"Exceptional summer warming leads to contrasting outcomes for methane cycling in small Arctic lakes of Greenland"

Sarah B. Cadieux[1,*], Jeffrey R. White[2] and Lisa M. Pratt[1]

[1]Department of Geological Sciences, Indiana University, Bloomington IN, USA
[2]School of Public and Environmental Affairs, Indiana University, Bloomington IN, USA
[*]now at: Earth and Environmental Science, University of Illinois at Chicago, Chicago Illinois, USA
Correspondence to: S. B. Cadieux (sbcadieux@gmail.com)

Abstract. In thermally stratified lakes, the greatest annual methane emissions typically occur during thermal overturn events. In July of 2012, Greenland experienced significant warming that resulted in substantial melting of the Greenland Ice Sheet and enhanced runoff events. This unusual climate phenomenon provided an opportunity to examine the effects of short-term natural heating on lake thermal structure and methane dynamics and compare these observations with those from the following year when temperatures were normal. Here, we focus on methane concentrations within the water column of 5 adjacent small lakes on the ice-free margin of Southwest Greenland under open-water and ice-covered conditions from 2012-2014. Enhanced warming of the epilimnion in the lakes under open-water conditions in 2012 led to strong thermal stability and the development of anoxic hypolimnions in each of the lakes. As a result, during open-water conditions, mean dissolved methane concentrations in the water column were significantly ($p < 0.0001$) greater in 2012 than in 2013. In all of the lakes, mean methane concentrations under ice-covered conditions were significantly ($p < 0.0001$) greater than under open-water conditions, suggesting spring overturn is currently the largest annual methane flux to the atmosphere. As the climate continues to warm, shorter ice cover durations are expected, which may reduce the winter inventory of methane and lead to a decrease in total methane flux during ice-melt. Under open-water conditions, greater heat income and warming of lake surface waters will lead to increased thermal stratification and hypolimnetic anoxia, which will consequently result in increased water column inventories of methane. This stored methane will be susceptible to emissions during fall overturn, which may result in a shift in greatest annual efflux of methane from spring melt to fall overturn. The results of this study suggest that inter-annual variation in ground-level air temperatures may be the primary driver of changes in methane dynamics because it controls both the duration of ice over and strength of thermal stratification.

1 Introduction

Methane (CH_4) emissions from freshwater environments are expected to increase with warming climates (Juutinen et al., 2009; Yvon-Durocher et al., 2011; Yvon-Durocher et al., 2014; Tan and Zhuang 2015a,b) but quantitative modeled projections of emissions are poorly constrained (Bastviken et al., 2011; Rasilo et al., 2015; Sepulveda-

Jauregui et al., 2015; Tan et al., 2015). Observations of seasonal and annual lake CH_4 dynamics in the Arctic are necessary to define source estimates in models and understand the impact warming may have on greenhouse gas emissions. Currently, in the Arctic, small lakes (surface area < 10 km^2) are abundant (Downing et al., 2006; Downing, 2010) and emit substantially more CH_4 per unit area than larger lakes (Bastviken et al., 2004; Cole et al., 2007; Juutinen et al., 2009; Wik et al., 2016), and seasonal variability of CH_4 emissions are influenced by energy input and organic carbon availability (Tan et al., 2015). However, climate change will lead to in variations in heat balance, temperature profiles and vertical mixing in lakes (Jankowski et al., 2006; MacIntyre et al., 2009; Hinkel et al., 2012; Butcher et al., 2015), causing many variations to both lake structure (Livingstone 2003; Coats et al., 2006) and CH_4 dynamics.

Microbial production of CH_4 by methanogens is dependent upon anoxia, temperature, and the amount and quality of organic carbon substrates (Liikanen et al., 2003; Kankaala et al., 2006; Duc et al., 2010; Borrel et al., 2011). A large proportion of the CH_4 produced in lakes is consumed by aerobic or anaerobic oxidation (Frenzel et al., 1990; Bastviken et al., 2002; Kankaala et al., 2007; Dzyuban, 2010; Martinez-Cruz et al., 2015). Aerobic microbial oxidation of methane (MOx) depends on the availability of both CH_4 and O_2, wherein higher MOx rates are usually found at the oxic/anoxic interface where both CH_4 and O_2 are present in high concentrations (Bastviken et al., 2002; Dzyuban 2010). Excess CH_4 that escapes MOx and reaches the upper mixed layer of the water column (epilimnion) is available for emission to the atmosphere by molecular diffusion under open-water conditions. Emission by ebullition and plants results in a direct flux of CH_4 to the atmosphere with limited oxidation in the water column (Keppler et al., 2006; Walter et al., 2006; Walter et al., 2007; Nisbet et al., 2009; Wik et al., 2013; Greene et al., 2014).

In lakes, the amounts of CH_4 in the water column (hereafter referred to as inventory) and CH_4 available for diffusive emissions (hereafter referred to as active CH_4) are strongly influenced by thermal stratification and seasonal overturns (Kankaala et al., 2007; López Bellido et al., 2009; Encinas Fernandez et al., 2014). Arctic lakes that are deep enough to stratify are usually dimictic (spring and autumn turnover) or cold monomictic (spring turnover) in areas without perennial ice cover. During thermal stratification, a lack of mixing between the epilimnion and anoxic hypolimnion suppresses gas transfer between these layers, allowing CH_4 to accumulate below the oxycline (hereafter referred to as storage) (Fig. 1; Bastviken et al., 2004; Sepulveda-Jauregui et al., 2015). During mixing from autumn turnover, all CH_4 previously stored in the hypolimnion is susceptible to MOx and/or diffusion (Encinas Fernandez et al., 2014). Under ice cover, CH_4 can accumulate and is either stored under ice or within the ice (Fig. 1; Walter et al., 2006; Walter Anthony et al., 2012; Sepulveda-Jauregui et al., 2015). In spring, the break-up of the ice and mixing allows stored CH_4 to be oxidized or emitted from the system through diffusion or ebullition (Juutinen et al., 2009; López Bellido et al., 2009; Karlsson et al., 2013; Greene et al., 2014; Jammet et al., 2015). Emissions of stored CH_4 during overturn events accounts for up to 40% of the total annual flux in lakes globally (Michmerhuizen et al., 1996; Juutinen et al., 2009; López Bellido et al., 2009; Encinas Fernandez et al., 2014; Jammet et al., 2015).

Over the last three decades, increasing atmospheric temperatures have resulted in increased lake temperatures and decreases in ice cover (Weyhenmeyer et al., 2011; Kraemer et al., 2015). Warming of surface waters will lead to increased thermal stratification and hypolimnetic anoxia, which should cause higher inventories of dissolved CH_4 stored in the hypolimnion of the water column. In addition to changes to thermal structure, warming and thawing of permafrost in the Arctic may allow organic carbon, nutrients and ions that were previously frozen in sediments to be transported into aquatic systems and become available for microbial utilization (Kokelj et al., 2009; Lougheed et al., 2011; Weyhenmeyer et al., 2011). Experimental laboratory incubation studies have also demonstrated that microbial CH_4 production significantly increases with increased temperature (Duc et al., 2010; Lofton et al., 2013; Fuchs et al., 2016).

On the ice-free margin of southwest Greenland, hundreds of thousands of Holocene lakes perched on continuous permafrost cover the landscape (Anderson et al., 2001; Anderson and Stedmon, 2007; Jorgensen and Andreasen, 2007). As a result of amplified warming in the Arctic over the past 20 years (IPCC, 2013), Greenland has experienced significant mass loss of the Greenland Ice Sheet (Nghiem et al., 2012; van As et al., 2012; Hall et al., 2013; Hanna et al. 2013; Hanna et al., 2014). Despite the abundance of lakes on the ice-free margin of Greenland and intense changes to the landscape as the result of warming, there are only a few published studies that have measured CH_4 in Greenlandic lakes (Walter Anthony et al., 2012; Webster et al., 2015; Cadieux et al., 2016; Goldman et al., 2016).

The anomalously warm summer in Greenland 2012, which resulted in substantial surface melt of the Greenland Ice Sheet (GIS) (Nghiem et al., 2012; Hanna et al., 2014) provides an opportunity to examine the effects of surface water heating on CH_4 dynamics in lakes. In this study, we quantify the depth inventories of CH_4 under both open-water and ice-covered conditions for 5 adjacent small lakes on the ice-free margin of Southwest Greenland from 2012 to 2014. In doing so, we are able to look at differences in CH_4 spatially among the lakes, seasonally by comparing open-water conditions to ice-covered conditions, and annually. The study lakes are ice-covered for 9-10 months of the year, leading us to predict that methane concentrations would be significantly greater under ice-covered conditions as opposed to open-water conditions. Under open-water conditions, we hypothesized that warmer conditions in the summer of 2012 would lead to increased thermal stratification and significantly greater CH_4 concentrations under open-water conditions than in 2013.

2 Study Area

The study area lies between the village of Kangerlussuaq, Greenland at the head of Søndre Strømfjord and the active terminus of the Russell Glacier (Fig. 2). The region has continuous permafrost extending from 50 cm below the surface to 130 m at Kangerlussuaq and 500 m at the ice sheet (Jorgensen and Andreasen, 2007). Soils in the region are not well-developed, composed of till and glaciofluvial deposits (Van Tatenhove and Olesen, 1994). Precipitation

in the Kangerlussuaq region is low, with annual precipitation < 150 mm yr^{-1}. Dwarf shrubs (*Salix*, *Vaccinium* and *Betula*) and graminoids (*Carex* and *Calamagrostis*) dominate the tundra vegetation in the region.

This paper focuses on 5 small lakes (surface area < 3 ha, maximum depth < 8 m), with a range of different morphometries and aquatic chemistries (Table 1). The lake names used herein (EVV Upper Lake, EVV Lower Lake, Teardrop Lake, Potentilla Lake and South Twin Lake) are informal based on local surficial features. The study lakes are part of a series of lakes within a narrow valley overlying a structural shear zone extending from the Russell Glacier to the Søndre Strømfjord (Fig. 2). The lakes are, at most, 6 km apart and are subject to the same climatic forcing. All lakes in the study are dimictic, exhibiting ice cover from late October to early June. Currently the study lakes are all hydrologically closed basins, with no active inflow or outflow channels observed from 2011-2014. Groundwater seepage into the lakes is assumed to be limited due to continuous permafrost.

In summer 2012, a blocking high-pressure system formed a heat dome over Greenland, leading to widespread surface melting of the Greenland ice sheet (GIS) (Hall et al., 2013; Hanna et al., 2014; Nghiem et al., 2012). As a result, this circulation pattern produced mean daily ground-level air temperatures in Kangerlussuaq that were the highest on record (Hanna et al., 2014). Weather data from a local Geological Survey of Denmark and Greenland (GEUS) station (van As et al., 2011; Fig. 2) showed that mean monthly ground-level temperatures for June-August in 2012 were ~2° C higher than in 2013 (Fig. 3). Correspondingly, mean air pressure from May to August of 2012 was higher than in 2013 (Fig. 3). Mean monthly wind speeds in the Kangerlussuaq region ranged from 1.52 m s^{-1} in June 2012 to 3.51 m s^{-1} in May of 2013 (Fig. 3). At the Kangerlussuaq airport, average temperatures from May to August of 2013 were within the range observed from 1996-2011, suggesting 2013 weather is typical for the region (data retrieved from weatherunderground.com).

