EARTH AND ENVIRONMENTAL SCIENCES

December 28, 2016

Dear Editorial Board,

Thank you for your timely handing of this manuscript. We are pleased that the reviews were positive and support publication of the work in *Biogeosciences*. The reviews were thoughtful, in depth and strengthened the manuscript. In the revised manuscript, we have made every effort to incorporate the suggestions of the two reviewers.

One of the major revisions suggested by reviewers was that it is difficult to correlate a specific weather phenomenon to CH_4 dynamics in the lakes and that many of our discussion points are over interpreted. We agree with the reviewer that at this level we are unable to specifically demonstrate that differences in internal CH_4 dynamics are directly correlated to temperature differences annually and seasonally without repeated years of data to conduct a statistical analysis. Without the ability to collect more data, we revised the discussion of the manuscript to be explicit that this is a possible result of warmer temperatures, by stating that our results correlate with the specific weather and are not the result of. In addition, within the revised version we have focused on making some discussion points more speculative in order to avoid over interpreting.

The reviews brought to our attention that there are previous studies on multiyear dissolved CH_4 concentration in the water column at similar latitudes that we were not previously aware of. We have added the suggested references, and accordingly refocused the paper's importance to the difference between a warm year and a "typical year".

Another significant concern was in regards to methodology and preparation not being fully described. To improve this aspect of the manuscript, we have clarified and expanded the methods.

In the following pages, we have provided a detailed response (in blue) to reviewer comments (which are included here verbatim).

We look forward to publication of this manuscript in *Biogeosciences* once revisions have been deemed acceptable.

Thank you for your consideration.

Sincerely,

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Anonymous Referee #1

Summary

The manuscript describes a study on dissolved CH4 concentration in five arctic shallow lakes located in Greenland. They used here five data sets (from summer 2012 to winter 2014) on the Southwest ice-free margin of Greenland. The aim of the study was focused on the effect of one high warming event occurred in summer 2012 on CH4 concentration profiles and compared it with subsequent years (2013 and 2014). The study of CH4 dynamics in lakes is a topic of broad scientific interest as lakes represent an important source of this gas to the atmosphere.

I recognize that it is a difficult task to study lakes in these extreme environments, and data coming from them are therefore valuable. The manuscript is not very clear in demonstrating how the warm 2012 summer influenced CH4 dynamics in these lakes. Even, this study shows minor effects of the 2012 warm summer on CH4 dynamics (showed in Figure 7), and it is very difficult to correlate the minor effects to any particular phenomena (showed in Figure 8).

Likewise, the authors should always make clear when data have been previously published. I was surprised that several data in Tables, Figures (Figure 6 and 7) and Map (Figure 2) are the same (or at least very similar) than those reported in another manuscript from the same authors (Cadieux et al. 2016); and no reference is made to that previous study (and/or indicated in those tables and figures). I also want to point out, that there are strong similarities in the DOC and pH data presented in Table 1 and Table 2 (for DOC) for open-water conditions 2012 in this manuscript and data presented in Table 1 for open water conditions in 2013 from Cadieux et al. (2016).

The manuscript is well written, although some sections are not totally mature yet and therefore the manuscript lacks a clear focus and structure. I think that some of the analysis are speculative and/or over-interpreted and numerous issues in the method section must be better addressed.

First, we thank the reviewer for their positive comments on the paper and feel they have raised some valid concerns. The reviewer is correct in noticing that some data and parts of figures are in Cadieux et al. 2016. However, its important to note that in Cadieux et al. 2016, only 3 lakes (EVV Upper lake, Teardrop lake, and Potentilla lake) are discussed for only open water conditions in 2013 and ice covered conditions 2014. In order to be explicit about data that is previously published, we have revised tables and figures to cite which lakes and data points have been previously published.

The reviewer is also correct in noticing that in Table 1, these physico-chemical characteristics of the lakes in open-water conditions in 2012 are the same as in Cadieux et al. (2016) - which is inaccurately labeled water conditions for 2013 when they are 2012. For the paper here, we revised the table text to include that this data is also in Cadieux et al. 2016 and will take steps to revise the other paper so both match.

Specific comments

The introduction contains mixed statements related to temperature effects on CH4 production/oxidation/storage in the water column (e.g. temperature dependencies on CH4 production is described in two sentences in second and fourth paragraphs). I would recommend reorganizing the ideas to improve the introduction flow (which should go from general to specific).

