes, but thermokarst and high closure lakes were significantly greater than low and no closure lakes (tested at $\alpha = 0.05$; Figure 2-4).

2.3.3. Methane and Carbon Dioxide Accumulation vs Dissolved Organic Matter

CH₄, CO₂, and DIC are products of organic matter decomposition, and as expected were strongly interrelated. CH₄ was strongly and significantly related to CO₂ ($r^2 = 0.81$, $P < 0.001$; Figure 2-5A) and DIC ($r^2 = 0.44$, $P < 0.001$; Figure 2-5B), and CO₂ was also strongly related to DIC ($r^2 = 0.77$, $P < 0.001$; Figure 2-5C). Substrate quantity (i.e., DOC and CDOM) were significantly related to CH₄ and CO₂. Increasing DOC was directly related to increasing CH₄ ($r^2 = 0.66$, $P < 0.001$; Figure 2-6A) and CO₂ ($r^2 = 0.81$, $P < 0.001$; Figure 2-6B). Additionally, CH₄ increased with decreasing pH (i.e., increasing H⁺ concentration; $r^2 = 0.59$, $P < 0.001$; Figure 2-7). Increasing CDOM levels (i.e., water colour) was also directly related to increasing CH₄ ($r^2 = 0.64$, $P < 0.001$; Figure 2-8A) and CO₂ ($r^2 = 0.74$, $P < 0.001$; Figure 2-8B).

Carbon quality plots showed that DOM aromaticity generally declines (i.e., SUVA₂₅₄ declines) with corresponding declines in the inferred molecular weight of the DOM (i.e. a(250):a(365) increases). The plot, however, revealed a group of five outlying lakes (L511, L278, L56, L275, and L527a) with low DOM aromaticity, but high molecular weight. After excluding the outliers, aromaticity decreased as molecular weight decreased ($r^2 = 0.76$, $P < 0.001$; Figure 2-9A). We compared SUVA₂₅₄ to another indicator of DOM molecular weight, S_R (which like a(250):a(365) also decreases as molecular weight decreases), to check for the aforementioned outliers, but in this case only three lakes (at S_R values > 2) are clearly outliers (Figure 2-9B). S_R, however, showed no relation with DOM aromaticity when regressed with or without outliers. Increasing DOM molecular weight (a(250):a(365)) corresponded with increasing levels of CH₄, or in other words CH₄ was lowest where DOM quality was highest ($r^2 = 0.65$, $P < 0.001$; Figure 2-10A). DOM aromaticity (SUVA₂₅₄) was not statistically related to CH₄ levels (Figure 2-10B). CO₂ also increased with increasing molecular weight (i.e., decreasing DOM quality, $r^2 = 0.41$, $P < 0.001$; Figure 2-10C) and was not related to DOM aromaticity (SUVA₂₅₄, Figure 2-10D).

Given the potential importance of DOM quality in relating to CH₄ accumulation, we also compared under-ice CH₄ levels to open-water pCO₂ levels. Considering the constant daylight at this latitude, macrophyte production is high in Delta lakes to the degree that the majority of these lakes absorb CO₂, as the summer progresses. Generally, under-ice

CH₄ levels were highest in lakes that absorbed the most CO₂ during open-water. Under-ice CH₄ levels during 2014 show strong inverse relations with late summer CO₂ partial pressures (pCO₂) from 2005 ($r^2 = 0.66$, $P < 0.001$; Figure 2-11A), 2006 ($r^2 = 0.59$, $P < 0.05$; Figure 2-11B), and 2014 ($r^2 = 0.43$, $P < 0.001$; Figure 2-11C). The molecular weight of under-ice DOM during 2014 ($a(250):a(365)$), was also related to late summer pCO₂ levels from 2005 ($r^2 = 0.37$, $P < 0.001$; Figure 2-12A), 2006 ($r^2 = 0.60$, $P < 0.05$; Figure 2-12B), and 2014 ($r^2 = 0.52$, $P < 0.001$; Figure 2-12C). Based on the above, DOM molecular weight was highest in lakes absorbing the most CO₂, i.e., DOM quality was highest in lakes absorbing the least CO₂. Thermokarst-affected lakes were excluded from regression of under-ice CH₄ and DOM molecular weight against pCO₂. Although CH₄ and DOM quality were strongly related to late summer pCO₂ levels, relations with submerged macrophyte density were relatively weak. CH₄ increased along with submerged macrophyte density ($r^2 = 0.36$, $P < 0.05$; Figure 2-13A), as did CO₂ ($r^2 = 0.20$, $P = 0.055$; Figure 2-13B).

Since under-ice CH₄ and DOM molecular weight were strongly related to DOM quantity (i.e., DOC) and late summer pCO₂, we explored the relationships of DOM quality and quantity with submerged macrophyte density and sill elevation, which are more direct indicators of primary productivity in Mackenzie Delta lakes. The sill elevation gradient was strongly related to under-ice CH₄ and CO₂ (Figure 2-2), as well as DOM quantity and quality. Under-ice DOC was positively related to sill elevation ($r^2 = 0.36$, $P < 0.001$; Figure 2-14A), but not submerged macrophyte density (Figure 2-14B). After excluding thermokarst-affected lakes and another regression outlier (but retaining DOM outliers from Figure 2-9), DOM molecular weight declined with increasing sill elevation ($r^2 = 0.33$, $P < 0.01$; Figure 2-14C). Declining molecular weight was weakly related to increasing submerged macrophyte density ($r^2 = 0.11$, $P = 0.12$; Figure 2-14D).

2.3.4. Potential Drivers of Under-ice Methane Accumulation

We explored the potential drivers of under-ice CH₄ accumulation by using AICc (i.e., AIC adjusted for small sample size) to evaluate all possible CH₄ predictors in multiple regression. Prior to AICc comparison, we screened the variables for correlation with CH₄ and multicollinearity between predictor variables (see correlation matrices in Appendix A).

We excluded variables not significantly ($\alpha = 0.05$) correlated with CH_4 , and dropped variables due to collinearity: we removed CO_2 and HCO_3^- in favour of DIC (i.e., a composite of CO_2 , HCO_3^- , and CO_3^{2-}), and dropped CDOM (was highly correlated with DOC, DIC, pH and $a(250):a(365)$). The remaining variables included were chlorophyll *a*, lake area, total suspended sediments (TSS), sill elevation, ice thickness, and macrophyte density. We performed three AICc analyses: (1) with data from all 29 survey lakes; (2) excluding outliers from the regression of CH_4 against $a(250):a(365)$ (L15a and L181; see Figure 2-10A); and (3) including only the lakes with macrophyte data (Table 2-4). In the first analysis, the regression coefficients of DIC ($P < 0.001$) and inferred DOM molecular weight ($P < 0.05$) were significant across all averaged models. In the second analysis (excluding outliers) the model-averaged regression coefficient for DIC was only significant to $P < 0.10$, whereas pH ($P < 0.001$) and DOM molecular weight ($P < 0.01$) were highly significant. Only DIC ($P < 0.10$) had a near-significant regression coefficient in the third analysis (lakes with macrophyte data); macrophyte density was not a predictor variable in the best model selected by AIC. Surprisingly, model-averaged regression coefficients for DOC were not significant in any of the AICc analyses. Overall, the predictor variables account for 85% of the variance in ambient CH_4 using all data, and 85% of the variance when excluding L15a and L181 (Table 2-5 and Figure 2-15). Using only the lakes with macrophyte data 86% of the variance in ambient CH_4 can be explained, however, macrophyte biomass is not a predictor variable in the AICc-identified model.

To directly assess the importance of DOM quality and quantity in driving under-ice CH_4 accumulation, we plotted DOM molecular weight and aromaticity against the residuals of regression of CH_4 against DOC (i.e., $\text{CH}_4 \sim \text{DOC}$). DOM molecular weight was closely related to $\text{CH}_4 \sim \text{DOC}$ residuals, where positive residuals were related to higher molecular weight and negative residuals were related to lower molecular weight ($r^2 = 0.50$, $P < 0.001$; Figure 2-16A). In other words, increases in CH_4 relative to DOC were related to increases in DOM molecular weight. DOM aromaticity on the other hand was not related to the residuals of the regression of CH_4 against DOC (Figure 2-16B). Together, DOM molecular weight and DOC (both regression coefficients significant to $P < 0.001$) explain 67% of the variance in CH_4 (Figure 2-16C).

We further assessed the importance of DOM quality and quantity in driving under-ice CH₄ accumulation with multiple regression models. Given the results of the AIC and above partial regression analyses, we used DOC, DOM molecular weight, DIC, and pH as predictors of CH₄ accumulation. We performed six multiple regression analyses: models A1-A3 with all observations ($n = 29$), and models B1-B3 without Lakes 15a and 181 ($n = 27$). Model A1 included DOC, DOM molecular weight, DIC, and pH as predictors ($r^2 = 0.76$), where DIC ($P = 0.03$) and pH ($P = 0.003$) regression coefficients were significant, but coefficients for DOC ($P = 0.72$) and DOM molecular weight ($P = 0.17$) were not significant (Table 2-6, Figure 2-17A). Dropping DOC (model A2) did not affect the DOM molecular weight coefficient ($P = 0.17$) or the r^2 (0.77), but the coefficients for DIC and pH improved in significance ($P < 0.001$). After dropping DOC and DOM molecular weight (model A3), regression using DIC and pH resulted in an r^2 of 0.76, which is the same result as model A1.

Considering the effect that excluding Lakes 15a and 181 had on the outcome of the AIC analyses, models B1-B3 were constructed without these two lakes (Table 2-6, Figure 2-17D to F). As in A1, DOC ($P = 0.87$) did not have a significant regression coefficient in B1 ($r^2 = 0.85$), but the coefficient for DOM molecular was significant ($P = 0.003$), as well as for DIC ($P = 0.09$) and pH ($P < 0.001$). Dropping DOC (model B2) did not change the r^2 (0.85), and the regression coefficients for DIC ($P = 0.02$), pH ($P < 0.001$), and DOM molecular weight ($P = 0.002$) remained significant. Regressing with only DIC and pH (model B3) reduced the r^2 to 0.78.

2.4. Discussion

2.4.1. Dissolved Organic Matter Decomposition

Our finding that CH₄ accumulation is greatest in lakes that are summertime CO₂ absorbers (i.e., highly productive lakes), higher in sill elevation, and higher in DOC concentration supports the postulation of Tank et al. (2009) that a significant portion of carbon fixed in Mackenzie Delta lakes is later converted to CH₄. Furthermore, DOM aromaticity was not statistically related to observed CH₄ levels, however, it did indicate a group of five high closure lakes with high DOM molecular weight, yet anomalously low

DOM aromaticity. Low DOM aromaticity in the anomalous lakes must indicate a greater abundance of autochthonous DOM, which fueled under-ice microbial communities and resulted in high levels of CH₄.

The relationship of increasing under-ice CH₄ accumulation with increasing molecular weight of ambient DOM is indicative of a complex, microbially active under-ice habitat in Mackenzie Delta lakes. Since high levels of CH₄ coincide with high DOM molecular weight, it is likely that a significant portion of the low molecular weight DOM was consumed, along with higher redox potential electron acceptors, and converted into CO₂ and other low molecular weight DOM, thereby creating the conditions required for methanogenesis. In the light-limited under-ice environment, the relation of high CH₄ with high molecular weight DOM likely indicates that the low molecular weight DOM was processed microbially, and a significant portion eventually converted to CH₄. Consequently, it is likely that as labile DOM is utilized, higher molecular weight DOM accumulates under-ice. We found increasing DOC (i.e., DOM quantity) to be strongly related to increasing CH₄, but it was not a significant predictor of CH₄ when combined in multiple regression with DOM molecular weight, pH, and DIC (i.e., CO₂ and HCO₃⁻). This does not mean that DOC is not an important factor driving methanogenesis. Instead, it highlights the importance of organic matter decomposition into carbon forms (i.e., CO₂ and acetate) readily utilizable by methanogens, and that microbial communities are more active, diverse, and dynamic (i.e., shift in community structure according to changing redox conditions) in lakes with greater CH₄ levels.

Considering that our results suggest a gradient of microbial activity in Mackenzie Delta lakes, under-ice CH₄ oxidation (MOX) is also an important consideration. High under-ice MOX rates have been observed in other Arctic regions (Kankaala et al. 2006, Greene et al. 2014, Martinez-Cruz et al. 2015), and may be linked to NO₃⁻ and SO₄²⁻ availability (Bertilsson et al. 2013). MOX may play an important part in regulating the accumulation of CH₄ in Mackenzie Delta lakes during the winter and warrants future investigation.

2.4.2. Comparison of 2014 and 1995 Under-Ice Gases

Although limited to measurements from Inuvik region lakes, our current measurements echo Pipke's (1996) in that the lowest levels of CH₄ and CO₂ are found in no closure lakes, intermediate levels in low closure lakes, and highest levels in high closure lakes. Pipke (1996) also established that under-ice dissolved CH₄ and CO₂ in lakes increases in parallel with increasing hydrologic isolation (i.e., closure class), and that CH₄ levels tend to increase along a west-east gradient across the Delta (i.e., lakes in the Inuvik region accumulate more CH₄ than lakes in the central Delta, which accumulate more CH₄ than lakes in the western region of the Delta). Our results diverge in the relative differences in CH₄ between lake closure classes. CH₄ levels in 2014 high closure lakes are similar to 1994 levels, but 2014 low closure CH₄ levels are higher than 1994, and our CH₄ levels in no closure lakes are lower than 1994. Since CH₄ is increasing in some lakes, decreasing in others, but not changing in the rest implies a complex interaction of variables underlying methanogenesis that we cannot fully resolve due to low overlap of lakes between the two surveys.

Methanogenesis is dependent on temperature, substrate availability, and redox potential, therefore changes (or lack thereof) between past and present CH₄ levels would be due to differences in one or varying combinations (or none) of these factors. Although winter air temperatures have generally increased over the past twenty years (Lesack et al. 2014), temperature is not likely to explain why CH₄ has not changed in high closure lakes, increased in low closure lakes, but decreased in no closure lakes because: (i) winter still lasts for an extended period of time, but may end earlier in the year; (ii) air temperatures are still well below freezing; (iii) water column temperatures remain between 0 and 4°C; and (i-iii) should affect each lake equally. However, it seems possible that lake sediments might be storing more heat during the summer, which may translate to greater methanogenesis during the winter, but no sediment temperature data is presently available to explore this further. Greater organic matter decomposition rates should result in decreasing redox potential due to consumption of electron absorbers, which would also result in greater CH₄ accumulation. In particular, SO₄ is significantly negatively related to CH₄ during under-ice conditions in Delta lakes ($r^2 = 0.67$, $P < 0.001$; Figure 2-18). Mackenzie River flood waters are a significant source of SO₄ in Delta lakes, but lake-river

connectivity does not necessarily equate to SO_4 prominence in the lakes (Lesack et al. 1998). Lengthening in no closure lake-river connection time, but shortening in high closure lake-river connection time has been observed due to climate change (e.g., rises in sea level and decreases in ice-jamming effects; Lesack and Marsh 2007), which has currently unknown consequences on the biogeochemistry of Mackenzie Delta lakes. Accordingly, future investigation on the cycling of sulphur and other electron receptors (i.e., Fe(III) , Mn(IV) , NO_3^- , and O_2) relative to changes in lake-river connection time may lead to greater understanding of the impact of climate change on under-ice DOM processing and under-ice CH_4 accumulation in Mackenzie Delta lakes. In any case, differences in CH_4 accumulation in lakes between 1994 and 2014 due to changes in SO_4^{2-} delivery during that time are highly speculative. It is more likely that the differences in CH_4 accumulation are an artefact of an imperfect comparison between the sets of lakes sampled in 1994 versus 2014.

2.4.3. Thermokarst Lakes

Although thermokarst is likely to have somewhat increased since Pipke's (1996) study 20 years ago, thermokarst does not seem to be a differentiating factor between lakes during the winter, and does not appear to directly explain why low closure lakes during 2014 accumulate more CH_4 than low closure lakes in 1994. Most lakes in the Mackenzie Delta are affected by thermokarst to some degree (Tank 2009), and thermokarst has a significant effect on CO_2 levels during the open-water period (Tank et al. 2009). Thermokarst has been shown to be increasingly prominent in the Arctic as temperatures increase, and typically results in more CH_4 emissions after adding permafrost carbon into lakes (Walter et al. 2006, Walter Anthony et al. 2010, Martinez-Cruz et al. 2015, Sepulveda-Jauregui et al. 2015). Although thermokarst effects have increased due to climate change in lakes upland of the Mackenzie Delta (Burn and Kokelj 2009), lakes within the Mackenzie Delta may have been impacted by increasing temperature to a lesser extent because of the significant moderating effect that this mass of water bodies has on ground temperature (Burn and Kokelj 2009). High closure lakes in the Delta are the most susceptible to thermokarst (Tank et al. 2011), however, we did not find that lakes known to be thermokarst-affected accumulated more CH_4 than high closure lakes. We cannot resolve the impact of thermokarst on the under-ice environment

in Mackenzie Delta lakes, but we can conclude that thermokarst-affected lakes do not accumulate more CH₄ and CO₂ than other Mackenzie Delta lakes of comparable closure classes. Our results suggest that the hydrologic and primary productivity gradients have a greater influence than thermokarst on under-ice CH₄ accumulation in this system.

2.5. Conclusions

Even though they are small in area and shallow in depth, Mackenzie Delta lakes accumulate a significant amount of CH₄ during the winter. Lakes that are greater CO₂ sinks during the late summer period are greater CH₄ accumulators during the winter, and appear to contain highly active under-ice microbial communities. This suggests that the greater supply of autochthonous carbon available in the more productive lakes sustains highly active microbial communities, which while processing this DOM consume electron acceptors and release CO₂, thus supporting a rich environment for methanogenesis. Although thermokarst-affected lakes do not appear to accumulate more CH₄ than other lakes of comparable closure classes, additional studies involving dating ¹⁴C and detailed bathymetry are required to resolve what effect thermokarst has on winter CH₄ production in Mackenzie Delta lakes. As a whole, the amount of CH₄ in Mackenzie Delta lakes seems to have slightly increased over the past 20 years, where lakes experiencing intermediate connection with the Mackenzie River experienced the greatest gains. Climate induced changes in Mackenzie Delta flooding hydrology may alter the cycling of CH₄-inhibiting electron absorbers, which has unknown consequences on under-ice CH₄ accumulation. Future studies should also focus on the impact of climate induced changes in lake-river connectivity on the composition and microbial metabolism of ions regulating the wintertime redox environment in Mackenzie Delta lakes.

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2.7. Tables

Table 2-1. Dissolved CH₄ and CO₂ Measured Under-ice in 2014 (refer to Table 1-1 for lake coordinates, area, and sill elevation).

Lake	Closure Class	CH ₄ (μmol L ⁻¹)	CO ₂ (μmol L ⁻¹)	Ice Thickness (cm)	Snow Depth (cm)	Unfrozen Water Depth (cm)
L302a	No	10.6	112.6	105	6	55
L15a	No	29.1	271.6	75	8	50
L129	No	20.2	192.9	106	11	40
L4	No	103.3	460.9	98	6	107
L85a	No	8.7	458.4	90	9	55
L501	Low	267.3	667.2	85	13	38
L80	Low	3.5	217.0	73	9	124
L107	Low	174.8	269.8	80	6	31
L300	Low	391.4	508.7	73	7	18
L85b	Low	121.9	355.0	63	7	97
L141	Low	722.0	771.6	78	7	29
L511	Low	1227.1	1860.5	83	8	46
L87	Low	280.2	284.3	77	7	41
L111	Low	637.9	772.0	80	7	47
L184	Low	524.6	854.3	71	7	45
L280	Thermokarst	218.1	590.2	75	7	169
L538	Low	572.6	703.0	84	6	38
L131	High	538.2	615.6	58	6	49
L278	High	1187.5	1559.3	66	7	63
L287	High	514.3	474.0	79	7	187
L134	High	141.7	270.5	72	6	95
L56	High	849.6	1005.2	72	10	69
L275	High	938.6	975.2	65	5	137
L520	Thermokarst	376.6	495.9	81	6	208
L522	High	95.8	525.9	75	5	306
L143	Thermokarst	832.0	888.6	77	7	190
L181	Thermokarst	1076.9	905.1	57	7	152
L186	High	480.2	434.6	64	7	368
L527a	High	1181.1	1635.0	70	10	93

Table 2-2. Tukey Adjusted *P*-Values of Between Year Multiple Comparisons of 2014 to 1994 Cross-Delta and Inuvik Region Only Under-ice Accumulation of CH₄, CO₂, and DIC in Mackenzie Delta Lakes

Comparison		Cross-Delta		
2014	1994	CH ₄	CO ₂	DIC
High	High	0.56	1.00	0.64
High	Low	0.03	0.92	0.14
High	No	<0.001	0.13	0.91
Low	High	1.00	0.97	0.33
Low	Low	0.86	1.00	0.04
Low	No	0.03	0.79	0.66
No	High	0.01	0.07	0.03
No	Low	0.16	0.17	0.004
No	No	0.92	0.80	0.08
2014	1994	Inuvik Region		
High	High	1.00	1.00	0.35
High	Low	0.02	0.72	0.64
High	No	0.006	0.001	0.90
Low	High	0.34	0.97	0.19
Low	Low	0.59	0.99	0.42
Low	No	0.25	0.01	0.98
No	High	<0.001	0.13	0.01
No	Low	0.49	0.66	0.04
No	No	0.87	0.93	0.93

Significance at $\alpha = 0.05$ is indicated in **bold**.

Table 2-3. Tukey Adjusted *P*-Values of Within Year Multiple Comparisons of Under-ice Accumulation of CH₄, CO₂, and DIC in Mackenzie Delta Lakes

Comparison	2014	1994-CD	1994-IN
CH ₄			
High/Low	0.55	0.44	0.02
High/No	<0.001	<0.001	0.004
Low/No	0.04	0.16	0.99
CO ₂			
High/Low	0.89	0.99	0.81
High/No	0.06	0.10	0.003
Low/No	0.34	0.39	0.08
DIC			
High/Low	1.00	0.83	1.00
High/No	0.44	0.99	0.08
Low/No	0.65	0.49	0.20

CD: Cross-Delta transect.

IN: Inuvik only transect.

Significance at $\alpha = 0.05$ is indicated in **bold**.

Table 2-4. Results of Second Order Akaike's Information Criteria (AICc) Model Selection Analysis, Showing Model-averaged AICc Weights of Under-ice CH₄ Predictor Variable Coefficients.

Predictor	All Study Lakes (<i>n</i> = 29)	L181 and L15a Removed (<i>n</i> = 27)	Lakes with Macrophyte Data (<i>n</i> = 15)
DIC	1.00(+) ***	0.88(+)	0.75
pH	0.89(-)	1.00(-) ***	0.88
<i>a</i> (250): <i>a</i> (365)	1.00(-) *	1.00(-) **	0.42
Chlorophyll <i>a</i>	0.93	0.16	0.00
Area	0.83	0.21	0.07
TSS	0.23	0.06	0.31
Sill	0.16	0.09	0.00
DOC	0.11	0.11	0.03
Ice thickness	0.05	0.06	0.00
Macrophytes	n/a	n/a	0.22

AICc weights (from 0 to 1) indicate relative variable importance when comparing across all possible combinations of predictor variables (i.e., 1 indicates the variable is present in 100% of the best assessed models). Weights in bold (italics) indicate significance of model-averaged regression coefficients at $\alpha = 0.05$ ($\alpha = 0.10$), where * $P < 0.05$, ** $P < 0.01$, and *** $P < 0.001$.

Table 2-5. Multiple Regression Models Identified by Second Order Akaike Information Criterion (AICc) Analyses for Under-ice Survey.

Regression Equation	AICc Weight	n	Adjusted r ²	P-Value
All data				
Model: $\sqrt{\text{CH}_4} = 82.1 + 21.2\log_{10}(\text{DIC}) - 15.4\text{pH} - 19.2\log_{10}(A_{\text{ratio}}) + 4.6\log_{10}(\text{Chl}) - 2.5\log_{10}(\text{Area})$	0.16	29	0.85	<0.001
P-value: 0.06 <0.001 0.01 0.01 0.02 0.02				
Lakes 15a and 181 removed (i.e., Aratio outliers)				
Model: $\sqrt{\text{CH}_4} = 168.2 + 13.3\log_{10}(\text{DIC}) - 24.2\text{pH} - 25.1\log_{10}(A_{\text{ratio}})$	0.19	27	0.85	<0.001
P-value: <0.001 0.01 <0.001 <0.001				
Lakes with macrophyte data				
Model: $\sqrt{\text{CH}_4} = 296.3 + 25.5\log_{10}(\text{DIC}) - 48.9\text{pH} - 3.8\sqrt{\text{TSS}}$	0.12	15	0.86	<0.001
P-value: 0.002 0.01 <0.001 0.048				

AICc weights indicate the likelihood of the model being the best from among all the models assessed in each respective analysis (i.e., for a model weight of 0.23, there is a 23% chance the model is the best from among all the models assessed for the given data).

A_{ratio} : $a(250):a(365)$, inferred DOM molecular weight, where increasing $a(250):a(365)$ indicates decreasing DOM molecular weight.

Chl: chlorophyll *a*.

P-values for respective regression coefficients are provided below estimates.

Table 2-6. Multiple Regression Models to Predict the (square root) Concentration (μM) of Under-ice CH_4 in Mackenzie Delta Lakes from DOC (mg L^{-1}), DIC (μM), pH, and DOM Molecular Weight (A_{ratio} , inferred from $a(250):a(365)$, where increasing values indicate decreasing molecular weight).

Model		Intercept	log ₁₀ (DOC)	log ₁₀ (DIC)	pH	log ₁₀ (A _{ratio})	Adjusted r ²	RMSE	n
All data									
A1	Coefficient	123.9	3.3	23.0	-24.7	-12.4	0.76	5.001	29
	P-value	0.02	0.72	0.03	0.003	0.17			
A2	Coefficient	127.7		25.9	-26.2	-11.6	0.77	4.913	29
	P-value	0.01		<0.001	<0.001	0.17			
A3	Coefficient	153.0		26.6	-31.3		0.76	5.004	29
	P-value	0.002		<0.001	<0.001				
Lakes 15a and 181 removed (i.e., A _{ratio} outliers)									
B1	Coefficient	170.0	-1.2	14.3	-24.8	-24.9	0.85	3.297	27
	P-value	<0.001	0.87	0.09	<0.001	0.003			
B2	Coefficient	168.2		13.3	-24.2	-25.1	0.85	3.843	27
	P-value	<0.001		0.02	<0.001	0.002			
B3	Coefficient	199.2		18.9	-34.0		0.78	4.647	27
	P-value	<0.001		0.007	<0.001				

RMSE: root mean standard error.

2.8. Figures

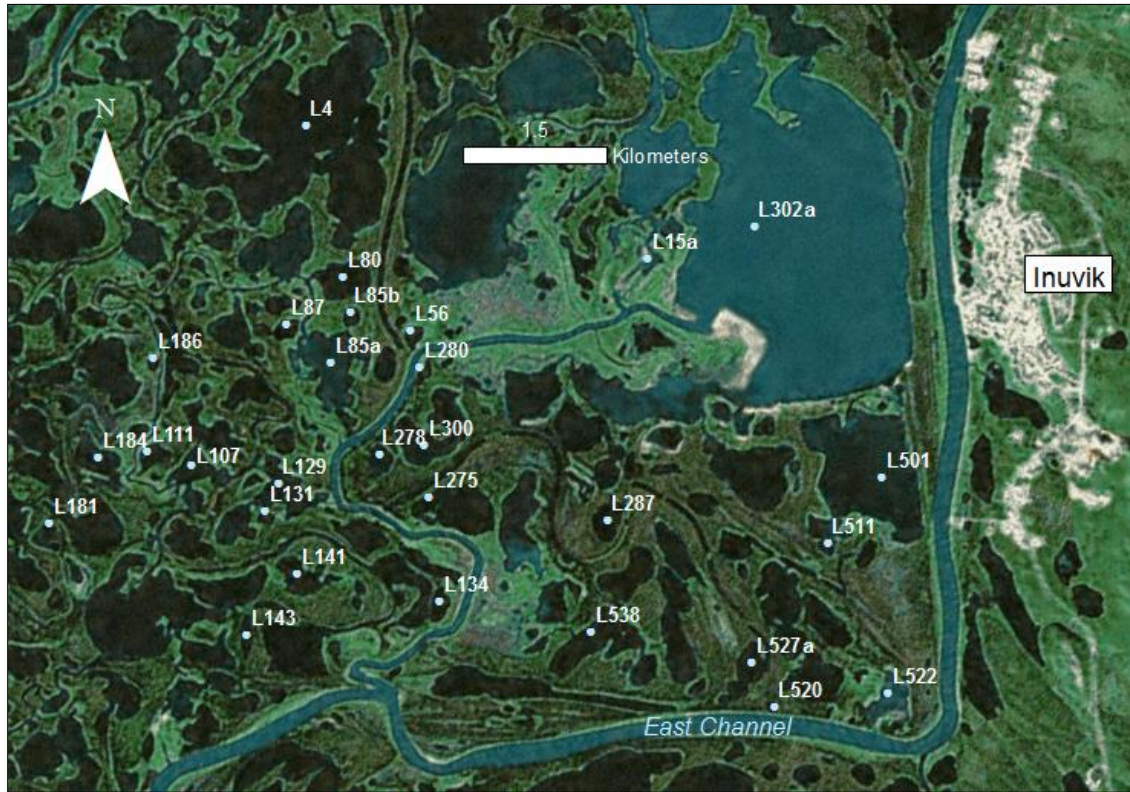


Figure 2-1. Location of Mackenzie Delta lakes sampled during May 2014.

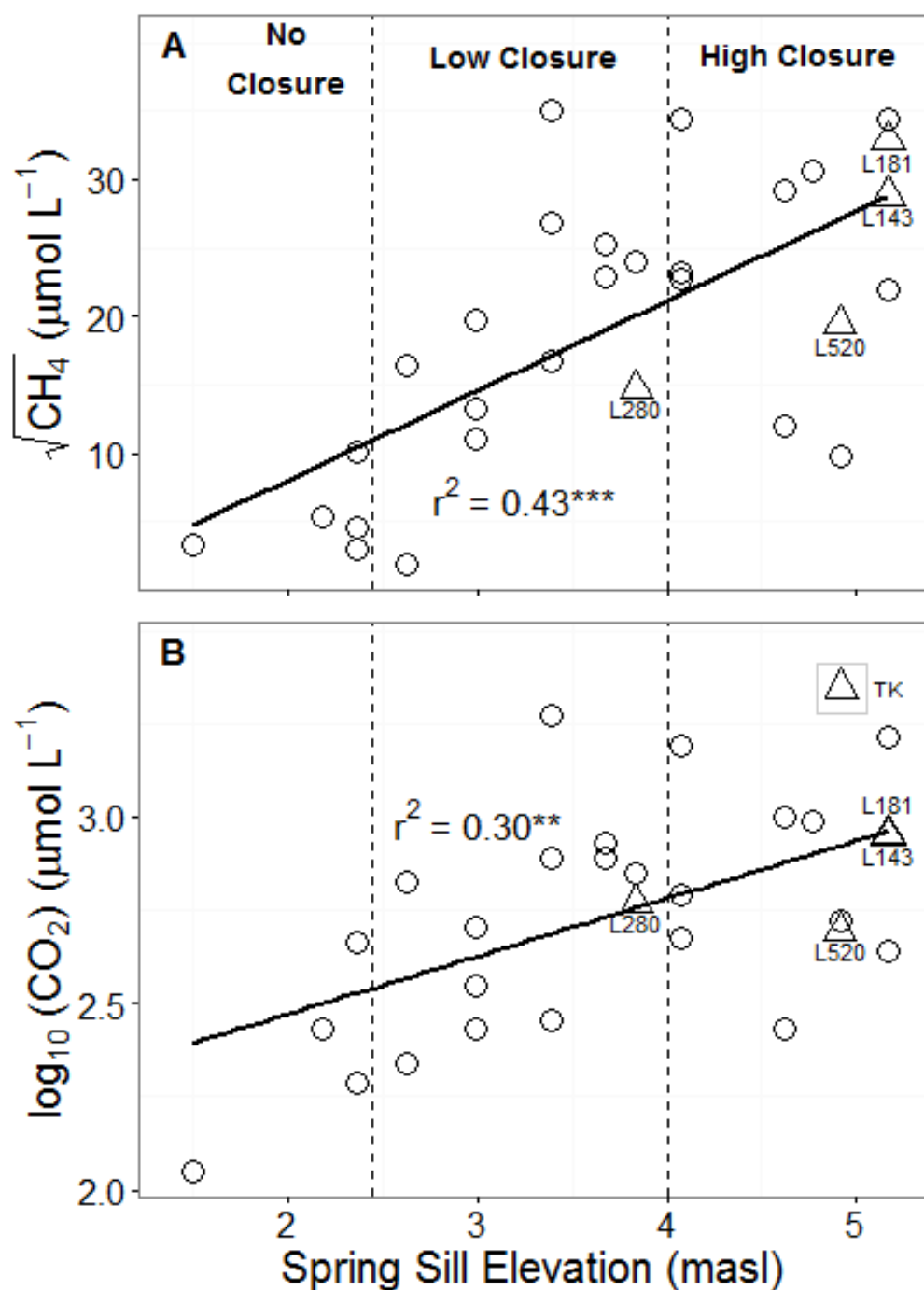


Figure 2-2. Under-ice CH_4 (A) and CO_2 (B) regressed against spring sill elevation.

Dashed lines delineate no, low, and high closure lakes. Lakes were grouped into closure classes as in previous studies of lakes in the same study area of the Mackenzie Delta (e.g., Lesack and Marsh 2010). Thermokarst (TK)-affected lakes are drawn as triangles, and are the same lakes (L143, L181, and L520) as identified in previous studies (e.g., Tank et al. 2009a) and in Chapter 3 (L280; L115 was not sampled under-ice in May 2014). All points are included in regressions. Adjusted r^2 values are reported. $^{**} P < 0.01$; $^{***} P < 0.001$.

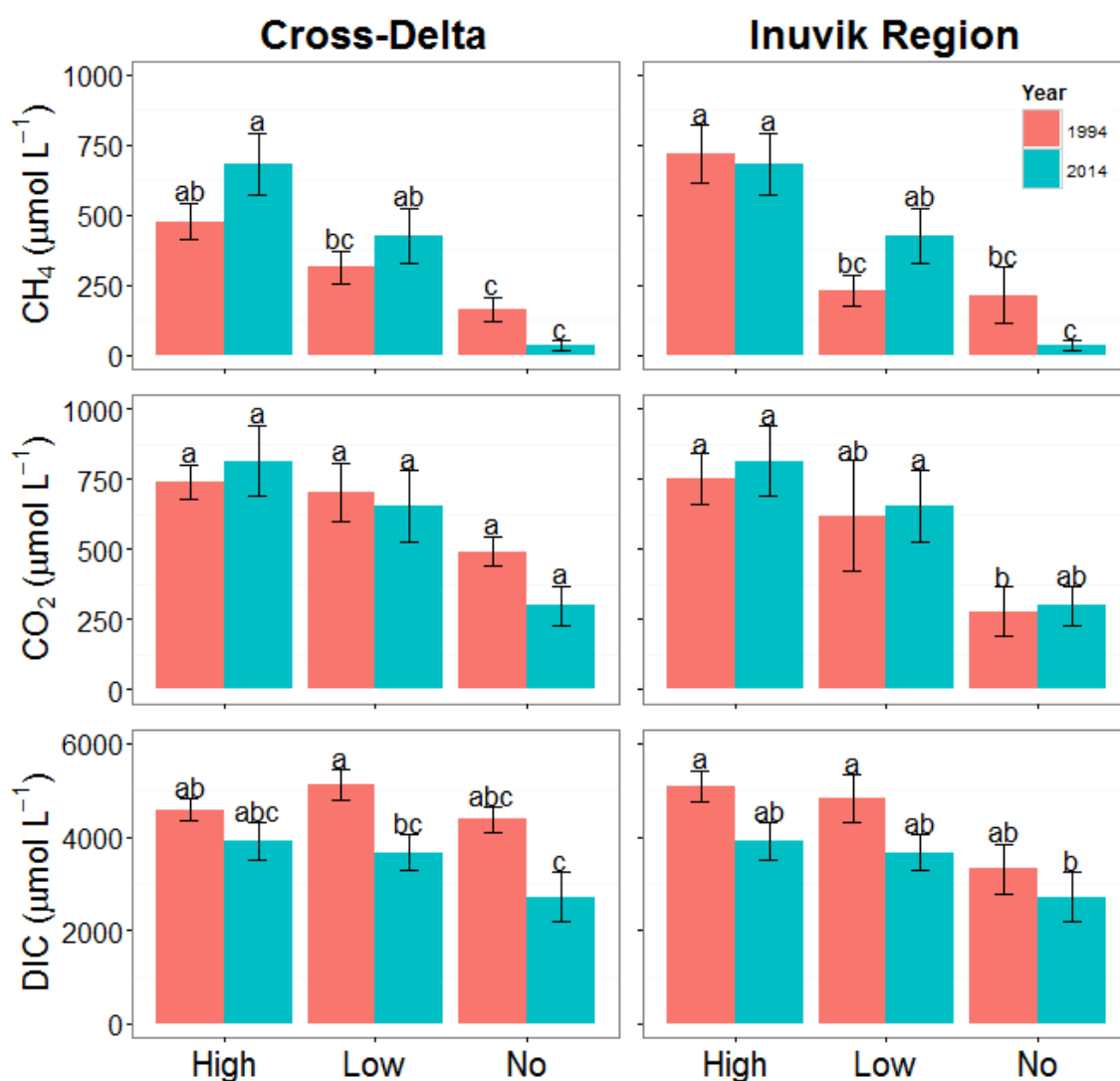


Figure 2-3. Mean CH₄, CO₂, and DIC under-ice in high, low, and no closure Mackenzie Delta lakes.

The 2014 survey included sampling of Inuvik region lakes only. Plots in the left column of the panel include all lakes in the cross-Delta survey by Pipke (1996). Plots on the right column of the panel include lakes surveyed by Pipke (1996) from the Inuvik region only. Error bars are ± 1 standard error of mean concentrations. Differing letters above error bars, within each panel, indicate significant difference at $\alpha = 0.05$ between lake type for CH₄, CO₂, and DIC, respectively.

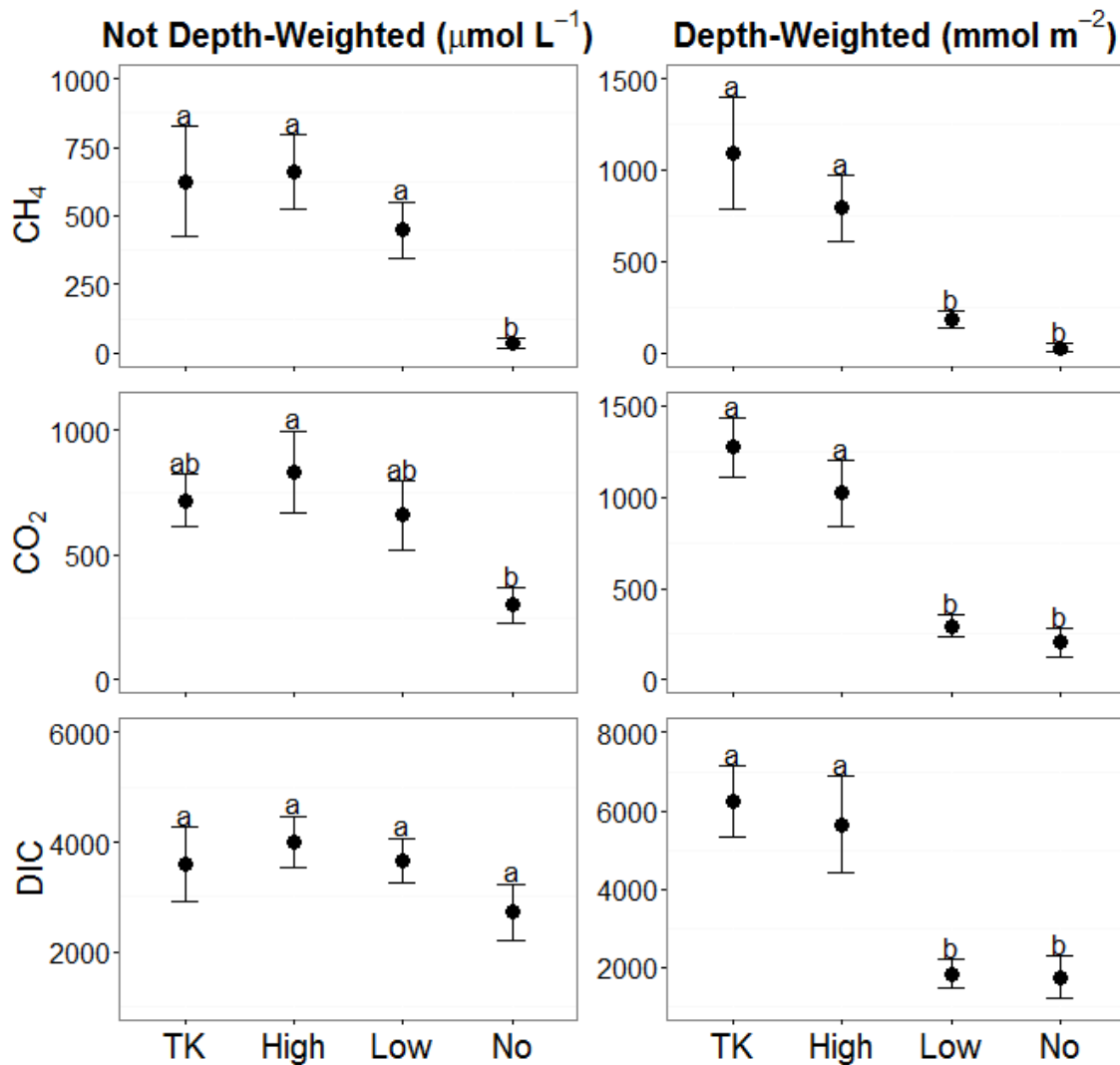


Figure 2-4. Comparison of CH₄ (top row), CO₂ (middle row), and DIC (bottom row) in Thermokarst (TK)-affected and high, low, and no closure lakes using mean under-ice (left column) and depth-weighted (right column) concentrations.

Points indicate the mean of each variable. Error bars are ± 1 standard error of mean concentrations. Differing letters above error bars indicate significant difference at $\alpha = 0.05$ between lake type for CH₄, CO₂, and DIC, respectively. Depth-weighted concentrations were obtained by multiplying mean under-ice concentrations by depth of unfrozen water at the sampling location.

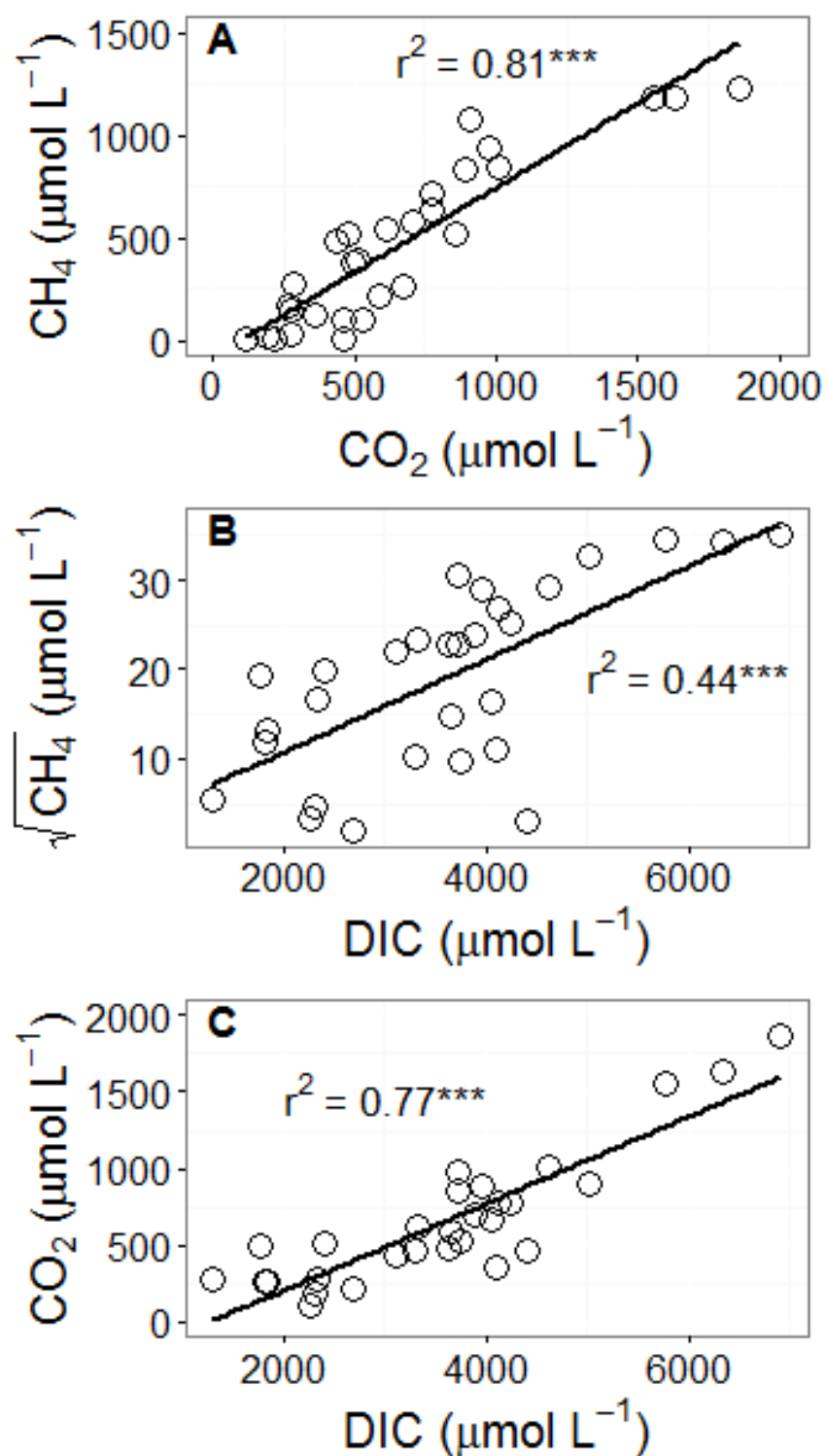


Figure 2-5. May 2014 under-ice relation between CH_4 and CO_2 (A), CH_4 and DIC (B), and CO_2 and DIC (C).

Adjusted r^2 values are reported. *** $P < 0.001$.

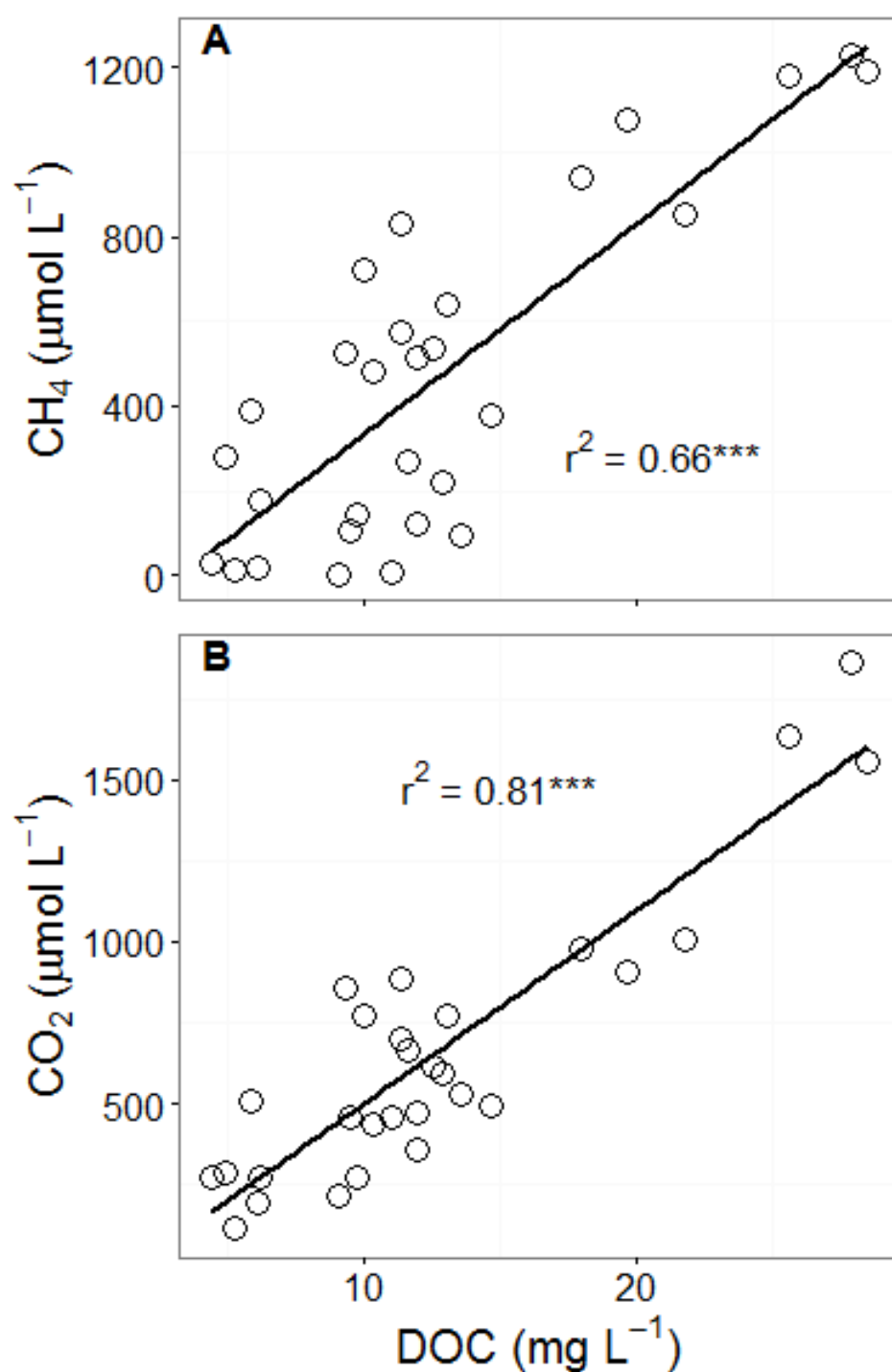


Figure 2-6. May 2014 under-ice relation of CH₄ (A) and CO₂ (B) to DOC. Adjusted r^2 values are reported. *** $P < 0.001$.

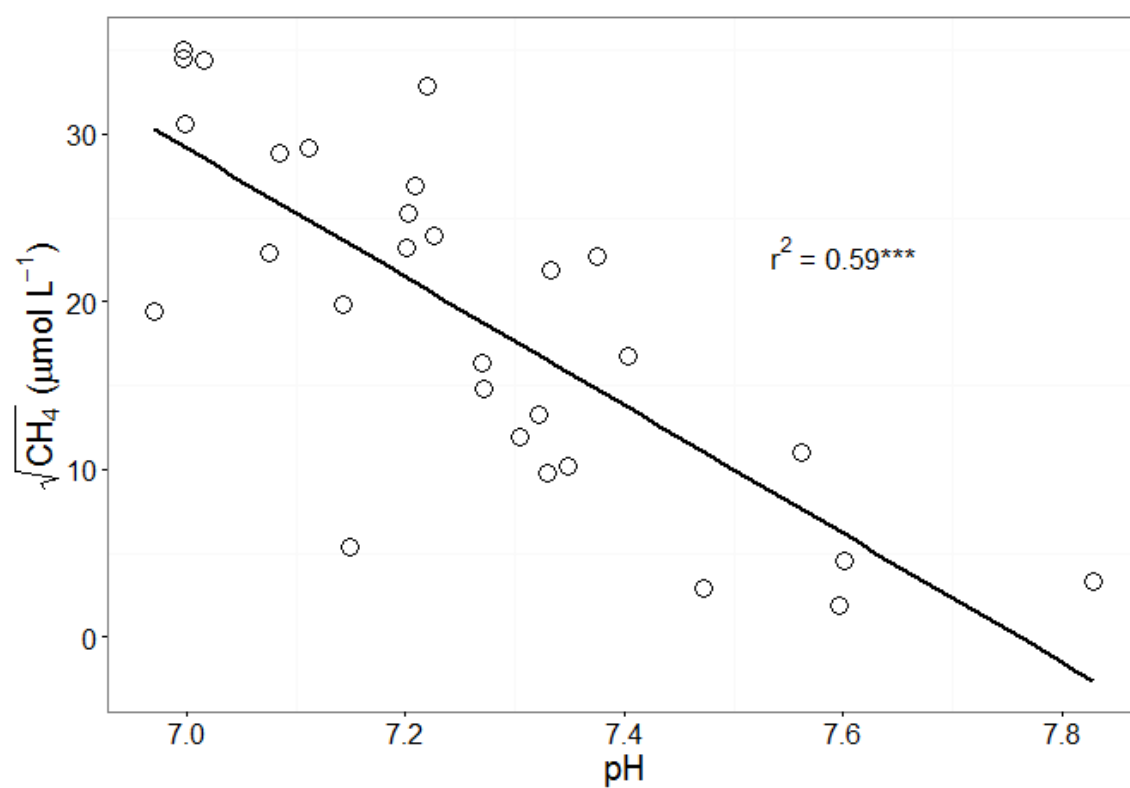


Figure 2-7. May 2014 under-ice relation of CH₄ to pH.
Adjusted r² value is reported. *** $P < 0.001$.