3 Methods

3.1 Sample collection and water chemistry analysis
Lakes were sampled in July of 2012 and 2013 and in April of 2013 and 2014 in order to measure both summer and winter stratification. Hereafter, July samplings will be referred to as open water and April samplings as ice covered. Only EVV Upper lake and Potentilla lake were sampled during all four sampling dates. All samples and measurements were taken at a location above maximum water depth (Z_{max}). Under open-water conditions, samples and measurements were collected using an inflatable Alpaca raft (Anchorage, AK, USA), and under ice-covered conditions, when each lake was covered by ~ 2 m of ice, a hole (~30 cm in diameter) was augered through the ice in order to sample. Temperature (T, °C), pH, dissolved oxygen (DO, mg L^{-1}), oxidation-reduction potential (ORP, mV) and specific conductivity (mS cm^{-1}) were measured using a YSI 6093 Data Sonde (Yellow Springs Inc., Yellow Springs, OH, USA) deployed at vertical intervals of 0.5 m depth.

Water for chemical analysis was collected from the water column using a Narrow Diameter Supernova™ electronic submersible pump. Samples were frozen, and transported to Indiana University, where all chemical analyses were

conducted. Dissolved organic carbon (DOC) was analyzed from filtered samples that were acidified using hydrochloric acid (HCl), and analyzed via high-temperature oxidation using a Shimadzu total organic carbon analyzer following methods described in Oviedo-Vargas et al. (2013) (corresponding Method Detection Limit (MDL) = 0.15 mg C L^{-1}). Concentrations of ions were analyzed using a Dionex ICS 2000 Ion Chromatograph using a CS12A analytical cation column, CSRS 300 4 mm suppressor, and 20 mM methanesulfonic acid eluent for cations and AS11-HC analytical anion column, ASRS 4 mm suppressor and 30 mM potassium hydroxide eluent for anions.

4.2 CH$_4$ collection

With the exception of Potentilla lake under ice-covered conditions in 2014, water samples for dissolved CH$_4$ in the water column were collected using an electronic submersible pump. Samples were collected at 0.25-1.0 m intervals through the water column and were immediately stripped in the field using a headspace-equilibrium technique (Westendorp 1985) to extract CH$_4$ from water. At each depth interval, 500 mL of water was collected into a 1 L Erlenmeyer flask and vigorously shaken for 1 minute. Headspace gas in the flask was displaced into a Cali-5-Bond bag using surficial lake water (Cadieux et al., 2016). Under ice-covered conditions in 2014, dissolved CH$_4$ in Potentilla lake was collected using a string of passive diffusion bags (PDBs) deployed in the lake for 5 days in order to obtain a high-resolution profile of dissolved CH$_4$ in the water column (Goldman et al., 2016). The PDBs are composed of a polyethylene membrane with a protective plastic mesh and are commercially available from EON Products Inc. (Georgia, USA). After 5 days, PDBs were retrieved from the lake and dissolved gas was sampled immediately in the field using the equilibrium gas stripping method described above. Further details regarding PDB methodology, preparation and applicability can be found in Goldman et al. (2016).

Profundal sediment samples were taken from Z$_{max}$ of each lake during ice-covered conditions and open water conditions in 2013 using a Wildco push-coring device. Cores were transferred back to the laboratory at Kangerlussuaq International Science Support (KISS) facility and immediately refrigerated at 4° C and processed within 24 hours of collection. Dissolved gas in the sediment was sampled using an equilibrium gas stripping method similar to that used for the water-column CH$_4$. Sediment cores were sub-sectioned into 6-10 cm intervals and each subsection was put into a 8 L Nalgene bottle with zero-CH$_4$ water to create 2 L sediment-water slurry, which was vigorously hand shaken for 5 minutes to displace gas from the sediment-slurry into the headspace (Cadieux et al., 2016). The volume of pore water in the sediment core was calculated by drying an additional subsection of sediment. The concentration of CH$_4$ in the sediment cores was calculated as moles of CH$_4$ per unit volume of pore water in the sediment.

Littoral sediment CH$_4$ bubble samples were collected during open-water conditions of both 2012 and 2013 by physically disturbing the sediment in order to release entrained gas bubbles. Gas bubbles were collected using a large plastic funnel (28 cm diameter) with a gas-tight sampling tube and 3-way Luer-Lok valve attached to the neck (Cadieux et al., 2016). We were unable to quantify the volume of sediment samples, therefore concentrations of CH$_4$

in gas collected from littoral sediments cannot be converted into pool size of CH_4 in the littoral sediments, and are only an approximation of CH_4 concentration.

4.3 Concentration of CH_4

The concentrations of water-column CH_4 and sediment CH_4 were measured using a Los Gatos Research (LGR) Methane Carbon Isotope Analyzer (MCIA) (LGR, Mountain View CA, USA) that was operated at KISS (Cadieux et al., 2016). All samples were processed within 24 hours of collection. The total concentration of CH_4 in each sample was corrected for dilution and calculated from the sum of the measured headspace partial pressure and the dissolved CH_4 remaining after gas stripping, according to Henry's law using values from Lide and Fredrikse (1995). Instrumental uncertainty on CH_4 concentrations from the MCIA was ± 0.5 ppmv, which is one standard deviation of the values for gas standards analyzed during sample runs.

4.4 Inventory of dissolved CH_4

Bathymetric data were collected under open-water conditions in 2013 using a LOWRANCE HDS-5 Gen2 depth-sonar built with GPS and processed by ciBio Base software by Contour Innovations LLC (Minneapolis, MN, U. S.). The area and volume of water were derived and measured from bathymetric data. The total inventory of dissolved CH_4 in each lake was calculated by multiplying CH_4 concentrations for each depth interval by the volume of each depth interval. It was assumed that CH_4 concentrations within each depth interval were homogenous both horizontally and vertically. During open-water conditions, the depth intervals for active and storage pools were defined by redox conditions, where the storage depths are defined as intervals with DO < 1 mg L^{-1}. The active depths were associated with the oxic epilimnion where dissolved gases are susceptible to diffusive exchange with the atmosphere and exposed to atmospheric oxygen. Under ice cover, the size of the CH_4 storage pool was assumed to be that contained in the volume of water below ice.

4.5 Statistical Analyses

Statistical analyses were made using IBM SPSS Statistics. Concentrations of CH_4 and chemical variables for all study lakes during each season were assessed for normal distribution via the Kolmogorov-Smirnov test, and were found to be non-normally distributed. Student's *t* test of unequal variance was used for testing statistically significant differences in concentrations of CH_4 between open-water and ice-covered conditions, as well as from one year to another. Systematic changes in aquatic chemistry and CH_4 concentrations were analyzed using linear regression, in order to assess if CH4 concentrations were related to variables such as DO, temperature, DOC and conductivity.

5 Results

5.1 Thermal structure and DO profiles

Under open-water conditions, all lakes were thermally stratified in 2012 (Fig. 4). Thermal stratification, expressed in terms of temperature difference ($\Delta T = T_{0m} - T_{zmax}$), was > 12 °C in all lakes except for EVV Lower lake, where $\Delta T \approx$ 7 °C. For all lakes under open-water conditions, epilimnetic temperatures were significantly warmer (n=30, $p <$ 0.0001) and bottom waters were cooler in 2012 than in 2013 (Fig. 4). Under open-water conditions in 2013, various levels of thermal stratification were observed, ranging from thermally stratified in EVV Upper lake and Potentilla lake ($\Delta T \approx 9$°C) to isothermal in EVV Lower lake ($\Delta T \approx 1$ °C; Fig. 4). Under ice-covered conditions in both 2013 and 2014, lakes were nearly isothermal ($\Delta T < 2$ °C) except for Potentilla lake which was weakly thermally stratified under ice cover, with $\Delta T \approx 4$ °C in both years.

Clinograde DO profiles were observed in all lakes under open-water conditions in 2012, wherein DO was saturated and in equilibrium with the atmosphere in the surface waters and became increasingly undersaturated down the water column (Fig. 5). Anoxia (DO < 0.5 mg L^{-1}) was measured in the bottom waters of all lakes except for Teardrop lake. In EVV Upper lake, Potentilla lake and South Twin lake, the bottom 2 to 2.5 m of the water column was anoxic. Similar clinograde DO trends were observed under open-water conditions in 2013, although stratification was weaker, (Fig. 5) and anoxia was limited to the bottom 1 m of the water column in EVV Upper lake and Potentilla lake. All lakes exhibited complete anoxia below the ice with the exception of Potentilla lake in both years. Measurable DO was observed under ice in Potentilla lake, with a clinograde profile from suboxic conditions (7.0 – 5.0 mg L^{-1}) below the ice to 4.5 m and anoxic conditions from 5.5 m to the sediment/water interface.

5.2 Aquatic chemistry

Ionic composition varied markedly lake to lake as well as seasonally and annually (Table 2). According to a salinity classification scheme based on specific conductivity (Stewart and Kantrud, 1971), under open-water conditions in 2012, two of the study lakes were dilute (.04-0.5 mS cm^{-1}; EVV Upper and Potentilla), one was slightly brackish (0.5-2 mS cm^{-1}; EVV Lower), and two were moderately brackish salinity, with maximum specific conductivity exceeding 2 mS cm^{-1} (Table 2). The anion abundance followed $HCO_3^- > DOC^-/Cl^- > SO_4^{2-}$ in most of lakes, regardless of conductivity. DOC$^-$ represents the estimated charge on DOC based upon the anionic charge deficit (Driscoll and Newton, 1985) (Fig. 6). EVV Upper lake was the only lake where $SO_4^{2-} > Cl^-$. Sulfate accounted for 12 % of the total anion abundance in EVV Upper lake, relative to < 3 % in the other lakes. Cation abundance in dilute lakes followed $Ca^{2+} > Mg^{2+} > Na^+ > K^+$, whereas in slightly brackish lakes, $Mg^{2+} > Na^+ > Ca^{2+} > K^+$ was observed (Fig. 6). Overall, conductivity and ionic compositions were higher under ice-covered conditions than open-water conditions (Table 2). However, under open-water conditions in 2012, mean specific conductivity was significantly higher in all lakes than in 2013 (n=53, $p < 0.0001$).

Under open-water conditions in 2012, concentrations of DOC ranged from median of 11 mg L^{-1} (Potentilla lake) to 92 mg L^{-1} (Teardrop lake; Table 2). Under ice-covered conditions, DOC was higher than open-water conditions (Table 2). No consistent trends were observed for DOC between open-water conditions in 2012 and 2013.

5.3 Concentrations of CH$_4$

5.3.1 Dissolved water column CH$_4$

Concentrations of dissolved CH$_4$ were significantly greater under open-water conditions in 2012 than in 2013 (*n*=38, p=0.008; Fig. 6). Under open-water conditions in 2012, dissolved CH$_4$ concentrations in the surface waters of the study lakes ranged from 1.2 – 28 µM (Fig. 7; Table 3). In all of the lakes, CH$_4$ concentrations increased down the water column and were greatest in the bottom waters (Fig. 7). The highest concentration of dissolved CH$_4$ (640 µM) was observed at 4.5 m in South Twin lake. Similar to 2012, in 2013 CH$_4$ concentrations increased down the water column in all lakes except for Teardrop lake. Under open-water conditions in 2013, concentrations of CH$_4$ in at the water-air interface ranged from 0.88 – 3.5 µM (Fig. 7). In Teardrop lake, CH$_4$ was < 10 µM though the water column, ranging from 1.4 to 8.1 µM (Fig. 7). The highest concentration of CH$_4$ (150 µM) was observed at 5.0 m in EVV Upper lake.

