# SEDIMENT EMISSION AND WATER COLUMN OXIDATION OF METHANE IN ALASKAN ARCTIC LAKES

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## ABSTRACT

## GABRIEL E. McGOWAN: Sediment Emission and Water Column Oxidation of Methane in Alaskan Arctic Lakes (Under the direction of Stephen C. Whalen)

Methane (CH<sub>4</sub>) is a greenhouse gas and is important in lacustrine food webs. Cycling of CH<sub>4</sub> in arctic lakes is poorly quantified, though arctic wetlands are key to the atmospheric CH<sub>4</sub> budget. Sediment emission and water column oxidation of CH<sub>4</sub> were studied in 3 shallow and 3 deep Alaskan arctic lakes during the 2010 and 2011 thaw seasons. Sediment CH<sub>4</sub> emission was oxygen-regulated and significantly higher in shallow lakes, averaging 1.39 mmol m<sup>-2</sup> d<sup>-1</sup>. Methane comprised a larger fraction of sediment catabolism in shallow lakes. Water column CH<sub>4</sub> oxidation was significantly greater in shallow lakes, averaging 0.16 mmol m<sup>-2</sup> d<sup>-1</sup>, with specific rates in bottom waters among the highest reported. Air-water CH<sub>4</sub> exchange ranged up to 1.94 mmol m<sup>-2</sup> d<sup>-1</sup> in shallow lakes, similar to rates reported for tropical lakes. The data show that CH<sub>4</sub> is important in C cycling in shallow Alaskan arctic lakes, which emit considerable CH<sub>4</sub> despite extensive CH<sub>4</sub> oxidation.

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### I. INTRODUCTION AND REVIEW OF THE LITERATURE

#### i. Context and Relevancy

Anthropogenic emissions since the Industrial Revolution, primarily from fossil fuel combustion and changes in land use patterns, have led to a marked increase in global atmospheric mixing ratios of the greenhouse gases carbon dioxide ( $CO_2$ ), methane ( $CH_4$ ), and nitrous oxide ( $N_2O$ ). Linked to these emission increases has been a warming of the global climate system, manifested in rising average surface and ocean temperatures, pervasive wasting of glaciers and sea ice, and increases in average sea levels (IPCC, 2007).

Globally, there was a 0.74°C increase in surface temperatures between 1906 and 2005 (IPCC 2007), and 2009 and 2010 are the warmest years on record (Foster and Rahmstorf, 2011). The IPCC predicts that global average temperature will be 1.4°C warmer than it is today by 2050; for areas above 60°N latitude, temperatures are predicted to rise 2.5°C by 2050, and as much as 7°C by 2100 (Kattsov et al., 2005). The Arctic has already warmed substantially since the last ice age, and is currently experiencing its warmest temperatures in 400 y (Overpeck et al., 1997). Observed effects of this warming on the continental Arctic include permafrost degradation (Osterkamp and Romanovsky, 1999; Osterkamp et al., 2000; Clow and Urban, 2002; Romanovsky et al., 2002, Yoshikawa and Hinzman, 2003), a longer annual ice-free period for lakes and rivers (Magnuson et al., 2000), and a longer growing season (Stow et al., 2003; Jia et al., 2003).

#### ii. Methane as a Greenhouse Gas

Methane accounts for about 20% of all radiative forcing by trace atmospheric constituents, and is about 21 times more efficient as a greenhouse gas on a per molecule basis than CO<sub>2</sub> (Whalen, 2005). Ice core records indicate that the atmospheric CH<sub>4</sub> mixing ratio correlates closely with atmospheric temperature (Wuebbles and Hayhoe, 2002). The current atmospheric  $CH_4$  mixing ratio is thought to be the highest over the last 650,000 y or more (Spahni et al., 2005), and has increased from 650 to around 1800 parts per billion by volume (ppbv) in the last 200 y (Lelieveld et al., 1998). This mixing ratio represents an increase of about 30% from early 1980s levels (IPCC, 2007). The rate of increase slowed in the late 1980s and the 1990s (Dlugokencky et al., 1998; Simpson et al., 2002), and the atmospheric  $CH_4$  mixing ratio was roughly constant in the early 2000s (Dlugokencky et al., 2003). However, in recent years the CH<sub>4</sub> mixing ratio has begun to increase again (Rigby et al., 2008). Natural wetlands represent the single largest source of  $CH_4$  to the atmosphere, releasing about 145 Tg of  $CH_4$  each year, which corresponds to around 24% of total annual CH<sub>4</sub> emissions from all identified sources (Lelieveld et al., 1998); methane emissions from freshwater lakes are estimated to exceed those from the oceans (Bastviken et al., 2004).

#### iii. The Arctic as an Atmospheric Methane Source

Approximately 50% of global wetlands are located in the Arctic and sub-Arctic (Matthews, 2000), and about 14% of the global soil carbon pool is stored in tundra environments (Post et al., 1982). As such, many research efforts have focused on quantifying CH<sub>4</sub> dynamics in and emission from Arctic tundra, and reported magnitudes of annual

emission vary between around 8 Tg and 68 Tg CH<sub>4</sub> (Whalen and Reeburgh, 1988, 1990a, 1992; Bartlett et al., 1992; Reeburgh, 1996; Zhuang et al., 2004). Arctic wetlands undergo an annual CH<sub>4</sub> emission cycle defined by the ice-free summer growing season, which accounts for most of the total yearly CH<sub>4</sub> emitted (Whalen, 2005). In the last half century, Arctic tundra ecosystems have shifted from net sinks to net sources of carbon (Oechel et al., 1993, 1995, 2000). Climate change is expected to increase CH<sub>4</sub> release from high latitude wetlands because of greater organic matter production during a longer growing season, as well as enhanced availability of organic matter due to permafrost thaw (e.g. Gedney et al., 2004; Hinzman et al., 2005; Zimov et al., 2005; Walter et al., 2006, 2008). However, climate change effects on emission-limiting CH<sub>4</sub> oxidation are uncertain (Whalen and Reeburgh, 1990a&b, 1992) and atmospheric CH<sub>4</sub> mixing ratios in the Arctic have been stable recently (Dlugokencky et al., 2009).

Permafrost underlies most of the Arctic, and changes in its extent and characteristics have been shown to correlate with fluctuations in climatic cycles (Lachenbruch and Marshall., 1986; Osterkamp, 2005). Arctic Alaska permafrost has warmed about 3°C since the 1980s (Osterkamp, 2005; Clow and Urban, 2002), leading to an increase in the occurrence of thermokarst features and the extent of the active layer (Nelson et al., 1998). Such changes in the permafrost regime can strongly influence carbon budgets in affected regions, in part by increasing nutrient availability in soils (IPCC, 2007); permafrost soils can have as much as thirty times the carbon content of unfrozen mineral soils (Zimov et al., 2005). Large increases in CH<sub>4</sub> release from high latitude wetlands undergoing permafrost thaw have been reported (e.g. Lawrence and Slater, 2005; Wickland et al., 2006), and isotope

analyses have shown much of the carbon in this  $CH_4$  dates to the Pleistocene and was previously stored in permafrost (Walter et al., 2006).

Lentic environments integrate watershed processes by accruing organic matter inputs, and substrate availability is, after the presence of  $O_2$ , the limiting factor to methanogenesis (Whalen, 2005). Therefore, it is conceivable that tundra lake sediments may surpass tundra soils in CH<sub>4</sub> production, and methanogenesis is expected to intensify with climate change. However, controls on CH<sub>4</sub> emission from Arctic lakes may differ fundamentally from those in tundra due to the nature of lake carbon cycling processes, and relatively few studies have attempted to constrain these processes in the shallow lakes and ponds that cover roughly 20 to 40% of the surface area of the Alaskan Arctic tundra (Livingstone et al., 1958; Black, 1969; Sellman et al., 1975).

#### iv. Lake Biogeochemical Processes

Lakes are generally heterotrophic systems, functioning as net atmospheric  $CO_2$ sources, and rely on detritus as a primary carbon source (del Giorgio et al., 1999; Cole et al., 2000; Hanson et al., 2003). This detritus is composed of mostly allochthonous dissolved organic carbon (DOC) and mostly autochthonous particulate organic carbon (POC) fractions; DOC tends to be more significant in oligotrophic lakes, where internal production is low (Biddanda et al., 2001). Decomposition, consisting of anaerobic and aerobic respiration as well as fermentation, provides a steady baseline energy source to the lake ecosystem and yields  $CO_2$  and  $CH_4$  (Wetzel, 2001). On a whole-lake basis, anaerobic processes can represent as much as 60% of carbon metabolism, with methanogenesis accounting for as much as 80% of anaerobic carbon mineralization (Bastviken et al., 2003). The exchange of

organic matter and nutrients across the sediment-water interface, coupled with microbefacilitated oxidation and reduction reactions, drives many lake biogeochemical processes. In turn, the spatial distribution and magnitude of these processes are largely dictated by dissolved oxygen conditions resulting from physical influences.

#### v. Methane in Lake Carbon Budgets

Under anoxic conditions in moist soils, wetlands and lake sediments, a suite of energy-yielding hydrolytic and fermentative reactions, catalyzed by anaerobic acid-forming bacteria, act on detritus to yield  $CO_2$  and saturated fatty-acid compounds. Methanogens, obligate anaerobes, metabolize these products in the terminal degradation step, methanogenesis, which can proceed along two primary pathways, although some groups show limited use of other simple compounds such as methylated amines (Wetzel, 2001). In the acetotrophic pathway, the fermentative intermediate acetate is disproportionated to  $CO_2$ and  $CH_4$ ; in the hydrogenotrophic pathway, hydrogen from organic acids enzymatically reduces  $CO_2$  to  $CH_4$ :

 $CH_3COOH \rightarrow CO_2 + CH_4$  (acetotrophic pathway);

 $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$  (hydrogenotrophic pathway).

Methane formed by these processes diffuses or bubbles upwards from the anaerobic zone of production, and is either oxidized under aerobic conditions by methanotrophic bacteria via

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_1$$

or emitted to the atmosphere (Utsumi et al., 1998a&b). Emission of  $CH_4$  from tundra soils is modulated by oxidation in the oxic surficial sediment layer (Whalen and Reeburgh, 1990). In contrast,  $CH_4$  diffusing from anoxic lake sediments is subject to oxidation in both oxic surficial sediments and an extensive, highly aerobic overlying water column prior to emission to the atmosphere (e.g. Fallon et al., 1980, Rudd and Taylor, 1980, Kuivila et al., 1988, Frenzel et al., 1990, Utsumi et al., 1998a&b, DeAngelis and Scranton, 1993, Kankaala et al., 2006). Most CH<sub>4</sub> oxidation in lakes occurs at the sediment-water interface if the bottom water is oxic, or in the water column at the lowest oxic depth, as these locations provide high concentrations of both O<sub>2</sub> and CH<sub>4</sub>. Above this zone, the process is limited by CH<sub>4</sub> concentration, and below, by O<sub>2</sub> concentration (Welch et al., 1980; Griffiths et al., 1982). Therefore, while CH<sub>4</sub> production in lake sediments may be greater in magnitude than in moist tundra soils due to more intense organic matter loading, lake sediment-generated CH<sub>4</sub> may be subject to more extensive oxidation prior to efflux from the lake surface. Methane that bubbles from anaerobic sediments, which may be an order of magnitude greater in quantity than CH<sub>4</sub> diffusing from anaerobic sediments, is not subject to significant oxidation unless trapped under ice cover (Walter et al., 2006, 2008).

Methanogenesis and CH<sub>4</sub> oxidation in lake sediments has been the subject of much research because of their role in lacustrine and global carbon budgets. Reported rates of net CH<sub>4</sub> release from the sediment of eutrophic, stratified lakes are often on the order of 10 mmol CH<sub>4</sub> m<sup>-2</sup>d<sup>-1</sup> (e.g. Rudd and Hamilton, 1978; Bedard and Knowles, 1991; Sweerts et al., 1991); for one artificially hyper-eutrophic lake, flux of CH<sub>4</sub> from profundal sediments into the anoxic hypolimnia averaged 35.8 mmol m<sup>-2</sup>d<sup>-1</sup>, a quantity of C equivalent to about 54% of all particulate C that settled from the water column (Fallon et al., 1980). For less productive lakes with oxic hypolimnia, and shallow, oxic zones of eutrophic lakes, net CH<sub>4</sub> fluxes from the sediments are typically < 1 mmol m<sup>-2</sup>d<sup>-1</sup> (e.g. Rudd and Hamilton, 1978; Kuivila et al., 1988). Ramlal et al. (1994) measured an average benthic CH<sub>4</sub> flux of

1.41mmol m<sup>-2</sup>d<sup>-1</sup> in a shallow Arctic tundra lake in Canada, and estimated that methanogenesis accounted for the majority of anoxic decomposition in the lake. In lakes with oxic bottom water,  $CH_4$  consumption in the oxidized microzone of the sediments can reduce net  $CH_4$  release by about 16 to 93% compared to the flux into the oxic surficial sediment layer from the anaerobic zone (Kuivila et al., 1988; Frenzel et al., 1990; Sweerts et al., 1991).

Water column microbial  $CH_4$  oxidation has been widely studied because of its dual role as a regulator of  $CH_4$  flux to the atmosphere and a pathway for carbon transfer from the benthic to the pelagic zone. Measurements and estimates of the proportion of CH<sub>4</sub> produced in lake sediments that is oxidized vary with lake characteristics. In general a significant fraction of this CH<sub>4</sub> is metabolized into CO<sub>2</sub> before it reaches the water-air interface; the percent of total CH<sub>4</sub> production accounted for by oxidation varies from about 30 to 94% (Fallon et al., 1980, Rudd and Taylor, 1980, Kuivila et al., 1988, Frenzel et al., 1990, Utsumi et al., 1998a&b, DeAngelis and Scranton, 1993, Kankaala et al., 2006). Several studies have examined  $CH_4$  oxidation in lakes with characteristics similar to those in this study, i.e. oligotrophic or mesotrophic lakes with highly oxic water columns. Estimates of the extent of lake CH<sub>4</sub> oxidized generally fall at the higher end of the range in the literature, between about 70% and 95%, with depth integrated rates of oxidation 0.05 to 6 mmol  $m^{-2}d^{-1}$  (Kuivila et al., 1988; Frenzel et al., 1990; Utsumi et al, 1998a&b; Kankaala et al., 2006). Area-based oxidation rates are higher in more productive lakes due to higher CH<sub>4</sub> concentrations, e.g. 23.3 mmol  $m^{-2}d^{-1}$  in Lake Mendota (Fallon et al., 1980).

Furthermore, CH<sub>4</sub> is an important vector of carbon and energy transfer from microbes in anoxic sediments to the oxic water column (Bastviken et al., 2003). Lake water column

organic carbon production from CH<sub>4</sub> oxidation can be comparable in magnitude to organic carbon production by all heterotrophic bacteria (Hessen and Nygaard, 1992), and even that by photosynthesizers on a seasonal basis (Utsumi et al., 1998b). The pivotal role of CH<sub>4</sub> dynamics in high-latitude lake carbon cycling has been illustrated by several groups: Bastviken et al. (2003) put methanotrophic bacterial production at 0.3 to 7% of organic C production by autotrophs in Swedish sub-Arctic lakes, while low  $\delta^{13}$ C values in zooplankton point to the importance of CH<sub>4</sub>-derived carbon in some pelagic food webs (Bastviken et al., 2003; Kanaaka et al., 2006). A study that artificially fertilized an Arctic lake with CH<sub>4</sub> found that the resulting CH<sub>4</sub> oxidation could account for 12% or more of the total lake respiration rate (Welch et al., 1980). In summary, CH<sub>4</sub> is important both in lacustrine food web dynamics and the global climate system, and these roles are likely magnified in the Arctic due to simple trophic structures (Roots, 1989) and the significance of high latitudes as a source of atmospheric CH<sub>4</sub>.

#### vi. Study Goals

The overall objective of this study was to assess critical components of  $CH_4$  cycling dynamics in representative Arctic lakes. To this end, I measured trace gas exchange at the sediment-water interface, including both  $CH_4$  and key gases ( $CO_2$ ,  $O_2$ ) associated with  $CH_4$  exchange, and oxidation of  $CH_4$  in the water column, and I estimated rates of air-water  $CH_4$  exchange. I focused on identifying any differences in the magnitude, characteristics and importance of these processes between shallow and deep Arctic lakes, and contrasted my data with lakes in more heavily studied regions. This study will provide a baseline measure of the importance of  $CH_4$  in the C budgets of Arctic lakes, against which the impact of future

climates can be appraised, and will provide input for process-based models and policy makers concerned with climate change.

#### II. METHODS

#### i. Study Sites

This study was conducted on six lakes located approximately 20 km north of the Phillip Smith Mountains in the Arctic Foothills region of Alaska. The landscape is completely underlain by permafrost and the vegetation is mostly tussock tundra, wet sedge tundra and dwarf shrub communities. The average annual surface temperature in the area is -8.4°C and lakes of this region are covered by ice for all but 3 months of the year, with snow cover present for 6 to 8 months. Deep lakes are thermally stratified from the end of June through mid-September, and shallow lakes circulate intermittently or continuously throughout the thaw season. Lakebeds are mostly comprised of soft sediment substrate, though deep lakes have more extensive areas of rocky bottom; macrophytes are largely absent from study lakes, occurring sparsely around the perimeter if at all. Study lakes are representative of the greater region in terms of mixing regime, physiochemical and biological characteristics, and size. Three shallow and three deep lakes around 2 m and 6 m, respectively (Table 1).

