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Accelerated warming in the Arctic contributes to the formation of landscape features known as thermokarsts, or ground surface depressions created by the thermal degradation of permafrost. As a significant portion of the global carbon pool is stored in high latitude ecosystems, it is of concern that accelerated permafrost thaw and the resulting formation of thermokarst features along lake margins may act as a positive feedback to climate warming by influencing the delivery of methanogenic substrates to arctic lake sediments. We designed an experiment to determine how thermokarst features may impact arctic lake sediment methanogenesis. We investigated 3 lakes with the presence of a thermokarst feature adjacent to their banks, and 3 lakes without this landscape feature in the foothills of the Brooks Range, Alaska. Using a sediment core incubation method, methanogenesis, methane oxidation and net sediment CH₄ flux to the water column were compared between lake types. Although a significant difference in CH₄ production was not found between lake types, a negative trend was found between methanogenesis and distance from shoreline in both lake types. Sediment traps served as a proxy to assess material delivered by an adjacent thermokarst feature. Although sedimentation rates were significantly greater in traps near a thermokarsting shore than those opposite, the organic matter content in the traps was lower near thermokarsts. Regression models suggested that the catchment area/lake area ratio, water column DOC (mg/L), dissolved oxygen (mg/L) and glacial till were the most useful variables for

predicting sediment methanogenesis in arctic lakes. However, our study does not suggest that thermokarst activity along lake shores enhances methanogenesis in lake sediments.

AN EXAMINATION OF THE INFLUENCE OF THERMOKARST ACTIVITY ON
ARTIC LAKE SEDIMENT METHANOGENESIS

by

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Approved by

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This project is dedicated to the memory of my good friend Shane Straight,
who is proud of me somewhere.

APPROVAL PAGE

This thesis has been approved by the following committee of the Faculty of The Graduate School at The University of North Carolina at Greensboro.

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TABLE OF CONTENTS

| | Page |
|---|------|
| LIST OF TABLES..... | vii |
| LIST OF FIGURES..... | viii |
| CHAPTER | |
| I. INTRODUCTION..... | 1 |
| II. MATERIALS AND METHODS | 7 |
| Study Sites..... | 7 |
| Sampling and Laboratory Methods..... | 8 |
| Data Analysis | 14 |
| III. RESULTS..... | 16 |
| Sedimentation..... | 16 |
| Sediment Trap % OM | 17 |
| Sediment % OM..... | 17 |
| DOC and DIC..... | 18 |
| Methane Oxidation and Sediment CH ₄ Flux to the Water Column..... | 20 |
| IV. DISCUSSION | 21 |
| Sedimentation..... | 21 |
| % Sediment OM Content..... | 23 |
| Methanogenesis and Methane Oxidation..... | 23 |
| V. CONCLUSION | 31 |

| | |
|---------------------------|----|
| REFERENCES | 33 |
| APPENDIX A: TABLES | 40 |
| APPENDIX B: FIGURES | 45 |

LIST OF TABLES

| | Page |
|--|------|
| Table 1. Study Sites | 41 |
| Table 2. DOC, DIC, $\delta^{13}\text{C}$ -DOC, and $\delta^{13}\text{C}$ -DOC values for bank runoff (Thermokarst or Reference Lake) and water column (Epilimnion and hypolimnion) | 42 |
| Table 3. Methanogenesis, methane oxidation and sediment CH_4 flux to the atmosphere ($\mu\text{molCH}_4/\text{m}^2/\text{day}$) by depth in thermokarst and reference lake | 43 |
| Table 4. Regression Equations for Lake Sediment Methanogenesis | 44 |
| Table 5. Regression Equations for Lake Sediment Methane Oxidation | 45 |

LIST OF FIGURES

| | Page |
|---|------|
| Figure 1. Study Sites | 46 |
| Figure 2. Sampling Methods..... | 47 |
| Figure 3. AFDM sedimentation rates for A) lakes with the presence of an adjacent thermokarst feature and B) reference lakes without the presence of an adjacent thermokarst feature | 48 |
| Figure 4. Percent organic matter of sedimentation between opposite traps placed within A) Reference Lakes and B) Thermokarst Lakes | 49 |
| Figure 5. Sediment % OM content by lake type | 50 |
| Figure 6. Mean rate of methanogenesis by sampling depth (bank, intermediate and maximum depth sampled) in reference and thermokarst lakes..... | 51 |
| Figure 7. Log $\mu\text{mol CH}_4/\text{m}^2/\text{day}$ by lake depth (m) | 52 |

CHAPTER I

INTRODUCTION

It is well documented that human activities have altered the global carbon cycle and influenced the composition of the atmosphere since the onset of the industrial revolution (Vitousek 1994). The combustion of fossil fuels for energy has increased the release of carbon-containing greenhouse gases, such as carbon dioxide (CO₂) and methane (CH₄), which account for an increased net retention of solar radiation, or radiative forcing (Lelieveld et al. 2002). As greenhouse gases diminish the net loss of infrared heat to space, they contribute to an increase in the surface temperature of the earth (IPCC 2007). Conservative estimates conclude that the average temperature of the earth's surface has increased by approximately 1.2-1.4°F in the last century, with eight of the warmest years on record occurring in the last decade (Hansen et al. 2000). Although accurate predictions of climate change prove difficult, recent climate models estimate that the average temperature of the Earth's surface may increase from 3.2 to 7.2°F above current levels by the conclusion of this century (Hergerl et al. 2007)

While CO₂ receives a great deal of attention when considering climate models, atmospheric CH₄ is a radiatively important greenhouse gas; it is 21 times more effective at trapping heat in the atmosphere on a molar basis than is carbon dioxide (ACIA 2005, Whalen 2005). Over the past two centuries, anthropogenic activities such as rice cultivation, mining, fossil fuel use and livestock production have increased the

concentration of CH₄ in our atmosphere from approximately 650 to nearly 1780 parts per billion by volume (ppbv) (Lelieveld et al. 2002). Additionally, saturated environments, such as those found in northern wetlands, have been identified as important natural sources of CH₄ (Walter et al. 2007). Therefore, a better understanding of the factors influencing both ecosystem and anthropogenic controls of CH₄ production is critical when considering future climate warming. However, the accuracy of climate change predictions depends on unknown factors, such as the levels of future greenhouse gas emissions, and the resulting response of ecosystem processes that may influence climate in regions such as the Arctic.

Arctic regions, including Northern Alaska, are unique environments that may have an impact on global climate in several ways. As a portion of the Arctic is perennially covered with snow and ice, a fraction of the solar energy reaching the earth's surface is reflected back to space, which is known as albedo (Pinty and Verstraete 1992). Therefore, the undisturbed cryosphere, present in the Arctic as snow, ice sheets, glaciers, and sea ice, mitigates surface warming by solar radiation inputs (McBean et al. 2005). However, climate change in the Arctic may significantly diminish this albedo effect as warming disturbs the negative annual radiation balance created by the cryosphere (Hinzman et al. 2005). Currently, evidence from terrestrial, marine and atmospheric studies indicates that the climate of the Arctic has experienced significant warming in the last three decades (Arctic Climate Impact Assessment (ACIA) 2004, Hinzman et al. 2005, Schuur et al. 2008). Recent studies estimate that the annual average temperature in the Arctic increased by approximately 1°C, and that average winter temperatures

increased by approximately 2-4°C between 1954 and 2003 (Bowden et al. 2008). Warmer air temperatures have been cited as a principle climate driver influencing permafrost thawing and degradation, reduced ice cap mass and increased recession, reduced glacial mass, and earlier snowmelt (Hinzman et al. 2005). As a consequence of this altered climatic state, the Arctic is currently experiencing a system-wide response to warming. These responses may influence hydrological and biogeochemical cycling in both terrestrial and aquatic systems (Schuur et al. 2008).

In terrestrial systems, warmer air temperatures in the Arctic may influence the transport of carbon from permafrost, or perennially frozen ground. It is estimated that nearly one third of the global soil carbon pool is sequestered in high latitude systems, representing one of the largest pools of stored organic carbon (Schuur et al. 2008, Quesada et al. 2006). Carbon density is often higher in near-surface permafrost, as organic carbon is derived from plant growth and photosynthesis. Although the permafrost carbon pool is variable regionally, conservative estimates conclude that all permafrost zones, both continuous and discontinuous, collectively contain approximately 1024 Pg C in the top 3 meters (Schuur et al. 2008). Since the retreat of the most recent glacial ice sheets during the Holocene, these ancient carbon stores have remained frozen, and thus largely unavailable to microbial decomposition.

As the Arctic ecosystem plays an important role in the global carbon budget, climate warming may subsequently release carbon sequestered in the upper permafrost layers in regions such as Northern Alaska (Ping et al. 1997). In particular, thermal degradation of permafrost may contribute to the collapse of the overlying ground surface,

creating a landscape depression known as a thermokarst (Walter et al 2007). Any changes in the active, or “seasonally thawed”, layer of permafrost may influence the transport of water, solutes and particulate materials. Thermokarst depressions may, therefore, transfer thawed organic carbon previously unavailable for microbial decomposition to receiving bodies of water including lakes.

Lake sediments are an important site for landscape derived organic matter (OM) mineralization, as anaerobic processes within freshwater environments can account for as much as 60% of lake carbon metabolism (Bastviken et al. 2003). Methanogenic bacteria in lakes meet their energy and growth requirements by producing CH₄ from the anaerobic decomposition of OM in aquatic sediments. CO₂ or acetic acid may serve as the terminal electron acceptor in methanogenesis. Acetoclastic methanogens dissimilate acetate to CO₂ and CH₄ in the acetoclastic pathway while hydrogenotrophic methanogens use H₂ as an electron donor to reduce CO₂, with CH₄ as a product (Whalen 2005). Methane oxidizing bacteria derive energy from the aerobic consumption of CH₄. Thus, the release of CH₄ in arctic lakes reflects the net production and heterotrophic consumption of CH₄ by the microbial community in sediments (Whalen 2005).