Under ice-covered conditions, the mean concentrations of dissolved CH$_4$ were significantly greater than under open-water conditions (*n*=29, *p* <0.0001; Fig. 7). In 2013, CH$_4$ concentrations under ice cover were relatively uniform down the water column in EVV Upper lake (102-150 µM) and EVV Lower lake (340-360 µM) and ranged from 450-690 µM in South Twin lake. Only in Potentilla lake did CH$_4$ increase down the water column from 1.3 µM under the ice to 812 µM at the sediment-water interface (Fig. 7). The mean concentrations of dissolved CH$_4$ under ice cover in 2013 were significantly greater than in 2014 (n=29; *p* < 0.0001; Fig. 7). In 2014, dissolved CH$_4$ concentrations increased down the water column from below ice cover to the sediment-water interface in all of the three lakes, from 49 – 68 µM in EVV Upper lake, 190-360 µM in Teardrop lake and 0.3-220 µM in Potentilla lake (Fig. 7).

Linear relationships between aquatic chemistry and CH$_4$ concentrations were weak (Fig. 8; r^2 values for regressions ranged from 0.20 – 0.35). The highest CH$_4$ concentrations were correlated to both lower temperatures and lower DO, however the lowest CH$_4$ concentrations did not correlate to highest temperatures or DO (Fig. 8a & b). Overall, high concentrations of CH$_4$ were related to high conductivity and DOC (Fig. 8c & d).

5.3.2 Whole-lake inventories and pool sizes of CH$_4$

In all the lakes, the total inventory of CH$_4$ in the water column was higher under ice-covered conditions in 2013 and lower under open-water conditions in 2013 (Fig. 9 a). Under open water conditions, total dissolved CH$_4$ was 2 – 20 times greater in 2012 than in 2013. During all sampling dates, EVV Upper lake had the lowest CH$_4$ inventory among the lakes (Fig. 9 a).

Under open water conditions, the inventories of both the stored and active pools of CH$_4$ varied between lakes and years (Fig. 9 b & c). In 2012, the majority (> 50%) of the total dissolved CH$_4$ inventory in the water column of EVV Upper lake and Potentilla lake was associated with the hypolimnion (Fig. 9 b). EVV Lower lake was the only lake in

2012 wherein the majority of the total inventory of CH_4 occurred in the active pool of the epilimnion. In 2013, with the exception of EVV Upper lake, the majority of the total CH_4 inventory was in the active pool in all of the lakes (Fig. 9 c). EVV Upper lake was the only lake where the majority of the total CH_4 inventory was associated with the hypolimnion (Fig. 9 c). We saw no evidence of holes or moats in the ice in any of the lakes at the end of ice-covered conditions in 2013 or 2014, suggesting that the total inventories are likely relatively well conserved.

5.3.3 Sediment CH_4

In all lakes, the concentrations of CH_4 in porewaters of profundal sediments were an order of magnitude greater than dissolved CH_4 concentrations in the water column (Table 4). Under ice cover in 2013, profundal CH_4 concentrations were greater than under open-water conditions in 2013 for all of the lakes. Littoral sediment CH_4 gas bubble concentrations in Potentilla and South Twin lake were greater in 2012 than 2013, whereas in Teardrop lake, concentrations of CH_4 were greater in 2013 (Table 4). Overall, the maximum littoral sediment CH_4 gas bubble concentration was 473,000 ppmv in EVV Upper lake in 2013 and the minimum was 166,000 ppmv in Potentilla 2013.

6 Discussion

6.1 Spatial variation in aquatic chemistry and methane concentrations

Aquatic chemistry of the study lakes during mid-summer varied considerably among lakes with no discernable spatial trends. Chemical characteristics in each lake likely reflect interactions between basin-specific factors such as bedrock geology, basin morphometry and macrophyte community composition. Geology in the Kangerlussuaq region has been generally described as dominated by granodioritic gneisses (Anderson et al. 2001; Jensen et al. 2002). Despite large differences in conductivity, HCO_3^- was the dominant anion in the lakes. However, we have observed and measured sections of SO_4^{2-} minerals locally, occurring in orange-brown, thinly bedded outcrops interpreted as weathered, sulfide-rich metasediments (unpublished data). Elevated SO_4^{2-} in only EVV Upper lake leads us to suspect there is sulfide-rich, metasedimentary bedrock in the basin of this lake that has contributed to the anomalously high SO_4^{2-}. In addition, pods of marble have been described in the region previously (Taylor and Kalsbeek 1990), although they were not identified locally. These localized marble pods could be responsible for increased Ca^{2+} in Teardrop lake. Previous work in the Kangerlussauq regions suggests that anomalously high concentrations of DOC may be associated with abundance of littoral macrophytes (Lim and Douglas 2003; Lim et al 2005; Anderson and Stedmon 2007). The lowest DOC concentrations were from Potentilla lake, which had a comparatively lower density of macrophytes in comparison to the other lakes. The relative density of macrophyte communities in these hydrologically closed basins may strongly influence DOC concentrations in the lakes.

In the water column, CH_4 concentrations are directly related to both conductivity and DOC, wherein high CH_4 concentrations correspond with both high conductivity and DOC (Fig. 8). However, we do not find a direct relationship between maximum CH_4 concentration and aquatic chemistry variables. Under open-water conditions of

2012, the maximum CH_4 concentration in the water column was from the hypolimnion of South Twin lake. While South Twin lake did exhibit relatively high conductivity, DOC concentrations were relatively low. Similarly, the highest CH_4 concentration was measured in Potentilla lake in 2013 under ice-covered conditions, corresponding to the lowest conductivity and DOC measured in the study. The lowest concentrations of CH_4 in all of the lakes were from epilimnetic waters, despite the wide range in aquatic chemistry lake-to-lake. In addition, EVV Upper lake had significantly higher concentrations of SO_4^{2-} than the other lakes in the study. Competition for substrates favors sulfate reduction (SR) and methanogenesis typically does not occur until SO_4^{2-} is exhausted and SR rates have decreased (Lovely & Klung 1983, Lovely & Klung 1986, Scholten et al., 2002, Ward & Winfrey 1985). However, EVV Upper lake did not have the lowest concentrations of CH_4 in the water column, suggesting there was sufficient reduced carbon substrates to fuel both SR and methanogenesis. Therefore, while aquatic chemistry in the water column could be a factor influencing CH_4 production, at the level of this investigation, it alone is likely insufficient to explain the variation in CH_4 concentrations observed lake-to-lake, as well as seasonally and annually.

6.2 Effect of temperature on lake stratification

Ground-level air temperatures strongly influence the thermal stratification of lakes during the open-water season. Warm ground-level air temperatures during open-water conditions in 2012 (Fig. 3) resulted in epilimnetic temperatures being 1.5 – 5 °C higher in all of the study lakes relative to open-water conditions in 2013 (Fig. 4). Increased epilimnetic temperatures under open-water conditions in 2012 are consistent with both predictive models and measured temperatures indicating that warming climates result in higher epilimnetic temperatures (Honzo and Stefan, 1993; Fang et al., 2009; Jankowski et al., 2006; Adrian et al., 2009; Coats et al., 2006). As a result of warmer epilimnetic waters, stronger thermal stratification occurred during open-water conditions in 2012 than in 2013, with ΔT 4 – 9 °C higher in 2012 (Fig. 4). In addition, wind speeds were significantly lower and air pressures were higher during open-water conditions in 2012 compared with 2013 (Fig. 3), leading to reduced mixing of the water column and greater heat transfer to shallower epilimnia. Temperature and thermal structure strongly influence DO concentrations in lakes, wherein stronger thermal stratification leads to increased anoxia in the hypolimnion (Hanson et al., 2006; Adrian et al., 2009; Foley et al., 2012). For example, the extremely warm European summer of 2003 resulted in stronger thermal stratification and hypolimnetic DO depletion in Swiss lakes (Jankowski et al., 2006). Similarly, as a result of strong thermal stratification in 2012, the hypolimnia of EVV Upper lake, EVV Lower lake, Potentilla and South Twin lake were anoxic. For comparison, 1-34 % of water column in the lakes was anoxic in 2012, whereas the percentages decreased to 0-7 % in 2013.

6.3 Effects of temperature on CH_4

Ground-level air temperature differences result in warmer surface waters and increased stratification between 2012 and 2013 but a weak linear relationship is observed between water temperatures and dissolved CH_4 concentrations (Fig. 8). Both the highest and lowest CH_4 concentrations are observed in waters < 5 °C. In freshwater environments, the concentration of dissolved CH_4 reflects the balance between CH_4 production and CH_4 consumption by anaerobic

or aerobic oxidation (Duc et al., 2010; Dzyuban, 2010; Encinas Fernandez et al., 2014; Kankaala et al., 2007; Martinez-Cruz et al., 2015; Segarra et al., 2015; Smemo and Yavitt 2011). Methane production is affected by temperature, where higher temperatures result in increased production (Duc et al., 2010). However, methanogenesis only occurs under anaerobic conditions (Borrel et al., 2011; Valentine et al., 1994; Yvon-Durocher et al., 2011). Under open-water conditions in all of the lakes, the majority of the water column is oxygenated (Fig. 5), therefore production was likely minimal in the water column in both 2012 and 2013. Concentration of CH_4 and DO are inversely related, wherein highest concentrations occur in anoxic waters and decrease with increasing DO (Fig. 8), suggesting MOx is driving the concentration of CH_4 in the water column. However, consumption of CH_4 by microbial methane oxidation is not strongly influenced by temperature (Duc et al., 2010) and has only been demonstrated to increase with increasing temperatures under CH_4 saturated conditions (Lofton et al., 2013).

Despite the absence of a strong linear relationship between water temperature and CH_4 concentrations, warmer ground-level air temperatures correspond with increased CH_4 both in the water column and the sediments in the study lakes at the time of sampling. Under open-water conditions, CH_4 concentrations in the water column were significantly greater in 2012 than in 2013 (Fig. 8), corresponding with increased ground-level air temperatures. Similarly, under ice-covered conditions, ground-level air temperatures were ~ 6 ℃ higher in 2013 than in 2014 and CH_4 concentrations in the water column were greater for the 2 lakes in which there is data for both years (Fig. 9). The CH_4 concentration differences occur throughout the water column, but are more pronounced in the bottom waters close to the sediment-water interface. It is possible that increased ground-level air temperatures result in increased production of CH_4 in the profundal sediments, which lead to increased concentrations in the bottom waters of each lake. However, under open-water conditions in 2012, the bottom water temperatures were colder than in 2013, suggesting profundal sediments were not warmer due to increased ground-level air temperatures. More likely, the higher CH_4 concentrations in the bottom waters during open-water conditions in 2012 were the result of increased thermal stratification and subsequent anoxia, allowing a buildup of CH_4 in the bottom waters.

The concentrations of CH_4 from profundal sediments during ice-covered conditions in 2013 were greater than from open-water conditions in 2013 (Table 4). While ground-level air temperatures were significantly colder during the 2013 ice-covered season compared to the 2013 open-water season (Fig. 3), the higher concentrations of CH_4 during ice-covered conditions may be a relic of the anomalously warm conditions from the previous open-water conditions in 2012. In the littoral sediments, where there is data for consecutive years, gas bubble CH_4 concentrations from 2012 were higher than in 2013 (Table 4), further suggesting that warmer ground-level air temperatures result in increased CH_4 production, consistent with experimental studies of methanogenesis response to higher temperature (Duc et al., 2010; Hoj et al., 2008; Lofton et al., 2013). However, it is important to note that littoral CH_4 concentrations are an estimate, as a volume of sediment/sample was unmeasured. Therefore, it is possible that the increase in littoral CH_4 concentrations is not the result of increased CH_4 production, but of a different amount of sediment disturbed.