Thank you for this suggestion to strengthen the introduction. In order to go from general to specific, as well as remove repetitive information, the organization now goes from discussion of lakes and climate, to methane production and consumption, to focus of this study.

Likewise, it is necessary to carefully review the literature to avoid controversial state- ments like the authors indicate at the end of the introduction "This work provides the first measurements of dissolved CH4 concentrations under both open-water and ice- covered conditions for consecutive years in small, Arctic lakes". From the literature that I know (and for sure I am missing a vast amount of studies), there are previous studies or multiyear dissolved CH4 concentrations in water column, in similar latitudes. Some of these previous works measured dissolved CH4 concentration through and over sev- eral years. I suggest some readings: Kaankala et al. (2006), Bellido et al. (2009), Karlsson et al. (2013), Greene et al. (2014), Miettinen et al. (2015), Tan et al. (2015), among others.

We appreciate the reviewer bringing this to our attention. Previously, in our literature search, we had not found Karlsson et al. (2013), Miettienen et al. 2015 and Greene et al. 2014 which all also describe both multiyear and multiseason results. The others described above are only for one season or one year. We have removed this sentence accordingly.

The description of the methods is the most important section to understand what the authors did. This section has to be improved substantially. Firstly, I found a number of cases in which devices or sample preparation are not full described (e.g. electronic submersible pump, total organic carbon analyzer, passive diffusion bags PDBs, HCl concentration, dilution correction for CH4 measurements). Secondly, littoral sediment CH4 bubble sampling method (used in this manuscript) is a very unspecific method. While in Cadieux et al. (2016) the method was used in combination with the isotopic analysis (isotopic values are helping to understand CH4 dynamics), in this manuscript, values of CH4 are given without determining the volume of sediment samples (as com- mented in the method section). Therefore, what is the point to include very speculative values of CH4 concentration from the littoral. Thirdly, I consider it would be necessary to describe briefly the methods, even if they are previously described (Cadieux et al. 2016), to avoid excessive self-citation and tedious reading. Finally, the statistical anal- yses need to be clarified. Some of them does not make sense, as written, and specific information is required to understand how data analysis was made e.g., mean/median temperature and CH4, profile values, seasonal, sectional.

The reviewer makes good point that this paper would be strengthened by describing the methods in more detail. We revised the methods section in the following ways in an attempt to address the concerns noted above:

- Regarding the DOC measurement, a reference has been added to describe the questions of methodology (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.).

- We specified the model and type of electronic submersible pump: "*Water for chemical analysis was collected from the water column using a Narrow Diameter Supernova™ electronic submersible pump.*"

- The methods for dissolved methane sampling have been briefly expanded: "*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).*"

- We acknowledge that the littoral methane concentrations are speculative, as we did not measure a concentration of sediment in order to normalize lake-to-lake. We have added a statement to explicitly state that this is just an estimation: "*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.*"

- In order to not over-analyzed results, the following was added to the littoral CH_4 section: *"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."

- Statistical analysis section has been clarified as to what was tested and why: "*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 CH_4 concentrations were related to variables such as DO, temperature, DOC and conductivity.*"

Through the results and discussion section some Figures are used to explain variations and significant differences between lakes. In data from Figure 7, it is impossible to note the range reported in surface waters and depth axes are missing in some sub-figures (making impossible to see clearly the depth profile). Moreover, in data analysis from Figure 8 (wrongly named Figure 7 in Page 9, Line 307), it is impossible to see when CH4 vs. DO and CH4 vs. T are related or not. Likewise, some discussion sections are not well focused on the main issue and over interpret results. Some examples are:

Regarding the figures, Line 307 was revised to Figure 8 and depth axes have been added to all of the panels in figure 7.