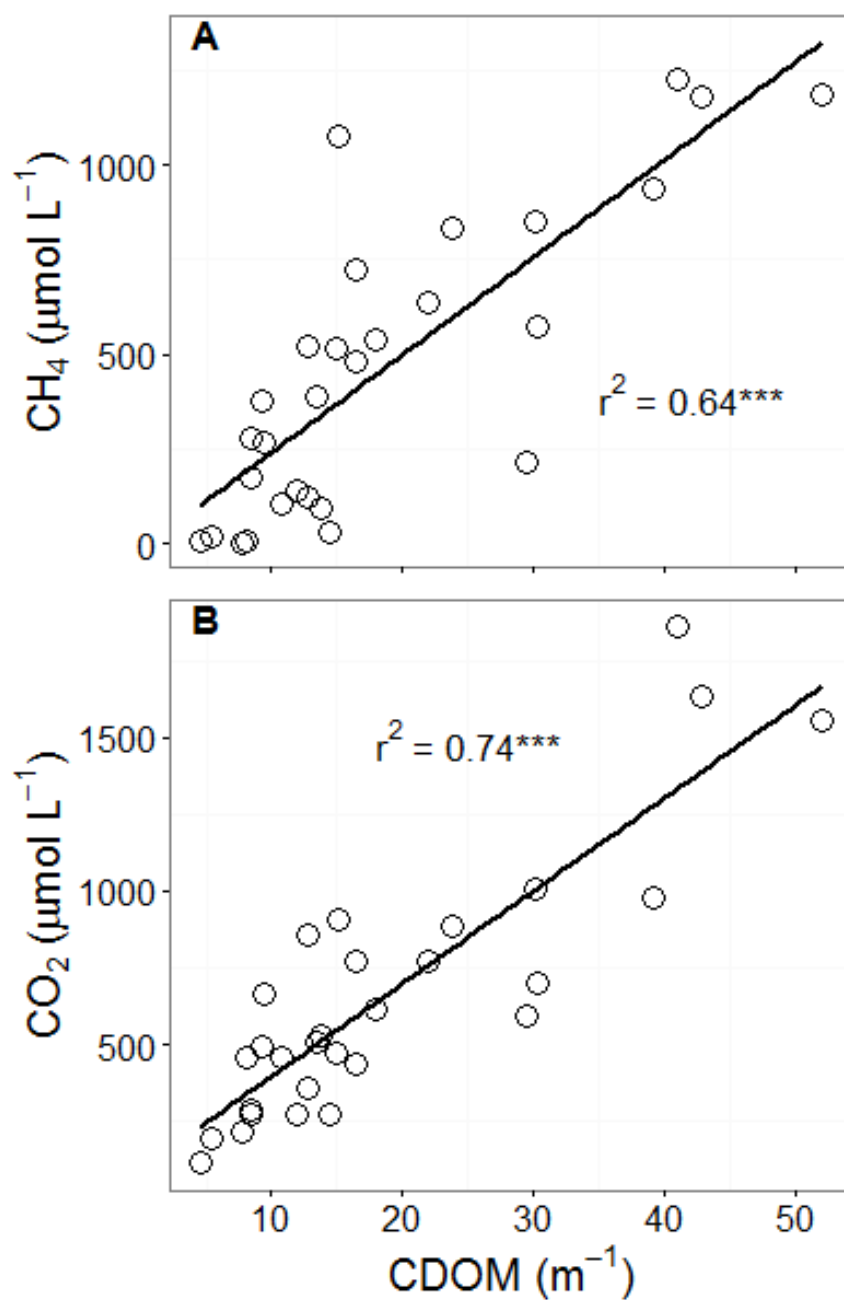


Figure 2-8. May 2014 under-ice relation of CH_4 (A) and CO_2 (B) to CDOM. CDOM (chromophoric dissolved organic matter) measured at $\lambda = 350$ nm. Increasing CDOM indicates increasing water colour. Adjusted r^2 values are reported. *** $P < 0.001$.

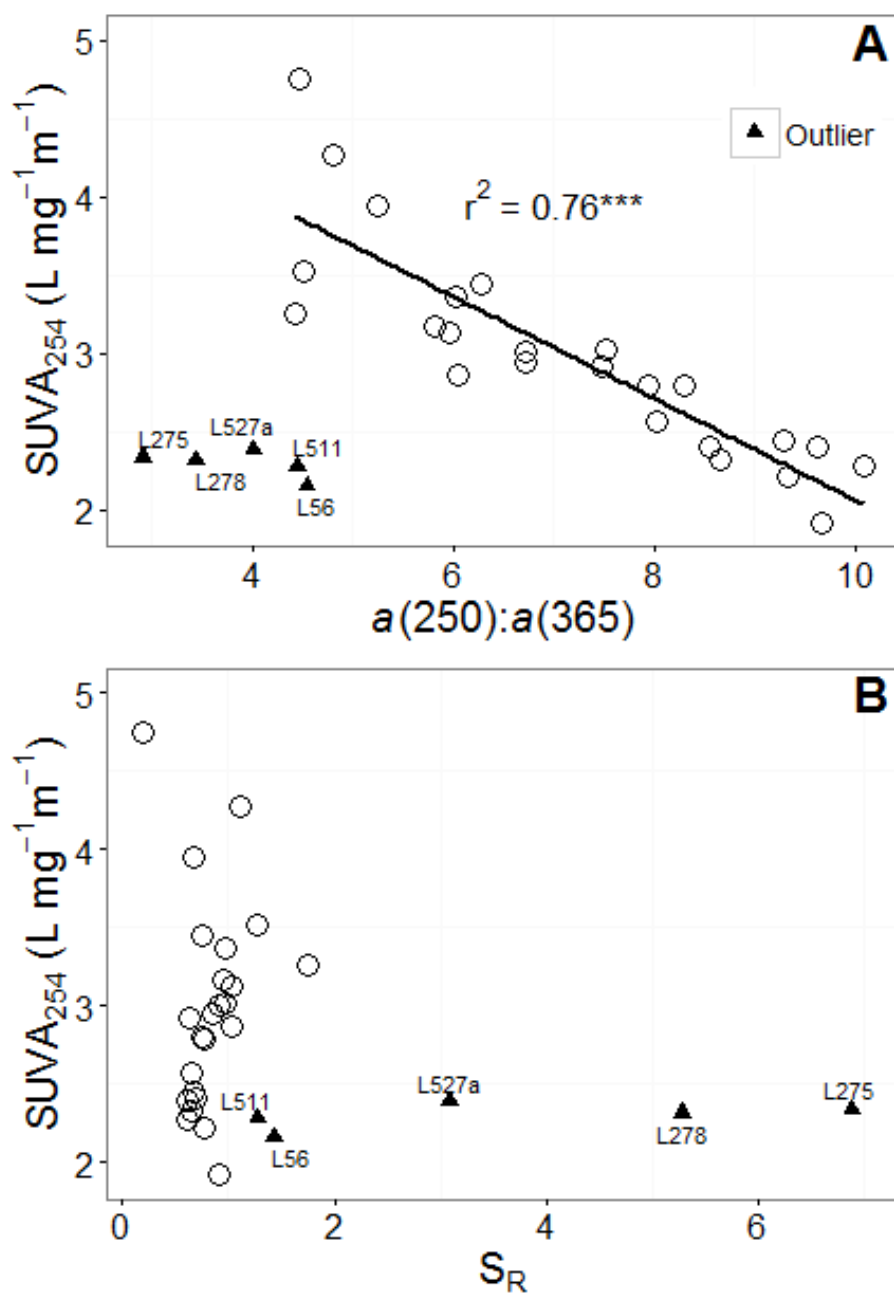


Figure 2-9. May 2014 under-ice relation of DOM aromaticity (SUVA₂₅₄) and inferred molecular weight measured as $a(265):a(365)$ (A) and S_R (B). Increasing $a(265):a(350)$, and increasing S_R , indicates decreasing molecular weight. The outlying measurements (triangles) did not originate from lakes known to be thermokarst-affected. Outliers were excluded from regression. Adjusted r^2 value is reported. *** $P < 0.001$.

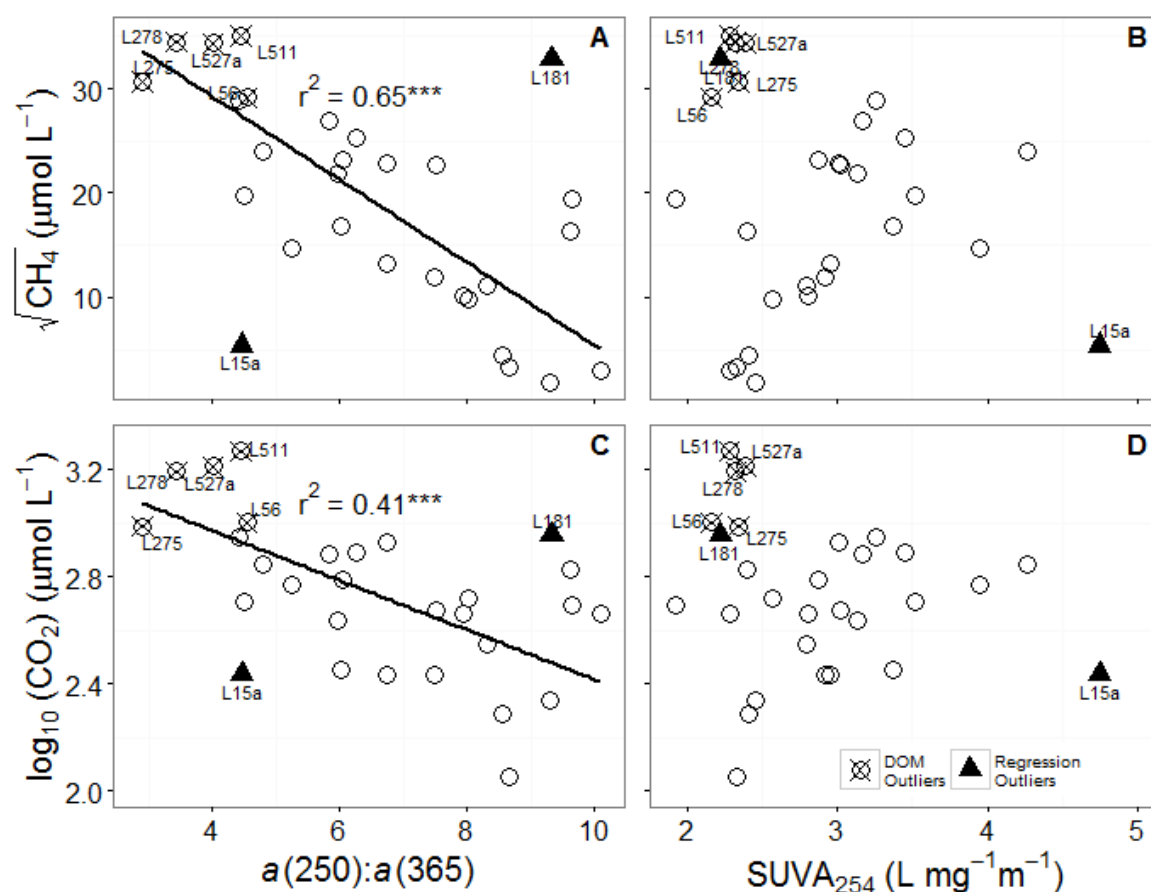


Figure 2-10. Regression of May 2014 under-ice CH_4 (A and B) and CO_2 (C and D) against inferred DOM molecular weight [$a(265):a(365)$] and aromaticity (SUVA_{254}).

Increasing $a(265):a(350)$ indicates decreasing DOM molecular weight, and increasing SUVA_{254} indicates increasing DOM aromaticity. DOM outliers from Figure 2-9 are shown as circles with x's, and are included in regressions (A and C). Outliers from the regression of CH_4 and $a(265):a(350)$, shown as triangles were excluded from regression. Adjusted r^2 values are reported. $^{***} P < 0.001$.

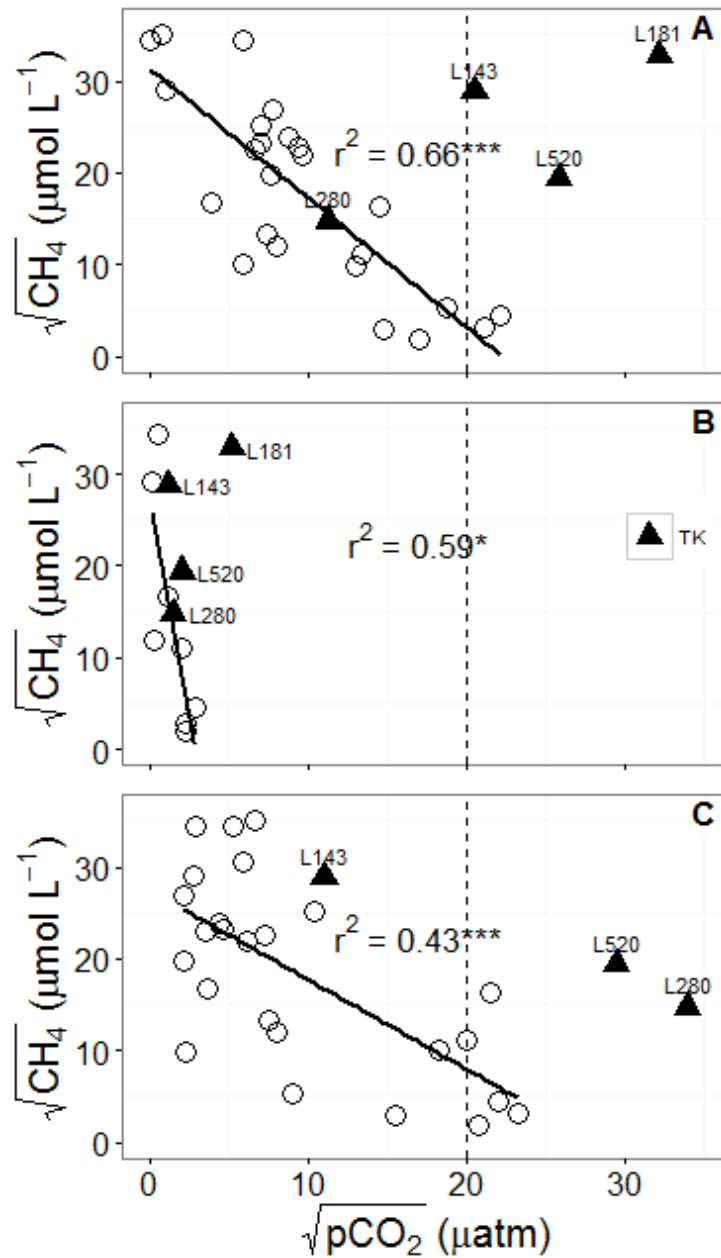


Figure 2-11. Relation of under-ice CH₄ accumulation with late summer CO₂ partial pressure.

CO₂ partial pressures (pCO₂) were obtained during surveys of 40 lakes in August 2005 (A), 16 lakes August 2006 (B), and 40 lakes August 2014 (C). Under-ice dissolved CH₄ measurements were obtained in May 2014 in the same lakes CO₂ flux was measured during the 2005 and 2006 surveys. Thermokarst (TK)-affected lakes are drawn as triangles, and are the same lakes (L143, L181, and L520) as identified in previous studies (e.g., Tank et al. 2009); L280 was determined to be TK-affected as per Chapter 3. The dashed line indicates atmospheric pCO₂, where measurements to the left of the line indicate CO₂ absorption, and measurements to the right of the line indicate CO₂ emission, where greater departure from atmospheric saturation implies stronger absorption or emission. TK-affected lakes were excluded from regression. Adjusted r^2 values are reported. * $P < 0.05$; and *** $P < 0.001$.

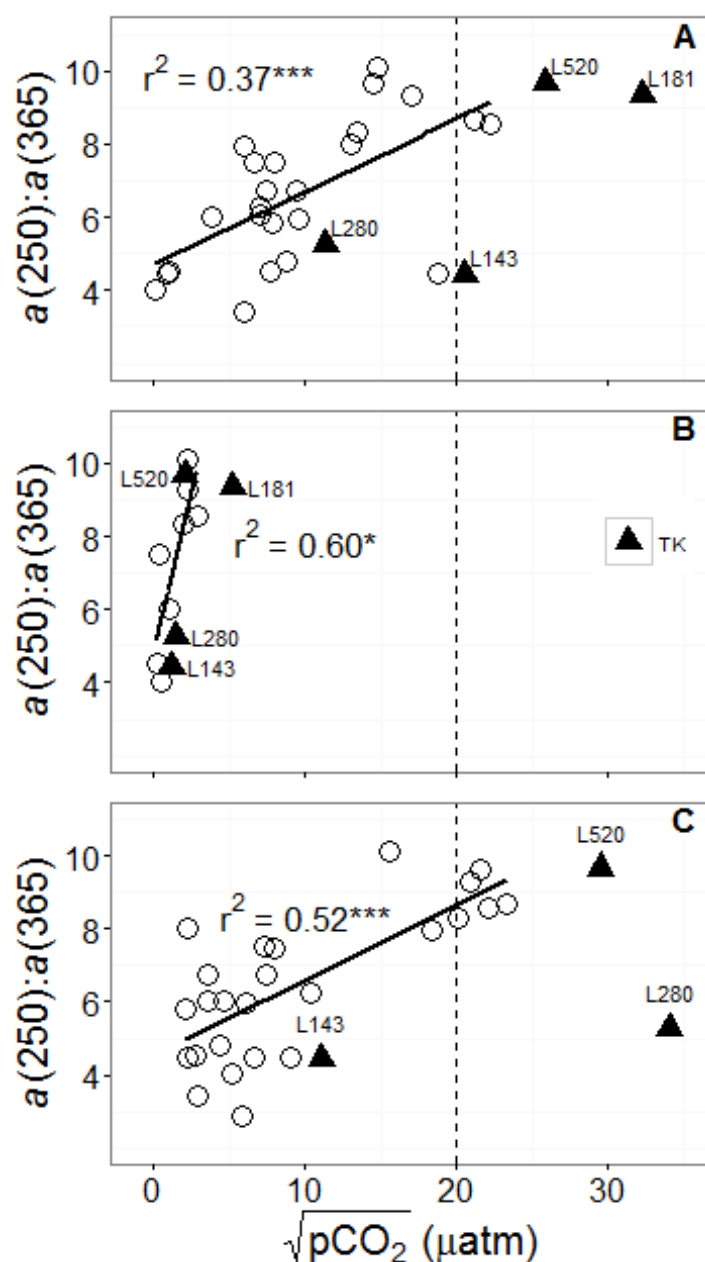


Figure 2-12. Relation of under-ice inferred DOM molecular weight [$a(250):a(365)$] accumulation with late summer CO_2 partial pressure.

Increasing $a(250):a(365)$ indicates decreasing DOM molecular weight. CO_2 partial pressures (pCO_2) were obtained during surveys of 40 lakes in August 2005 (A), 16 lakes August 2006 (B), and 40 lakes August 2014 (C). Under-ice $a(250):a(365)$ measurements were obtained in May 2014 in the same lakes CO_2 flux was measured during the 2005 and 2006 surveys. Thermokarst (TK)-affected lakes are drawn as triangles, and are the same lakes (L143, L181, and L520) as identified in previous studies (e.g., Tank et al. 2009); L280 was determined to be TK-affected as per Chapter 3. The dashed line indicates atmospheric pCO_2 , where measurements to the left of the line indicate CO_2 absorption, and measurements to the right of the line indicate CO_2 emission. TK-affected lakes were excluded from regression. Adjusted r^2 values are reported. * $P < 0.05$; and *** $P < 0.001$.

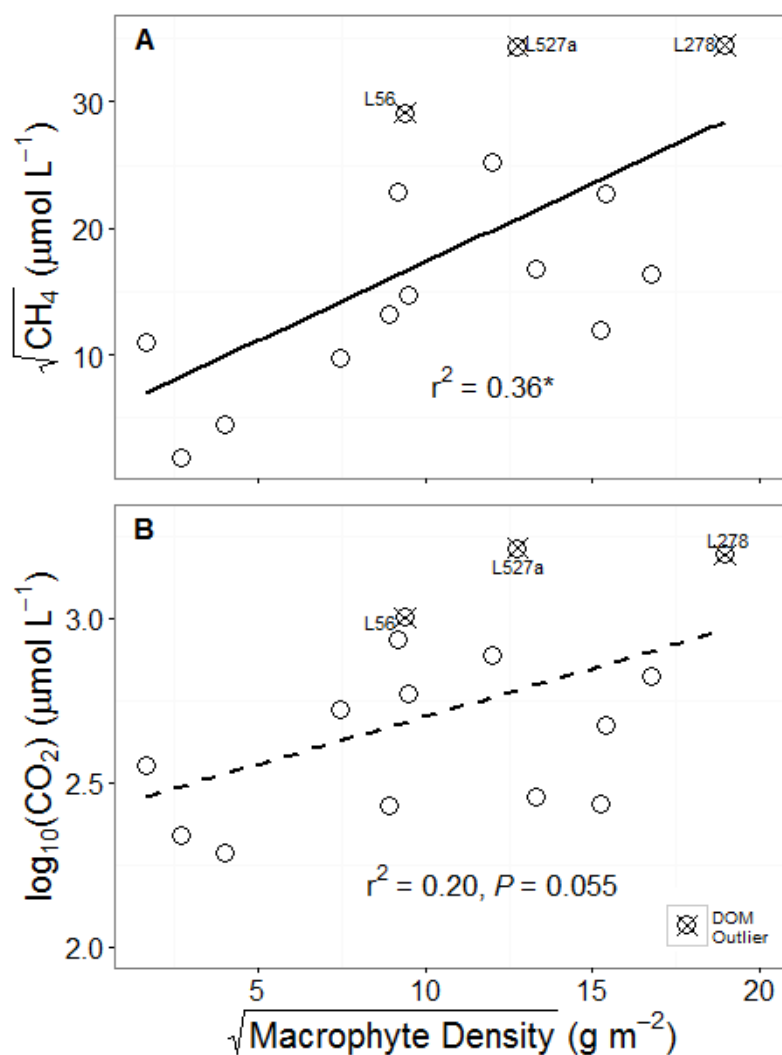


Figure 2-13. Under-ice CH_4 (A) and CO_2 (B) regressed against submerged macrophyte density.

DOM outliers from Figure 2-9 are shown as circles with x's. All points are included in regressions. A regression line was fit where relation is significant (A), and a dashed line was fit where regression is nearly significant (B). Submerged macrophyte densities were obtained from Squires et al. (2002). Adjusted r^2 values are reported. * $P < 0.05$.

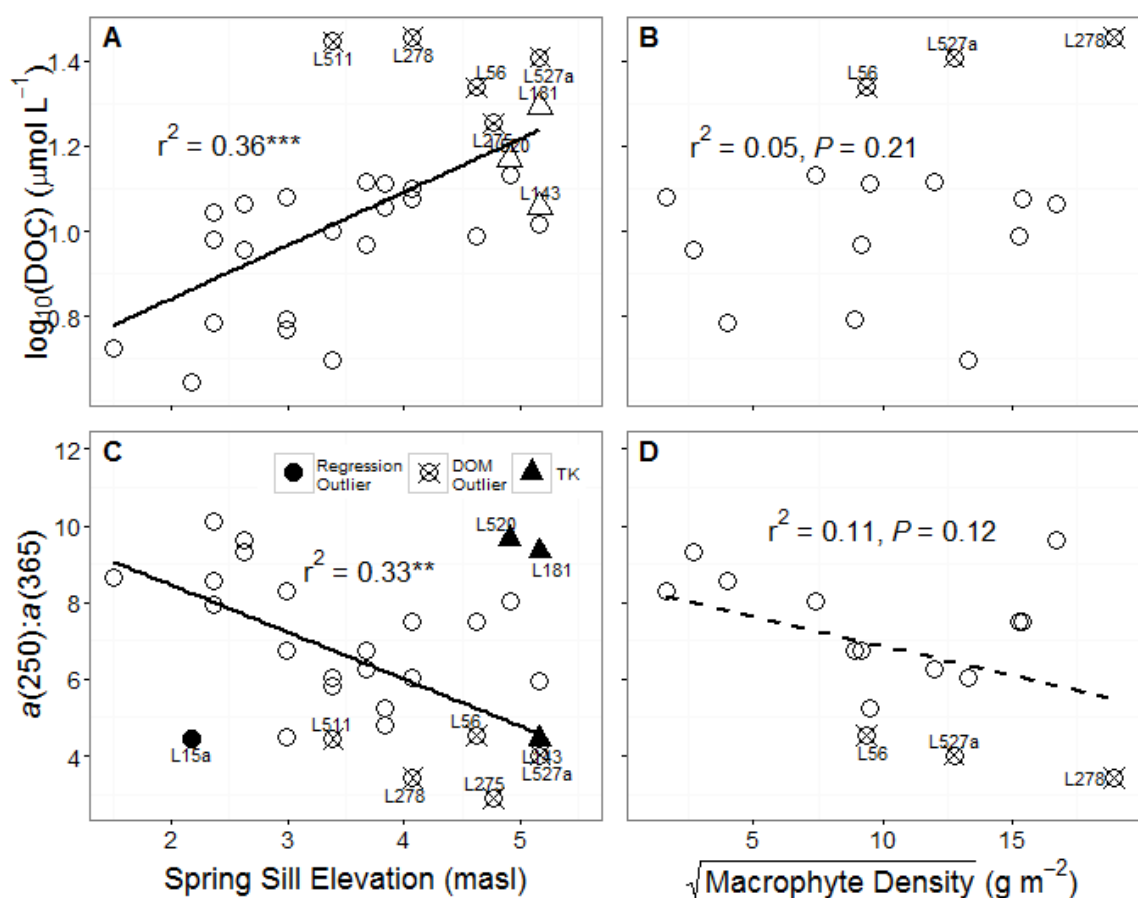


Figure 2-14. Under-ice DOC regressed against spring sill elevation (A) and submerged macrophyte density (B), and inferred DOM molecular weight regressed against spring sill elevation (C) and submerged macrophyte density (D).

Increasing $a(250):a(365)$ indicates decreasing DOM molecular weight. DOM outliers from Figure 2-9, shown as circles with x's, are included in all regressions. Thermokarst (TK)-affected lakes are shown as triangles, and where non-shaded are included in regressions. Shaded-in triangles (circles) are TK lakes (outliers) that have been excluded from regression. A regression line was fit where relation is significant (A and C), and a dashed line was fit where regression is nearly significant (D). Submerged macrophyte densities were obtained from Squires et al. (2002). Adjusted r^2 values are reported. $** P < 0.01$; $*** P < 0.001$.

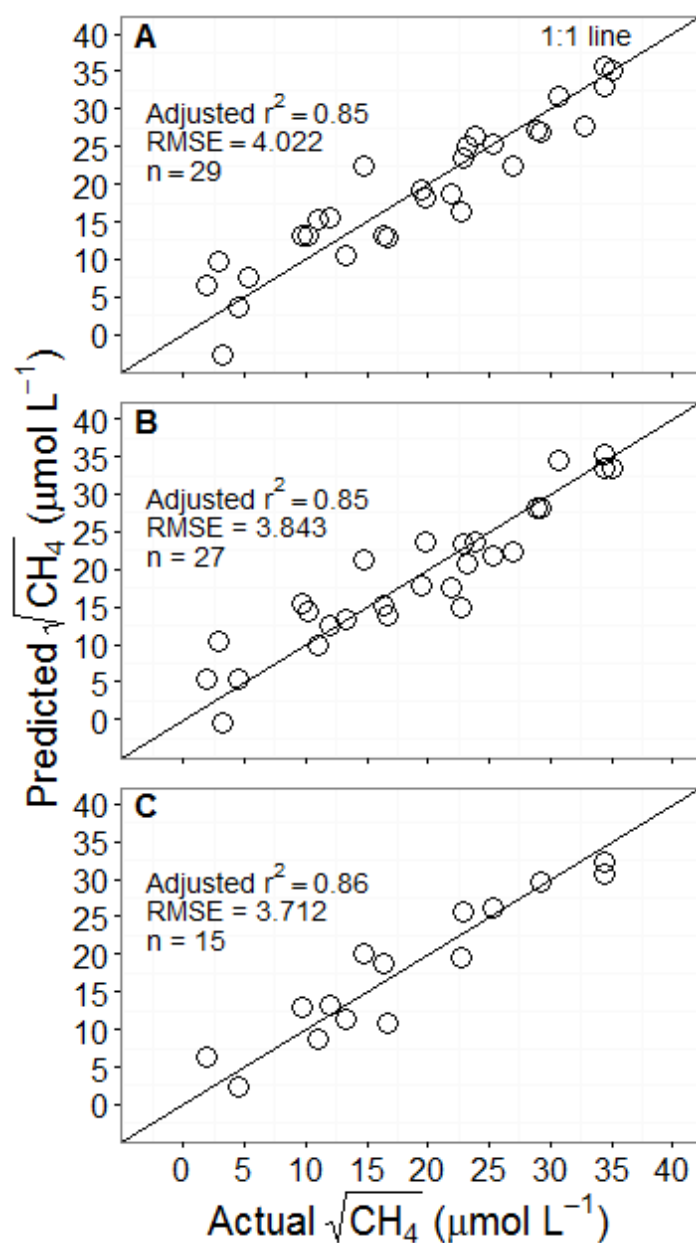


Figure 2-15. AIC-selected multiple regression models for under-ice dissolved CH_4 accumulation, using all data (A), excluding dissolved organic matter (DOM) molecular weight ($a(250):a(365)$) outliers (L181 and L15a, B), and using the subset of lakes with submerged macrophyte density (C).

Predictor variables are:

- (A) DIC, pH, $a(250):a(365)$, chlorophyll a , and area;
- (B) DIC, pH, and $a(250):a(365)$; and
- (C) DIC, pH, and TSS.

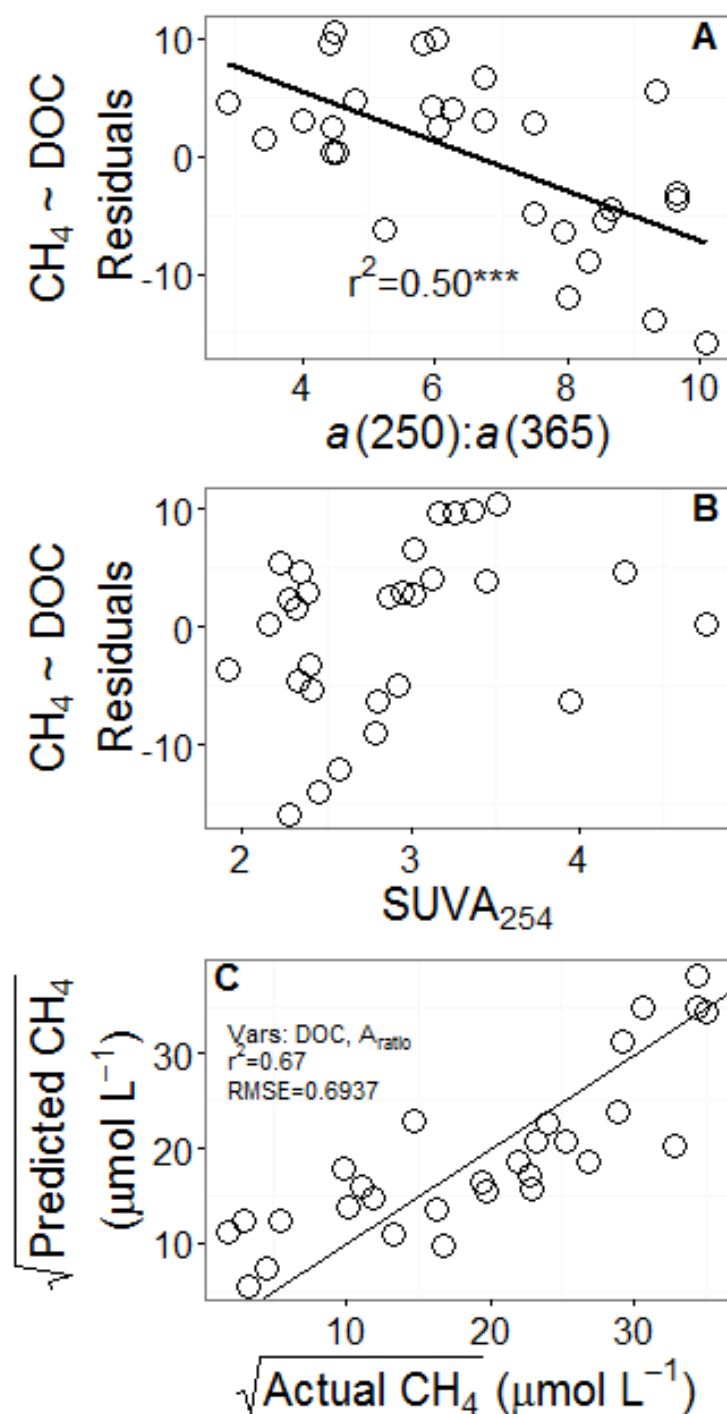


Figure 2-16. Residuals of under-ice CH_4 regressed against DOC plotted against DOM molecular weight (A) and aromaticity (B), and multiple regression for CH_4 using DOC and DOM molecular weight as predictor variables.

Increasing $a(250):a(365)$ indicates decreasing DOM molecular weight. Increasing SUVA_{254} indicates increasing DOM aromaticity. Adjusted r^2 value reported. *** $P < 0.001$.

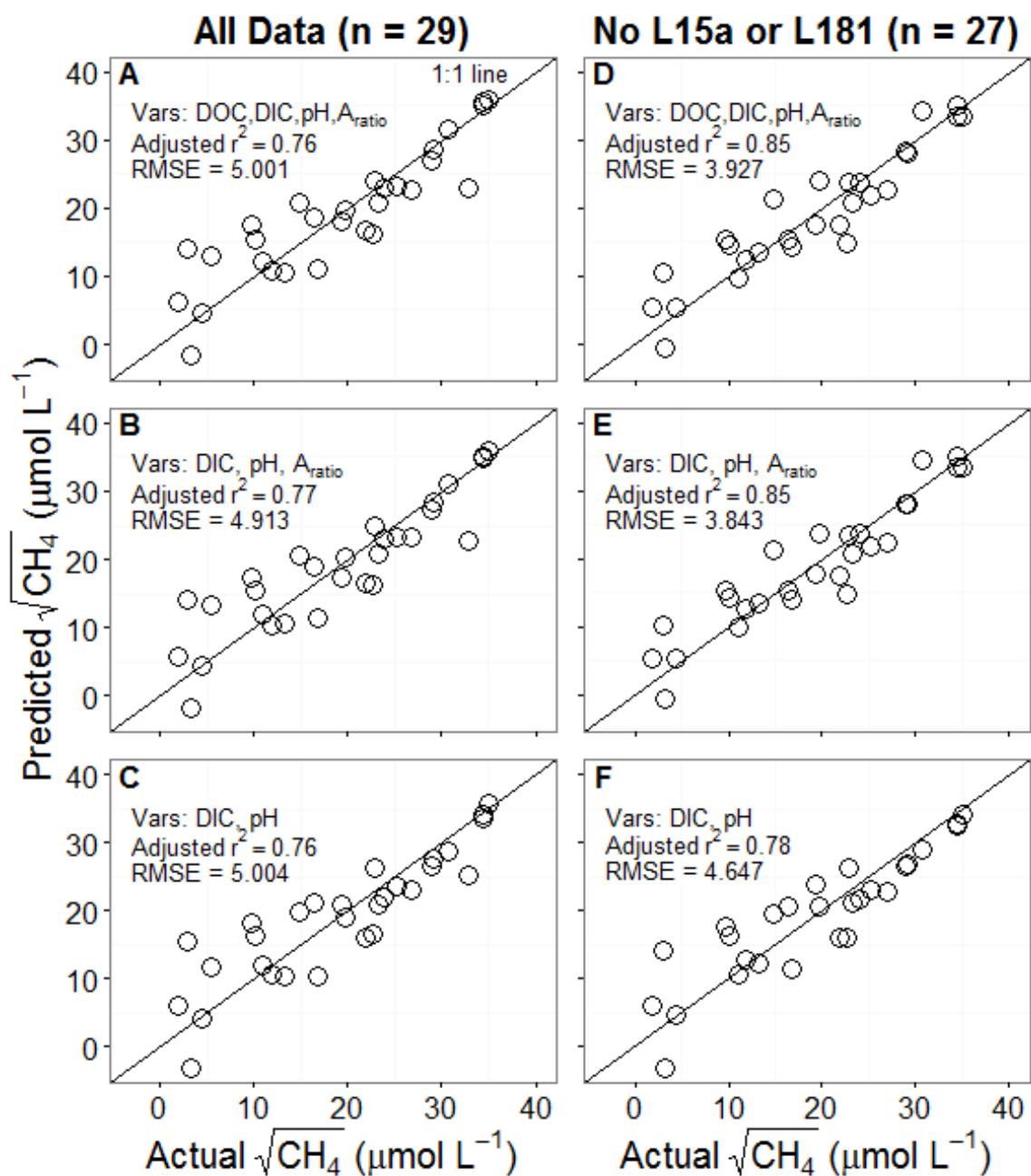


Figure 2-17. Multiple regression for under-ice CH_4 using all data (A-C) and excluding dissolved organic matter (DOM) molecular weight (A_{ratio} : $a(250):a(365)$) outliers (L181 and L15a, D-F).

Note that regression coefficients for DOC are not significant in A or D, and regression coefficients for A_{ratio} are not significant in A or B, but are significant in D and E (see Table 2-6). Vars: CH_4 predictor variables.

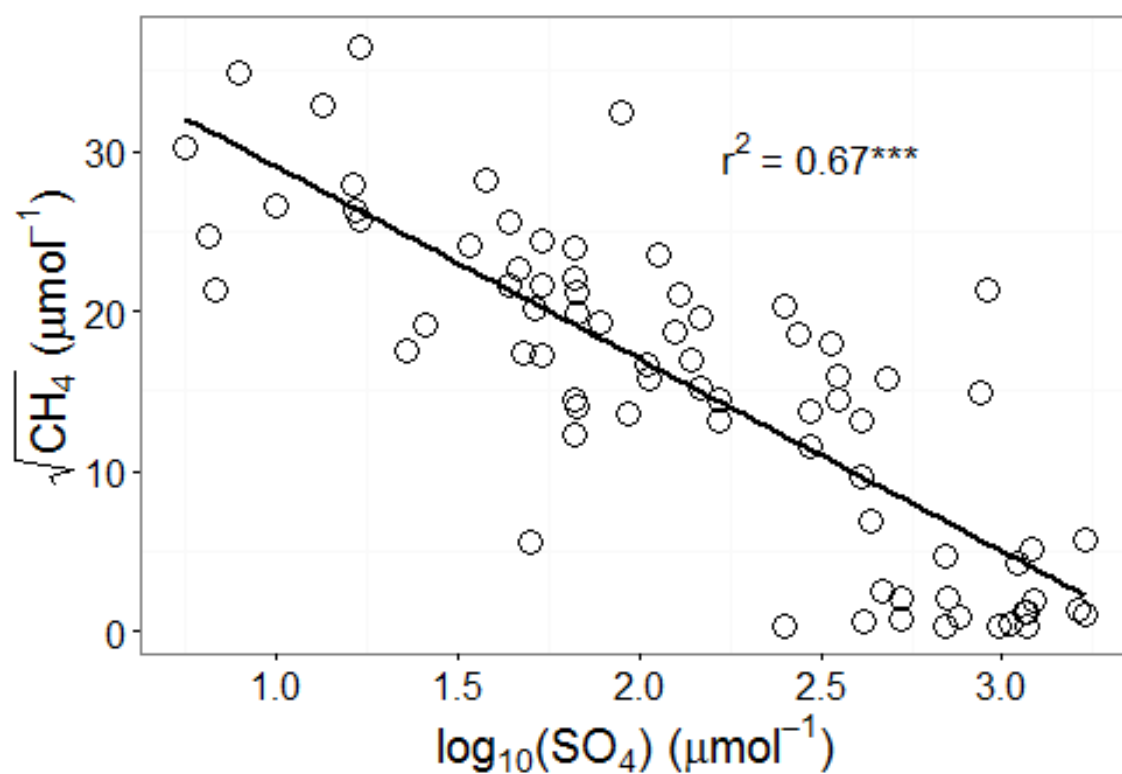


Figure 2-18. Negative relation between under-ice CH_4 and SO_4 in Mackenzie Delta lakes, data from Pipke (1996).
Adjusted r^2 values are reported. *** $P < 0.001$.

Chapter 3.

Open-Water Methane Dynamics in Mackenzie Delta Lakes

3.1. Introduction

Lakes are significant sources of methane (CH_4) to the atmosphere, and with over 45,000 lakes (Figure 3-1) (Emmerton et al. 2007) the Mackenzie Delta has the potential to produce a considerable amount of CH_4 emissions. CH_4 is a greenhouse gas that is 34 times as potent (normalized over a 100 year time scale) than carbon dioxide (CO_2) (Myhre et al. 2013), but seasonal CH_4 dynamics in the Mackenzie Delta are relatively unknown. As discussed in the previous chapter, CH_4 accumulates under-ice in Mackenzie Delta lakes, where lakes that are the most productive (i.e., CO_2 absorbers during the open-water period) tend to have the highest in situ levels of CH_4 prior to ice-out. The majority of Mackenzie Delta lakes are near neutral in terms of CO_2 , but the net CO_2 balance is significantly altered by thermokarst (thawing permafrost) additions of carbon into the lakes (Tank et al. 2009). Past investigations of partial pressures (p) of CH_4 in Mackenzie Delta lakes during the open-water period suggest that the lakes are CH_4 emitters, where pCH_4 in lake water ranges from 100-5,000 times more than atmospheric pCH_4 (Tank et al. 2009). The open-water dynamics of pCO_2 in Mackenzie Delta lakes have been linked to variable carbon sources (Tank et al. 2011), but open-water pCH_4 dynamics have been previously under-investigated.

Mackenzie Delta lakes are surrounded by permafrost, which limits input of water from subsurface and groundwater flows, and have small catchments that limit input from precipitation. The Mackenzie Delta experiences ice cover 7-8 months each year, and the open-water season takes place from June-October (Emmerton et al. 2007). The spring flood is the dominant hydrologic event in the Mackenzie Delta. Meltwater from warm southern reaches of the Mackenzie River flow north to the ice-covered Delta causing water levels to rise very quickly and flooding to occur (Mackay 1963, Marsh and Hey 1989). Not all lakes receive the same influx of water because Mackenzie Delta lakes occur at different elevations (Figure 1-2), and this difference of elevation between a lake and the Mackenzie River limits the influx of floodwater (Mackay 1963, Marsh and Hey 1989). Mackenzie Delta lakes have been operationally defined as no closure lakes (lowest elevation and connected to the river for most, if not all of the year), low closure lakes (intermediate elevation and connected to the river for part of the year), and high closure lakes (highest elevation and only connected to the river in intermittent years)(Mackay

1963, Marsh and Hey 1989). Thermokarst-affected lakes (i.e., lakes receiving an input of terrestrially-derived carbon due to melting permafrost) are also prominent in the Mackenzie Delta, and are usually a subset of high closure lakes (Burn and Kokelj 2009, Tank et al. 2009a, 2011).

The influx of spring river water increases total suspended sediments in the lake water column, where lakes with higher connection times to the river have higher sediment loading and sedimentation (Pipke 1996, Hay et al. 1997, Squires and Lesack 2003b). Less sedimentation occurs in lakes with lower connectivity resulting in conditions that allow submerged macrophytes to occur (Squires and Lesack 2003b). By late summer, the dense mats of submerged macrophytes are so productive that Mackenzie Delta lakes tend to absorb CO₂ (Tank et al. 2009). High closure lakes tend to be macrophyte-rich, so have a greater capacity to absorb CO₂ than low and no closure lakes. During the winter, macrophyte carbon appears to fuel a considerable amount of methanogenesis such that high closure lakes accumulate more CH₄ than lakes of lower elevation (Chapter 2). Thermokarst lakes also accumulate high levels of CH₄ during the winter, but conversely to other Mackenzie Delta lakes, tend to emit CO₂ during the open-water period (Tank et al. 2009). In other regions, thermokarst addition of carbon into lakes due to rising temperatures have been shown to result in enhanced levels of CH₄ emissions (Walter et al. 2006, Walter Anthony et al. 2010, Martinez-Cruz et al. 2015, Sepulveda-Jauregui et al. 2015), but the influence of thermokarst on CH₄ in lakes of the Mackenzie Delta has not been previously investigated.

3.1.1. Objectives

The open-water (i.e., ice-free) period for lakes in the Mackenzie Delta lasts for approximately 150 days, from late May or early June to October. The CH₄ dynamics in Mackenzie Delta lakes over this time period are important to understand because: (i) substantial generation of greenhouse gas (GHG) emissions to the atmosphere may occur; and (ii) changes in the pattern of pCH₄ throughout the course of summer, and along the hydrological gradient, may reveal mechanisms that could limit the escape of CH₄ to the atmosphere. CH₄ oxidation (MOX) is a function performed by CH₄ consuming bacteria that has the potential to re-route CH₄-derived energy into aquatic food webs.

Understanding the open-water dynamics are thus essential to figuring out the overall role of CH₄ in this system.

The same processes regulating CH₄ during the winter as discussed in Chapter 2 (e.g., temperature, substrate availability, and redox conditions) are also prevalent during the open-water period. Specifically of interest to this Chapter are the trends in pCH₄ throughout the open-water period, and what mechanisms might drive these patterns. Also of interest is the relative importance of dissolved organic matter (DOM)-quality, and quantity (i.e., dissolved organic carbon, DOC) in explaining patterns of open-water pCH₄ versus their importance in explaining under-ice CH₄. The questions we sought to answer in this chapter are detailed below.

Question 1: What kind of seasonal variability in CH₄ concentrations occurs during the open-water period, and how are lake closure and CH₄ concentrations related?

Hypothesis: CH₄ will decrease in all lakes throughout the open-water period. Mackenzie Delta lakes are well aerated in open-water conditions, which results in an environment with high redox potential, and therefore lower potential for CH₄ production. Macrophyte-rich lakes are stronger CH₄ producers than thermokarst-affected lakes because DOM-quality for methanogens is higher in macrophyte-rich lakes.

Question 2: How are seasonal trends in CH₄ concentrations related to dissolved organic matter (DOM)?

Hypothesis: CH₄ will be highest in lakes with higher quality DOM, i.e., macrophyte-rich lakes are stronger CH₄ producers than thermokarst lakes because DOM-quality for methanogens is higher in macrophyte-rich lakes.

3.2. Methods

3.2.1. Preparation of Sampling Bottles

All gas, DOC, CDOM, and other limnological samples collected in storage containers as detailed in Section 2.2.1.

3.2.2. Field Sampling

We sampled 43 Mackenzie Delta lakes (Table 1-1, Figure 3-1), which included the subset of 29 lakes sampled during May 2014 (Chapter 2). Open-water sampling took place in 2014 during 3 helicopter surveys (one in each month of June, July, and August) of the 43 lakes, and weekly surveys of a subset of 6 lakes. The June survey took place approximately 2 weeks after ice-out. During the 43 lake surveys, gas samples were obtained by gently scooping surface water into a bucket while lying flat on helicopter floats. While submerged in the bucket, serum bottles septa were pierced with a hypodermic needle, which was carefully removed when water stopped flowing into the bottle (i.e., pressure was equilibrated between the bottle and water). Serum bottles were kept submerged for 5-10 seconds to allow the stopper to reseal, then we swirled the bottles to dissolve the KCl. Samples for DOC, CDOM, chlorophyll *a*, and TSS were collected by pumping lake water directly into the prepared 1 L bottles. In situ water temperature, water conductivity, atmospheric pressure, and water depth were measured for each sampling event survey. During the 6 lake surveys, lakes were accessed by boat, and surface water was sampled directly rather than from a bucket. Samples for DOC, CDOM, chlorophyll *a*, and TSS were obtained by directly filling the prepared 1 L bottles with surface water. In situ water temperature, conductivity, atmospheric pressure, and water depth were measured at every sampling event.

3.2.3. Laboratory Analysis

All gas samples were analyzed at Simon Fraser University (Burnaby, British Columbia, Canada) by gas chromatography as detailed in Section 2.2.3. Also refer to Section 2.2.3 for details regarding CDOM, DOC, chlorophyll *a*, and TSS analysis. Nutrient

samples were analyzed by the University of Alberta Biogeochemical Analytical Service Laboratory (BASL) in Edmonton, Alberta.

3.2.4. Calculations and Data Acquisition

Refer to Section 2.2.4 for gas, pH, and DOM calculation methods.

Connection times were calculated using Mackenzie River (East Channel at Inuvik) water levels (referenced to the datum used in previous work, e.g., Lesack et al. 2010) at hydrometric station 10LC002 available online from the Water Survey of Canada (<http://wateroffice.ec.gc.ca/>), and summer and spring lake sill elevations. We assumed ice-out and flooding at the lakes to closely coincide with East Channel peak water levels, so we used the day of peak East Channel peak water levels as a time reference point for comparison. Submerged macrophyte density (g m^{-2}) and organic matter content (%) were obtained from Squires et al. (2002).

3.2.5. Statistics

We used second order Akaike Information Criterion (AICc) to assess the importance of open-water pCH_4 predictor variables for each 43 lake survey (Burnham and Anderson 2002). Refer to Section 2.2.5 for details regarding use of AICc to evaluate importance of predictor variables. We also compared a number of indices for comparing DOM molecular weight and aromaticity, including:

$$\text{CH}_4 \sim a(250):a(365) + \text{SUVA}_{254};$$

$$\text{CH}_4 \sim a(250):a(365);$$

$$\text{CH}_4 \sim \text{SUVA}_{254};$$

$$\text{CH}_4 \sim S_R + S_{275-295} + S_{350-400};$$

$$\text{CH}_4 \sim S_R;$$

$$\text{CH}_4 \sim S_{275-295};$$

$$\text{CH}_4 \sim S_{350-400}; \text{ and}$$

$$\text{CH}_4 \sim S_{300-600}.$$

Of these indices, only $S_{300-600}$ is not described in Section 2.2.4. Similar to the other spectral slope (S) indices, it was calculated by modeling napierian absorbances from $\lambda = 300-600$ nm. Increasing $S_{300-600}$ indicates decreasing DOM molecular weight, and decreasing $S_{300-600}$ indicates increasing DOM molecular weight and aromaticity (Markager and Vincent 2000).

Correlation matrices for all measurement variables from each 43 lake survey are presented in Appendix A. Data analyses were performed in RStudio, version 3.2.5 (RStudio Team 2016).

3.3. Results

3.3.1. Seasonal Methane Trends

Identification of Thermokarst Lakes

We tracked $p\text{CO}_2$ levels in our study lakes to potentially identify new thermokarst-affected lakes in addition to lakes which were identified as affected by thermokarst in previous studies (Squires et al. 2002, Tank et al. 2009). Since $p\text{CO}_2$ levels in Mackenzie Delta lakes consistently drop below atmospheric equilibrium during late summer, where higher elevation lakes are the greatest CO_2 absorbers, lakes that do not follow this trend are typically affected by thermokarst. We observed two clear outliers (L280 and L115) when regressing $p\text{CO}_2$ and sill elevation (Figure 3-2A; $r^2 = 0.15$, $P < 0.01$), which we further examined by grouping lakes into closure classes according to sill elevation (e.g., Lesack et al. 2010; Figure 3-2B). We also verified the presence of thermokarst along the margins of L280 and L115 using Google Earth as per Tank et al. (2009). Lakes L280 and L115, in addition to L520, L181, and L143, are considered thermokarst lakes in subsequent analyses.

43-lake Monthly Surveys

Increases in $p\text{CH}_4$ were strongly related to increases in spring sill elevation in early summer ($r^2 = 0.44$, $P < 0.001$; Figure 3-3A) and mid-summer ($r^2 = 0.30$, $P < 0.001$; Figure 3-3B), but were poorly related in late summer ($r^2 = 0.05$, $P = 0.09$; Figure 3-3C).

Considering that pCH_4 levels in thermokarst affected lakes did not exhibit anomalous trends compared to high and low closure lakes, pCH_4 in thermokarst-affected lakes was not excluded from regressions. There was one outlier excluded from pCH_4 against sill elevation regressions, however, which was the same outlier lake (L302a, aka “Big Lake”) observed by Tank et al. (2009).

pCH_4 generally decreased throughout the open-water period, but never fell below atmospheric equilibrium. In the early summer, mean pCH_4 was highest in thermokarst lakes at 8,480 μatm , and decreased along the spring sill elevation gradient, where pCH_4 was 6,995 μatm in high closure lakes, 1,814 μatm in low closure lakes, and 292 μatm in no closure lakes (Table 3-1, Figure 3-4). The same pattern held for the mid-summer and late summer surveys. In the mid-summer, pCH_4 was 2,985 μatm in thermokarst lakes, 1,791 μatm in high closure lakes, 1,186 μatm in low closure lakes, and 749 μatm in no closure lakes. In the late summer, pCH_4 was 1,585 μatm in thermokarst lakes, 1,020 μatm in high closure lakes, 893 μatm in low closure lakes, and 678 μatm in no closure lakes. pCH_4 decreased in thermokarst, high closure, and low closure lakes throughout the summer, but increased in no closure lakes after early summer (Figure 3-4).

6-lake Weekly Surveys

pCH_4 generally increased over the open-water period in the lowest elevation lakes (Figure 3-5). In the intermediate elevation lakes (L87 and L280) and high closure lake (L56), pCH_4 is highest after ice-out and decreases over the summer. Ice-out is assumed to coincide with peak water levels (i.e., flooding of lakes). At 4.958 masl (referenced to the pre-1990 Water Survey Canada datum), peak water levels at the East Channel (at Inuvik) of the Mackenzie River are within normal ranges (Lesack et al. 2013). L520, a lake identified as thermokarst-affected in previous studies has 2 pCH_4 peaks: first around 2 weeks following flood, and another around 60 days following flood. The thermokarst lake we identified in 2014, L280 (see above), does not exhibit the same temporal trend in pCH_4 as L520.