Arctic lakes, which comprise up to 48% of the land surface in some regions of the Arctic, may contribute as much as 6% annually (~24.2 Tg CH₄ yr⁻¹) to the global atmospheric CH₄ budget (Walter et al 2006). In response to climate warming, acetoclastic CH₄ production may increase due to increases in the import of dissolved organic carbon (DOC) into lakes from the terrestrial environment. In particular, thermokarsts may be responsible for the delivery of labile OM previously sequestered in

the permafrost to the sediments of arctic lakes (Walter et al 2006). Therefore, increased CH₄ emissions from microbial decomposition in lake sediments (as a result of enhanced delivery of thermokarst-derived DOC) may constitute a landscape process that acts as a positive feedback capable of influencing the future radiative forcing of climate change. As the impact of active thermokarsts on methanogenesis in lake sediments remains uncertain, my objectives for this study were to: 1) determine the importance of thermokarst activity on methanogenesis and methane oxidation in arctic lake sediments, and 2) determine if the proximity relative to an active thermokarst feature significantly affects CH₄ production in arctic lake sediments. As a means of evaluating the factors that may affect methanogenesis, I compared lakes with and without an active thermokarst feature adjacent to their banks in terms of rates of sedimentation, lake sediment OM content as a function of depth, determined differences in sediment DOC, and finally determined differences in DOC that may be supplied to lake sediments from the banks. I hypothesized that thermokarst activity alters CH₄ production in arctic lake sediments compared to lakes without the presence of an adjacent thermokarst feature on their banks. Additionally, I hypothesized that proximity to a shoreline thermokarst feature, measured as differences in the mean rate of methanogenesis between samples taken adjacent to the thermokarst feature, at an intermediate depth, and at a maximum depth from the thermokarst disturbance, affects methanogenesis within a lake. I hypothesized that sediment methanogenesis is significantly greater in thermokarst lakes than in reference lakes due to the enhanced delivery of organic substrates from melting permafrost. I further hypothesized that both sediment % OM and sediment DOC will differ between

lake types. Finally, I hypothesized that thermokarst lakes will differ from reference lakes in terms of sediment % OM and sediment DOC.

CHAPTER II

MATERIALS AND METHODS

Study Sites

Six lakes near Toolik Field Station, Alaska ($68^{\circ} 37' 53''$ N, $149^{\circ} 36' 20''$ W) in the Northern Foothills of the Brooks Range were sampled for this study (Fig. 1). Lakes in this region are oligotrophic to ultraoligotrophic, relatively shallow, and remain ice-covered for about 9 months of the year (Hershey et al. 2006). The region is dominated by tundra, and underlain with continuous permafrost. Three reference lakes (NE12, Toolik and E1) were compared to lakes with thermokarsts along their banks (NE14, Campsite and I-Minus). The thermokarst activity differed between the three thermokarst lakes in this study, as Campsite, I Minus and NE14 showed qualitatively low, medium and high thermokarst activity respectively. Reference lakes were chosen primarily on the basis of similarities in glacial till age (Hershey et al. 2006) and maximum depth to the thermokarst lakes. Physical data for the thermokarst and reference lakes are shown in Table 1.

Sampling and Laboratory Methods

A total of 24 polycarbonate cylindrical cores, 50.8 cm in length and 5 cm in outer diameter, with an inner diameter of 4.6 cm, were used to collect sediment samples from each lake by gravity coring. In each lake, 8 cores (3 controls, 4 treatments and 1 core for sediment organic content analysis) were taken at the shallow bank directly adjacent to the thermokarst, or in an area of similar bottom morphometry, in reference lakes.

Additionally, 8 cores were taken at both intermediate and maximum depths. Intermediate depths were defined as the median value between the bank and maximum depth sampled. All sediment cores were filled with lake water and capped with rubber stoppers before being transported back to the lab.

In order to determine the influence of thermokarst activity on methanogenesis, the processes of methanogenesis and methane oxidation were examined independently.

Methyl fluoride, CH_3F , was used to distinguish total methanogenesis from net sediment CH_4 flux. At low concentrations, such as 1.5%, CH_3F is known to be a selective inhibitor of methane oxidation by aerobic methanotrophic bacteria in natural systems (Janssen and Frenzel 1997). Therefore, each control core (without the addition of a CH_3F inhibition treatment) provides a measure of the net CH_4 flux from lake sediments, or the portion of CH_4 produced that was not oxidized. Treatment cores (which contain 1.5% CH_3F) estimated the rate of gross methanogenesis in lake sediments, because methane oxidation was expected to be inhibited. The rate of methane oxidation was estimated as the difference between sediment CH_4 flux (control cores) and the rate of methanogenesis (1.5% methyl fluoride treatment cores).

Upon returning to the lab, all 24 cores from each lake were extruded into shorter cores (30 cm in length and 5 cm in outer diameter, with an inner diameter of 4.6 cm) for experimental manipulation. Approximately 13 cm of sediment were extruded into the short cores with care taken not to disturb the sediments. Actual sediment heights were recorded for all cores. Overlying lake water remained in the short core headspace, and each core was capped with an airtight acrylic stopper fitted with a septum for sampling. Once all 24 cores had been extruded, treatments were applied using water collected from the study lake.

A saturated stock solution of CH_3F in control water from the study lakes was made at the beginning of each experiment in order to prepare subsequent treatments. Lake water of the same origin (epilimnion or hypolimnion) to the sediment cores was added to the rim of a large serum vial. A stopper was then placed on the lid of the serum vial, followed by the placement of a needle through the stopper in order to displace water from the vial as pressure was applied. A 60ml syringe was filled with CH_3F gas, purged, and then filled again with CH_3F to limit potential contamination from the presence of ambient gases. The syringe was inserted into the vial through the stopper and inverted. As gas was forced into the vial, water from the vial was displaced via the needle. The CH_3F saturated solution in the serum vial was capped with a crimp seal and shaken vigorously. This CH_3F saturated solution was diluted to a 1.5% CH_3F treatment solution using study lake water in a 1L cubitainer.

For each lake, twelve 1.5% CH_3F treatment cores (4 per depth) were prepared by removing the overlying headspace water from each sediment core, leaving approximately

2 cm of headspace water over the surface of the sediment. Treatment water was slowly dripped down an inverted syringe plunger in order to minimize the amount of disturbance to the sediment surface within the treatment core. A floating magnetic stir bar was placed approximately 6 cm above the sediment in both control and treatment cores. Finally, all sediment cores were capped with a fitted acrylic septum cap with an airtight sampling port. Nine control cores (3 per depth) were prepared using a similar method as the treatment cores, with the exception of replacing the overlying headspace water with untreated lake water (hypolimnetic or epilimnetic) from each sample depth. One additional core from each depth was taken for sediment OM analysis.

All 21 experimental cores were incubated for 24 h in a water bath at 8°C, which represented the median water temperature at all sampling locations. The cores were placed on a circular wooden table with a support to hold a rotating magnet, which was suspended from the center apparatus and attached to a motor turning at 1 rpm. The movement of the magnet rotated the floating magnetic stir bars to prevent an oxygen gradient from forming within the cores. After all 21 cores were placed in the incubation chamber, an initial time zero (T_0) sample was collected. The septa sampling cap was removed from each of the incubation cores in order to sample the headspace water. A syringe with a cannula attachment was used to remove 3-ml of water from the headspace, which was then injected into a labeled 12-ml exetainer that had been previously evacuated with helium gas and returned to 1 atm followed by the addition of 0.1ml 1N HCl in order to halt microbial activity. The sampled volume was replaced with 3ml of treatment or control water, depending on the sample of origin. This process was repeated

for all cores at 12 hours (T_1) and 24 hours (T_2). The exetainers were then shaken, inverted and allowed to sit for at least 24 hours. Headspace gas was analyzed with a gas chromatograph for ppm CH_4 .

Three separate depths were sampled along a transect to evaluate whether or not CH_4 production decreases from samples taken from a bank depth to samples taken at a maximum depth in the absence (reference lakes) or presence (thermokarst-influenced lakes) of an active thermokarst (Figure 2). The CH_3F treatment experiment previously described was used to measure CH_4 production at each of these depths in order to determine if proximity to a thermokarst significantly alters the mean rate of sediment methanogenesis. The sampling and incubation methods were identical to those used to determine differences in CH_4 production between lake types, as three separate depths replicated in each lake satisfied both objectives simultaneously.

Sediment traps were placed in the water column of each lake in order to quantify thermokarst influence on sediment deposition. The traps consisted of four 4"x12" PVC pipes which held four 3"x12" clear plastic mailing tubes open at the top to collect settling particulate matter within a lake. In order to maintain water column position, each trap was anchored to the bottom of the lake, and buoyed at the surface.

Two sediment traps were placed in each of the six lakes. The first trap was placed one meter above the water-sediment interface near the thermokarst-eroded bank, while the second trap was placed at a similar depth and distance from the shoreline on the opposite side of the lake. In reference lakes, opposite traps were placed at similar depths and approximate distances from the shore relative their thermokarst comparison lakes.

Each trap remained at each site for a minimum of two weeks. The water and sediment from each of four sediment trap cylinders was filtered through three replicate pre-ashed glass fiber filters with a 0.7 μm nominal pore size. The filters were dried at 65°C for 48 hours and re-weighed. One filter from each sediment trap replicate was used to determine sedimentation rate, calculated in $\text{mg}/\text{m}^2/\text{day}$ dry mass. Filters were then combusted in a furnace for 1 hr at 500° C, after which, the filters were re-weighed in order to determine ash-free dry mass (AFDM). Percent organic content of each filter was estimated operationally as the fraction of pre-ashed dry weight that was subsequently combusted in the furnace (i.e., mass loss on ignition).