#### ii. Field Sampling

All samples were collected from an inflatable raft, or an aluminum boat. Sampling locations were at mean depth ( $\overline{z}$ ) and at or near maximum depth ( $z_{max}$ ) of each study lake. Sampling focused on three lakes (GTH 99, GTH 114, GTH 100) in the summer of 2010, and three lakes (GTH 112, NE14, Toolik Lake) in the summer of 2011.

Triplicate acrylic benthic chambers, two opaque and one translucent, were deployed by boat at  $\overline{z}$  in each lake under calm conditions during the ice-free season. Benthic chambers were used to measure sediment-water exchange of dissolved inorganic carbon (DIC;  $CO_{2(aq)}$ +  $HCO_3^-+CO_3^{2-}$ ),  $CH_4$ , and  $O_2$ , with the clear chamber controlling for the effects of benthic photosynthetic activity. Sediment-water exchange rates for target variables were taken to be representative of whole-lake processes, as Whalen et al. (2008) have reported that  $\overline{z}$  is a key indicator of the relative importance of benthic and pelagic production.

Each benthic chamber consisted of a 30cm by 30cm box, 20cm in height, covering 900cm<sup>2</sup> of sediment surface, and isolating a volume of water that varied between chambers (7.5 to 16.9L), depending on the depth to which it was embedded in the sediments when lowered into place. Galvanized steel chain was strung along the external, upper rim of the chambers to enhance sediment penetration. The chambers were turned 90° from upright and lowered until positioned just above the sediment-water interface, then returned to horizontal and lowered to the sediment surface. This ensured that the water trapped in the benthic chamber was from the bottom stratum. Chambers were fitted with a stirring device driven by a 1 rpm motor (Hankscraft Motors) powered by a 12V rechargeable battery. Neodynium magnets transmitted power from the motor to the stirring device to continuously circulate the chamber-isolated water parcel. *In vitro* testing indicated that added rhodamine dye was

completely homogenized in <15 min, as demonstrated by fluorescence measurements conducted repeatedly on chamber-trapped water.

Benthic chambers were sampled through 10m of 2.4mm diameter Tygon tubing extending from 5cm into the chamber top to the lake surface. A 5mm diameter tube fitted to the top of the chamber facilitated venting of surficial water during deployment and inflow of replacement water during sampling. Sampling volumes were kept to a minimum to prevent significant dilution of benthic chamber contents by replacement water. At 4h after deployment (designated zero time;  $T_0$ ), and at 1 or 2 d intervals thereafter to a maximum of 23 d, chambers were sampled using a standard protocol described below. If  $T_0$  samples were turbid or showed uncharacteristic concentrations of dissolved gases, sediments were considered disturbed and chamber was subsequently redeployed.

Chamber sampling was initiated by flushing the sampling tube with 90ml of chamber water (equivalent to twice the sampling tube volume). Thereafter, quadruplicate 10ml samples were collected by syringe for duplicate DIC (hereafter referred to as CO<sub>2</sub>) and CH<sub>4</sub> analyses, and two 5ml syringes were drawn for dissolved O<sub>2</sub> analysis and immediately stored on ice.

Water column profiles of selected physicochemical variables were taken at 0.5 to 3 m intervals at  $z_{max}$  and at the site of chamber deployment ( $\overline{z}$ ). These profiles were taken when the chambers were initially deployed, and at 1 to 3 subsequent time points during the chamber sampling time series, except at  $\overline{z}$  in GTH 100 where only one profile was taken. Profiles of photosynthetic photon flux density (PPFD) were determined at  $z_{max}$  (taken to be representative of PPFD down the water column at all lake locations) and only at time of initial chamber deployment (LiCor LI-250 Quantum meter fitted with a LI-192SA

underwater  $2\pi$  quantum sensor). Dissolved O<sub>2</sub> and temperature profiles were determined with a YSI Model 85 multiparameter water quality meter. Surface water samples were directly collected by hand into sampling vessels, or by syringe for subsequent injection into sampling vessels, while samples from depth were collected with a Van Dorn-type sampler.

On retrieval from each sampling depth, the Van Dorn sampler was carefully opened at the top and duplicate 10 ml syringe samples were collected for  $CH_4$  analysis. The Van Dorn sampler was then closed and duplicate 43 ml samples for  $CH_4$  oxidation rate studies were collected into amber vials, which had first been overflowed with about three volumes of sample water. Vials were sealed using Teflon-lined caps, eliminating any air in the headspace. The distal end of the sampling hose was constricted to ensure gentle flow and avoid degassing while vials were filled. Two additional 43 ml samples of surface water were collected to use as killed controls. The Van Dorn sampler was then used to fill opaque polyethylene bottles with sample water for DOC and chlorophyll a (chl *a*) analysis. Profiles of  $CH_4$  oxidation rates, DOC, and chl *a* were collected only once per lake.

All syringe-collected samples for chamber  $CH_4$  and DIC and water column  $CH_4$ analyses were injected into 30 ml serum vials filled with high purity  $N_2$  and precharged with 0.5 ml of 2.5 N HCl to arrest biological activity and convert all DIC to  $CO_2$ . Prior to injecting 10 ml water samples into these serum vials, an equal volume of  $N_2$  gas was removed from each vial to maintain an internal pressure of 1 atm.

#### iii. Experimental and Analytical

All samples were returned to a laboratory at Toolik Field Station (TFS) within 4 h of collection. Dissolved O<sub>2</sub> samples were analyzed immediately using a miniature Winkler

titration technique modified from Carpenter (1965). Unfiltered water from depth profiles was passed through ashed Whatman 47 mm GF/F filters. Filtrate was acidified with 0.2 ml of 2.5 N HCl and stored at 4°C in acid-rinsed and combusted (550°C) amber pyrex bottles for DOC while filter-trapped material was extracted for 24 h at -5°C in buffered 90% acetone solution for chl *a* analysis (Wetzel and Likens, 2000). Filters were pulverized midway through extraction; this procedure was shown by Whalen et al. (2008) to give a chl *a* yield not significantly different from grinding. Following Welchmeyer (1994), chl *a* was analyzed fluorometrically (Turner Designs TD70 fluorometer). This technique does not involve an acidification step but maintains a desensitized response to phaeopigments and chl *b*. Dissolved organic C was analyzed by high-temperature catalytic combustion (Shimadzu TOC-V<sub>CPH</sub> total organic carbon analyzer).

Methane and CO<sub>2</sub> analyses were performed via flame ionization detection (FID-GC) and thermal conductivity detection (TCD-GC) gas chromatography (Shimadzu GC-8A instruments), respectively. Operating conditions for FID-GC analysis were the following: 1/8" diameter x 1 m length molecular sieve 5A (60/80) column; column temperature = 90°C; injector and detector temperatures = 140°C; carrier gas = ultra-high purity N<sub>2</sub> at 33 ml min<sup>-1</sup> flow rate. Precision of analysis was <1% at 10 ppm CH<sub>4</sub>. Operating conditions for TCD-GC analysis were the following: 1/8" x 2m porapak N column (80/100); column temperature = 40°C; injector detector temperatures = 140°C, current = 140 mA; carrier gas = ultra-high purity He at 30 ml min<sup>-1</sup> flow rate. Precision of analysis was <1% at 351 ppm CO<sub>2</sub> (Whalen and Reeburgh, 2000).

Rates of  $CH_4$  oxidation were measured using biogenically produced <sup>14</sup> $CH_4$  (Daniels and Zeikus, 1983) with a specific activity of 517 MBq mmol<sup>-1</sup>. Aliquots (100µl) of stock

solution were diluted into a calibrated 24.3 ml serum vial filled with ultra-high purity N<sub>2</sub> to make a working standard. To prepare samples for incubation, 0.5 ml of this working <sup>14</sup>CH<sub>4</sub> standard was injected through the Teflon septa of the 43 ml sample vials while venting displaced water with an adjacent needle through the sealing septum. Killed (via 0.5 ml formaldehyde) controls were similarly treated. Sample vials were hand-shaken for 3 min, placed on a rotating carousel (6 rpm) in 15°C water bath and incubated in the dark for up to 24 h. Incubations were terminated by injecting 0.5 ml of 4 N NaOH through septa and hand shaking. Sample vials were then uncapped and placed on a shaker table under a fume hood for 12 h to vent unreacted <sup>14</sup>CH<sub>4</sub>. Thereafter 8 ml aliquots of unfiltered water were placed in scintillation vials with 10 ml of Aquasol-2 scintillation cocktail. Additional subsamples were filtered (0.22 µm Millipore nitrocellulose membrane), and the filtrate similarly treated. Filters were placed in Scintisafe scintillation cocktail, and all samples were assayed for  $\beta$ activity on Packard TriCarb Liquid Scintillation counter.

#### iv. Calculations and Statistics

Attenuation coefficients ( $K_d$ ; m<sup>-1</sup>) for radiant energy in the water column were calculated following Kirk (1994). Attenuation of radiant energy by the clear acrylic benthic chambers was determined empirically by placing the LiCOR meter beneath a clear chamber directly below a light source *in vitro* and comparing PPFD measurements to those taken without the chamber in place. Toolik Field Station Environmental Data Center (EDC) incident irradiance data (*http://toolik.alaska.edu/edc/weather/data\_query.php*; collected with LiCor LI-190SB quantum sensor), along with  $K_d$  for radiant energy,  $\overline{z}$ , 6% surface reflectance (Carrignan and Planas, 1994) and the empirically determined 20% attenuation by clear

acrylic, were used to estimate PPFD incident on the lake bottom beneath clear benthic chambers during deployment in each lake.

Headspace mixing ratios for  $CH_4$  and  $CO_2$  in serum vials were converted to mol L<sup>-1</sup> basis, while concentrations in the aqueous phase in serum vials were calculated from temperature-corrected values of Henry's constant (Weiss 1974; Yamamoto 1976). *In situ*  $CH_4$  and  $CO_2$  concentrations were computed as the sum of aqueous and gaseous phases in serum vials. Rates of sediment-water exchange of gases were calculated as the linear rate of change in mass m<sup>-2</sup> sediment surface d<sup>-1</sup>. If the slope of this linear fit was not significant at the p<0.05 level, then the rates of change in mass of the dissolved constituent in the chamber during each sampling interval were averaged to obtain an exchange rate.

Rates of CH<sub>4</sub> utilization (respiration + assimilation into biomass) were calculated by multiplying the fraction of added <sup>14</sup>CH<sub>4</sub> utilized time<sup>-1</sup> (specific oxidation rate,  $k_{CH4}$ ) times the ambient CH<sub>4</sub> concentration for whole water samples. Turnover times (d) were calculated as the reciprocal of the specific oxidation rate. Biomass-incorporated CH<sub>4</sub> was estimated from  $\beta$  activity on filter-trapped particulates, while respired CH<sub>4</sub> was estimated from radioactivity associated with the filtrate. This latter quantity included <sup>14</sup>CO<sub>2</sub> plus DO<sup>14</sup>C.

Estimates of CH<sub>4</sub> emissions from study lakes to the atmosphere (mmol m<sup>-2</sup> d<sup>-1</sup>) were obtained using a simple stagnant film gas transfer model (Broecker and Peng, 1974). This formulation presumes a well-mixed gas phase, and that molecular diffusion through a laminar surface layer is the limiting step for transfer from the aqueous phase. Molecular diffusivities (D; m<sup>2</sup> s<sup>-1</sup>) of CH<sub>4</sub> were determined for observed temperatures using a temperature dependence relationship extrapolated from data presented by Broecker and Peng (1974). The laminar surface layer thickness z (m) was parameterized by wind speed

according to the relationship found by Kling et al. (1992) for lakes in the same study area. Wind speed data were obtained from the TFS EDC

(*http://toolik.alaska.edu/edc/weather/data\_query.php*), and wind speeds at TFS were assumed representative of wind speeds throughout the study region at a given time. The ratio of *D* to *z* is an estimate of the piston velocity. Solubility coefficients ( $K_s$ ) for CH<sub>4</sub> were estimated based on temperature according to Wanninkhof (1992). The atmospheric partial pressure of CH<sub>4</sub> was assumed to be 1.8 µatm, and used with solubility coefficients and observed surface water CH<sub>4</sub> concentrations to obtain a concentration gradient across the laminar surface layer. A range of potential lake surface CH<sub>4</sub> efflux rates was calculated for each study lake based on the minimum and maximum surface temperature and CH<sub>4</sub> concentrations observed.

The Mann-Whitney U test and the Wilcoxon signed range test were used for comparisons of means between lake size classes or dark and clear chambers when the data were not normally distributed. This was often the case due to the small sample size (6 study lakes). Elsewhere, the t-test was used to assess significance. Values of p<0.05 were considered significant. Because of the small sample population, the power of such tests is limited, but the results are still more informative than qualitative assessments.

#### III. RESULTS

## i. Geomorphology of Study Lakes

All study lakes are located in the vicinity of 68°N, 149°W. Lakes in the shallow size class average 2.1 to 2.2 m depth, while average depth ( $\overline{z}$ ) in deep lakes is 6 to 7m (Table 1). The maximum depth ( $z_{max}$ ) for shallow lakes is 4.1 to 6.7m, while  $z_{max}$  in deep lakes is 15.7 to 26.3 m. Lake volume and surface area range from  $15 \times 10^3$  to  $87 \times 10^3$  m<sup>3</sup> and 0.7 to 4.0 ha, respectively, in the shallow lakes. Deep lake volumes and surface areas are larger, ranging from  $351 \times 10^3$  to  $10950 \times 10^3$  m<sup>3</sup> and 5.4 to 148.8 ha, respectively. Catchment areas are 13 to 59 ha for shallow lakes, while deep lake values are larger, measuring from 77 to 6760 ha. Overall, the ratio of catchment area: lake surface area varies from 3.0 to 45.4 and shows no trend with respect to lake size class.

Table 1: Location, size class, and geomorphology of study lakes.									
Study Lake	Latitude (N)	Longitude (W)	Size Class	z <sub>max</sub> (m)	7 (m)	Volume (10 <sup>3</sup> m <sup>3</sup> )	Surface area (ha)	Catchment area (ha)	Catchment:Lake area ratio
GTH 99	68° 29′ 38″	149° 35′ 59″	Shallow	4.1	2.1	15	0.7	13	18.5
GTH 112	68° 40′ 17″	149° 14' 54"	-	6	2.2	62	2.8	30	10.7
GTH 114	68° 40' 45″	149° 13′ 44″	-	6.7	2.2	87	4	59	14.8
GTH 100	68° 29′ 38″	149° 35′ 59″	Deep	15.7	6.4	351	5.4	93	17.2
NE14	68° 40′ 31″	149° 37′ 27″	-	18.7	6	1617	25.2	77	3
Toolik	68° 38' 00″	149° 36′ 15″	-	26.3	7	10950	148.8	6760	45.4

#### ii. Water Column Studies

Both shallow and deep lakes stratify thermally during the ice-free season, although shallow lakes mix intermittently in some years. Deep and shallow lakes showed both similarities and differences in physicochemical and biological properties at  $z_{max}$ . Profiles of dissolved O<sub>2</sub> concentration were orthograde in the deep lakes (Figure 1), but heterograde in the shallow lakes (Figure 2). While chl *a* concentration profiles varied in shape (Figures 3 and 4), mean concentrations averaged 5.6 µg l<sup>-1</sup> in shallow lakes, significantly higher than the mean of 1.0 µg l<sup>-1</sup> in deep lakes. Similarly, DOC concentrations showed no pattern down the water column in either lake type (Figures 3 and 4), but were significantly greater on average at  $z_{max}$  in the shallow lakes at 538 µM compared to 382 µM in the deep lakes (Table 2). Average DOC concentrations at  $z_{max}$  showed no relationship with the ratio of catchment area to lake surface area (R<sup>2</sup> < 0.001).



Figure 1: Depth profiles of temperature,  $O_2$  concentration,  $CH_4$  concentration, and volume-based  $CH_4$  oxidation rates in deep lakes. Horizontal dashed line corresponds to  $\overline{z}$ , the mean depth of the lake.

At  $z_{max}$ , water column concentrations of CH<sub>4</sub> were extremely low, 0.06 to 0.35  $\mu$ M, at all depths in the deep lakes (Figure 1; Table 2). Methane concentrations were relatively low, 0.28 to 6.08  $\mu$ M, in shallow lakes down to the depth of O<sub>2</sub> depletion in the hypolimnia, but still generally exceeded concentrations observed throughout the entire water column in deep lakes (cf. Figures 1 and 2). However, a spike in CH<sub>4</sub> concentration occurred in the hypoxic bottom waters of the shallow lakes, where maximum concentrations of 15.5, 52.6, and 17.9  $\mu$ M were observed in GTH 99, GTH 112, and GTH 114, respectively. These CH<sub>4</sub> concentrations were an order of magnitude or more higher than surface water concentrations in shallow lakes and exceeded concentrations in deep lakes by two orders of magnitude or more.