3.3.2. DOM-Quality and Quantity

43-lake Monthly Surveys

The DOM-quality indices with the strongest statistical relations to pCH₄ during each of the 43 lake open-water surveys were $a(250):a(365)$ and SUVA₂₅₄ (Table 3-2). Increases in the $a(250):a(365)$ ratio indicates decreasing DOM molecular weight, whereas increasing SUVA indicates increasing DOM aromaticity. DOM-quality was subsequently assessed using these two indices in all following analyses. In situ pCH₄ was statistically higher in lakes with lower molecular weights of DOM (i.e., increasing $a(250):a(365)$) in the early summer ($r^2 = 0.17$, $P < 0.01$), but was weakly related to molecular weight in mid-summer ($r^2 = 0.06$, $P = 0.06$) and unrelated in late summer (Figure 3-6A). In situ pCH₄ was also statistically higher in lakes with lower DOM aromaticity (i.e., decreasing SUVA values) during mid-summer ($r^2 = 0.16$, $P < 0.05$) and early summer ($r^2 = 0.22$, $P < 0.01$), and unrelated to DOM aromaticity during late summer (Figure 3-6B). The decrease in DOM molecular weight (Figure 3-6A) and aromaticity (Figure 3-6B) as the summer progressed is indicative of DOM photolysis (Tank et al. 2011).

DOM quantity, rather than quality was more strongly related to pCH₄. Although not related in the early summer (Figure 3-7A), CDOM (i.e., water colour measured as naperian absorbance at $\lambda = 350$ nm) increased with pCH₄ during mid-summer ($r^2 = 0.22$, $P < 0.01$; Figure 3-7B) and late summer ($r^2 = 0.09$, $P < 0.05$; Figure 3-7C). Increasing DOC was strongly related to increasing pCH₄ in the early summer ($r^2 = 0.23$, $P < 0.001$; Figure 3-8A) and mid-summer ($r^2 = 0.55$, $P < 0.001$; Figure 3-8B), but was less strongly related in late summer ($r^2 = 0.09$, $P < 0.05$; Figure 3-8C).

6-lake Weekly Surveys

DOM molecular weight (measured as $a(250):a(365)$; Figure 3-9A) and aromaticity (measured as SUVA₂₅₄; Figure 3-9B) steadily decreased throughout the open-water period, and also decreased as sill elevation increased in the 6 intensively studied lakes. The decrease in DOM molecular weight and aromaticity throughout the open-water period is likely due to DOM photolysis (Tank et al. 2011). DOM aromaticity drops sharply around 30 and 70 days after the spring flood peak in Lake 280 (Figure 3-9B). Since no parallel changes are observed in DOM molecular weight for Lake 280 (Figure 3-9A), the aromaticity drops in L280 may be due to concurrent addition of DOC (Figure 3-10). The DOC spikes could originate from macrophyte exudates during a period of high production,

or from thermokarst carbon. $p\text{CO}_2$ in the six lake subset generally decreases in the lakes (Figure 3-11), which reflects an increase in macrophyte activity over the measurement period. Considering that $p\text{CO}_2$ levels in L280 also coincide with the DOC spikes (Figure 3-10), the DOC spikes in L280 are not likely to be macrophyte exudates. Since decreases in DOM molecular weight and aromaticity (Figure 3-9A and B) were concurrent with DOC spikes, photolysis of thermokarst carbon is the more likely explanation and further suggests that L280 is a thermokarst lake.

3.3.3. $p\text{CH}_4$ Along the Productivity Gradient

Primary production in Mackenzie Delta lakes can be observed by seasonal decreases in $p\text{CO}_2$, which is also closely linked to winter CH_4 accumulation, sediment organic matter content, and submerged macrophyte biomass. Water column $p\text{CO}_2$ was not significantly related to $p\text{CH}_4$ levels during the summer (Figure 3-12). Under-ice CH_4 in the water column at the end of winter (measured in May 2014; see Chapter 2) was strongly related to open-water $p\text{CH}_4$ in the early summer ($r^2 = 0.40$, $P < 0.001$; Figure 3-13A) and mid-summer ($r^2 = 0.27$, $P < 0.01$; Figure 3-13B), but was not statistically related by late summer (Figure 3-13C). Sediment organic matter was not significantly related to $p\text{CH}_4$ in the water column during any of the seasonal surveys (Figures 3-14A to C), though it showed a weak trend in early summer (Figure 3-14A). However, submerged macrophyte biomass was strongly related to water-column $p\text{CH}_4$ in early summer ($r^2 = 0.37$, $P < 0.01$; Figure 3-14D), and showed a weaker but near-significant statistical trend in mid-summer ($r^2 = 0.15$, $P = 0.06$; Figure 3-14E), but was not statistically related by late summer (Figure 3-14F). Furthermore, pH was not related to $p\text{CH}_4$ in early summer, mid-summer, or late summer (Figure 3-15A to C). Although $p\text{CH}_4$ was highest in lakes of smallest area during the early summer ($r^2 = 0.40$, $P < 0.001$, Figure 3-16A) and, to a lesser extent during mid-summer ($r^2 = 0.07$, $P = 0.07$, Figure 3-16B), area and $p\text{CH}_4$ were not related by late summer (Figure 3-16C). An outlier lake, L521 was excluded from regressions of $p\text{CH}_4$ and area.

3.3.4. Potential Seasonal Drivers of pCH₄

Considering that winter CH₄ accumulation in Mackenzie Delta lakes is driven by products of DOM decomposition, DOM quality, and lake-river connectivity (Chapter 2), we also explored these as potential drivers of water column pCH₄ during the open-water period. We evaluated all possible combinations of pCH₄ predictor variables (pCO₂, pH, DOM molecular weight ($\alpha(250):\alpha(365)$) and aromaticity (SUVA₂₅₄), area, spring sill elevation, and DOC) with AICc (i.e., AIC adjusted for small sample size) for each survey of lakes. Prior to AICc analyses, we screened the variables for correlation with CH₄ and multicollinearity between predictor variables (see correlation matrices in Appendix A), and determined it was not necessary to drop any variables due to collinearity. The relative importance of predictor variables was highly seasonal (Table 3-3). During the early summer, pCO₂ and spring sill elevation, which is a composite variable for increasing primary productivity, were significant predictors of pCH₄. In the mid-summer, DOC was the only predictor of pCH₄ with a significant model-averaged regression coefficient. For the late summer, area was a significant predictor when outliers were included, however, once removing outliers (L302a, L521, and all thermokarst lakes), none of the predictor variables explained late summer pCH₄ well. After excluding outliers and thermokarst lakes, 62% of the variance in pCH₄ could be explained during the early summer, 53% in mid-summer, and 4% in late summer multiple regressions (Table 3-4). Models were relatively well fit in early and mid-summer, with or without outliers (Figure 3-17A to D), however, late summer models were poor fits (Figure 3-17E and F).

Similar to Section 2.3.4, we directly evaluated the relation of DOM quality and quantity with pCH₄ by plotting DOM molecular weight and aromaticity against the residuals of regression of pCH₄ against DOC (i.e., pCH₄ ~ DOC). DOM molecular weight was closely related to pCH₄ ~ DOC residuals during early summer (Figure 3-18A), where positive residuals were related to lower molecular weight and negative residuals were related to higher molecular weight ($r^2 = 0.19$, $P < 0.01$). In other words, increases in early summer pCH₄ ~ DOC residuals were related to decreases in DOM molecular weight, which is the opposite of what we observed during winter. Similarly, early summer pCH₄ ~ DOC residuals were related to decreases in DOM aromaticity ($r^2 = 0.10$, $P < 0.05$; Figure 3-18B). DOM molecular weight and aromaticity were unrelated to pCH₄ and DOC during

mid and late summer (Figure 3-18C to F). Since DOM molecular weight and aromaticity were not related to the partial regression of pCH₄ and DOC during mid- and late summer, we only conducted multiple regression from DOC and DOM molecular weight and aromaticity for the early summer survey. Together, DOC and DOM molecular weight and aromaticity can explain up to 41% of the variance in early summer pCH₄ (Figure 3-19), where the regression coefficient of DOC was significant ($\alpha = 0.05$) with or without Lakes 4 and 107 (outliers from Figures 3-18A and B), DOM molecular weight was significant when including all data, but not without outliers, and DOM aromaticity was not significant with or without outliers.

We also compared pCH₄ to total nitrogen and total phosphorous. These data were only available for the subset of six lakes, and the following relationships were based on data collected throughout the open-water period (i.e., not based on seasonal relationships). pCH₄ increased with increasing total nitrogen ($r^2 = 0.36$, $P < 0.01$; Figure 3-20A), and decreased with increasing total phosphorous ($r^2 = 0.32$, $P < 0.01$; Figure 3-20B). Total nitrogen was related to DOM quantity and quality (Figure 3-21), where increases in total nitrogen were related to increasing DOC ($r^2 = 0.79$, $P < 0.001$), decreasing DOM molecular weight ($r^2 = 0.67$, $P < 0.001$), and decreasing DOM aromaticity ($r^2 = 0.70$, $P < 0.001$). Total phosphorous did not appear to be related to DOM quantity or quality (Figure 3-22).

3.4. Discussion

3.4.1. Seasonal Variation in pCH₄

Water column pCH₄ levels among Mackenzie Delta lakes were always above atmospheric levels. To our knowledge seasonal measurements from other Arctic deltas are not in the literature, however, our CH₄ measurements are comparable to other Arctic and sub-Arctic regions in North America (Table 3-5). As we expected: pCH₄ (i) in thermokarst and high and low closure lakes declined significantly throughout the open-water period, and (ii) average levels in thermokarst-affected and high closure lakes respectively were about 2,800% and 2,300% higher than no closure lakes in the early summer shortly after ice-out, 300% and 140% higher in mid-summer, and 130% and 50%

higher in late summer (mid-summer difference in thermokarst and no closure lakes was significant, otherwise mid and late summer differences among the lake classes were not statistically different). Unlike the other lake classes, $p\text{CH}_4$ in no closure lakes increased from early to midsummer, although not significantly, before decreasing slightly into late summer. Considering that the lakes reaerate upon exposure to the atmosphere after ice-out, and that temperatures are relatively low, the high $p\text{CH}_4$ levels observed in the early summer could be partly explained as residual winter CH_4 rather than CH_4 that was produced after ice-out. Reaeration of the water column raises the redox potential of the water column, which when fully mixed deepens the surface sediment reduction zone and limits methanogenesis to subsurface sediment.

3.4.2. DOM Decomposition and Photolysis

Early Summer

As expected, we found increasing $p\text{CH}_4$ to be related to increasing DOM quality (i.e., decreasing DOM molecular weight and aromaticity), which is the opposite of the trend that we observed under-ice (Chapter 2). During the winter, DOM molecular weight increases as CH_4 increases, which suggests that under-ice ambient DOM reflects the amount of decomposition that has occurred. During the early summer, however, the positive relation between increasing DOM quality (i.e., decreasing molecular weight and aromaticity) and the partial regression of $p\text{CH}_4$ against DOC suggests that labile DOM is fueling microbial communities in these lakes, a portion of which is converted into CH_4 . During the winter and early and mid-summer there is a sharp gradient in CH_4 levels among lakes in the Mackenzie Delta, where CH_4 levels increased with increasing substrate availability, which is inherently due to differences in sill elevation and primary production. Considering the AIC and partial regression results together, DOM quantity and quality as well as spring sill elevation and $p\text{CO}_2$ are highly related to early summer $p\text{CH}_4$. This suggests that carbon cycling during the early summer is less driven by primary production and DOM photolysis, both of which become more prominent as the summer progresses, and more so driven by microbial activity and the Mackenzie Delta hydrological gradient. The timing of the early summer survey was roughly two weeks following the spring flood, which affects the lakes to varying degrees according to lake elevation relative to the river. Higher elevation lakes are connected to the Mackenzie River for shorter durations, and

this lower lake-river contact time results in less flushing of the lakes (Lesack and Marsh 2010), thus microbial activity are likely disturbed to a lesser degree in higher elevation lakes than lower elevation lakes after ice-out. Consequently, this may allow for greater organic matter decomposition in higher elevation lakes, which may result in greater substrate for methanogens, thus culminating in more CH₄ production in higher elevation lakes.

Mid-summer

Mid-summer pCH₄ levels were also related to DOM quantity, but not quality, and sill elevation, however, unlike in early summer the observed pattern is likely shaped to a large extent by DOM photolysis. The spring flood delivers a pulse of sediments into the lakes, which increases light attenuation, and when sediments settle out of the water column DOM photolysis occurs given the long Arctic summer days. DOM photolysis can occur at a substantial rate in Mackenzie Delta lakes (Gareis 2007), and is likely responsible for the seasonal decrease in DOM molecular weight and aromaticity we observed. Considering that DOM photolysis is very unlikely to occur in the sediment, which is where methanogenesis should be occurring since the lakes are well aerated during mid-summer, and DOM in the water column has been affected by photolysis, water column DOM quality is not likely to reflect DOM quality in anoxic sediment. As such, DOM quantity and lake elevation remain as significant predictors of mid-summer pCH₄, which suggests that the apparent gradient of increasing organic matter decomposition, and microbial activity, with increasing hydrologic isolation persists into mid-summer in Mackenzie Delta lakes.

Late Summer

DOM quantity and quality were weakly related to late summer pCH₄, and there was no significant trend in pCH₄ across the lake-river connectivity gradient, which was unexpected. Furthermore, DOM quality and quantity, pCO₂, and pH can individually explain only up to 9% of the variance in late summer pCH₄, which is not improved with multiple regression. This suggests that water column DOM photolysis has no direct effect on methanogenesis during the later summer, however, DOM photolysis could contribute to water column methanogenesis after anoxia is established under-ice during the winter.

Late summer DOM is lower in molecular weight and aromaticity due to photolysis and may serve as a labile microbial substrate at the onset of winter.

Nitrogen

The relationships we observed between total nitrogen and DOM suggest a strong influence on CH₄ cycling within the lakes. The majority of total nitrogen was primarily TDN (over 86%), and given that TDN is primarily DON in these lakes (Tank 2009), the highly significant relationship to DOC suggests that organic matter processing and release of inorganic nitrogen from DOM may have a strong effect on CH₄ dynamics. However, rather than microbial processing of organic matter, it may be that photolysis plays a more critical part in processing DOM and mineralizing nutrients for methanogens. Total nitrogen was positively related to DOC, decreasing DOM molecular weight, and decreasing DOM aromaticity, where decreasing DOM molecular weight and aromaticity in Mackenzie Delta lakes is indicative of DOM photolysis (Gareis 2007, Tank et al. 2011). This suggests that the 24 hour Arctic summer daylight may have a more complex interaction with CH₄ dynamics than what may be assumed considering that anoxic sediment zones are likely sheltered from sunlight. To our knowledge there are no studies linking methanogenesis to DOM photolysis in the literature.

3.4.3. Ebullition and MOX

Since there is certainly a substrate availability and quality gradient among the lakes, no temperature gradient (assessed with a one-factor (closure class) ANOVA, $P = 0.27$), and similar redox (i.e., well aerated) conditions exist among the lakes, why is there such a lack of variability in late summer pCH₄? During the early summer, pCH₄ levels were related to indicators of autochthonous production (e.g., submerged macrophyte biomass) as well as increasing DOM quality, but not during late summer. Considering that late summer pCH₄ was higher than early summer pCH₄ in no closure lakes, and that no closure lakes produce the least CH₄ over the winter, factors other than decreasing methanogenesis in the higher elevation lakes during over the course of the summer are likely driving late summer pCH₄ patterns in Mackenzie Delta lakes.

We propose two hypothesis to explain the lack of variation in late summer $p\text{CH}_4$ among lakes. Firstly, we hypothesize that there is variability in CH_4 ebullition between Mackenzie Delta lakes. CH_4 produced in the anoxic sediment zone either escapes to the atmosphere via ebullition, or diffuses upwards through the oxygenated surface sediments and across the sediment-water interface before reaching the water column and eventually the atmosphere (Segers 1998, Bastviken et al. 2004). As seen in Chapter 2, under-ice CH_4 accumulation is strongly related to late summer primary production with increasing lake elevation. Considering that the lakes are not covered in ice, CH_4 ebullition is not likely to effect $p\text{CH}_4$ levels (Greene et al. 2014). Therefore, it may be the case that late summer CH_4 ebullition also increases with lake elevation.

Secondly, differences in MOX may explain the late summer trends of $p\text{CH}_4$. MOX can significantly reduce the amount of CH_4 observed in lakes (Rudd et al. 1974, Bédard and Knowles 1997, Horz et al. 2002, Bastviken et al. 2003, 2008). MOX can occur in anoxic (via anaerobic SO_4^{2-} reduction) and oxygenated sediments, throughout the overlying benthos, and the water column, which leaves water column CH_4 as the net balance between CH_4 flux across the sediment-water interface and water column MOX and diffusion into the atmosphere (Figure 1-4). Consequently, if MOX is greater in high closure and thermokarst lakes than low and no closure lakes, then ambient $p\text{CH}_4$ in high closure and thermokarst lakes under-represents the amount of organic matter decomposition in the lakes. Isotopic signatures of zooplankton suggest CH_4 oxidizing bacteria are an important part of food webs in Mackenzie Delta lakes (Tank 2009), which suggests that MOX could play a significant role in limiting CH_4 emissions from these lakes. We discuss CH_4 ebullition and MOX in more detail in the following chapter.

3.4.4. Thermokarst-Affected Lakes

Although thermokarst dramatically alters $p\text{CO}_2$ dynamics in Mackenzie Delta lakes, it was surprising that we did not observe similar effects in $p\text{CH}_4$ dynamics. In the late summer, ambient $p\text{CO}_2$ levels in the lakes is the net balance between microbial processing of DOC (the efficiency of which is significantly altered by DOM quality), CO_2 production from DOM photolysis, and submerged macrophyte-driven primary production (which is primarily driven by light availability). The late summer decline of $p\text{CO}_2$ with

increasing sill elevation is a well-defined trend in the lakes, and departures from this trend are clear indications of allochthonous input of carbon from thermokarst (Tank et al. 2009). In this manner, and with supporting aerial imagery showing shoreline slumping, we identified two new thermokarst-affected lakes in addition to those previously identified. $p\text{CH}_4$ levels were consistently highest in thermokarst lakes, though not always significantly so. Assuming that higher $p\text{CH}_4$ levels indicate greater rates of CH_4 production, it is possible that thermokarst lakes in the Mackenzie Delta also produce more CH_4 by ebullition. In other regions, lakes affected by thawing of yedoma (ice and organic-rich) permafrost have been shown to produce significantly more CH_4 than thermokarst-affected lakes in non-yedoma permafrost regions, and lakes that received organic-rich permafrost were prone to release considerably more CH_4 via ebullition (Kling et al. 1992, Walter et al. 2006, Walter Anthony et al. 2010, Sepulveda-Jauregui et al. 2015). The Mackenzie Delta is underlain by permafrost that is rich in organic matter content (Kokelj and Burn 2005, Burn and Kokelj 2009, Nguyen et al. 2009, Hugelius et al. 2014, Schuur et al. 2015), and CH_4 ebullition is known to occur during the winter as evidenced by bubbles trapped in ice and “hotspots” (holes in ice) where ebullition has prevented ice from forming (Figure 3-23). As discussed in the following chapter, due to a small sample size we were unable to resolve potential differences in late summer CH_4 ebullition to account for a lack of variation in late summer $p\text{CH}_4$ between lakes of different closure type and thermokarst extent, however this does seem to be a plausible explanation. Additional study is required to determine the relationship between thermokarst versus primary production and CH_4 ebullition in Mackenzie Delta lakes.

3.5. Conclusion

Regardless of the season, Mackenzie Delta lakes are consistent CH_4 emitters throughout the open-water period. Although allochthonous carbon input via thermokarst drastically affects $p\text{CO}_2$ balances in these lakes, $p\text{CH}_4$ levels in thermokarst lakes are not dramatically higher than lakes of comparable closure class, but are indeed higher than in other Mackenzie Delta lakes. Considering that winter, early summer, and mid-summer CH_4 levels in the lakes are strongly linked to sill elevation and DOM quality and quantity, the weak relationships of these variables with late summer $p\text{CH}_4$ suggests that significant

differences in MOX and/or CH₄ ebullition occur along the sill elevation gradient, where MOX and ebullition must be increasingly important in higher elevation lakes. In terms of climate change, increasing temperatures are linked to increasing incidence of thermokarst-related inputs of permafrost carbon to lakes, which lead to enhancement of CH₄ emissions from Arctic lakes. In addition to direct impacts of temperature and thawing permafrost, Mackenzie Delta lakes are subject to the dynamic hydrology of the Mackenzie River. Climate change has a significant effect on spring-time Mackenzie River ice jamming, and subsequent flooding of lakes, which has unknown ecological consequences. Future studies regarding the effects of climate change on CH₄ in Mackenzie Delta lakes requires parallel understanding of the effects of climate change on the Mackenzie River and the flooding ecohydrology of these lakes.

3.6. References

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3.7. Tables

Table 3-1. Summary of Respective Mean, Maximum, and Minimum Partial Pressures (p) of CH₄ (µatm) in Thermokarst (TK)-Affected Lakes, High Closure Lakes, Low Closure Lakes, and No Closure Lakes Measured During Early Summer, Mid-Summer, and Late Summer 2014.

Closure Class	Number of Lakes	Mean	Maximum	Minimum	Standard Deviation
<i>Early Summer</i>					
TK	5	8,480	12,642	3,585	3,485
High	12	6,995	27,675	607	7,281
Low	14	1,814	5,619	73.46	1,847
No	5	292	736	93	275
<i>Mid-Summer</i>					
TK	5	2,985	5,279	1,372	1,790
High	13	1,791	3,175	712	756
Low	18	1,186	2,848	213	720
No	5	749	2,332	93	912
<i>Late Summer</i>					
TK	4	1,585	3,192	688	1,158
High	13	1,020	2,293	494	443
Low	20	893	1,687	370	383
No	5	678	997	113	356

Maximum (minimum) refers to the highest (lowest) individual lake pCH₄ level in respective closure classes. Standard deviation is given to reflect the spread of measurements within each lake class.

Table 3-2. Second Order Akaike's Information Criteria (AICc) Weights of DOM-Quality Indices as Predictors of Dissolved CH₄ (only top 4 weights for each season are shown).

Predictors	w _i	Δ _i
<i>All Data (n = 155)</i>		
<i>a(250):a(365)</i>	0.52	0.00
<i>a(250):a(365) + SUVA₂₅₄</i>	0.21	1.80
<i>SUVA₂₅₄</i>	0.19	1.99
<i>S₃₀₀₋₆₀₀</i>	0.02	6.30
<i>June Data (n = 36)</i>		
<i>a(250):a(365)</i>	0.71	0.00
<i>a(250):a(365) + SUVA₂₅₄</i>	0.23	2.28
<i>S₃₀₀₋₆₀₀</i>	0.03	6.54
<i>SUVA₂₅₄</i>	0.02	7.25
<i>July Data (n = 41)</i>		
<i>a(250):a(365) + SUVA₂₅₄</i>	0.49	0.00
<i>a(250):a(365)</i>	0.25	1.33
<i>SUVA₂₅₄</i>	0.25	1.37
<i>S₃₀₀₋₆₀₀</i>	0.01	7.67
<i>August Data (n = 42)</i>		
<i>a(250):a(365)</i>	0.30	0.00
<i>SUVA₂₅₄</i>	0.21	0.75
<i>a(250):a(365) + SUVA₂₅₄</i>	0.19	0.95
<i>S₃₅₀₋₄₀₀</i>	0.08	2.66

AICc weights (from 0 to 1) indicate relative variable importance when comparing across all possible combinations of predictor variables (i.e., 1 indicates the variable is present in 100% of the best assessed models).

Four analyses were performed: (i) using all measurements; (ii) using June (early summer) measurements only; (iii) July (mid-summer) measurements only; and (iv) late summer (August) measurements only.

Indices of DOM molecular weight include *a(250):a(365)*, *S₃₀₀₋₆₀₀*, and *S₃₅₀₋₄₀₀*, where S refers to spectral slope. *SUVA₂₅₄* refers to DOM aromaticity (see methods for full descriptions).

Table 3-3. Results of Second Order Akaike's Information Criteria (AICc) Model Selection Analysis, Showing Model-averaged AICc Weights of Seasonal pCH₄ Predictor Variable Coefficients.

Predictor	Early Summer		Mid-Summer		Late Summer	
	All Data	Outliers ¹ Removed	All Data	Outliers ¹ Removed	All Data	Outliers ² Removed
	(n = 36)	(n = 30)	(n = 41)	(n = 35)	(n = 41)	(n = 35)
pCO ₂	0.97(+)	0.95(+)*	0.10	0.12	0.10	0.17
pH	0.19	0.17	0.09	0.12	0.10	0.25
<i>a(250):a(365)</i>	0.23	0.13	0.26	0.12	0.48	0.18
SUVA ₂₅₄	0.11	0.16	0.09	0.11	0.33	0.15
Area	0.59	0.29	0.09	0.13	0.97(-)*	0.13
Sill	1.00(+)**	1.00(+)**	0.84	0.60	0.14	0.12
DOC	0.34	0.42	1.00(+)**	1.00(+)**	0.66	0.39

¹Outliers include all thermokarst lakes (L115, L143, L181, L280, and L520) and L302a.

²Outliers include all thermokarst lakes (L115, L143, L181, L280, and L520), L302a, and L521.

AICc weights (from 0 to 1) indicate relative variable importance when comparing across all possible combinations of predictor variables (i.e., 1 indicates the variable is present in 100% of the best assessed models). Weights in bold (italics) indicate regression coefficient is significant to $\alpha = 0.05$ ($\alpha = 0.10$) with sign given in brackets.

a(250):a(365): inferred dissolved organic matter (DOM) molecular weight, where increasing ratio indicates decreasing molecular weight.

SUVA₂₅₄: DOM aromaticity, where increasing values indicate increasing aromaticity.

* $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$.

Table 3-4. Multiple Regression Models Identified by Second Order Akaike Information Criterion (AICc) Analyses for Open-water Surveys.

Regression Equation	AICc Weight	n	Adjusted r ²	P-Value
Early Summer 43 Lake Survey				
<i>All data</i>				
Model: $\log_{10}(\text{pCH}_4) = 1.55\log_{10}(\text{pCO}_2) - 0.24\log_{10}(\text{Area}) + 2.36\log_{10}(\text{Sill}) - 2.15$	0.13	36	0.66	<0.001
P-value: 0.007 0.045 0.004 0.3				
<i>Outliers excluded: all thermokarst lakes (L115, L143, L181, L280, and L520) and L302a</i>				
Model: $\log_{10}(\text{pCH}_4) = 2.05\log_{10}(\text{pCO}_2) + 2.04\log_{10}(\text{DOC}) + 3.59\log_{10}(\text{Sill}) - 7.53$	0.14	30	0.62	<0.001
P-value: 0.004 0.10 <0.001 0.002				
Mid-summer 43 Lake Survey				
<i>All data</i>				
Model: $\log_{10}(\text{pCH}_4) = 0.45 + 2.46\log_{10}(\text{DOC}) + 0.76\log_{10}(\text{Sill})$	0.18	41	0.68	<0.001
P-value: 0.2 <0.001 0.02				
<i>Outliers excluded: all thermokarst lakes (L115, L143, L181, L280, and L520) and L302a</i>				
Model: $\log_{10}(\text{pCH}_4) = 0.48 + 2.51\log_{10}(\text{DOC}) + 0.62\log_{10}(\text{Sill})$	0.17	35	0.53	<0.001
P-value: 0.3 <0.001 0.08				
Late Summer 43 Lake Survey				
<i>All data</i>				
Model: $\log_{10}(\text{pCH}_4) = 1.95 - 0.09\log_{10}(\text{Area}) + 0.75\log_{10}(\text{DOC}) + 0.09A_{\text{ratio}}$	0.11	41	0.34	<0.001
P-value: 0.007 0.01 0.03 0.09				
<i>Outliers excluded: all thermokarst lakes (L115, L143, L181, L280, and L520), L302a, and L521</i>				
Model: $\log_{10}(\text{pCH}_4) = 2.54 + 0.42\log_{10}(\text{DOC})$	0.08	35	0.04	0.13
P-value: 0.007 0.13				

Note that the regression in Figure 3-8C of pCH₄ against DOC gives a different result than the outliers excluded regression for the late summer survey in the above table because the regression in Figure 3-8C only excludes L302a.

A_{ratio}: a(250):a(365), which is inferred dissolved organic matter (DOM) molecular weight, where increasing ratio indicates decreasing molecular weight.

P-values for multiple regression coefficients are given below respective predictor variables.

AICc weights indicate the likelihood of the model being the best from among all the models assessed in each respective analysis (i.e., for a model weight of 0.13, there is a 13% chance the model is the best from among all the models assessed for the given data).

Table 3-5. Depth-Corrected Dissolved CH₄ (mmol m⁻²) in North American Lakes and Ponds.

Source	Location/Lake Type	Timeframe	Number of Lakes	CH ₄
Present study	Thermokarst	June 2014	5	2.58 - 57
Present study	High closure	June-August 2014	13	0.77 - 88
Present study	Low closure	June-August 2014	14	0.38 - 16
Present study	No closure	June 2014	5	0.12 - 3.42
Laurion et al. (2010)	Nunavik	July 2007	13	0.08 - 0.88
Laurion et al. (2010)	Nunavut	July 2007	21	0.04 - 10
Hamilton et al. (1994)	Manitoba (coastal fen ponds)	June-October 1990	10	0.06 - 58
Hamilton et al. (1994)	Manitoba (interior fen ponds)	June-October 1990	10	0.32 - 48
Hamilton et al. (1994)	Manitoba (Kinosheo bog)	June-October 1990	10	0.18 - 43.80
Martinez-Cruz et al. (2015)	Alaska (yedoma)	June/July 2011	7	8.42 - 424
Martinez-Cruz et al. (2015)	Alaska (non-yedoma)	June/July 2011	23	5.61 - 247

3.8. Figures



Figure 3-1. Location of Mackenzie Delta lakes sampled during open-water 2014. Yellow text indicates the subset of 6 lakes, which were sampled weekly as well as during the 43 lake surveys.

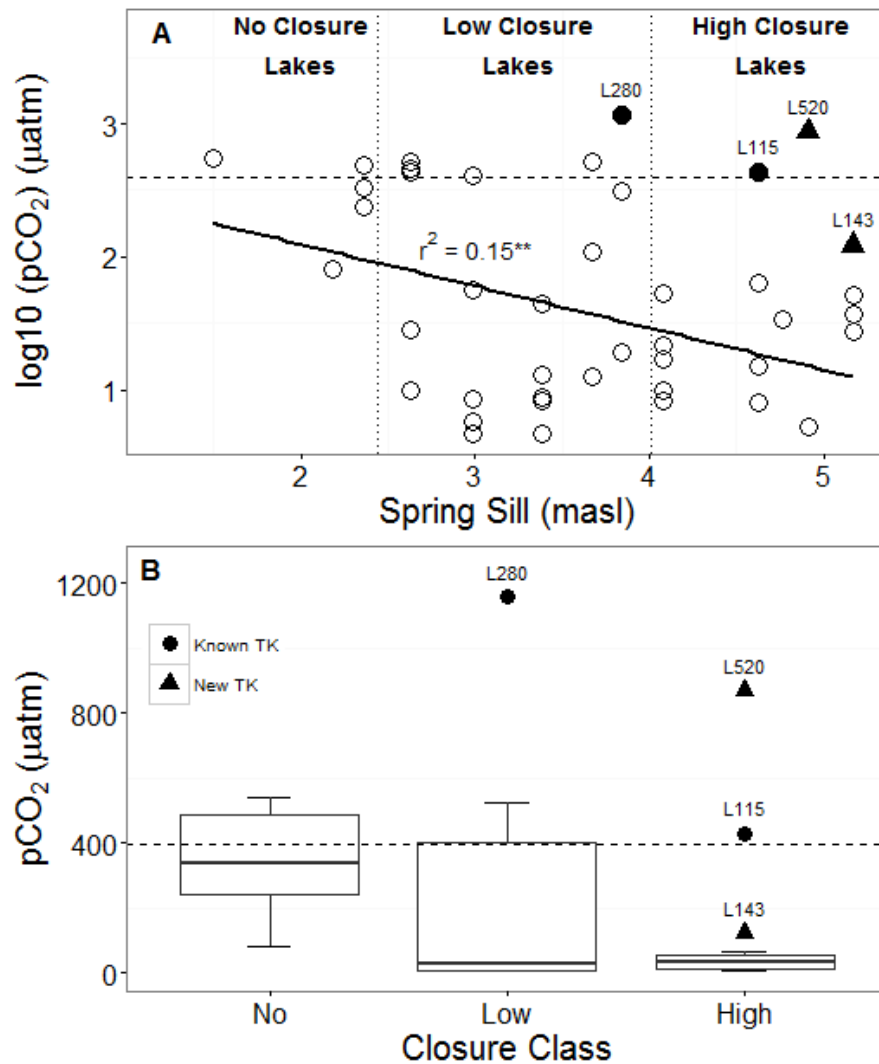


Figure 3-2. Identification of thermokarst (TK) lakes through regression of 2014 late summer pCO₂ levels against spring sill elevation (A) and distribution of pCO₂ within historically defined closure classes.

Dotted lines delineate no, low, and high closure lakes, and dashed lines indicate atmospheric pCO₂. Lakes were grouped into closure classes as in previous studies of lakes in the same study area (e.g., Lesack and Marsh 2010). “Known TK” are lakes known to be thermokarst (TK)-affected (L143 and L520; L181 is another TK lake, but was not sampled during late summer 2014) and are drawn as triangles, and “New TK” are lakes that are likely newly identified as TK-affected. Boxes indicate the first quartile (bottom of box), median (line within box), and third quartile (top of box) of pCO₂ measurements. Whiskers indicate maximum and minimum measurements that are within 1.5 times the interquartile range, where values beyond the whiskers are outliers (i.e., TK-affected). pCO₂ outliers from the late summer survey are considered TK lakes in subsequent analyses. Adjusted r^2 values are reported. $^{**} P < 0.01$.

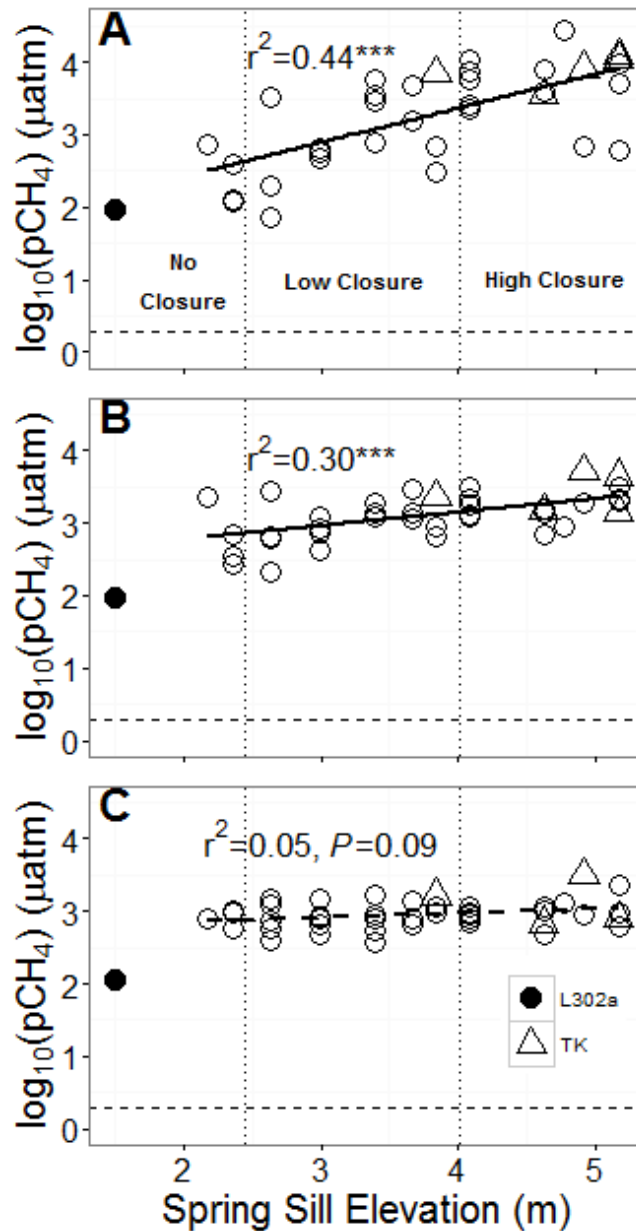


Figure 3-3. Regression of pCH_4 against sill elevation from surveys of 43 Mackenzie Delta Lakes during early summer (A), mid-summer (B), and late summer (C) of 2014.

Dotted lines delineate no, low, and high closure lakes, and dashed lines indicate atmospheric pCH_4 . Hollow triangles indicate thermokarst (TK)-affected lakes. TK lakes did not exhibit unusual pCH_4 levels, thus were included in regressions. L302a was excluded from regressions. A regression line was fit where relationship is significant (A and B), and a dashed line was fit where regression was nearly significant (C). Adjusted r^2 values are reported. *** $P < 0.001$.

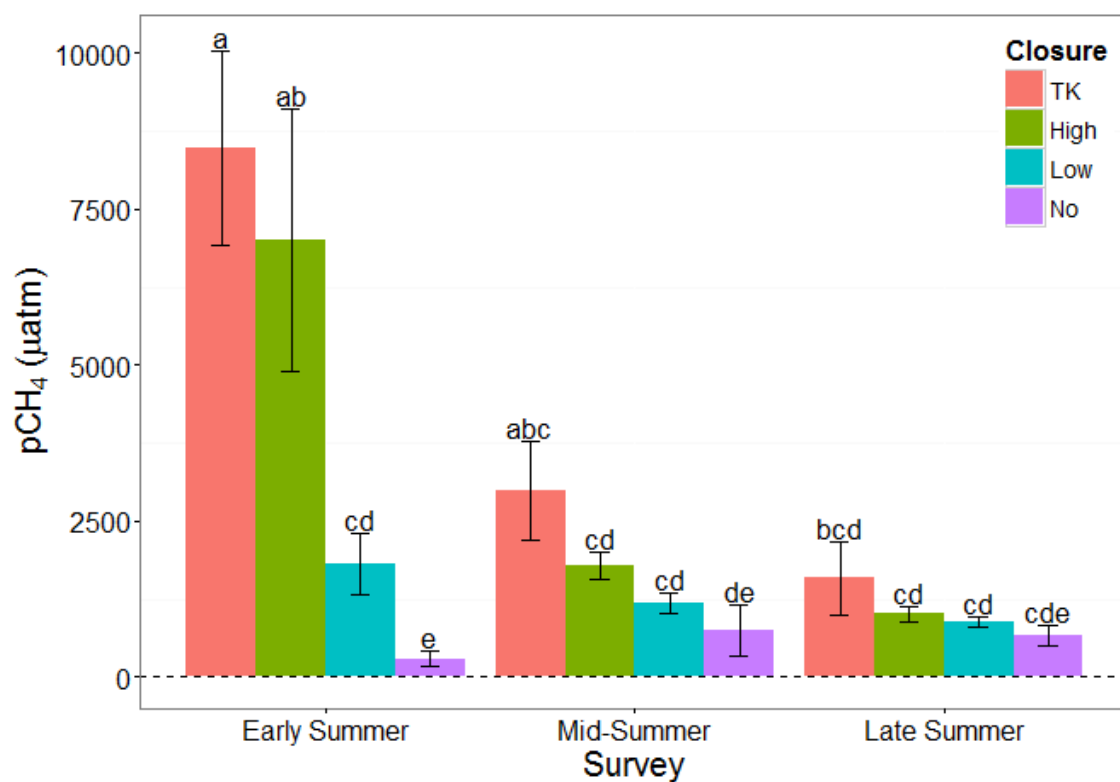


Figure 3-4. Mean pCH₄ in Mackenzie Delta lakes in the early summer, mid-summer, and late summer 43-lake surveys.

Atmospheric pCH₄ indicated with dashed line. Error bars are ± 1 standard error of mean concentrations. Differing letters above error bars indicate significant difference at $\alpha = 0.05$.

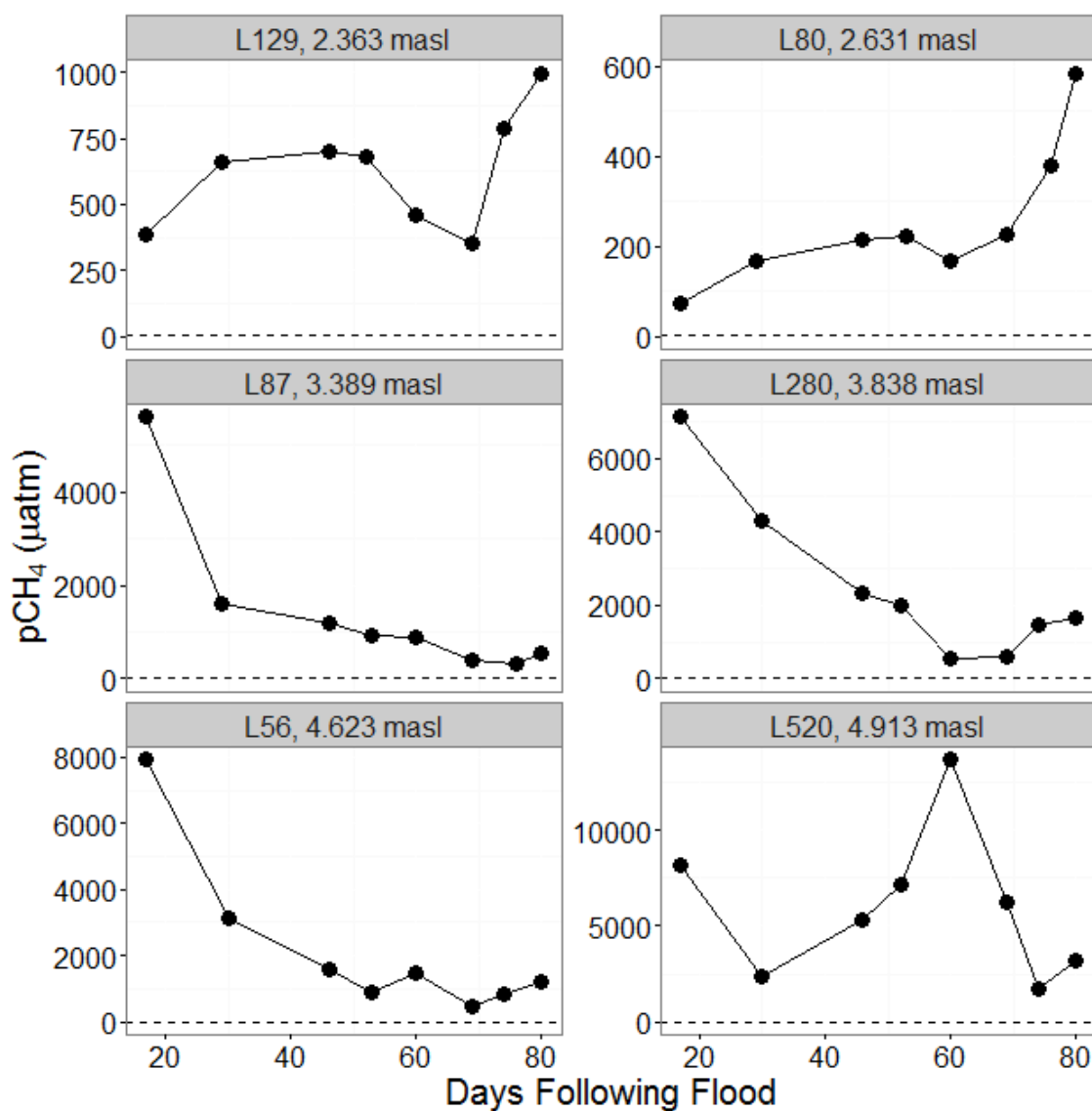


Figure 3-5. pCH₄ in 6 intensively studied Mackenzie Delta lakes.

Atmospheric pCH₄ indicated with dashed lines. Spring sill elevation (masl) for each lake is indicated on each plot. Lake 280 and Lake 520 are thermokarst lakes. Days following flood approximates time since ice-out, which was assumed to occur on the day of peak water at East Channel.

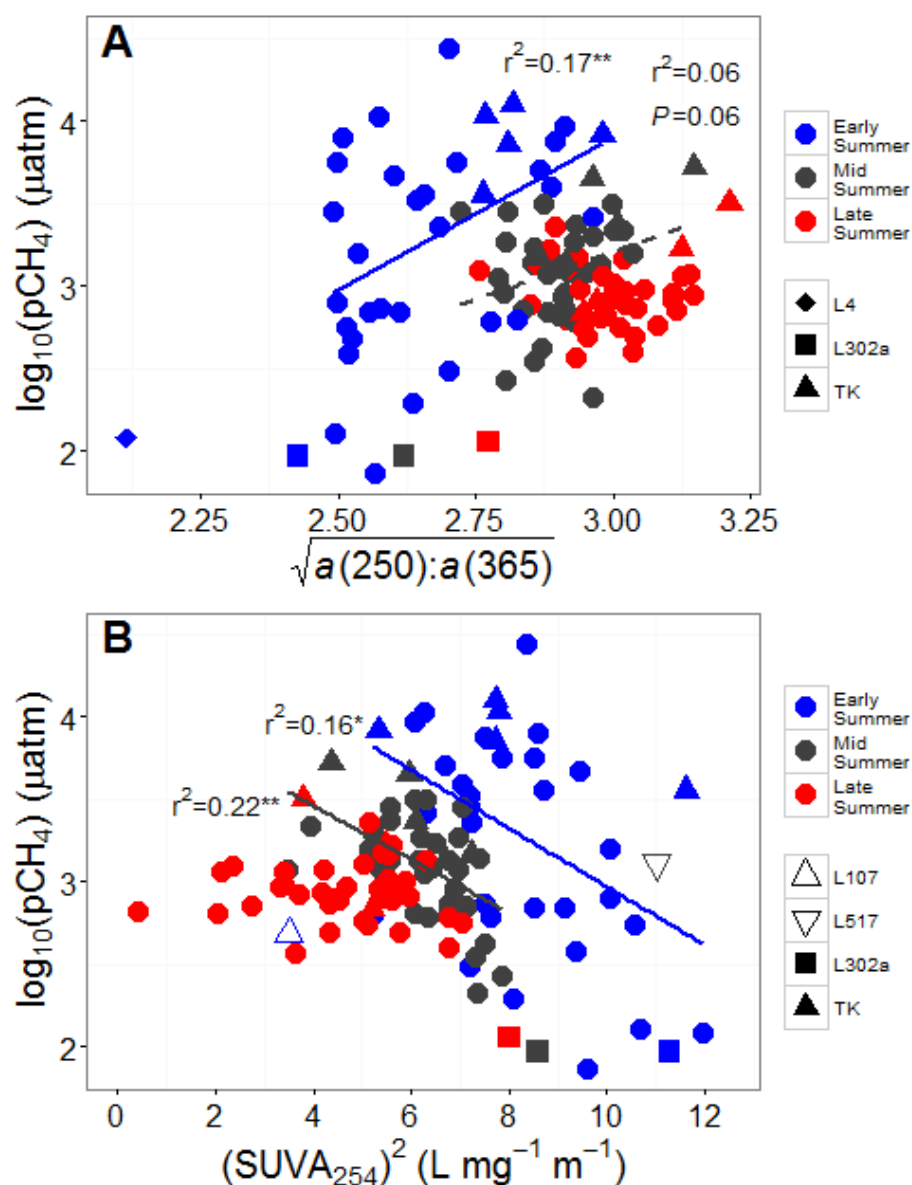


Figure 3-6. Levels of pCH₄ during early, mid, and later summer versus (A) inferred molecular weight ($a(250):a(365)$) and (B) aromaticity ($SUVA_{254}$) of dissolved organic matter (DOM).

Increasing $a(250):a(365)$ indicates decreasing DOM molecular weight, and increasing $SUVA_{254}$ indicates increasing DOM aromaticity. Thermokarst (TK) lakes did not exhibit unusual pCH₄ levels, thus were included in regressions, but L302a was excluded from regressions. L4 was excluded from early summer DOM molecular weight regression. L107 and L517 were excluded from early and mid-summer DOM aromaticity regressions, respectively. A regression line was fit where relationship is significant, and a dashed line was fit where regression is nearly significant. Adjusted r^2 values are reported. * $P < 0.05$; ** $P < 0.01$.

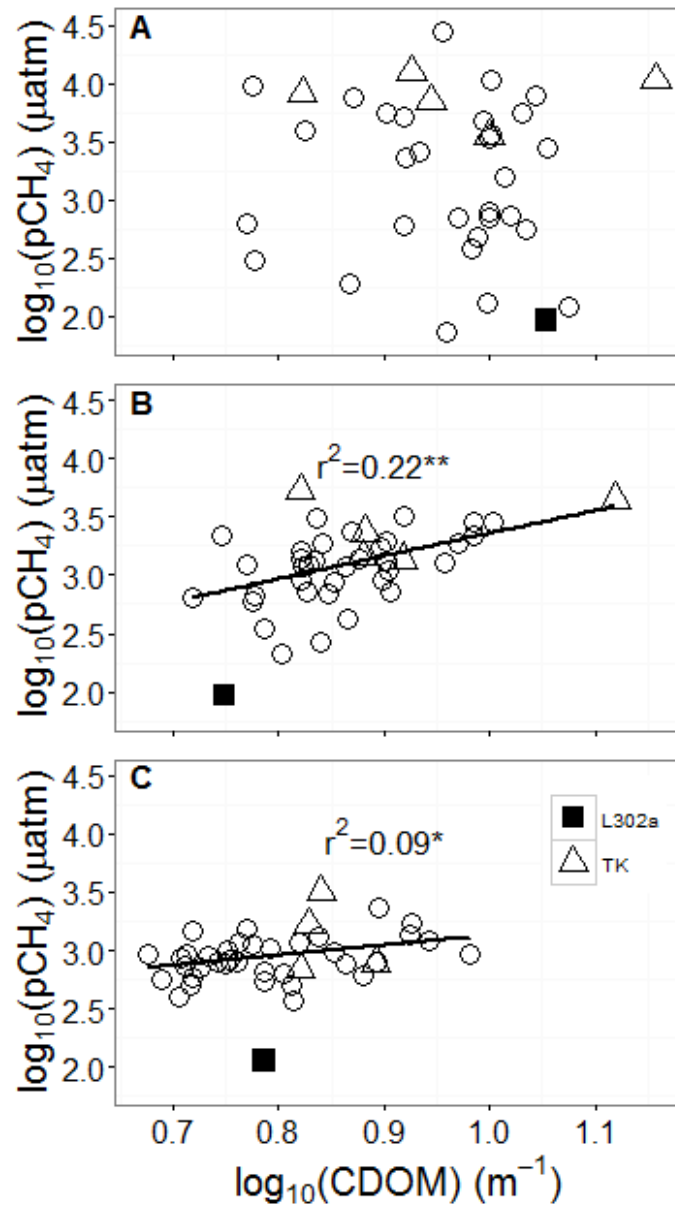


Figure 3-7. Regression of pCH₄ against CDOM from surveys of 43 Mackenzie Delta Lakes during early summer (A), mid-summer (B), and late summer (C) of 2014.

Hollow triangles indicate thermokarst (TK)-affected lakes. TK lakes did not exhibit unusual pCH₄ levels, thus were included in regressions. Adjusted r^2 values are reported. * $P < 0.05$; ** $P < 0.01$.

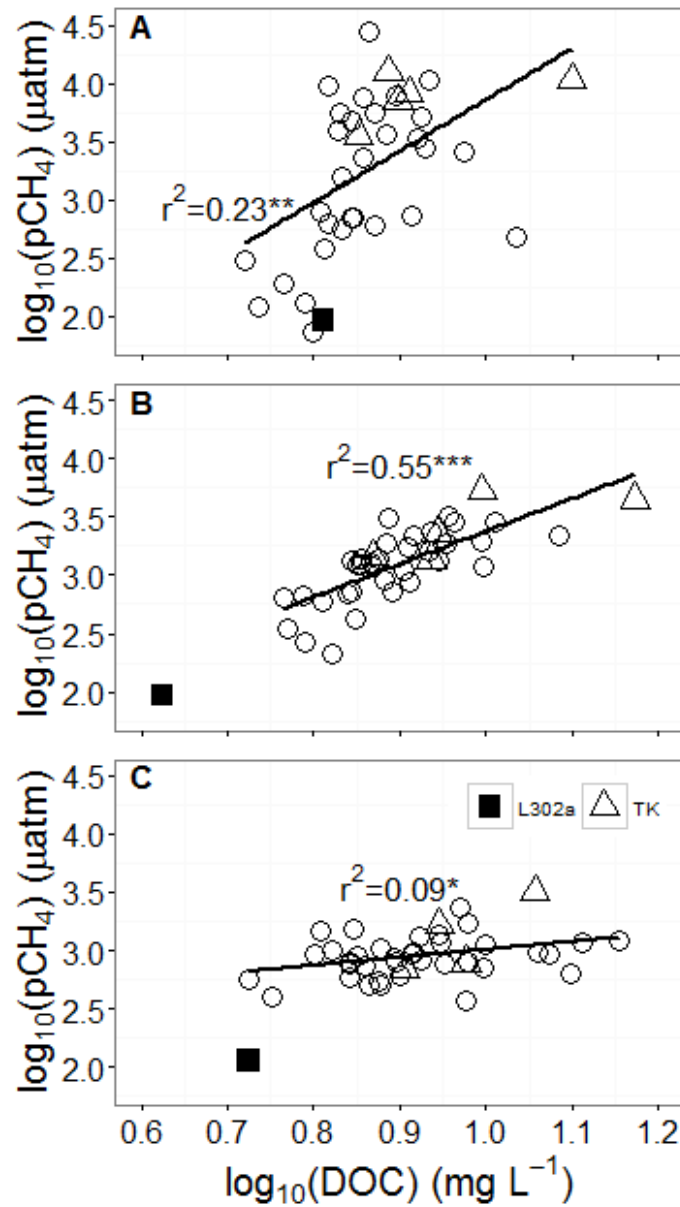


Figure 3-8. Regression of pCH_4 against DOC from surveys of 43 Mackenzie Delta Lakes during early summer (A), mid-summer (B), and late summer (C) of 2014.

Hollow triangles indicate thermokarst (TK)-affected lakes. TK lakes did not exhibit unusual pCH_4 levels, thus were included in regressions. L302a was excluded from regressions. Adjusted r^2 values are reported. * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$.