One core from each depth sampled from each lake was analyzed for % OM and surficial sediment $\delta^{13}\text{C}$. Each core was sampled every mm for the first 5 millimeters, and then sampled every 5 mm thereafter to a depth of 6 cm. A clamp was used to secure the sediment core in a vertical position over a core extruding device (29 cm long x 48 cm diameter) with an attached ruler. In this manner, the core was able to be extruded at regular mm distance intervals downcore, and sediment samples at each distance interval were carefully scraped into a labeled microcentrifuge tube. Each sample was then dried in a drying oven at 65°C for 48 hours and shipped back to UNCG for laboratory analysis.

A known weight (mg) of sediment sample from each distance interval downcore was placed in an aluminum foil packet and combusted in a furnace for 1 hr at 500° C, then re-weighed in order to determine ash-free dry mass (AFDM). Percent organic content of each sediment sample was determined as the fraction of pre-ashed weight that was combusted in the furnace. For each lake, three samples of surficial sediment at each

sampling depth were analyzed for $\delta^{13}\text{C}$ by the U.C. Davis Stable Isotope Facility using isotope ratio mass spectrometry.

In an effort to understand the sources of carbon that may become available to the sediment microbial community, water samples of both DOC and DIC were taken from the runoff along adjacent banks and in the water column within each lake. DOC and DIC samples were taken from ground water runoff and bank soils adjacent to all study lakes. The water samples taken at each lake were placed in 40ml amber vials containing either 0.1mL HCl (DOC samples) or 0.1 mL HgCl_2 (DIC samples), then shipped for analysis by the U.C. Davis Stable Isotope Facility. DOC and DIC were analyzed for ^{13}C using an O.I. Analytical Model 1010 TOC Analyzer interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer. A 20-mL aliquot of sample was transferred into a heated digestion vessel and reacted sequentially with phosphoric acid then with sodium persulfate to convert DIC and DOC each into a pulse of CO_2 . The two sequential CO_2 pulses liberated by the chemical treatments were carried in a helium flow to an infra-red gas analyzer (IRGA), then to the isotope ratio mass spectrometer where the $^{13}\text{C}/^{12}\text{C}$ ratios were measured and compared to ratios of laboratory standards calibrated against NIST Standard Reference Materials. CH_4 samples in the water column of each lake (epilimnion and hypolimnion) were taken by injecting 8ml of lake water into purged 12 ml exetainers with the addition of 0.1ml HCl. After vigorously shaking each exetainer, a 2.5ml sample of headspace gas was injected into a gas chromatograph for analysis of water column CH_4 . Finally, temperature ($^{\circ}\text{C}$) and dissolved oxygen (mg/L) were measured at each sample depth within each lake using a YSI minisonde.

Data Analysis

After checking for normality, a two-sample t-test was used to compare mean values of CH₄ production ($\mu\text{mol CH}_4/\text{m}^2/\text{day}$) between lake types. Two-sample t-tests were used to compare sedimentation rates and % OM between sediment traps placed on opposing sides of each lake, and also to compare sedimentation rates and % sediment trap OM content between lake types. As methanogenesis values in reference lakes were not normally distributed, a Kruskal-Wallis non-parametric test was used to determine if mean rate of methanogenesis was significantly different among reference lakes. A two-way ANOVA was used to determine if lake type (presence or absence of a thermokarst feature) significantly effects CH₄ production in lake sediments. A one-way ANOVA was used to determine if CH₄ production in lake sediments changed significantly from samples taken near the bank of an active thermokarst to samples taken at intermediate and maximum depths within lakes affected by thermokarst erosion. Similarly, a one-way ANOVA was used to determine whether CH₄ production in lake sediments changed significantly from samples taken near the bank to samples taken at intermediate and maximum depths within each reference lake. Finally, multiple regression analysis was used to predict sediment methanogenesis and methane oxidation from all variables measured, which included: lake type (thermokarst or reference), glacial till, temperature (°C), dissolved oxygen (mg/L), sediment % OM content, water column DOC and the catchment area/lake area ratio. Lakes were assigned rank ages according to the age of the underlying glacial surface according to the methods of Hershey et al. (2006). All

significant relationships reported are those with a p-value < 0.05 . Statistical analyses were conducted using SPSS 15.0 Data Analysis software.

CHAPTER III

RESULTS

Sedimentation

The sedimentation rates were variable among thermokarst lakes, as the mean rates of Lakes NE14, Campsite and I Minus were 90.4, 38.2 and 33.5 mg/m²/day respectively (Figure 3a). Within each thermokarst lake, traps placed near an adjacent thermokarst feature had significantly greater rates of sedimentation than those placed near the opposite bank (Figure 3a). The greatest within-lake difference in sedimentation rate was found in lake NE14, which qualitatively exhibited the greatest degree of thermokarst activity; mean sedimentation rate in the trap located near the thermokarst bank (116.6 mg/m²/day) was significantly greater than the trap placed near the opposite bank (55.3 mg/m²/day) (Figure 3a). No significant differences in sedimentation rate (mg/m²/day) were found between opposing sediment traps within reference lakes (Figure 3b), but were quite variable among different reference lakes, as the mean rates of Lakes E1, NE12 and Toolik were 33.4, 180.7 and 13.1 mg/m²/day respectively.

Sediment Trap % OM

When both traps within a lake were considered, reference lakes had significantly greater % of sedimentation represented by OM than thermokarst lakes. Significant differences in % OM of sedimentation were not found between traps placed on opposite sides of reference lakes (Figure 4a). The % OM of sediment trap material of Lake NE12 was unable to be determined due to the complete combustion of sediment filters. In thermokarst lakes Campsite and I Minus, a significant difference in % OM of sediment trap material was not found between traps placed near an active thermokarst bank and those placed opposite (Figure 4b). However, the percent of sedimentation represented by OM was significantly lower in traps placed near the active thermokarst shore than those placed opposite in thermokarst lake NE14 (Figure 4b), which exhibited the greatest degree of thermokarst activity.

Sediment % OM

Reference lake sediments had a significantly greater % OM (21.3%) than thermokarst lakes (12.4%) (Figure 5). This relationship remained consistent when comparing the sediment %OM at each depth between lake types, as the mean % sediment OM content for reference lakes at the bank (22.7%), intermediate (20.1%) and the maximum depth (20.1%) were greater than that of reference lakes at similar depths (16.1%, 10.1% and 11% respectively).

DOC and DIC

Water column DOC and DIC (mg/L) values did not differ significantly between thermokarst and reference lakes ($p = 0.06$, $t = 1.69$, $df = 4$, Table 2). Bank runoff DOC (mg/L) values were not significantly different between samples taken from reference banks and thermokarst lake banks. The largest bank material runoff DOC value obtained from all lakes (70.5 mg/L) was from Lake NE14, which exhibits the largest degree of thermokarst activity. In thermokarst lakes, the DOC and DIC values from thermokarst runoff declined with degree of thermokarst activity, as DOC values for Lake NE14, I-Minus and Campsite were 70.5, 17.3 and 2.3 mg/L, respectively. DIC values collected from thermokarst runoff in lakes NE14, I-Minus and Campsite had DIC values of 77.9, 22.4 and 1.3 mg/L respectively. Reference lakes were intermediate in DIC (Table 2).

Methanogenesis

Methanogenesis was detected at all depths in both lake types, and rates were variable (198 – 7300 $\mu\text{mol}/\text{m}^2/\text{day}$ in reference lakes and 241 – 2109 $\mu\text{mol}/\text{m}^2/\text{day}$ in thermokarst lakes; Table 3). The mean rates of methanogenesis at all depths were greater in reference lakes (1737.2 $\mu\text{mol CH}_4/\text{m}^2/\text{day}$) than thermokarst lakes (987.9 $\mu\text{mol CH}_4/\text{m}^2/\text{day}$). However, this difference was not significant ($t = 0.67$, $df = 4$, $p = 0.27$, Figure 6). Although the mean rate of methanogenesis was significantly different between reference lakes (Kruskal-Wallis test, $\chi^2 = 7.77$, $d.f. = 2$, $p = 0.02$), there was no significant difference in the mean rate of methanogenesis between thermokarst lakes. There was a weak negative trend indicating that the mean rate of methanogenesis

declined with depth when both lake types were considered (linear regression, $R^2 = 0.18$, $p = 0.08$, Figure 7).

The relationship between depth and methanogenesis was variable when considering lakes individually. Rates of CH_4 production in thermokarst lake Campsite, which qualitatively exhibited the smallest degree of thermokarst erosion of the three disturbed lakes, were found to decrease significantly with depth from an adjacent thermokarst feature (linear regression, $p < 0.0001$, $R^2 = 0.73$). Although the rate of methanogenesis did not change significantly with depth in reference lake Toolik, rates of methanogenesis were found to increase significantly with depth in reference Lake E1 (linear regression, $p = 0.042$, $R^2 = 0.35$) whereas rates of methanogenesis in reference lake NE12 were found to decrease significantly with depth (linear regression, $p = 0.003$, $R^2 = 0.59$).

As there was no significant difference in methanogenesis by lake type, multiple regression equations were constructed to determine what measured variables were most useful for predicting methanogenesis in all lakes studied. Multiple regression analysis based on all available data suggested that glacial till, dissolved oxygen (mg/L) the catchment area:lake area ratio and water column DOC (mg/L) were the most useful variables for predicting sediment methanogenesis in arctic lakes (Table 4).

Methane Oxidation and Sediment CH₄ Flux to the Water Column

A significant difference in methane oxidation or sediment CH₄ flux was not found between lake types ($p = 0.158$, $t = 1.47$, d.f. = 4, $p = 0.118$, $t = -1.17$, d.f. = 4 respectively). Although Lake E1 showed greatest mean rate of methanogenesis, all CH₄ produced there was consumed by methane oxidizing bacteria (MOB) at the intermediate and maximum depths sampled (Table 3). Similarly, methane oxidation was found to completely consume all CH₄ produced at the maximum depth sampled in thermokarst lake NE14 (Table 3).