Figure 2: Depth profiles of temperature,  $O_2$  concentration,  $CH_4$  concentration, and volume-based  $CH_4$  oxidation rates in shallow lakes. Horizontal dashed line corresponds to  $\overline{z}$ , the mean depth of the lake.

Profiles of CH<sub>4</sub> oxidation rates in the water column at  $z_{max}$  effectively mirrored CH<sub>4</sub> concentration profiles, with rates in deep lakes centering around 0.007 µmol L<sup>-1</sup> d<sup>-1</sup>, but increasing by a factor of about 3 near the hypolimnetic sediments (Figure 1; Table 2). Methane oxidation rates were as low as 0.001 µmol L<sup>-1</sup> d<sup>-1</sup> in the epilimnia of shallow lakes, but were higher by as much as four orders of magnitude or more (up to 43 µmol L<sup>-1</sup> d<sup>-1</sup>) in the hypoxic hypolimnia, where CH<sub>4</sub> concentrations were elevated (Figure 2), and significantly higher than deep lake rates. First-order rate constants,  $k_{CH4}$  (d<sup>-1</sup>), corresponding to these CH<sub>4</sub>

oxidation rates were significantly higher in the shallow lakes at all depths than in the deep lakes, with average values varying from 0.41 to  $1.12 \text{ d}^{-1}$  in shallow lakes and 0.025 to 0.095  $\text{d}^{-1}$  in deep lakes. First order rate constants for CH<sub>4</sub> oxidation increased markedly in the bottom waters of the shallow lakes, showing a maximum of 3.64  $\text{d}^{-1}$  in Lake GTH 112 (Table 2).



Figure 3: Depth profiles of chlorophyll a (chl a) and dissolved organic carbon (DOC) concentrations in deep lakes. Horizontal dashed line corresponds to  $\overline{z}$ , the mean depth of the lake.

Similarly distinct differences were observed between lake classes at the  $\overline{z}$  sampling station. In all shallow lakes and in NE14, the sediment-water interface at this sampling station corresponded to a depth above the observed thermocline at the  $z_{max}$  sampling station, and profiles of temperature and dissolved O<sub>2</sub> were roughly orthograde to the lake bottom (Figures 1 and 2); in GTH 100 and in Toolik Lake, the lake bottom at the  $\overline{z}$  sampling station

corresponded to a depth within the thermocline at the deep sampling station but dissolved  $O_2$  profiles were still roughly orthograde to the lake bottom. Other water column properties at this sampling station (DOC, chl *a*, CH<sub>4</sub> concentration, CH<sub>4</sub> oxidation rate and  $k_{CH4}$ ) showed relatively little variation from the lake surface to the bottom in each lake. However, chl *a* and DOC concentrations were significantly greater in shallow lakes than in deep lakes, averaging 5.12 versus 0.99 µg L<sup>-1</sup> and 540 versus 359 µM, respectively (Table 2), and mean DOC concentrations at  $\overline{z}$  showed no relationship with the ratio of catchment area to lake surface area (R<sup>2</sup> = 0.03). Similarly, the mean water column CH<sub>4</sub> concentration, CH<sub>4</sub> oxidation rate, and  $k_{CH4}$ , while lower on average in all lakes at  $\overline{z}$  than at  $z_{max}$ , were all significantly higher in shallow lakes than in deep lakes, by one or two orders of magnitude (Table 2).





Table 2: Mean and (range) of water column concentrations of chlorophyll a (chl <i>a</i> ), dissolved organic-C (DOC), and CH <sub>4</sub> , and mean and
(range) of volume-based and specific ( $k_{CH4}$ ) rates of CH <sub>4</sub> oxidation in study lakes at the deepest point ( $z_{max}$ ) and mean depth ( $\overline{z}$ ) of each
lake.

Study Lake	Z <sub>max</sub>	Size Class	Chl <i>α</i> (µg L <sup>-1</sup> )	DOC (µM)	Volume-based CH <sub>4</sub> oxidation rate (μmol L <sup>-</sup> <sup>1</sup> d <sup>-1</sup> )	<i>k<sub>CH4</sub></i> (d <sup>-1</sup> )	CH₄ (μM)
GTH 99	4.1	Shallow	1.43 (1.12-1.81)	377 (326-393)	0.84 (0.013-4.10)	0.72 (0.016-2.85)	2.14 (0.63-15.5)
GTH 112	6.0	-	6.98 (1.78-9.87)	591 (507-632)	7.63 (0.46-43.0)	1.12 (0.355-3.64)	7.96 (0.28-52.6)
GTH 114	6.7	-	7.59 (2.98-28.3)	618 (561-665)	4.01 (0.001-21.3)	0.41 (0.001-1.21)	1.24 (0.37-17.9)
GTH 100	15.7	Deep	0.91 (0.63-1.67)	374 (336-432)	0.008 (0.0001-0.023)	0.095 (0.001-0.234)	0.18 (0.06-0.32)
NE14	18.7	-	0.50 (0.26-0.95)	333 (192-462)	0.005 (0.0001-0.025)	0.025 (0.001-0.139)	0.20 (0.06-0.35)
Toolik	26.3	-	1.27 (0.51-2.15)	436 (314-591)	0.009 (0.0001-0.020)	0.061 (0.001-0.137)	0.18 (0.13-0.27)
	Z						
GTH 99	2.1	Shallow	1.26 (1.12-1.36)	390 (386-393)	0.017 (0.013-0.018)	0.018 (0.016-0.023)	1.20 (0.90-1.67)
GTH 112	2.2	-	9.36 (8.84-9.87)	575 (507-618)	0.476 (0.445-0.510)	0.368 (0.345-0.391)	2.37 (1.28-6.08)
GTH 114	2.2	-	3.34 (2.98-3.54)	645 (625-665)	0.004 (<0.001-0.008)	0.004 (0.001-0.006)	0.48 (0.40-0.57)
GTH 100	6.4	Deep	1.09 (0.66-1.67)	391 (362-432)	0.002 (<0.001-0.006)	0.015 (<0.001-0.05)	0.25 (0.21-0.32)
NE14	6.0	-	0.30 (0.26-0.34)	316 (192-511)	0.0002 (0.0001-0.0003)	0.001 (0.001-0.003)	0.13 (0.06-0.29)
Toolik	7.0	-	1.35 (0.99-1.86)	370 (314-402)	0.002 (<0.001-0.007)	0.015 (0.001-0.046)	0.19 (0.14-0.27)
#### iii. Methanotrophic Bacterial Growth Efficiency and Production

When entire volume-based <sup>14</sup>CH<sub>4</sub> utilization data were considered, estimates of total CH<sub>4</sub> oxidation rates (whole water samples) agreed on average to within 11% of rates independently estimated by summing values found for <sup>14</sup>CH<sub>4</sub>-C respired (radiolabeled filtrate) and <sup>14</sup>CH<sub>4</sub>-C incorporated into biomass (radiolabeled filter-trapped material). By both measures, CH<sub>4</sub> oxidation rates in NE14 were very low, approaching the sensitivity limits of the <sup>14</sup>CH<sub>4</sub> method, and showed the most variability. Excluding data for NE14, CH<sub>4</sub> oxidation rate estimates by the whole water and respiration-biomass summation measures agreed to within 6%.

Percent incorporation of assimilated <sup>14</sup>CH<sub>4</sub> into biomass, or methanotrophic bacterial growth efficiency (MBGE), varied from 23% to 48%, with the highest value associated with the most uncertainty in NE14 (Table 3). Excluding these data, percent incorporation showed lower lakewise variability, from 23% to 39%. The average growth efficiency for the shallow lakes (33%) was not significantly different from the average growth efficiency in the deep lakes (36%).

	μmol C m <sup>-2</sup> d <sup>-1</sup>					
Study Lake	Size Class	Growth Efficiency (%)	Respired- CH <sub>4</sub>	Biomass- CH₄	Total CH₄ Oxidation	CH₄ oxidation biomass production as % of phytoplankton primary production
GTH 99	Shallow	39.4	71.3	41.4	112.7	1.1%
GTH 112	-	22.6	977.2	292.2	1269.4	4.6%
GTH 114	-	37.4	256.0	135.8	391.8	1.6%
GTH 100	Deep	28.2	8.2	4.0	12.1	0.08%
NE14	-	48.4	2.2	1.9	4.1	-
Toolik	-	30.6	13.3	6.0	19.4	0.1%

Table 3: Whole-lake methanotrophic production estimates and comparisons to area-based phytoplankton primary production estimates for some study lakes

Depth-integrated rates of biomass production from methanotrophy varied by more than a factor of 100 (Table 3). The lowest rate, 1.9  $\mu$ mol C m<sup>-2</sup> d<sup>-1</sup>, occurred in NE14, and the highest rate of 292  $\mu$ mol C m<sup>-2</sup> d<sup>-1</sup> was observed in GTH 112. The mean rate of 157  $\mu$ mol C m<sup>-2</sup> d<sup>-1</sup> for methanotrophic biomass production in the shallow lakes was significantly higher than the mean of 4  $\mu$ mol C m<sup>-2</sup> d<sup>-1</sup> for the deep lakes. Prior work has measured whole-lake phytoplankton primary production rates in all study lakes (Miller et al., 1986; Whalen et al., 2006, 2008) except NE14; whole-lake estimates of methanotrophic biomass production correspond to 1 to 5% of these values in shallow lakes, compared to about 0.1% in GTH 100 and Toolik (Table 3).

## iv. Radiant Energy and Sediment-Water Gas Exchange

Attenuation coefficients ( $K_d$ ) for photosynthetically active radiation (PAR) in shallow lakes were significantly greater than deep lake values, averaging 1.26 m<sup>-1</sup> compared to 0.43 m<sup>-1</sup> (Table 4). Radiant energy at the sediment surface during deployment corresponded to 1.9 to 4.2% of that incident on the lake surface in GTH 112, GTH 114, GTH 100, and Toolik. Much larger proportions of surface-incident PAR penetrated to the sediment surface in GTH 99 and NE14, at 19.8 and 22.3%, respectively. Field irradiance at the sediment surface during deployment was a function of weather conditions, incubation length,  $\overline{z}$  and  $K_d$ . This quantity was greatest in GTH 99 and NE14 at 4.50 and 5.26 mol photons m<sup>-2</sup> d<sup>-1</sup>, respectively, while values for the other study lakes were roughly similar and one or two orders of magnitude smaller (Table 4).

Table 4: Attenuation coefficients for underwater irradiance ( $K_d$ ), mean lake depth ( $\overline{z}$ ), photosynthetic photon flux density(PPFD) at sediment surface in clear benthic chamber, and percent of lake sediment surface area at or above compensation depth (1% PPFD) for photosynthesis.

Lake	Size Class	K <sub>d</sub>	<u>z</u> (m)	Mean incubation PPFD, $\overline{z}$ (mol photons m <sup>-2</sup> d <sup>-1</sup> )	% of sediment area at or above 1% PPFD penetration
GTH 99	Shallow	0.77	2.1	4.50	100
GTH 112	-	1.57	2.2	1.12	69
GTH 114	-	1.44	2.2	0.90	81
GTH 100	Deep	0.62	6.4	0.42	54
NE14	-	0.25	6.0	5.26	100
Toolik	-	0.46	7.0	0.97	74

A representative time series of benthic chamber dissolved gas concentrations is shown in Figure 5. In all lakes, both clear and dark benthic chambers showed net dissolved O<sub>2</sub> consumption (negative flux). Overall, area-based rates of dissolved O<sub>2</sub> loss varied from 0.62 to 3.09 mmol  $m^{-2} d^{-1}$  in the shallow lakes, and from 0.29 to 2.16 mmol  $m^{-2} d^{-1}$  in the deep lakes. Dissolved O<sub>2</sub> consumption rates were higher in dark chambers than clear chambers in all lakes except GTH 99 and GTH 100. Dissolved O<sub>2</sub> consumption rates in GTH 100 were roughly the same in both dark and clear chambers, while in GTH 99 dissolved O<sub>2</sub> consumption in the clear chamber exceeded that in the dark chambers by more than a factor of two (Table 5). Otherwise, dissolved O<sub>2</sub> consumption in light chambers was 19 to 85% of mean values for dark chambers. Excluding data from GTH 99, these ratios were inversely related to field irradiance at the clear chamber sediment surface ( $R^2 = 0.86$ ) and percent penetration of incident PAR to the sediment surface at  $\overline{z}$  (R<sup>2</sup> = 0.85). When the entire data were considered, the dissolved O<sub>2</sub> flux in light chambers showed no relationship to either epipelic chl a ( $R^2 = 0.21$ ) or field irradiance at the clear chamber sediment surface  $(R^2 = 0.13).$ 



Figure 5: Representative (GTH 114) benthic chamber time series for changes in dissolved  $CH_4$ ,  $CO_2$ , and  $O_2$  concentrations.

Table 5: Benthic chamber sediment-water exchange rates for  $O_2$ ,  $CO_2$ , and  $CH_4$  (mmol m<sup>-2</sup> d<sup>-1</sup>); estimates of gross photosynthesis (PS) and predicted dark  $CO_2$  flux (mmol m<sup>-2</sup> d<sup>-1</sup>) based on respiratory quotient of 0.85 for aerobic respiration; and comparison of predicted and observed dark chamber  $CO_2$  flux. Standard error of the mean for duplicate dark chambers given in parentheses. Negative values indicate flux into the sediment.

Study Lake	Size Class	O <sub>2</sub>	CO2	CH₄	Gross PS	Predicted dark CO₂ flux (0.85* Gross PS)	Predicted dark CO₂ flux as % of observed
GTH 99 Dark	Shallow	-0.62 (0.17)	6.78 (2.09)	2.02 (0.22)	-0.73	1.83	27%
GTH 99 Clear	-	-1.35	2.45	0.69			
GTH 112 Dark	-	-1.35 (0.10)	8.08 (0.41)	2.37 (0.33)	0.38	6.74	83%
GTH 112 Clear	-	-0.97	6.42	2.48			
GTH 114 Dark	-	-3.09 (0.06)	8.02 (0.29)	0.65 (0.09)	1.19	5.29	66%
GTH 114 Clear	-	-1.90	4.28	0.24			
GTH 100 Dark	Deep	-1.18 (0.12)	2.77 (0.21)	0.007 (0.001)	0.03	1.95	70%
GTH 100 Clear	-	-1.15	1.92	-0.001			
NE14 Dark	-	-1.53 (0.01)	6.62 (0.06)	0.390 (0.011)	1.24	2.96	45%
NE14 Clear	-	-0.29	1.91	0.002			
Toolik Dark	-	-2.16 (0.22)	6.17 (0.71)	0.383 (0.063)	0.32	4.40	68%
Toolik Clear	-	-1.84	3.72	0.017			

All benthic chambers in all lakes showed net  $CO_2$  emission (positive flux; cf. Figure 5), with rates of  $CO_2$  production greater in the dark chambers than in the clear chamber in each lake (Table 5). Considering all lakes,  $CO_2$  efflux was significantly greater in dark chambers, averaging 6.41 mmol m<sup>-2</sup> d<sup>-1</sup>, than in clear chambers, which averaged 3.45 mmol m<sup>-2</sup> d<sup>-1</sup>. The difference between dark and clear chamber  $CO_2$  fluxes was significantly greater in the shallow lakes than in the deep lakes. Additionally, dark  $CO_2$  production was significantly higher in the shallow lakes than in deep lakes, averaging 7.63 mmol m<sup>-2</sup> d<sup>-1</sup> compared to 5.19 mmol m<sup>-2</sup> d<sup>-1</sup>.

Gross photosynthesis in the clear benthic chamber during incubation was approximated by using the difference in  $O_2$  loss between the clear and dark chambers (Table 5). The expected rate of  $CO_2$  accumulation from aerobic decomposition was estimated by adding the difference in  $O_2$  consumption between clear and dark chambers to the observed  $CO_2$  flux in the clear chamber, asssuming a RQ (molar ratio of  $CO_2$  produced to  $O_2$  consumed) of 0.85 for aerobic decomposition (Boyd, 1973; Hanson and Tenore, 1981). These predicted dark chamber  $CO_2$  accumulation rates were 45 to 83% of observed dark chamber  $CO_2$  production in all study lakes except GTH 99, where the predicted rate was 27% of the observed due to greater  $O_2$  depletion in the clear chamber than the dark chambers (Table 5).

There was a net accumulation of CH<sub>4</sub> in all benthic chambers in all lakes (cf. Figure 5) except for the clear chamber in GTH 100 where essentially no flux was observed (Table 5). However, CH<sub>4</sub> emitted from the sediment was subject to oxidation in the chamberisolated water parcel potentially underestimating sediment surface CH<sub>4</sub> efflux. Experimental values of  $k_{CH4}$  at  $\overline{z}$  in each lake (Table 6) were used with chamber CH<sub>4</sub> concentration and volume data to calculate an average rate of oxidation in chamber-isolated water. This value was added to the observed sediment-water CH<sub>4</sub> flux (Table 5) to give an improved estimate of CH<sub>4</sub> efflux to the overlying water (Table 6). The calculated increase in sediment-water CH<sub>4</sub> flux over the observed values was notable only in GTH 112, where fluxes increased by 25 and 30% in the dark and clear chambers, due to order of magnitude higher values of  $k_{CH4}$  and rapid CH<sub>4</sub> accumulation. Table 6: Specific ( $k_{CH4}$ ) rates of CH<sub>4</sub> oxidation at depth of benthic chamber deployment ( $\overline{z}$ ), CH<sub>4</sub> oxidation rates in benthic chamber water and corrected CH<sub>4</sub> flux from sediments (mmol m<sup>-2</sup> d<sup>-1</sup>), and comparison of corrected CH<sub>4</sub> fluxes between dark and clear chambers.