Without temperature data for profundal and littoral sediments, it is impossible to directly determine whether warmer temperatures result in an increase in CH_4 production or if other factors may influence production of CH_4. However, because bottom water temperatures were colder during open-water conditions in 2012 than in 2013 (Fig. 4), it is unlikely that profundal sediments were warmer in response to warmer ground-level air temperatures. In addition to temperature, methanogenesis is also influenced by the amount and quality of organic carbon substrates (Borrel et al., 2011; West et al., 2012). Lakes in this study are all embedded within continuous permafrost, with an active layer < 0.5 m thick. It is possible that the anomalously warm conditions in 2012 resulted in warming and thickening of the active permafrost layer, which could have caused organic carbon, nutrients and ions to enter the lakes and be available for microbial utilization (Adrian et al., 2009; Kokelj et al., 2009; Lougheed et al., 2011; Weyhenmeyer and Karlsson, 2009). However, under open-water conditions, DOC was only higher in one lake in 2012 compared to 2013 and DOC concentrations during ice-covered conditions in 2013 and 2014 were similar (Table 2). Significantly higher specific conductivity during open-water conditions in 2012 compared to 2013 was observed for all of the lakes (Table 2), which could be attributed to an additional source from permafrost thaw. Increases in DOC and conductivity were observed in thaw ponds in Western Siberia during the anomalous hot summer of 2012, but were attributed to evapoconcentration effects (Pokrovsky et al., 2013). In the Greenlandic lakes, significant water level changes between the two consecutive years of this study were not observed, so it is unlikely that the higher conductivity in 2012 was the result of evaporation.

6.4 Effects of stratification on CH_4

Enhanced thermal stratification and anoxia during open-water conditions in 2012 corresponded with significantly higher CH_4 concentrations in the water column. The most notable difference in CH_4 concentrations between 2012 and 2013 occurred within the bottom waters, which were anoxic in 2012. Under open-water conditions in 2012, the amount of CH_4 stored in the hypolimnion was 2 to 300 times higher than in 2013. The higher CH_4 concentrations may be the result of increased CH_4 production due to more extensive anaerobic conditions. However, the higher CH_4 concentrations were more likely the result of larger pools of anoxic waters in 2012 allowing for a buildup of CH_4 that corresponded in increased CH_4 storage in the water column (Fig. 8). During fall overturn, the storage pool of CH_4 is susceptible to diffusion and/or oxidation (Encinas Fernandez et al., 2014; Kankaala et al., 2007; López Bellido et al., 2009). If half of the stored CH_4 is emitted during fall overturn, as suggested by results from Fernandez et al., (2014), the autumn overturn CH_4 flux would be significantly larger in 2012 than that in 2013 as a result of the more extensive anoxia in 2012.

Weaker thermal stratification during open water conditions in 2013 meant that 93 –100 % of the water column in the lakes had DO concentrations > 1 mg L^{-1}. When CH_4 diffusing from anoxic sediments reaches oxic sediment or water, the majority of it is oxidized (Bastviken et al., 2002; Dzyuban, 2010; Kankaala et al., 2007). MOx is highly efficient at consuming CH_4 thereby lowering CH_4 concentrations. The percentage of CH_4 oxidized can be estimated by assuming that CH_4 at the water-air interface originates from diffusion through the water column from the profundal sediments. Given that an increased proportion of the water column was oxic under open-water conditions

2013, we initially hypothesized that the percentage of CH_4 oxidized would be greater in 2013 than in 2012. However, under open-water conditions in 2013, the percentage of CH_4 oxidized was similar to, or less, than in 2012. Consistent with CH_4 oxidation rates from Alaskan lakes, MOx controls CH_4 concentrations when DO is present (Martinez-Cruz et al., 2015). Under warm conditions in 2012, not only were CH_4 concentrations in sediments and anoxic waters elevated, but the percentage of CH_4 oxidized was also higher. Several studies suggest that MOx is important for mitigating CH_4 emissions to the atmosphere (Martinez-Cruz et al., 2015; Milucka et al., 2015; Segarra et al., 2015). However, despite the likelihood that MOx was more efficient in 2012 under warmer conditions, CH_4 concentrations in the stored pool were higher in 2012 than in 2013.

While significant variations in CH_4 concentrations and inventories were observed under between the consecutive years under open-water conditions, the amount of CH_4 stored under ice cover was significantly greater than that stored in the anoxic hypolimnion under open-water conditions (Fig. 3-6). For South Twin lake, the CH_4 storage under ice cover in 2013 was more than an order of magnitude greater than that stored in the hypolimnion during open-water conditions in 2012, and in Lower lake it was two orders of magnitude greater (Fig. 3-6). In these small Greenlandic lakes, emissions during spring overturn currently reflects the largest potential flux of CH_4 to the atmosphere. Similarly, in other Arctic lakes, CH_4 emissions during spring overturn after ice-breakup are usually larger than CH_4 emissions during autumn overturns (Juutinen et al., 2009; López Bellido et al., 2009; Karlsson et al., 2013; Miettinen et al., 2015).

6.5 Implications for a warmer Arctic
In the Arctic, lakes are ice covered for more than 8 months of the year (Belzile et al., 2001). The study lakes here are ice covered ~10 months of the year. At sampling under ice-covered conditions, lakes have been covered ~8 months. In each of the study lakes, CH_4 concentrations are significantly higher under ice-cover conditions compared to open-water conditions (Fig. 7), which is also observed in other Northern latitude lakes that are ice covered the majority of the year (Juutinen et al., 2009; Martinez-Cruz et al., 2015). Ice cover impedes gas exchange between the water and the atmosphere, promoting buildup of CH_4 in the water column leading to increased CH_4 storage (Bastviken et al., 2004; Juutinen et al., 2009; Martinez-Cruz et al., 2015; Phelps et al., 1998). No holes or moats were observed in the ice cover during sampling, therefore the total inventory of CH_4 in the water column under ice-covered conditions was stored. Similar to stored CH_4 during stratification in open-water conditions, CH_4 stored under ice is susceptible to emission to the atmosphere during spring overturns during and after ice breakup.

Projected climate change is expected to change ice cover characteristics in lakes (Fang and Stefan 2009; Mueller et al., 2009). Ice coverage duration has already decreased for many lakes as ground-level air temperatures have increased (Bertilsson et al., 2013; Weyhenmeyer et al., 2011). As perennially ice covered lakes begin to develop open water periods for at least some portions of the year, the number of seasonally frozen lakes will increase (Mueller et al., 2009). Currently, the largest efflux of CH_4 from our study lakes will most likely occur during ice-breakup and spring overturn, consistent with other Arctic lakes (Karlsson et al., 2013; Miettinen et al., 2015).

Changes in the duration of seasonal ice-cover will result in changes in inventories of under-ice CH_4. We predict that
475 as the duration of ice cover decreases, the amount of CH_4 stored under ice cover will likely decrease due to the shorter time for accumulation. If the amount of stored CH_4 under ice-cover decreases, this will potentially reduce the amount of CH_4 emitted during ice-breakup and spring overturn.

In addition to a decrease in ice cover, our results also suggest an increase in ground-level air temperatures will result in enhanced thermal stability and anoxia in Arctic lakes, as we observed during open-water conditions in 2012. The
480 duration of open-water thermal stratification will also likely increase in concert with the decrease in ice cover. The combined effects of extended season and greater strength of stratification are likely to be development of higher CH_4 inventories in the water column during open-water periods. Conceptually, as anoxic zones expand in space and duration, the influence of methanogenic sediments on water column inventories of methane should increase. Currently, small lakes emit substantially more CH_4 per unit area than larger lakes during open-water conditions
485 (Bastviken et al., 2004; Cole et al., 2007; Juutinen et al., 2009). Small, shallow likes are more susceptible to thermal change due to increased ground-level air temperatures and will likely continue to be major CH_4 contributors to the atmosphere. In fact, our results suggest that increased warming in the Arctic will result in greater summer inventories of CH_4 and consequently larger emissions of CH_4 to the atmosphere during autumn overturn in small lakes.
490

7 Conclusions

Over the past half century, the Arctic has warmed at a rate greater than the global average, and climate models predict further polar amplification, with the Arctic continuing to warm at a faster rate than other regions. The anomalously warm summer of 2012 in Greenland corresponded with significantly higher CH_4 concentrations under
495 open-water conditions in a series of small lakes compared to the following year. Stronger thermal stratification under warmer conditions lead to increased CH_4 storage in the lakes. With impending warming climate, increased stratification and CH_4 storage in lakes will likely lead to greater potential fluxes during fall overturn. Currently, in these small, seasonally ice covered Arctic lakes, the greatest concentrations of CH_4 in the water column are occurring under ice-covered conditions. Changes in seasonal ice cover will result in changes in under ice CH_4
500 inventories, and consequently lead to reductions in the amount of CH_4 emitted during ice-breakup and spring overturn. These results suggest that inter-annual variation in ground-level air temperatures may be the primary driver of changes in methane dynamics because it controls the both the strength of thermal stratification and duration of ice cover. We predict that as the climate continues to warm, the greatest annual efflux of CH_4 from small arctic lakes will shift from spring overturn to fall overturn.
505

8 Acknowledgements

Funding for this work was provided by NASA ASTEP Grant #NNX11AJ01G. We thank Contour Innovations LLC for assistance with bathymetric maps and Amy Goldman, Seth Young and Yongbo Peng for assistance in the field with sample collection. For logistical support, we thank Polar Field Services, Inc., Kangerlussuaq International

510   Science Support and Ruth Droppo for logistical support. Weather data from the Programme for Monitoring of the Greenland Ice Sheet (PROMICE) and the Greenland Analogue Project (GAP) was provided by the Geological Survey of Denmark and Greenland (GEUS) at http://www.promice.dk.

9 Literature Cited

515   Adrian, R., O'Reilly, C.M., Zagarese, H., Baines, S.B., Hessen, D.O., Keller, W., Livingstone, D.M., Sommaruga, R., Straile, D., Van Donk, E., Weyhenmeyer, G.A. and Winder, M.: Lakes as sentinels of climate change, Limnol Oceanogr, 54, 2283-2297, 2009.

Anderson, N.J., Harriman, R., Ryves, D.B. and Patrick, S.T.: Dominant factors controlling variability in the ionic composition of West Greenland lakes, Arct Antarct Alp Res, 33, 418-425, 2001.

520   Anderson, N.J. and Stedmon, C.A.: The effect of evapoconcentration on dissolved organic carbon concentration and quality in lakes of SW Greenland, Freshwater Bio 52, 280-289, 2007.

Bastviken, D., Cole, J., Pace, M. and Tranvik, L.: Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate, Global Biogeochem Cy 18, doi:10.1029/2004GB002238, 2004.

525   Bastviken, D., Ejlertsson, J. and Tranvik, L.: Measurement of methane oxidation in lakes: a comparison of methods. Environ Sci Technol, 36, 3354-3361, 2002.

Bastviken, D., Tranvik, L., Downing, J.A., Crill, P.M. and Enrich-Prast, A.: Freshwater methane emissions offset the continental carbon sink, Science, 331, 50, 2011.

Belzile, C., Vincent, W.F., Gibson, J.A.E. and Hove, P.V.: Bio-optical characteristics of the snow, ice, and water
530   column of a perennially ice-covered lake in the High Arctic, Can J Fish Aquat Sci, 58, 2405-2418, 2001.

Bertilsson, S., Burgin, A., Carey, C.C., Fey, S.B., Grossart, H.-P., Grubisic, L.M., Jones, I.D., Kirillin, G., Lennon, J.T., Shade, A. and Smyth, R.L.: The under-ice microbiome of seasonally frozen lakes, Limnol Oceanogr 58, 1998-2012, 2013.

Borrel, G., Jezequel, D., Biderre-Petit, C., Morel-Desrosiers, N., Morel, J.P., Peyret, P., Fonty, G. and Lehours,
535   A.C.: Production and consumption of methane in freshwater lake ecosystems, Res Microbiol, 162, 832-847, 2011.