CHAPTER IV

DISCUSSION

Thawing permafrost associated with climate warming has been reported in many areas (ACIA 2005, Hergerl et al. 2007), a process which lead to increased development of thermokarst features (Bowden et al. 2008). However, the impacts of increased thermokarst activity and permafrost thaw on the biogeochemical composition of aquatic fresh water ecosystems and the resulting ecological responses of the benthic microbial communities to sediment inputs from thermokarst activity are relatively unknown. Here, we discuss the results from studies of six arctic lakes with or without the influence of thermokarst activity on their shores, and consider factors that may affect variability in sedimentation, sediment OM content, and ultimately differences in sediment methanogenesis between lake types.

Sedimentation

The rates of sedimentation for all six lakes were calculated from sediment traps placed at comparable depths on opposing sides of each lake. Sedimentation rate served as a proxy for thermokarst activity. Although there are shortcomings to sediment traps (Wetzel and Balson 1992), this method still provides an index of impact of thermokarst on sedimentation. In this study, traps placed near an adjacent thermokarst feature had significantly greater rates of sedimentation than those placed near the

opposite bank at similar depths in thermokarst lakes (Figure 3a), suggesting the method captured at least part of the impact of thermokarst on sedimentation.

As expected, the greatest difference in sedimentation rate was found in lake NE14, which exhibited the greatest degree of thermokarst activity. These data are consistent with river data, as those in a 0.9 km² subwatershed of the Toolik River in which researchers concluded that thermokarst activity delivered more sediment to the subwatershed than was normally delivered in 18 years from an 132 km² adjacent river basin (Bowden et al. 2008). Therefore, these data further support that thermokarst activity enhances sediment delivery to adjacent bodies of water.

However, the material delivered is largely inorganic in composition (Figure 4b). Several studies of Alaskan, Yukon Territory and Siberian watersheds with varying degrees of permafrost degradation conclude that the export of DOM from watersheds is likely to decline with permafrost degradation (Maclean et al. 1999, Striegl et al. 2005, Carey 2003). Such a decline in DOM export in areas of permafrost degradation may be due to an increase in adsorption by exposed mineral soils, such as those found on the exposed surfaces of thermokarst depressions (Frey and McClelland 2009).

The quality and rate at which organic particles, both autochthonous and allochthonous, are deposited on the sediment surface exerts a strong influence on the abundance and activity of sediment microbes, as OM and associated nutrients potentially available to sediment bacteria play a dominant role in sediment microbial production rates (Kalf 2002). Substrate supply is a primary control for methanogenesis, and the addition of methanogenic substrates (direct or indirect) typically enhances the microbial

production of CH₄ (Whalen 2005). Therefore, any changes in the delivery of methanogenic substrates to the sediment-water interface by thermokarst activity may alter rates of sediment methanogenesis compared to undisturbed lakes.

% Sediment OM Content

Comparison of % OM in sediment samples between lake types also suggests that thermokarst activity enhances the delivery of inorganic rather than organic materials, as thermokarst lake sediments had significantly lower % organic content than reference lake sediments at all depths ($t = -4.13$, $df = 3$, $p = 0.013$, Figure 5). One explanation for these results may be that increased hydrological contact with the mineral soils, such as the exposed mineral soils of thermokarst erosion, may enhance the delivery of inorganic material to lake sediments in permafrost regions (Kokelj et al. 2005), as mineral soils have the potential to stabilize organic materials onto charged surfaces. In contrast, arctic lakes without the influence of thermokarst activity on their shores may exhibit greater hydrological contact with organic soils coupled with a reduced amount of contact with mineral soils (Vincent and Laybourn-Parry 2008). This factor may have accounted for the greater % OM content found in both the sediments and sediment traps of non-thermokarst lakes in this study.

Methanogenesis and Methane Oxidation

Despite significant differences between lake types in sedimentation and % sediment OM content, there was no significant difference in the rate of methanogenesis

($\mu\text{mol CH}_4/\text{m}^2/\text{day}$) between lakes types (Figure 6), and methanogenesis was not found to change significantly with depth (Figure 7). Although Kling et al. (1992) did not find any significant correlation between size, depth or latitude and CH_4 emission in arctic lakes, several studies have found that lake methanogenesis is easily predicted by factors such as lake morphometry, depth, organic input and temperature (Bartlett et. al 1992, Kelly and Chynoweth 1981, Zeikus and Winfrey 1976). In order to determine what measured variables served as the best predictors for lake sediment methanogenesis, multiple regression models based on all available data were constructed.

Differences in dissolved oxygen concentrations were found to explain approximately 6% of sediment methanogenesis, with a negative Pearson's correlation coefficient of -0.355 (Table 4). As methanogenesis is a strictly anaerobic process, lake sediment methanogenesis is negatively correlated with hypolimnetic O_2 saturation, and is often optimized when O_2 saturation is below 5% (Juutinen et al. 2008). Once anaerobic conditions are established, temperature and organic substrate are critical limiting factors for methanogenesis, as warmer temperatures and direct (H_2 or acetate) or indirect (glucose or leaf leachate) methanogenic substrates enhance CH_4 production in sediments (Segers 1998). Factors such as water temperature and the composition of organic materials deposited in lake sediments may vary both between and within lakes.

The interaction variable between depth (m) and the temperature of the sampling location ($^{\circ}\text{C}$) was found to be a significant predictor of sediment methanogenesis in the presence of other measured variables, and temperature exhibited positive Pearson's correlation coefficients (0.228, $p = 0.04$) with sediment methanogenesis (Table 4). Spatial

variation in sediment CH₄ production within lakes may occur due to a heterogeneous distribution of OM and temperature along a gradient of lake zonation. Littoral sediments in lakes typically are warmer and receive a majority of the OM loading from terrestrial sources. In contrast, profundal sediments, characterized by low temperatures, are often richer in OM derived from autochthonous sources (Murase and Sugimoto 2001). The results of this study indicated that there was a weak negative trend between lake depth and methanogenesis in both lake types (One-way ANOVA, $p = 0.06$). However, a significant relationship was not found in either lake type between depth and sediment organic content, and sediment OM was not found to be a reliable predictor in either regression model.

The Q_{10} of most methanogens is approximately 2.4, with an optimum of approximately 35°C (Kelly and Chynoweth 1981). Additionally, there is evidence that sediment methanogen density is correlated with lake sediment temperature (Zeikus and Winfrey 1976). The average water temperatures of samples taken at the bank and maximum depth of each lake were 10.2°C and 4.7°C, respectively. However, all cores were incubated at 8°C for 24h to measure the rate of sediment methanogenesis. Although this temperature represented a realistic mean between temperatures found at lakes for each core sample, controlling for temperature in all cores from all lakes limited this study's ability to estimate rate of methanogenesis within a lake or on a whole-lake basis. However, incubating cores at the same temperature provided the opportunity to evaluate effects of sediment type or quality on rate of methanogenesis. A study of lake methanogenesis at three depths (shallow, intermediate and maximum) found that lake

methanogenesis increased with depth when incubating sediment samples at similar temperatures to their origin in a lake (Zeikus and Winfrey 1976).

Regression analysis and subsequent Pearson's correlation coefficients suggest that glacial surface may influence sediment methanogenesis (Table 4). Glacial deposits of the older (50,000-120,000 years old) Itkillik I drifts of the central Brooks Range glacial succession contain soils that are generally more moist and acidic than the soils of the younger (11,500-25,000) Itkillik II glacial drifts (Hamilton 2002). Additionally, the total soil organic C (g/m^2) is considerably different with regard to the two glacial surfaces, as previous studies found Itkillik I drifts contained 373 g/m^2 soil organic carbon compared to Itkillik II drifts which contained 701 g/m^2 soil organic carbon (Hobbie et al. 2002). DOC values in the water column of thermokarst Lake I- Minus (younger surface) were elevated compared to that of Lake NE14 (older surface), and the analysis of a Pearson's correlation matrix yielded a negative correlation between the age of the underlying glacial surface of a lake and water column DOC values (-0.224). These factors suggest that thermokarst erosion from younger, carbon-rich soils may influence sediment methanogenesis as a pathway for DOC metabolism to a greater extent than thermokarst erosion from older glacial surfaces. However, this study was not designed to determine the contribution of permafrost derived OM as fuel for methanogenesis, thus, further research on this topic is needed.

Water column DOC (mg/L) was found to be a reliable predictor of sediment methanogenesis only in the presence of other variables (Table 4). Water column DOC (epilimnion and hypolimnion) was significantly greater in reference lakes than in

thermocarst lakes ($t = 1.97$, d.f. = 4, $p = 0.04$). A study of 22 lakes in small upland catchments in Northwest Canada (11 pristine lakes and 11 lakes affected by thermocarst slumping) also found that the mean DOC concentration in pristine lakes was greater than the mean concentration in thermocarst lakes (Kokelj et al. 2005). A Pearson's product-moment correlation coefficient indicates that there is a significant positive relationship between water column DOC and the catchment area:lake area ratio in reference lakes ($r = .979$, $n = 3$, $p < 0.001$), suggesting that the shallow, organic soils surrounding reference lakes may enhance the transport of DOC to lakes. In contrast, a negative relationship between these two variables was found in thermocarst lakes ($r = -.443$, $n = 3$, $p = 0.08$), suggesting that the percentage of the catchment area disturbed by thermocarst erosion exerts a negative influence on DOC concentrations in the water column of thermocarst lakes. A similar negative relationship between percentage of lake catchment area affected by disturbance (a factor unmeasured in this study) and water column DOC concentrations was found in a study of Canadian thermocarst lakes (Kokelj et al. 2005). However, regression models indicated that water column DOC values explained only 3% of the variation in sediment methanogenesis (Equation 4, Table 4). Therefore, it is reasonable to conclude that although thermocarst erosion has an influence on DOC concentration in lake water compared to reference lakes, water column DOC values alone are not reliable predictors for arctic lake methanogenesis.