Study Lake	Size Class	<i>k<sub>CH4</sub></i> (d⁻¹)	Chamber water CH₄ oxidation (mmol m <sup>-2</sup> d <sup>-1</sup> )	Corrected CH₄ flux from sediments (mmol m <sup>-2</sup> d <sup>-1</sup> )	Difference, dark and clear corrected CH <sub>4</sub> flux (mmol m <sup>-2</sup> d <sup>-1</sup> )
GTH 99 Dark	Shallow	0.018	0.041	2.06	1.35
GTH 99 Clear	-	0.018	0.020	0.71	(Clear 34% of dark)
GTH 112 Dark	-	0.372	0.590	2.96	-0.27
GTH 112 Clear	-	0.372	0.750	3.23	(Clear 109% of dark)
GTH 114 Dark	-	0.005	0.003	0.651	0.41
GTH 114 Clear	-	0.005	0.002	0.240	(Clear 37% of dark)
GTH 100 Dark	Deep	0.044	<0.001	0.007	0.008
GTH 100 Clear	-	0.044	<0.001	-0.001	(Clear -11% of dark)
NE14 Dark	-	0.002	0.001	0.390	0.388
NE14 Clear	-	0.002	<0.001	0.002	(Clear 0.5% of dark)
Toolik Dark	-	0.045	0.015	0.398	0.381
Toolik Clear	-	0.045	<0.001	0.017	(Clear 4.3% of dark)

Corrected sediment-water CH<sub>4</sub> fluxes were significantly larger in dark chambers than in the clear chambers except in GTH 112 and GTH 100, where fluxes were similar for all chambers. Excluding these data, clear chamber CH<sub>4</sub> fluxes corresponded to an average of 19% of dark chamber fluxes. Rates of CH<sub>4</sub> exchange in deep lake clear chambers averaged 0.01 mmol m<sup>-2</sup> d<sup>-1</sup>, significantly lower than the 1.39 mmol m<sup>-2</sup> d<sup>-1</sup> observed in the shallow lakes. Similarly, dark chamber CH<sub>4</sub> fluxes were significantly higher in the shallow lakes, at 1.89 mmol m<sup>-2</sup> d<sup>-1</sup> on average compared to a mean of 0.27 mmol m<sup>-2</sup> d<sup>-1</sup> in the deep lakes.

Lake sediment catabolism consists of both anaerobic and aerobic respiration processes, which oxidize organic C compounds to  $CO_2$ , as well as fermentation, the disproportionation of organic C compounds to  $CO_2$  and  $CH_4$ . Total flux of  $CO_2$  and  $CH_4$ from sediments to the water column thus provides a measure of sediment heterotrophy, and the  $CH_4$  fraction of this flux is an index of the importance of  $CH_4$  in overall C mineralization. Methane accounted for 20% of sediment catabolism on average in the shallow lakes,

significantly higher than the mean of 2% in the deep lakes (Table 7). Considering all benthic chambers, corrected sediment-water  $CH_4$  flux was significantly correlated ( $R^2 = 0.40$ ) with C sedimentation rates given in Bretz (2012).

Table 7: Net sediment inorganic C flux (mmol m <sup>-2</sup> d <sup>-1</sup> ) and percent							
contribution of CH <sub>4</sub> to inorganic C flux							
Study Lake	CH4 % of Inorganic C Flux						
GTH 99 Dark	8.8	23.3					
GTH 99 Clear	3.2	22.5					
GTH 112 Dark	11.0	26.8					
GTH 112 Clear	9.7	33.5					
GTH 114 Dark	8.7	7.5					
GTH 114 Clear	4.5	5.3					
GTH 100 Dark	2.8	0.3					
GTH 100 Clear	1.9	0.0					
NE14 Dark	7.0	5.6					
NE14 Clear	1.9	0.1					
Toolik Dark	6.6	6.1					
<b>Toolik Clear</b>	3.7	0.5					

# v. Stagnant film model of CH<sub>4</sub> emission to atmosphere

Maximum and minimum estimates for  $CH_4$  release from the lake surface to the atmosphere were generated from end member observations of water temperature and  $CH_4$  concentration at the lake surface. Maximum and minimum estimates of lake surface  $CH_4$  efflux averaged 1.34 and 0.58 mmol m<sup>-2</sup> d<sup>-1</sup>, respectively, in the shallow lakes. These values were significantly higher than the respective means of 0.22 mmol m<sup>-2</sup> d<sup>-1</sup> and 0.12 mmol m<sup>-2</sup> d<sup>-1</sup> estimated for the deep lakes (Table 8). GTH 112 had the highest estimated CH4 efflux, at 1.94 mmol m<sup>-2</sup> d<sup>-1</sup>, and NE14 showed the lowest, 0.11 mmol m<sup>-2</sup> d<sup>-1</sup>. Corrected clear

chamber  $CH_4$  fluxes were positively related to maximum estimated  $CH_4$  evasion from the lake surface ( $R^2 = 0.76$ ).

Table 8: Stagnant film model-estimated lake CH <sub>4</sub> emissions, with surface temperatures and CH <sub>4</sub>									
concentrations.									
Study Lake	Size Class	T (°C) range	Surface CH₄ (µM) range	Minimum flux (mmol m <sup>-2</sup> d <sup>-1</sup> )	Maximum flux (mmol m <sup>-2</sup> d <sup>-1</sup> )				
GTH 99	Shallow	12.8-15.6	0.84-1.67	0.71	1.52				
GTH 112	-	13.2-17.2	0.74-2.02	0.64	1.94				
GTH 114	-	13.6-17.4	0.47-0.57	0.40	0.55				
GTH 100	Deep	13.5-15.8	0.16-0.25	0.14	0.23				
NE14	-	13.4-14.8	0.13-0.29	0.11	0.25				
Toolik	-	12.5-15.4	0.15-0.21	0.12	0.19				

## IV. DISCUSSION AND CONCLUSIONS

## i. Water Column Studies

Overall, differences between the deep and the shallow lakes in water column physicochemical characteristics, methanotrophic production, sediment-water exchange of CH<sub>4</sub> and estimated CH<sub>4</sub> emissions point to the shallow lakes as more productive systems. While the shallow lakes are likely subject to more mixing during the ice-free season, they nonetheless demonstrated heterograde  $O_2$  profiles at  $z_{max}$ , while orthograde profiles were found in the deep lakes despite the presence of a thermocline. These findings illustrate the previously reported extreme oligotrophy of the deep lakes, and relative productivity of the shallow lakes versus deep lakes in this region (Sierszen et al., 2003; Whalen et al., 2006, 2008). With the exception of a large maximum at depth in GTH 114 (28.32 µg L<sup>-1</sup>), the chl *a* concentrations observed (0.26 to 9.87 µg L<sup>-1</sup>; Table 2) were similar to previous reports for lakes in the Arctic Foothills region, which range from 0.12-7.4 µg L<sup>-1</sup> (Kling et al., 1992; Levine and Whalen, 2001; Sierszen et al., 2003; LaPierriere et al., 2003; Crump et al., 2003; Whalen et al., 2006, 2008), as well as those given for lakes elsewhere in the Arctic, which center around 1.5 µg L<sup>-1</sup> (Hamilton et al., 2001; Lim et al., 2001; Michelutti et al., 2003).

In oligotrophic lakes, phytoplankton production and watershed inputs are the dominant contributors to DOC concentrations (Wetzel, 2001). In Arctic lakes, allochthonous inputs are highest during the spring thaw due to elevated runoff, while autochthonous production increases in significance later in the summer (Whalen and Cornwell, 1985), when most field sampling was performed. As with chl a, DOC concentrations were significantly higher in shallow lakes, suggesting greater overall productivity. Measured concentrations of DOC (192 to 665  $\mu$ M) were similar to others reported for lakes in the Arctic Foothills region, which center around 400 to 500 µM (Whalen and Cornwell, 1985; Kling et al., 2000; Crump et al., 2003), and comparable to the lower end of literature values for temperate, boreal, and sub-Arctic lakes (Howard et al., 1971; Chau et al., 1977; Fallon et al., 1980; Mattson and Likens, 1993; Michmerhuizen et al., 1996; Bastviken et al., 2002; Bastviken et al., 2004), which show values varying from 150 to 1800  $\mu$ M. The decoupling of drainage size and DOC content, together with the high degree of homogeneity in vegetation between study lake drainages, suggests that elevated DOC in shallow lakes may have been related to autochthonous sources. Kling et al. (2000) noted a similar lack of relationship between DOC and catchment area in a chain of small lakes in the study area.

Deep lake CH<sub>4</sub> concentrations of 0.06 to 0.35  $\mu$ M (Table 2) are among the lowest recorded. These values are similar to the lowest concentrations previously reported for unfertilized lakes in the study region during summer (Kling et al., 1992), other high latitude lakes (Welch et al., 1980; Bartlett et al., 1992; Bastviken et al., 2004), and a mesotrophic, temperate lake with an oxic hypolimnion (Lidstrom and Somers, 1984; Kuivila et al., 1988), which give CH<sub>4</sub> concentrations of 0.09 to 2.32 uM. In contrast, my observation of elevated CH<sub>4</sub> concentrations (up to 52.6  $\mu$ M) in the bottom water of the shallow lakes extend to the

Arctic similar observations of CH<sub>4</sub> accumulation in O<sub>2</sub>-depleted hypolimnia of natural and human-impacted lakes in sub-Arctic to temperate regions, which generally show hypolimnetic CH<sub>4</sub> concentrations of 30 to 80  $\mu$ M (Rudd and Hamilton, 1978; Harrits and Hanson, 1980; Lilley and Baross, 1988; Liu et al., 1996; Bastviken et al., 2002; Kankaala et al., 2006).

Remarkably, volume-based rates of CH<sub>4</sub> oxidation varied over five orders of magnitude (Table 2). In accord with CH<sub>4</sub> concentrations, CH<sub>4</sub> oxidation rates of <0.001 to 0.025 umol L<sup>-1</sup> d<sup>-1</sup> in the deep lakes compare favorably to the lowest values reported. These vary from <0.001 to 0.144 µmol L<sup>-1</sup> d<sup>-1</sup> in lakes of varying trophic status and latitudes (Lilley and Baross, 1988; Utsumi et al., 1998a&b; Bastviken et al., 2002; Bastviken et al., 2004; Sundh et al., 2005; Kankaala et al., 2006). On the other hand, the CH<sub>4</sub> oxidation rates of up to 43 µmol L<sup>-1</sup> d<sup>-1</sup> in the shallow lakes exceeded rates of about 0.5 to 5 µmol L<sup>-1</sup> d<sup>-1</sup> (Welch et al., 1980) in a CH<sub>4</sub>-fertilized Canadian Arctic lake, and surpassed the highest observed rates of about 17 to 30 µmol L<sup>-1</sup> d<sup>-1</sup> in eutrophic north-temperate and sub-Arctic lakes (Rudd and Hamilton, 1975; Harrits and Hanson, 1980).

Specific rates of CH<sub>4</sub> oxidation are independent of CH<sub>4</sub> concentration, allowing cross-site comparison of methanotrophic activity. Values from <0.0001 to 0.234 d<sup>-1</sup> in deep lakes are toward the low end of values of 0.001 to 1.0 d<sup>-1</sup> reported for the Hudson River (de Angelis and Scranton, 1993) and for marine waters (Kelly, 2003) and temperate and boreal lakes of varying trophic status (Utsumi et al. 1998a&b; Bastviken et al., 2003). Although  $k_{CH4}$  values for surface waters in shallow lakes fall within the range given elsewhere, the highest  $k_{CH4}$  values in bottom waters of shallow lakes (1.21 to 3.64 d<sup>-1</sup>) exceed previous reports for lacustrine environments and translate to CH<sub>4</sub> turnover times of 0.83 to 0.29 d.

Collectively, remarkably high summer concentrations of hypolimnetic  $CH_4$  in waters characterized by a short ice-free season and intermittent circulation, and correspondingly high values for  $CH_4$  oxidation and  $k_{CH4}$ , indicate the importance of  $CH_4$  in carbon cycling in the water columns of shallow Arctic Foothills lakes.

# ii. Methanotrophic Bacterial Growth Efficiency and Methanotrophic Production

Methanotrophic bacterial growth efficiency ranged from 23 to 48% (Table 3), with no difference between shallow and deep study lakes. King (1993) reported that MBGE in aquatic environments varied between 15 and 80%, and Bastviken et al. (2003) found a similar range, 6 to 77%, in boreal lakes of varying trophic status; MBGE values measured in this study fall within this range, but were somewhat more constrained, suggesting similar methanotrophic consortium and kinetics across all study lakes. Growth efficiencies similar to those found here indicate dominance by Type II methanotrophs (Auman et al., 2000).

The average area-based CH<sub>4</sub> oxidation rate of 0.591 mmol m<sup>-2</sup> d<sup>-1</sup> for shallow lakes was significantly higher than the average of 0.012 mmol m<sup>-2</sup> d<sup>-1</sup> for deep lakes (Table 3), despite the depth difference (Table 1). Nonetheless, for all study lakes, area-based rates of CH<sub>4</sub> oxidation were similar to the lowest previously observed, which show a generalized decrease with increasing latitude. Reported areal rates of CH<sub>4</sub> oxidation range to 20 mmol m<sup>-</sup> <sup>2</sup> d<sup>-1</sup> in eutrophic and mesotrophic temperate lakes (Rudd and Hamilton, 1978; Fallon et al., 1980; Striegl and Michmerhuizen, 1996; Utsumi et al., 1998 a&b), 4.3 mmol m<sup>-2</sup> d<sup>-1</sup> in eutrophic and oligotrophic boreal lakes (Bastviken et al., 2002; Kankaala et al., 2006), and 0.83 mmol m<sup>-2</sup> d<sup>-1</sup> in a CH<sub>4</sub>-fertilized Arctic lake (Welch et al., 1980). The extraordinarily high volume-based rates of CH<sub>4</sub> oxidation in bottom waters of shallow study lakes do not

compensate for reduced hypolimnetic volume, resulting in low area-based rates of CH<sub>4</sub> oxidation in waters of Arctic Foothill lakes.

Area-based estimates of methanotrophic biomass production in shallow lakes corresponded to 1 to 5% of phytoplankton production, compared to about 0.1% in deep lakes (Table 3), again pointing to a greater role for  $CH_4$  in C cycling in shallow lakes than in deep lakes. Percentages similar to those calculated for the shallow lakes, 0.3 to 7%, were reported for boreal lakes of variable productivity by Bastviken et al. (2003), while a higher range, 5 to 10%, was found by Kankaala et al. (2006) for a highly humic boreal lake. The relative importance of  $CH_4$  as a potential energy source for pelagic food webs in these lakes appears to be roughly similar to benthic food webs, as Bretz (2012) found that methanotrophic biomass production was 1.2 to 6.3% of epipelic primary production.

Compared to the deep study lakes, the shallow lakes have a thinner oxic water column into which  $CH_4$  diffusing upward from the sediments can be attenuated by methanotrophs. Nonetheless, the shallow lakes exhibited significantly greater volume-based, areal, and specific  $CH_4$  oxidation rates. Combined with the larger lake-surface  $CH_4$ emissions predicted for the shallow lakes, these data strongly suggest a greater  $CH_4$  source in the sediment of the shallow lakes. In turn, this implies that the shallow lakes, on a per-unitarea basis, are stronger drivers of carbon cycling, an inference supported by their elevated chl *a* and DOC concentrations and previous work (e.g. Desortova, 1981; O'Brien et al., 1992; Whalen et al., 2006).

#### iii. Sediment-Water Exchanges and the Role of Radiant Energy

Dissolved  $O_2$  concentrations in the benthic chambers declined slowly, and approached the levels of depletion observed in the hypolimnia of the shallow lakes (<50 µM) only in GTH 112. Still, all lake sediments showed net  $O_2$  consumption under clear benthic chambers at  $\overline{z}$ , indicating that the sediments were net heterotrophic. The range of benthic  $O_2$ depletion rates observed here (Table 5) borders, and frequently falls short of, the low end of literature values of 1.6 to 32 mmol m<sup>-2</sup> d<sup>-1</sup> compiled by Pace and Prairie (2005) for lake sediments worldwide, pointing to the oligotrophic nature of lakes in the study region.

The lack of correlation between  $O_2$  flux in the clear chambers and either epipelic chl *a* or field irradiance at the sediment surface further points to the complexity of factors influencing dissolved  $O_2$  exchange at the sediment-water interface. Nonetheless, the higher rate of  $O_2$  consumption in the clear chamber than in the dark chambers in GTH 99 reported here is abstruse. Sediment oxygen demand results from aerobic respiration as well as oxidation of reduced chemical species such as  $Fe^{2+}$  and  $Mn^{2+}$  diffusing upward from anaerobic regions of the sediment to oxic zones. Sediment particles and interstitial water contain reduced chemical constituents, and it is feasible that chamber deployment disturbed the sediments enough to enhance  $O_2$  consumption in the light chamber of GTH 99 by mobilizing such species (e.g. Adams et al., 1982).