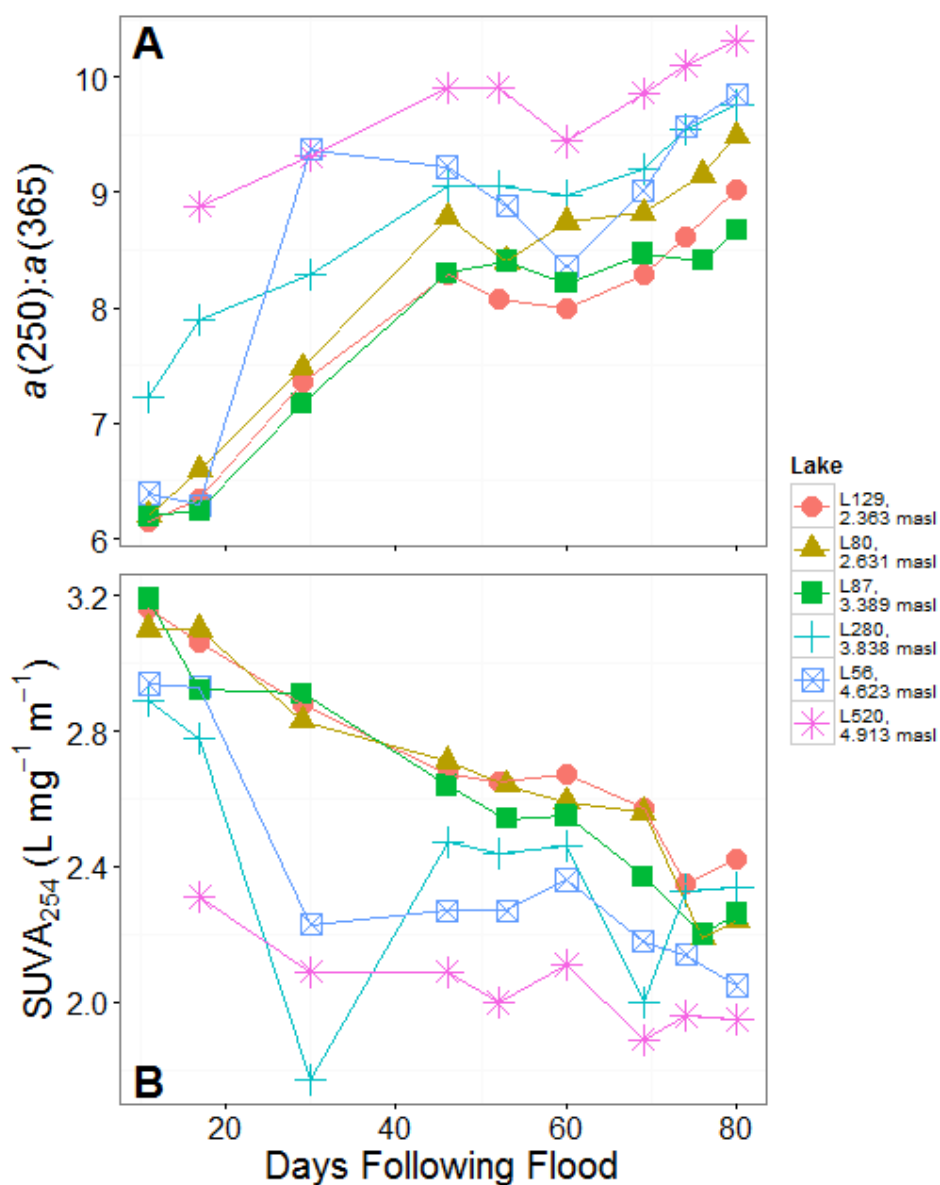


Figure 3-9. DOM molecular weight (A) and aromaticity (B) during summer 2014 in 6 intensively studied lakes.

Increasing $a(250):a(365)$ indicates decreases DOM molecular weight. Increasing $SUVA_{254}$ indicates increases DOM aromaticity. Lakes 280 and 520 are considered to be thermokarst lakes. Days following flood approximates time since ice-out, which was assumed to occur on the day of peak water at East Channel.

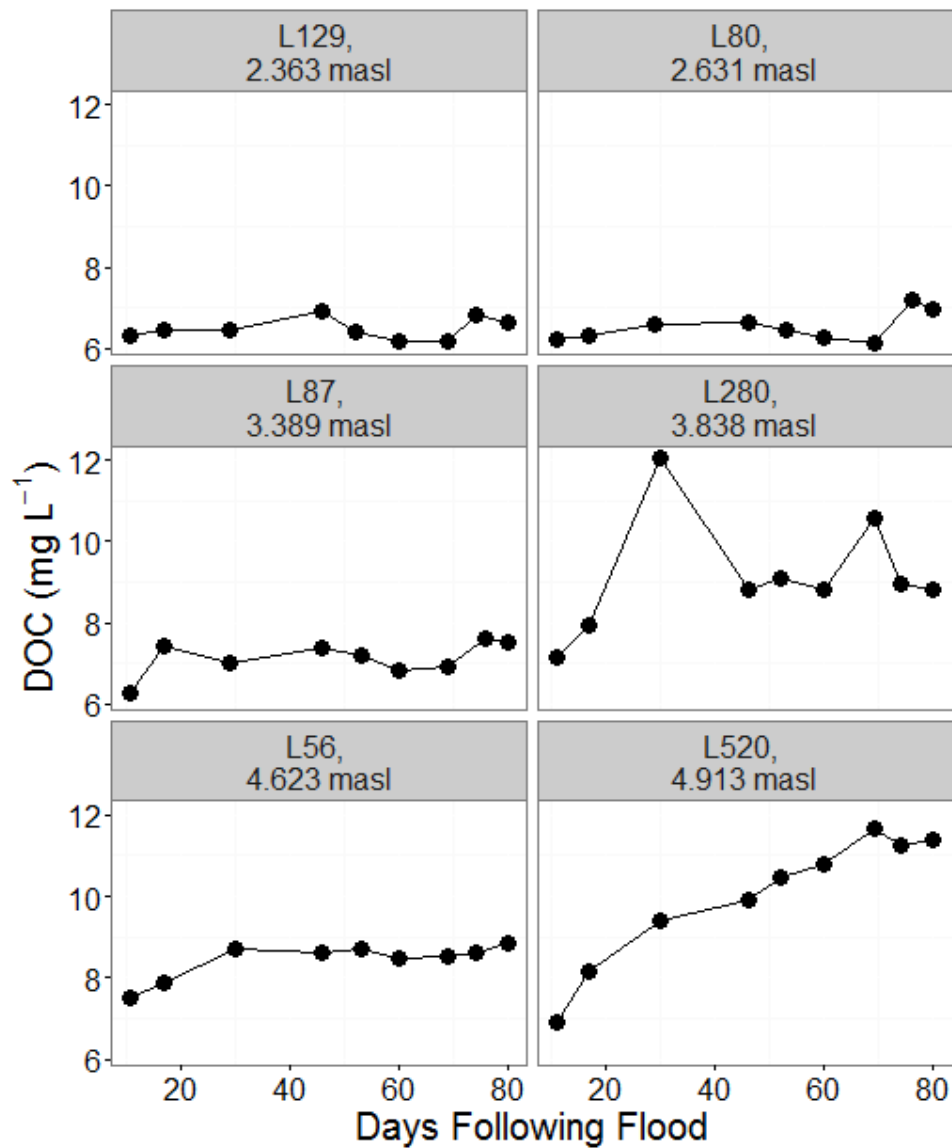


Figure 3-10. DOC in 6 intensively studied Mackenzie Delta lakes.

Spring sill elevation (masl) for each lake is indicated on each plot. Lakes 280 and 520 are thermokarst lakes. Days following flood approximates time since ice-out, which was assumed to occur on the day of peak water at East Channel.

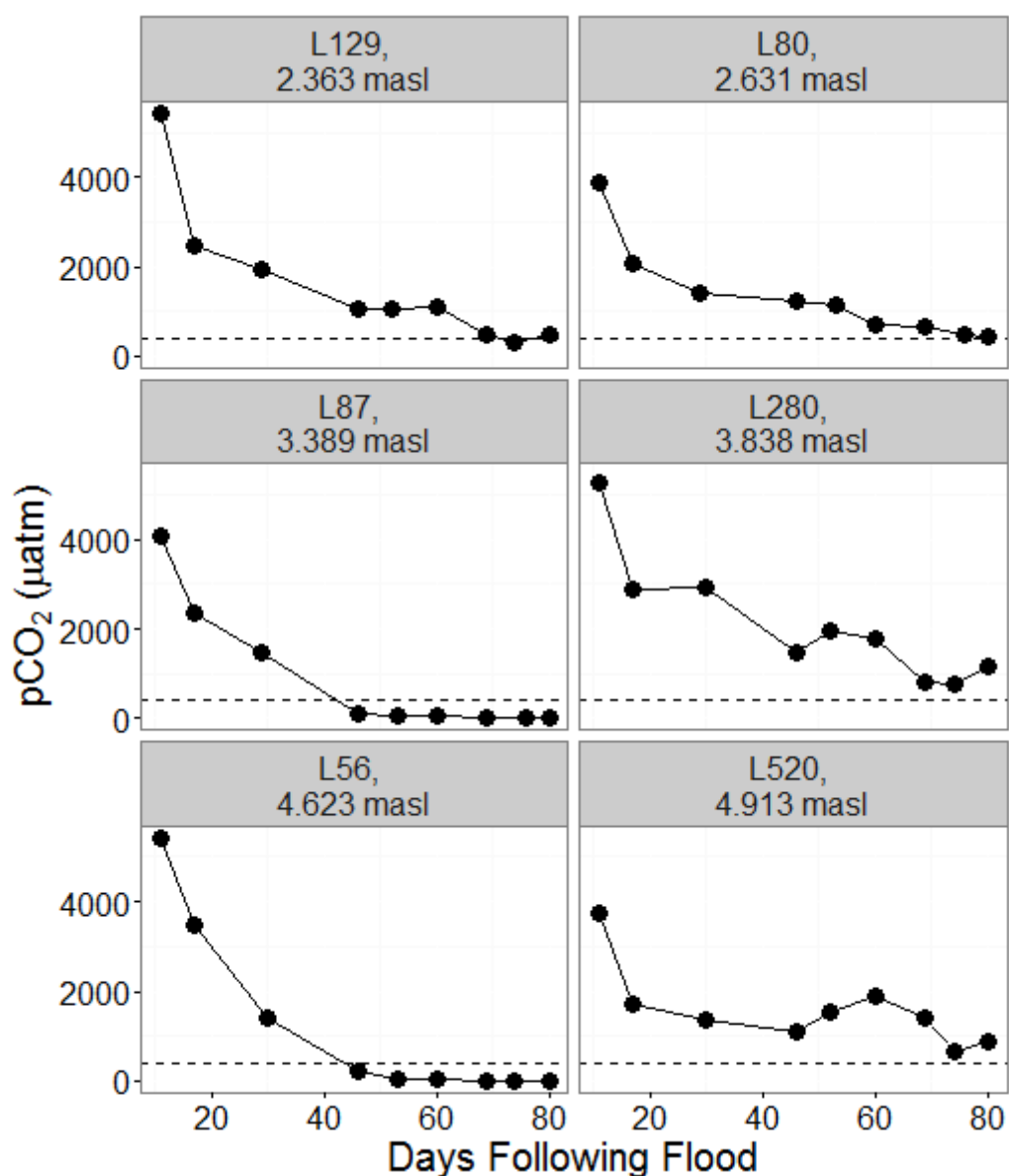


Figure 3-11. $p\text{CO}_2$ in 6 intensively studied Mackenzie Delta lakes.

Atmospheric $p\text{CO}_2$ indicated with dashed lines. Spring sill elevation (masl) for each lake is indicated on each plot. Lakes 280 and 520 are thermokarst lakes. Days following flood approximates time since ice-out, which was assumed to occur on the day of peak water at East Channel.

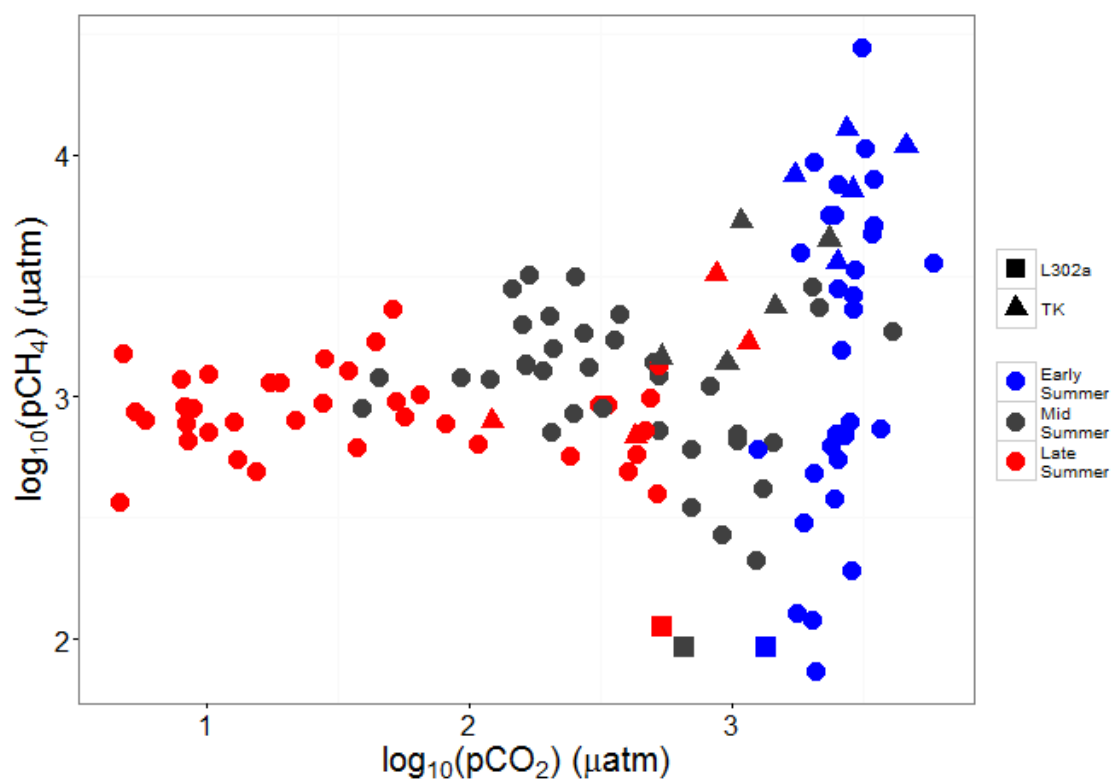


Figure 3-12. Early summer, mid-summer, and late summer plot of pCH_4 against pCO_2 .

Triangles indicate thermokarst (TK)-affected lakes.

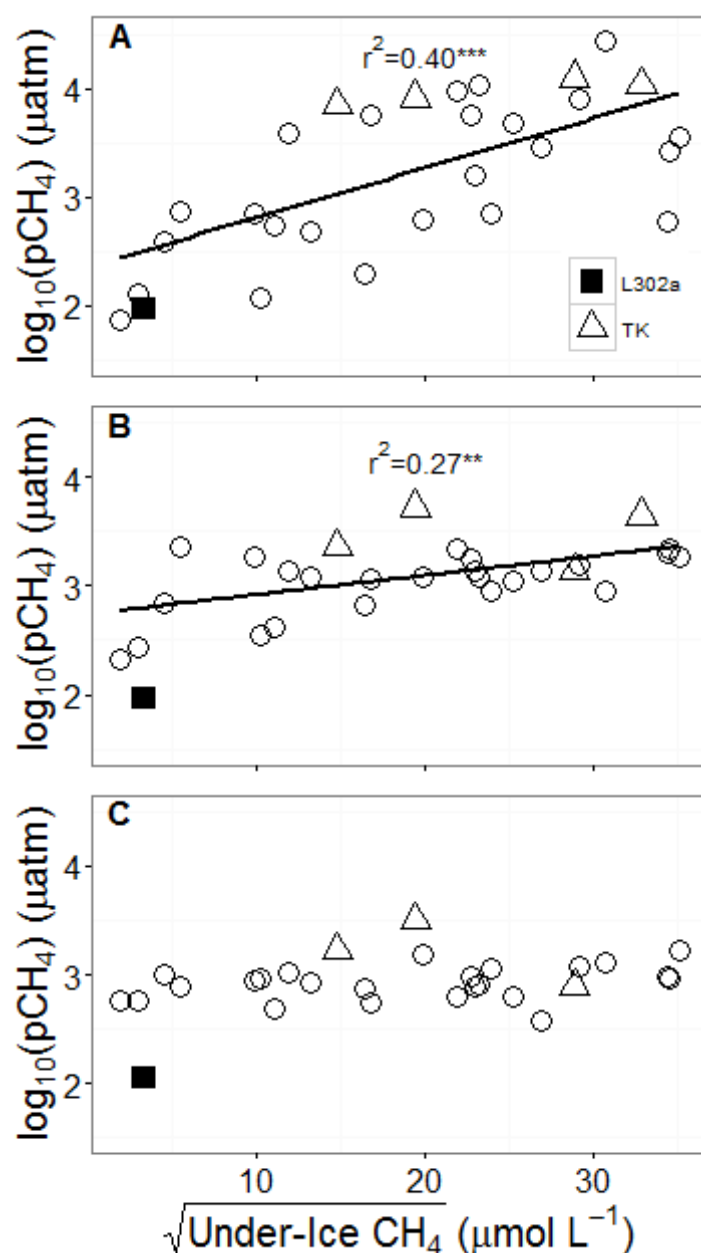


Figure 3-13. Regression of early summer (A), mid-summer (B), and late summer (C) pCH_4 against 2014 under-ice CH_4 .

Triangles indicate thermokarst (TK)-affected lakes. TK lakes were included in regressions, but L302a was excluded from regressions. A regression line was fit where relationship is significant. Adjusted r^2 values are reported. $^{**} P < 0.01$; $^{***} P < 0.001$.

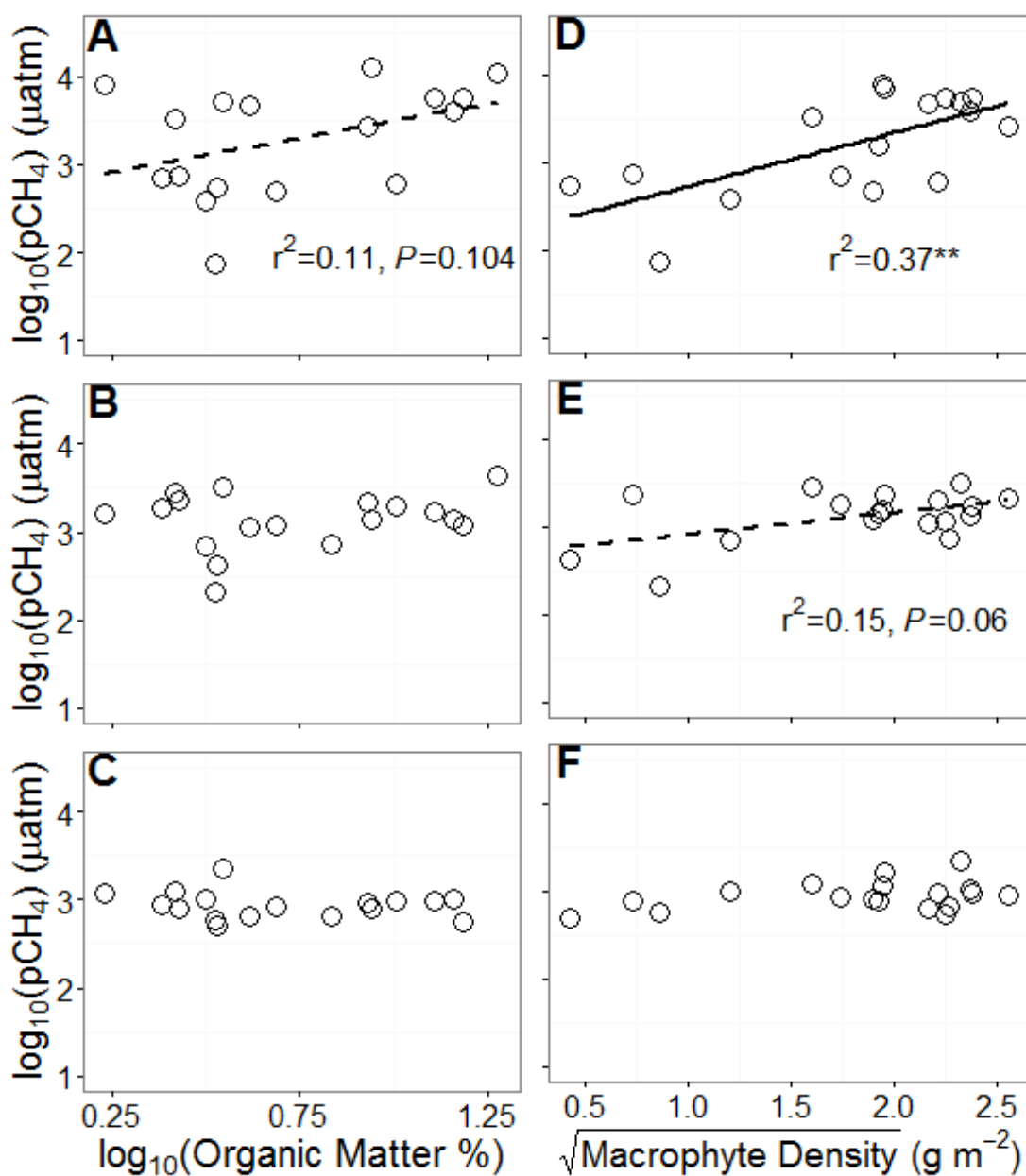


Figure 3-14. Regression of early summer (A and D), mid-summer (B and E), and late summer (C and F) pCH₄ against sediment organic matter (A-C) and submerged macrophyte density (D-F).

A regression line was fit where relationship is significant (D), and dashed lines were fit where regression is nearly significant (A and E). Adjusted r^2 values are reported. $^{**} P < 0.01$.

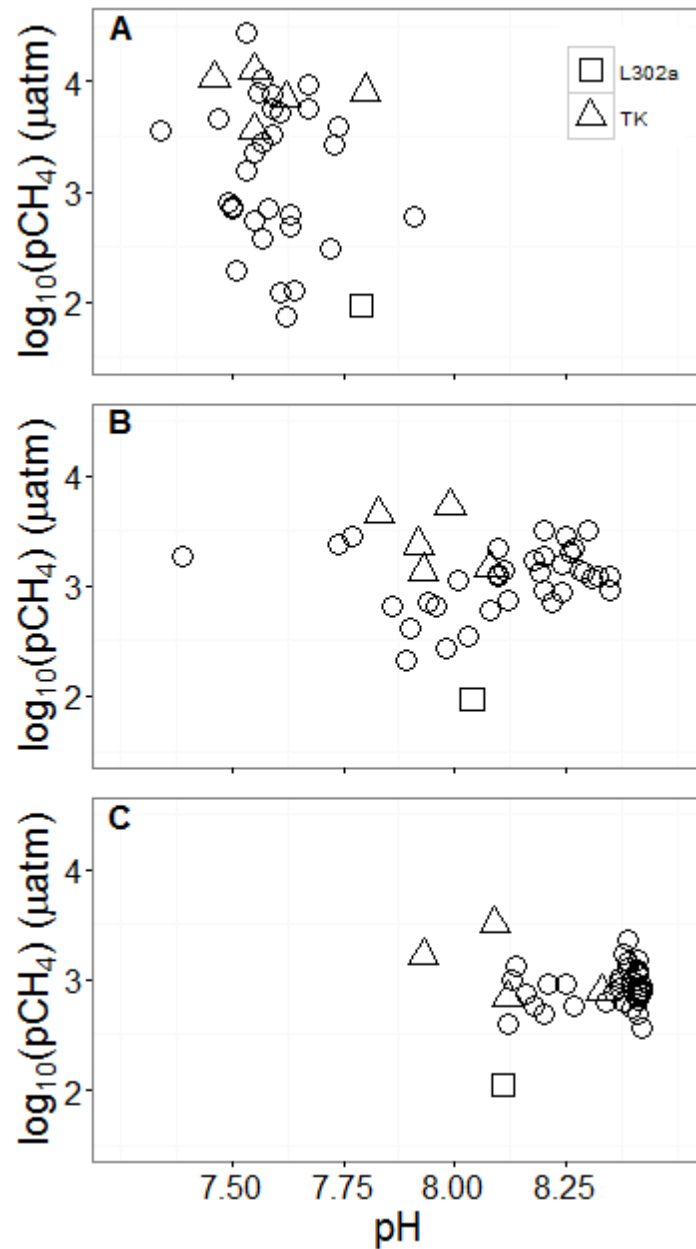


Figure 3-15. Plots of early summer (A), mid-summer (B), and late summer (C) pCH_4 against pH.

Triangles indicate thermokarst (TK)-affected lakes.

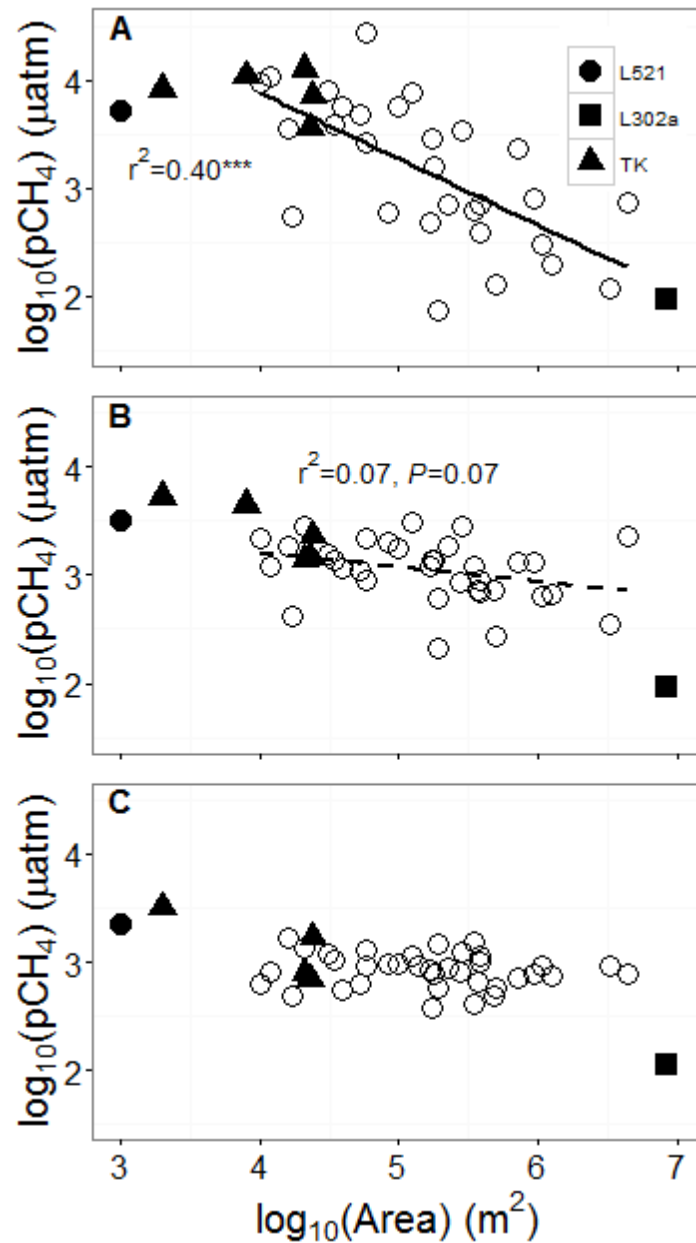


Figure 3-16. Regression of early summer (A), mid-summer (B), and late summer (C) pCH₄ against Area.

Triangles indicate thermokarst (TK)-affected lakes. Lakes 521 (shaded circle) and 302a (shaded square) showed high leverage, so were considered outliers. TK lakes, L521, and L302a were excluded from regressions. A dashed regression line was fit where relation is nearly significant. Adjusted r^2 values are reported. *** $P < 0.001$.

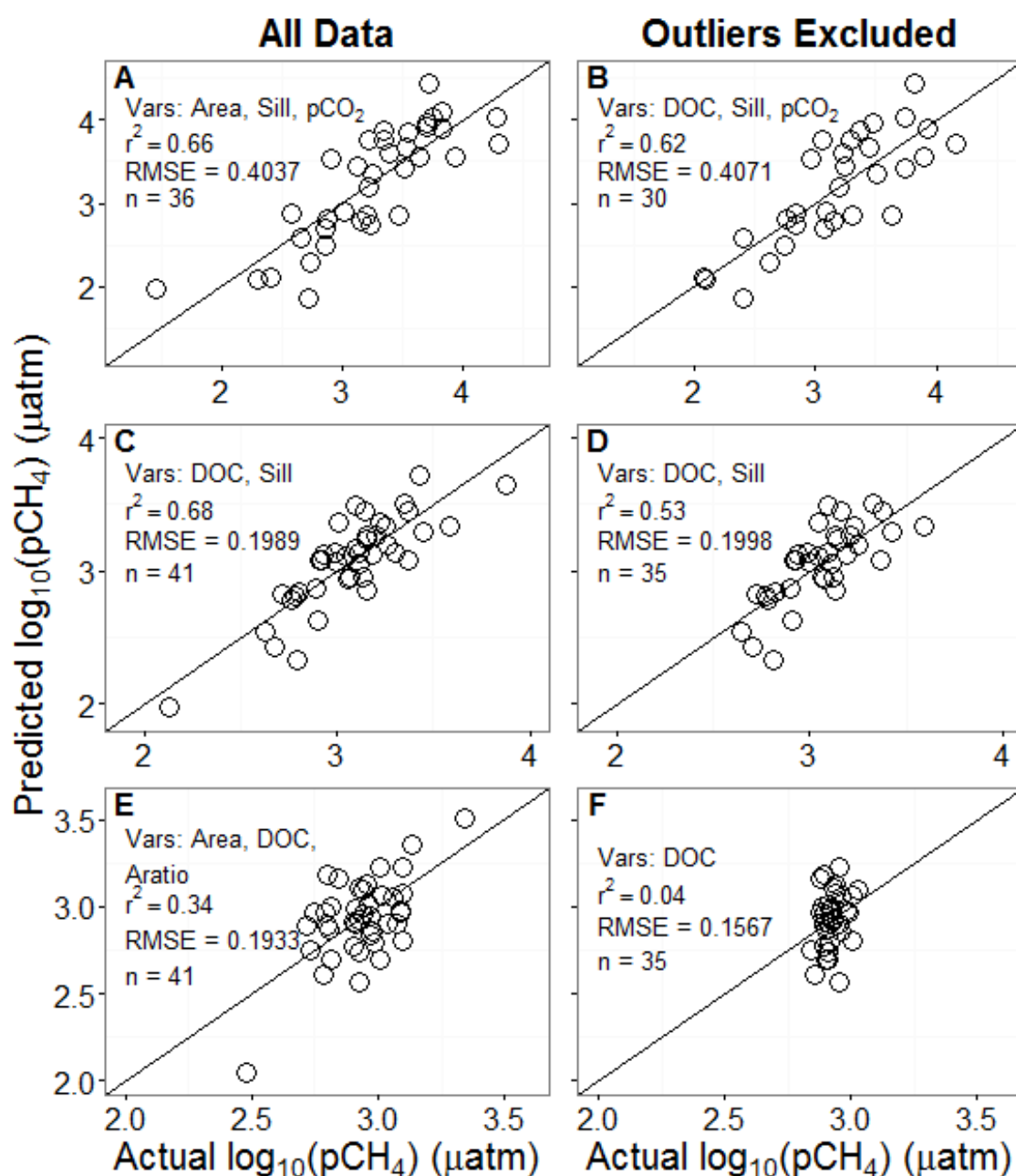


Figure 3-17. AIC-selected multiple regression models for predicting pCH_4 during early (A and B), mid (C and D), and late summer (E and F), and using all data (A, C, and E) and excluding outliers (B, D, and F).

Note that regression coefficients are not significant ($\alpha = 0.05$) for DOC in (B), Sill in (D), Aratio (i.e., $a(250):a(365)$, inferred DOM molecular weight) in (E), and DOC in (F, refer to Table 3-4). Vars: CH_4 predictor variables. Outliers excluded from (B) and (D) include all thermokarst lakes (L115, L143, L181, L280, and L520) and L302a. Outliers excluded from (F) include all thermokarst lakes (L115, L143, L181, L280, and L520), L302a, and L521.

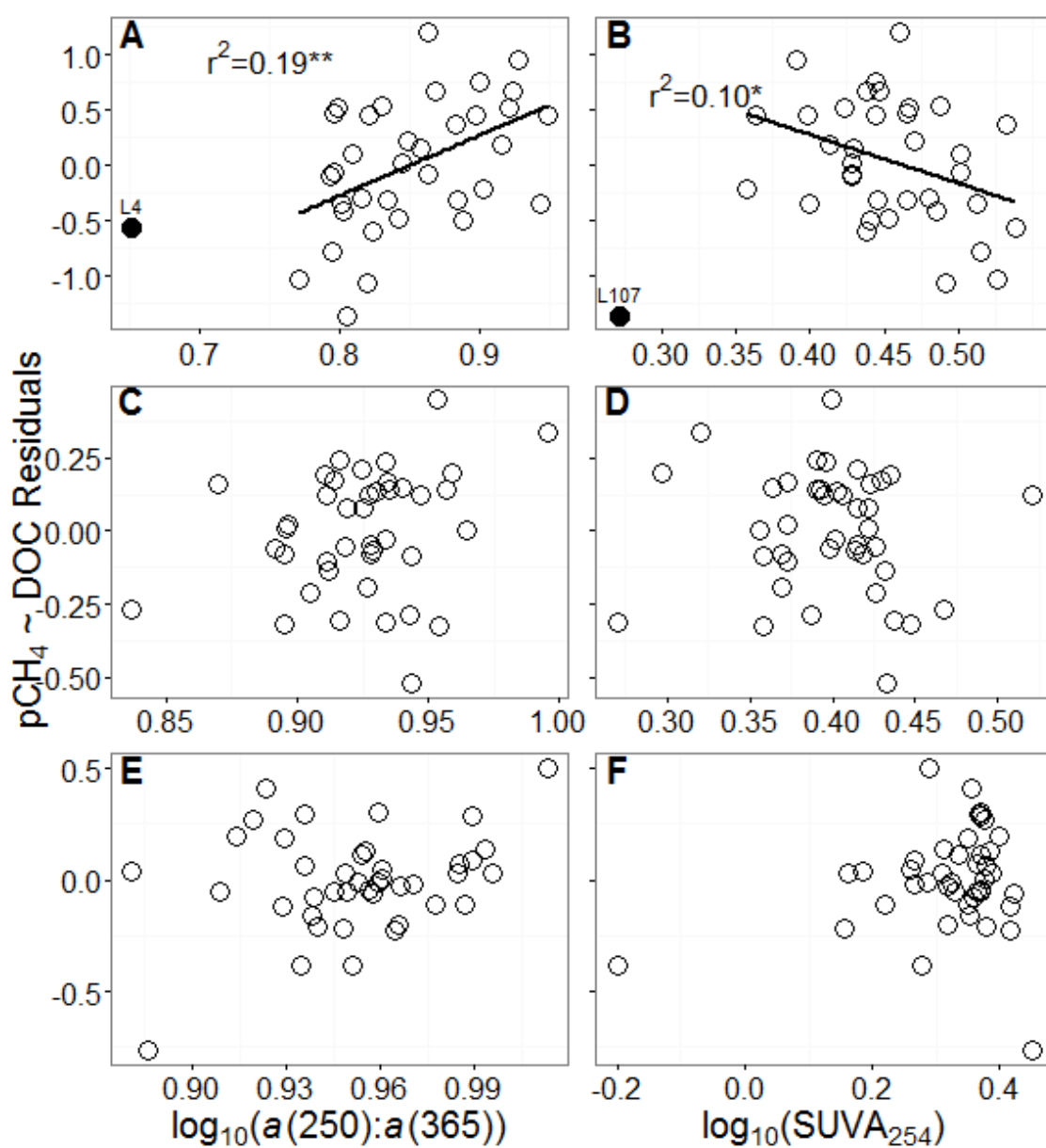


Figure 3-18. Residuals of pCH₄ regressed against DOC plotted against early (A and B), mid (C and D), and late summer (E and F) DOM molecular weight (A, C, and E) and aromaticity (B, D, and F).

Increasing $a(250):a(365)$ indicates decreasing DOM molecular weight. Increasing $SUVA_{254}$ indicates increasing DOM aromaticity. Lakes 4 and 107 (shaded circles) are outliers from early summer plots). Adjusted r^2 values reported. * $P < 0.05$; ** $P < 0.01$.

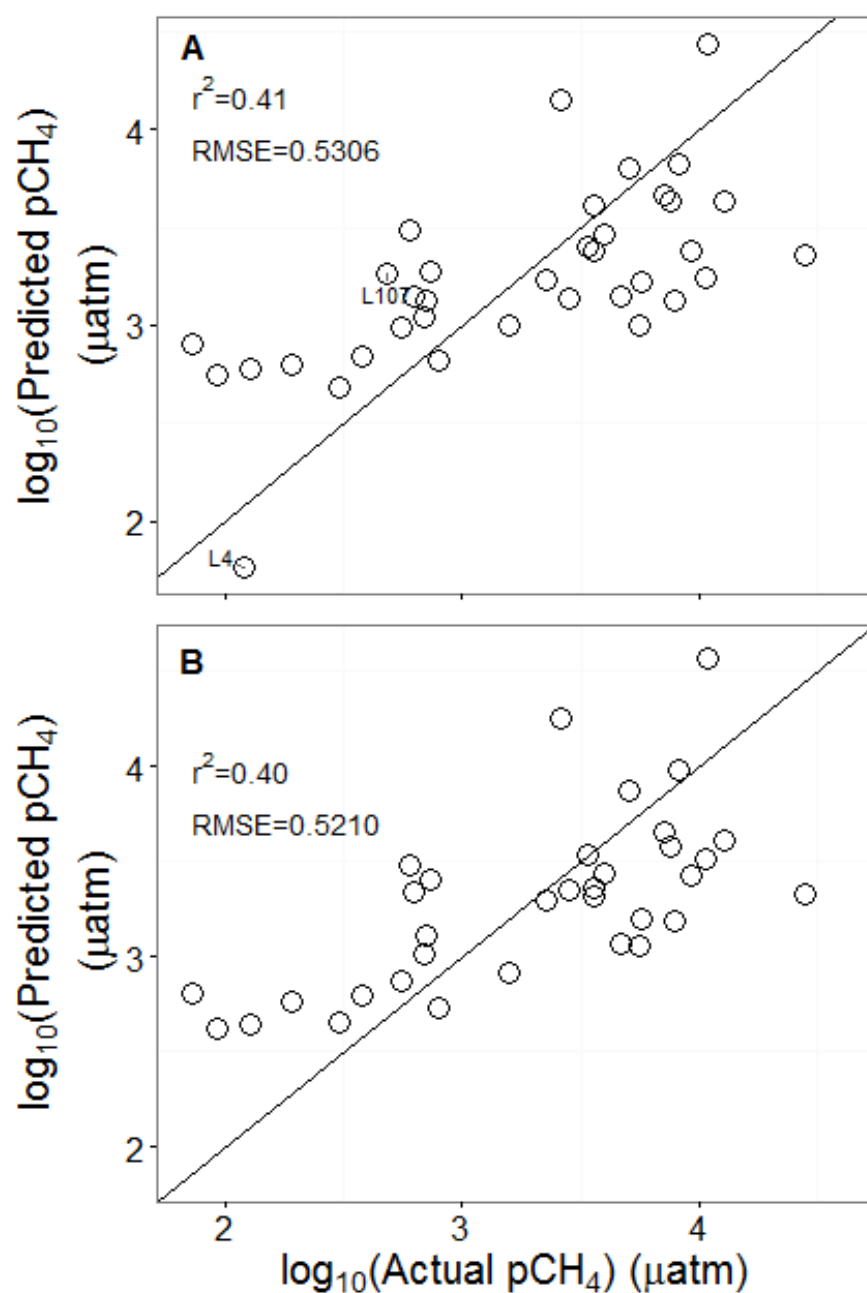


Figure 3-19. Multiple regression for predicting $p\text{CH}_4$ during early summer from DOC and DOM molecular weight and aromaticity using all data (A) and without outliers (Lakes 4 and 107 from Figure 3-18A and B, respectively) (B).

Note that regression coefficient for DOC is significant in (A) and (B), DOM molecular weight (i.e., $a(250):a(365)$) significant in (A), but not (B), and DOM aromaticity (i.e., SUVA_{254}) is not significant in either multiple regression (significance tested at $\alpha = 0.05$ for all regression coefficients).

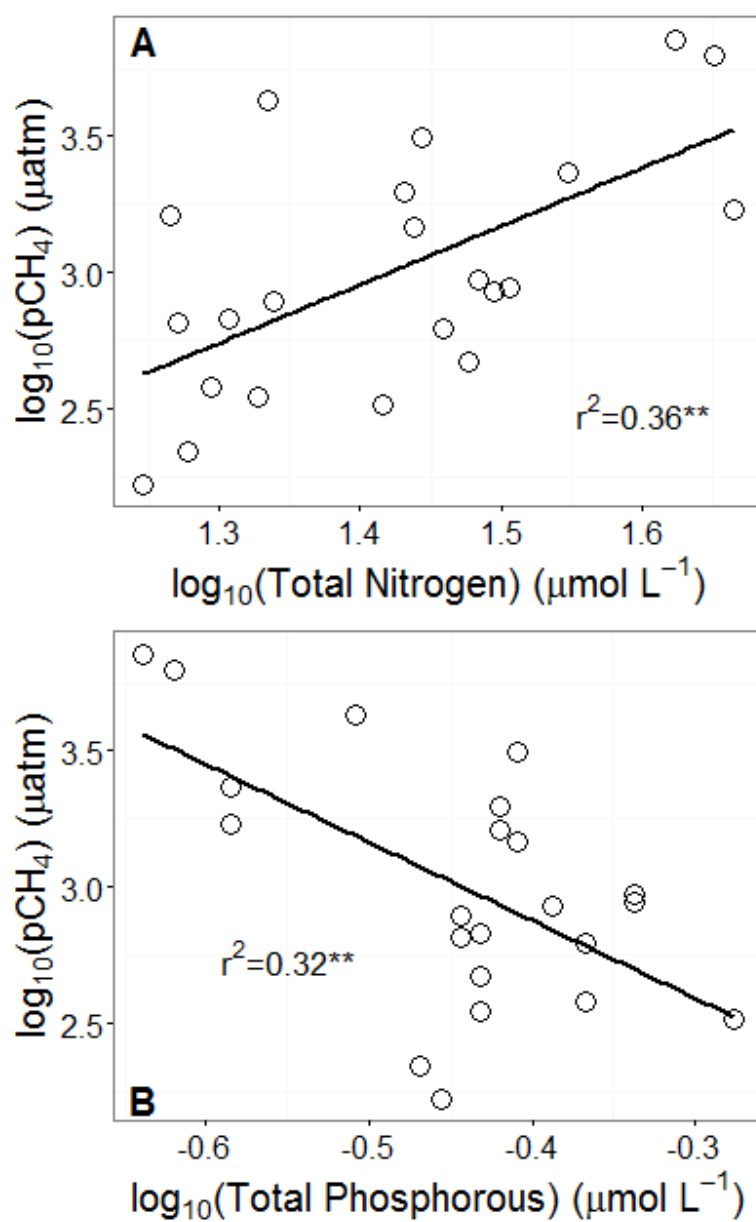


Figure 3-20. Relationship between pCH_4 and total nitrogen (A) and total phosphorous (B).

Adjusted r^2 values are reported. $** P < 0.01$.

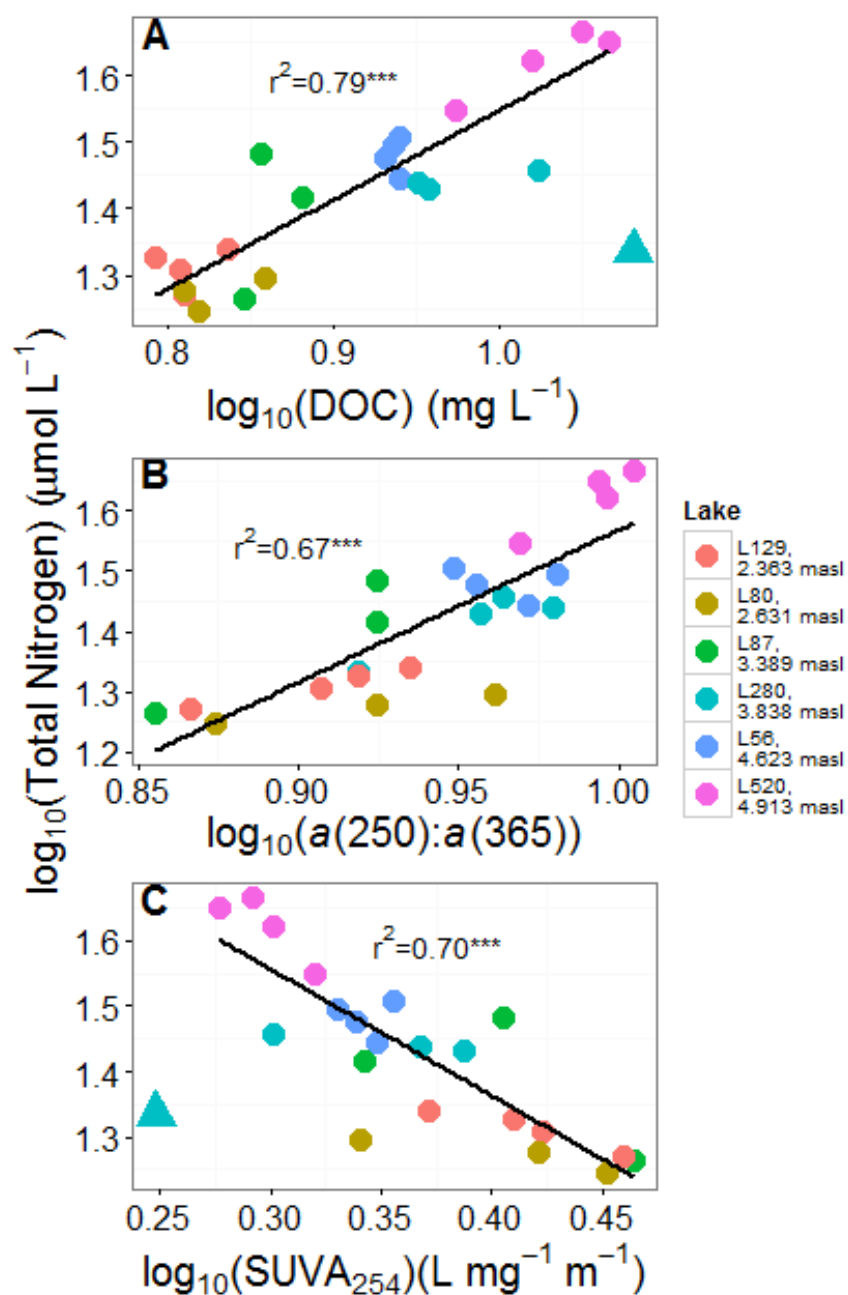


Figure 3-21. Relationship between total nitrogen and dissolved organic carbon (DOC) (A), dissolved organic matter (DOM) molecular weight (B), and DOM aromaticity (C) in the six intensively studied lakes.

Increasing $\text{a}(250):\text{a}(365)$ indicates decreasing DOM molecular weight. Increasing SUVA_{254} indicates increasing DOM aromaticity. Triangles (L280) in (A) and (C) were considered outliers and were excluded from respective regressions. Adjusted r^2 values are reported. *** $P < 0.001$.

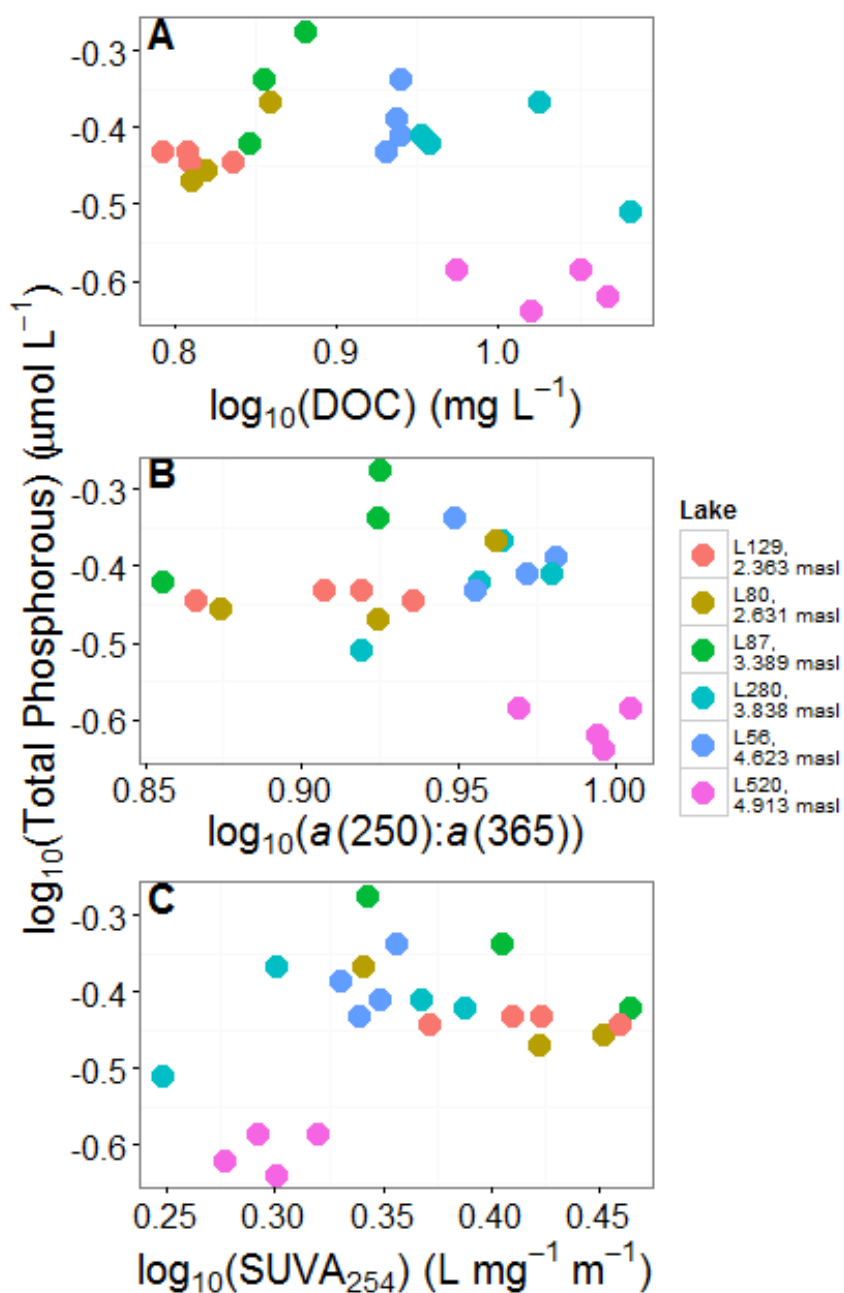


Figure 3-22. Relationship between total nitrogen and dissolved organic carbon (DOC) (A), dissolved organic matter (DOM) molecular weight (B), and DOM aromaticity (C) in the six intensively studied lakes.

Increasing $a(250):a(365)$ indicates decreasing DOM molecular weight. Increasing SUVA_{254} indicates increasing DOM aromaticity.

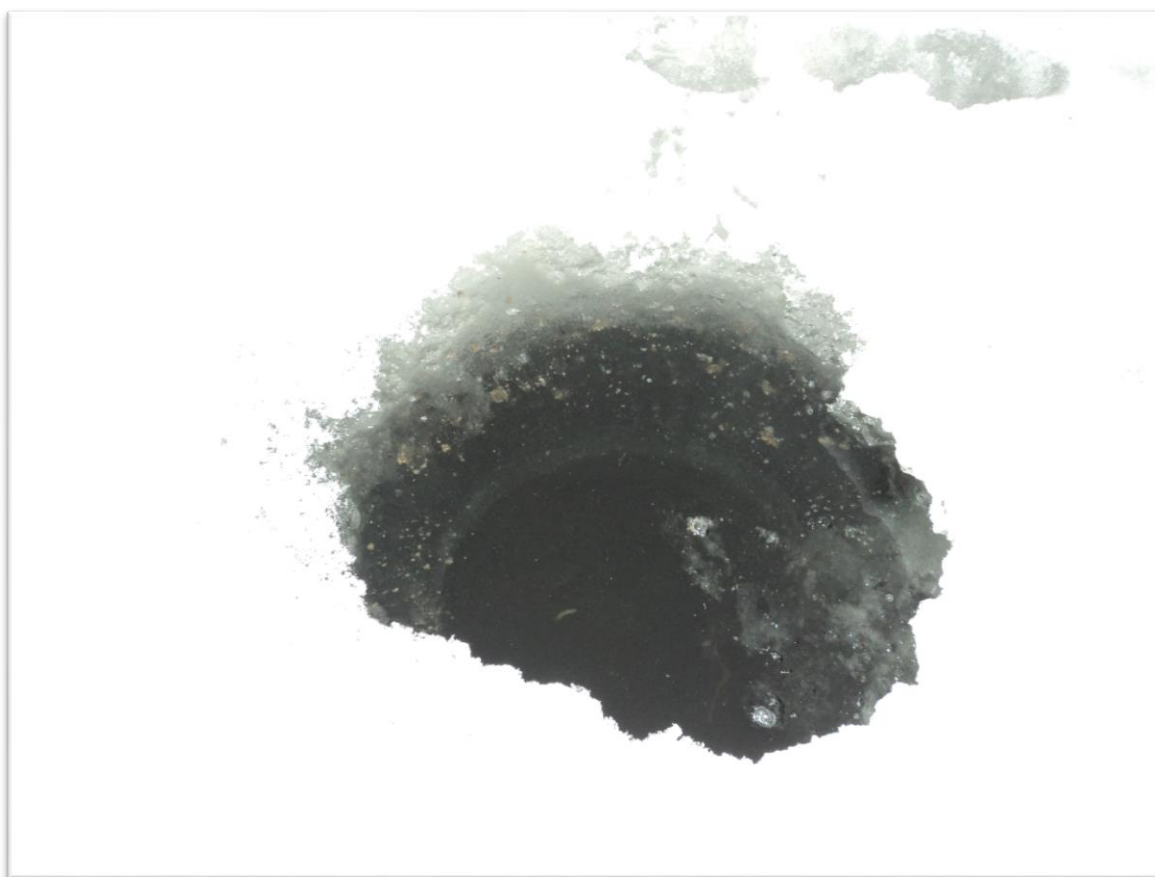


Figure 3-23. Hole in ice at Lake 134 that is likely a CH₄ “Hotspot”, where intense CH₄ ebullition has likely prevented ice formation over the winter.