Approximately 31% of sediment methanogenesis was not explained by measured variables in regression models. This suggests that 1) larger sample sizes are needed at all depths to more accurately quantify CH_4 production, and 2) other, unmeasured variables

likely exist as important predictors regarding arctic lake methanogenesis. Landscape factors such as differences in active layer depths, glacial surface chemistry, runoff and vegetation may also influence the delivery of methanogenic substrates and sediment load to lakes, which may yield important differences between lake types. For instance, isotopic analysis of lake sediment $\delta^{13}\text{C}$ indicated that thermokarst erosion may contribute significant amounts of carbonate to the sediment microbial community. As the age of the landscape surrounding a lake can have a strong influence on lake biogeochemistry, the till from glaciations originating in the Brooks Range study site suggests that the basic till in the region is carbonate rich (Hamilton 2002). Over time, carbonates originating in glacial surfaces leach out, a factor which influences calcium and bicarbonate concentrations in lakes and streams in this region (Quesada et al. 2006). Stiller and Magaritz (1974) found that the $\delta^{13}\text{C}$ of CaCO_3 in lake sediments is typically enriched, with $\delta^{13}\text{C}$ values ranging from -3 to -1‰. The $\delta^{13}\text{C}$ of surficial sediment samples taken at the bank location of NE14 directly adjacent to the thermokarst input ranged from -5.45 to -4.49‰, which were considerably enriched compared to surficial sediments taken at the bank depths of all reference lakes (-28.16 to -30.74‰) and thermokarst lakes I-Minus and Campsite (-27.85 to -29.83 ‰). As NE14 demonstrates the greatest degree of thermokarst activity, these results suggest that thermokarst erosion may influence the delivery of carbonates to the lake sediment microbial community. Carbonate may also provide a carbon source for hydrogenotrophic methanogens, as bicarbonate may readily form water and carbon dioxide in an aqueous solution (Altheide et al. 2007). Therefore, methanogens utilizing the hydrogenotrophic pathway may utilize the free hydrogen and CO_2 from carbonate

precursors supplied by thermokarst erosion. As the rate of methanogenesis in sediment samples taken adjacent to the thermokarst in lake NE14 ($1042 \mu\text{mol CH}_4/\text{m}^2/\text{day}$) was greater than that found at the maximum depth of the lake ($660 \mu\text{mol CH}_4/\text{m}^2/\text{day}$), it cannot be ruled out that enhanced carbonate delivery from landscape erosion may be a factor influencing methanogenesis. However, as these lakes are supersaturated in CO_2 , it is unlikely that methanogens are limited by available CO_2 alone (Cole et al. 1994).

Thermokarst runoff DIC values provide additional indirect evidence of inorganic carbon delivery from thermokarst processes, as DIC values of thermokarst runoff from NE14 (55 to 78 mg/L) were elevated relative to bank runoff from reference lakes (14.46 to 56.33 mg/L), and were greater than DIC values obtained from the thermokarst runoff of I-Minus (22.39 mg/L) and Campsite (1.3 mg/L), which exhibit declining degrees of thermokarst activity respectively (Table 2). If indeed thermokarst processes enhance the delivery of carbonates to lake sediments, then there may be a trend in thermokarst lakes towards elevated alkalinity over time. Although hydrogenotrophic and acetoclastic methanogenesis may occur at pH values as low as 4, Goodwin and Zeikus (1987) demonstrated that the optimal pH for methanogenesis is typically between 5-6, with some alkaliphilic methanogens tolerating pH values between 8 and 9. Therefore, carbonate delivery from the weathering of exposed mineral soils, such as those exposed by thermokarst processes, may provide indirect substrates for methanogens, which may stimulate CH_4 production regardless of slightly alkaline conditions.

Methane oxidation was not found to differ significantly between reference and thermokarst lakes when all depths were considered ($p = 0.158$, $t = 1.47$, d.f. = 4), and

regression analysis indicated that the most useful predictors of methane oxidation from all variables measured were rate of sediment methanogenesis ($\mu\text{mol CH}_4/\text{m}^2/\text{day}$) and hypolimnetic DO (mg/L) (Table 5). Although known freshwater methane-oxidizing bacteria are predominately obligate methanotrophs, all are obligate aerobes capable of acquiring energy from the oxidation of CH_4 when terminal electron acceptors such as oxygen are present (Whalen 2005, Brune et al. 2000). All lakes sampled contained hypolimnetic oxygen, and methanogenesis was detected at all depths within each lake. Therefore, CH_4 and O_2 availability are main factors limiting the activity of methanotrophs, as they occur primarily at the oxic/anoxic interface in aquatic sediments (Lampert and Sommer 1997, Brune et al. 2000, Le Mer and Roger 2001). The input of degradable OM to the sediment is correlated with both methanogenesis and methane oxidation (Brune et al. 2000), and DOC loading to lakes from the landscape in this region is very high (Whalen and Cornwell 1985). However, neither water column DOC nor the %OM of lake sediments was found to be reliable predictors of either microbial process in the absence of other variables.

The amount of carbon stored in the OM of arctic permafrost is considerable. However, the results of this study do not indicate that climate warming-induced permafrost thaw and subsequent thermokarst erosion along lake margins significantly enhances lake sediment methanogenesis. Furthermore, the isotopic results coupled with the sediment trap and sediment organic content indicate that thermokarst erosion may enhance the delivery of weathering products, such as carbonates, to the surficial sediments adjacent to thermokarst features.

CHAPTER VI

CONCLUSION

Results of this study indicate that while rates of methanogenesis and methane oxidation are considerable in reference and thermokarst lakes, thermokarst lakes do not produce significantly greater rates of CH₄ than reference lakes. On a regional scale, the rates of arctic lake sediment methanogenesis recorded in this study (3-116 mg CH₄/m²/d) were within the range of those measured in northern wetlands (40 mg CH₄/m²/d), yet lower than rates measured in temperate (150 mg CH₄/m²/d) and tropical (199 mg CH₄/m²/d) wetlands (Cao et al. 1996). Methanogenesis does not change significantly from locations adjacent to lake shores to maximum depths within each lake type. Thermokarst activity does significantly enhance sediment delivery to lakes, with increases in inorganic sedimentation rate associated with degree of thermokarst activity within lakes. As a likely consequence, thermokarst lake sediments contain significantly less % OM than reference lakes. Additionally, the results of this study suggest that the carbon content of the glacial surface may influence DOC within the water column of thermokarst lakes. The most important factors pertaining to lake methanogenesis appear to be glacial till, DO (mg/L), the catchment area:lake area ratio, and the interaction variable between depth (m) and temperature (°C) and water column DOC concentration.

The effects of thermokarst activity on methanogenesis, methane oxidation and sediment CH₄ flux to the atmosphere are poorly understood in arctic lakes; therefore,

further research is needed to determine the effects of thermokarst erosion on arctic lake biogeochemistry, as thawing permafrost is likely to increase with climate warming in the Arctic environment. As the resulting ecological responses to increased permafrost thawing remain unknown, processes that may transfer permafrost carbon to the atmosphere, such as increased microbial decomposition of previously frozen organic carbon on the landscape, may represent a very significant potential feedback to climate change. However, it is not evident from this study that thermokarst erosion along shore margins in deep lakes acts as a positive feedback to climate warming in the Arctic.

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APPENDIX A. TABLES

Table 1. Study Sites. Each control lake (E1, Toolik, and NE12) was chosen as a complement to the three thermokarst lakes (I Minus, Campsite and NE14) based on similarities in maximum depth.

| Lake | Type | Location | Elevation (m) | Catchment Area:Lake Area | Maximum Depth (m) | Glacial Till |
|----------|-------------|--------------------------|---------------|--------------------------|-------------------|--|
| I Minus | Thermokarst | 68° 31' N, 149° 35' W | 825 | 5.8 | 15.5 | Drift of Iktillik Phase II, Outwash of Iktillik Phase II |
| E1 | Reference | 68°38' N, 149°33' W | 771 | 35.7 | 13.5 | Drift of Iktillik Phase I |
| Campsite | Thermokarst | 68° 36' N, 149° 11' W | 864 | 1.63 | 27.4 | Drift of Iktillik Phase I, Outwash of Iktillik Phase II |
| Toolik | Reference | 68° 38' N, 149° 36' W | 720 | 44.9 | 25 | Drift of Iktillik Phase II, Outwash of Iktillik Phase II |
| NE14 | Thermokarst | 149° 62' N, 68° 67' W | 699 | 3.23 | 18.2 | Drift of Iktillik Phase II, Active tundra earthflow |
| NE12 | Reference | 149° 62' N, 68° 66' W | 693 | 17 | 17.5 | Drift of Iktillik Phase II |

Table 2. DOC, DIC, $\delta^{13}\text{C}$ -DOC and $\delta^{13}\text{C}$ -DIC values for bank runoff (Thermokarst or Reference Lake) and water column (epilimnion and hypolimnion). Toolik Bank DIC data was unavailable.