Rates of benthic  $CO_2$  production measured in my dark chambers are comparable to the low-end values reported for other studies utilizing dark sediment core and benthic chamber incubations, while my clear chamber values are among the lowest observed. Reported rates extend to 132 mmol m<sup>-2</sup> d<sup>-1</sup> in marine environments, and from 2 to 28.4 mmol m<sup>-2</sup> d<sup>-1</sup> in temperate freshwaters (Anderson et al., 1986; Sweerts et al., 1986; Blackburn et al.,

1988; Hedin, 1990; Pulliam, 1993; Therkildsen and Lomstein, 1993; Ramlal et al., 1993). Ramlal et al. (1994) observed much higher rates of sediment respiration than those reported here in a shallow Canadian arctic lake, up to 47 mmol  $CO_2 \text{ m}^{-2} \text{ d}^{-1}$ , possibly related to the 80% macrophyte cover of sediments in that lake. Overall, the low rates of  $CO_2$  accumulation in benthic chambers further emphasize the oligotrophic status of the study lakes.

Oligotrophic systems are frequently considered to be dominated by aerobic decomposition (Holmer and Storkholm, 2001). The magnitude of excess CO<sub>2</sub> production beyond that predicted by aerobic respiration reflects the relative importance of anaerobic respiratory pathways (Pace and Prairie, 2005). Excluding GTH 99, expected dark chamber  $CO_2$  fluxes based on  $O_2$  consumption data were only 45 to 83% of observed values (Table 5). This suggests an important role for anaerobic pathways in sediment catabolism in these lakes. Methanogenesis is clearly important in the study lakes (Bretz, 2012). Other anaerobic respiratory processes potentially include reduction of iron, manganese, nitrate, and sulfate, which have variously been shown to be significant in mesotrophic and oligotrophic temperate lakes (Rich, 1980; Kuivila and Murray, 1984; Kuivila et al., 1989; Mattson and Likens, 1992). Sulfate reduction is unlikely here because typical water column concentrations of 20  $\mu$ M (Chalfant, 2004) are below the 100  $\mu$ M level that limits this microbial group (Sinke et al., 1992). High concentrations of both solid phase and dissolved iron have been reported for Toolik Lake sediments (Cornwell and Kipphut, 1992), indicating that Fe<sup>3+</sup> reduction is possible, and Fe<sup>3+</sup> reduction has been shown to be an important metabolic pathway in anaerobic zones of Alaskan Arctic coastal plain lakes (Lipson et al., 2010, 2011). The gradual diffusion of winter-accrued CO<sub>2</sub> from the sediments during summer (cf. Ramlal et al., 1994) is an additional possibility. However, further analysis of water and sediment

samples would be needed to make quantitative statements about these processes in the study lakes.

Arctic Foothills lakes are oligotrophic, with relatively shallow mean depths and high catchment area : lake area ratios, suggesting that their biogeochemical cycles may be driven by allochthonous inputs. However, sediment C mineralization and sediment-water CH<sub>4</sub> exchange here appear to be heavily influenced by autochthonous inputs, and the effect is magnified in shallow relative to deep lakes. The C:N ratios of sedimenting material were similar to those of phytoplankton biomass (Bretz, 2012), indicating dominance by autochthonously produced material. Water column chl *a* concentrations (an index of phytoplankton biomass) were higher in the shallow lakes, and overall were positively related ( $R^2 = 0.60$ ) to rates of C sedimentation. Rates of C sedimentation were also significantly higher in the shallow lakes, averaging 7.5 mmol m<sup>-2</sup> d<sup>-1</sup>, compared to 0.6 mmol m<sup>-2</sup> d<sup>-1</sup> in the deep lakes (Bretz, 2012). Furthermore, across all lakes, corrected clear chamber CH<sub>4</sub> fluxes correlated positively ( $R^2 = 0.40$ ) to C sedimentation rates.

The attenuation of lake sediment  $CH_4$  release by  $O_2$  has been previously observed in many lakes (e.g. Kuivila et al., 1988; Frenzel et al., 1980; Liikanen et al., 2003; Murase et al., 2005), and dissolved  $O_2$  was also a critical regulator of sediment-water  $CH_4$  flux in the study lakes. The highly oxic hypolimnia observed in the deep lakes during summer, and the small volume of shallow lake hypolimnia that experienced summer hypoxia, suggest that  $O_2$ regulates benthic  $CH_4$  fluxes for the majority of study lake area. The average extent of the surficial oxic sediment layer was significantly higher in the shallow lakes than in the deep lakes, varying from 110 to 210  $\mu$ m in the former compared with 230 to 315  $\mu$ m in the latter (Bretz, 2012). Across all lakes, corrected clear chamber  $CH_4$  exchange showed a significant inverse relationship ( $\mathbb{R}^2 = 0.70$ ) with the extent of the surficial oxic sediment layer (Figure 6), as has been reported for mesotrophic and eutrophic north-temperate and boreal lakes (Frenzel et al., 1990; Sweerts et al., 1991; Huttunen et al., 2006). Corrected CH<sub>4</sub> flux in the dark chambers significantly exceeded that in the clear chambers, likely due to decreased oxidized microzone thickness in the dark chambers during incubation. Oremland (1975) observed a similar discrepancy between clear and dark benthic chamber CH<sub>4</sub> fluxes in shallow, tropical marine waters.



Figure 6: Relationship between corrected clear chamber sediment-water CH<sub>4</sub> exchange rate and vertical extent of surficial oxic sediment. Oxic layer thickness from Bretz (2012).

King (1990) showed that  $CH_4$  efflux from the sediment-water interface in a wetland varied inversely with light influx, and that light regimes indirectly control  $CH_4$  fluxes from PAR-exposed wetland sediment by stimulating photosynthetic  $O_2$  production, which provides a favorable environment for  $CH_4$  oxidation. The majority (54 to 100%) of sediment area in the study lakes is shallower than the depth of 1% surface PAR penetration (Table 5), the compensation light intensity for photosynthesis (Reynolds, 2006). At shallower depths, epipelic photosynthesis may not always exceed community respiration (see above), but some  $O_2$  is generated to offset respiratory activity and reduce  $CH_4$  emission from the sediments.

The indirect effect of light on sediment CH<sub>4</sub> flux plays a unique role in arctic lakes, whose light regime is defined on a yearly, rather than diurnal, basis, with a continuous summer photoperiod, and no influx of radiant energy for roughly 9 months per year due to ice cover. Clear chamber CH<sub>4</sub> fluxes reflect typical summer conditions, while dark chamber CH<sub>4</sub> fluxes, which were significantly higher considering all data, may be similar to those that occur in the winter. As the sediment oxidized microzone diminishes in thickness, CH<sub>4</sub> flux from the sediment may increase and CH<sub>4</sub> could accrue in the ice-capped water column rather than diffusing to the atmosphere. This may lead to a large pulse of CH<sub>4</sub> from the lake during turnover after spring thaw. The importance of such storage fluxes has been established in boreal and temperate lakes (Strayer and Tiedje, 1978; Fallon et al., 1980; Michmerhuizen et al., 1996; Striegl and Michmerhuizen, 1998; Utsumi et al., 1998 a&b; Casper et al., 2000; Bastviken et al., 2002; Huttunen et al., 2003; Bastviken et al., 2004).

## iv. Evasion of CH<sub>4</sub> from the Lake Surface

For the duration of benthic chamber deployment, average estimated wind speeds were similar for all lakes and maximum and minimum observed temperatures over the entire sampling period were not significantly different between shallow and deep lakes. Therefore, stagnant film model-estimated CH<sub>4</sub> emissions depended primarily on surface CH<sub>4</sub> concentrations ( $R^2 = 0.99$ ), and thus were higher for shallow lakes. The maximum predicted CH<sub>4</sub> efflux averaged 1.34 mmol m<sup>-2</sup> d<sup>-1</sup> for the shallow lakes, somewhat higher than the mean of 0.43 mmol m<sup>-2</sup> d<sup>-1</sup> for lakes and rivers in the Arctic Foothills (Kling et al., 1992), while the average of 0.22 mmol m<sup>-2</sup> d<sup>-1</sup> for deep lakes is somewhat lower. Shallow lake CH<sub>4</sub> fluxes are also very similar to the mean of 1.3 mmol m<sup>-2</sup> d<sup>-1</sup> observed by Whalen and Reeburgh (1990) in Arctic Alaska ponds, but Bartlett et al. (1992) found greater CH<sub>4</sub> emissions than any observed here, averaging 4.8 mmol m<sup>-2</sup> d<sup>-1</sup>, in small (<10 km<sup>2</sup>) lakes with emergent macrophytes in the Yukon-Kuskokwim delta. Large (>10 km<sup>2</sup>) lakes in the same study had CH<sub>4</sub> effluxes centering around 0.24 mmol m<sup>-2</sup> d<sup>-1</sup>, very similar to those observed here for deep lakes Globally, shallow lake values compare well even to diffusive CH<sub>4</sub> fluxes reported for tropical lakes (about 1.1 mmol m<sup>-2</sup> d<sup>-1</sup>; Barlett et al., 1988; Devol et al., 1988; Boon and Mitchell, 1995), but here only apply for the brief ice-free season.

Considering all data, predicted CH<sub>4</sub> emissions from the study lakes compare favorably to the low end of CH<sub>4</sub> fluxes reported for terrestrial tundra environments in Alaska, which are as high as about 10 mmol m<sup>-2</sup> d<sup>-1</sup> during the thaw season, but average between <0.1 and 3.3 mmol m<sup>-2</sup> d<sup>-1</sup> (Whalen and Reeburgh, 1988, 1990a, 1992). The highly oxic water columns of Arctic lakes appear to effectively attenuate CH<sub>4</sub> emitted from the sediments, often leading to lower emissions from the lake surface than from soils in the surrounding tundra environments, where diffusing CH<sub>4</sub> must transit a less extensive oxic zone overlying the zone of CH<sub>4</sub> production. Notably, maximum estimated fluxes of CH<sub>4</sub> from the shallow lakes are very similar to the average range reported for Alaskan Arctic tundra, suggesting that rates of methanogenesis in the smallest lakes in the region are sufficient to overcome the effects of water column oxidation. Corrected clear chamber CH<sub>4</sub> fluxes were significantly related to maximum estimated CH<sub>4</sub> evasion from the lake surface (R<sup>2</sup> = 0.76), suggesting that water column methanotrophy is unable to completely compensate for elevated CH<sub>4</sub> efflux from the sediment.

#### v. Methane Mass Balance

My entire data can be combined into a conceptual model of summer  $CH_4$  cycling dynamics in Arctic Foothill lakes, incorporating the sediments as a  $CH_4$  source, with water column oxidation and surface evasion as sinks (Figure 7). The results of a simple, arithmetic mass balance are shown in Table 9. Considering both the minimum and the maximum predicted rates of CH<sub>4</sub> evasion to the atmosphere, all study lakes besides GTH 112 showed  $CH_4$  mass balances <0, that is,  $CH_4$  emissions were greater than implied by flux from the sediments and consumption in the water column. Kling et al. (1992) encountered a similar phenomenon in their study of CH<sub>4</sub> concentrations and emissions in surface waters from the same region, and suggested that groundwater flow imported significant CH<sub>4</sub>, subsidizing emissions. This likely accounts for the excess CH<sub>4</sub> emission to the atmosphere in most study lakes. The lone exception was GTH 112, where 7% to 47% of clear chamber sediment  $CH_4$ flux was unaccounted for by the mass balance as currently framed. Only one clear chamber was deployed in each lake; however, two dark chambers were deployed, with replicate measurements of sediment CH<sub>4</sub> emission showing an average coefficient of variation of 30%. Assuming a similar degree of spatial variation in clear chambers, excess sediment-water  $CH_4$ flux in GTH 112 can be accounted for by variability of this magnitude.



Figure 7: Conceptual model of CH<sub>4</sub> cycling dynamics in shallow and deep Arctic Foothill lakes. Arrows depicting sources and sinks and are sized to represent their approximate relative magnitude.

Ebullition is estimated to contribute 40-60% of total lake CH<sub>4</sub> emissions in some instances (Bastviken et al., 2004). Walter et al. (2006, 2008) and others (e.g. Zimov et al., 1997) have shown that CH<sub>4</sub> ebullition from Arctic lakes is a significant source of natural CH<sub>4</sub> to the atmosphere, and can account for as much as 95% of annual CH<sub>4</sub> emission from Arctic lakes. However, benthic chambers have a small footprint and ebullition is spatially heterogeneous (Casper et al., 2000; Ostrovsky, 2003; Walter et al., 2006, 2008) such that it is unlikely that an event would be captured in a chamber experiment, and chamber CH<sub>4</sub> time series data do not appear to reflect bubble episodes (cf. Figure 5). Overall, there is a marked contrast between the scale and form of  $CH_4$  cycling in deep and shallow lakes in the Arctic Foothills region (Figure 7; Table 9). Transport of  $CH_4$  from adjacent groundwater appears to account for essentially all  $CH_4$  emissions from deep lakes, as, on average, roughly all  $CH_4$  diffusing from the sediments (under light conditions) to the water column is consumed by methanotrophs. Ebullition likely plays a significant role, transporting  $CH_4$  directly to the atmosphere with minimal loss to methanotrophs, but this was not reflected in the results of this study. On average in both lake types, sediment-water  $CH_4$ flux under dark conditions exceeds areal water column oxidation at  $\overline{z}$ , suggesting that  $CH_4$ accumulation under winter ice and mass evasion at spring turnover are significant.

Table 9: Mass balance of CH <sub>4</sub> for study lakes and mean CH <sub>4</sub> mass balances for size classes. All units are mmol m <sup>-2</sup> d <sup>-1</sup> .										
Study Lake	Size Class	Corr. clear sed. CH₄ flux	Water col. CH₄ ox.	Min. est. surface emission	Max. est. surface emission	% Sed. CH₄ flux oxidized in water col.	% CH₄ flux Emitted	Max. balance	Min. balance	% Sed. CH₄ flux unaccounted for
GTH 99	Shallow	0.71	0.05	0.71	1.52	7	100-214	-0.05	-0.86	0
GTH 112	-	3.23	1.08	0.64	1.94	33	20-60	1.51	0.21	7 to 47
GTH 114	-	0.24	0.007	0.40	0.55	3	167-229	-0.17	-0.32	0
GTH 100	Deep	-0.001	0.011	0.14	0.23	-	-	-0.15	-0.24	0
<b>NE14</b>	-	0.002	0.001	0.11	0.25	50	5500-12500	-0.11	-0.25	0
Toolik	-	0.030	0.014	0.12	0.19	47	400-633	-0.10	-0.17	0
Size Class										
Shallow	Mean	1.39	0.38	0.58	1.34	27	42-96	0.43	-0.32	0-31
Deep	Mean	0.01	0.009	0.12	0.22	90	1200-2200	-0.12	-0.22	0

#### vi. Summary and Conclusions

Arctic Foothills lakes show marked contrasts in C cycling characteristics when subdivided by size. Deep lake values for  $CH_4$  concentration, water column  $CH_4$  oxidation rates, sediment  $CH_4$  emission, and surface evasion of  $CH_4$  are similar to the lowest reported globally, while shallow lake values are often similar to those reported for lower latitude lakes of higher trophic status. Thus,  $CH_4$  plays a more significant role in shallow Arctic lakes, both in their internal food web dynamics and in their contribution to the atmospheric  $CH_4$ budget and climate change. All aspects of the  $CH_4$  cycle in these systems appear to be strongly tied to autochthonous production in both the water column and epipelon.

Expected consequences of a warmer Arctic include enhanced delivery of nutrients and DOC to lacustrine systems (Hobbie et al., 1999; Prowse et al., 2006; Tank et al., 2011). Nutrients may stimulate phytoplankton production, increasing delivery of high quality C to the sediment (Kritzberg et al., 2005), and enhancing  $CH_4$  production. Conversely, elevated DOC may reduce radiant energy penetration in lake waters (Morris et al., 1995; Fee et al., 1996), decreasing phytoplankton production and resulting C sedimentation. While my findings indicate that lower C sedimentation would cause lower sediment  $CH_4$  emission, the impact of elevated turbidity on phytoplankton and epipelon production would accelerate  $O_2$ depletion in bottom waters and sediments. This effect would be amplified by strengthened lake stratification resulting from higher temperatures and a longer thaw season (Prowse et al., 2006). In turn, accelerated  $O_2$  depletion in bottom waters would reduce the thickness of the surficial sediment oxic layer. Therefore, the data suggest that projected climate warming in Arctic environments (e.g. Kattsov et al., 2005) will likely increase sediment-water  $CH_4$  flux. My data show that  $CH_4$  oxidation is an important component of C cycling in Alaskan Arctic lakes, particularly shallow ones, and  $k_{CH4}$  in shallow lake bottom waters in particular were extremely high. This suggests that water column communities of methanotrophs could be capable of mitigating future increases in sediment  $CH_4$  flux. However, air-water  $CH_4$ exchanges were strongly correlated to sediment  $CH_4$  fluxes, indicating that the sediment  $CH_4$ signal survived to the surface despite significant  $CH_4$  oxidation activity. Therefore, lake surface  $CH_4$  effluxes may increase proportionally with sediment  $CH_4$  fluxes in a warming climate. This analysis excludes  $CH_4$  emission via ebullition, which is expected to increase due to pervasive permafrost thaw (Zimov et al., 2005; Walter et al., 2006, 2008).