Butcher, J.B., Nover, D., Johnson, T.E. and Clark, C.M.: Sensitivity of lake thermal and mixing dynamics to climate change, Climatic Change, 129, 295-305, 2015.

Cadieux, S.B., White, J.R., Sauer, P.E., Peng, Y., Goldman, A.E. and Pratt, L.M.: Large fractionations of C and H
540   isotopes related to methane oxidation in Arctic lakes, Geochim Cosmochim Ac, 187, 141-155, 2016.

Coats, R., Perez-Losada, J., Schladow, G., Richards, R. and Goldman, C.: The warming of Lake Tahoe, Climatic Change, 76, 121-148, 2006.

Cole, J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L., Striegl, R.G., et al.: Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget, Ecosystems, 10, 171-184, 2007.

545   Downing, J.A.: Emerging global role of small lakes and ponds: little things mean a lot, Limnetica 29, 9-24, 2010.

Downing, J.A., Prairie, Y.T., Cole, J., Duarte, C.M., Tranvik, L.J., Strigel, R.G., et al.: The global abundance and size distribution of lakes, ponds, and impoundments, Limnol Oceanogr 51, 2388-2397, 2006.

Driscoll, C.T. and Newton, R.M.: Chemical Characteristics of Adirondack Lakes, Environ Sci Technol, 19, 1018-1024, 1985.

550 Duc, N.T., Crill, P. and Bastviken, D.: Implications of temperature and sediment characteristics on methane formation and oxidation in lake sediments, Biogeochemistry, 100, 185-196, 2010.

Dzyuban, A.N.: Dynamics of microbial oxidation of methane in the water of stratified lakes, Microbiology, 79, 822-829, 2010.

Encinas Fernandez, J., Peeters, F. and Hofmann, H.: Importance of the autumn overturn and anoxic conditions in the

555 hypolimnion for the annual methane emissions from a temperate lake, Environ Sci Technol, 48, 7297-7304, 2014.

Fang, X. and Stefan, H.G.: Simulations of climate effects on water temperature, dissolved oxygen, and ice and snow covers in lakes of the contiguous Unitied States under past and future climate scenarios, Limnol Oceanogr, 54, 2359-3270, 2009.

560 Frenzel, P., Thebrath, B. and Conrad, R.: Oxidation of methane in the oxic surface layer of a deep lake sediment (Lake Constance), FEMS Microbiol Ecol, 73, 149-158, 1990.

Fuchs, A., Lyautey, E., Motuelle, B. and Casper, P.: Effects of increasing temperatures on methane concentrations and methanogenesis during experimental incubation of sediments from oligo- and mesotrophic lakes, J Geophys Res-Biogeo, doi: 10.1002/2016JG003328, 2016.

565 Goldman, A.E., Cadieux, S.B., White, J.R. and Pratt, L.M.: Passive sampling method for high-resolution concentration and isotopic composition of dissolved methane in Arctic Lakes, Limnol Oceanogr-Meth 14, 69-78, 2016.

Greene, S.,Walter Anthony, K. M., Archer, D., Sepulveda-Jauregui, A., and Martinez- Cruz, K.: Modeling the impediment of methane ebullition bubbles by seasonal lake ice, Biogeosciences, 11, 6791–6811,

570 doi:10.5194/bg-11-6791-2014, 2014.

Hall, D.K., Comiso, J.C., DiGirolamo, N.E., Shuman, C.A., Box, J.E. and Koenig, L.S.: Variability in the surface temperature and melt extent of the Greenland ice sheet from MODIS, Geophys Res Lett, 40, 2114-2120, 2013.

Hanna, E., Fettweis, X., Mernild, S.H., Cappelen, J., Ribergaard, M.H., Shuman, C.A., et al.: Atmospheric and

575 oceanic climate forcing of the exceptional Greenland ice sheet surface melt in summer 2012, Int J Climatol 34, 1022-1037, 2014.

Hanna, E., Jones, J.M., Cappelen, J., Mernild, S.H., Wood, L., Steffen, K. and Huybrechts, P.: The influence of North Atlantic atmospheric and oceanic forcing effects on 1900-2010 Greenland summer climate and ice melt/runoff, Int J Climatol, 33, 862-880, 2013.

580 Hinkel, K.M., Lenters, J.D., Sheng, Y., Lyons, E.A., Beck, R.A., Eisner, W.R., et al.: Thermokarst lakes on the Arctic Coastal Plain of Alaska: Spatial and temporal variability in summer water temperature, Permafrost Periglac, 23, 207-217, 2012.

Hoj, L., Olsen, R.A. and Torsvik, V.L.,: Effects of temperature on the diversity and community structure of known methanogenic groups and other archaea in high Arctic peat. ISME J 2, 37-48, 2008.

585 IPCC: Summary for Policymakers, in: Stocker, T.F., Quin, D., Plattner, G.K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., et al. (Eds.), Climate Change 2013: The Physical Science Basics. Contribution of Working Group I to the Fifth Assessment Report on the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambride, United Kingdom, New York, NY, USA, 2013.

Jammet, M., Crill, P., Dengel, S. and Friborg, T.: Large methane emissions from a subarctic lake during spring
590 thaw: Mechanisms and landscape significance, J Geophys Res Biogeosci, 120, 2289-2305, doi: 10.1002/2015JG003137, 2015.

Jankowski, T., Livingstone, D.M., Buhrer, H., Forster, R. and Niederhauser, P.L Consequences of the 2003 European heat wave for lake temperature profiles, thermal stability, and hypolimnetic oxygen depletion: Implications for a warmer world, Limnol Oceanogr, 51, 815-819, 2006.

595 Jorgensen, A.S. and Andreasen, F. (2007) Mapping of permafrost surface using ground-penetrating radar at Kangerlussuaq Airport, western Greenland. Cold Reg Sci Technol 48, 64-72.

Juutinen, S., Rantakari, M., Kortelainen, P., Huttunen, J.T., Larmola, T., Alm, J., Silvola, J. and Marktikainen, P.J.: Methane dynamics in different boreal lake types, Biogeosciences, 6, 209-223, 2009.

Kankaala, P., Taipale, S., Nykänen, H. and Jones, R.I.: Oxidation, efflux, and isotopic fractionation of methane
600 during autumnal turnover in a polyhumic, boreal lake, J Geophys Res, 112, doi:10.1029/2006JG000336, 2007.

Kankaala, P., Huotari, J., Peltomaa, E., Saloranta, T., and Ojala, A.: Methanotrophic activity in relation to methane efflux and total heterotrophic bacterial production in a stratified, humic, boreal lake, Limnol. Oceanogr., 51, 1195–1204, 2006.

605 Karlsson, J., Giesler, R., Persson, J., Lundin, E.: High emission of carbon dioxide and methane during ice thaw in high latitude lakes, J. Geophys. Res. Lett., 40, 1–5, doi:10.1002/grl.50152, 2013.

Keppler, F., Hamilton, J.T., Brass, M. and Rockmann, T.: Methane emissions from terrestrial plants under aerobic conditions, Nature, 439, 187-191, 2006.

Kodovska, F.G-T., Sparrow, K.J., Yvon-Lewis, S.A., Paytan, A., Dimova, N.T., Lecher, A.L. and Kessler, J.D.:
610 Dissolved methane and carbon dioxide fluxes in Subarctic and Arctic regions: Assessing measurement techniques and spatial gradients, Earth Planet Sc Lett, 436, 43-55, 2016.

Kokelj, S.V., Zajdlik, B. and Thompson, M.S.: The impacts of thawing permafrost on the chemistry of lakes across the subarctic boreal-tundra transition, Mackenzie Delta region, Canada. Permafrost Periglac, 20, 185-199, 2009.

615 Kraemer, B.M., Hook, S., Huttula, T., Kotilainen, P., O'Reilly, C.M., Peltonen, A., et al.: Century-Long Warming Trends in the Upper Water Column of Lake Tanganyika, PLoS One, 10, e0132490, 2015.

Lide, D.R. and Fredrikse, H.P.R.: CRC handbook of chemistry and physics, 76 ed. CRC Press, Boca Raton, FL, 1995.

620 Liikanen, A., Huttunen, J.T., Murtoniemi, T., Tanskanene, H., Vaisanen, T., Silvola, J., et al.: Spatial and seasonal variation in greenhouse and nutrient dynamics and their interactions in the sediment of a boreal eutrophic lake, Biogeochemistry, 65, 83-103, 2003.

Lim, D. and Douglas, M.S.V.: Limnological characteristics of 22 lakes and ponds in the Haughton Crater Region of Devon Island, Nunavut, Canadian High Arctic, Arct Antarct Alp Res 35, 509-519, 2003.

625 Lim, D. Douglas, M.S.V. and Smol, J.P.: Limnology of 46 lakes and ponds on Banks Island, N.W.T., Canadian Arctic Archipelago, Hydrobiologia, 545, 11-32, 2005.

Lindgren, P.R., Grosse, G., Walter Anthony, K.M. and Meyer, F.J.: Detection and spatiotemporal analysis of methane ebullition on thermokarst lake ice using high-resolution optical aerial imagery, Biogeosciences 13, 27-44, 2016

Livingstone, D.M.: Impact of secular climate change on the thermal structure of a large temperate central European 630 lake, Climatic Change, 57, 205-225, 2003.

Lofton, D.D., Whalen, S.C. and Hershey, A.E. Effect of temperature on methane dynamics and evaluation of methane oxidation kinetics in shallow Arctic Alaskan lakes. Hydrobiologia 721, 209-222, 2013.

López Bellido, J., Tulonen, T., Kankaala, P. and Ojala, A.: CO_2 and CH_4 fluxes during spring and autumn mixing periods in a boreal lake (Pääjärvi, southern Finland), J Geophys Res, 114, G04007, 635 doi:10.1029/2009JG000923, 2009.

Lougheed, V.L., Butler, M.G., McEwen, D.C. and Hobbie, J.E.: Changes in Tundra Pond Limnology: Re-sampling Alaskan Ponds After 40 Years, Ambio, 40, 589-599, 2011.

Lovely, D.R. and Klung, M.J.: Sulfate reducers can out-compete methanogens at fresh-water sulfate concentrations. Appl Environ Microb, 45, 187-192, 1983.

640 Lovely, D.R. and Klung, M.J.: Model for the distribution of sulfate reduction and methanogenesis in freshwater sediments, Geochem Cosmochim Ac, 50, 11-18, 1986.

MacIntyre, S., Fram, J.P., Kushner, P.J., Bettez, N.D., O'Brien, J.O., Hobbie, J.E. and Kling, G.W.: Climate-related variations in mixing dynamics in an Alaskan arctic lake, Limnol Oceanogr 54, 2401-2417, 2009.

Martinez-Cruz, K., Sepulveda-Jauregui, A., Walter Anthony, K. and Thalasso, F.: Geographic and seasonal variation 645 of dissolved methane and aerobic methane oxidation in Alaskan lakes, Biogeosciences, 12, 4595-4606, 2015.

Michmerhuizen, C.M., Striegl, R.G. and McDonald, M.E.: Potential methane emission from north-temperate lakes following ice melt, Limnol Oceanogr, 41, 985-991, 1996.

Miettinen, H., Pumpanen, J., Heiskanen, JJ., Aaltonen, H., Mammarella, I., Ojala, A., Levula, J., and Rantakari, M.: 650 Towards a more comprehensive understanding of lacustrine greenhouse gas dynamics two-year measurements of concentrations and fluxes of CO_2, CH_4 and N_2O in a typical boreal lake surrounded by managed forests, Boreal Environ. Res. 20, 75–89, 2015.