| Thermokarst Lake | Sample Type | Date | DOC (mg/L) | $\delta^{13}\text{C}$-DOC | DIC (mmol/L) | $\delta^{13}\text{C}$-DIC |
|------------------------------|----------------------|-------------|-------------------|---|---------------------|---|
| I - Minus | Epilimnion | 25-Jul-08 | 6.5 | -27.1 | 0.5 | -7.3 |
| I - Minus | Hypolimnion | 14-Jul-08 | 6.0 | -28.1 | 0.6 | -10.8 |
| NE14 | Upper Thermokarst | 3-Jul-08 | 20.0 | -26.4 | 4.6 | -6.9 |
| NE14 | Lower Thermokarst | 3-Jul-08 | 70.5 | -21.8 | 6.5 | -7.7 |
| NE14 | Runoff Entering Lake | 3-Jul-08 | 3.7 | -26.4 | 1.7 | -3.9 |
| NE14 | Epilimnion | 3-Jul-08 | 3.0 | -23.8 | 1.7 | -3.9 |
| NE14 | Hypolimnion | 3-Jul-08 | 4.0 | -25.7 | 2.2 | -4.8 |
| Campsite | Thermokarst | 3-Jul-08 | 2.3 | -28.8 | 0.1 | -24.7 |
| Campsite | Epilimnion | 12-Jul-08 | 2.4 | -27.4 | 0.5 | -3.2 |
| Campsite | Epilimnion | 12-Jul-08 | 2.5 | -27.4 | -.5 | -3.8 |
| <u>Reference Lake</u> | | | | | | |
| Toolik | Hypolimnion | 7-Jul-08 | 4.7 | -27.9 | 0.8 | -7.7 |
| Toolik | Epilimnion | 7-Jul-08 | 5.0 | -28.6 | 0.7 | -5.2 |
| Toolik | Bank | 2-Jul-08 | 5.8 | -27.6 | N/A | N/A |
| E1 | Bank | 2-Jul-08 | 51.2 | -26.6 | 1.2 | -11.3 |
| E1 | Epilimnion | 1-Jul-08 | 6.6 | -27.7 | 0.7 | -6.2 |
| E1 | Hypolimnion | 1-Jul-08 | 6.0 | -26.8 | 0.8 | -7.3 |
| NE12 | Bank | 8-Jul-08 | 10.0 | -27.4 | 4.7 | -12.2 |
| NE12 | Epilimnion | 8-Jul-08 | 3.9 | -30.0 | 1.6 | -6.4 |
| NE12 | Hypolimnion | 18-Jul-08 | 2.8 | -27.8 | 2.0 | -7.1 |

Table 3. Methanogenesis, methane oxidation and sediment CH₄ flux to the atmosphere ($\mu\text{molCH}_4/\text{m}^2/\text{day}$) by depth in thermokarst and reference lakes. Depths represent low, intermediate and deep respectively. Methanogenesis, methane oxidation and sediment CH₄ flux are reported as mean and standard deviation at each depth.

| Lake | Thermokarst Present | Depth (m) | Methanogenesis ($\mu\text{mol CH}_4/\text{m}^2/\text{day}$) | CH ₄ Oxidation ($\mu\text{mol CH}_4/\text{m}^2/\text{day}$) | Net CH ₄ flux from the sediment to the water column ($\mu\text{mol CH}_4/\text{m}^2/\text{day}$) |
|-----------|---------------------|-----------|---|--|---|
| E1 | No | 5.6 | 4232 (\pm 1650) | 2242 (\pm 747) | 1990 |
| | | 7.3 | 347 (\pm 111) | 2159 (\pm 990) | 0 |
| | | 13.5 | 7300 (\pm 610) | 10556 (\pm 5967) | 0 |
| NE12 | No | 1.5 | 1718 (\pm 382) | 894 (\pm 307) | 824 |
| | | 9.4 | 262 (\pm 155) | 53 (\pm 4) | 208 |
| | | 16.8 | 202 (\pm 2) | 27 (\pm 54) | 175 |
| Toolik | No | 8.1 | 424 (\pm 158.42) | 210 (\pm 108) | 214 |
| | | 11.4 | 951 (\pm 247) | 426(\pm 176) | 525 |
| | | 19.1 | 198 (\pm 42) | 224 (\pm 109) | 0 |
| Campsite | Yes | 5.9 | 2109 (\pm 217) | 238 (\pm 127) | 1871 |
| | | 12.7 | 322(\pm 199) | 42 (\pm 40.8) | 280 |
| | | 18.3 | 242 (\pm 79) | 109 (\pm 117) | 133 |
| NE14 | Yes | 0.75 | 1042 (\pm 590) | 929 (\pm 517) | 113 |
| | | 9.3 | 1396 (\pm 632) | 84 (\pm 18) | 1312 |
| | | 18.2 | 660 (\pm 106) | 1168 (\pm 685) | 0 |
| I - Minus | Yes | 1.2 | 967 (\pm 307) | 420 (\pm 554) | 546 |
| | | 8.1 | 964 (\pm 174) | 111 (\pm 32) | 853 |
| | | 15.5 | 1191(\pm 300) | -314 (\pm 288) | 1190 |

Table 4. Regression Equations for Lake Sediment Methanogenesis. Abbreviations used: HDOC, water column dissolved organic carbon (mg/L); DO, hypolimnetic dissolved oxygen (mg/L); Till, Glacial Till (age rank); TxD, the interaction variable between temperature (°C) and depth of sample (m); CALA, catchment area:lake area. All significant equations are reported at $p < 0.05$

| Regression Equations | (n = 72) | Adj. R ² | Sig. |
|---|----------|---------------------|-------|
| 1. $\log \text{CH}_4 = 5.867 + 0.684(\text{Till})$ | | 0.39 | <0.01 |
| 2. $\log \text{CH}_4 = 6.882 + 0.622(\text{Till}) - 0.330(\text{TxD})$ | | 0.53 | <0.01 |
| 3. $\log \text{CH}_4 = 6.638 + 0.696(\text{Till}) - 0.268(\text{CALA}) - .257(\text{TxD})$ | | 0.60 | <0.01 |
| 4. $\log \text{CH}_4 = 4.885 + 0.514(\text{Till}) - 0.443(\text{CALA}) + .304(\text{HDOC}) - .179(\text{TxD})$ | | 0.63 | <0.01 |
| 5. $\log \text{CH}_4 = -3.411 + 1.269(\text{HDOC}) - 1.106(\text{CALA}) + .313(\text{Till}) - .124(\text{TxD}) - .117(\text{DO})$ | | 0.69 | <0.01 |

Table 5. Regression Equations for Lake Sediment Methane Oxidation. Abbreviations used: CH₄, methanogenesis; DO, hypolimnetic dissolved oxygen (mg/L). All significant equations are reported at p < 0.05

| Regression Equations | (n = 54) | Adj. R ² | Sig. |
|---|----------|---------------------|-------|
| 1. log methane oxidation = 8.733 + .619(DO) | | 0.38 | <0.01 |
| 2. log methane oxidation = 4.488 + .482(DO) + .447(logCH ₄) | | 0.56 | <0.01 |

APPENDIX B. FIGURES

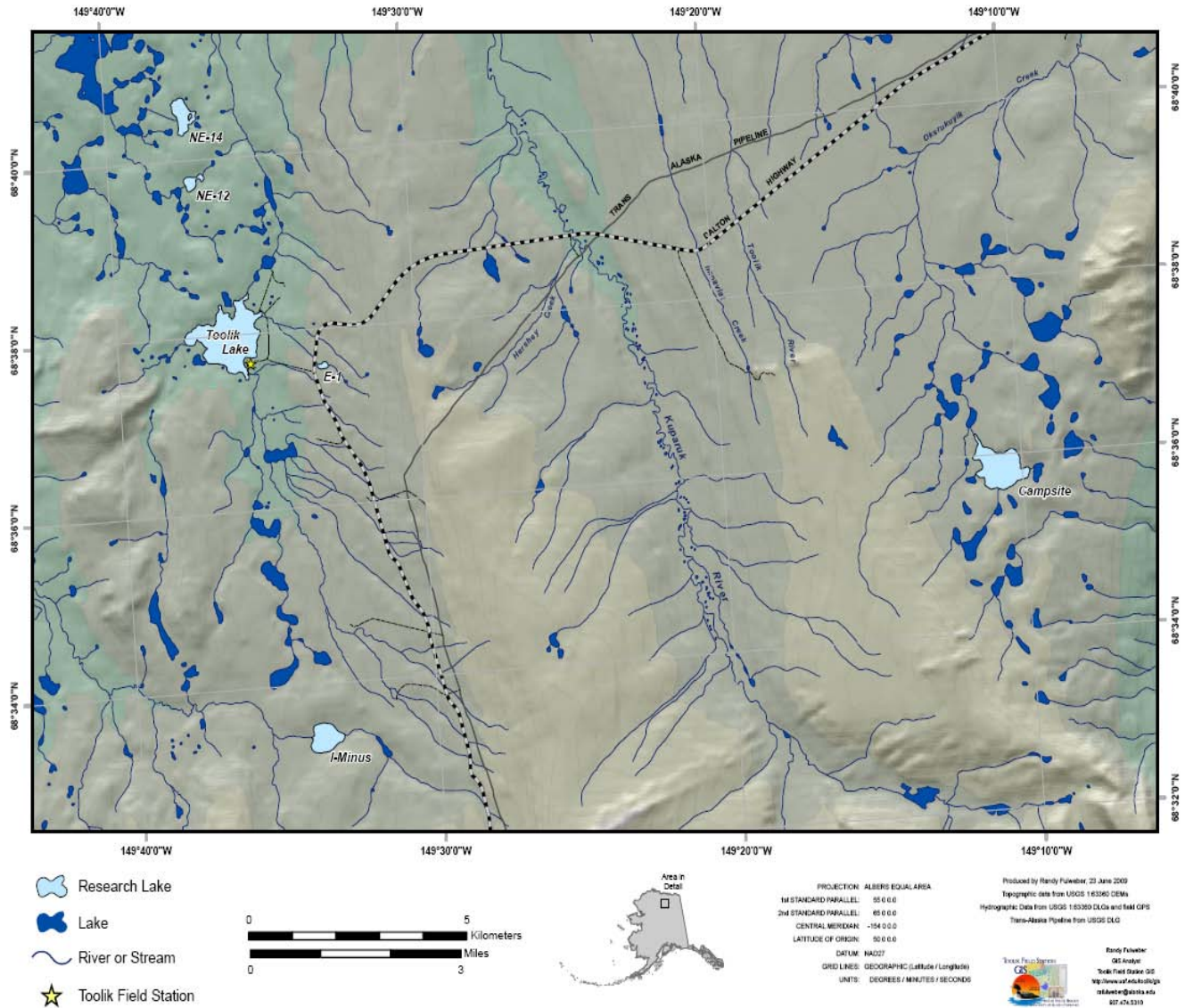


Fig 1: Study Sites. Six lakes were examined near Toolik Lake, Alaska (68° N, 149° W) in the Northern Foothills of the Brooks Range.