The role of  $CH_4$  as a currency of C and energy in Alaskan Arctic lakes is already significant, and seem likely to expand with climate change. However,  $CH_4$  cycling dynamics in Arctic lakes are intertwined with other processes, and the effects of climate-induced change on variables that influence organic matter input and sediment  $O_2$  levels must be considered in attempting to constrain potential climate feedbacks in high latitudes. Based on the data presented here, shallow Arctic lakes should factor prominently in the projections of climate modelers making recommendations to policymakers.

Table A.1: Profiles of temperature, dissolved $O_2$ , photosynthetic photon flux density, CH <sub>4</sub> ,										
chí <i>a</i> , an	chl a, and DOC taken at z <sub>max</sub> on 7/8/2010.									
z (m)	Т (°С)	O <sub>2</sub> (μM)	PPFD (µmol photons m <sup>-2</sup> s <sup>-1</sup> )	CH₄ (μM)	Chl a (ug/L)	DOC (µM)				
0.0	14.4	273	1166	1.53	1.12	393				
0.5	13.1	270	724	-	-	-				
1.0	12.8	268	532	1.52	1.36	386				
1.5	12.4	263	360	-	-	-				
2.0	12.3	265	253	1.95	1.31	390				
2.5	12.2	261	184	2.24	-	-				
3.0	12.1	253	112	-	1.55	326				
3.5	12.0	254	90	11.79	1.81	389				
4.0	11.9	46	52	15.46	-	-				

Appendix A	: GTH 99	depth	profile	data
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Table A.2: Profiles of temperature, dissolved $O_2$ , and $CH_4$ taken at $\overline{z}$ on 7/21/2010.							
z (m)	Т (°С)	O₂ (μM)	CH₄ (μM)				
0.0	12.9	278	0.93				
0.5	12.6	277	0.91				
1.0	12.4	276	0.90				
1.5	12.3	269	0.95				
2.0	12.2	268	1.12				

Table A.3: Profiles of temperature, dissolved $O_2$ , and $CH_4$ taken at $z_{max}$ on 7/21/2010.								
z (m)	T (°C)	O <sub>2</sub> (μM)	CH <sub>4</sub> (μM)					
0.0	12.8	292	0.87					
0.5	12.7	281	-					
1.0	12.6	277	0.83					
1.5	12.5	281	-					
2.0	12.1	268	0.97					
2.5	12.0	263	0.95					
3.0	11.8	260	-					
3.5	11.6	270	2.04					
4.0	11.3	243	2.42					

Table A.4: Profiles of temperature, dissolved								
$O_2$ , and CH <sub>4</sub> taken at $\overline{z}$ on 7/30/2010.								
z (m) Τ (°C) Ο <sub>2</sub> (μΜ) CH <sub>4</sub> (μΜ)								
0.0	12.9	279	1.67					
0.5	13.0	279	1.44					
1.0	13.0	263	1.46					
1.5	13.0	269	1.36					
2.0	13.0	263	1.22					

Table A.5: Profiles of temperature, dissolved					
O <sub>2</sub> , and CH	I₄ taken at z	z <sub>max</sub> on 7/30/	2010.		
z (m)	T (°C)	O₂ (μM)	CH₄ (μM)		
0.0	13.2	254	1.41		
0.5	13.2	251	-		
1.0	13.2	250	1.49		
1.5	13.0	248	-		
2.0	12.6	231	1.55		
2.5	12.2	217	2.33		
3.0	11.8	209	-		
3.5	11.3	222	2.69		
4.0	11.0	223	3.58		

Table A.6: Profiles of temperature, dissolved						
O <sub>2</sub>	, and $CH_4$ t	aken at z <sub>max</sub>	on 7/8/2011.			
z (m)	T (°C)	O₂ (μM)	$CH_4$ ( $\mu M$ )			
0.0	15.6	260	0.98			
0.5	15.5	257	-			
1.0	15.5	255	0.81			
1.5	15.3	251	0.97			
2.0	15.1	251	0.88			
2.5	14.3	268	0.93			
3.0	13.9	249	0.72			
3.5	13.3	225	0.63			
4.0	12.8	139	1.44			

Table B	Table B.1: Profiles of photosynthetic photon flux density, temperature, CH <sub>4</sub> , chl <i>a</i> , and					
DOC tal	ken at $z_{max}$ on 6/30/2	011.				
z (m)	PPFD (µmol photons m <sup>-2</sup> s <sup>-1</sup> )	T (°C)	z (m)	CH₄ (μM)	Chl a (ug/L)	DOC (µM)
0.0	199.70	13.2	0.0	1.29	9.65	507
1.0	29.03	13.3	0.5	1.29	9.87	578
2.0	4.61	13.3	1.0	1.28	8.84	618
3.0	0.78	9.5	2.0	1.30	9.10	598
4.0	0.16	7.0	3.5	0.55	2.66	632
5.0	0.04	6.4	5.7	11.82	1.78	615
5.8	0.03	6.2	-	-	-	-

A	ppendix	к <b>В</b> :	GTH	112 de	pth	profile	data
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Table B.2:	Profile of CH <sub>4</sub>
taken at $\overline{z}$	on 6/30/2011.
z (m)	CH₄ (μM)
0.0	1.31
0.5	1.30
1.0	1.30
1.5	1.34
2.0	1.28

Table B.3: Profiles of temperature, dissolved					
O <sub>2</sub> , and CH,	4 taken at $z_m$	<sub>ax</sub> on 7/6/20	11.		
z (m)	T (°C)	O <sub>2</sub> (μM)	$CH_4$ ( $\mu M$ )		
0.0	14.5	240	0.74		
0.5	14.5	238	-		
1.0	14.3	229	0.56		
1.5	13.6	227	-		
2.0	12.8	223	0.46		
2.5	12.4	220	-		
3.0	11.8	194	0.28		
3.5	10.1	125	-		
4.0	8.0	64	0.29		
4.5	7.1	64	9.23		
5.0	7.0	64	22.3		
5.5	6.8	64	32.4		

Table B.4:	Profiles of te	emperature,	aissoived		
O <sub>2</sub> , and CH <sub>4</sub>	₁ taken at zm	1ax on 7/13/	/2011.		
z (m)	T (°C)	O <sub>2</sub> (μM)	$CH_4$ ( $\mu M$ )		
0.0	14.6	193	1.53		
1.0	14.6	188	1.21		
2.0	14.7	187	1.29		
3.0	13.6	130	0.63		
4.0	8.6	38	18.23		
4.5	7.9	36	29.74		
5.0	7.5	35	41.93		
5.5	7.2	34	52.62		

Table B.5: Profiles of temperature, dissolved
$O_2$ , and CH <sub>4</sub> taken at $\overline{z}$ on 7/13/2011.

$O_2$ , and Cr	n <sub>4</sub> taken at 2	2 011 7/15/20	11.
z (m)	Т (°С)	O <sub>2</sub> (μM)	$CH_4$ ( $\mu M$ )
0.0	14.7	188	1.78
0.5	14.7	182	6.08
1.0	14.7	179	3.74
1.5	14.7	176	3.06
2.0	14.7	176	2.53

Table B.6: Profiles of temperature and dissolved $O_2$ taken at $z_{max}$ on 7/19/2011.					
z (m)	T (°C)	Ο <sub>2</sub> (μΜ)			
0.0	15.3	246			
1.0	15.0	238			
2.0	14.6	228			
3.0	13.8	180			
4.0	9.4	24			
5.0	7.6	22			
6.0	7.3	22			

Table C.1: Profiles of temperature, dissolved $O_2$						
and $CH_4$ taken at $z_{max}$ on 7/1/2010.						
z (m)	Т (°С)	O <sub>2</sub> (μM)	CH₄ (μM)			
0.0	16.9	260	0			
0.5	-	-	0.47			
1.0	17.0	240	-			
1.5	-	-	0.72			
2.0	16.3	215	-			
2.5	-	-	1.38			
3.0	14.1	187	-			
3.5	-	-	0.48			
4.0	10.0	100	-			
4.5	-	-	2.33			
5.0	7.4	51	-			
5.5	-	-	17.63			
6.0	7.0	48	-			

Appendix C: (	GTH 114 depth	profile data
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Table C.2: I	Profile of CH <sub>4</sub>
taken at $\overline{z}$ c	on 7/1/2010.
z (m)	CH₄ (μM)
0.0	0.57
0.5	0.54
1.0	0.54
1.5	0.54
2.0	0.56

z (m)	PPFD (μmol photons m <sup>-2</sup> s <sup>-1</sup> )	T (°C)	O <sub>2</sub> (μM)	Chl a (ug/L)	DOC (µM)			
0.0	799.0	17.4	252	-	-			
0.5	325.0	16.8	232	2.98	665			
1.0	162.0	14.6	245	-	-			
1.5	89.7	13.1	238	3.54	644			
2.0	38.3	12.5	245	-	-			
2.5	12.2	12.3	241	3.49	625			
3.0	11.0	12.1	225	-	-			
3.5	5.5	12.0	220	2.98	561			
4.0	-	11.9	223	-	-			
4.5	-	11.6	197	28.3	607			
5.0	-	9.6	50	-	-			
5.5	-	8.0	47	-	-			
6.0	-	7.1	47	4.20	605			

Table C.3: Profile of photosynthetic photon flux density, temperature, dis	ssolved
$O_2$ , chl $\alpha$ , and DOC taken at $z_{max}$ on 7/9/2010.	

Table C.4: Profiles of temperature, dissolved							
$O_2$ , and C	H <sub>4</sub> at z <sub>max</sub> t	aken on 7/2	4/2010.				
z (m)	T (°C)	O <sub>2</sub> (μM)	CH₄ (μM)				
0	13.7	352	-				
0.5	13.6	350	0.38				
1	13.5	341	-				
1.5	13.3	334	0.37				
2	13.2	323	-				
2.5	13.0	321	0.45				
3	12.7	319	-				
3.5	12.5	320	0.43				
4	12.4	318	-				
4.5	12.3	316	0.60				
5	12.2	306	-				
5.5	12.2	299	-				
6	12.1	258	2.21				

Table C.5: Profiles of temperatures, dissolved					
$O_2$ , and $C$	H₄ taken a	t <del>z</del> on 7/24/2	2010.		
z (m)	Т (°С)	O₂ (μM)	$CH_4$ ( $\mu M$ )		
0.0	13.6	347	0.46		
0.5	13.6	344	0.40		
1.0	13.5	338	0.46		
1.5	13.5	322	0.42		
2.0	13.0	298	0.42		

Table C.6: Profiles of temperature, dissolved						
O <sub>2</sub> , and C	H₄ taken a	t z <sub>max</sub> on 7/3	1/2010.			
z (m)	T (°C)	O <sub>2</sub> (μM)	CH₄ (μM)			
0	14	332	-			
0.5	13.9	325	0.48			
1	13.9	321	-			
1.5	13.9	320	0.46			
2	13.9	309	-			
2.5	13.8	310	0.50			
3	13.3	306	-			
3.5	13.1	297	0.51			
4	13.1	302	-			
4.5	13.1	301	0.64			
5	13.0	293	-			
5.5	13.0	290	-			
6	12.8	250	3.34			

Table C.7	Table C 7: Profiles of temperature dissolved						
O2, and C	O2, and CH4 taken at $\overline{z}$ on 7/31/2010.						
z (m)	T (°C)	O <sub>2</sub> (μM)	CH₄ (μM)				
0.0	14.0	333	0.50				
0.5	13.9	333	0.44				
1.0	13.8	322	0.44				
1.5	13.6	328	0.44				
2.0	13.4	325	0.43				

DOC, and CH <sub>4</sub> taken at $z_{max}$ on 7/8/2010.						
z (m)	PPFD (µmol photons m <sup>-2</sup> s <sup>-1</sup> )	T (°C)	O <sub>2</sub> (μM)	Chl a (ug/L)	DOC (µM)	CH₄ (μM)
0.0	972.21	15.8	260	0.66	380	-
0.5	-	-	-	-	-	0.16
1.0	435.31	12.8	261	-	-	-
1.5	315.4	-	-	-	-	-
2.0	221.37	12.3	257	-	-	-
2.5	170.96	-	-	-	-	-
3.0	120.5	12.1	256	0.94	432	0.15
3.5	90.4	-	-	-	-	-
4.0	68.72	12.0	259	-	-	-
4.5	47.56	-	-	-	-	-
5.0	37.39	8.3	259	-	-	-
6.0	19.45	6.8	248	-	-	0.12
7.0	11.16	5.8	238	1.67	362	-
8.0	6.61	5.3	230	-	-	-
9.0	-	5.0	221	-	-	0.06
10.0	-	4.8	201	0.68	361	-
11.0	-	4.7	190	-	-	-
12.0	-	4.6	190	-	-	0.07
13.0	-	4.6	195	0.63	336	-
13.5	-	-	-	-	-	0.10
14.0	-	4.9	-	-	-	-

# Appendix D: GTH 100 depth profile data

Table D.1: Profiles of photosynthetic photon flux density, temperature, dissolved O<sub>2</sub>, chl a,

Table D.2:	Profiles of te	emperature,	dissolved
O <sub>2</sub> and CH	4 taken at z <sub>ma</sub>	<sub>x</sub> on 7/28/20	)10.
z (m)	T (°C)	O <sub>2</sub> (μM)	$CH_4$ ( $\mu M$ )
0	13.5	9.1	0.44
1	13.5	9.13	-
2	13.5	8.27	-
3	13.2	8.71	0.49
4	12.7	8.92	-
5	11.1	8.87	-
6	8.2	8.24	0.26
7	6.4	7.45	-
8	5.7	7.31	-
9	5.2	6.76	0.24
10	5.0	6.24	-
11	4.8	5.93	-
12	4.8	5.76	0.31
13	4.8	5.76	-
14	4.7	-	0.25

$O_2$ , and CH	$_4$ taken at $\overline{2}$	z on 7/28/201	LO.
z (m)	T (°C)	O <sub>2</sub> (μM)	CH₄ (μM)
0	13.6	278.4375	0.25
0.5	13.6	279.375	-
1	13.6	274.0625	0.32
1.5	13.6	263.125	-
2	13.6	262.5	-
2.5	13.6	257.5	0.27
3	13.6	255.9375	-
3.5	13.2	265.3125	0.21
4	12.7	268.125	-
4.5	12	259.0625	0.22
5	11	269.375	-
5.5	10	263.4375	-
6	8.7	244.375	0.25

Table E.1: Profiles of photosynthetic photon flux density, temperature, dissolved O <sub>2</sub> , chl <i>a</i> ,							
DOC, and CH <sub>4</sub> taken at $z_{max}$ on 7/15/2011.							
z (m)	PPFD (μmol photons m <sup>-2</sup> s <sup>-1</sup> )	T (°C)	Ο <sub>2</sub> (μΜ)	Chl a (ug/L)	DOC (µM)	CH₄ (μM)	
0.0	939	14.8	217	0.286	192	0.15	
1.0	719	14.6	212	-	-	-	
2.0	508	14.5	209	-	-	0.14	
3.0	377	14.5	207	0.264	125	-	
4.0	320	14.4	203	-	-	0.14	
5.0	234	14.2	208	0.338	244	-	
6.0	187	13.9	220	-	-	0.27	
7.0	151	10.1	253	-	-	0.33	
8.0	123	8.6	260	0.408	382	0.34	
9.0	92	8	258	-	-	-	
10.0	76	7.7	256	-	-	0.34	
11.0	60	7.6	255	0.748	290	-	
12.0	44	7.3	247	-	-	0.29	
13.0	-	7.1	244	-	-	-	
14.0	-	6.9	225	0.948	300	0.24	
15.0	-	6.8	199	0.499	-	0.21	
15.5	-	-	-	-	-	0.20	

Appendix E: NE14 depth profile data

Table E.2: Profiles of temperature, dissolved O <sub>2</sub> ,							
and CH <sub>4</sub> tak	ten at $\overline{z}$ on 7/2	22/2011.					
z (m)	T (°C)	O <sub>2</sub> (μM)	CH₄ (μM)				
0.0	14.5	240	0.25				
1.0	14.5	238	-				
1.5	-	-	0.11				
2.0	14.5	234	-				
3.0	14.5	233	0.13				
4.0	14.5	233	0.13				
5.0	14.5	227	0.14				
6.0	14.5	227	0.13				
Table E.3: Profiles of temperature, dissolved $O_2$ ,							
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and CH <sub>4</sub> take	en at z <sub>max</sub> on	//22/2011.					
z(m)	T (°C)	O <sub>2</sub> (μM)	CH₄ (μM)				
0.0	14.3	225	0.13				
1.0	14.4	219	-				
2.0	14.4	215	-				
3.0	14.4	213	0.13				
4.0	14.4	212	-				
5.0	14.4	216	0.14				
6.0	14.4	212	-				
7.0	12.5	242	-				
8.0	9.6	261	0.30				
9.0	8.6	265	-				
10.0	8.3	269	-				
11.0	7.9	256	0.28				
12.0	7.6	251	-				
13.0	7.4	238	-				
14.0	7.1	215	0.18				
15.0	7.0	222	0.17				