We agree with the reviewer that it is difficult to note the range of surface water CH_4 concentrations in Figure 7. In order to clarify this, a new table has been made that defines the surficial values under open-water conditions in all of the lakes:

Table 3: CH_4 concentrations (μM) in surface waters 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

We also agree with the reviewer that in Figure 8 it is difficult to see the trend. This is because there is not a very statistically significant trend between CH_4 concentration and temperature/dissolved oxygen. This is why we had included r^2 values on each of the figures. We have gone through the text to ensure that we do not over analyze this non-significant trend.

i) competition for substrates favors sulfur reduction (SR) and methanogenesis typically does not occur until SO42- 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 CH4 in the water column, suggesting there was sufficient reduced carbon substrates to fuel both SR and methanogenesis. Therefore, while aquatic chemistry in the water 320 column may be a factor influencing CH4 production, it alone is insufficient to explain the variation in CH4 concentrations observed lake-to-lake, as well as seasonally and annually."

Give the small sample size for each lake, our statistical power is limited for aquatic chemistry. In keeping with the reviewer's suggestion, the last sentence has been revised to: "*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."*

ii) all section "6.3 Effects of temperature on CH4", and

In keeping with the reviewer's suggestion, we have revised section 6.3 to explicitly mention that the relationships observed are at a specific date and time. For example: "*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."*

iii) you don't have thorough information on the ice phenology to indicate that "Our re- sults suggest that changes in the duration of seasonal ice cover will, in turn, result in changes in inventories of under-ice CH4. As the duration of ice cover decreases, the amount of CH4 stored under ice 455 cover will likely decrease due to the shorter time for accumulation, potentially reducing the amounts of CH4 emitted during ice-breakup and spring overturn.". I think, the results are not reliable to support such statements.

We agree with the reviewer that we don't have dates for ice-in or ice-out or other ice phenology information. However, with the data we do have, we can speculate what may happen to CH_4 inventories as ice-cover duration decreased. In keeping with the reviewer's comments, we revised this section accordingly: "*Currently, the largest efflux of CH_4 from our study lakes occurs during ice-breakup and spring overturn. Changes in the duration of seasonal ice-cover will result in changes in inventories of under-ice CH_4. We predict that 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."*

References

Bellido, J. L., Tulonen, T., Kankaala, P., and Ojala, A.: CO2 and CH4 fluxes during spring and autumn mixing periods in a boreal lake (Paajarvi, southern Finland), J. Geophys. Res.-Biogeosci., 114, G04007, doi:10.1029/2009JG000923, 2009.

This was already included as Lopez Bellido.

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fractionations of C and H isotopes related to methane oxidation in Arctic lakes, Geochim. Cosmochim. Ac., 187, 141-155, 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, doi:10.5194/bg-11-6791-2014, 2014.

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.

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.

Miettinen, H., Pumpanen, J., Heiskanen, JJ., Aaltonen, H., Mammarella, I., Ojala, A., Levula, J., and Rantakari, M.: Towards a more comprehensive understanding of lacustrine greenhouse gas dynamics two-year measurements of concentrations and fluxes of CO2, CH4 and N2O in a typical boreal lake surrounded by managed forests, Boreal Environ. Res. 20, 75–89, 2015.

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. (note: for sure to develop the models, they used multi-year dissolved CH4 concentration data).

We thank the reviewer for including the full citations for the references suggested. These have been incorporated into the text.

Anonymous Referee #2

With a little focusing this interesting study could be a gem. The study demonstrates two mechanisms by which warming temperatures in Greenland could affect methane dynamics in small lakes. The first is during open water, increased stratification of the water column, which would presumably result in greater methane release during fall overturn and less overall methane oxidation. The second mechanism is that greater temps will result in less overall ice cover which would cause less methane storage un- der the ice and presumably more overall oxidation. These two processes or effects of increased temperature would seemingly have contradictory effects. I don't know the extent to which these two processes effects have been expounded in the literature, but this is the first time I've seen them presented. I would thus suggest to the authors that they make more of these observations, highlighting them in the abstract, and particularly in the article titles, which is rather weak right now, in my opinion. Per- haps something like " The contradictory nature of warming effects on lake methane emissions: increased stratification during ice free periods versus reduced ice cover." Needs work, but something along those lines. I would also suggest that these unique observations be expanded into a conceptual model in the discussion and conclusions.

Thank you for this positive review of our paper.

The reviewer has a valid point that the title could be modified to be more compelling. We have taken this into consideration and revised the title to: *"Exceptional summer warming leads to contrasting outcomes for methane cycling in small Arctic lakes of Greenland"*

Specific comments.

1. abstract. See above. ALSO focus on the effects these processes will have on overall annual lake methane emissions. That's what's important. You may not have the data, but speculate, and call for attention to what your have observed so it can be followed up.