Milucka, J., Kirf, M., Lu, L., Krupke, A., Lam, P., Littmann, S., et al.: Methane oxidation coupled to oxygenic photosynthesis in anoxic waters, ISME J, doi: 10.1038/ismej.2015.12, 2015.

655   Mueller, D.R., Van Hove, P., Antoniades, D., Jeffries, M.O. and Vincent, W.F.: High Arctic lakes as sentinel ecoystems: Cascading regime shifts in climate, ice cover, and mixing, Limnol Oceanogr, 54, 2371-2385, 2009.

Nghiem, S.V., Hall, D.K., Mote, T.L., Tedesco, M., Albert, M.R., Keegan, K., et al.: The extreme melt across the Greenland ice sheet in 2012, Geophys Res Lett, 39, doi:10.1029/2012GL053611, 2012.

660   Nisbet, R.E., Fisher, R., Nimmo, R.H., Bendall, D.S., Crill, P.M., Gallego-Sala, A.V., et al.: Emission of methane from plants, Proc Biol Sci, 276, 1347-1354, 2009.

Oviedo-Vargas, D., Royer, T.V., Johnson, L.T., 2013. Dissolved organic carbon manipulation reveals coupled cycling of carbon, nitrogen, and phosphorus in a nitrogen-rich stream. Limnology and Oceanography 58, 1196-1206.

665   Paytan, A., Lecher, A.L., Dimova, N., Sparrow, K.J., Kodovska, F.G-T., Murray, J., et al.: Methane transport from the active layer to lakes in the Arctic using Toolik Lake, Alaska, as a case study, PNAS, 112, 3636-3640, 2015.

Phelps, A.R., Peterson, K.M. and Jeffries, M.O.: Methane efflux from high-latitude lakes during spring ice melt, J Geophys Res, 103, 29029–29036, 1998.

670   Pokrovsky, O.S., Shirokova, L.S., Kirpotin, S.N., Kulizhsky, S.P. and Vorobiev, S.N.: Impact of western Siberia heatwave 2012 on greenhouse gases and trace metal concentration in thaw lakes of discontinuous permafrost, Biogeosciences, 10, 5349-5365, 2013.

Preston, D.L., Caine, N., McKnight, D.M., Williams, M.W., Hell, K., Miller, M.P., et al.: Climate regulates alpine lake cover phenology and aquatic ecosystem structure. Geophys Res Lett, accepted, doi:
675   10.1002/2016GL069036, 2016.

Rasilo, T., Prairie, Y.T. and Del Giorgio, P.A.: Large-scale patterns in summer diffusive CH_4 fluxes across boreal lakes, and contribution to diffusive C emissions, Global Change Biol 21, 1124-1139, 2015.

Scholten, J.C.M., van Bodegom, P.M., Vogelaar, J., van Ittersum, A., Hordijk, R., et al.: Effect of sulfate and nitrate on acetate conversion by anaerobic microorganisms in a freshwater sediment, FEMS Microbiol Ecol, 42,
680   375-385, 2002.

Segarra, K.E., Schubotz, F., Samarkin, V., Yoshinaga, M.Y., Hinrichs, K.U. and Joye, S.B.: High rates of anaerobic methane oxidation in freshwater wetlands reduce potential atmospheric methane emissions. Nat Comm 6, doi:10.1038/ncomms8477, 2015.

Sepulveda-Jauregui, A., Walter Anthony, K.M., Martinez-Cruz, K., Greene, S. and Thalasso, F.: Methane and
685   carbon dioxide emissions from 40 lakes along a north–south latitudinal transect in Alaska, Biogeosciences, 12, 3197-3223, 2015.

Smemo, K.A. and Yavitt, J.B.: Anaerobic oxidation of methane: an underappreciated aspect of methane cycling in peatland ecosystems?, Biogeosciences, 8, 779-793, 2011.

Stewart, R.E. and H. A. Kantrud. 1971. Classification of natural ponds and lakes in the glaciated prairie region, in:
690   Service, U.S.F.a.W. (Ed.). Resource Publication, Washington, D.C.

695

700

705

710

715

720

725

Tan, Z. and Zhuang, Q.: Arctic lakes are continuous methane sources to the atmosphere under warming conditions, Environ Res Lett, 10, 054016, 2015a.

Tan, Z. and Zhang, Q.: Methane emissions from pan-Arctic lakes during the 21st century: An analysis with process-based models of lake evolution and biogeochemistry, J Geophys Res Biogeosci, 120, 2641-2653, doi: 10.1002/2015JG003184, 2015b.

Tan, Z., Zhuang, Q., Water Anthony, K.: Modeling methane emissions from arctic lakes: Model development and site-level study, J. Adv. Model. Earth Syst., 07, doi:10.1002/2014MS000344., 2015.

Valentine, D.W., Holland, E.A. and Schimel, D.S.: Ecosystem and physiological controls over methane production in northern wetlands, J Geophys Res, 99, 1563-1571, 1994.

van As, D., Hubbard, A., Hasholt, B., Mikkelsen, A.B., van den Broeke, M. and Fausto, R.S.: Large surface meltwater discharge from the Kangerlussuaq sector of the Greenland ice sheet during the record-warm year 2012 explained by detailed energy balance observations, The Cryosphere, 6, 199-209, 2012.

van As, D., Fausto, R.S., Ahlström, A.P., Andersen, S.B., Andersen, M.L., Citterio, M., et al.: Programme for Monitoring of the Greenland Ice Sheet (PROMICE): first temperature and ablation record, Geological Geol Surv Den Greenl, 23, 73-76, 2011.

Van Tatenhove, F.G.M. and Olesen, O.B.: Ground temperature and related permafrost characteristics in west Greenland. Permafrost and Periglacial Processes, 5, 199-215, 1994.

Walter Anthony, K.M., Anthony, P., Grosse, G. and Chanton, J.: Geologic methane seeps along boundaries of Arctic permafrost thaw and melting glaciers, Nat Geosci, 5, 419-426, 2012.

Walter, K.M., Smith, L.C. and Chapin, F.S., III: Methane bubbling from northern lakes: present and future contributions to the global methane budget, Philos Trans A Math Phys Eng Sci, 365, 1657-1676, 2007.

Walter, K.M., Zimov, S.A., Chanton, J.P., Verbyla, D. and Chapin, F.S., III: Methane bubbling from Siberian thaw lakes as a positive feedback to climate warming, Nature, 443, 71-75, 2006.

Ward, D.M. and Winfrey, M.R.: Interactions between methanogenic and sulfate-reducing bacteria in sediments, Adv Aq Microbiol, 3, 141-179, 1985.

Webster, K.D., White, J.R. and Pratt, L.M.: Ground-level concentrations of atmospheric methane in southwest Greenland evaluated using open-path laser spectrocopy and cavity-enhanced absoprtion spectroscopy, Arct Antarct Alp Res, 47, 599-609, 2015.

West, W.E., Coloso, J.J. and Jones, S.E.: Effects of algal and terrestrial carbon on methane production rates and methanogen community structure in a temperate lake sediment, Freshwater Bio, 57, 949-955, 2012.

Westendorp, R.G.: A quantitation method for dynamic headspace analysis using multiple runs, J Chromatogr Sci, 23, 521-524, 1985.

Weyhenmeyer, G.A. and Karlsson, J: Nonlinear response of dissolved organic carbon concentrations in boreal lakes to increasing temperatures, Limnol Oceanogr, 54, 2513-2519, 2009.

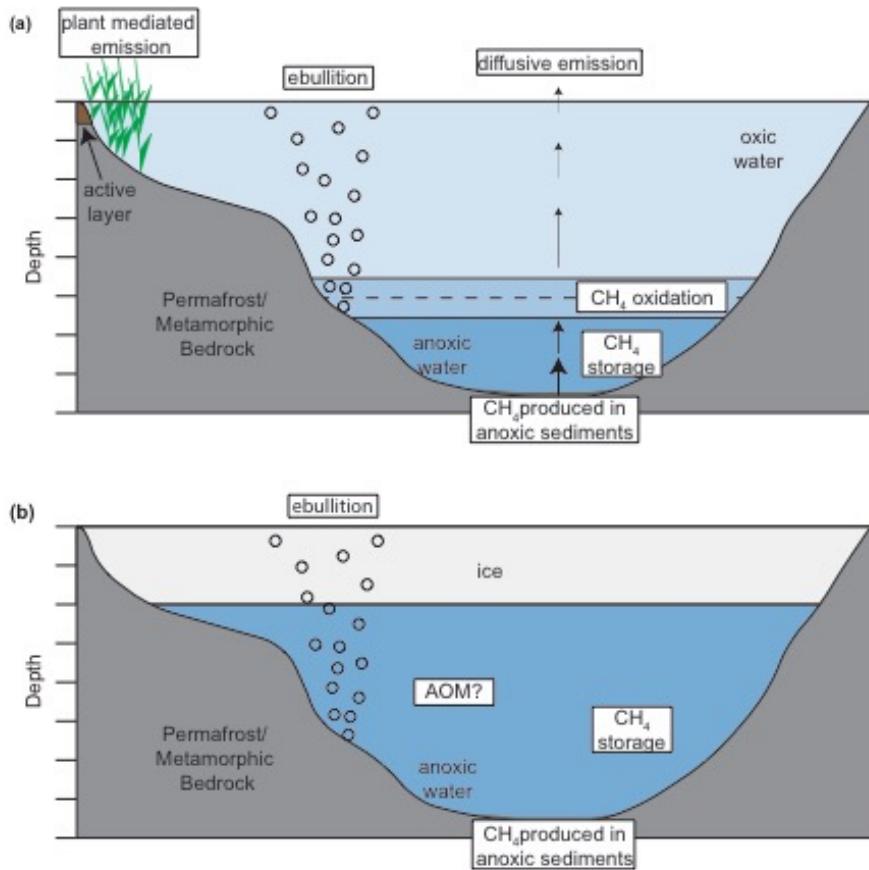
Weyhenmeyer, G.A., Livingstone, D.M., Meili, M., Jensen, O., Benson, B. and Magnuson, J.J.: Large geographical differences in the sensitivity of ice-covered lakes and rivers in the Northern Hemisphere to temperature changes, Global Change Bio, l17, 268-275, 2011.

Wik, M., Crill, P.M., Varner, R.K. and Bastviken, D.: Multiyear measurements of ebullitive methane flux from three subarctic lakes, J Geophys Res 18, 1307–1321, 2013.

730   Wik, M., Varner, R.K., Walter Anthony, K., MacIntyre, S. and Bastviken, D.: Climate-sensitive northern lakes and ponds are critical components of methane release, Nat Geosci, 9, 99-106, 2016.

Yvon-Durocher, G., Allen, A.P., Bastviken, D., Conrad, R., Gudasz, C., St-Pierre, A., et al.: Methane fluxes show consistent temperature dependence across microbial to ecosystem scales, Nature, 507, 488-491, 2014.

Yvon-Durocher, G., Montoya, J.M., Woodward, G.U.Y., Jones, J.I. and Trimmer, M.: Warming increases the

735   proportion of primary production emitted as methane from freshwater mesocosms, Global Change Biol, 17, 1225-1234, 2011.

10. Figures

740

Figure 1. Methane emission pathways and dynamics in a bedrock controlled thermokarst lacustrine system under both open-water and ice-covered conditions.