Table E.4:	Table E.4: Profiles of temperature, dissolved $O_2$ ,								
and CH <sub>4</sub> taken at $\overline{z}$ on 8/6/2011.									
z (m)	T (°C)	O <sub>2</sub> (μM)	$CH_4$ ( $\mu M$ )						
0.0	13.4	279	0.15						
1.0	13.5	276	-						
2.0	13.5	278	0.15						
3.0	13.5	273	0.07						
4.0	13.5	276	0.07						
5.0	13.5	268	0.06						
6.0	13.5	271	0.00						

6	1

Table E.5: Profiles of temperature, dissolved							
$O_2$ , and $CH_4$ taken at $z_{max}$ on 8/6/2011.							
z (m)	Т (°С)	O₂ (μM)	CH₄ (μM)				
0	13.5	270	0.16				
2	13.5	263	-				
4	13.5	262	0.16				
6	13.5	257	-				
7	13.5	258	-				
8	13.1	260	0.24				
9	10.2	298	0.35				
10	9.3	295	-				
11	9.0	290	0.32				
12	8.3	281	0.30				
13	7.7	258	0.14				

Table E.5: Profiles of temperature, dissolved								
$O_2$ , and $CH_4$ t	aken at z <sub>max</sub>	on 8/6/201	.1.					
z (m)	$CH_4$ ( $\mu M$ )							
0	13.5	270	0.16					
2	13.5	263	-					
4	13.5	262	0.16					
6	13.5	257	-					
7	13.5	258	-					
8	13.1	260	0.24					
9	10.2	298	0.35					

Table F.1: Profiles of photosynthetic photon flux density, temperature, dissolved O <sub>2</sub> , CH <sub>4</sub> ,								
chl a, and	DOC taken at z <sub>max</sub> or	n 7/12/20	11.					
z (m)	PPFD (µmol photons m <sup>-2</sup> s <sup>-1</sup> )	T (°C)	O <sub>2</sub> (μM)	$CH_4$ ( $\mu M$ )	Chl a (ug/L)	DOC (µM)		
0.0	292	15.3	263	0.15	1.26	4.02		
0.5	186	-	-	-	-	-		
1.0	110	15.3	260	-	-	-		
1.5	73	-	-	-	-	-		
2.0	60	15.2	260	0.08	1.03	-		
2.5	51	-	-	-	-	-		
3.0	43	15.2	260	-	-	-		
3.5	39	-	-	-	-	-		
4.0	31	15.1	256	-	0.99	314		
4.5	25	-	-	-	-	-		
5.0	20	14.4	253	0.09	-	-		
6.0	13.3	12.2	256	-	1.63	-		
7.0	8.1	9.8	263	0.11	-	-		
8.0	5	8.3	263	0.12	1.86	393		
9.0	3.1	6.8	254	0.11	2.15	515		
10.0	1.9	6.4	250	-	1.28	-		
11.0	-	5.9	243	0.11	-	-		
12.0	-	5.9	241	-	0.74	402		
13.0	-	5.6	238	0.17	-	-		
14.0	-	5.5	238	-	-	-		
15.0	-	5.4	231	0.15	0.51	591		
16.0	-	5.2	229	0.15	-	-		
17.0	-	5.0	226	-	-	-		

Appendix F: Toolik depth profile data

Table F.2: Profiles of temperature, dissolved O <sub>2</sub> , and								
CH₄ taken	at $\overline{z}$ on 7/14	4/2011.						
$z$ (m) T (°C) $O_2$ ( $\mu$ M) $CH_4$ ( $\mu$ M)								
0.0	14.8	256	0.17					
0.5	14.8	252	-					
1.0	14.7	254	-					
1.5	14.5	250	0.21					
2.0	14.5	246	-					
2.5	14.4	247	-					
3.0	14.4	250	0.18					
3.5	14.4	248	-					
4.0	14.3	251	0.19					
4.5	14.1	247	-					
5.0	14	245	0.27					
5.5	13.5	242	-					
6.0	13.1	247	0.25					
6.5	10.4	241	0.21					
7.0	8.5	233	0.20					
7.5	7.9	219	0.22					

Table F.3: Profiles of temperature, dissolved O <sub>2</sub> ,					
and $CH_4$ ta	ken at z <sub>max</sub> o	on 7/21/2011.			
z (m)	T (°C)	O₂ (μM)	CH₄ (μM)		
0.0	15.4	259	0.15		
1.0	15.0	256	-		
2.0	14.9	254	-		
3.0	14.7	249	0.15		
4.0	14.7	250	-		
5.0	14.6	244	-		
6.0	14.1	247	-		
7.0	12.1	247	-		
8.0	8.8	253	0.15		
9.0	7.1	243	-		
10.0	6.4	237	0.13		
11.0	6.1	233	-		
12.0	5.9	228	-		
13.0	5.7	226	0.13		
14.0	5.5	225	-		
15.0	5.4	223	-		
16.0	5.3	219	0.15		
17.0	5.2	215	-		

and CH <sub>4</sub> taken at $\overline{z}$ on 8/12/2011.							
z (m)	T (°C)	O₂ (μM)	CH₄ (μM)				
0.0	12.5	284	0.20				
2.0	12.4	277	0.16				
3.0	12.4	276	0.14				
4.0	12.4	273	0.15				
5.0	12.3	271	0.16				
6.0	12.2	273	0.20				

Table F.4: Profiles of temperature, dissolved O

respired Cactiv	respired Cactivity, and ratio of biomass-incorporated and respired Cactivity to whole water Cactivity.								
	Whole	Riomass	Respired	Total (biomass	Total activity :	Corrected	Corrected	Corrected	
Sample	water	DPM ml <sup>-1</sup>	DPM ml <sup>-1</sup>	+respired) DPM	whole water	Total DPM	<b>Biomass DPM</b>	Respired	
	DPM mL <sup>-1</sup>			mL⁻¹	activity	mL⁻¹	mL⁻¹	DPM mL <sup>-1</sup>	
Killed Control 1	7	5	46	51	-	-	-	-	
Killed Control 2	5	3	9	12	-	-	-	-	
0 m A	223	157	147	304	1.37	9	2	6	
0 m B	236	190	154	344	1.46	7	2	5	
1 m A	235	96	151	246	1.05	9	3	6	
1 m B	216	91	159	249	1.16	10	3	7	
2 m A	245	100	161	261	1.07	597	168	429	
2 m B	271	127	182	309	1.14	627	186	442	
3 m A	5115	1960	3333	5293	1.03	1081	330	751	
3 m B	5051	1935	3818	5753	1.14	1104	355	749	
3.5 m A	8431	2273	6192	8465	1.00	1381	423	959	
3.5 m B	7459	2386	5361	7747	1.04	1331	418	913	
4 m A	12680	3931	9259	13190	1.04	1774	615	1159	
4 m B	12681	3835	9196	13031	1.03	1773	590	1182	

Table G.1: GTH 99 <sup>14</sup>CH<sub>4</sub> oxidation experiment results for raw and corrected whole water <sup>14</sup>C activity, biomass-incorporated <sup>14</sup>C activity, and respired <sup>14</sup>C activity, and ratio of biomass-incorporated and respired <sup>14</sup>C activity to whole water <sup>14</sup>C activity.

rate, speci	rate, specific rate of $CH_4$ oxidation, and $CH_4$ turnover time.						
Sample	Ambient CH₄ (μM)	Total oxidation rate (μmol L <sup>-1</sup> d <sup>-1</sup> )	Biomass conversion rate (μmol L <sup>-1</sup> d <sup>-1</sup> )	$CH_4$ respiration rate (µmol L <sup>-1</sup> d <sup>-1</sup> )	Specific oxidation rate (d <sup>-1</sup> )	CH₄ turnover time (d)	
0 m A	0.98	0.02	0.01	0.01	0.02	50.41	
0 m B	0.98	0.02	0.01	0.01	0.02	43.93	
1 m A	0.81	0.01	0.01	0.01	0.02	64.11	
1 m B	0.81	0.01	0.01	0.01	0.02	63.14	
2 m A	0.88	0.01	0.01	0.01	0.02	59.85	
2 m B	0.88	0.02	0.01	0.01	0.02	49.44	
3 m A	0.72	0.34	0.13	0.22	0.48	2.10	
3 m B	0.72	0.38	0.13	0.25	0.53	1.88	
3.5 m A	0.63	0.59	0.16	0.43	0.94	1.07	
3.5 m B	0.63	0.51	0.16	0.35	0.81	1.23	
4 m A	1.44	4.24	1.27	2.98	2.95	0.34	
4 m B	1.44	3.96	1.17	2.79	2.76	0.36	

Table G.2: GTH 99 measured ambient  $CH_4$  concentration when  ${}^{14}CH_4$  oxidation experiment samples were collected (7/8/2011), calculated total  $CH_4$  oxidation rate, rate of conversion of  $CH_4$  to biomass,  $CH_4$  respiration rate, specific rate of  $CH_4$  oxidation, and  $CH_4$  turnover time.

Sample	Whole water DPM mL <sup>-1</sup>	Biomass DPM mL <sup>-1</sup>	Respired DPM mL <sup>-1</sup>	Total (biomass +respired) DPM mL <sup>-1</sup>	Total activity : whole water activity	Corrected Total DPM mL <sup>-</sup>	Corrected Biomass DPM mL <sup>-1</sup>	Corrected Respired DPM mL <sup>-1</sup>
Killed Control 1	6	4	6	10	-	-	-	-
Killed Control 2	9	4	7	11	-	-	-	-
0 m A	1794	366	1449	1815	1.01	1805	362	1442
0 m B	1801	418	1439	1857	1.03	1846	414	1432
0.5 m A	1688	425	1355	1780	1.05	1770	421	1349
0.5 m B	1749	466	1371	1837	1.05	1826	462	1364
1 m A	1704	426	1356	1782	1.05	1771	421	1350
1 m B	1606	438	1265	1703	1.06	1692	434	1258
2 m A	1730	391	1343	1734	1.00	1723	387	1336
2 m B	1774	486	1419	1905	1.07	1894	482	1413
3.5 m A	6126	1322	4803	6126	1.00	6115	1318	4797
3.5 m B	6123	1482	4817	6298	1.03	6288	1478	4810
5.7 m A	9032	1529	7510	9039	1.00	9028	1525	7503
5.7 m B	10985	2242	9064	11306	1.03	11296	2238	9058

Table G.3: GTH 112 <sup>14</sup>CH<sub>4</sub> oxidation experiment results for raw and corrected whole water <sup>14</sup>C activity, biomass-incorporated <sup>14</sup>C activity, and respired <sup>14</sup>C activity, and ratio of biomass-incorporated and respired <sup>14</sup>C activity to whole water <sup>14</sup>C activity.

iale, speci	The face of CH <sub>4</sub> UXI	uation, and $CH_4$ tu	mover time.			
Sample	Ambient CH₄ (µM)	Total oxidation rate (μmol L <sup>-1</sup> d <sup>-1</sup> )	Biomass conversion rate (μmol L <sup>-1</sup> d <sup>-1</sup> )	$CH_4$ respiration rate ( $\mu$ mol L <sup>-1</sup> d <sup>-1</sup> )	Specific oxidation rate (d <sup>-1</sup> )	CH₄ turnover time (d)
0 m A	1.29	0.48	0.10	0.38	0.37	2.69
0 m B	-	0.49	0.11	0.38	0.38	2.63
0.5 m A	1.29	0.47	0.11	0.36	0.36	2.75
0.5 m B	-	0.49	0.12	0.36	0.38	2.66
1 m A	1.28	0.47	0.11	0.36	0.36	2.75
1 m B	-	0.45	0.11	0.33	0.35	2.89
2 m A	1.30	0.46	0.10	0.36	0.35	2.83
2 m B	-	0.51	0.13	0.38	0.39	2.56
3.5 m A	0.55	0.85	0.18	0.66	1.55	0.65
3.5 m B	-	0.88	0.21	0.67	1.61	0.62
5.7 m A	11.82	33.11	5.59	27.52	2.80	0.36
5.7 m B	-	52.95	10.49	42.46	4.48	0.22

Table G.4: GTH 112 measured ambient  $CH_4$  concentration when  ${}^{14}CH_4$  oxidation experiment samples were collected (6/30/2011), calculated total  $CH_4$  oxidation rate, rate of conversion of  $CH_4$  to biomass,  $CH_4$  respiration rate, specific rate of  $CH_4$  oxidation, and  $CH_4$  turnover time.

Sample	Whole water DPM mL <sup>-1</sup>	Biomass DPM mL <sup>-1</sup>	Respired DPM mL <sup>-1</sup>	Total (biomass +respired) DPM mL <sup>-1</sup>	Total activity : whole water activity	Corrected Total DPM mL <sup>-</sup>	Corrected Biomass DPM mL <sup>-1</sup>	Corrected Respired DPM mL <sup>-1</sup>
Killed Control 1	18	5	17	23	-	-	-	-
Killed Control 2	14	4	12	16	-	-	-	-
0.5 m A	39	11	26	38	0.96	18	6	12
0.5 m B	39	11	25	36	0.93	17	6	11
1.5 m A	85	32	55	88	1.03	68	28	41
1.5 m B	79	26	48	74	0.94	54	21	33
2.5 m A	100	37	60	96	0.96	77	32	45
2.5 m B	85	37	55	92	1.08	73	33	40
3.5 m A	808	263	546	809	1.00	789	258	531
3.5 m B	794	263	545	808	1.02	789	259	530
4.5 m A	9540	3083	6507	9590	1.01	9570	3078	6492
4.5 m B	9619	3042	6617	9659	1.00	9640	3038	6602
6.0 m A	9309	3950	5885	9836	1.06	9816	3946	5871
6.0 m B	9551	4038	5632	9669	1.01	9650	4033	5617

Table G.5: GTH 114 <sup>14</sup>CH<sub>4</sub> oxidation experiment results for raw and corrected whole water <sup>14</sup>C activity, biomass-incorporated <sup>14</sup>C activity, and respired <sup>14</sup>C activity to whole water <sup>14</sup>C activity.

Sample	Ambient CH₄ (μM)	Total oxidation rate (μmol L <sup>-1</sup> d <sup>-1</sup> )	Biomass conversion rate (µmol L <sup>-1</sup> d <sup>-1</sup> )	CH₄ respiration rate (µmol L <sup>-1</sup> d <sup>-1</sup> )	Specific oxidation rate (d <sup>-1</sup> )	CH₄ turnover time (d)
0.5 m A	0.47	0.00	0.0002	0.0004	0.001	766.80
0.5 m B	-	0.00	0.0002	0.0004	0.001	824.23
1.5 m A	0.72	0.00	0.001	0.002	0.005	202.58
1.5 m B	-	0.00	0.001	0.002	0.004	255.22
2.5 m A	1.38	0.01	0.003	0.004	0.006	180.06
2.5 m B	-	0.01	0.003	0.004	0.005	189.80
3.5 m A	0.48	0.03	0.01	0.02	0.06	17.08
3.5 m B	-	0.03	0.01	0.02	0.06	17.10
4.5 m A	2.33	2.72	0.88	1.85	1.17	0.86
4.5 m B	-	2.76	0.87	1.89	1.19	0.84
6 m A	17.63	21.65	8.70	12.95	1.23	0.81
6 m B	-	20.94	8.75	12.19	1.19	0.84

Table G.6: GTH 114 measured ambient  $CH_4$  concentration when  $^{14}CH_4$  oxidation experiment samples were collected (7/1/2010), calculated total  $CH_4$  oxidation rate, rate of conversion of  $CH_4$  to biomass,  $CH_4$  respiration rate, specific rate of  $CH_4$  oxidation, and  $CH_4$  turnover time.

Sample	Whole water	Biomass	Respired	Total (biomass +respired)	Total activity : whole	Corrected Total DPM	Corrected Biomass DPM	Corrected Respired DPM
				DPM mL <sup>-1</sup>	water activity	mL⁻¹	mL⁻¹	mL⁻¹
Killed Control 1	8	6	9	15	-	-	-	-
Killed Control 2	12	3	8	12	-	-	-	-
0.5 m A	24	6	17	24	0.97	10	2	9
0.5 m B	19	6	11	17	0.89	4	1	3
3 m A	44	12	32	44	1.00	31	8	24
3 m B	36	11	30	41	1.15	28	7	21
6 m A	541	277	412	688	1.27	675	272	403
6 m B	466	161	359	520	1.12	507	156	350
9 m A	956	314	875	1190	1.24	1176	310	867
9 m B	886	286	773	1060	1.20	1046	282	765
12 m A	2052	856	1778	2634	1.28	2621	851	1770
12 m B	2043	730	1843	2573	1.26	2559	725	1834
13.5 m A	2445	1046	1980	3026	1.24	3013	1041	1972
13.5 m B	2465	857	1933	2790	1.13	2776	852	1924

Table G.7: GTH 100 <sup>14</sup>CH<sub>4</sub> oxidation experiment results for raw and corrected whole water <sup>14</sup>C activity, biomass-incorporated <sup>14</sup>C activity, and respired <sup>14</sup>C activity, and ratio of biomass-incorporated and respired <sup>14</sup>C activity to whole water <sup>14</sup>C activity.