Chapter 4.

The Role of Methane Oxidation in Regulating Methane Emissions from Mackenzie Delta Lakes

4.1. Introduction

Contrary to lakes in other Arctic regions, the net balance of carbon dioxide (CO₂) in Mackenzie Delta lakes has been shown to be near neutral, where some lakes tend to absorb more atmospheric CO₂ than they emit (Tank et al. 2009a). However, surface water concentrations of methane (CH₄), which is a greenhouse gas 34 times as potent (normalized over a 100 year time scale) than carbon dioxide (CO₂) (Myhre et al. 2013), persist in excess of equilibrium with the atmosphere throughout open-water conditions in Mackenzie Delta lakes (Chapter 3), which suggests that this system is a net source of carbon to the atmosphere. Furthermore, CH₄ accumulates in Mackenzie Delta lakes over the winter (Chapter 2), and constitutes an unknown portion of potential CH₄ emissions at ice-out. During the winter, ambient CH₄ levels in Mackenzie Delta lakes tend to be greater in lakes that are the most productive (i.e., CO₂ absorbers) in the late summer (Chapter 2).

4.1.1. Study Site

The Mackenzie Delta contains over 45,000 shallow lakes (mean depth = 1.5 m) (Emmerton et al. 2007), making it the largest delta in North America and the second largest in the circumpolar Arctic (Figure 4-1). Ice cover lasts for 7-8 months each year, and the open-water season takes place from June-October. Because Mackenzie Delta lakes occur at different elevations, lakes experience varying connectivity to the Mackenzie River (Figure 1-2). During the spring flood, meltwater from warm southern reaches of the Mackenzie River flow north to the ice-covered delta causing water levels to rise very quickly and flooding to occur (Mackay 1963, Marsh and Hey 1989). Differences in lake-river connectivity allow for operational definition of these lakes as: no closure lakes (lowest elevation and connected to the river for most, if not all of the year), low closure lakes (intermediate elevation and connected to the river for part of the year), and high closure lakes (highest elevation and only connected to the river in intermittent years) (Mackay 1963, Marsh and Hey 1989).

Since Mackenzie Delta lakes are surrounded by permafrost, which prevents input of water from subsurface and groundwater flows, and have small catchments that limit input from precipitation, the spring flood is the dominant hydrologic event in the delta. The

relative hydrologic isolation of Mackenzie Delta lakes results in differences in delivery of suspended sediments, dissolved ions, and allochthonous (terrestrial in origin) carbon between lakes, where sediment loading and sedimentation tends to decrease with increasing lake elevation (Pipke 1996, Hay et al. 1997, Squires and Lesack 2003). These differences amount to dense mats of submerged macrophytes in higher elevation lakes (Squires et al. 2002), which are so productive during the late summer that they tend to absorb CO_2 (Tank et al. 2009a), but tend to have higher levels of CH_4 during the winter and throughout the open-water period. Many lakes in the Mackenzie Delta are affected by thermokarst (i.e., terrestrially-derived carbon added to lakes due to thawing of permafrost), which tends to turn lakes into CO_2 emitters rather than absorbers. Thermokarst affected lakes are usually a subset of high closure lakes (Burn and Kokelj 2009, Tank et al. 2009a, 2011). Due to rising temperatures across the Arctic, the prevalence of thermokarst is expected to increase (ACIA 2005). Thermokarst addition of carbon into lakes has been shown to result in enhanced levels of CH_4 emissions in other Arctic regions (Walter et al. 2006, Walter Anthony et al. 2010, Martinez-Cruz et al. 2015, Sepulveda-Jauregui et al. 2015), as well as during early summer and mid-summer in Mackenzie Delta lakes (Chapter 3).

In Mackenzie Delta lakes, CH_4 produced in sediments either diffuses across the sediment-water interface into the water column, where it can be oxidized prior to diffusing to the atmosphere, or is emitted directly to the atmosphere by ebullition (Figure 1-4). Considering that the lakes are well mixed, dissolved (i.e., ambient) water column CH_4 reflects the net water column CH_4 oxidation (MOX) as well as the net MOX across the sediment-water interface. As discussed in Chapter 3, dissolved CH_4 in all Mackenzie Delta lakes is generally highest after ice-out and decreases throughout the year. High closure and thermokarst lakes tend to have higher levels of dissolved CH_4 during early and mid-summer, but during late summer there is little variation in dissolved CH_4 between lake types even though there are considerable differences in dissolved CO_2 dynamics due to thermokarst (i.e., melting of permafrost around lake margins and/or under the lake bottom). Considering that ambient CH_4 levels in Mackenzie Delta lakes are strongly linked to the hydrologic and productivity gradient during winter, early summer, and mid-summer, it is surprising that there is little variability in dissolved CH_4 between the lakes during late summer. This suggests that either MOX draws down late summer ambient CH_4 to a

greater extent in high closure and thermokarst lakes, and/or that proportionately more CH₄ escapes high closure and thermokarst lakes through ebullition than lower elevation lakes.

4.1.2. Methane Oxidation

MOX is a function performed by methanotrophs (i.e., CH₄ oxidizing bacteria, MOB) that regulates lake CH₄ emissions by consuming dissolved CH₄. MOX can occur either aerobically or anaerobically (through sulfate (SO₄⁻) reduction), and takes place primarily at the oxic-anoxic boundaries, such as at the sediment-water interface of mixed lakes, or in the metalimnion of stratified lakes (Rudd et al. 1976, Coleman et al. 1981, Capone and Kiene 1988, Bédard and Knowles 1997, Gentzel et al. 2012, Lofton et al. 2014). MOB activity is controlled by temperature, availability of CH₄ (CH₄ bubbles are not available for MOX), dissolved inorganic nitrogen (DIN), dissolved oxygen (DO), and pH (Rudd et al. 1976, Hanson and Hanson 1996, He et al. 2012). Lake morphology is also an important factor for MOX, where CH₄ oxidation is generally higher in deep, stratified water columns than in shallow, well mixed areas (Bastviken et al. 2008). A significant amount of MOX can take place in lakes. Investigations have found that 30-99% of the CH₄ produced in sediments can be oxidized and prevented from escaping into the atmosphere (Rudd et al. 1974, Segers 1998, Bastviken et al. 2008).

Traditionally, in-lake primary production has been considered as the primary source of carbon and energy flux through ecosystems, but it is increasingly apparent that CH₄-derived carbon (MDC) is also an important energy source in aquatic ecosystems. Non-traditional food webs include ecosystems that do not rely on photosynthetic carbon sources, and involve transfer of MDC up trophic levels through grazing. For example, consumption of MOB has been observed in Chironomids (Jones et al. 2008, Jones and Grey 2011, Gentzel et al. 2012, Hershey et al. 2015) as well as zooplankton (Bastviken et al. 2003, Kankaala et al. 2006a, 2006b, Taipale et al. 2008, Tank 2009). Food webs that are based on bacteria are usually not as efficient (where carbon respiration is greater than carbon incorporation into biomass) as those based on primary production, and further investigation is required to improve understanding of the nutritional value of MOB (Tank 2009, Gentzel et al. 2012).

In Mackenzie Delta lakes, isotopic evidence shows that MOB form an important part of zooplankton diet. Tank (2009) discovered depressed $\delta^{13}\text{C}$ values, which are indicative of zooplankton grazing on MOB. The evidence is clear that MDC serves as an energy and carbon source, but the relative importance of MOB compared to HB in Mackenzie Delta lakes has not been measured and is poorly understood in this system. The presence of MOB is a clear indication that MOX is occurring, even though Mackenzie Delta lakes are shallow, and that MOX may play an important part in regulating the amount of CH_4 emitted from Mackenzie Delta lakes.

4.1.3. Methane Emission

There are three pathways for CH_4 emission from lakes in well-mixed lakes during open-water conditions: (1) ebullition; (2) diffusive flux; and (3) aquatic vegetation-mediated flux (Pipke 1996, Bastviken et al. 2004, 2008, Walter Anthony et al. 2010). Ebullition involves the flux of CH_4 directly from sediment into the atmosphere, and can be observed as bubbles (Bastviken et al. 2008, Walter Anthony et al. 2010). Bubbles form in sediments because of the low solubility of CH_4 , resulting in quick saturation of dissolved CH_4 , which forces CH_4 out of solution (Walter Anthony et al. 2010). Factors that control the formation and release of CH_4 bubbles are: (i) changes to lake bottom currents; (ii) decrease in hydrostatic pressure as water levels decline; (iii) decrease in atmospheric pressure; (iv) bubble buoyancy in excess of threshold; and (v) sediment pore space (Walter Anthony et al. 2010, Scandella et al. 2011). The diffusive flux is a slower process than ebullition involving the diffusion of CH_4 from sediment into the water column. CH_4 in solution that avoids oxidation reaches the upper layer of the water column, and diffuses into the atmosphere following the atmospheric-water concentration gradient and the physical rate of exchange between the two mediums (Bastviken et al. 2008). Diffusive flux can also include CH_4 that accumulated in the anoxic zone of the water column. During the de-stratification and/or ice-out periods, this CH_4 is mixed into upper layers of the lake and can diffuse into the atmosphere, which is commonly referred to as ice-out or storage flux (Bastviken et al. 2004). A considerable amount of CH_4 accumulates in Mackenzie Delta lakes (Chapter 2), most of which is likely emitted to the atmosphere following ice-out (Pipke 1996). Finally, there is the flux through aquatic vegetation, where methanogenesis and MOX occurs at, near, or within plant roots in lake sediment (Segers 1998, Bastviken

et al. 2004). Ebullition and diffusion are the primary pathways for CH₄ emissions from lakes, whereas vegetation-mediated flux is more significant in wetlands with emergent macrophytes. Vegetation-mediated flux of CH₄ was not investigated in this study. Future studies should investigate this pathway considering that emergent macrophytes (*Equisetum fluviatile*) become increasingly prominent as the summer progresses in Mackenzie Delta lakes.

4.1.4. Objectives

CH₄ seeps associated with gas deposits have been studied in the northern parts of the Mackenzie Delta (Bowen et al. 2008), but CH₄ fluxes from biological origins have not been previously investigated. Considering the extent of thermokarst, high sediment organic matter content, and dissolved CH₄ concentrations in excess of equilibrium with the atmosphere, Mackenzie Delta lakes are likely strong emitters of CH₄ especially if water column MOX rates are low. Our objectives for this chapter are detailed below.

Question 1: How is lake closure status related to open-water CH₄ oxidation (MOX) in Mackenzie Delta lakes?

Hypothesis: Thermokarst lakes should have the greatest MOX rates because they are comparatively deeper, connected lakes should have the lowest MOX rates because they contain the least CH₄, and macrophyte-rich lakes should have intermediate MOX rates. MOX should increase throughout the open-water period coinciding with increasing submerged macrophyte production (i.e., decreasing dissolved CO₂) to account for the decrease in ambient CH₄ observed during the open-water period.

Question 2: How is lake closure status related to CH₄ emission from Mackenzie Delta lakes?

Hypothesis: Thermokarst lakes have higher CH₄ ebullition rates than macrophyte-rich lakes because of additions of permafrost carbon, but lower CH₄ emissions because thermokarst lakes have higher MOX rates. Lakes with high river

connectivity produce the least amount of CH₄, and are relatively weak emitters of CH₄.

4.2. Methods

4.2.1. Methane Oxidation

Every 1-2 weeks during open-water conditions in 2014 (June through August) and again in June 2015, MOX rates were measured using in situ incubations in a subset of 6 lakes (Figure 4-1). In situ incubations involve measurement of the decline over time of CH₄ in containers suspended in the water column (Michmerhuizen et al. 1996, Striegl and Michmerhuizen 1998, Utsumi et al. 1998, Bastviken et al. 2008). Gas-tight cubitainers (Reliance Fold-a-Carrier, Reliance Products LP, Winnipeg, MB) with flexible walls and 10 L capacity were used instead of rigid bottles to allow repeated sampling from the same container without pressure changes or introduction of gas or water to compensate for the loss of sampled water (Bastviken et al. 2008). To ensure cubitainers were gas-tight, we tested for CH₄ leakage by determining molecular diffusion coefficients for cubitainers filled with CH₄-infused distilled, deionized water (0.2 µm filtered prior to CH₄ infusion), which were submersed into water baths maintained at room temperature, and exposed to ambient room air, for 24 hours. We found no correction for CH₄ leakage was necessary. In 2014, duplicate cubitainers (triplicate in 2015) were setup at the center of each lake. To fill a cubitainer, the cubitainer was fully submerged and then water from within 0.5 m of the water surface was gently pumped into the cubitainers using a battery powered submersible pump with rubber tubing. Once filled and all air bubbles escaped, a minimum of 30 L of water was flushed through the cubitainer. After the cubitainer was flushed, the hose was gently removed and the cubitainer was sealed with a butyl rubber stopper. The pump and tubing were flushed with lake water for a minimum of 5 minutes prior to sampling. A 1 mL syringe (with the plunger removed) was pierced through the stopper and fitted with a 3-way stopcock to allow sampling of the cubitainer. Samples were withdrawn from the cubitainers by attaching a hypodermic needle to the stopcock to enable direct transfer into prepared serum bottles. In 2014, due to logistical constraints concerning serum bottles initial samples were taken from the lake surface (at the same

time and exact location the cubitainer was being filled). In 2015, initial samples were taken directly from the cubitainers. After initial samples were taken, the cubitainer would be tied to a rope that had one end attached to an anchor and the other end to a float. Cubitainers were left in situ for 24 hours, after which time we would return to collect final samples. Lake DO was measured with a calibrated YSI model 32 during filling of cubitainers, and was measured again in the cubitainers and in the lake after final CH₄ samples were obtained to ensure cubitainers did not become anoxic. All cubitainer CH₄ samples were taken in duplicate. We collected samples for nutrients (TDN, PN, TDP, PP, and PC) and other limnological parameters (DIC, DOC, CDOM, chlorophyll *a*, depth, and temperature) concurrent with cubitainer deployments in 2014, but not in 2015.

4.2.2. Methane Emissions

Floating Chambers

The floating chamber method is a commonly used method to measure CH₄ emissions in lakes (Matthews et al. 2003, Bastviken et al. 2004, 2008, Cole et al. 2010, Bartosiewicz et al. 2015). The method involves using gas tight chambers to capture CH₄ escaping from the water column. The method is based on Fick's first law,

$$F = k * (C_w - \alpha C_A), \quad [1]$$

where F is the diffusive flux, k is piston velocity, α is the chemical enhancement factor (for CH₄, α is 1 because it is a chemically inert gas), C_w is the gas concentration measured in the water, and C_A is the gas concentration in the air (i.e., floating chamber) given equilibrium with the water (as per Henry's Law). The temporal increase in C_A would decrease gas flux into the chamber over longer-term deployments, therefore flux into the chamber would be non-linear. Assuming constant C_w , k can be determined analytically. The solution for k , as outlined by Bastviken et al. (2004) and Cole et al. (2010) involves the following steps. Firstly, the mass of gas crossing the area of the chamber (A , m²) over time is the flux, F :

$$F = \frac{dM}{dt * A}. \quad [2]$$

Secondly, substituting into Equation (Eq. 1) and using the ideal gas law to convert to mass and partial pressures, Eq. 3 is obtained:

$$\frac{dP}{dt} = \frac{k * K_h * R * T * A}{V} * (P_w - P), \quad [3]$$

where, K_h is the Henry's law constant for CH₄ (mol m⁻³ Pa⁻¹), R is the ideal gas constant (8.314 m³ Pa K⁻¹ mol⁻¹), T is temperature (K), V is the volume of the chamber (m³), and P_w and P are the respective partial pressures (Pa) of CH₄ in the surface water and chamber. Lastly, to determine k over the chamber deployment period, Eq. 3 is integrated to produce the following (MacIntyre et al. 1995, Cole et al. 2010):

$$k = \frac{\frac{V}{K_h * R * T * A} \ln \frac{P_w - P_i}{P_w - P_f}}{t_f - t_i}, \quad [4]$$

where subscripts i and f refer to initial and final conditions. We determined K_h from Bunsen solubility coefficients for CH₄ (Yamamoto et al. 1976), which we converted to the appropriate units (mol m⁻³ Pa⁻¹) by multiplying by 0.000440319 (Sander 2014).

The floating chamber method has been shown to result in overestimation of gas diffusion fluxes from lakes due to increased turbulence at the air-water interface unless some key modifications are met (Matthews et al. 2003). Primarily, these include adjusting buoyant collars around the chambers so that ~3 cm of the lip of each chamber extends below the water surface, and that deployments last for 24 hours (Bastviken et al. 2004). Spatial homogeneity in diffusion in combination with variability in ebullition requires deployment of 12-15 floating chambers per lake in transects from the lake shore to lake centre. The placement of chambers along the water surface has a significant impact on CH₄ estimates. Due to mixing, diffusive CH₄ has limited variability across the water surface, but CH₄ bubbles (ebullition) occur with a high degree of variability (Bastviken et al. 2004, Cole et al. 2010, Walter Anthony et al. 2010). Given homogeneity in diffusive flux, chambers not affected by ebullition will have similar concentrations of CH₄, whereas ebullition occurs with great variation across the water surface, and will not affect all chambers (Bastviken et al. 2004). Comparison of the variation in k_{600} between chambers allows for the determination of the respective fluxes (Bastviken et al. 2004), where:

$$\frac{k_{gas\ 1}}{k_{gas\ 2}} = \left(\frac{Sc_{gas\ 1}}{Sc_{gas\ 2}} \right)^n, \quad [5]$$

and

$$k_{600} = \left(\frac{600}{Sc_{gas\ 2}} \right)^n * k_{gas\ 2}. \quad [6]$$

Exponents $n = -0.5$ or -0.67 can be used, where -0.5 is correct for describing gas fluxes at liquid surfaces (Csanady 1990) and has been used in other in other studies using chamber deployments on lakes similar in size to our study lakes (Bastviken et al. 2004, Cole et al. 2010, Bartosiewicz et al. 2015). k_{600} values are k values normalized to the Schmidt number (Sc , dimensionless) of CO_2 at $20^\circ C$ in freshwater, which is 600. For simplicity, Sc numbers can be determined from temperature (Wanninkhof 1992); however, our intention was to compare chamber-derived k_{600} to wind-based models as well as a model of average wind speeds in Alaska, therefore we determined Sc for CH_4 from the kinematic viscosity of H_2O and the molecular diffusion coefficient of CH_4 as follows. Sc is defined as:

$$Sc = \frac{\nu}{D}, \quad [7]$$

where ν is the kinematic viscosity of water ($m^2\ s^{-1}$), and D ($m^2\ s^{-1}$) is the coefficient of molecular diffusion. The kinematic viscosity of water, ν is defined as:

$$\nu = \frac{\nu_B * 10}{\rho}, \quad [8]$$

where ν_B is the dynamic viscosity of water ($Pa\ s^{-1}$), ρ is the density of water ($g\ cm^{-3}$), and 10 is a conversion factor to return ν in units of $cm^2\ s^{-1}$. The dynamic viscosity of water, ν_B can be computed as (CRC Handbook of Chemistry and Physics, Weast 1983):

$$\nu_B = 10^{-3} * 10^A, \quad [9]$$

where

$$A = \frac{1301}{998.333 + 8.1855(T-20) + 0.00580(T-20)^2}, \quad [10]$$

and T is temperature in °C. The density of water, ρ can be computed as (CRC Handbook of Chemistry and Physics, Weast 1983):

$$\rho = \frac{999.83952 + 16.945176(T) - 7.987041 \times 10^{-3}(T)^2 - 46.170461 \times 10^{-6}(T)^3 + 105.56302 \times 10^{-6}(T)^4 - 280.54253 \times 10^{-12}(T)^5}{1 + 16.879850 \times 10^{-3}(T)} \times 10^{-3}, \quad [11]$$

where T is temperature in °C. The molecular diffusion coefficient of CH₄, D is defined as (MacIntyre et al. 1995):

$$D = (10^{-6}T) / (v_B \times 1000 \times V_c^{0.629}), \quad [12]$$

where V_c is 98.6, the critical volume for CH₄.

When k values (Eq. 5) from chambers that received CH₄ ebullition are converted to k_{600} and compared to k_{600} values from other chambers during the same deployment, chambers that received ebullition can be distinguished from chambers that did not receive ebullition (Bastviken et al. 2004). By finding each chamber's $k_{600} / \text{Minimum } k_{600}$ ratio, where *Minimum k_{600}* is the smallest chamber-derived k_{600} determined from the same deployment of chambers as the chamber's k_{600} , chambers receiving ebullition can be distinguished from chambers not receiving ebullition. Once $k_{600} / \text{Minimum } k_{600}$ ratios are computed for all chambers across all deployments, frequency distribution assessment allows for clear delineation between chambers receiving CH₄ diffusion only versus chambers receiving diffusion and ebullition. Bastviken et al. (2004) use $k_{600} / \text{Minimum } k_{600}$ of 2 (i.e., chambers with a piston velocity twice as high than the chamber with the lowest piston velocity) as the distinguishing boundary, where ratios <2 indicate chambers received CH₄ diffusion only, and ratios ≥ 2 indicate ebullition and diffusion were received. Based on the work by Bastviken et al. (2004), chambers deployed 1-2 m in depth (which is the mean depth of Mackenzie Delta lakes) have a ~60% probability of receiving CH₄ ebullition. After distinguishing ebullition from diffusion between chambers, we determined k [Eq. 5] for chambers receiving diffusion only and used k to calculate diffusion flux [Eq. 1]. For chambers receiving ebullition, lake average k_{600} values during the same

deployment were used to calculate k [Eq. 6], which was then used to calculate diffusion flux [Eq. 1]. Ebullition was calculated as the difference between the amount of CH₄ in the chamber at the end of the sampling period and the amount of CH₄ that diffused into the chamber.

Gas diffusion rates at the air-water interface depend on a concentration gradient and k [Eq. 1]. A number of wind-based models have been empirically determined to approximate k . Wind is critically important in gas fluxes across the air-water interface in determining the thickness of the stagnant film layer, where increases in wind speed correspond with decreases in the thickness of the stagnant film layer, which results in a higher k . Using wind speeds measured at the Inuvik Airport (<http://climate.weather.gc.ca/>), we compared our chamber fluxes to models derived by Cole and Caraco (1998):

$$k_{600} = 2.07 + 0.215u^{1.7}, \quad [13]$$

Crusius and Wanninkhof (2003):

$$k_{600} = 0.168 + 0.228u^{2.2}, \quad [14]$$

and Wanninkhof (1992):

$$k_{600} = 0.45u^{1.64}, \quad [15]$$

where u is wind speed (m/s). We also compared our results to the stagnant film layer (z) method used by Kling et al. (1992), which was constructed using average z thickness of 200 μm :

$$F = D * z^{-1} * (C_w - C_A). \quad [16]$$

Sampling Protocol

In 2014, we surveyed 2 lakes on 4 occasions beginning in July and ending in August. Given logistical constraints, we were only able to deploy 6 chambers on one lake (L129, a no closure lake) and 9 on the other (L280, a low closure, thermokarst lake). We used HDPE buckets that when submerged below the water surface 0.03 m had an internal

volume of 0.0076 m³ and open-mouth area of 0.040 m². Once deployed on the first sampling occasion in July 2014, chambers were not removed until August 2014. In June 2015, we deployed 15 chambers in 6 lakes (L129, L80, L87, L280, L56, and L520). Chambers were never directly tied to an anchor. As recommended by Bastviken et al. (2004), chambers were attached to a float that separated the line connecting to the anchor. In this way disturbance to the chamber during sampling can be minimized. Sampling of the chamber involved withdrawing initial samples with 60 mL plastic syringes through a 3-way stopcock on one end of 0.30 m of Nalgene tubing, the other end of which was attached to a 1 mL plastic syringe (with the plunger removed) fitted through a hole (sealed with silicon grease) drilled through the bottom of the chamber. Prior to each chamber sampling, the 60 mL syringe was used to mix the contents of the chamber by pumping the full syringe volume six times without introducing air into the chamber. The syringes used to sample the chamber were fitted with 3-way stopcocks to prevent leakage of gas in between transfer to storage vials (13.5 mL Vacutainer serum vials, prepared by flushing with ultra-zero air, and evacuation to 27" Hg). In 2014, samples were transferred to storage vials in the laboratory (within 3 hours), and in 2015 samples were transferred in the field within 5 minutes of collection. Dissolved CH₄ samples were obtained from 0.10 m below the water surface, and within ~1 m of the respective chamber.

4.2.3. Methane Mass Balance and Sediment Diffusion

We utilized a mass balance model (see Figure 1-4) of dissolved CH₄ to compare MOX and atmospheric diffusion rates to CH₄ storage in the water column. We also used the model to estimate diffusion from the sediment into the water column by integrating the change in water column storage of dissolved CH₄ over time:

$$SED = \frac{d}{dt}Storage + MOX_D + DIF, \quad [17]$$

where *SED* is CH₄ sediment diffusion at time, $\frac{d}{dt}Storage$ is the change in dissolved depth-weighted CH₄ over time, *MOX_D* is depth-weighted MOX, and *DIF* is the diffusion of CH₄ from the water column to the atmosphere, which was calculated using the Cole and Caraco (1998) model for determining *k₆₀₀*. Considering that together pH and dissolved CH₄ can explain 75% of the variance in MOX (see results), we used a multiple regression

model with these two predictor variables to determine MOX in instances where dissolved CH₄ measurements were available, but MOX measurements were not.

4.2.4. Mackenzie Delta Methane Emission Extrapolations

We estimated mean annual CH₄ emissions in thermokarst and high, low, and no closure lakes as the seasonal sums of: (i) ice-out (i.e., storage) flux; (ii) diffusion flux; and (iii) ebullition flux. For each flux component, we calculated delta-wide closure class fluxes as:

$$Class\ Flux = \frac{\sum(Individual\ lake\ flux) * (Lake\ area)}{Surveyed\ area} * Delta\ area\ of\ closure\ class, [18]$$

where we corrected *Delta area of closure classes* given in Lesack and Marsh (2010) to reflect the proportion of thermokarst lakes within the surveyed area (Tank et al. 2009a).

Diffusion fluxes were determined using respective early, mid-, and late summer surface water CH₄ concentrations (Chapter 3). We used wind speeds from the Inuvik Airport to calculate k_{600} values using Eq. 13 (Cole and Caraco 1998), which were used to determine k [Eq. 6] and then CH₄ diffusion fluxes [Eq. 1]. We assumed the open-water period to last from June through October, and that our early, mid-, and late summer diffusion fluxes were representative of average June, July, and August fluxes, respectively, and that our August fluxes are representative of September and October fluxes.

Ebullition fluxes were derived from the empirical relationship between ebullition measured with floating chambers and diffusion (as determined using the Cole and Caraco (1998) method of calculating k_{600}). Considering that ice-out fluxes should take into account winter time ebullition, our estimate includes open-water ebullition only.

4.2.5. Sampling Container Preparation and Laboratory Analyses

Serum bottles for dissolved CH₄ were prepared as detailed in Chapter 2.2.1. CH₄ in serum vials and bottles were analyzed as detailed in Chapter 2.2.3, and salinity,

temperature, and pressure corrected concentrations were determined as detailed in Chapter 2.2.4. All samples were analyzed at SFU, Burnaby, BC.

4.2.6. Statistics

Data analyses were performed in RStudio, version 3.2.5 (RStudio Team 2016). Given our small sample size, we assessed the importance of all MOX predictor variables with second order Akaike Information Criterion (AICc). We followed the methodology for AIC outlined in Chapter 2.2.5. Comparisons of chamber-derived k_{600} values against wind-based models were done with pairwise t-tests, and we report P -values uncorrected and corrected for multiple comparisons between groups. We report adjusted r^2 for all relationships. We used Box-Cox transformations to meet assumptions of normality and homoscedasticity where required (Sokal and Rohlf 1995).

4.3. Results

4.3.1. Methane Oxidation

Seasonal Patterns in MOX

We measured MOX rates ranging from $2.47 \text{ mmol m}^{-3} \text{ day}^{-1}$ to below our detection limit (assumed to be $0 \text{ mmol m}^{-3} \text{ day}^{-1}$). In 2014, the MOX measurements initially began 29 days after ice-out; we assumed ice-out to coincide with peak water levels in East Channel of the Mackenzie River at Inuvik. Initial MOX measurements in 2015 began 14 days after ice-out, but in this case were limited to two measurements from each lake over a course of 14-25 days following peak waters in East Channel. MOX rates were highest early in the open-water period, and decreased as the summer progressed (Figure 4-2). MOX was greatest in the higher elevation lakes, and lower in the lowest elevation lakes). When considering all MOX measurements from 2014 and 2015, over 50% of the variance in MOX can be explained by ambient CH_4 concentration ($r^2 = 0.50$, $P < 0.001$; Figure 4-3). The overall decrease in MOX over the open-water period appears to be primarily driven by the general trend of ambient CH_4 in Mackenzie Delta lakes, which decreases throughout the open-water period (Chapter 3). However, MOX rates per unit substrate

(i.e., Normalized MOX; Figure 4-2) also generally declined after the early open-water period.

Potential Drivers of MOX

To resolve what factors could potentially account for the ~50% of variation in MOX (Figure 4-3) that were not accounted for by substrate concentration, we regressed all possible combinations of limnological variables against Normalized MOX and assessed the relative importance of variables with AIC. These variables included nutrients, pH, chlorophyll *a*, DO, physical parameters (water column depth and temperature), and DOM quantity and quality (2014 MOX measurements only because some variables were not re-measured in 2015). Due to their ecological significance as established in the literature, we included all of the aforementioned variables in the AIC analysis even if no significant correlation was observed with Normalized MOX (Appendix A). Model averaged coefficients and weights show that pH is the only variable measured in 2014 having a significant averaged regression coefficient with Normalized MOX (Table 4-1). The best model determined by AIC had a weight of 0.1 (i.e., 10% chance of being the best model from among all models considered in the analysis) and included TDP, *a*(250):*a*(365) (i.e., DOM molecular weight), and pH (multiple regression $r^2 = 0.66$, $P < 0.001$); however, TDP and *a*(250):*a*(365) did not have significant AIC model averaged regression coefficients with Normalized MOX (Table 4-1). pH shows highly significant negative relation to MOX when regressed with MOX ~ CH₄ residuals ($r^2 = 0.53$, $P < 0.001$; Figure 4-4A), as well as with Normalized MOX ($r^2 = 0.54$, $P < 0.001$; Figure 4-4B). Neither TDP ($r^2 = -0.01$, $P = 0.38$; Figure 4-5A) or *a*(250):*a*(365) ($r^2 = -0.05$, $P = 0.78$; Figure 4-5B) show any relation with Normalized MOX. Subsequently, we constructed a multiple regression model using all 2014 and 2015 measurements to predict MOX using dissolved CH₄ and pH (Figure 4-6), which can account for 75% of the variance in MOX ($P < 0.001$).

4.3.2. Floating Chambers

Ebullition Detection

The threshold between chambers receiving only diffusion of CH₄ from lake surface waters versus chambers also receiving ebullition was resolved for 135 chamber deployments, based on calculations of k_{600} / Minimum k_{600} ratios. Bastviken et al. (2004)

used a ratio of 2 as a threshold, and following their methodology, 2.3 was taken as the threshold for detecting ebullition in our chambers (Figure 4-7).

On the August 12-13, 2014 deployment in L280, chamber k_{600} values exceeded 3 m day⁻¹, which is 3x as high as the average of all k_{600} values for 2014 (measured in L280 and L129 only), and 2x as high as the values measured over the same time period in L129. This means that all 9 chambers in L280 had to have received ebullition. Since k cannot be determined in a lake if all chambers receive ebullition, diffusion and ebullition flux rates were estimated for that date in L280 by using the k_{600} value from L129 measured during the same time period.

Ebullition Correction

A small percentage of chambers (13%, including all August 12th L280 chambers) had CH₄ concentrations greater than equilibrium with surface water likely from high ebullition. With chamber CH₄ concentrations greater than equilibrium with surface water, CH₄ would diffuse into the lake from the chamber and emissions would be underestimated. To correct for this, we constructed a simple mass balance model (Bastviken et al. 2010). We considered ebullition to be constant and took into account diffusion out of the chamber:

$$\frac{dm}{dt} = A * Ebullition - A * Diffusion, \quad [19]$$

when integrated and rearranged yields:

$$Ebullition = \frac{m_0 e^{-At} - m_t}{e^{-At} - 1}, \quad [20]$$

where m_0 is the moles of CH₄ in the chamber at start of deployment, and m_t is the moles of CH₄ in the chamber at end of deployment. Corrected ebullition rates were 20 ± 1% (mean ± standard error [SE]) greater than uncorrected ebullition rates for these chambers. For all (n = 144) chambers deployed in 2014 and 2015, 51% received ebullition based on our detection method. This is consistent with the probability expected by Bastviken et al. (2004) for lakes 1-2 m in depth, which is in the range of depths of lakes/chamber deployments in our study.

Diffusion and Ebullition Among Lakes and Seasons

In 2015, floating chambers were deployed on 6 lakes, whereas in 2014 only 2 lakes were sampled. 2015 measurements were obtained in mid-June, whereas 2014 measurements were obtained from late July to mid-August. Ebullition was variable within the lake types in 2015, and was highest in high closure lakes and/or thermokarst lakes (Figure 4-8). The proportion of total (i.e., diffusion and ebullition) flux consisting of ebullition from Lake 280 in 2015 was comparable to estimates from 2014, however, ebullition from L129 was much greater in 2015 than it was in 2014. Since ebullition is spatially variable, the discrepancy is likely partly due to the difference in the number of chambers deployed on the lake each year: 6 chambers were deployed on L129 throughout 2014, but 15 were deployed in 2015. Overall, ebullition ranged from 0.05 to 1.58 mmol m⁻² day⁻¹ in the lower elevations lakes (L129, L80, and L87), 0.86 to 7.16 mmol m⁻² day⁻¹ in thermokarst lakes (L520 and L280), and at 13.17 mmol m⁻² day⁻¹ was highest in the high elevation lake (L56, Table 4-2).

For our deployments in 2 lakes in 2014, CH₄ emission was greater in the thermokarst lake (Lake 280) than in the no closure lake (Lake 129). Chamber-derived diffusion ranged from 0.42 to 2.22 (mean = 1.07) mmol m⁻² day⁻¹ in Lake 129, and 1.23 to 3.82 (mean = 1.93) mmol m⁻² day⁻¹ in Lake 280 (Table 4-2; Figure 4-9). Chamber-derived diffusion exceeded ebullition for the majority of the open-water period in L129, but ebullition exceeded diffusion throughout the measurement period in L280, where at the final sampling date ebullition was 4x as high as diffusion and formed 80% of total CH₄ emission (i.e., diffusion + ebullition). Ebullition was also considerably more variable in L280, where the ebullition rate on August 12th was 3x greater than what we measured one week earlier.

When combining 2014 and 2015 measurements, CH₄ diffusion was very strongly related to ambient water-column CH₄ ($r^2 = 0.91$, $P < 0.001$; Figure 4-10), which is as expected [Eq. 1]. Ebullition was strongly related to water-column CH₄ ($r^2 = 0.53$, $P = 0.002$; Figure 4-11A), and chamber-derived CH₄ diffusion ($r^2 = 0.67$, $P < 0.001$; Figure 4-11B). We also compared ebullition to wind-derived CH₄ diffusion (as per Cole and Caraco (1998) method), and used the relationship ($r^2 = 0.52$, $P < 0.01$; Figure 4-12) to estimate ebullition rates for Mackenzie Delta-wide flux extrapolations. Ebullition was also plotted against

spring sill and lake area, but no significant relation was observed (Figure 4-13). Although CH₄ ebullition did not appear to be related to under-ice CH₄ or spring sill, it may be a case of insufficient statistical power to detect the relation because of small sample size.

Comparison of Chambers with Wind Models

Chamber-derived CH₄ diffusion rates were similar to three wind-based (Wanninkhof 1992, Cole and Caraco 1998, Crusius and Wanninkhof 2003) and a model of Alaskan lakes (Kling et al. 1992) that uses an average 200 µm stagnant film layer thickness (Table 4-3). Criticisms of diffusion fluxes determined using the floating chamber are based on the possibility for chambers to enhance turbulence at the water-air interface as the chamber moves up and down on the water surface (e.g., Matthews et al. 2003). This increase in turbulence artificially increases k , which results in overestimations of diffusion, however, designing chambers to allow openings to extend below the water surface has been shown to mitigate surface turbulence and produce reliable diffusion estimates (e.g., Basviken et al. 2004 and Cole et al. 2010). Consequently, we built our chambers to extend below the water surface, and we tested the reliability of our diffusion fluxes by comparing chamber-derived k_{600} values to wind model-derived k_{600} values (k_{600} values are normalized piston velocities, thus allowing for comparison across environmental gradients). We found no statistically significant difference in k_{600} between the wind-based models and our chamber-derived lake average k_{600} values, however, the Kling et al. (1992) model was significantly different from our measurements ($P = 0.0011$; Table 4-4). Our chamber-derived k_{600} values were closest to the Cole and Caraco (1998) model ($16 \pm 14\%$ [mean coefficient of variation [CV] $\pm$ standard deviation]), but the differences were somewhat greater in the cases of the Crusius and Wanninkhof (2003) model ($22 \pm 15\%$), the Wanninkhof (1992) model ($35 \pm 17\%$), and the Kling et al. (1992) model ($46 \pm 20\%$). Considering the high similarity, we used the Cole and Caraco (1998) model to determine CH₄ diffusion fluxes from Mackenzie Delta lakes in subsequent analyses.

4.3.3. Methane Mass Balance

Methane Loss to Atmospheric Diffusion versus MOX

The rates of diffusion to the atmosphere plus MOX measured in the 6 intensively studied lakes are sufficiently high to account for removing the majority of CH₄ stored in the water columns on a daily basis during most of the open water period (Figure 4-14). The majority of CH₄ stored in the water column of the 6 intensively studied lakes after the first 40 days of open water appears to be lost to the atmosphere through diffusion rather than reduction by water column MOX (Figure 4-14). In the lowest elevations lakes (129 and 80), CH₄ storage and diffusion to the atmosphere increased over the summer. CH₄ storage and diffusion to the atmosphere were highest following ice-out and steadily decreased over the summer in the intermediate elevation lakes (87 and 280) and high elevation lake (56). In Lake 520 (thermokarst lake), CH₄ storage and diffusion fluctuated over summer, where both were high following ice-out and decreased until approximately 30 days following ice-out, then increased 4-fold over the next 20 days (i.e., until 60 days following ice-out), and decreased again at the end of summer. The percentage of CH₄ losses (sum of MOX and diffusion to the atmosphere) due to MOX were greatest within 30 days of ice-out (up to 50% losses through MOX) and decreased over the summer in all six lakes (Figure 4-15). When considering all measurements, MOX accounts for $18 \pm 3\%$ (mean $\pm$ SE) of CH₄ losses, therefore $82 \pm 3\%$ of dissolved CH₄ losses from these lakes are due to diffusion to the atmosphere.

Methane Sediment Flux

Seasonal sediment diffusion (i.e., diffusion of CH₄ from sediment into the water column) patterns (Figure 4-16), inferred from mass balance calculations between total CH₄ losses (diffusion to the atmosphere plus MOX) and changes in water column CH₄ storage, were somewhat similar to the general patterns of CH₄ storage in the lakes. Rates of sediment diffusion appeared to be much lower in the two lowest elevation lakes (Lakes 129 and 80) than in the higher elevation lakes. This was expected, but may also be a result of not accounting for changes in water column CH₄ storage as a result of water renewal in these lakes during their connection time with the river. Inferred sediment diffusion also appeared to increase until around 40-50 days after ice-out, in contrast to the pattern in the other lakes. In the four higher elevation lakes, inferred sediment diffusion

was generally as expected, trending from higher during early open-water to lower rates during later open-water, with the exception of Lake 520. Lake 520 exhibited an unusual pattern, where sediment diffusion spiked up around 50 days following ice-out, then decreased into late summer. Sediment diffusion was highly related to dissolved CH₄ ($r^2 = 0.89$, $P < 0.001$; Figure 4-17A), but not pH (Figure 4-17B) or CO₂ (Figure 4-17C). As expected, DOM quantity and quality were positively related to sediment diffusion. Sediment diffusion increased with increasing DOC ($r^2 = 0.58$, $P < 0.001$; Figure 4-18A), increased with decreasing DOM molecular weight ($r^2 = 0.30$, $P < 0.01$; Figure 4-18B), and also increased with decreasing DOM aromaticity ($r^2 = 0.34$, $P < 0.01$; Figure 4-18C). Sediment diffusion was also related to increasing TDN ($r^2 = 0.44$, $P < 0.001$; Figure 4-19A) and decreasing PP ($r^2 = 0.37$, $P < 0.01$; Figure 4-19B).

4.3.4. Mackenzie Delta Methane Emissions

Representative Open-Water Fluxes

Estimates of CH₄ emissions from the full suite of lakes in the Mackenzie Delta are summarized in Table 4-5. The open-water emission fluxes are based on direct measurements of CH₄ concentrations during three helicopter surveys of 43 lakes, which were sampled at least once in June, July, and August of 2014. CH₄ diffusion to the atmosphere per unit lake area was estimated for each of the lakes from Equation 1, where we used the Cole and Caraco (1998) model to determine k from average wind speed, and the CH₄ concentration, temperature, and barometric pressure measured at each lake on the day of each survey. CH₄ ebullition to the atmosphere for each lake on the day of each helicopter survey was then estimated from the statistical relation between the Cole and Caraco-based diffusion values and our direct measurements of chamber-based ebullition (Figure 4-12). There was also strong correspondence between the results from the Cole and Caraco model versus our direct chamber-based diffusion measurements conducted in our smaller set of 6 study-lakes. The areal-weighted average of both the diffusion and ebullition fluxes was then estimated for each of the representative lake classes (based on known areas for each of the surveyed lakes relative to the total area of all lakes surveyed) within the set of 43 lakes for each of the 3 surveys (Figure 4-20).

Coinciding with the seasonality of surface water CH₄ concentration (Chapter 3), the areal-weighted flux rates of diffusion and ebullition to the atmosphere for each of the lake classes (Figure 4-20, Table 4-5) was generally highest in June (early summer), and thereafter decreased into July (mid-summer) and August (late-summer). Diffusion flux rates were consistently highest in thermokarst lakes (June, July, and August: 219, 74.1, and 18.0 mg m⁻² day⁻¹). Diffusion from high closure lakes (108, 49.1, 12.2 mg m⁻² day⁻¹) was higher than low closure lakes (22.1, 34.4, and 13.7 mg m⁻² day⁻¹) in June and July, but not in August. Diffusion from no closure lakes (7.3, 25.4, and 7.6 mg m⁻² day⁻¹) was highest in July, and similar in June and August. Because the model for estimating ebullition flux rates is driven by the diffusion fluxes, the ebullition fluxes follow a similar pattern to the above. The results (Figure 4-20) suggest the ebullition fluxes are a more dominant component of the total daily flux rates early (June survey) during the open-water period compared to later (August survey).

Representative Ice-out Fluxes

The ice-out emission fluxes from the full suite of lakes in the Mackenzie Delta (Table 4-5) are based on direct measurements of CH₄ concentrations beneath the ice-cover of 29 lakes (from among the 43 lakes surveyed during open-water) at the end of winter (early May), plus measurements of subsequent concentrations in those same lakes during the open-water helicopter survey in June. CH₄ mass storage per unit lake area was estimated for each of the 29 lakes on the date of each survey from the concentration of water column CH₄ multiplied by the mean depth of unfrozen water (in the May survey) or mean open-water depth (in the June survey). The ice-out flux to the atmosphere per unit lake area of each lake was then estimated as the per area change in mass storage of CH₄ from the May survey to the June survey, and assuming that any additional CH₄ entering the lake-water via diffusion from the bottom sediments or being consumed within the lake via MOX during the time window between the two surveys was small relative to the change in lake storage. The areal-weighted average of May and June CH₄ storage plus ice-out fluxes was then estimated for each of the representative lake classes (based on known areas for each of the surveyed lakes relative to the total area of all lakes surveyed) within the set of 29 lakes (Figure 4-21).

Overall, storage of CH₄ in the lakes by the June survey date was quite small relative to the May survey values (Figure 4-21), with the inferred ice-out flux appearing to account for a purge of nearly all the CH₄ stored in the lakes over the winter. The inferred CH₄ ice-out fluxes among the 29 lakes surveyed accounted for an average of $94.8 \pm 0.9\%$ (mean $\pm$ SE) of the end-of-winter CH₄ storage (Figure 4-22). Moreover, it is highly likely that all of the CH₄ from winter storage was emitted to the atmosphere by the time of the June survey, given that post ice-out fluxes of CH₄ from the sediments within the lakes is sufficiently high to account for the amounts of CH₄ storage measured during the June survey. As expected, the inferred ice-out flux rates were closely related to the lake elevation gradient. CH₄ ice-out fluxes were significantly related to spring sill elevation ($r^2 = 0.73$, $P < 0.001$; Figure 4-23A) and lake area ($r^2 = 0.40$, $P < 0.001$; Figure 4-23B). The areal-weighted ice-out flux for each of the lake classes (Figure 4-21, Table 4-5) was highest in thermokarst lakes (15.81 g m^{-2}), followed by high (10.59 g m^{-2}), low (1.97 g m^{-2}), and no closure lakes (0.44 g m^{-2}), thus closely following the sill elevation and lake productivity gradient.

Delta-Wide Methane Fluxes

Estimates of total CH₄ fluxes for the entire Mackenzie Delta during open-water were obtained by scaling the estimates of per day flux rate for each lake class (Figure 4-20) to the total estimated area in the Delta represented by each lake class. Specifically, the water surface area of all lakes in the Mackenzie Delta is 3331 km^2 (Emmerton et al. 2007), where the estimated lake area within each lake class is 60.6% no closure, 24% low closure, 12.3% high closure, and 3.1% thermokarst (Lesack and Marsh 2010). Scaling the per day fluxes to an annual flux was based on assuming the results for each of three helicopter surveys was representative of a 30 day window during the open-water period. Because no CH₄ data was available for September and October, daily open-water fluxes for this period were taken to be equivalent to the values for the August survey. Given that daily flux values during September-October were expected to be low, as were observed during the August survey, the overall error in the total Delta open-water flux that was introduced by utilizing the August values to estimate the September-October period is likely small. Estimates of ice-out CH₄ fluxes for the entire Delta were obtained by scaling the per area estimates for each lake class (Figure 4-21) to the total estimated area in the Delta represented by each lake class (analogous to the open-water case).

Based on the above scaling of our lake survey measurements, then summing the open-water diffusion and ebullition fluxes, plus the ice-out fluxes, we estimate Mackenzie Delta lakes to annually emit 35.8 Gg of CH₄ (Figure 4-24). Ebullition formed approximately 50% of this estimate, ice-out 24%, and diffusion 26% of annual emissions from these lakes. This translates to open-water CH₄ fluxes of 9.13 Gg yr⁻¹ by diffusion and 18.24 Gg yr⁻¹ by ebullition. Our ice-out CH₄ flux of 8.41 Gg yr⁻¹ is within the range of Pipke's (1996) similarly calculated "Method 2B", which yielded a range of 6.29 to 15.63 Gg yr⁻¹.

4.4. Discussion

Seasonal Decrease in Water Column MOX

Our measured MOX rates (up to 2.47 mmol m⁻³ day⁻¹) are comparable with other studies conducted in Arctic regions (Table 4-6). MOX rates in the Mackenzie Delta generally decreased from early to later in the open period. This trend is partly related to a decrease in dissolved CH₄ (i.e., substrate), which decreases over the open-water period (Chapter 3). The trend, however, may also be related to other factors that drive a seasonal decline in MOX rates per unit CH₄ over the open-water season. We hypothesized that high closure lakes would exhibit higher MOX rates than thermokarst-affected lakes and low closure lakes, however, this was only the case in the first half of the summer. By late summer, MOX rates ranged from near detection limits up to only 0.5 mmol m⁻³ day⁻¹ among all lakes. We sampled for MOX at the center of each lake and approximately 0.30 m below the water surface, and since the lakes are well mixed, our measurements should be representative of average water column MOX.

Considering the general decline in MOX rates over the summer (Figure 4-2), it is not likely that differences in water column MOX explain why CH₄ is similar between lakes during the late summer (see Chapter 3). Instead, differences in MOX at the sediment-water interface could be quite different between the lakes, where higher elevation and more productive lakes (i.e., with greater potential for methanogenesis) have more sediment-water MOX than lower elevation lakes (i.e., with lower potential for methanogenesis). However, since the lakes are well mixed and highly productive during late summer such that DO should be at saturation, sufficient supply of DIN would be

required to allow for MOX at the sediment-water interface to occur (Rudd et al. 1976, Smith and Lewis 1992). Since DIN is low in the water column of the lakes, rapid DIN release through DON decomposition, or from sediments, would be required to sustain high levels of MOX at the sediment-water interface. Further study of DIN cycling at the sediment-water interface may help to advance our understanding of seasonal MOX dynamics in the benthic environment of Mackenzie Delta lakes.

Effects of pH on MOX

The inverse statistical relation between MOX and pH was surprising. In Mackenzie Delta lakes where primary production rates are high, pH can reach values higher than 10 (Tank et al. 2009b). In these lakes alkalization exerts a strong pressure on microbial communities, forcing adaptation and resulting in shifting of microbial community structure (Tank et al. 2009b). The stress of high pH significantly alters DOC processing, and yields reduced bacterial growth efficiency with increasing pH, but the biochemical consequences of increasing pH on methanotrophs are relatively unknown. Given the effect of pH on microbial DOC processing, however, increasing pH may indirectly impact nitrogen availability in well mixed, oxygenated Delta lakes. If DIN is low, methanotrophs may also exhibit depressed MOX rates at DO levels near saturation (Rudd et al. 1976, Smith and Lewis 1992). In the water column, MOX rates are usually highest in the thermocline, where DO levels are below saturation, and competition for DIN is low. Considering that Mackenzie Delta lakes are shallow and well-mixed, therefore well-aerated, and low in DIN (typically $<10 \mu\text{g L}^{-1}$) it is not surprising that we observed low MOX rates in the water column of the six study lakes. DIN is likely the product of microbial processing of dissolved organic nitrogen (DON) in Delta lakes, and may partly explain the link between pH and MOX. If increasing pH slows microbial processing of DON, thereby decreasing the mineralization of DIN, then water column MOX should also decrease.

The decrease in MOX as the summer progressed may also be partly explained by bacterial grazers. Although elevated pH has a negative effect on bacteria, heterotrophic nanoflagellates (HNANs; i.e., bacterial grazers) have been observed to tolerate high pH in Delta lakes (Tank et al. 2009b). Previous studies in Delta lakes have identified significant negative correlations of high zooplankton abundances and low bacterial abundances (Riedel 2002), as well as isotopic evidence of grazing on methanotrophs

(Tank 2009). Tank (2009) observed depressed zooplankton $\delta^{13}\text{C}$ signatures (thus indicating grazing of methanotrophs) significantly correlated with coincident measurements of dissolved CH_4 in early summer shortly after ice-out, which were measured in the same 6 lakes that we studied. Resultant mixing models constructed by Tank (2009) show that methanotrophs form a small, but consistent contribution to zooplankton biomass in early summer and late summer, and that methanotrophs are more important to zooplankton shortly after ice-out. The observations by Tank (2009) coincide with our timeline: highest MOX rates were observed at ice-out and decreased throughout the summer. However, considering that methanotrophs contribute a small amount to zooplankton biomass during late summer (Tank 2009), it is not likely that grazing pressure alone causes the decrease in MOX as the summer progresses. Instead, it is more likely a combination of an oxygen-rich water-column, insufficient supply of DIN, perhaps due to pH-related suppression of microbial processing of DON, and bacterial grazing that regulate MOX as the summer progresses in Mackenzie Delta lakes.

Methane Emissions Using Chambers

Our results generally show that CH_4 diffusion and ebullition fluxes from the water surface to the atmosphere were higher in high elevation and thermokarst lakes than in low elevation lakes connected to the river, with fluxes from the thermokarst lakes somewhat higher than in the high elevation lakes. Since diffusion is dependent on concentration gradients, diffusion fluxes to the atmosphere closely reflected the seasonal variation in water column CH_4 and generally decreased over the summer. Ebullition was closely related to water column CH_4 , and generally decreased over the sampling period (late July to mid-August) in the 2 lakes where we obtained measurements, but spiked at the very last sampling date (8-fold increase Lake 280, and 17-fold in L129). These spikes are likely due to changes in hydrostatic pressure (i.e., water levels), temperature, and atmospheric pressure. As described in Section 4.1.3, ebullition increases due to (i) changes to lake bottom currents; (ii) decrease in hydrostatic pressure as water levels decline; (iii) decrease in atmospheric pressure; (iv) bubble buoyancy in excess of threshold; and (v) sediment pore space. The ebullition spikes in Lakes 280 and 129 (Figures 4-21 and 4-22, respectively) coincide with decreasing hydrostatic pressure, atmospheric pressure, and water levels, and increasing temperature. Decreases in atmospheric pressure due to changes in weather over the sampling period (from sunny and clear, to raining, then sunny

and clear) coincided with the emission spikes, which has also been observed in other studies (Bartosiewicz et al. 2015). Decreases in hydrostatic pressure have been shown to decrease effective stress below sediment tensile strength, in effect allowing bubbles to escape the sediment (Scandella et al. 2011). Considering that the sediments in the highly productive Delta lakes are rich in organic matter (Squires and Lesack 2003), these sediments are likely to have low tensile strength and greater elasticity, which would make them more sensitive to changes in hydrostatic pressure than the less productive lakes with lower sediment organic matter content. Given that over 50% of CH₄ emitting from Mackenzie Delta lakes consists of ebullition, additional study regarding the mechanics of ebullition from these lakes is warranted.