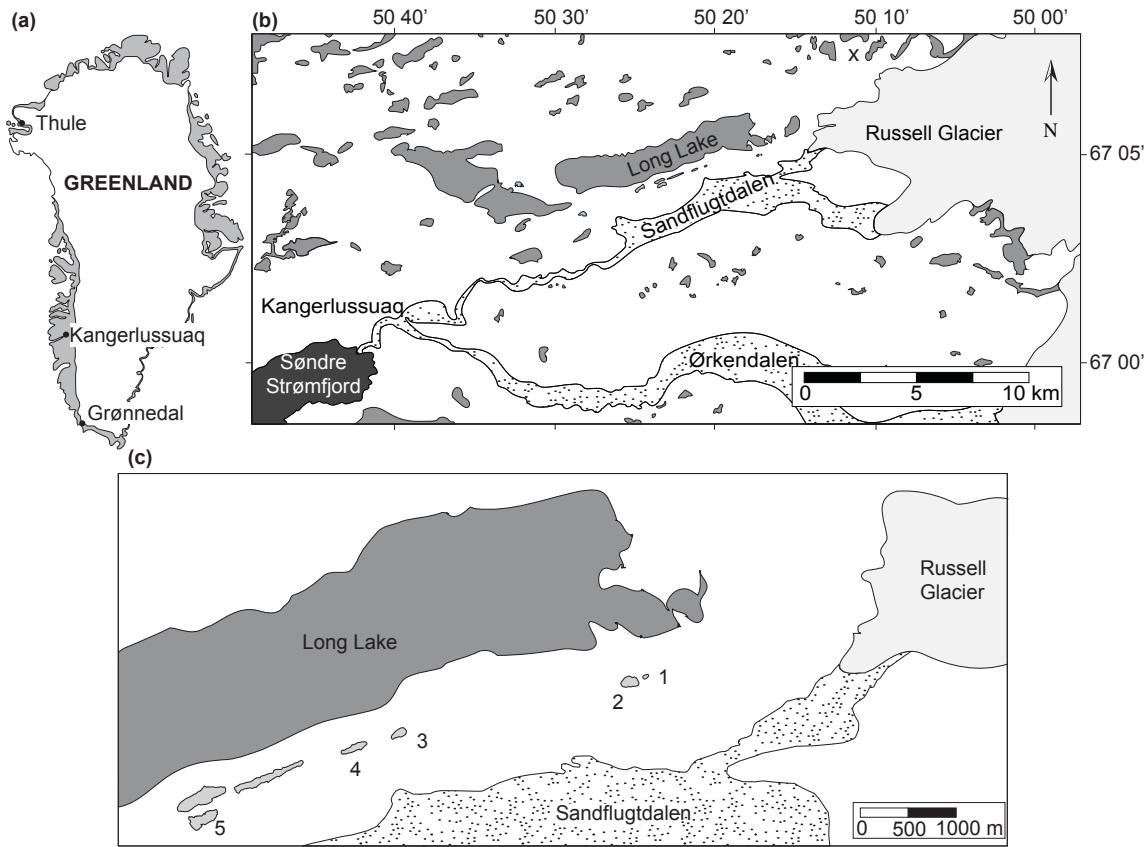



Figure 2. **a)** Greenland, showing Kangerlussuaq; **b)** Regional map of Kangerlussuaq and the inland ice margin, including Sandflugtdalen and Ørkendalen which are two major proglacial valley sandur systems. X marks the location of the Geological Survey of Denmark and Greenland (GEUS) weather station. **c)** Study area map of lakes relative to the Russell Glacier, Long Lake and Sandflugtdalen sandur. 1) EVV Upper lake; 2) EVV Lower lake; 3) Teardrop lake; 4) Potentilla lake; 5) South Twin lake. Figure is modified from Cadieux et al. 2016.

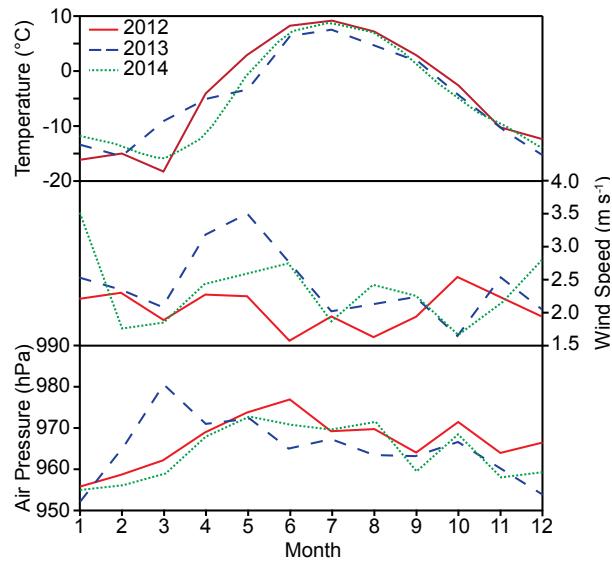



Figure 3. Mean monthly temperature, wind speed and air pressure for Kangerlussuaq from 2012 (red solid line), 2013 (blue dashed line) and 2014 (green dotted line). Data from the Program for Monitoring of the Greenland Ice Sheet (PROMICE) and the Greenland Analog Project (GAP) were provided by the Geological Survey of Denmark and Greenland at http://www.promice.dk.

755

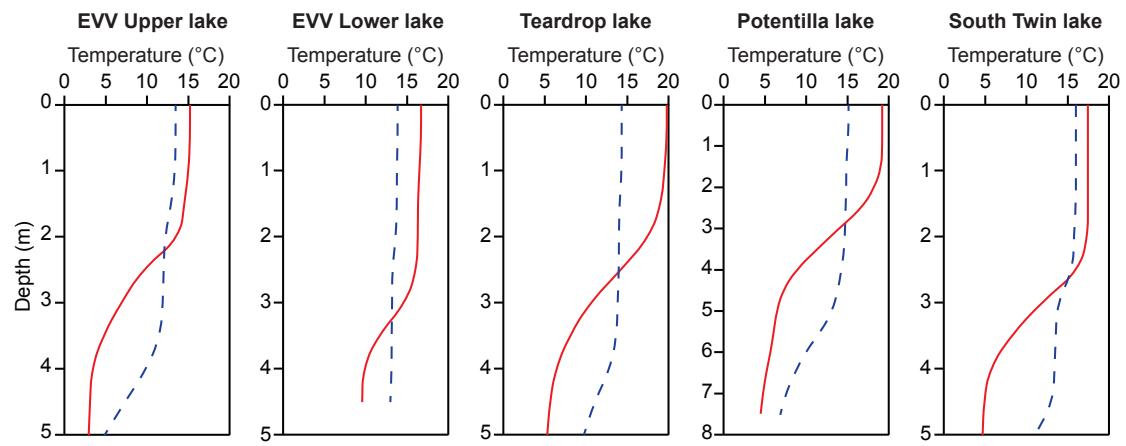



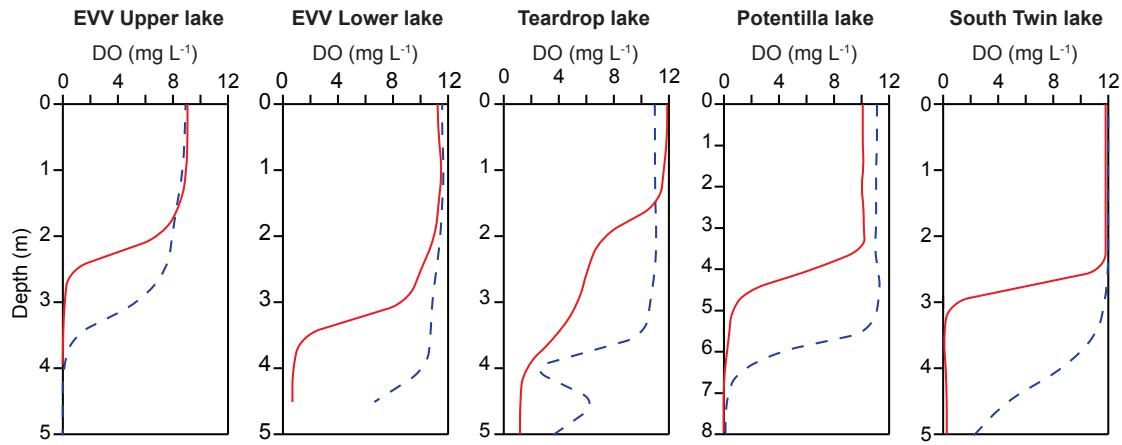
Figure 4. Profiles of temperature under open-water conditions in 2012 (red solid line) and 2013 (blue dashed line).

760

Figure 5. Profiles of DO under open-water conditions in 2012 (red solid line) and 2013 (blue dashed line).