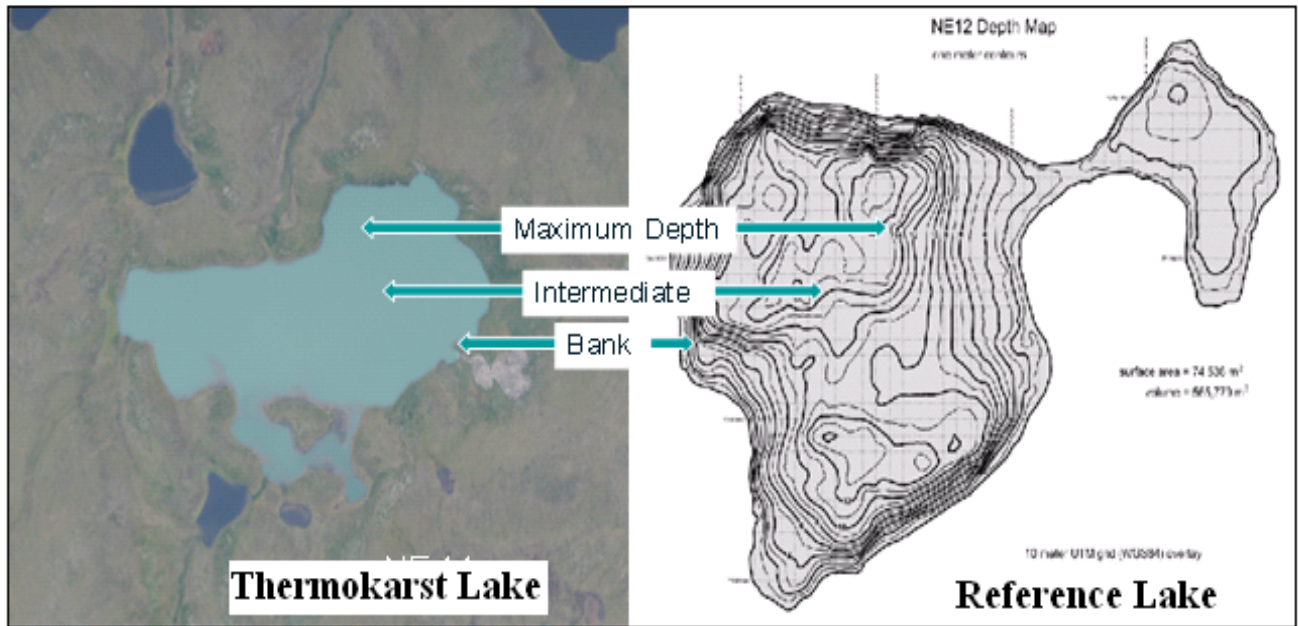


Figure 2: Sampling Methods. 21 sediment cores (7 shallow, 7 bank and 7 intermediate) were sampled from reference lakes (E1, Toolik and NE12) at similar depths from their thermokarst lake counterparts (I Minus, Campsite, and NE14 respectively). Bathymetric maps facilitated the location of these depths in reference lakes.

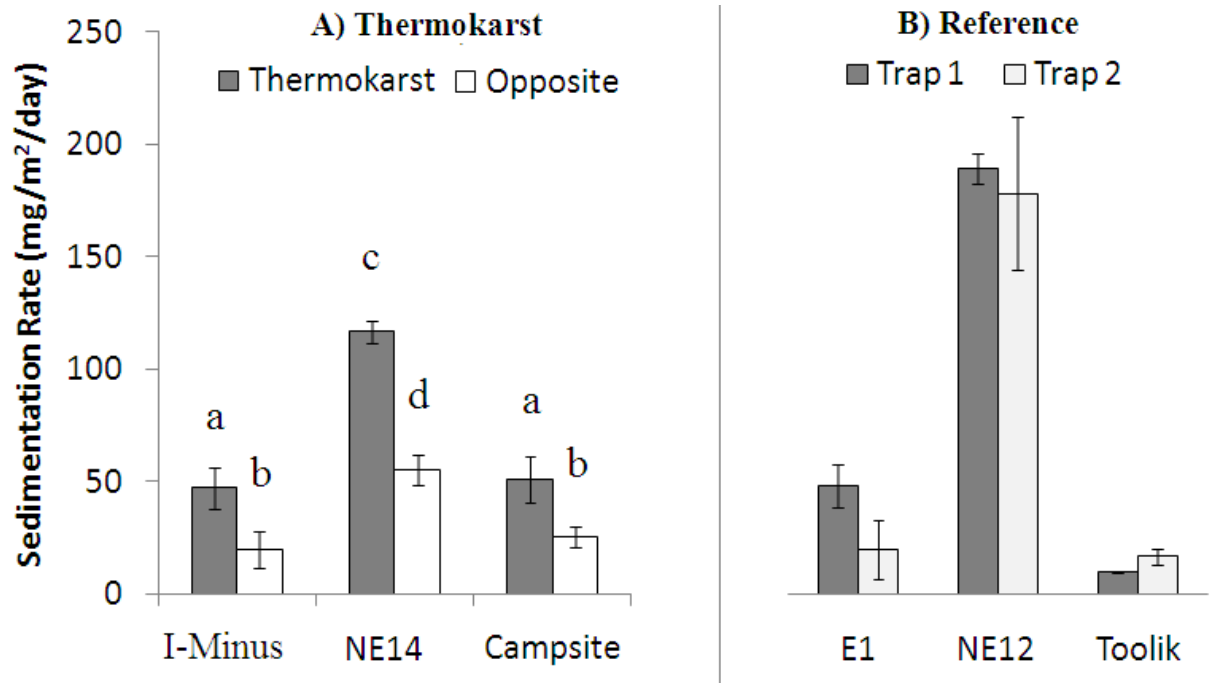


Figure 3. AFDM sedimentation rates for A) lakes with the presence of an adjacent thermokarst feature and B) reference lakes without the presence of an adjacent thermokarst feature. Significant differences in sedimentation rate were not found between sediment traps placed on opposite sides of all three reference lakes. Significant differences in sedimentation rate were found between sediment traps placed near an active thermokarst and sediment traps placed opposite of the active thermokarst for all three lakes with the presence of an adjacent thermokarst feature. Standard error is reported as SEM ($n = 4$). Significant differences between sediment traps are denoted by different letters.

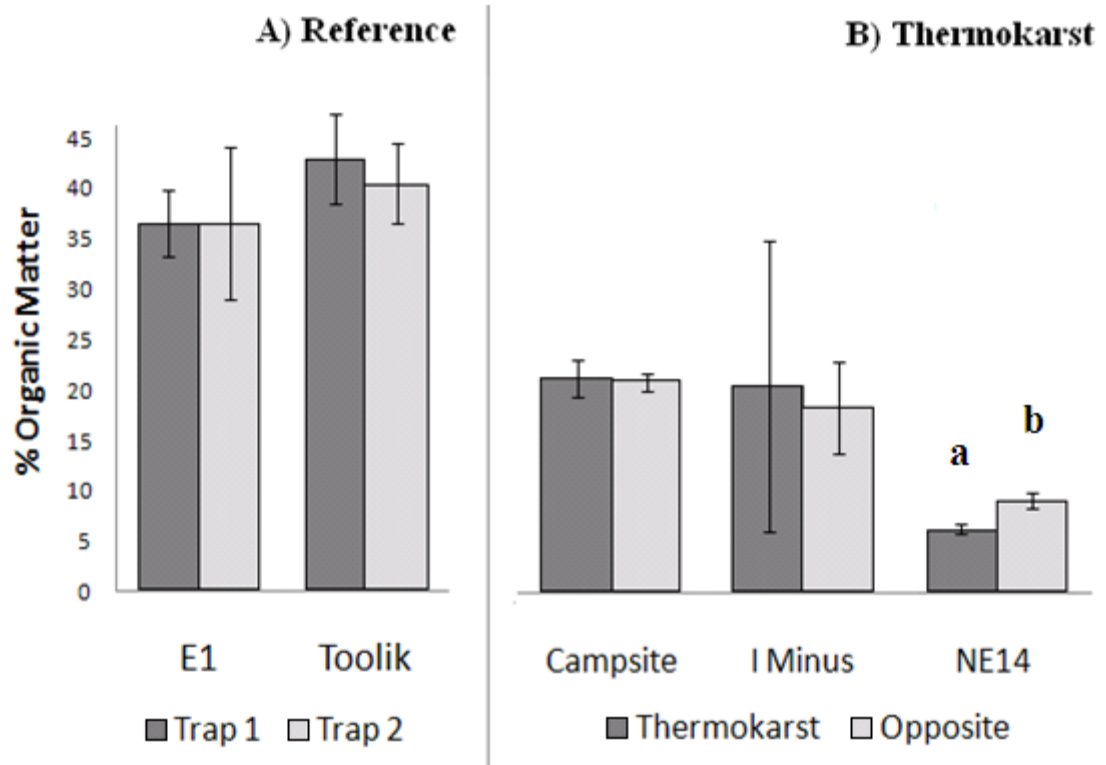


Figure 4. Percent organic matter of sedimentation between opposite traps placed within A) Reference Lakes and B) Thermokarst Lakes. Standard error is reported as SEM (n = 4) Significant differences between opposite traps placed within each lake are denoted by different letters.