Our floating chamber measurements of CH₄ diffusion agree well with wind-based models using wind speeds measured at the Inuvik Airport. We followed the floating chamber method as described by Bastviken et al. (2004), which has been described as best used in lakes with low wind (i.e., < 3.0 m s⁻¹). Lakes in our study region are below the tree line and have small surface area, thus are relatively wind-sheltered. Localized wind studies are clearly required to obtain improved gas flux estimates, however, for studies interested in comparing fluxes between lake types, use of wind speeds from the Inuvik Airport seems reasonable. Although our spatio-temporal coverage of CH₄ ebullition was low, differences in ebullition between lake classes was substantial. Given the stark contrast in CH₄ ebullition between lake types, deployment of bubble traps should be a greater priority than wind studies. The floating chamber method appeared to work well during the early summer, but during late summer CH₄ ebullition rates grew considerably higher than expected such that in some chambers CH₄ would diffuse from the chambers back into the water. Furthermore, the floating chamber method is highly labor intensive, so methods such as bubble traps that allow longer-term deployments would be more efficient and practical, and likely would produce more accurate results in high ebullition environments. Bubble traps (Hamilton et al. 1994, Walter Anthony et al. 2010, Sepulveda-Jauregui et al. 2015) could also be used to measure wintertime CH₄ ebullition, which is particularly important for advancing our understanding of the effects of thermokarst on CH₄ emissions from Mackenzie Delta lakes, and ice bubble storage, which can contribute ~10% of annual CH₄ emissions (Greene et al. 2014).

Methane Water Column Storage and Sediment Flux

Sediment fluxes generally increased over the summer, however, this observation may be limited due to not taking flushing rates into account. The general seasonal increase in sediment flux from Lakes 129 and 80 suggests that as water levels decline, flushing of CH₄ from lake to river declines, which would result in increasing CH₄ storage in the lake. Consequently, increasing sediment fluxes from lakes connected to the river may be an artifact of decreasing flushing rates and not necessarily increases in methanogenesis. The other four lakes are not expected to be affected by flushing with the river to the same extent as Lakes 129 and 80 because of lower connection times, so it is not surprising to observe divergent seasonal trends between the lakes. In any case, since we did not measure water inflows and outflows we cannot resolve this possibility. Future studies of CH₄ budgets in these lakes must certainly be accompanied by detailed water budgets.

Mackenzie Delta lakes are shallow (mean depth 1.5 m) and well mixed over the open-water period, however, the 4-fold increase in CH₄ storage from 30 to 50 days after ice-out in Lake 520 (Figure 4-14) suggests stratification occurred at some point before mid-summer especially because a similar pattern was not observed in the other lakes. Since Lake 520 is deeper (mean depth of 2.2 m, maximum 4.4 m) due to thermokarst than other Mackenzie Delta lakes, it is possible that stratification occurred, which potentially resulted in hypolimnetic anoxia. Anoxia would lead to dissolved CH₄ accumulation in the hypolimnion, and after mixing could explain the observed pattern of CH₄ storage in Lake 520. Lake 280 is also a thermokarst lake, but is shallower (mean depth of 1.6 m, maximum 3.4 m) and also has a greater surface area (24,000 m²) than Lake 520 (2,000 m²). Considering the relatively small surface area, Lake 520 may not be as sensitive to wind-driven mixing as other Mackenzie Delta lakes. Since Lake 520 is small and shallow, buoyancy-driven mixing (e.g., Bartosiewicz et al. 2015) should also be considered in future studies of CH₄ dynamics in this lake and other thermokarst-deepened Mackenzie Delta lakes.

Although the above described scenario may explain the high CH₄ diffusion from sediment to water (i.e., sediment flux) for Lake 520 (over 300 mg m⁻² day⁻¹), our other estimates were generally comparable to other regions (Table 4-7). Sediment fluxes from

the lower elevation lakes generally increased over the summer and were highest at the end of our sampling period, whereas higher elevation lakes (with the exception of Lake 520) generally decreased over the summer and were lowest at the end of summer. This reconciles with what we observed in Chapter 3, where CH_4 increased towards the end of summer in no closure lakes, but CH_4 in thermokarst and low and high closure lakes decreased over the summer and were lowest by the end of summer. Considering that high ebullition rates are possible towards the end of summer, but sediment flux was generally lowest towards the end of summer, it is not likely that decreases in methanogenesis over the summer in the higher elevation lakes explain why late summer levels of CH_4 in all lakes regardless of elevation gradient. Instead, it is likely that MOX at the sediment-water interface increases over the open-water period, which regulates ambient levels of CH_4 in the water column of these lakes. Therefore, it appears that MOX at the sediment-water interface significantly reduces CH_4 emissions from Mackenzie Delta lakes.

MOX at the Sediment-Water Interface

Sediment flux of CH_4 into the water-column (i.e., the balance of dissolved CH_4 escaping oxidation at the sediment-water interface) was significantly related to nutrients and DOM quality and quantity, which was consistent with what we observed in Chapter 3. Further to the discussion in Chapter 3, since TDN is primarily DON in these lakes (Tank 2009), it seems that organic matter processing and release of inorganic nitrogen from DOM has a positive effect on sediment CH_4 flux, but it is not clear how this affects the balance between methanogenesis and MOX at the sediment-water interface, nor is it clear how the dynamics of bacterial DOM processing versus DOM photolysis affect nutrient availability for methanogenesis and sediment-water MOX. What is clear is that sediment fluxes generally increase over the summer in the lower elevation lakes, decrease in intermediate elevation lakes and high elevation lakes, but is variable in deeper thermokarst lakes. This suggests that MOX at the sediment-water interface increases as the summer progresses, and also increases along the lake elevation gradient. Since Mackenzie Delta lakes are shallow, they should be relatively well mixed, and because methanotrophs are sensitive to high levels of DO, high levels of DIN would be required to sustain high rates of MOX (Rudd et al. 1976, Smith and Lewis 1992). Considering that sediment nitrogen in relation to sediment organic matter tends to increase along the lake

elevation gradient (Squires et al. 2003), it seems possible that there may be sufficient DIN available to sustain high rates of MOX at the sediment-water interface assuming that the processes (microbial or photolysis) behind organic matter decomposition do not inhibit methanotrophs in the surface sediment environment. Furthermore, pH tends to be higher in the more productive higher elevation lakes. Since increasing pH has a significant negative effect on MOX in the water column, it seems likely that MOX at the sediment-water interface would also be affected. Although this complicates our hypothesis that MOX at the sediment-water interface increases over the summer in the higher elevation lakes, it may be the case that increases in sediment pore water pH may be somewhat buffered compared to the water column considering the abundance of ion exchange sites in the sediment. Consequently, future studies should seek to understand the DIN, DO, and pH dynamics in the sediment in addition to the composition of sediment microbial communities to fully understand the role of MOX at the sediment water interface in regulating CH₄ emissions from Mackenzie Delta lakes.

MOX Reduction of Ice-out Flux

One key uncertainty with our CH₄ ice-out estimate is whether or not MOX could significantly reduce the ice-out flux. From our various measurements, we have developed statistical models yielding MOX rates and diffusion rates to the atmosphere as a function of ambient CH₄ levels (plus other measures) in our lake-waters during open-water. Whereas we have measurements of under-ice CH₄ storage in our set of study lakes, it is possible to only crudely estimate ambient CH₄ concentrations in the lakes immediately post ice-out because of dilution effects from melting lake-ice and snow, plus the layer of flood-water from the river that mixes with water derived directly from each lake. Potentially using such corrected concentrations of ambient CH₄ to project potential MOX and diffusion rates to the atmosphere at that point in time is greatly oversimplified. In any case, projected ambient CH₄ concentrations at the time of ice-out are considerably outside the range of concentrations from which the MOX and diffusion models were developed. There are also potential interaction effects in the chemistry of mixing lake-water (very high DIC, lower pH) with floodwater from the river (lower DIC, higher pH). Moreover, upon initial removal of the ice cover, CH₄ concentrations in most of the lakes are super-saturated and may effervesce, bubbling out directly to the atmosphere and thus escaping MOX. It is very difficult to quantify these potential effects. Never-the-less, if we take a simplified scenario

assuming atmospheric diffusion is a function of ambient CH₄ concentrations in typical Delta lakes, as was used for our floating-chamber measurements of CH₄ diffusion, the projected CH₄ diffusion rates (Cole and Caraco (1998) method) for dilution-corrected concentrations ranging up to 800 µmol L⁻¹ at ice-out are shown in Figure 4-27. Similarly, if we use the relationship between ambient CH₄ concentrations and MOX (Figure 4-3; the regression model in Figure 4-6 was not used because of the great uncertainty from interaction effects in the chemistry of mixing lake-water), the projected MOX rates at ice-out are also shown in Figure 4-27.

Comparing the projected CH₄ diffusion and MOX rates, the rate of increase in MOX with respect to dissolved CH₄ is slightly lower than that of diffusion (Figure 4-27), which suggests overall that diffusion into the atmosphere is likely the more dominant CH₄ removal process at ice-out. However, considering the small difference in slopes, there appears to be very high potential for MOX to significantly reduce the CH₄ ice-out flux and to fuel a productive community of methanotrophs. It is unknown how methanotroph activity changes in response to ice-out, but since they are already active (to varying degrees) before the ice melts (Martinez-Cruz et al. 2015) and that MOX rates increase with CH₄ availability, methanotrophs should respond relatively quickly if sufficient oxygen and DIN are available. That being said, these projected growth rates would require very high methanotroph cell division rates in order for MOX to approach the rates of CH₄ diffusion to the atmosphere. Methanotroph growth kinetics are unknown in this system, and warrant further investigation to determine to what degree MOX might be able to keep pace with atmospheric diffusion at ice-out.

Methane Ice-out Flux

Our ice-out flux amounts to approximately 24% of total CH₄ emissions (diffusion and ebullition) from Mackenzie Delta lakes. Although our CH₄ ice-out flux estimate is within the range predicted by Pipke (1996), it assumes homogenous lake bathymetry and does not directly take into account CH₄ trapped in ice. Our depth-weighted CH₄ concentrations (i.e., CH₄ storage) assumed that the depth at the sampling location was representative of mean lake depth. This further assumes that there is little variation in lake morphology. Thermokarst lakes are typically deeper than other lakes in the Mackenzie Delta, and likely have relatively uneven basins. Future investigation of lake

bathymetry would help refine CH₄ ice-out fluxes, and may also improve our understanding of thermokarst in Mackenzie Delta lakes.

Ice-trapped bubbles have been shown to be a significant component of CH₄ ice-out flux in other areas (e.g., Walter et al. 2006, Walter Anthony et al. 2010, Sepulveda-Jauregui et al. 2015) and are very likely to also be important in Mackenzie Delta lakes. Ebullition occurs during the winter, and CH₄ bubbles are either sealed in ice during downward ice growth, or bubbles exchange gases with the water column (Greene et al. 2014). We did notice ice-trapped bubbles in many lakes, and future efforts to investigate Mackenzie Delta CH₄ fluxes should take ice bubble fluxes into account. CH₄ ebullition has been positively related to thermokarst in other areas, and it could be that thermokarst lakes in the Mackenzie Delta produce more CH₄ ice bubbles than other lakes.

Mackenzie Delta Lakes are Sources of Carbon to the Atmosphere

Our CH₄ emission rates generally compare well to other Arctic regions (Table 4-8). Even though our ebullition estimates are based on measurements from only 6 lakes, most compare well to mean fluxes of comparable lake types north of 50° latitude. Additional ebullition measurements from more lakes over the open-water period are required to refine our estimate.

Using our ice-out, diffusion, and ebullition fluxes in Table 4-5, and assuming the global warming potential over 100 years (GWP₁₀₀) of CH₄ is 34-times that of CO₂ (Myhre et al. 2013) (i.e., CO₂-equivalents (eq) of CH₄ = mass CH₄ * 34), we estimate Mackenzie Delta lakes to contribute 1.2 Tg of CO₂-equivalents (eq) to the atmosphere per year. Because of high rates of late summer primary production, Mackenzie Delta lakes are near neutral on an annual basis in terms of CO₂ (excluding thermokarst lakes). However, CH₄ constitutes a considerable leak of carbon in this system that offsets any CO₂ absorption because it is the more productive lakes that emit the most CH₄. High closure lakes constitute the greatest carbon leak, where up to 3.7 g m⁻² of CO₂ is absorbed per year (Tank et al. 2009a), but 0.46 Tg of CO₂-eq are lost annually as CH₄. Important to note is that our estimates are likely to primarily consist of biogenic CH₄, and not geogenic CH₄. Substantial geogenic CH₄ seeps associated with natural gas deposits have been observed in a number of lakes in the northern half of the Delta (Bowen et al. 2008), which could add

considerably to our estimates. Moreover, a substantial portion of the water surface area in the Mackenzie Delta also consists of distributary river channels (Emmerton et al. 2007), which have not been included in our analysis.

4.5. Conclusion

Consistent with the trend of dissolved CH_4 observed in the previous chapter, MOX decreases during the open-water period in all lakes, and CH_4 sediment fluxes generally increase in no closure lakes, but decrease in low and higher elevation lakes as the summer progresses. Considering that CH_4 sediment flux generally decreases over the summer, it is likely that MOX at the sediment-water interface increases over the open-water period. If MOX at the sediment-water interface is indeed considerable in Mackenzie Delta lakes, then the contribution of CH_4 -derived carbon to benthic food webs may also be significant. Furthermore, MOX at the sediment-water interface could also be substantially reducing the amount of CH_4 diffusing from lakes. In other CH_4 -rich regions, methanotrophs have been shown to comprise a large portion of chironomid biomass, which then serves as a shunt for delivering CH_4 -derived carbon up the food chain. Future investigations should focus on benthic community food webs to resolve the various carbon-utilization pathways apparently occurring and within the sediments. Patterns of CH_4 emissions from Mackenzie Delta lakes reflect the general seasonal decrease in dissolved CH_4 , however, we need to better understand how seasonal patterns of ebullition are driven in the Delta. These late summer emission events indicate that methanogenesis does not necessarily slow over the summer, which further suggests that MOX at the sediment-water interface may be responsible for regulating CH_4 levels from intermediate and higher elevation lakes in the Mackenzie Delta. Future studies should focus on quantifying MOX at the sediment-water interface and improving our understanding behind the mechanics of ebullition in these lakes. It is clear that there are many dimensions of CH_4 cycling in Mackenzie Delta lakes, and further study is required in order to fully understand how climate change may affect CH_4 emissions from Mackenzie Delta lakes. Two areas of focus are recommended: (i) MOX at the sediment-water interface; and (ii) ebullition.

4.6. References

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4.7. Tables

Table 4-1. Results of Akaike's Information Criteria (AIC) Model Selection Analysis, Showing Model-averaged Normalized Methane Oxidation (MOX) Predictor Variable Coefficients and AICc Weights.

Predictor	Coefficient	Standard Error	P-Value	AICc Weight
pH	-2.43	0.61	<0.001	1
TDP	2.09	1.79	0.26	0.7
<i>a</i> (250): <i>a</i> (365)	0.15	0.16	0.35	0.57
DOC	0.03	0.05	0.60	0.29
DO	0.03	0.07	0.65	0.26
PN	0.02	0.09	0.83	0.08
PC	0.00	0.01	0.85	0.07
Depth	-0.02	0.10	0.87	0.06
SUVA	-0.04	0.16	0.80	0.12
Chlorophyll <i>a</i>	0.01	0.10	0.92	0.03
PP	0.03	0.33	0.92	0.03
TDN	-0.02	0.19	0.93	0.03
CDOM	0.01	0.05	0.87	0.06
Temperature	0.00	0.01	0.98	0.03

AICc weights (from 0 to 1) indicate relative variable importance when comparing across all possible combinations of predictor variables (i.e., 1 indicates the variable is present in 100% of the assessed models).

Table 4-2. Floating Chamber CH₄ Diffusion and Ebullition from 6 Mackenzie Lakes Measured in 2014 and 2015.

Lake	Date	Lake Area (m ²)	Spring Sill (masl)	Closure	Average Depth (m)	Temperature (°C)	Dissolved CH ₄ (μmol L ⁻¹)	Number of Chambers	k_{600} (m day ⁻¹)	Diffusion (mmol m ⁻² day ⁻¹)	Ebullition (mmol m ⁻² day ⁻¹)	Total Emission (mmol m ⁻² day ⁻¹)	Ebullition % of Total Emission
L129	20140725	378000	2.363	No	2.5	17.63	1.26	6	0.84	0.97	0.22	1.19	18
L280	20140725	24000	3.838	TK	2.0	18.20	2.08	8	0.70	1.36	3.30	4.65	71
L129	20140729	378000	2.363	Con	1.5	13.36	0.77	5	1.19	0.66	0.06	0.71	8
L280	20140729	24000	3.838	TK	2.3	14.12	0.98	9	1.68	1.23	1.91	3.14	61
L129	20140806	378000	2.363	No	1.7	12.43	0.71	6	0.81	0.42	0.16	0.59	28
L280	20140806	24000	3.838	TK	2.2	13.12	1.20	9	1.37	1.32	5.78	7.11	81
L280	20140812	24000	3.838	TK	2.2	15.49	2.53	9		3.82	16.11	19.93	81
L129	20140812	378000	2.363	No	1.4	15.03	1.50	6	1.73	2.22	2.78	5.00	56
L87	20150612	39000	3.389	Low	1.4	14.06	0.53	15	0.78	0.32	0.09	0.40	21
L520	20150614	2000	4.913	TK	1.9	16.09	3.33	13	0.80	2.37	0.86	3.23	27
L80	20150615	193000	2.631	Low	3.0	14.34	0.15	14	1.10	0.12	0.05	0.17	29
L129	20150616	378000	2.363	No	1.8	13.53	0.53	15	0.96	0.40	1.58	1.98	80
L280	20150617	24000	3.838	TK	2.3	14.17	2.84	15	1.21	2.85	7.16	10.01	72
L56	20150617	31000	4.623	High	1.2	15.22	7.99	14	0.84	5.79	13.47	19.25	70

k_{600} : piston velocity (k) normalized to Schmidt number of 600.

TK: thermokarst lake.

Average depth determined using all chambers per deployment.

Dissolved CH₄ is the average surface water concentration across all chambers.

Table 4-3. CH₄ Diffusion (mmol m⁻² day⁻¹) Measured with Floating Chambers, Three Wind-Based Models (Cole, Wan, and Cru), and a Model of Alaskan Lakes (ALA).

Lake	Date	Floating Chambers	Cole	Wan	Cru	Kling
L129	20140725	0.97	1.36	1.52	1.86	0.81
L280	20140725	1.36	2.02	2.25	2.75	1.19
L129	20140729	0.66	0.70	0.73	0.77	0.45
L280	20140729	1.23	0.83	0.88	0.93	0.53
L129	20140806	0.42	0.48	0.38	0.30	0.41
L280	20140806	1.32	0.81	0.64	0.51	0.68
L280	20140812	3.82	2.48	2.65	2.92	1.56
L129	20140812	2.22	1.44	1.54	1.69	0.90
L87	20150612	0.32	0.38	0.32	0.24	0.31
L520	20150614	2.37	2.20	1.58	1.33	2.09
L80	20150615	0.12	0.11	0.10	0.07	0.09
L129	20150616	0.40	0.42	0.40	0.28	0.31
L280	20150617	2.85	2.11	1.76	1.34	1.72
L56	20150617	5.79	6.14	5.13	3.90	5.01

Diffusion for L280 obtained on 20140812 were based on k_{600} from L129, therefore were excluded from comparison of models.

Cole: Cole and Caraco (1998)

Wan: Wanninkhof (1992)

Cru: Crusius and Wanninkhof (2003)

Kling: Kling et al. (1992)

Table 4-4. Results of Paired t-test Comparison of Floating Chamber-Derived and Wind Model-Derived k_{600} Values.

Comparison	Bonferroni Adjusted <i>P</i> -Value	Unadjusted <i>P</i> -Value
Cole-FC	1.00	0.30
Wan-FC	1.00	0.18
Cru-FC	1.00	0.19
Kling-FC	0.0011	<0.001
Wan-Cole	1.00	0.18
Cru-Cole	1.00	0.29
Kling-Cole	<0.001	<0.001
Cru-Wan	1.00	0.42
Kling-Wan	0.002	<0.001
Kling-Cru	0.14	0.014

FC: floating chamber

Cole: Cole and Caraco (1998)

Wan: Wanninkhof (1992)

Cru: Crusius and Wanninkhof (2003)

Kling: Kling et al. (1992)

Table 4-5. Areal-weighted CH₄ Flux Extrapolations from Mackenzie Delta Thermokarst (TK), High, Low, and No Closure Lakes.

Lake Class	Diffusion Flux (mg m ⁻² d ⁻¹)	Ebullition Flux (mg m ⁻² d ⁻¹)	Ice-out Flux (mg m ⁻²)	Cross-Delta Area (km ²)	Diffusion per Lake Class (Mg d ⁻¹)	Ebullition per Lake Class (Mg d ⁻¹)	Diffusion per Lake Class (Gg)	Ebullition per Lake Class (Gg)	Total Diffusion per Interval (Gg)	Total Ebullition per Interval (Gg)	Total Ice-out (Gg)	Total Flux per Interval (Gg)
JUNE									2.97	9.32		12.29
TK	219	886		103	22.5	91.3	0.68	2.74				
High	108	426		409	44.1	174.4	1.32	5.23				
Low	22.12	39.19		793	17.5	31.1	0.53	0.93				
No	7.32	6.90		2026	14.8	14.0	0.44	0.42				
JULY									3.19	6.15		9.34
TK	74.08	177		103	7.6	18.2	0.23	0.55				
High	49.14	94.19		409	20.1	38.5	0.60	1.16				
Low	34.39	56.54		793	27.3	44.8	0.82	1.35				
No	25.39	51.05		2026	51.4	103.4	1.54	3.10				
AUGUST									0.99	0.92		1.91
TK	18.02	21.29		103	1.9	2.2	0.06	0.07				
High	12.20	11.24		409	5.0	4.6	0.15	0.14				
Low	13.70	13.48		793	10.9	10.7	0.33	0.32				
No	7.55	6.57		2026	15.3	13.3	0.46	0.40				
SEPTEMBER AND OCTOBER									1.98	1.85		3.83
TK	18.02	21.29		103	1.9	2.2	0.11	0.13				
High	12.20	11.24		409	5.0	4.6	0.30	0.28				
Low	13.70	13.48		793	10.9	10.7	0.65	0.64				
No	7.55	6.57		2026	15.3	13.3	0.92	0.80				

Lake Class	Diffusion Flux (mg m ⁻² d ⁻¹)	Ebullition Flux (mg m ⁻² d ⁻¹)	Ice-out Flux (mg m ⁻²)	Cross-Delta Area (km ²)	Diffusion per Lake Class (Mg d ⁻¹)	Ebullition per Lake Class (Mg d ⁻¹)	Diffusion per Lake Class (Gg)	Ebullition per Lake Class (Gg)	Total Diffusion per Interval (Gg)	Total Ebullition per Interval (Gg)	Total Ice-out (Gg)	Total Flux per Interval (Gg)
ICE-OUT												8.41
TK			15806	103	1628						1.63	
High			10589	409	4331						4.33	
Low			1969	793	1562						1.56	
No			440	2026	892						0.89	
OVERALL												35.79

Flux rates for closure classes obtained as per Eq. 18.

Surveyed flux is the surveyed flux divided by the surveyed area.

Cross-Delta areas of high, low, and no closure lakes were obtained from Lesack and Marsh (2007) and reflects the two additional TK lakes (L280 and L115) identified in Chapter 3. The cross-Delta area of TK lakes was based on the proportion of these lakes in the surveyed area (Tank et al. 2009a). We considered L302a a no closure lake rather than outlier lake.

Delta-wide flux = Flux Rate * Cross-delta Area.

Diffusion fluxes are calculated for June, July, and August using samples obtained as per Chapter 3, and September and October fluxes are estimated from August diffusion rates. Diffusion is assumed to occur over the entire open-water period (150 days).

Ebullition fluxes were calculated from diffusion rates following the relationship in Figure 4-11. Ebullition was assumed to occur over the entire open-water period.

Table 4-6. CH₄ Oxidation Rates (mmol m⁻³ day⁻¹) Measured in Lakes in the Mackenzie Delta, Alaska, and Mid-western USA.

Study	Region	Number of Lakes	Minimum	Maximum
Present study	Mackenzie Delta	6	0	2.47
Martinez-Cruz et al. (2015)	Alaska	30	1.25	33.67
Lofton et al. (2014)	Alaska	2	0.053	8.16
Kankaala et al. (2006a)	Finland	1	0.02	18
Bastviken et al. (2003)	Wisconsin	3	0.00063	2.44
Striegl and Michmerhuisen (1998)	Minnesota	2	0	200

Table 4-7. Mean (min, max) CH₄ Diffusion from Sediments into Water Column Measured in Mackenzie Delta Lakes and Other Regions, Where all Measurements are of Diffusion into Overlying Water that is Oxid.

Study	Lake	Region	CH ₄ Sediment Diffusion (mg CH ₄ m ⁻² day ⁻¹)
Present study	L129	Mackenzie Delta	17.8 (3.7-36.2)
Present study	L280	Mackenzie Delta	104 (19.6-285)
Present study	L520	Mackenzie Delta	214 (67.7-402)
Present study	L56	Mackenzie Delta	85.5 (19.6-285)
Present study	L80	Mackenzie Delta	5.4 (1.0-9.0)
Present study	L87	Mackenzie Delta	45.7 (6.9-216)
Bastviken et al. 2008	Paul	Wisconsin, USA	51.5
Bastviken et al. 2009	Peter	Wisconsin, USA	48.4
Bastviken et al. 2010	Hummingbird	Wisconsin, USA	37.9
Rudd and Hamilton 1978	227	Experiment Lakes Area, Ontario	12.8
Roy et al. 1996	Lake Ontario	Hamilton Harbour, Ontario	0-83.1

Table 4-8. CH₄ Ice-out, Diffusion, and Ebullition Emission Rates Measured in the Mackenzie Delta and Comparable Regions.

Study	Region	Number of lakes	Flux (mg CH ₄ m ⁻² day ⁻¹)
Ice-out Flux			
Present study	Thermokarst	4	15806
Present study	High closure	6	10589
Present study	Low closure	14	1969
Present study	No closure	5	440
Michmerhuizen et al. (1996)	Wisconsin/Minnesota	19	10-2970
Sepulveda-Jauregui et al. (2015)	Alaska	40	0-39000
Diffusion			
Present study	Thermokarst	5	104
Present study	High closure	13	56.3
Present study	Low closure	20	23.4
Present study	No closure	5	13.4
Wik et al. (2016)	Beaver ponds	733 lakes	117 (1-147)
Wik et al. (2016)	Glacial/post-glacial lakes	and ponds	12.5 (3-18)
Wik et al. (2016)	Peatland ponds	north of	86.1 (26-122)
Wik et al. (2016)	Thermokarst	~50°N	33.2 (3-38)
Ebullition			
Present study	Thermokarst	2	361
Present study	High closure	1	177
Present study	Low closure	2	36.4
Present study	No closure	1	21.5
Wik et al. (2016)	Beaver ponds	733 lakes	83.8
Wik et al. (2016)	Glacial/post-glacial lakes	and ponds	32.2 (9-58)
Wik et al. (2016)	Peatland ponds	north of	58.5
Wik et al. (2016)	Thermokarst	~50°N	87.5 (7-132)

Ice-out fluxes are mg CH₄ year⁻¹.

Diffusion and ebullition fluxes from this study are the average of June, July, and August fluxes.

Fluxes in brackets are minimum and maximum, where numbers outside brackets are mean fluxes.

4.8. Figures



Figure 4-1. Map of Mackenzie Delta lakes where methane oxidation and emission chambers were deployed.

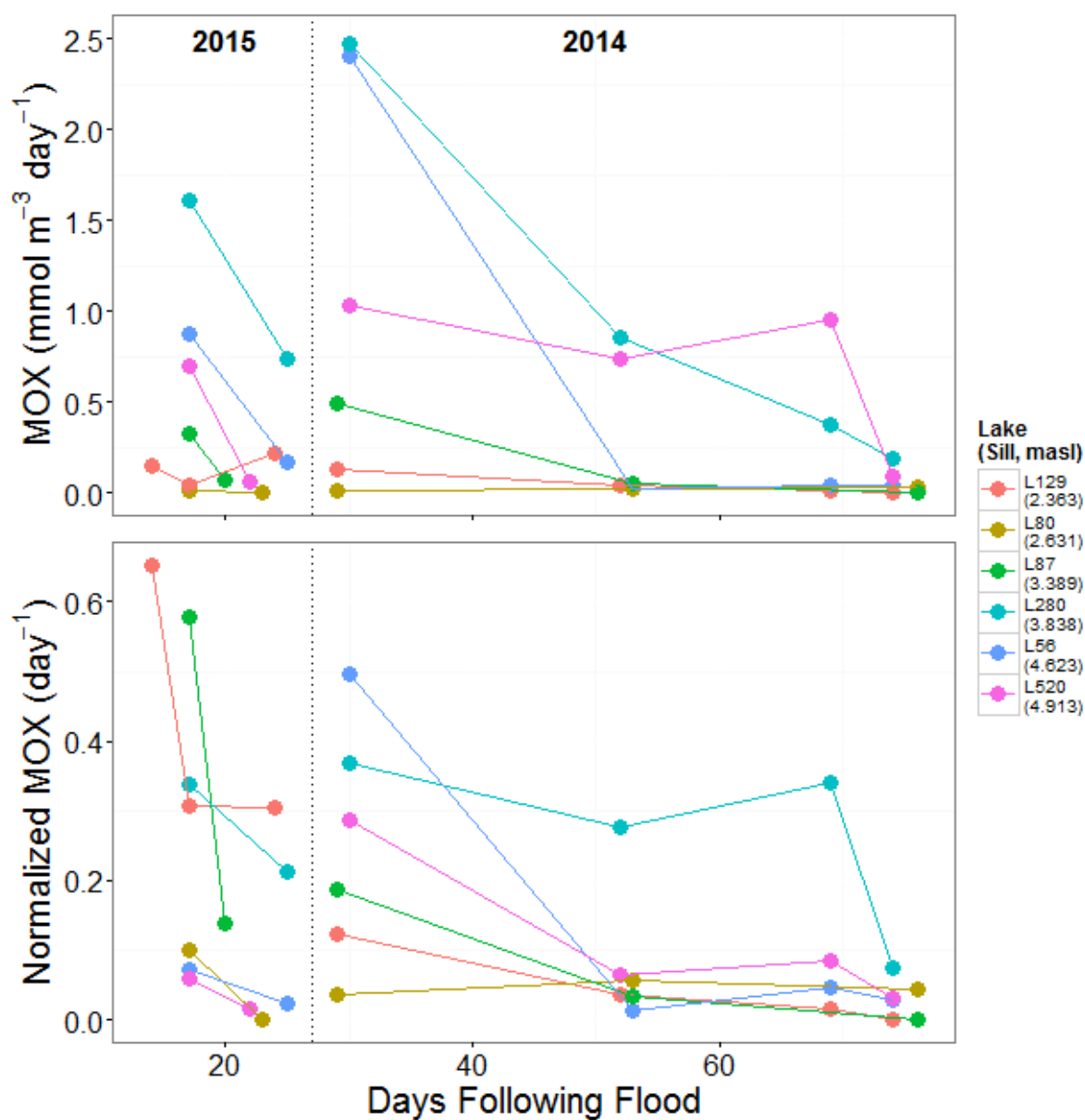


Figure 4-2. CH₄ oxidation (MOX) rates (top) and Normalized MOX rates (i.e., oxidation per unit CH₄; bottom) measured in 6 lakes of varying sill elevation during open-water conditions in 2014 and 2015.

Days following flood approximates time since ice-out, which was assumed to occur on the day of peak water at East Channel. The dotted line is drawn to show the separation between 2014 and 2015 measurements.

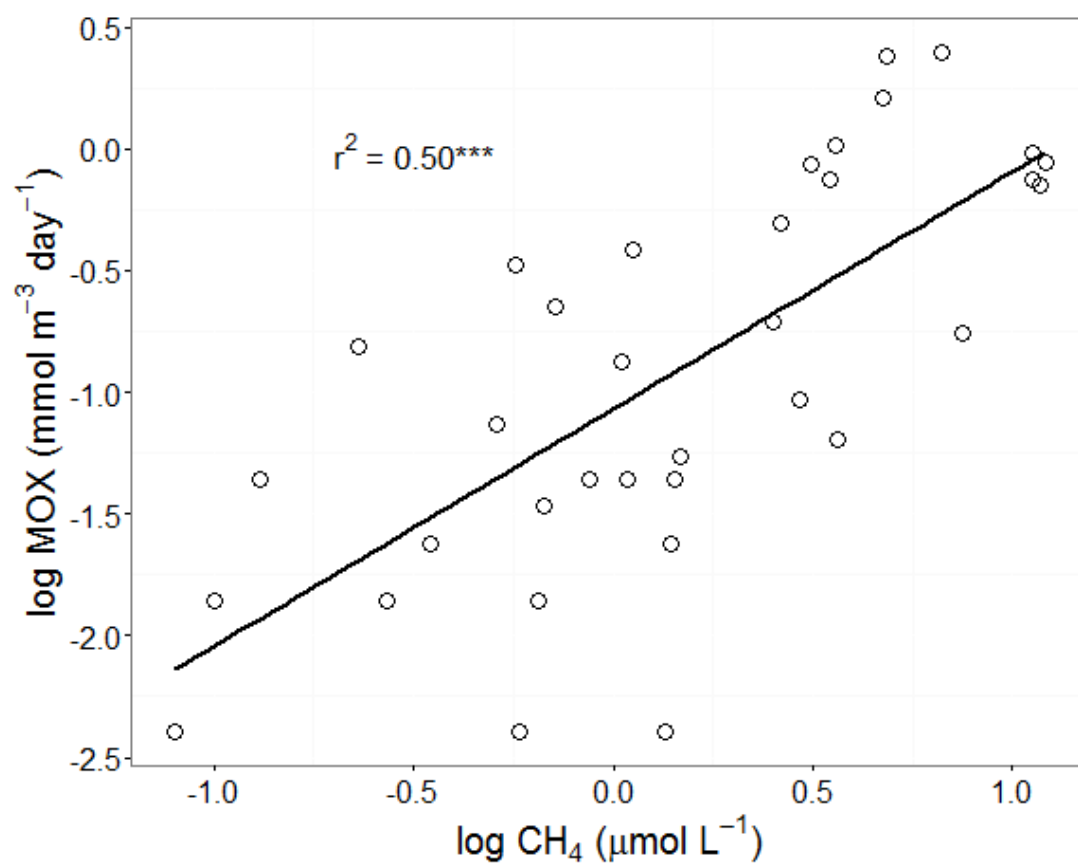


Figure 4-3. Regression of CH₄ oxidation (MOX) against ambient CH₄ using measurements taken from 6 lakes throughout the summer 2014 and shortly after ice-out in 2015.

MOX values of half the smallest MOX measurement ($0.005 \text{ mmol m}^{-3} \text{ day}^{-2}$) were added to 0 values prior to $\log_{10}$ transformation. Adjusted r^2 is shown. $^{***}P < 0.001$.

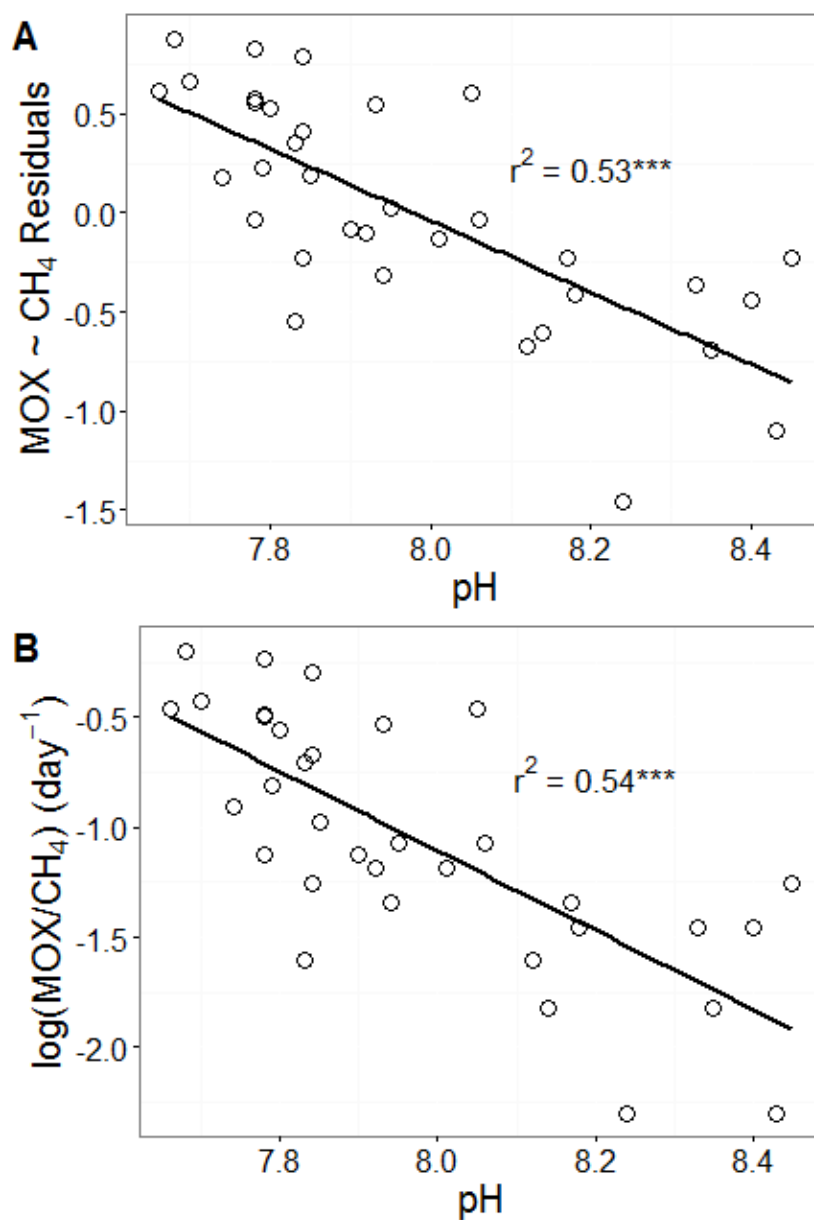


Figure 4-4. Regression of substrate corrected (normalized) CH₄ oxidation rates (MOX) against pH using measurements taken from 6 lakes throughout the summer 2014 and shortly after ice-out in 2015.

Residuals from the regression shown in Figure 3-2 are plotted against pH in panel (A). In panel (B), Normalized MOX values were obtained by dividing measured MOX by ambient CH₄. Half the smallest MOX measurement (0.005 mmol m⁻³ day⁻²) was added to all MOX measurements to allow log₁₀ transformation. Adjusted r^2 values are shown. *** $P < 0.001$.

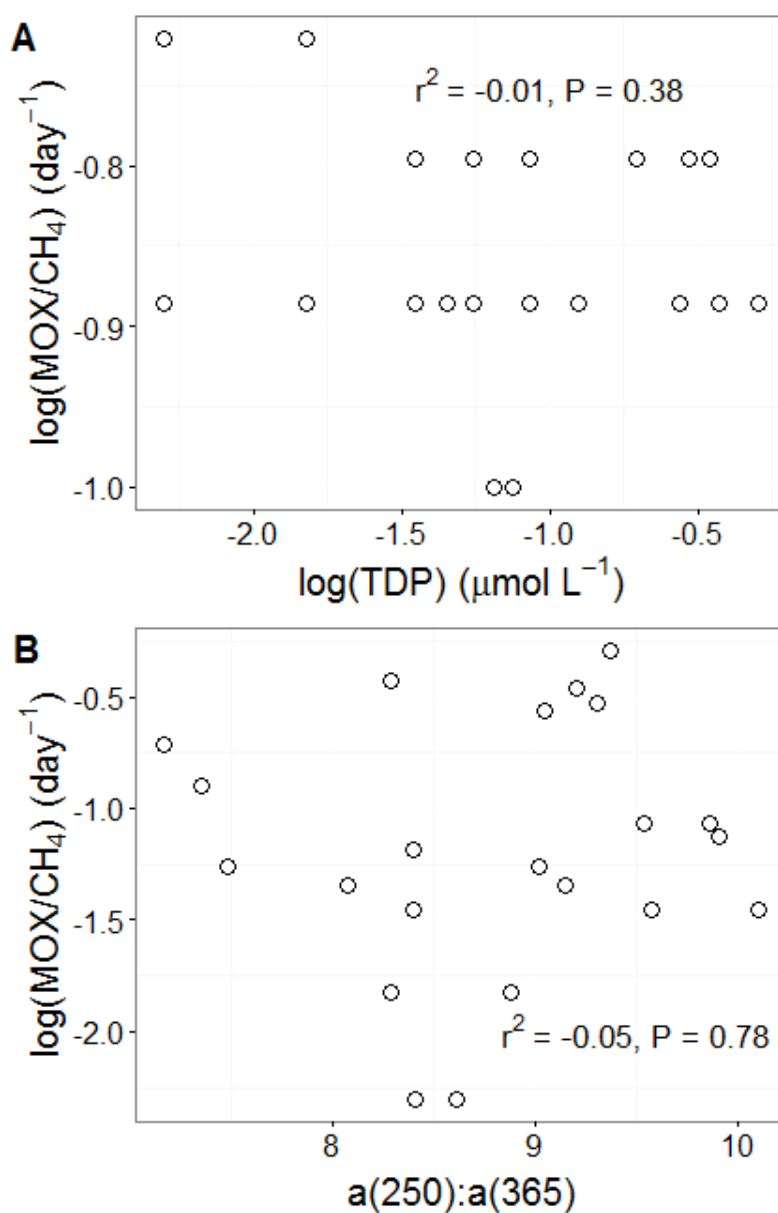


Figure 4-5. Regression of substrate corrected (Normalized) CH₄ oxidation (MOX) against TDP (A) and $a(250):a(365)$ (B).

Normalized MOX values were obtained by dividing measured MOX by ambient CH₄. Half the smallest MOX measurement ($0.005 \text{ mmol m}^{-3} \text{ day}^{-2}$) was added to all MOX measurements to allow $\log_{10}$ transformation. Adjusted r^2 values are shown. Increasing $a(250):a(365)$ indicates decreasing DOM molecular weight.

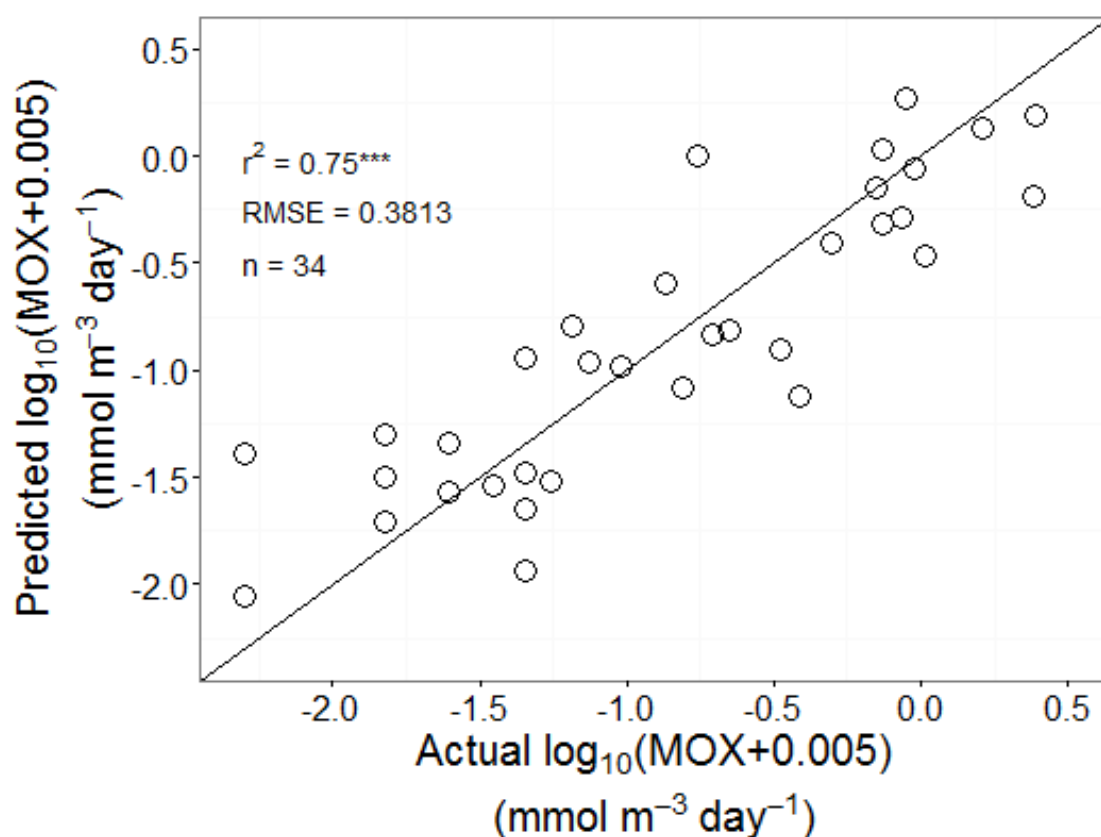


Figure 4-6. Multiple Regression of CH_4 oxidation (MOX) using pH and dissolved CH_4 and pH as predictor variables.

Half the smallest MOX measurement ($0.005 \text{ mmol m}^{-3} \text{ day}^{-2}$) was added to all Normalized MOX measurements to allow $\log_{10}$ transformation. Adjusted r^2 value is shown. Diagonal line is 1:1 line of predicted to actual measurements. Regression equation is:

$\log_{10}(\text{MOX}+0.005) = 0.8897 \cdot \log_{10}(\text{CH}_4) - 1.7742 \cdot \text{pH} + 13.1134$, where the slopes and intercept are all significant to $P < 0.001$.

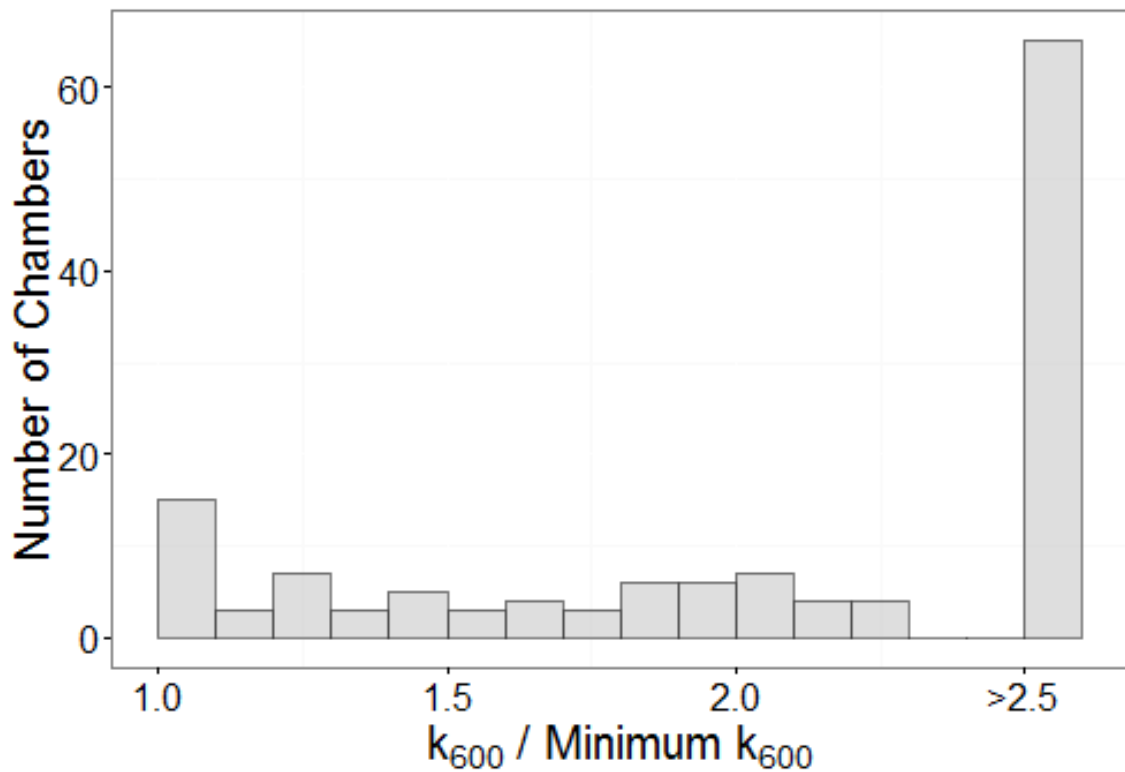


Figure 4-7. Distribution of $k_{600} / \text{Minimum } k_{600}$ ratios from each floating chamber (n=135).

k_{600} values are piston velocities normalized to Schmidt numbers of 600 for CO_2 , thus allowing for comparison of piston velocities of different gases at different temperatures. Minimum k_{600} is the minimum k_{600} measured by a chamber per lake during a measurement period, and $k_{600} / \text{minimum } k_{600}$ is the k_{600} of a chamber divided by the minimum k_{600} measured at the lake. The probability of a chamber receiving ebullition is 0.48 if excluding the 9 measurements on August 12, 2014 from L280 (excluded from Figure 4-6). Assuming all 9 chambers from L280 on August 12, 2014 received ebullition, the probability of a chamber receiving ebullition increases to 0.51.

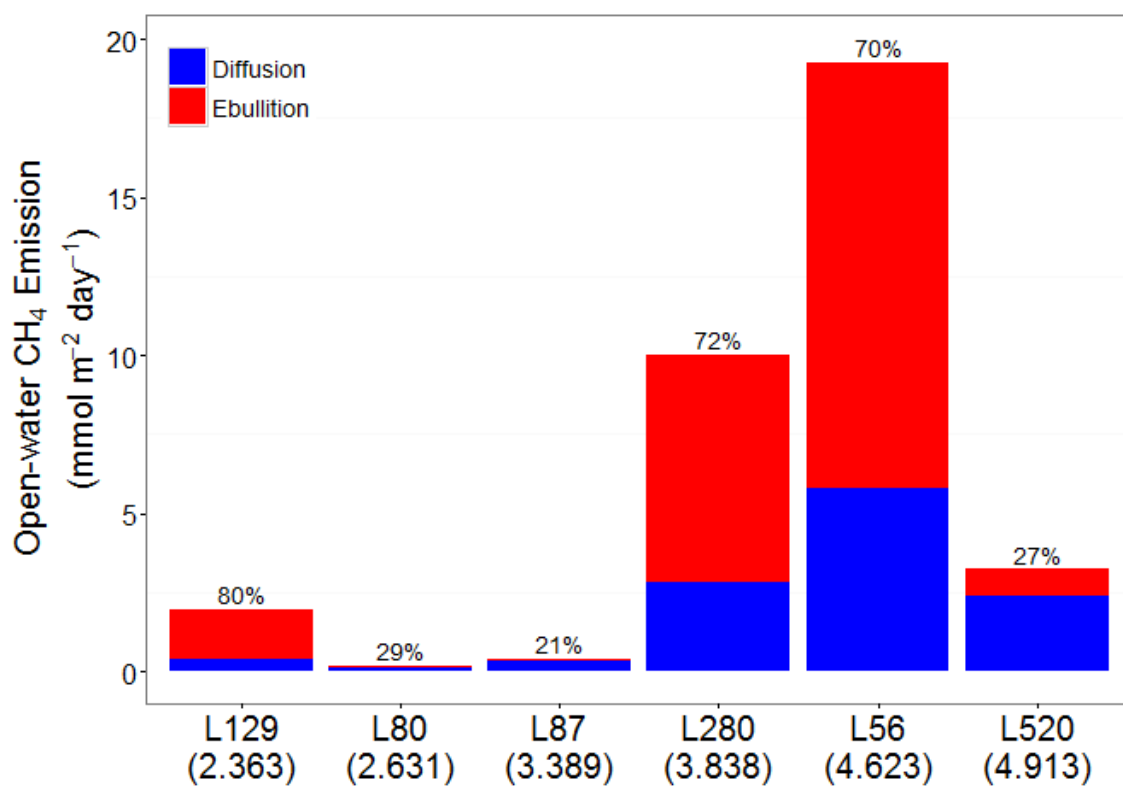


Figure 4-8. Diffusion, ebullition, and total CH₄ emission measured during 2015 in 6 Mackenzie Delta lakes.

Numbers in parentheses beneath lake numbers indicate spring sill elevation (masl). Numbers above bars indicate percentage of total flux being ebullition.