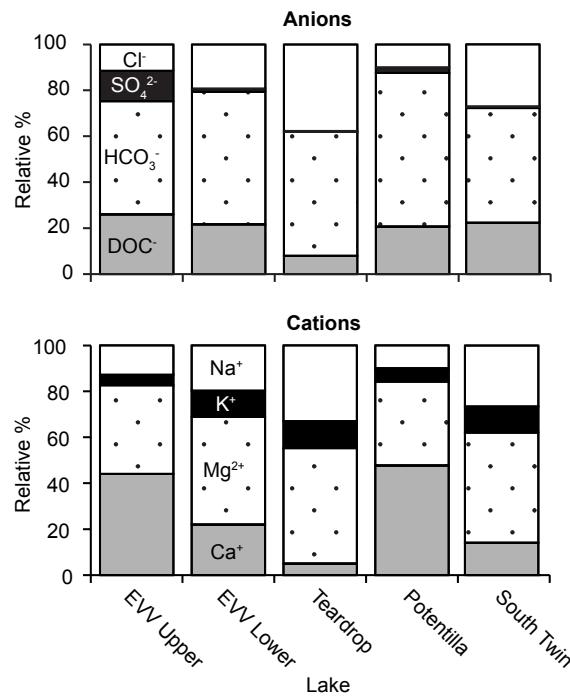
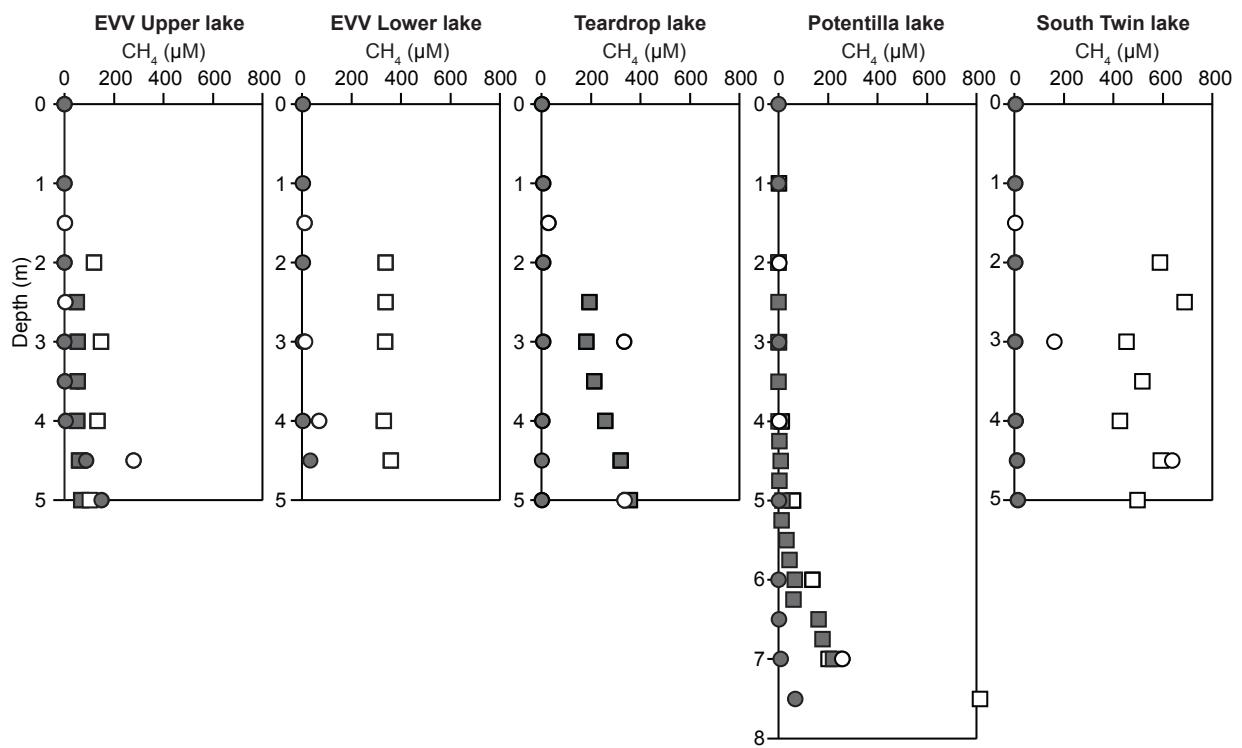
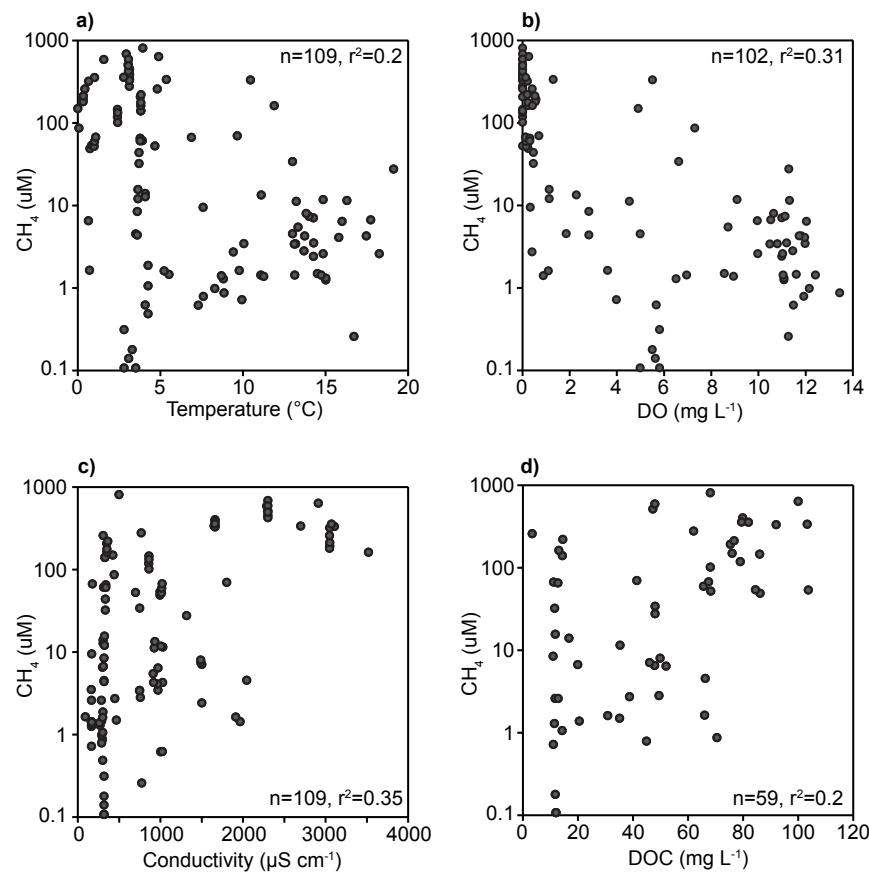



Figure 6. Relative percentages of median total charge associated with anions and cations in water samples from each

765 of the study lakes. We assign the equivalents of missing anionic charge to DOC (Driscoll and Newton, 1985). In all

study lakes, HCO_3^- was the dominant anion. SO_4^{2-} was the least abundant anion in all lakes except EVV Upper lake.

There was no dominant cation from lake-to-lake.

770   Figure 7. Profiles of dissolved CH_4 under open water conditions (circles) in July 2012 (open) and July 2013 (closed) and ice-covered conditions (squares) in April 2013 (open) and April 2014 (closed). Concentrations of CH_4 under open water condition in 2013 and ice covered conditions in 2014 can also be seen in Cadieux et al. 2016.

775   Figure 8. Relationships between dissolved CH_4 concentrations from 2012-2014 and **a)** temperature, **b)** DO, **c)** conductivity, and **d)** DOC.

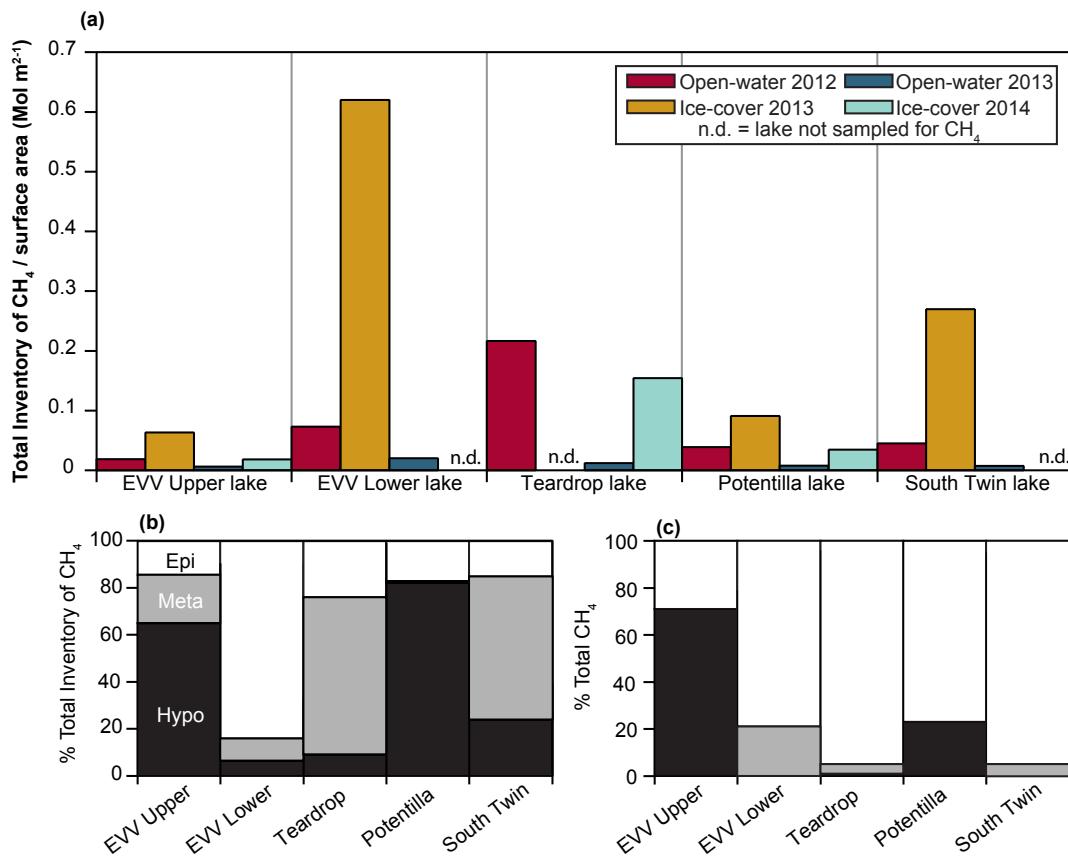



Figure 9. **a)** Total inventory (moles) of CH_4 in the water column of each lake under both open-water conditions in July 2012 (black) and July 2013 (grey) and ice-covered conditions in April 2013 (white) and April 2014 (hashed-lines). For seasons where the inventory was low, total moles are written above the bars; n.d. refers to seasons when a given lake was not measured. **b & c) Relative** pool sizes (% of total) of dissolved CH_4 under open water conditions in July 2012 (b) and July 2013 (c). Pools are defined by redox conditions, where the stored pool (black) is the sum of CH_4 from intervals where DO < 1 mg L^{-1}, gray represents the suboxic pool, and the active pool (white) is the sum of CH_4 from well mixed surface intervals potentially available for direct exchange with the atmosphere.

11 Tables

Table 1. Morphometrics and median physico-chemical characteristics of lakes under open-water conditions in 2012.

	Z_{max} (m)	Fetch (m)	Surface area (ha)	Volume (m^3)	pH	Specific Conductivity (mS cm^{-1} °C)	DOC (mg L^{-1})
EVV Upper*	5.5	68	0.22	5,200	7.0 (11)	0.7 (11)	38.7 (4)
EVV Lower	4.5	180	1.5	31,000	8.9 (10)	1.2 (10)	38.4 (2)
Teardrop*	5.25	160	0.97	34,000	9.2 (11)	4.3 (11)	92.0 (4)
Potentilla *	8.0	280	1.6	160,000	7.2 (15)	0.4 (15)	11.4 (3)
South Twin	5.5	310	3.1	120,000	7.9 (11)	4.0 (11)	20.5 (3)

sample size is in parentheses

 * Can also be found in Cadieux et al. 2016

Table 2. Seasonal and annual variation in median specific conductivity and DOC

	Open Water 2012*	Ice Cover 2013	Open Water 2013	Ice Cover 2014
Specific Conductivity (mS cm^{-1})				
EVV Upper lake	0.7 (10)	1.5 (10)	0.5 (11)	1.0 (10)
EVV Lower lake	1.2 (8)	2.9 (7)	1.0 (9)	n.d.
Teardrop lake	4.3 (10)	n.d.	1.9 (11)	3.1 (10)
Potentilla lake	0.4 (15)	0.5 (15)	0.3 (16)	0.4 (13)
South Twin lake	4.0 (10)	4.0 (9)	1.2 (9)	n.d.
DOC (mg L^{-1})				
EVV Upper lake	39 (4)	79 (3)	48 (4)	76 (6)
EVV Lower lake	38 (2)	80 (2)	49 (2)	n.d.
Teardrop lake	92 (3)	n.d.	58 (4)	77 (3)
Potentilla lake	11 (3)	17 (4)	11 (3)	12 (9)
South Twin lake	21 (3)	110 (2)	48 (3)	n.d.

n.d. refers to seasons when a given lake was not measured

sample size is in parentheses

*open water conditions for EVV Upper lake, Teardrop lake, and South Twin lake can also be found in Cadieux et al. (2016).

Table 3. Concentrations of CH4 (uM) in surface waters (0.5 m) under open-water conditions in 2012 and 2013

	2012	2013
EVV Upper	2.7	0.9
EVV Lower	11.5	2.7
Teardrop	27.8	2.4
Potentilla	2.6	1.3
South Twin	4.3	3.5

825

Table 4. Ranges of CH_4 concentrations in profundal sediments and littoral sediment gas bubbles

	Profundal (mM)		Littoral (ppmv)	
	Ice Cover 2013	Open Water 2013	Open Water 2012	Open Water 2013
EVV Upper lake	0.7-1.9 (6)	0.3-0.7 (5)	n.d.	473,000 (1)
EVV Lower lake	2.7 (1)	0.8-1.9 (5)	n.d.	332,000 (1)
Teardrop lake	n.d.	0.5-1.2 (5)	378,000 (1)	372,000-404,000 (2)
Potentilla lake	1.5-2.0 (4)	1.0-1.4 (5)	320,000 (1)	166,000-262,000 (2)
South Twin lake	1.4-3.4 (3)	0.4-2.2 (4)	434,000 (1)	228,000-238,000 (2)

830

835

n.d. refers to seasons when a given lake was not measured

sample size is in parentheses