We agree with the reviewer that adding more regarding the possible overall methane emissions and highlighting the shift from spring emission to fall emission is important to highlight in the abstract. The later part of the abstract has been revises as follows to include these suggestions: "*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.*"

2. page 3, lines 90-95. Your hypothesis. Why did you hypothesize that warmer conditions would lead to higher methane concentrations? Say "increased stratification" here. Explicitly state it. Advance a hypothesis about ice cover. Return to these hypotheses in your discussion.

We hypothesized that warmer conditions would lead to higher methane concentrations, because warmer conditions would lead to increased stratification. This sentence has been revised to increased stratification in order to clarify.

The reviewer makes a good point that a hypothesis should be stated regarding ice cover. Accordingly, the following hypothesis has been added about ice cover: "*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.*"

3. Lines 95-100. Permafrost soil? Anything you can tell us about it? Peat? Mineral soil? OM content? Does it thaw under the lake (thaw bulb) to make the methane you observe?

The soil is composed predominantly of till and glaciofluvial deposits. While there are talics in the area, our observations do not suggest there are talics below any of the study lakes here. In response to this comment, we have added the following sentence to further define soils in the

region: *"Soils in the region are not well-developed, composed of till and glaciofluvial deposits (Van Tatenhove and Olesen, 1994)."*

4. line 112. define GIS

GIS stands for the Greenland Ice Sheet, and has been defined in the text accordingly. It is also defined in the introduction.

5. line 126 define EVV

EVV stands for Epidode Vein Valley and is an informal name to describe an outcrop close in proximity to the lakes. We have revised the study area section to include further information regarding the names of the lakes: "*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"*

6. line 211. what is Clinograde?

A clinograde oxygen profile is when dissolved oxygen values decrease with depth. This term is defined in the later part of the sentence:*"wherein DO was saturated and in equilibrium with the atmosphere in the surface waters and became increasingly under saturated down the water column."*

7. line 225. "moderately brackish salinity? What was the salinity in o/oo? Is "brackish" the right term? Like 5-10 o/oo?

These are terms from Stewart and Kantrud paper, which has been added to the references. In terms of salinity, brackish here would be >2 ‰.

8. Line 307-308. confusing. Is the sentence messed up?

This sentence did need to be clarified. It has been revised to state: "*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."*

9. Line 308 do you mean figure 8? Not 7?

Yes, thank you

10. Line 315 sulfate reduction not sulfur.

Done. Thank you

11. Line 352. Inversely related?

Yes, this should be inversely related and has been revised.

12. Lines 415-425. I don't follow this too well. How do you know that the % of CH4 oxidized is

the same over the two years? Do you have measurements of MOX> ? Doesn't this kind of blow your theory that more temp and more stratification will result in more methane release with fall overturn? How is the MOX the same across years, or even known at all?

The way we determined that the same amount of CH_4 was oxidized was by assuming all the methane in the surface water originated from the sediment. By doing that, what is at the surface is a percentage of the initial methane (at the sediment-water interface). Therefore, we don't have the measurements of MOX, just an estimate of the % of methane oxidized. We have revised this paragraph to emphasize that this isn't an estimate of MOX, but an estimate of the amount of methane oxidized.

Even though the amount oxidized at the time of stratification is the same, it doesn't change that under warmer conditions with increased stratification in 2012 there is more methane in the anoxic waters, which is what would be emitted during fall overturn.

13. Develop around line 425-460 the effects of a shorter ice covered period. Make a solid conceptual model centered on your figures. What is the interplay between increased stratification during ice free in contrast with less ice cover? How does this interplay affect annual methane flux as temperatures warm> I would think that there would be less MOX under stratified conditions, and certainly less under ice.

We agree with the reviewers concern and expanded the relevant discussion to better articulate the conceptual model as informed by our results: "*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 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 (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.*"

14. Conclusions. Point out that these two processes are contradictory.

In response to this suggestion, the conclusions have been revised to explicitly point out that these two processes are contradictory, leading to the inclusion of the following sentence: "*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.*"

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

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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-

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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).

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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

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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 augured 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

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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

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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.

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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.

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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.

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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

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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.

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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

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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 ºC 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.

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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

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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).

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Changes in the duration of seasonal ice-cover will result in changes in inventories of under-ice CH_4. We predict that 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 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 (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.