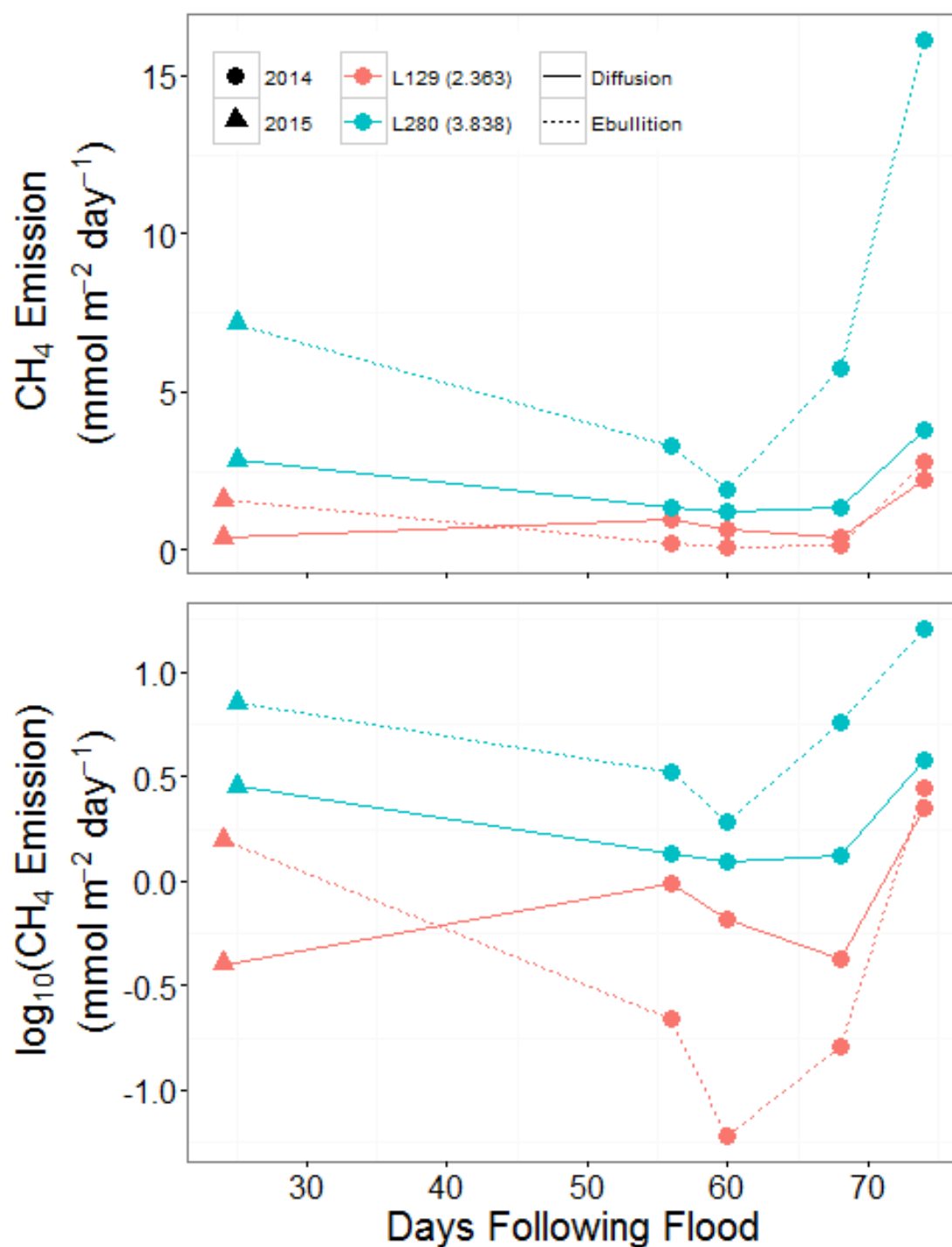


Figure 4-9. Time series of CH₄ emissions measured in 2 lakes in 2014 and 2015. Untransformed emissions are shown in the top panel, and log₁₀ transformations are shown in the bottom panel. Triangles indicate measurements from 2015, and circles indicate measurements from 2014. Dashed lines indicate ebullition, and non-dashed lines indicate diffusion. Days following flood approximates time since ice-out, which was assumed to occur on the day of peak water at East Channel.

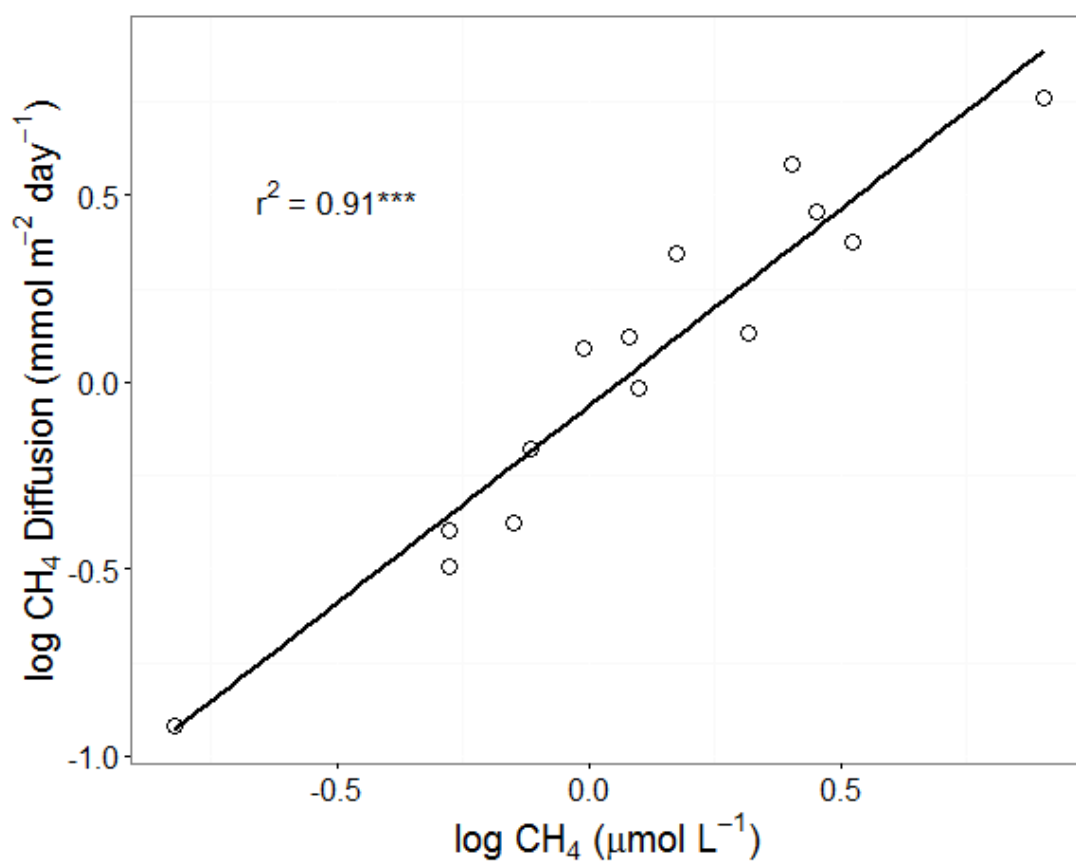


Figure 4-10. Diffusion measured with floating chambers in 2 lakes in 2014, and 6 lakes in 2015.

Measurements were obtained in 2014 (2 lakes were sampled 4 times each) and 2015 (6 lakes, including the 2 lakes from 2014, were sampled once). Adjusted r^2 is shown. *** $P < 0.001$.

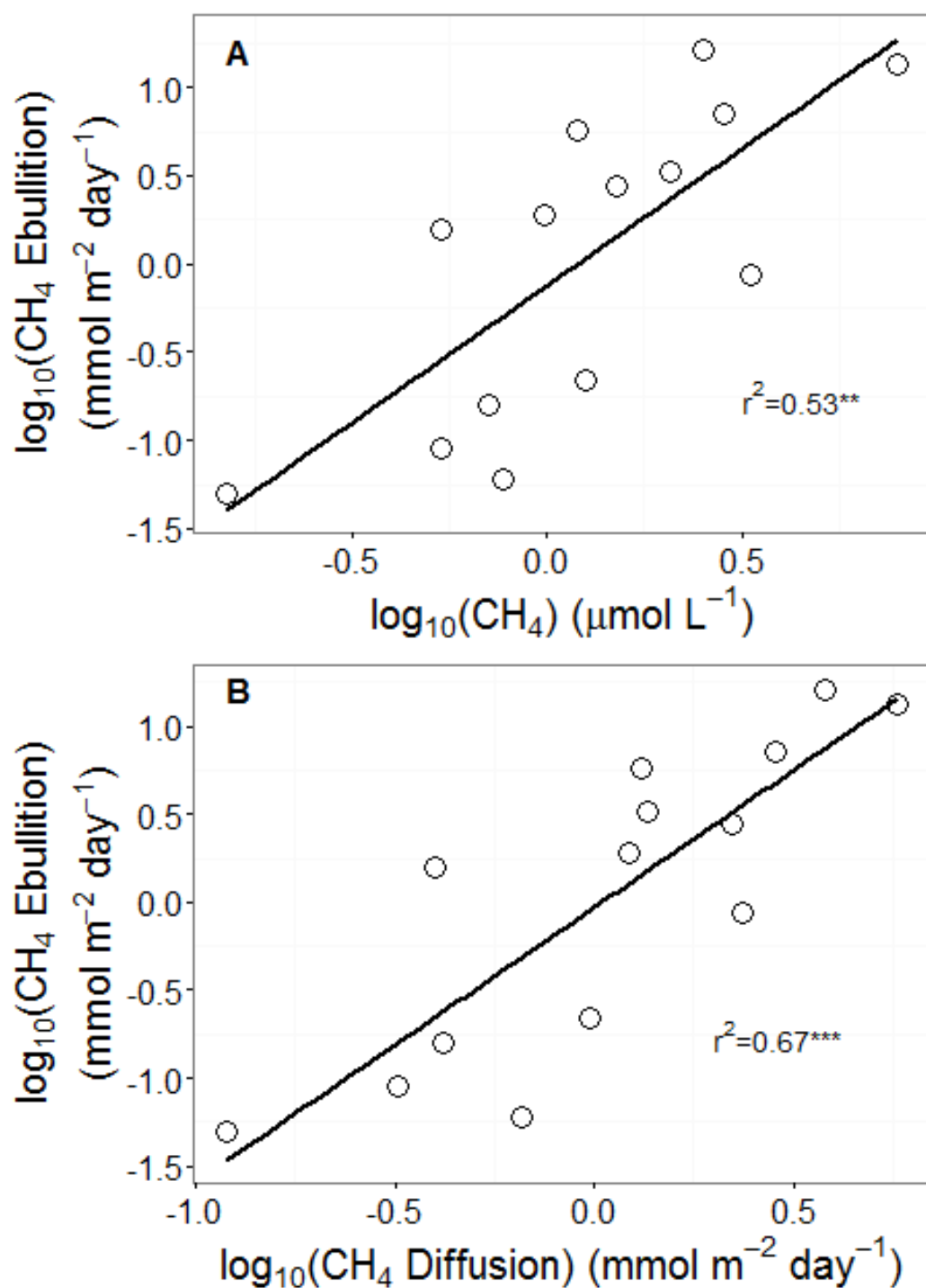


Figure 4-11. Ebullition measured with floating chambers in 2 lakes in 2014, and 6 lakes in 2015 plotted against dissolved CH_4 (A) and chamber-derived CH_4 diffusion.

Measurements were obtained in 2014 (2 lakes were sampled 4 times each) and 2015 (6 lakes, including the 2 lakes from 2014, were sampled once). Adjusted r^2 is shown. $^{**}P < 0.01$; $^{***}P < 0.001$.

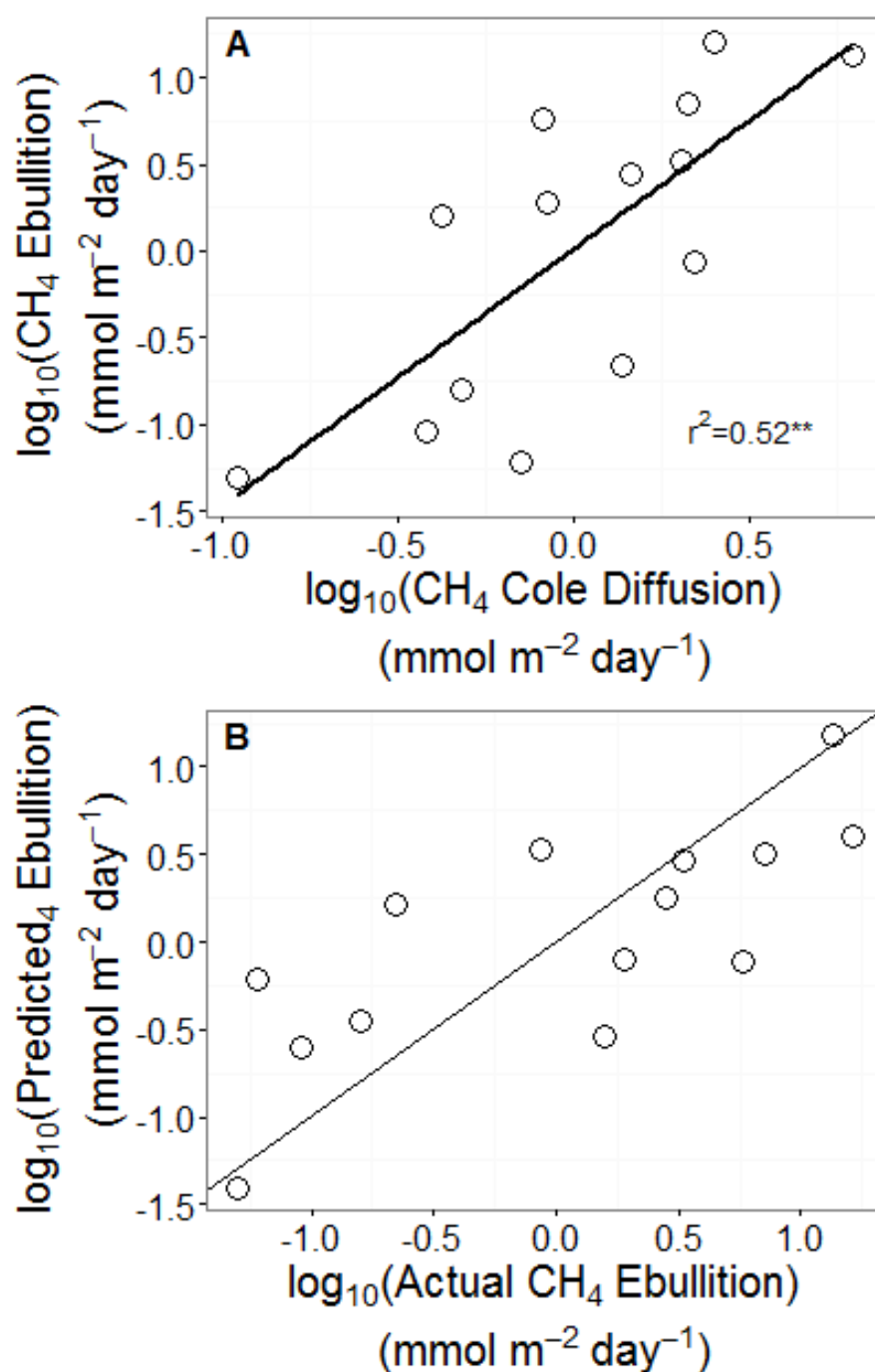


Figure 4-12. CH₄ ebullition regressed (A) from CH₄ diffusion, and model fit (B) of linear regression.

Ebullition measurements were obtained in 2014 (2 lakes were sampled 4 times each) and 2015 (6 lakes, including the 2 lakes from 2014, were sampled once). Diffusion measurements were determined using the Cole and Caraco (1998) method for calculating k_{600} . The equation used to calculate ebullition in subsequent analyses was:

$$\log_{10}(\text{Ebullition}) = 1.48146 \cdot \log_{10}(\text{Diffusion}) + 0.01725. \quad \text{Adjusted } r^2 \text{ is shown. } **P < 0.01.$$

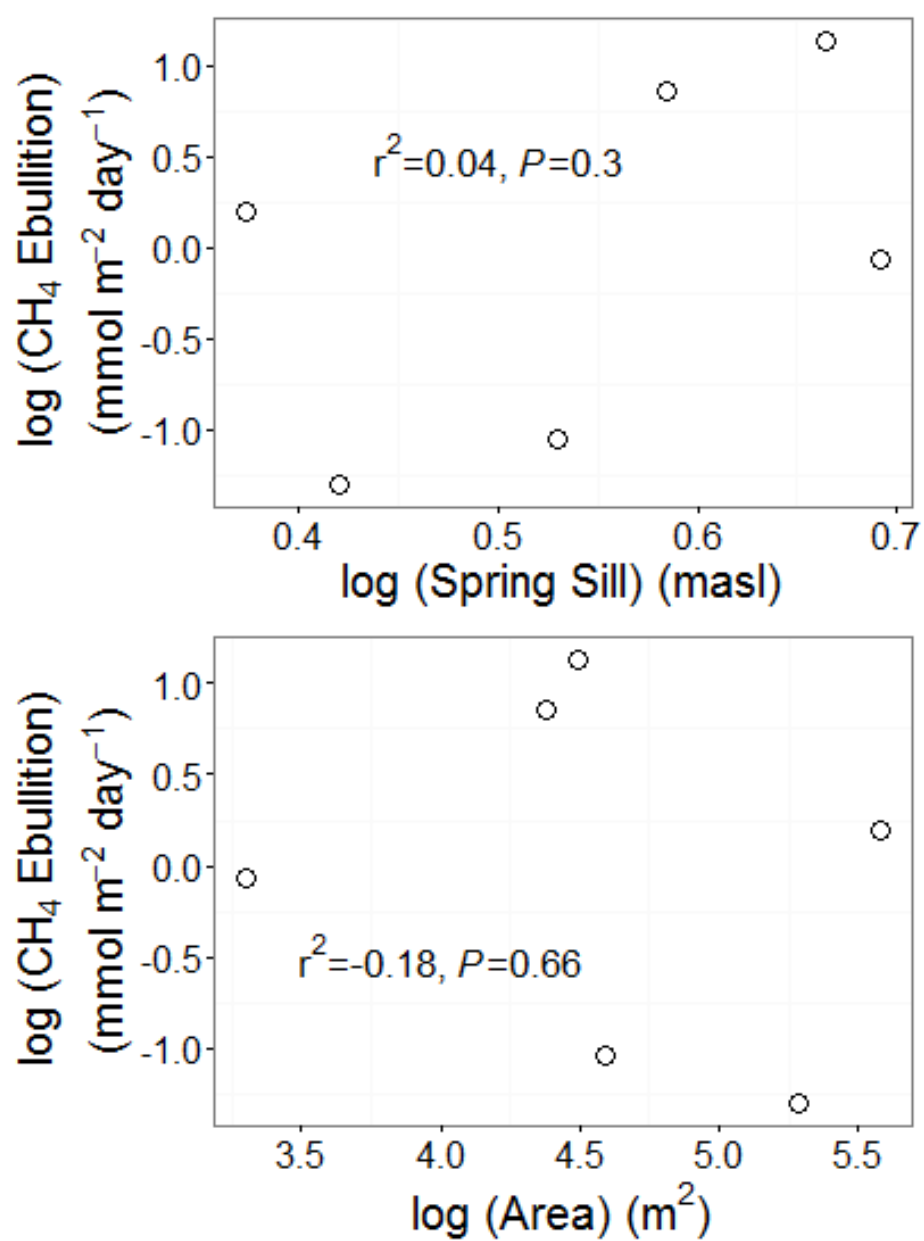


Figure 4-13. CH₄ Ebullition plotted against spring sill elevation (top) and lake Area (bottom).

Measurements were obtained in 2015 from 6 Mackenzie Delta lakes. Adjusted r^2 is shown.

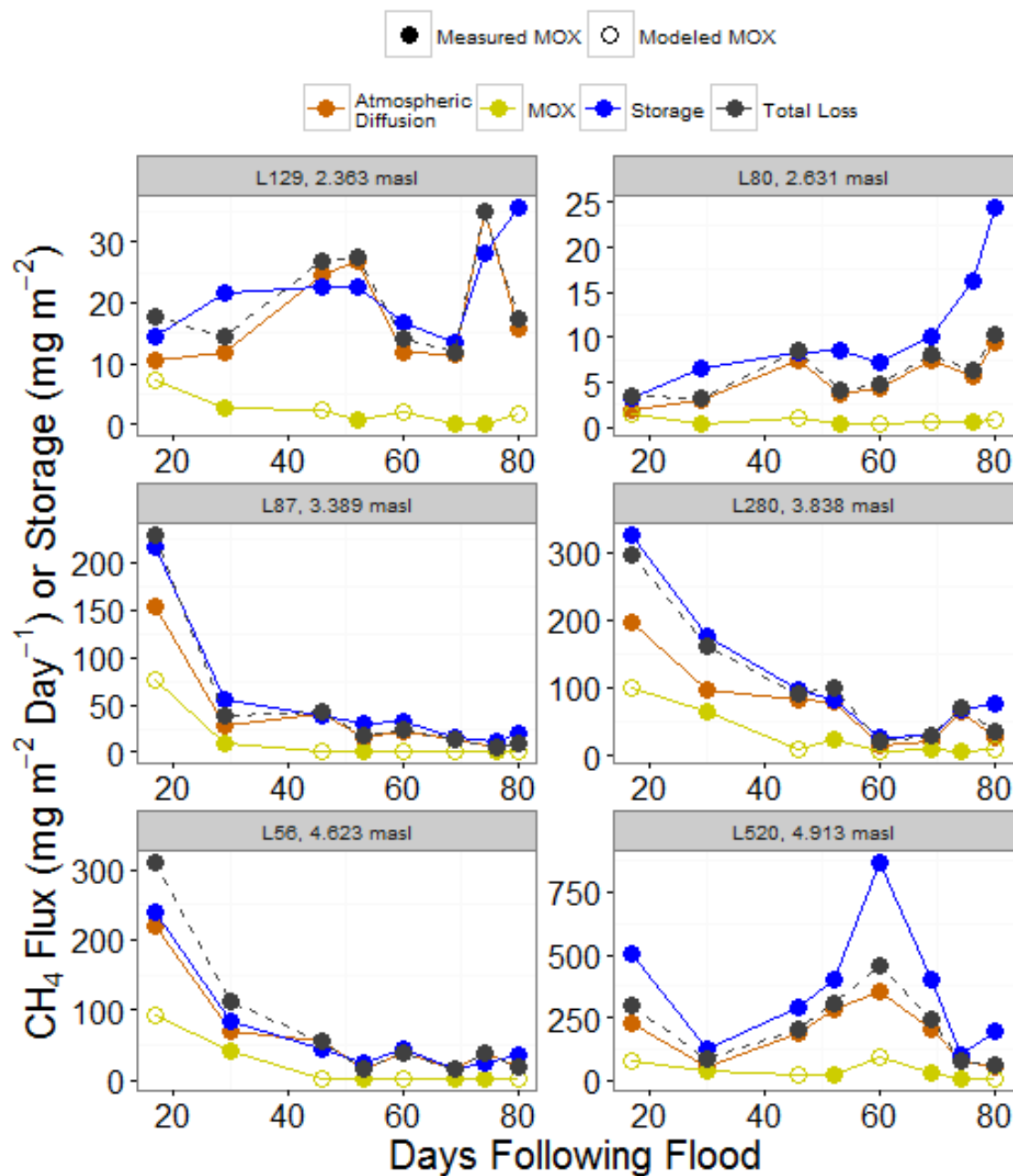


Figure 4-14. Mass balance of CH_4 fluxes, which include diffusion from the water column to the atmosphere and CH_4 oxidation (MOX), the sum of which accounts for total CH_4 lost from the lakes, and CH_4 water column storage of six Mackenzie Delta lakes in 2014.

Days following flood approximates time since ice-out, which was assumed to occur on the day of peak water at East Channel. Measured MOX indicates MOX rates actually measured, whereas Modeled MOX indicates values predicted from the model shown in Figure 4-6. CH_4 storage was determined by multiplying in situ CH_4 concentrations by mean water depth.

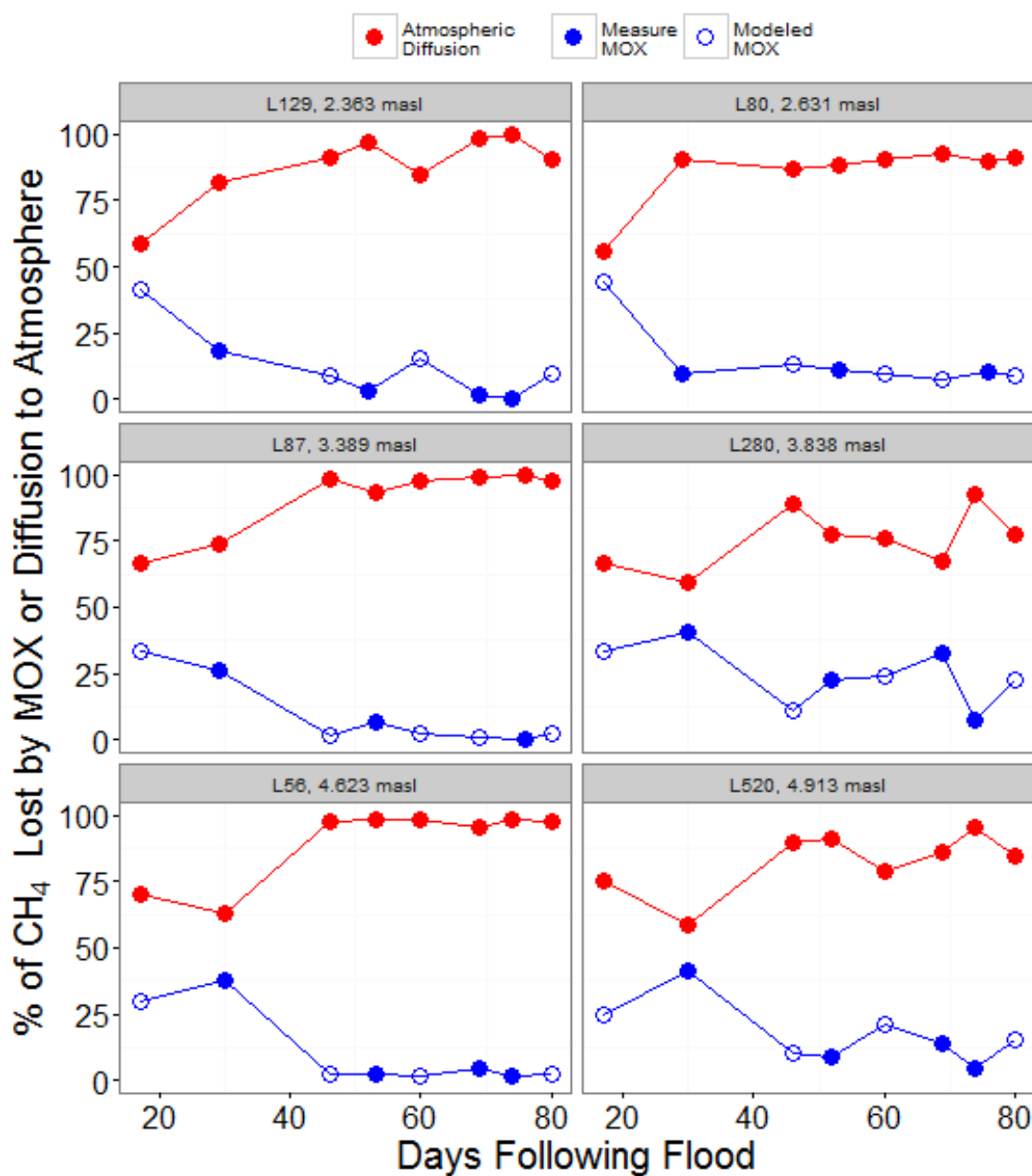


Figure 4-15. Percentage (%) of CH₄ lost from six Mackenzie Delta lakes due to CH₄ oxidation (MOX) or diffusion to the atmosphere.

Days following flood approximates time since ice-out, which was assumed to occur on the day of peak water at East Channel. Measured MOX indicates MOX rates actually measured, whereas Modeled MOX indicates values predicted from the model shown in Figure 4-6.

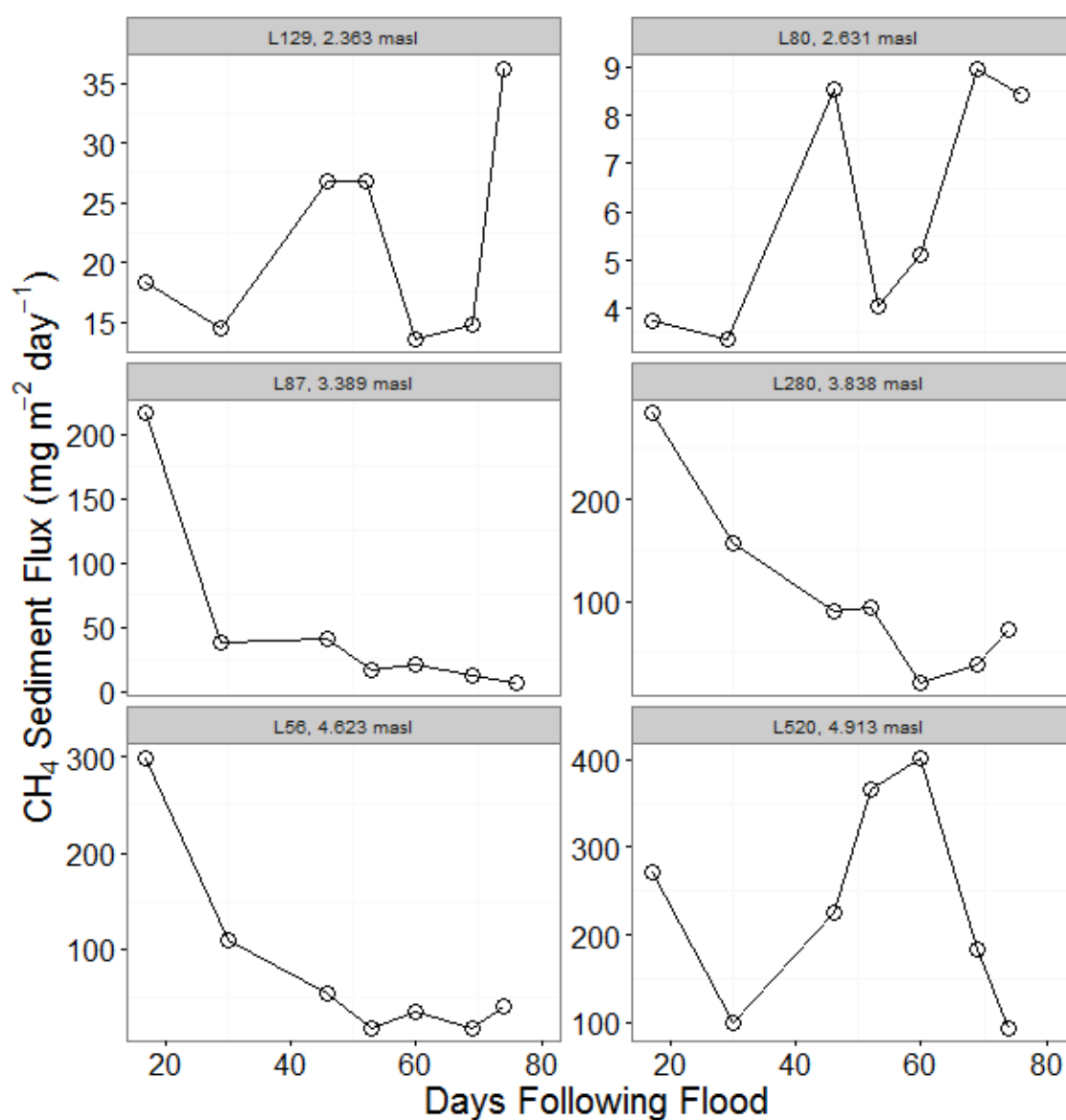


Figure 4-16. CH₄ diffusing into the water column from the sediment (i.e., sediment flux) in six Mackenzie Delta lakes.

Days following flood approximates time since ice-out, which was assumed to occur on the day of peak water at East Channel.

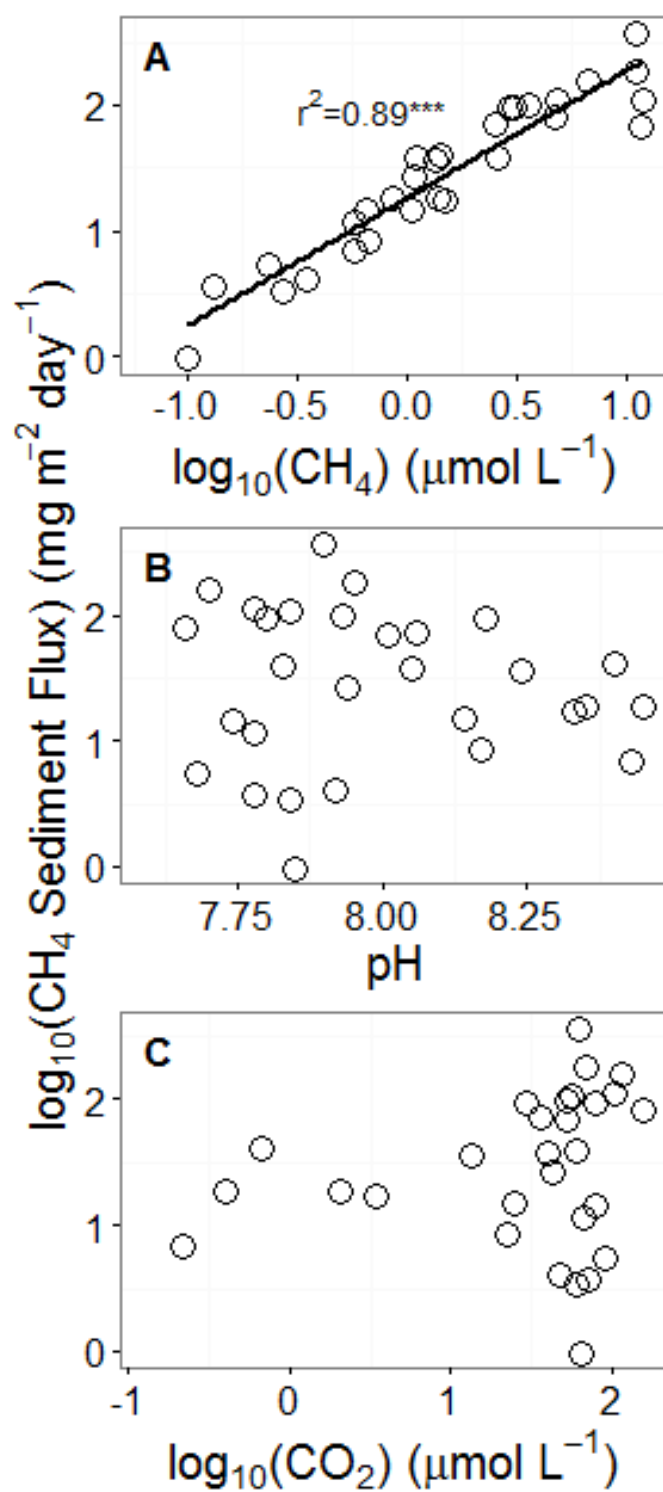


Figure 4-17. CH_4 diffusing into the water column from the sediment (i.e., sediment flux) regressed against dissolved CH_4 (A), pH (B), and dissolved CO_2 (C).

Adjusted r^2 value is reported. *** $P < 0.001$.

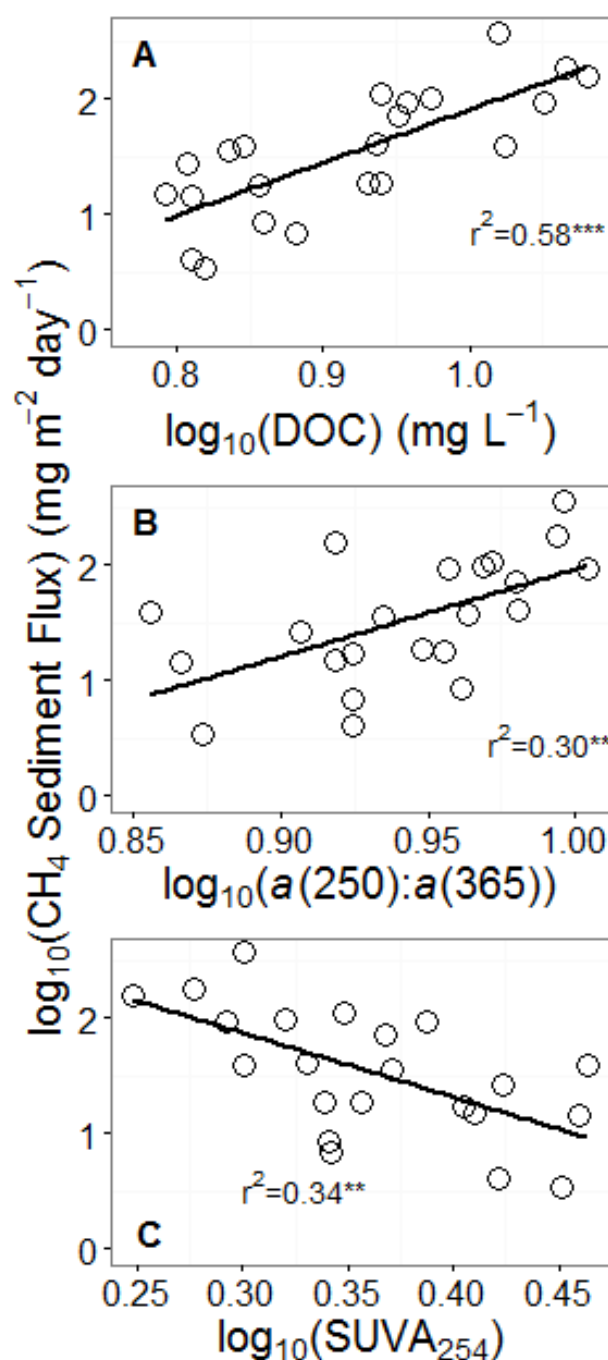


Figure 4-18. CH_4 diffusing into the water column from the sediment (i.e., sediment flux) regressed against DOC (A), dissolved organic matter DOM molecular weight, and DOM aromaticity (C).

Sediment diffusion is the flux of CH_4 from the sediment into the water column. DOC describes DOM quantity. $a(250):a(365)$ and SUVA_{254} are proxies for DOM quality, where increasing $a(250):a(365)$ indicates decreasing DOM molecular weight, and increasing SUVA_{254} indicates increasing DOM aromaticity. Measurements were obtained from 6 lakes throughout 2014. Adjusted r^2 values are reported. $^{**} P < 0.01$; $^{***} P < 0.001$.

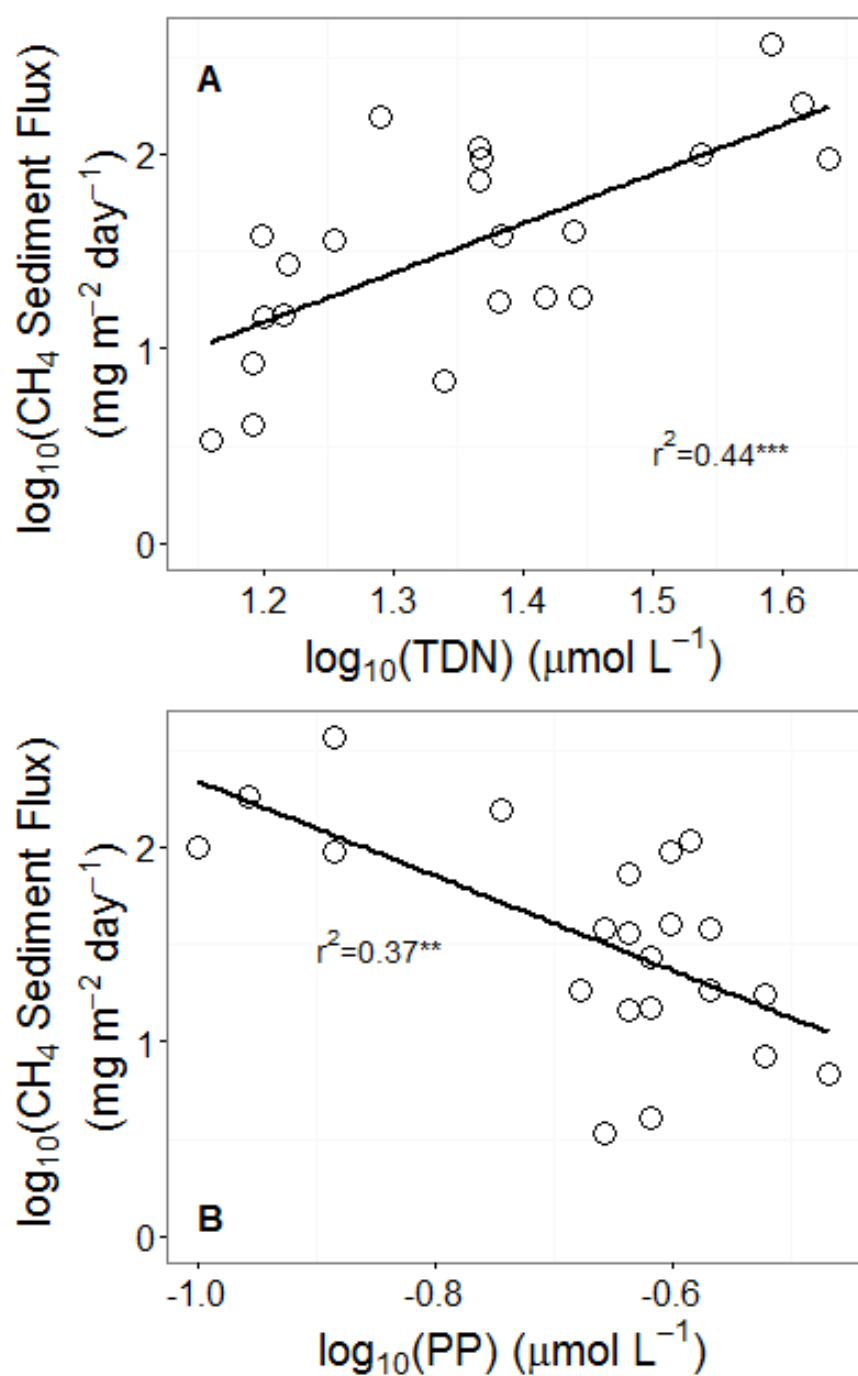


Figure 4-19. CH_4 diffusing into the water column from the sediment (i.e., sediment flux) regressed against TDN (A) and PP (B).

Sediment diffusion is the flux of CH_4 from the sediment into the water column. Measurements were obtained from 6 lakes throughout 2014. Adjusted r^2 values are reported. $^{**} P < 0.01$; $^{***} P < 0.001$.

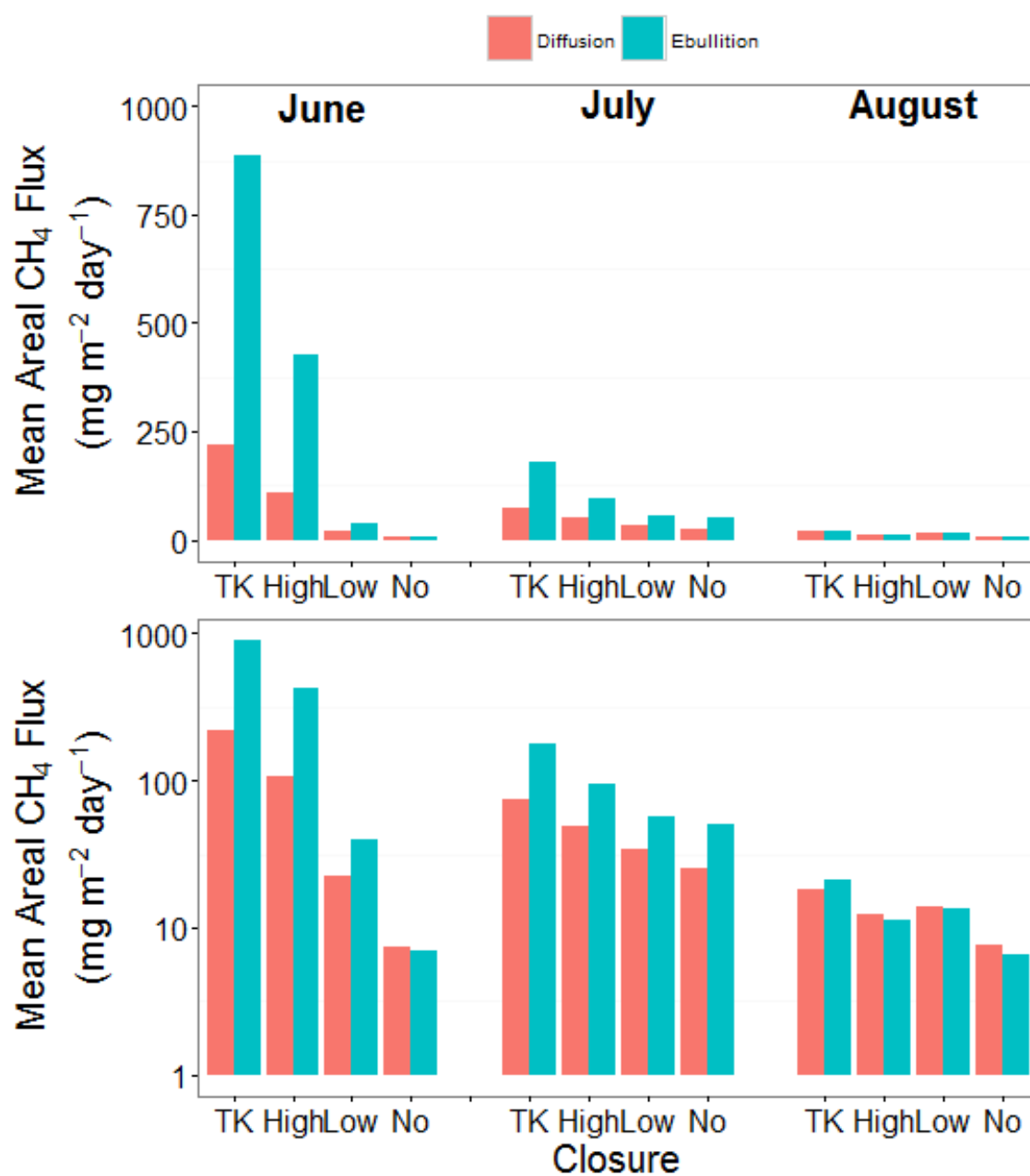


Figure 4-20. Areal-weighted mean CH₄ diffusion and ebullition from thermokarst (TK) and high, low, and no closure lakes based on data collected during June, July, and August surveys of 43 lakes in 2014, where the top panel shows fluxes on non-transformed scale, and bottom panel shows fluxes on log-transformed scale.

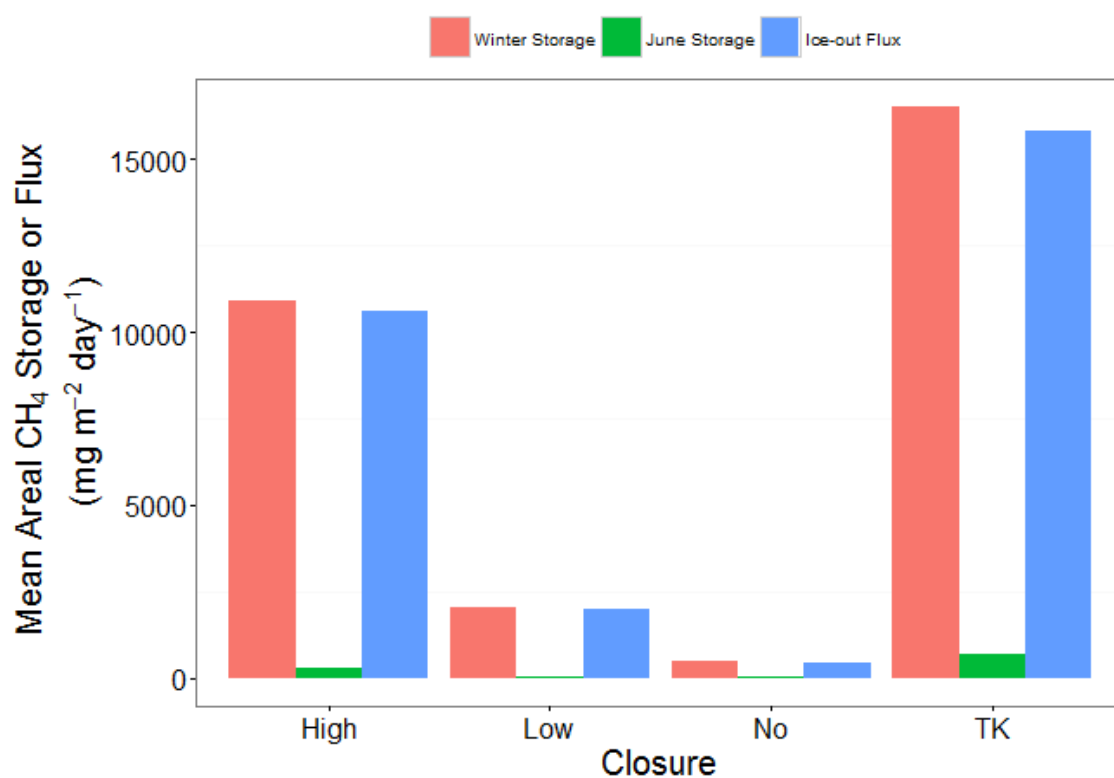


Figure 4-21. Areal-weighted CH₄ storage and ice-out fluxes in thermokarst (TK) and, high, low, and no closure lakes estimated from 29 lakes sampled during 2014.

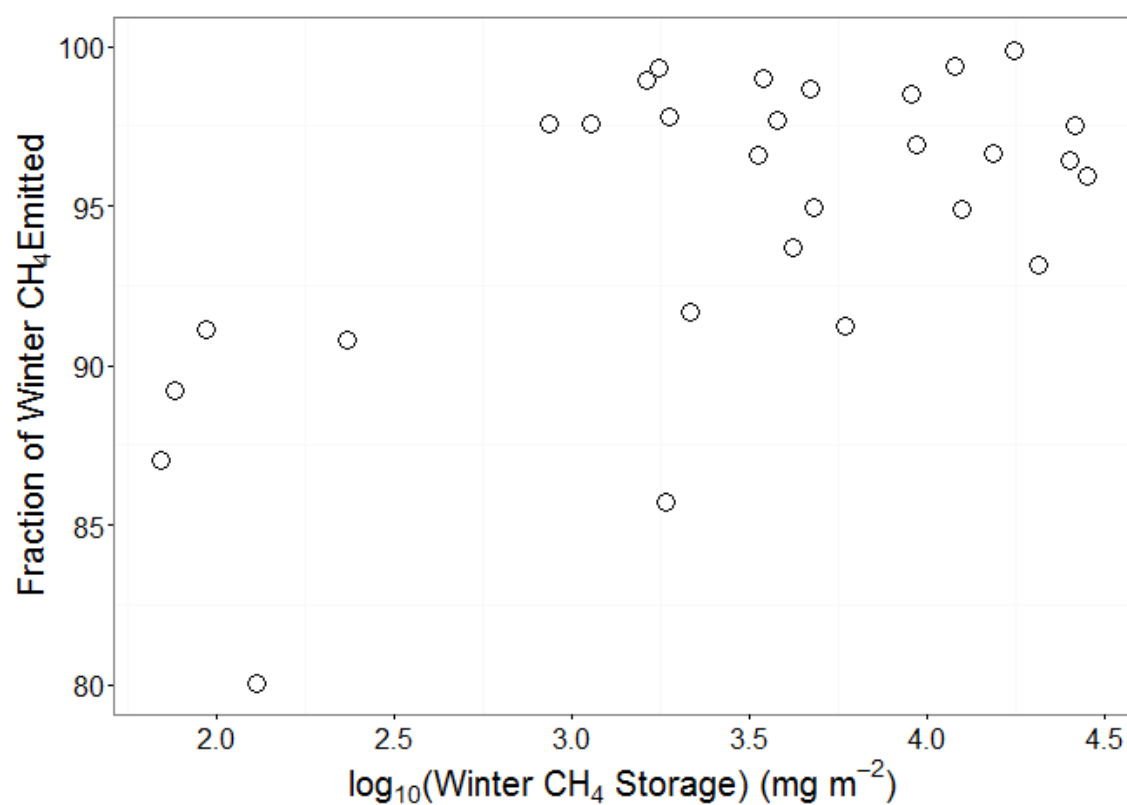


Figure 4-22. Fraction of winter CH₄ storage emitted at ice-out estimated for 29 lakes sampled during 2014.