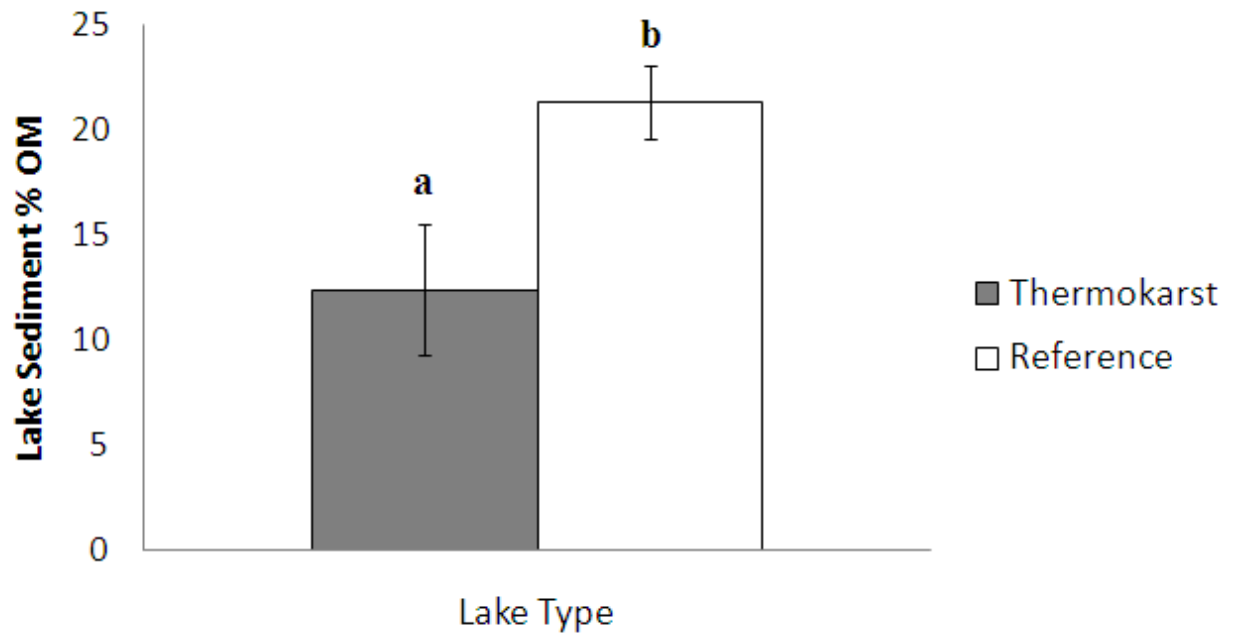


Figure 5. Sediment % OM content by lake type. Standard error is reported as SEM (n= 3). The mean % OM content in lake sediment samples (bank, intermediate and Zmax) in reference lakes (21.3%) was significantly greater than that of thermokarst lakes (12.4%) ($t = -4.38$, $df = 4$, $p = 0.006$). Standard error is reported as SEM (n= 3). Significant differences between lake types are denoted by separate letters.

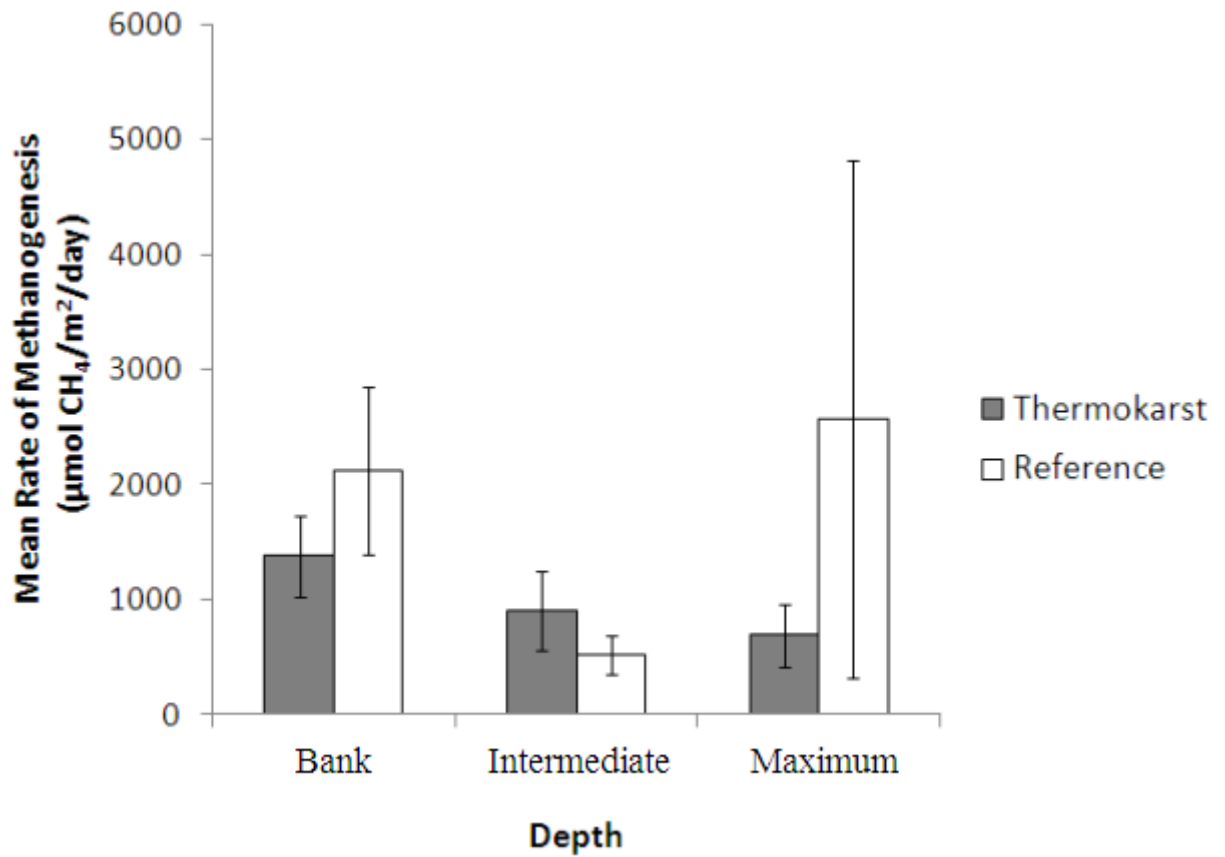


Figure 6. Mean rate of methanogenesis by sampling depth (bank, intermediate and maximum depth sampled) in reference and thermokarst lakes. There was no significant difference in mean rate of methanogenesis between lake types at any depth sampled. When all depths were considered at once, there was no significant difference in the median rate of methanogenesis between lake types after log transformation to meet the assumptions for normality ($p = 0.3$, $t = 0.6$, $df = 2$). Standard error is reported as SEM ($n = 3$).

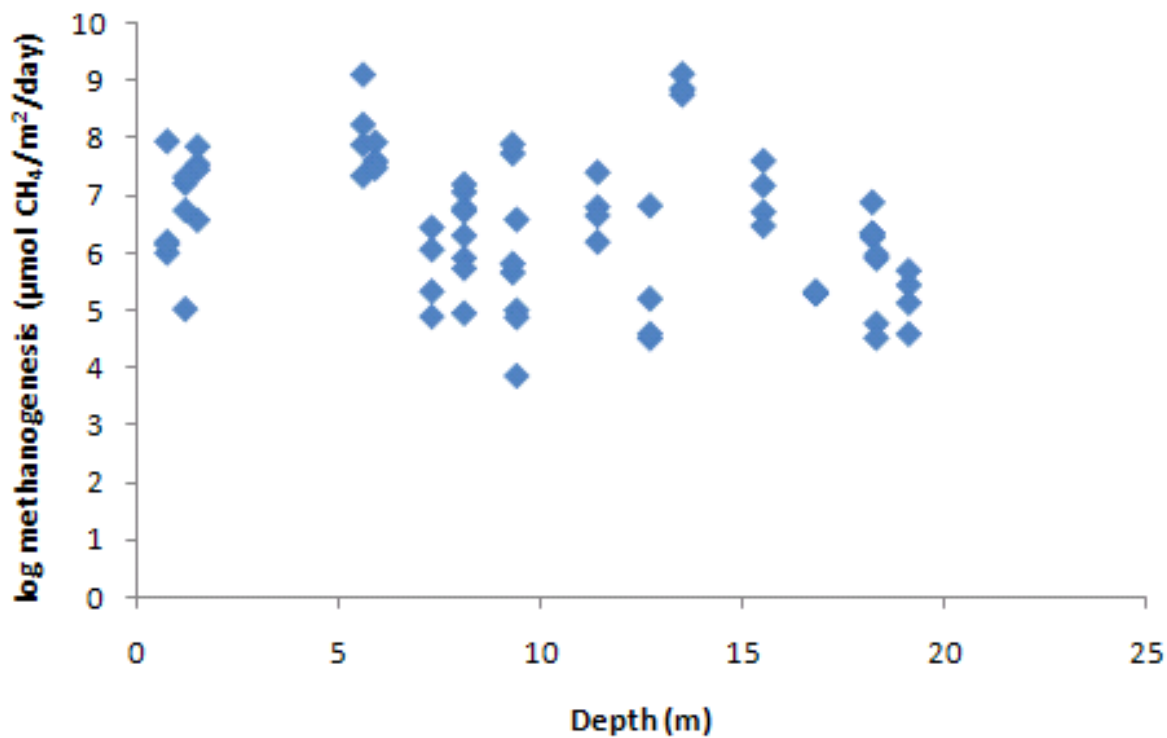


Figure 7. Log $\mu\text{mol CH}_4/\text{m}^2/\text{day}$ by lake depth (m). No significant difference in median rate of CH_4 production ($\mu\text{mol CH}_4/\text{m}^2/\text{day}$) was found between lake types after accounting for differences in depth.