Sample	Ambient CH₄ (μM)	Total oxidation rate (μmol L <sup>-1</sup> d <sup>-1</sup> )	Biomass conversion rate (μmol L <sup>-1</sup> d <sup>-1</sup> )	$CH_4$ respiration rate (µmol L <sup>-1</sup> d <sup>-1</sup> )	Specific oxidation rate (d <sup>-1</sup> )	CH₄ turnover time (d)
0.5 m A	0.16	0.0001	0.00002	0.0001	0.0007	1346.97
0.5 m B	-	4E-05	0.00001	0.0000	0.0003	3626.50
3 m A	0.15	0.0003	0.0001	0.0003	0.002	445.48
3 m B	-	0.0003	0.0001	0.0002	0.002	500.41
6 m A	0.12	0.006	0.002	0.004	0.05	20.06
6 m B	-	0.005	0.001	0.003	0.04	26.89
9 m A	0.06	0.005	0.001	0.004	0.09	11.29
9 m B	-	0.005	0.001	0.003	0.08	12.76
12 m A	0.07	0.01	0.005	0.01	0.21	4.78
12 m B	-	0.01	0.004	0.01	0.20	4.91
13.5 m A	0.10	0.02	0.01	0.02	0.24	4.09
13.5 m B	-	0.02	0.01	0.02	0.22	4.48

Table G.8: GTH 100 measured ambient  $CH_4$  concentration when  $^{14}CH_4$  oxidation experiment samples were collected (7/8/2010), calculated total  $CH_4$  oxidation rate, rate of conversion of  $CH_4$  to biomass,  $CH_4$  respiration rate, specific rate of  $CH_4$  oxidation, and  $CH_4$  turnover time.

				Total (biomass	Total activity :	Corrected	Corrected	Corrected
Sample	Whole water	Biomass	Respired	+respired) DPM	, whole water	Total DPM	<b>Biomass DPM</b>	Respired DPM
·			DPIVI ML	mL <sup>-1</sup>	activity	mL⁻¹	mL⁻¹	mL⁻¹
Killed Control 1	6	2	4	6	-	-	-	-
Killed Control 2	5	3	3	6	-	-	-	-
0 m A	11	6	7	13	1.15	7	4	3
0 m B	20	5	10	14	0.71	8	2	6
3 m A	30	15	15	30	1.00	24	13	11
3 m B	21	11	15	25	1.20	19	8	11
5 m A	26	24	16	41	1.55	35	22	13
5 m B	19	18	13	31	1.59	25	15	10
8 m A	26	17	17	34	1.32	28	15	13
8 m B	24	13	16	29	1.20	23	10	12
11 m A	78	58	61	119	1.52	112	55	57
11 m B	68	45	52	96	1.41	90	42	48
14 m A	1263	803	1056	1860	1.47	1853	801	1052
14 m B	1219	737	1012	1749	1.43	1743	734	1009

Table G.9: NE14 <sup>14</sup>CH<sub>4</sub> oxidation experiment results for raw and corrected whole water <sup>14</sup>C activity, biomass-incorporated <sup>14</sup>C activity, and respired <sup>14</sup>C activity, and ratio of biomass-incorporated and respired <sup>14</sup>C activity to whole water <sup>14</sup>C activity.

Sample	Ambient CH₄ (µM)	Total oxidation rate (μmol L <sup>-1</sup> d <sup>-1</sup> )	Biomass conversion rate (μmol L <sup>-1</sup> d <sup>-1</sup> )	CH₄ respiration rate (µmol L <sup>-1</sup> d <sup>-1</sup> )	Specific oxidation rate (d <sup>-1</sup> )	CH₄ turnover time (d)
0 m A	0.13	6E-05	4E-05	3E-05	0.0005	2066.86
0 m B	-	8E-05	2E-05	6E-05	0.0006	1717.61
3 m A	0.13	0.0002	1E-04	0.0001	0.002	585.75
3 m B	-	0.0002	8E-05	0.0001	0.001	730.15
5 m A	0.14	0.0003	0.0002	0.0001	0.002	400.32
5 m B	-	0.0002	0.0001	9E-05	0.002	564.40
8 m A	0.30	0.0006	0.0003	0.0003	0.002	496.63
8 m B	-	0.0005	0.0002	0.0003	0.002	613.22
11 m A	0.28	0.002	0.001	0.001	0.01	122.98
11 m B	-	0.002	0.001	0.001	0.01	153.41
14 m A	0.18	0.03	0.01	0.01	0.14	6.98
14 m B	-	0.02	0.01	0.01	0.13	7.45

Table G.10: NE14 measured ambient  $CH_4$  concentration when  ${}^{14}CH_4$  oxidation experiment samples were collected (7/22/2011), calculated total  $CH_4$  oxidation rate, rate of conversion of  $CH_4$  to biomass,  $CH_4$  respiration rate, specific rate of  $CH_4$  oxidation, and  $CH_4$  turnover time.

				Total (biomass	Total activity :	Corrected	Corrected	Corrected
Sample	Whole water	Biomass	Respired	+respired) DPM	, whole water	Total DPM	<b>Biomass DPM</b>	Respired DPM
		DPIVI ML	DPIVI ML	mL <sup>-1</sup>	activity	mL⁻¹	mL⁻¹	mL⁻¹
Killed Control 1	14	21	5	8	-	-	-	-
Killed Control 2	5	3	3	6	-	-	-	-
0 m A	9	6	10	16	1.73	9	2	6
0 m B	11	5	9	14	1.27	7	2	5
3 m A	12	6	10	16	1.37	9	3	6
3 m B	11	6	11	17	1.51	10	3	7
8 m A	624	172	433	604	0.97	597	168	429
8 m B	616	189	445	634	1.03	627	186	442
10 m A	1070	333	755	1088	1.02	1081	330	751
10 m B	1090	359	752	1111	1.02	1104	355	749
13 m A	1334	426	962	1388	1.04	1381	423	959
13 m B	1300	422	917	1338	1.03	1331	418	913
16 m A	1793	619	1162	1781	0.99	1774	615	1159
16 m B	1719	594	1186	1780	1.04	1773	590	1182

Table G.11: Toolik <sup>14</sup>CH<sub>4</sub> oxidation experiment results for raw and corrected whole water <sup>14</sup>C activity, biomass-incorporated <sup>14</sup>C activity, and respired <sup>14</sup>C activity to whole water <sup>14</sup>C activity.

Sample	Ambient CH₄ (μM)	Total oxidation rate ( $\mu$ mol L <sup>-1</sup> d <sup>-1</sup> )	Biomass conversion rate (µmol L <sup>-1</sup> d <sup>-1</sup> )	$CH_4$ respiration rate (µmol L <sup>-1</sup> d <sup>-1</sup> )	Specific oxidation rate (d <sup>-1</sup> )	CH₄ turnover time (d)
0 m A	0.15	9E-05	2E-05	7E-05	0.0006	1569.01
0 m B	-	7E-05	2E-05	5E-05	0.0005	2109.28
3 m A	0.15	1E-04	3E-05	6E-05	0.0006	1550.60
3 m B	-	0.0001	3E-05	8E-05	0.0007	1351.90
8 m A	0.15	0.01	0.002	0.005	0.04	22.73
8 m B	-	0.01	0.002	0.005	0.05	21.63
10 m A	0.13	0.01	0.003	0.007	0.08	12.34
10 m B	-	0.01	0.003	0.007	0.08	12.07
13 m A	0.13	0.01	0.004	0.009	0.10	9.54
13 m B	-	0.01	0.004	0.009	0.10	9.92
16 m A	0.15	0.02	0.01	0.01	0.14	7.31
16 m B	-	0.02	0.01	0.01	0.14	7.32

Table G.12: Toolik measured ambient  $CH_4$  concentration when  ${}^{14}CH_4$  oxidation experiment samples were collected (7/21/2011), calculated total  $CH_4$  oxidation rate, rate of conversion of  $CH_4$  to biomass,  $CH_4$  respiration rate, specific rate of  $CH_4$  oxidation, and  $CH_4$  turnover time.

Appendix H:	Sediment-water exc	hange data for	r dissolved O	<sup>1</sup> 2, CO <sub>2</sub> , a	and CH <sub>4</sub>
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Table H.1: Volumes of water trapped in benthic chambers used to calculate exchange rates for dissolved  $\mathsf{O}_2,\,\mathsf{CO}_2,\,\mathsf{and}\,\mathsf{CH}_4.\,$  Volumes were calculated based on depth of chamber penetration into sediment. Chamber GTH 99 GTH 112 GTH 114 GTH 100 NE14 Toolik Dark A Volume (L) 7.48 16.09 16.88 14.18 16.31 13.61

Dark B		_0.00	20100	10:01		_0.0_
Volume (L)	11.19	15.75	16.61	15.30	13.61	16.09
Clear						
Volume (L)	14.68	15.98	15.47	15.75	14.63	14.29

Table H.2: Time series of dissolved  $O_2$ ,  $CO_2$ , and  $CH_4$  concentrations in GTH 99 benthic chambers.

-	Dark	Dark	Clear	Dark A	Dark B	Clear	Dark A	Dark B	Clear
Days	$AO_2$	$BO_2$	O <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub>	$CH_4$	$CH_4$	$CH_4$
	(μM)	(µM)	(µM)	(µM)	(µM)	(µM)	(µM)	(µM)	(μM)
0.0	268.7	255.7	266.4	1053.1	1033.9	964.3	1.75	1.68	1.98
1.8	163.1	162.5	412.3	1439.2	1473.7	793.5	17.58	24.73	38.42
4.0	134.7	124.0	378.5	1435.5	1491.0	684.4	82.28	94.19	100.16
5.8	119.8	122.8	367.8	1661.3	1697.4	812.4	121.45	134.66	67.40
8.0	105.6	108.0	311.4	1757.7	1777.6	827.9	145.86	174.92	35.30
11.1	127.5	137.6	296.6	1788.4	1808.6	842.4	197.34	207.46	51.59
12.9	99.1	105.6	267.5	2042.4	2090.7	983.7	255.63	289.54	23.28
14.8	91.9	115.1	256.3	2077.7	2038.0	932.5	307.77	275.30	57.52
17.9	102.0	108.0	189.8	2419.9	2482.3	1182.7	326.88	353.22	90.54

Sentine chambers.									
	Dark	Dark	Clear	Dark A	Dark B	Clear	Dark A	Dark B	Clear
Days	$AO_2$	$BO_2$	O <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub>	$CH_4$	$CH_4$	$CH_4$
	(µM)	(μM)	(µM)	(µM)	(µM)	(µM)	(µM)	(µM)	(µM)
0.0	209.4	227.2	232.7	209.8	202.7	213.8	4.97	1.26	3.28
1.4	128.7	158.4	154.3	365.1	324.8	343.5	28.35	6.81	22.61
3.0	110.3	109.8	100.8	441.8	416.6	426.3	31.51	7.49	48.95
4.0	102.6	106.8	105.6	456.7	443.9	460.6	59.68	21.01	64.67
5.9	105.5	124.5	119.8	534.1	505.6	488.7	72.29	37.01	94.50
8.3	86.6	110.9	119.3	685.1	598.7	596.1	83.73	47.91	98.73
9.3	79.5	106.2	105.0	693.7	608.0	575.9	102.32	51.78	89.09
11.2	66.4	90.2	97.3	794.1	696.4	655.7	166.05	89.51	136.21
13.0	62.3	89.0	117.5	880.4	790.7	724.9	218.50	109.41	184.28
14.9	46.3	65.8	89.6	1008.5	906.4	844.3	295.76	142.94	244.96

Table H.3: Time series of dissolved  $O_2$ ,  $CO_2$ , and  $CH_4$  concentrations in GTH 112 benthic chambers.

Table H.4: Time series of dissolved  $O_2$ ,  $CO_2$ , and  $CH_4$  concentrations in GTH 114 benthic chambers.

	Dark	Dark	Clear	Dark A	Dark B	Clear	Dark A	Dark B	Clear
Days	$AO_2$	$BO_2$	O <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub>	$CH_4$	$CH_4$	$CH_4$
	(μM)	(μM)	(µM)	(µM)	(µM)	(µM)	(µM)	(µM)	(µM)
0.0	268.7	255.7	266.4	158.1	174.6	159.7	0.53	0.62	0.73
1.8	118.6	112.7	129.3	401.1	415.5	343.6	1.54	7.17	9.98
4.0	115.1	123.4	133.5	456.5	501.4	405.2	4.81	17.02	9.58
5.8	103.2	106.8	120.4	526.2	575.2	449.9	10.27	24.31	6.85
7.9	89.0	103.8	132.3	598.9	654.0	465.4	16.12	33.92	13.51
10.8	94.3	98.5	137.6	671.9	732.0	505.7	23.55	45.42	17.84
12.8	83.1	73.0	149.5	748.6	850.4	542.9	36.22	55.32	21.90

Sentine enambers.										
	Dark	Dark	Clear	Dark A	Dark B	Clear	Dark A	Dark B	Clear	
Days	$AO_2$	$BO_2$	O <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub>	$CH_4$	$CH_4$	$CH_4$	
	(µM)	(µM)	(µM)	(µM)	(µM)	(µM)	(µM)	(µM)	(µM)	
0.0	248.0	245.6	259.8	760.7	722.7	741.4	0.18	0.18	0.18	
1.8	242.6	230.2	252.1	863.1	802.4	805.5	0.29	0.15	0.14	
4.0	199.3	218.9	247.4	767.8	754.7	714.8	0.17	0.11	0.10	
5.8	165.5	177.4	228.4	857.6	817.2	771.5	0.18	0.25	0.22	
8.0	149.5	176.8	204.1	893.1	829.9	773.1	0.11	0.13	0.11	
11.2	147.7	160.8	202.9	967.4	919.1	875.9	0.76	0.29	0.33	
12.9	128.1	138.2	182.1	1018.7	945.5	869.9	0.44	0.18	0.17	
14.9	105.0	110.3	155.4	1011.3	929.3	840.2	0.18	0.25	0.22	
18.0	137.0	132.3	150.1	1160.7	1001.8	970.8	2.18	0.73	0.23	

Table H.5: Time series of dissolved  $O_2$ ,  $CO_2$ , and  $CH_4$  concentrations in GTH 100 benthic chambers.

Table H.6: Time series of dissolved  $O_2$ ,  $CO_2$ , and  $CH_4$  concentrations in NE14 benthic chambers.

Dark A Davs	Dark B Days	Clear Days	Dark A $O_2$	Dark B $O_2$	Clear O <sub>2</sub>	Dark A CO <sub>2</sub>	Dark B CO <sub>2</sub>	Clear CO <sub>2</sub>	Dark A CH <sub>4</sub>	Dark B CH <sub>4</sub> (IIM)	Clear CH₄ (µM)
0.0	0.0	0.0	281.2	200 1	303.7	1709 5	(μινι) 1681 7	<u>(μινι)</u> 1679 6	0.34	0.25	0.19
0.0	0.0	0.0	201.2	290.1	303.7	1709.5	1001.7	1079.0	0.54	0.25	0.19
1.8	1.0	2.0	179.2	252.7	287.1	1738.9	1722.1	1741.7	0.36	0.42	0.27
4.0	3.0	3.9	120.4	143.6	287.1	1941.7	1879.5	1914.0	0.55	0.84	0.22
4.9	4.9	7.0	119.2	128.7	227.8	1946.8	2155.4	1800.8	2.02	1.78	0.27
7.0	8.0	8.8	99.7	92.5	245.6	1981.3	2180.6	1738.2	7.50	8.76	0.26
8.9	9.8	11.0	118.6	84.2	275.8	2205.1	2195.1	1785.7	13.81	13.14	0.30
12.0	12.0	12.9	87.8	94.9	262.2	2241.0	2190.2	1781.2	25.56	20.45	0.43
13.8	13.8	-	78.9	114.5	-	2297.8	2405.1	-	35.19	28.74	-
16.0	-	-	92.0	-	-	2316.9	-	-	42.23	-	-
17.8	-	-	94.9	-	-	2381.0	-	-	50.46	-	-

	Dark	Dark	Clear	Dark A	Dark B	Clear	Dark A	Dark B	Clear	
Days	$AO_2$	$BO_2$	O <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub>	$CH_4$	$CH_4$	$CH_4$	
	(µM)	(μM)	(µM)	(µM)	(µM)	(µM)	(µM)	(µM)	(µM)	
0.0	285.3	278.8	277.0	745.3	764.1	748.5	0.80	0.28	0.35	
2.2	189.2	249.7	228.4	932.1	834.2	836.0	3.38	3.22	1.11	
4.2	112.7	198.7	169.7	1009.8	887.5	893.5	2.83	1.92	0.44	
6.7	110.9	163.7	134.1	1069.6	923.0	933.6	10.32	2.52	0.36	
9.1	124.6	121.6	125.2	1124.4	1039.0	995.9	19.38	7.22	0.99	
11.7	90.2	105.6	104.4	1250.7	1135.7	1071.0	29.61	11.25	2.32	
14.2	92.5	115.7	113.3	1324.0	1201.7	1079.1	46.31	17.30	1.70	

Table H.7: Time series of dissolved  $O_2$ ,  $CO_2$ , and  $CH_4$  concentrations in Toolik benthic chambers.

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