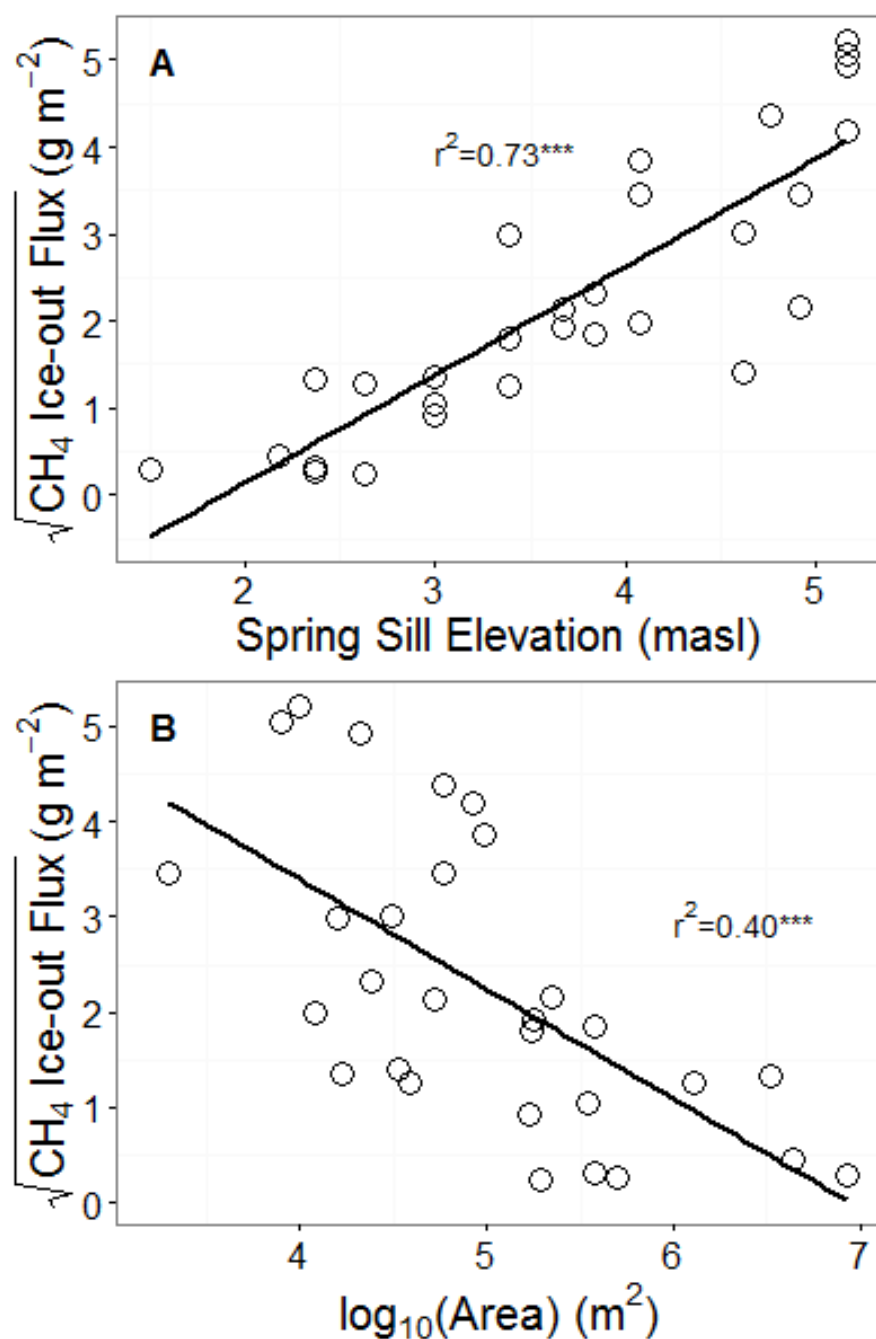


Figure 4-23. CH₄ ice-out flux in lakes of varying elevation (A) and area (B). Ice-out flux is the difference in mass of CH₄ prior to ice-out and approximately two weeks following ice melt, thus not accounting for potential MOX. Adjusted r^2 values are reported. *** $P < 0.001$.

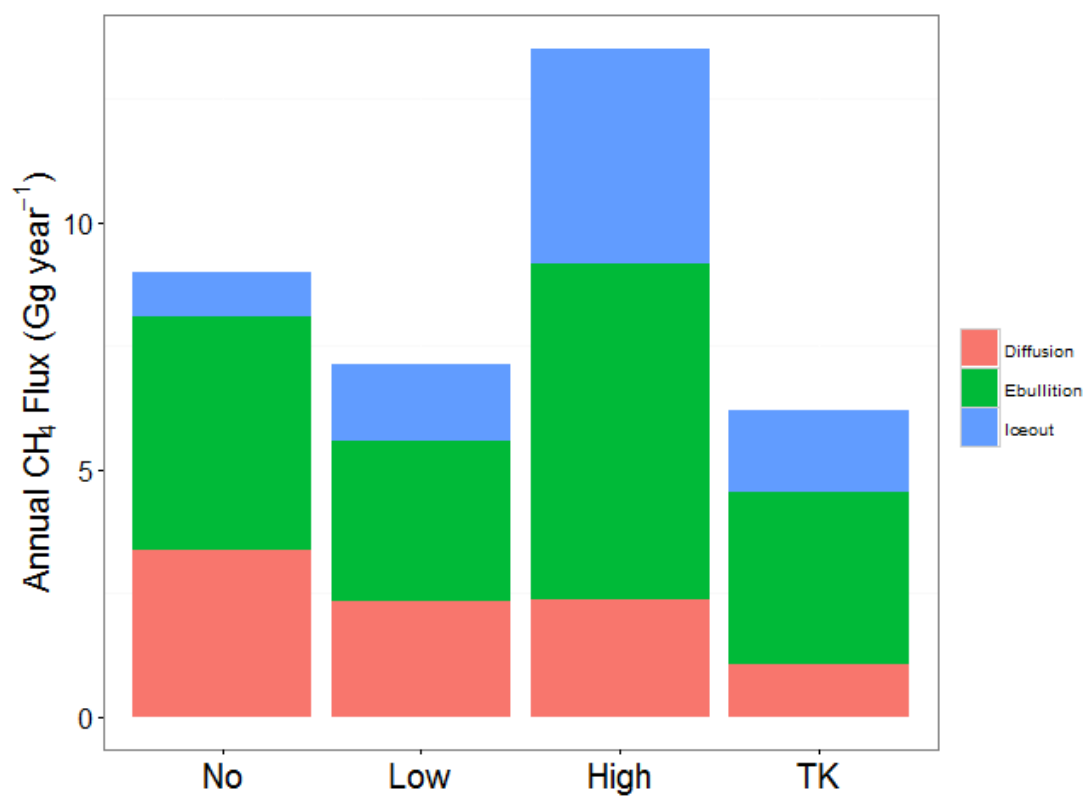


Figure 4-24. Extrapolated annual fluxes of CH₄, separated into diffusion, ebullition, and ice-out, in thermokarst (TK) and high, low, and no closure lakes.

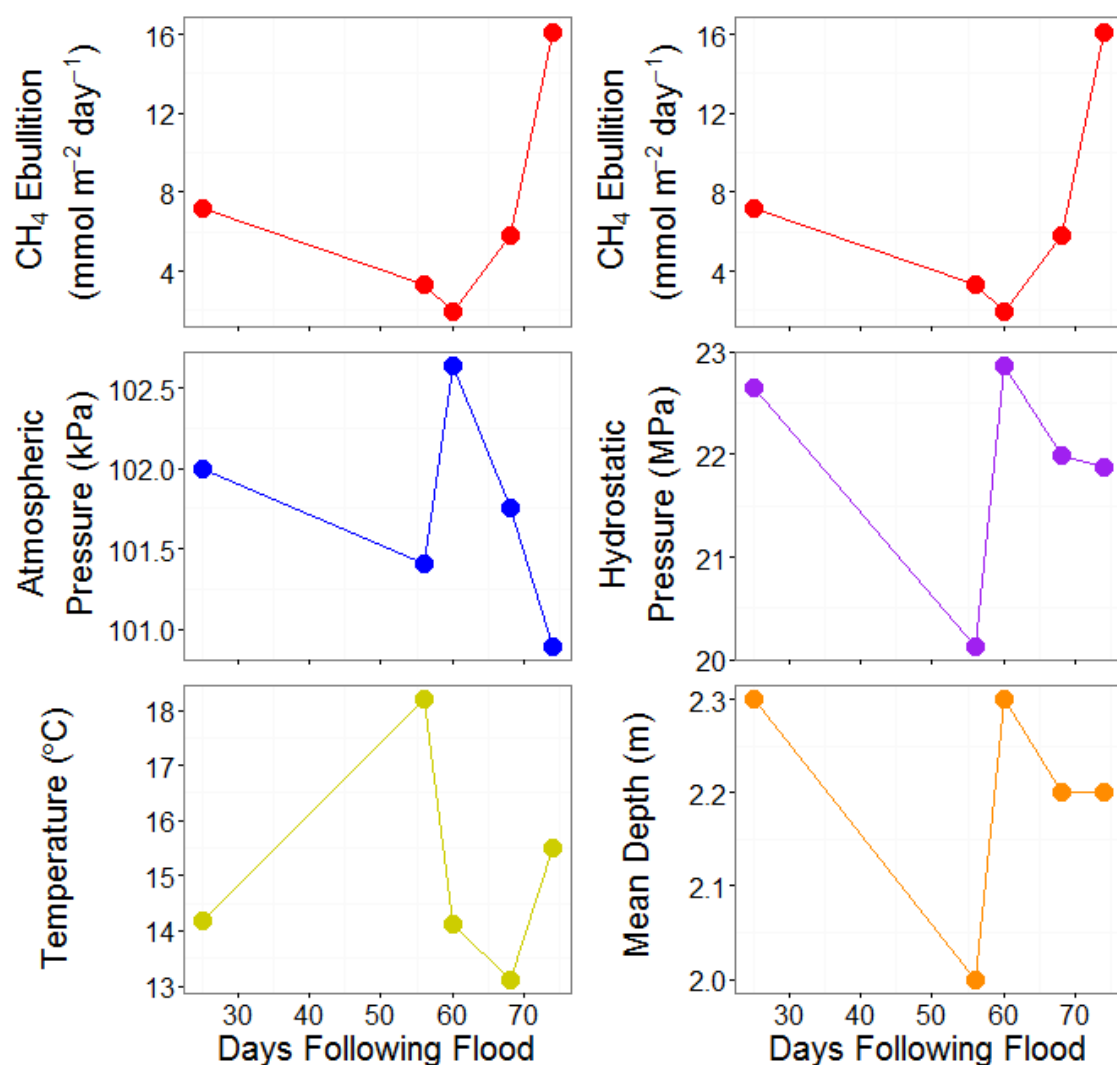


Figure 4-25. CH₄ ebullition, atmospheric pressure, temperature, hydrostatic pressure, and mean depth during 2014 at Lake 280.

Days following flood approximates time since ice-out, which was assumed to occur on the day of peak water at East Channel. CH₄ ebullition was plotted in both columns to facilitate comparison. Hydrostatic pressure was determined as: $p_h = (\rho gh + p_{atm}) * 1000$, where p_h is hydrostatic pressure (kPa), ρ is the density of water (calculated as per Eq. 11, kg m⁻³), g is gravitational acceleration (9.81 m s⁻²), h is the mean depth of the lake (determined from depths at floating chamber location, m), p_{atm} is atmospheric pressure (kPa), and 1000 is to convert to units of MPa.

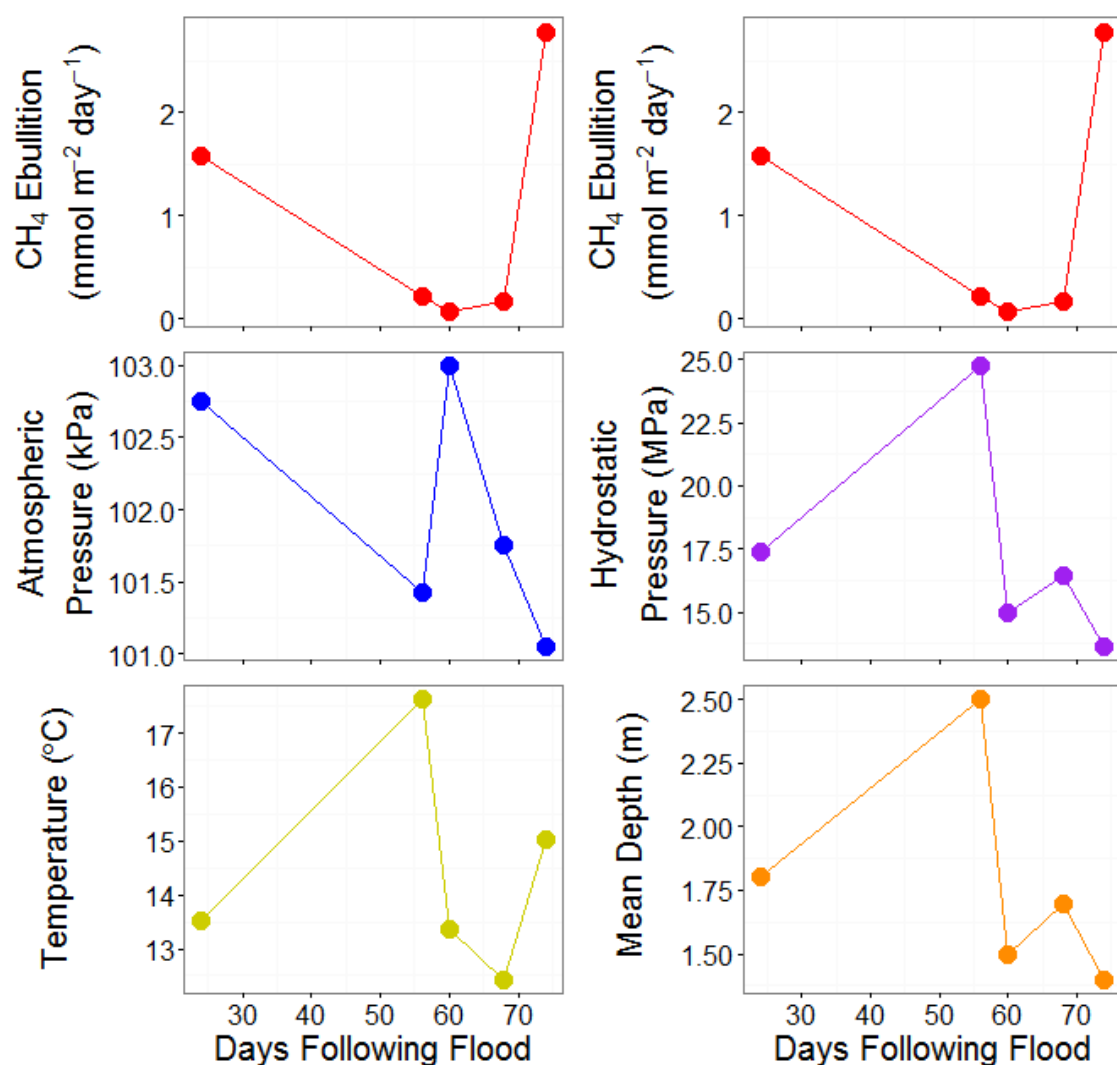


Figure 4-26. CH₄ ebullition, atmospheric pressure, temperature, hydrostatic pressure, and mean depth during 2014 at Lake 129.

Days following flood approximates time since ice-out, which was assumed to occur on the day of peak water at East Channel. CH₄ ebullition was plotted in both columns to facilitate comparison. Hydrostatic pressure was determined as described in the previous figure.

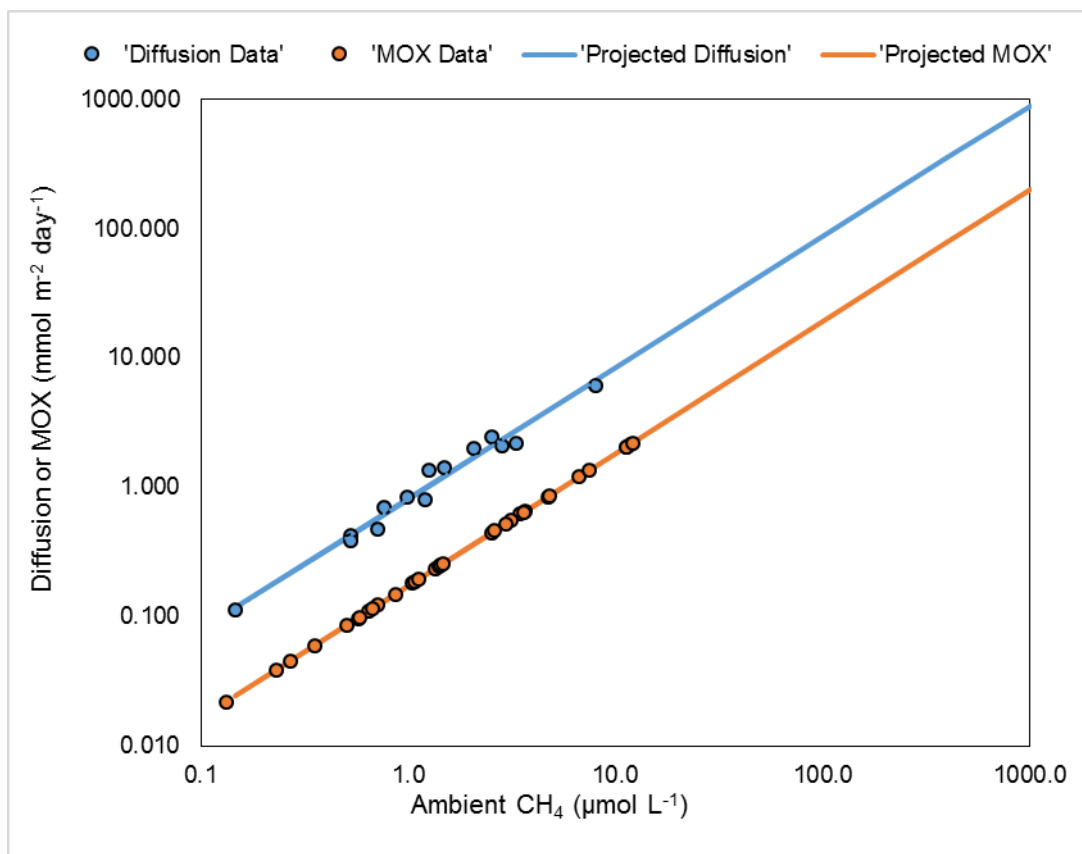


Figure 4-27. Projection of CH₄ oxidation (MOX) and diffusion to the atmosphere at ice-out relative to ambient dissolved CH₄.

'Diffusion Data' were measured using the Cole and Caraco (1998) model for determining k , and show the relationship between diffusion and ambient CH₄, which was used to determine 'Projected Diffusion'. Similarly, 'Projected MOX' was determined using the relationship between MOX and ambient CH₄ (see Figure 4-3). The data points on the lines are intended to simply mark the range of ambient CH₄ concentrations from which the projections were based, and do not include all the original data. Note both y and x axes have been log₁₀ transformed.

Chapter 5.

Thesis Summary

Chapter 2

Under-ice dissolved CH₄ was measured at the end of winter during May 2014 in 29 Mackenzie Delta lakes over a range of river connectivity and limnological characteristics known from prior work. Although CH₄ levels are trending upwards in low closure lakes, current CH₄ levels are not statistically different from levels measured 20 years ago. CH₄ levels increased along the sill elevation gradient, showed a strong, positive relationship with DOM (i.e., substrate) quantity, DIC, and pH, and were highest in lakes that are strong late summer CO₂ absorbers. CH₄ levels increased with DOM molecular weight, which suggests that a significant portion of the low molecular weight DOM is highly microbially active and converted to CH₄, thus resulting in the accumulation of less labile, higher molecular weight DOM over the winter.

Chapter 3

Dissolved CH₄ was measured during 3 surveys of 43 lakes in June, July, and August 2014, and in a subset of 6 lakes on a weekly basis in between the 43 lake surveys. In intermediate and higher elevation lakes, CH₄ was generally highest in June and decreased over the summer. CH₄ in no closure lakes generally increased throughout the open-water period. Although CH₄ levels in thermokarst-affected lakes were higher than other lakes throughout the summer, we did not find statistically significant differences in CH₄ levels between thermokarst-affected and lakes of comparable closure classes. We hypothesized that increases in dissolved CH₄ levels would correspond with decreases in dissolved CO₂ due to high macrophyte production in late summer (i.e., lakes that are CO₂ sinks would be sources of CH₄), however, no statistical relationship was found. DOM quantity and quality were positively and strongly related to CH₄ during early and mid-summer, but were weakly related in late summer. Overall, late summer dissolved CH₄ was not explained well by any lake water variable we measured. This suggests that the importance of MOX and CH₄ ebullition must increase throughout the open-water period.

Chapter 4

Every 1-2 weeks during open-water conditions in 2014 (June through August), water column MOX rates were measured in 6 lakes, and CH₄ emission rates (measured

with floating chambers) were tracked in a subset of 2 lakes. Water column MOX and CH₄ emission rates were measured again in June 2015 in a subset of 6 lakes. Water column MOX was highest after ice-out, and decreased throughout the open-water period. After correcting for ambient CH₄ (i.e., substrate) we unexpectedly found that pH has a significant negative relationship with MOX. pH increases throughout the open-water period in Mackenzie Delta lakes, corresponding with high rates of macrophyte production, and can reach levels over a pH of 10. Since water-column MOX is minor throughout the open-water period, the lack of inter-lake variation in late summer dissolved CH₄ could be the result of MOX at the sediment-water interface. Diffusion of CH₄ from sediments into the water columns of Mackenzie Delta lakes is significantly impacted by DOM quantity and quality, and TDN and PP. Considering they are poorly associated with water column MOX, these variables could be associated with sediment methanogenesis.

CH₄ emissions are seasonally variable in Mackenzie Delta lakes. Diffusion and ebullition were closely related to CH₄ levels, but CH₄ ebullition appears to be more variable and is likely highly sensitive to relatively abrupt changes in water levels and meteorological conditions. The chamber method resulted in CH₄ diffusion rates consistent with wind-based models that used averaged wind speeds from the Inuvik Airport. However, future studies would benefit from the use of “bubble traps” rather than floating chambers due to high rates of ebullition experienced on a number of occasions. Mackenzie Delta lakes emit 35.79 Gg of CH₄ to the atmosphere, where 24% is emitted at ice-out, 50% by ebullition, and 26% via open-water diffusion.

Significance of Research

The significance of our findings is threefold. Our results have for the first time quantified how lakes in Arctic deltas that are more isolated from river inflows are typically sinks for CO₂, and that the lakes absorbing the most CO₂ tend to be greater sources of CH₄ to the atmosphere. High carbon-quality, as determined by the within-lake mix of carbon from in situ photosynthesis and allochthonous DOM, appear to be more important than thermokarst in affecting the balance between CH₄ and CO₂ yields to the atmosphere in Arctic deltas. Secondly, our results suggest the importance of considering CH₄ not only as a greenhouse gas, but also as an alternative fuel for food webs in Arctic delta lakes.

Our results provide the first estimates of MOX rates within water-columns of such study systems, which is an important step in linking CH₄ to higher trophic levels. We also documented the novel finding that increasing pH, as a function of high photosynthetic rates, has a negative effect on MOX. Thirdly, our results suggest the potential importance of DOM photolysis for affecting carbon-quality and fueling methanogenic communities. As photolysis increases DOM lability over the open-water period, in combination with DOM release from senescing macrophytes, late summer DOM may consequently serve as a labile microbial substrate at the onset of winter, effectively fueling methanogenesis throughout the ice-covered period. Melting of permafrost in thermokarst lakes of the Arctic deltas may enhance their CH₄ levels, however, further work is needed to assess the effects of climate change on CH₄ cycling in Arctic delta lakes more generally.

Appendix A.

Correlation Matrices

Table A1. Correlation Matrix (Pearson's r) of Box-Cox Transformed Variables from Winter 2014 Survey.

	CH ₄	CO ₂	DOC	DIC	pH	CDO M	A _{ratio}	SUV A	TSS	HCO ₃ ⁻	CO ₃ ²⁻	OM	Mac	Chlorop	Temp	S.Cond	Salinity	Area	Sill	Snow	Ice	Depth
CH ₄	1	0.88	0.72	0.68	-0.78	0.81	-0.61	-0.12	0.69	0.56	-0.32	0.46	0.64	0.56	-0.23	0.19	0.18	-0.55	0.70	-0.06	-0.50	0.04
CO ₂	0.88	1	0.83	0.83	-0.82	0.86	-0.53	-0.16	0.70	0.73	-0.26	0.21	0.51	0.45	-0.17	0.29	0.26	-0.42	0.62	0.08	-0.42	0.05
DOC	0.72	0.83	1	0.84	-0.57	0.75	-0.26	-0.50	0.58	0.78	-0.01	0.14	0.34	0.44	0.00	0.34	0.30	-0.54	0.63	0.06	-0.41	0.34
DIC	0.68	0.83	0.84	1	-0.40	0.69	-0.30	-0.33	0.50	0.98	0.27	0.18	0.30	0.30	-0.08	0.17	0.13	-0.26	0.35	0.26	-0.24	0.05
pH	-0.78	-0.82	-0.57	-0.40	1	-0.75	0.62	-0.01	-0.67	-0.23	0.76	-0.20	-0.64	-0.40	0.24	-0.38	-0.36	0.43	-0.64	0.09	0.43	-0.02
CDOM	0.81	0.86	0.75	0.69	-0.75	1	-0.79	0.10	0.54	0.58	-0.29	0.11	0.44	0.41	-0.14	0.10	0.08	-0.40	0.62	-0.09	-0.49	0.14
A _{ratio}	-0.61	-0.53	-0.26	-0.30	0.62	-0.79	1	-0.39	-0.35	-0.16	0.45	0.00	-0.42	-0.14	0.21	0.10	0.09	0.14	-0.36	0.16	0.32	0.15
SUVA	-0.12	-0.16	-0.50	-0.33	-0.01	0.10	-0.39	1	-0.25	-0.32	-0.20	-0.01	0.05	0.02	-0.12	-0.39	-0.37	0.22	-0.09	-0.20	-0.04	-0.21
TSS	0.69	0.70	0.58	0.50	-0.67	0.54	-0.35	-0.25	1	0.38	-0.35	0.23	0.40	0.39	-0.26	0.35	0.32	-0.32	0.56	-0.09	-0.38	0.08
HCO ₃ ⁻	0.56	0.73	0.78	0.98	-0.23	0.58	-0.16	-0.32	0.38	1	0.44	0.15	0.19	0.25	-0.01	0.10	0.06	-0.21	0.27	0.28	-0.20	0.07
CO ₃ ²⁻	-0.32	-0.26	-0.01	0.27	0.76	-0.29	0.45	-0.20	-0.35	0.44	1	-0.09	-0.61	-0.18	0.28	-0.34	-0.35	0.23	-0.36	0.22	0.23	0.09
OM	0.46	0.21	0.14	0.18	-0.20	0.11	0.00	-0.01	0.23	0.15	-0.09	1	0.71	0.62	-0.02	-0.14	-0.12	-0.49	0.45	-0.25	-0.31	0.15
Mac	0.64	0.51	0.34	0.30	-0.64	0.44	-0.42	0.05	0.40	0.19	-0.61	0.71	1	0.50	-0.44	0.10	0.10	0.03	0.42	0.00	-0.08	-0.15
Chlorop	0.56	0.45	0.44	0.30	-0.40	0.41	-0.14	0.02	0.39	0.25	-0.18	0.62	0.50	1	-0.25	0.09	0.07	-0.36	0.44	-0.34	-0.37	-0.01
Temp	-0.23	-0.17	0.00	-0.08	0.24	-0.14	0.21	-0.12	-0.26	-0.01	0.28	-0.02	-0.44	-0.25	1	-0.26	-0.22	-0.25	0.23	-0.17	-0.21	0.52
S.Cond	0.19	0.29	0.34	0.17	-0.38	0.10	0.10	-0.39	0.35	0.10	-0.34	-0.14	0.10	0.09	-0.26	1	0.99	-0.09	0.10	0.07	0.11	0.00
Salinity	0.18	0.26	0.30	0.13	-0.36	0.08	0.09	-0.37	0.32	0.06	-0.35	-0.12	0.10	0.07	-0.22	0.99	1	-0.13	0.13	0.04	0.09	0.04
Area	-0.55	-0.42	-0.54	-0.26	0.43	-0.40	0.14	0.22	-0.32	-0.21	0.23	-0.49	0.03	-0.36	-0.25	-0.09	-0.13	1	-0.78	0.16	0.62	-0.42
Sill	0.70	0.62	0.63	0.35	-0.64	0.62	-0.36	-0.09	0.56	0.27	-0.36	0.45	0.42	0.44	0.23	0.10	0.13	-0.78	1	-0.25	-0.66	0.52
Snow	-0.06	0.08	0.06	0.26	0.09	-0.09	0.16	-0.20	-0.09	0.28	0.22	-0.25	0.00	-0.34	-0.17	0.07	0.04	0.16	-0.25	1	0.21	-0.28
Ice	-0.50	-0.42	-0.41	-0.24	0.43	-0.49	0.32	-0.04	-0.38	-0.20	0.23	-0.31	-0.08	-0.37	-0.21	0.11	0.09	0.62	-0.66	0.21	1	-0.28
Depth	0.04	0.05	0.34	0.05	-0.02	0.14	0.15	-0.21	0.08	0.07	0.09	0.15	-0.15	-0.01	0.52	0.00	0.04	-0.42	0.52	-0.28	-0.28	1

CDOM: water colour, measured as $a(350)$; A_{ratio}: $a(250):a(265)$; OM: sediment organic matter content; Mac: submerged macrophyte density; Chlorop: chlorophyll a concentration; Temp: water temperature; S.Cond: specific conductivity; Snow: depth of snow overlying lake ice; Ice: ice thickness; Depth: depth of unfrozen water. Note: all outliers included.

Table A2. P-values for Table A1 (Winter 2014) Correlation Coefficients (bold indicates significant at $\alpha = 0.05$).

	CH ₄	CO ₂	DOC	DIC	pH	CDO M	A _{ratio}	SUV A	TSS	HCO ₃ ⁻	CO ₃ ²⁻	OM	Mac	Chlo rop	Tem p	S.Co nd	Sali nity	Area	Sill	Sno w	Ice	Dept h
CH ₄		0.00	0.00	0.00	0.00	0.00	0.00	0.54	0.00	0.00	0.09	0.09	0.01	0.00	0.23	0.33	0.35	0.00	0.00	0.77	0.01	0.84
CO ₂	0.00		0.00	0.00	0.00	0.00	0.00	0.41	0.00	0.00	0.18	0.45	0.05	0.01	0.37	0.13	0.18	0.02	0.00	0.68	0.02	0.79
DOC	0.00	0.00		0.00	0.00	0.00	0.18	0.01	0.00	0.00	0.97	0.63	0.21	0.02	1.00	0.08	0.11	0.00	0.00	0.76	0.03	0.07
DIC	0.00	0.00	0.00		0.03	0.00	0.12	0.08	0.01	0.00	0.16	0.53	0.27	0.11	0.66	0.38	0.51	0.17	0.07	0.18	0.22	0.81
pH	0.00	0.00	0.00	0.03		0.00	0.00	0.95	0.00	0.22	0.00	0.47	0.01	0.03	0.22	0.04	0.05	0.02	0.00	0.65	0.02	0.94
CDOM	0.00	0.00	0.00	0.00	0.00		0.00	0.61	0.00	0.00	0.13	0.69	0.10	0.03	0.47	0.62	0.69	0.03	0.00	0.66	0.01	0.48
A _{ratio}	0.00	0.00	0.18	0.12	0.00	0.00		0.04	0.06	0.40	0.01	1.00	0.12	0.48	0.28	0.62	0.63	0.48	0.06	0.40	0.09	0.44
SUVA	0.54	0.41	0.01	0.08	0.95	0.61	0.04		0.18	0.09	0.29	0.98	0.87	0.90	0.53	0.03	0.05	0.25	0.64	0.31	0.84	0.27
TSS	0.00	0.00	0.00	0.01	0.00	0.00	0.06	0.18		0.04	0.06	0.40	0.14	0.04	0.17	0.06	0.09	0.09	0.00	0.63	0.04	0.69
HCO ₃ ⁻	0.00	0.00	0.00	0.00	0.22	0.00	0.40	0.09	0.04		0.02	0.60	0.49	0.19	0.95	0.61	0.77	0.27	0.16	0.14	0.31	0.70
CO ₃ ²⁻	0.09	0.18	0.97	0.16	0.00	0.13	0.01	0.29	0.06	0.02		0.76	0.02	0.34	0.14	0.07	0.06	0.23	0.06	0.25	0.23	0.65
OM	0.09	0.45	0.63	0.53	0.47	0.69	1.00	0.98	0.40	0.60	0.76		0.01	0.01	0.94	0.61	0.67	0.07	0.09	0.37	0.27	0.60
Mac	0.01	0.05	0.21	0.27	0.01	0.10	0.12	0.87	0.14	0.49	0.02	0.01		0.06	0.10	0.71	0.73	0.91	0.12	0.99	0.77	0.60
Chlorop	0.00	0.01	0.02	0.11	0.03	0.03	0.48	0.90	0.04	0.19	0.34	0.01	0.06		0.19	0.63	0.73	0.06	0.02	0.07	0.05	0.94
Temp	0.23	0.37	1.00	0.66	0.22	0.47	0.28	0.53	0.17	0.95	0.14	0.94	0.10	0.19		0.17	0.26	0.19	0.24	0.38	0.27	0.00
S.Cond	0.33	0.13	0.08	0.38	0.04	0.62	0.62	0.03	0.06	0.61	0.07	0.61	0.71	0.63	0.17		0.00	0.62	0.60	0.74	0.56	0.99
Salinity	0.35	0.18	0.11	0.51	0.05	0.69	0.63	0.05	0.09	0.77	0.06	0.67	0.73	0.73	0.26	0.00		0.51	0.51	0.83	0.65	0.84
Area	0.00	0.02	0.00	0.17	0.02	0.03	0.48	0.25	0.09	0.27	0.23	0.07	0.91	0.06	0.19	0.62	0.51		0.00	0.39	0.00	0.02
Sill	0.00	0.00	0.00	0.07	0.00	0.00	0.06	0.64	0.00	0.16	0.06	0.09	0.12	0.02	0.24	0.60	0.51	0.00		0.19	0.00	0.00
Snow	0.77	0.68	0.76	0.18	0.65	0.66	0.40	0.31	0.63	0.14	0.25	0.37	0.99	0.07	0.38	0.74	0.83	0.39	0.19		0.27	0.14
Ice	0.01	0.02	0.03	0.22	0.02	0.01	0.09	0.84	0.04	0.31	0.23	0.27	0.77	0.05	0.27	0.56	0.65	0.00	0.00	0.27		0.14
Depth	0.84	0.79	0.07	0.81	0.94	0.48	0.44	0.27	0.69	0.70	0.65	0.60	0.60	0.94	0.00	0.99	0.84	0.02	0.00	0.14	0.14	

CDOM: water colour, measured as $a(350)$; A_{ratio}: $a(250):a(265)$; OM: sediment organic matter content; Mac: submerged macrophyte density; Chlorop: chlorophyll a concentration; Temp: water temperature; S.Cond: specific conductivity; Snow: depth of snow overlying lake ice; Ice: ice thickness; Depth: depth of unfrozen water. Note: all outliers included.

Table A3. Correlation Matrix (Pearson's r) of Box-Cox Transformed Variables from Early Summer 2014 Survey.

	pCH ₄	pCO ₂	DIC	pH	CDOM	A _{ratio}	SUVA	Area	Sill	Con	DOC	Temp	Depth	Chl
pCH ₄	1	0.47	0.55	-0.19	-0.07	0.55	-0.35	-0.72	0.71	-0.65	0.51	0.64	-0.28	-0.20
pCO ₂	0.47	1	0.60	-0.85	0.34	0.03	-0.02	-0.28	0.13	-0.09	0.42	0.13	-0.34	0.34
DIC	0.55	0.60	1	-0.09	-0.01	0.51	-0.41	-0.48	0.40	-0.39	0.58	0.59	-0.48	0.02
pH	-0.19	-0.85	-0.09	1	-0.44	0.31	-0.26	0.01	0.12	-0.16	-0.13	0.27	0.11	-0.44
CDOM	-0.07	0.34	-0.01	-0.44	1	-0.64	0.48	0.11	-0.27	0.23	0.38	-0.24	-0.18	0.29
A _{ratio}	0.55	0.03	0.51	0.31	-0.64	1	-0.55	-0.58	0.65	-0.64	0.29	0.60	-0.07	-0.27
SUVA	-0.35	-0.02	-0.41	-0.26	0.48	-0.55	1	0.32	-0.32	0.28	-0.51	-0.47	0.29	0.29
Area	-0.72	-0.28	-0.48	0.01	0.11	-0.58	0.32	1	-0.72	0.70	-0.48	-0.59	0.11	0.12
Sill	0.71	0.13	0.40	0.12	-0.27	0.65	-0.32	-0.72	1	-0.97	0.33	0.60	-0.05	-0.16
Con	-0.65	-0.09	-0.39	-0.16	0.23	-0.64	0.28	0.70	-0.97	1	-0.34	-0.56	0.00	0.12
DOC	0.51	0.42	0.58	-0.13	0.38	0.29	-0.51	-0.48	0.33	-0.34	1	0.47	-0.50	-0.06
Temp	0.64	0.13	0.59	0.27	-0.24	0.60	-0.47	-0.59	0.60	-0.56	0.47	1	-0.33	-0.56
Depth	-0.28	-0.34	-0.48	0.11	-0.18	-0.07	0.29	0.11	-0.05	0.00	-0.50	-0.33	1	0.08
Chl	-0.20	0.34	0.02	-0.44	0.29	-0.27	0.29	0.12	-0.16	0.12	-0.06	-0.56	0.08	1

Note: all outliers included

A_{ratio}: a(250):a(365)

Con: 2014 connection time

Temp: lake temperature

Chl: Chlorophyll a

Table A4. *P-values* for Table A3 (early summer 2014) Correlation Coefficients (bold indicates significance at $\alpha = 0.05$).

	pCH ₄	pCO ₂	DIC	pH	CDOM	A _{ratio}	SUVA	Area	Sill	Con	DOC	Temp	Depth	Chl
pCH ₄		0.00	0.00	0.27	0.67	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.09	0.24
pCO ₂	0.00		0.00	0.00	0.04	0.85	0.91	0.09	0.44	0.61	0.01	0.47	0.04	0.04
DIC	0.00	0.00		0.61	0.95	0.00	0.01	0.00	0.02	0.02	0.00	0.00	0.00	0.91
pH	0.27	0.00	0.61		0.01	0.07	0.13	0.94	0.49	0.34	0.45	0.11	0.53	0.01
CDOM	0.67	0.04	0.95	0.01		0.00	0.00	0.51	0.12	0.19	0.02	0.16	0.29	0.08
A _{ratio}	0.00	0.85	0.00	0.07	0.00		0.00	0.00	0.00	0.00	0.09	0.00	0.69	0.12
SUVA	0.04	0.91	0.01	0.13	0.00	0.00		0.06	0.06	0.10	0.00	0.00	0.08	0.08
Area	0.00	0.09	0.00	0.94	0.51	0.00	0.06		0.00	0.00	0.00	0.00	0.54	0.48
Sill	0.00	0.44	0.02	0.49	0.12	0.00	0.06	0.00		0.00	0.05	0.00	0.79	0.35
Con	0.00	0.61	0.02	0.34	0.19	0.00	0.10	0.00	0.00		0.04	0.00	0.99	0.48
DOC	0.00	0.01	0.00	0.45	0.02	0.09	0.00	0.00	0.05	0.04		0.00	0.00	0.73
Temp	0.00	0.47	0.00	0.11	0.16	0.00	0.00	0.00	0.00	0.00	0.00		0.05	0.00
Depth	0.09	0.04	0.00	0.53	0.29	0.69	0.08	0.54	0.79	0.99	0.00	0.05		0.62
Chl	0.24	0.04	0.91	0.01	0.08	0.12	0.08	0.48	0.35	0.48	0.73	0.00	0.62	

Note: all outliers included

A_{ratio}: a(250):a(365)

Con: 2014 connection time

Temp: lake temperature

Chl: Chlorophyll a

Table A5. Correlation Matrix (Pearson's r) of Box-Cox Transformed Variables from Mid-summer 2014 Survey

	pCH ₄	pCO ₂	DIC	pH	CDOM	A _{ratio}	SUVA	Area	Sill	Con	DOC	Temp	Depth	Chl
pCH ₄	1	0.02	0.19	-0.02	0.53	0.45	-0.45	-0.61	0.59	-0.58	0.79	0.36	-0.21	-0.21
pCO ₂	0.02	1	0.78	-0.93	0.02	0.02	0.20	0.13	-0.19	0.12	-0.10	-0.13	0.32	0.46
DIC	0.19	0.78	1	-0.66	0.13	0.16	-0.13	-0.16	-0.10	0.04	0.19	0.03	0.18	0.46
pH	-0.02	-0.93	-0.66	1	0.00	-0.03	-0.17	-0.16	0.10	-0.05	0.08	0.13	-0.28	-0.45
CDOM	0.53	0.02	0.13	0.00	1	-0.17	0.13	-0.35	0.30	-0.31	0.75	0.21	-0.48	0.01
A _{ratio}	0.45	0.02	0.16	-0.03	-0.17	1	-0.54	-0.41	0.49	-0.43	0.39	0.31	0.31	-0.15
SUVA	-0.45	0.20	-0.13	-0.17	0.13	-0.54	1	0.47	-0.40	0.38	-0.52	-0.22	0.02	0.32
Area	-0.61	0.13	-0.16	-0.16	-0.35	-0.41	0.47	1	-0.69	0.67	-0.65	-0.70	-0.01	0.29
Sill	0.59	-0.19	-0.10	0.10	0.30	0.49	-0.40	-0.69	1	-0.97	0.59	0.63	0.04	-0.43
Con	-0.58	0.12	0.04	-0.05	-0.31	-0.43	0.38	0.67	-0.97	1	-0.57	-0.59	-0.06	0.38
DOC	0.79	-0.10	0.19	0.08	0.75	0.39	-0.52	-0.65	0.59	-0.57	1	0.37	-0.33	-0.20
Temp	0.36	-0.13	0.03	0.13	0.21	0.31	-0.22	-0.70	0.63	-0.59	0.37	1	0.21	-0.35
Depth	-0.21	0.32	0.18	-0.28	-0.48	0.31	0.02	-0.01	0.04	-0.06	-0.33	0.21	1	0.11
Chl	-0.21	0.46	0.46	-0.45	0.01	-0.15	0.32	0.29	-0.43	0.38	-0.20	-0.35	0.11	1

Note: all outliers included

A_{ratio}: a(250):a(365)

Con: 2014 connection time

Temp: lake temperature

Chl: Chlorophyll a

Table A6. *P-values* for Table A5 (mid-summer 2014) Correlation Coefficients (bold indicates significance at $\alpha = 0.05$).

	pCH ₄	pCO ₂	DIC	pH	CDOM	A _{ratio}	SUVA	Area	Sill	Con	DOC	Temp	Depth	Chl
pCH ₄		0.91	0.24	0.89	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.19	0.20
pCO ₂	0.91		0.00	0.00	0.91	0.88	0.22	0.41	0.25	0.46	0.54	0.42	0.04	0.00
DIC	0.24	0.00		0.00	0.40	0.32	0.41	0.32	0.55	0.81	0.24	0.84	0.26	0.00
pH	0.89	0.00	0.00		0.99	0.85	0.30	0.33	0.53	0.75	0.60	0.41	0.07	0.00
CDOM	0.00	0.91	0.40	0.99		0.29	0.43	0.02	0.06	0.05	0.00	0.18	0.00	0.96
A _{ratio}	0.00	0.88	0.32	0.85	0.29		0.00	0.01	0.00	0.00	0.01	0.05	0.05	0.34
SUVA	0.00	0.22	0.41	0.30	0.43	0.00		0.00	0.01	0.01	0.00	0.16	0.89	0.04
Area	0.00	0.41	0.32	0.33	0.02	0.01	0.00		0.00	0.00	0.00	0.00	0.97	0.07
Sill	0.00	0.25	0.55	0.53	0.06	0.00	0.01	0.00		0.00	0.00	0.00	0.82	0.00
Con	0.00	0.46	0.81	0.75	0.05	0.00	0.01	0.00	0.00		0.00	0.00	0.69	0.01
DOC	0.00	0.54	0.24	0.60	0.00	0.01	0.00	0.00	0.00	0.00		0.02	0.03	0.21
Temp	0.02	0.42	0.84	0.41	0.18	0.05	0.16	0.00	0.00	0.00	0.02		0.18	0.02
Depth	0.19	0.04	0.26	0.07	0.00	0.05	0.89	0.97	0.82	0.69	0.03	0.18		0.50
Chl	0.20	0.00	0.00	0.00	0.96	0.34	0.04	0.07	0.00	0.01	0.21	0.02	0.50	

Note: all outliers included

A_{ratio}: a(250):a(365)

Con: 2014 connection time

Temp: lake temperature

Chl: Chlorophyll a

Table A7. Correlation Matrix (Pearson's r) of Box-Cox Transformed Variables from Late Summer 2014 Survey

	pCH ₄	pCO ₂	DIC	pH	CDOM	A _{ratio}	SUVA	Area	Sill	Con	DOC	Temp	Depth	Chl
pCH ₄	1.00	-0.06	0.07	0.07	0.29	0.26	-0.29	-0.52	0.41	-0.35	-0.40	0.25	0.06	-0.16
pCO ₂	-0.06	1.00	0.94	-0.91	-0.12	-0.01	0.30	-0.05	-0.22	0.15	0.33	-0.25	0.22	0.06
DIC	0.07	0.94	1.00	-0.84	-0.04	0.06	0.28	-0.16	-0.13	0.06	0.26	-0.10	0.20	0.05
pH	0.07	-0.91	-0.84	1.00	0.15	-0.11	-0.31	0.01	0.26	-0.22	-0.32	0.23	-0.25	0.03
CDOM	0.29	-0.12	-0.04	0.15	1.00	-0.50	0.02	-0.49	0.38	-0.42	-0.57	0.32	-0.28	0.27
A _{ratio}	0.26	-0.01	0.06	-0.11	-0.50	1.00	-0.23	-0.13	0.25	-0.17	0.01	-0.04	0.53	-0.26
SUVA	-0.29	0.30	0.28	-0.31	0.02	-0.23	1.00	-0.01	-0.14	0.07	0.76	0.08	-0.04	-0.12
Area	-0.52	-0.05	-0.16	0.01	-0.49	-0.13	-0.01	1.00	-0.67	0.65	0.34	-0.46	-0.18	-0.16
Sill	0.41	-0.22	-0.13	0.26	0.38	0.25	-0.14	-0.67	1.00	-0.98	-0.39	0.23	0.31	0.15
Con	-0.35	0.15	0.06	-0.22	-0.42	-0.17	0.07	0.65	-0.98	1.00	0.35	-0.17	-0.32	-0.13
DOC	-0.40	0.33	0.26	-0.32	-0.57	0.01	0.76	0.34	-0.39	0.35	1.00	-0.16	0.08	-0.25
Temp	0.25	-0.25	-0.10	0.23	0.32	-0.04	0.08	-0.46	0.23	-0.17	-0.16	1.00	-0.22	0.16
Depth	0.06	0.22	0.20	-0.25	-0.28	0.53	-0.04	-0.18	0.31	-0.32	0.08	-0.22	1.00	-0.01
Chl	-0.16	0.06	0.05	0.03	0.27	-0.26	-0.12	-0.16	0.15	-0.13	-0.25	0.16	-0.01	1.00

Note: all outliers included

A_{ratio}: a(250):a(365)

Con: 2014 connection time

Temp: lake temperature

Chl: Chlorophyll a

Table A8. *P-values* for Table A7 (late summer 2014) Correlation Coefficients (bold indicates significance at $\alpha = 0.05$).

	pCH ₄	pCO ₂	DIC	pH	CDOM	A _{ratio}	SUVA	Area	Sill	Con	DOC	Temp	Depth	Chl
pCH ₄		0.72	0.67	0.65	0.06	0.09	0.07	0.00	0.01	0.02	0.01	0.11	0.70	0.30
pCO ₂	0.72		0.00	0.00	0.45	0.95	0.06	0.74	0.16	0.34	0.03	0.11	0.15	0.69
DIC	0.67	0.00		0.00	0.80	0.71	0.08	0.30	0.43	0.69	0.10	0.53	0.20	0.76
pH	0.65	0.00	0.00		0.33	0.50	0.05	0.93	0.09	0.16	0.04	0.15	0.11	0.84
CDOM	0.06	0.45	0.80	0.33		0.00	0.89	0.00	0.01	0.01	0.00	0.04	0.08	0.09
A _{ratio}	0.09	0.95	0.71	0.50	0.00		0.14	0.40	0.12	0.30	0.97	0.79	0.00	0.09
SUVA	0.07	0.06	0.08	0.05	0.89	0.14		0.94	0.38	0.64	0.00	0.59	0.80	0.46
Area	0.00	0.74	0.30	0.93	0.00	0.40	0.94		0.00	0.00	0.03	0.00	0.26	0.30
Sill	0.01	0.16	0.43	0.09	0.01	0.12	0.38	0.00		0.00	0.01	0.14	0.04	0.35
Con	0.02	0.34	0.69	0.16	0.01	0.30	0.64	0.00	0.00		0.02	0.28	0.04	0.43
DOC	0.01	0.03	0.10	0.04	0.00	0.97	0.00	0.03	0.01	0.02		0.31	0.61	0.11
Temp	0.11	0.11	0.53	0.15	0.04	0.79	0.59	0.00	0.14	0.28	0.31		0.16	0.32
Depth	0.70	0.15	0.20	0.11	0.08	0.00	0.80	0.26	0.04	0.04	0.61	0.16		0.95
Chl	0.30	0.69	0.76	0.84	0.09	0.09	0.46	0.30	0.35	0.43	0.11	0.32	0.95	

Note: all outliers included

A_{ratio}: a(250):a(365)

Con: 2014 connection time

Temp: lake temperature

Chl: Chlorophyll a

Table A9. Correlation Matrix (Pearson's r) of Box-Cox Transformed Normalized Methane Oxidation (MOX) Variables.

	NOX	pH	Depth	TDN	TDP	PN	PP	PC	DOC	CDOM	A _{ratio}	SUVA	Temp	DO	Chl
NOX	1	-0.72	0.48	0.09	-0.20	-0.38	-0.33	-0.40	0.42	0.58	0.06	-0.11	0.44	-0.39	-0.56
pH	-0.72	1	-0.67	0.22	0.56	0.53	0.39	0.41	-0.13	-0.66	0.28	-0.21	-0.56	0.79	0.67
Depth	0.48	-0.67	1	0.26	-0.55	-0.62	-0.75	-0.35	0.42	0.33	0.18	-0.18	0.18	-0.57	-0.44
TDN	0.09	0.22	0.26	1	0.11	-0.16	-0.58	-0.13	0.77	-0.09	0.82	-0.72	-0.08	0.30	0.04
TDP	-0.20	0.56	-0.55	0.11	1	0.23	0.38	0.01	0.00	0.02	-0.06	-0.07	-0.20	0.50	0.09
PN	-0.38	0.53	-0.62	-0.16	0.23	1	0.72	0.89	-0.31	-0.40	0.02	0.14	-0.34	0.50	0.61
PP	-0.33	0.39	-0.75	-0.58	0.38	0.72	1	0.50	-0.57	-0.26	-0.36	0.36	-0.12	0.33	0.36
PC	-0.40	0.41	-0.35	-0.13	0.01	0.89	0.50	1	-0.22	-0.38	0.04	0.07	-0.34	0.39	0.59
DOC	0.42	-0.13	0.42	0.77	0.00	-0.31	-0.57	-0.22	1	0.22	0.68	-0.86	-0.03	0.04	-0.21
CDOM	0.58	-0.66	0.33	-0.09	0.02	-0.40	-0.26	-0.38	0.22	1	-0.44	0.27	0.42	-0.56	-0.62
A _{ratio}	0.06	0.28	0.18	0.82	-0.06	0.02	-0.36	0.04	0.68	-0.44	1	-0.79	-0.24	0.50	0.16
SUVA	-0.11	-0.21	-0.18	-0.72	-0.07	0.14	0.36	0.07	-0.86	0.27	-0.79	1	0.23	-0.29	-0.07
Temp	0.44	-0.56	0.18	-0.08	-0.20	-0.34	-0.12	-0.34	-0.03	0.42	-0.24	0.23	1	-0.43	-0.50
DO	-0.39	0.79	-0.57	0.30	0.50	0.50	0.33	0.39	0.04	-0.56	0.50	-0.29	-0.43	1	0.40
Chl	-0.56	0.67	-0.44	0.04	0.09	0.61	0.36	0.59	-0.21	-0.62	0.16	-0.07	-0.50	0.40	1

Note: all outliers included

NOX: normalized methane oxidation (i.e., MOX per unit CH₄)

A_{ratio}: a(250):a(365)

Temp: lake temperature

Chl: Chlorophyll a

Table A10. *P*-values for Table A9 (Normalized Methane Oxidation) Correlation Coefficients (bold indicates significance at $\alpha = 0.05$).

	NOX	pH	Depth	TDN	TDP	PN	PP	PC	DOC	CDOM	A _{ratio}	SUVA	Temp	DO	Chl
NOX		0.00	0.02	0.71	0.38	0.08	0.13	0.06	0.05	0.00	0.78	0.62	0.04	0.07	0.01
pH	0.00		0.00	0.32	0.01	0.01	0.07	0.06	0.56	0.00	0.21	0.34	0.01	0.00	0.00
Depth	0.02	0.00		0.24	0.01	0.00	0.00	0.11	0.05	0.13	0.41	0.42	0.41	0.01	0.04
TDN	0.71	0.32	0.24		0.62	0.48	0.01	0.55	0.00	0.68	0.00	0.00	0.73	0.18	0.87
TDP	0.38	0.01	0.01	0.62		0.30	0.08	0.98	1.00	0.93	0.80	0.77	0.37	0.02	0.69
PN	0.08	0.01	0.00	0.48	0.30		0.00	0.00	0.16	0.07	0.92	0.53	0.12	0.02	0.00
PP	0.13	0.07	0.00	0.01	0.08	0.00		0.02	0.01	0.25	0.10	0.10	0.60	0.14	0.10
PC	0.06	0.06	0.11	0.55	0.98	0.00	0.02		0.33	0.08	0.86	0.76	0.13	0.07	0.00
DOC	0.05	0.56	0.05	0.00	1.00	0.16	0.01	0.33		0.32	0.00	0.00	0.90	0.85	0.34
CDOM	0.00	0.00	0.13	0.68	0.93	0.07	0.25	0.08	0.32		0.04	0.23	0.05	0.01	0.00
A _{ratio}	0.78	0.21	0.41	0.00	0.80	0.92	0.10	0.86	0.00	0.04		0.00	0.27	0.02	0.47
SUVA	0.62	0.34	0.42	0.00	0.77	0.53	0.10	0.76	0.00	0.23	0.00		0.31	0.19	0.75
Temp	0.04	0.01	0.41	0.73	0.37	0.12	0.60	0.13	0.90	0.05	0.27	0.31		0.04	0.02
DO	0.07	0.00	0.01	0.18	0.02	0.02	0.14	0.07	0.85	0.01	0.02	0.19	0.04		0.07
Chl	0.01	0.00	0.04	0.87	0.69	0.00	0.10	0.00	0.34	0.00	0.47	0.75	0.02	0.07	

Note: all outliers included

NOX: normalized methane oxidation (i.e., MOX per unit CH₄)

A_{ratio}: a(250):a(365)

Temp: lake temperature

Chl: Chlorophyll a