Comment [SBC1]: Conceptual model based on suggestion from reviewer 2

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 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 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.

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10. Figures

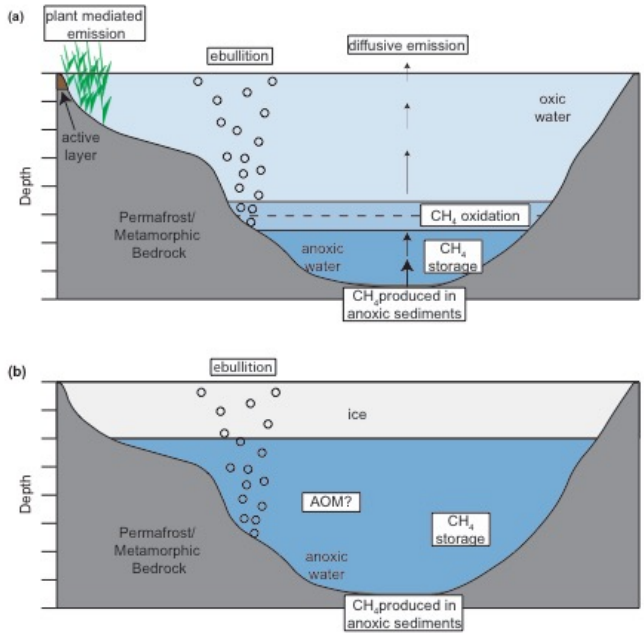
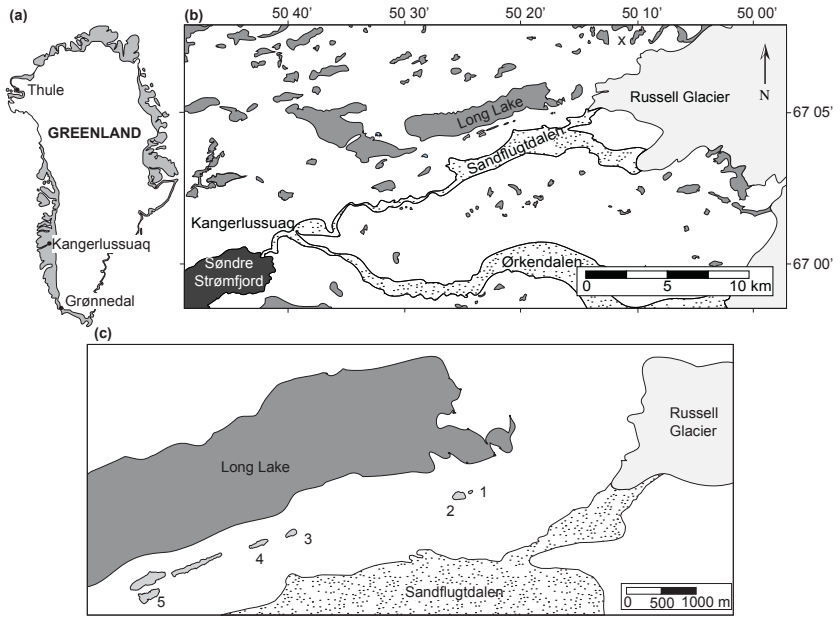


Figure 1. Methane emission pathways and dynamics in a bedrock controlled thermokarst lacustrine system under both open-water and ice-covered conditions.



860 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.

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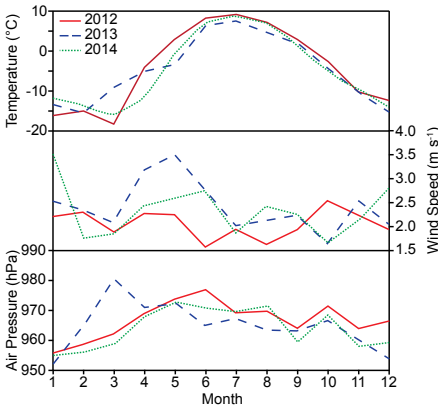

Figure 3. Mean monthly temperature, wind speed and air pressure for Kangerlussuaq from 2012 (red solid line), 2013 (blue dashed line) and 2014 (green dotted line). Data from the Program for Monitoring of the Greenland Ice Sheet (PROMICE) and the Greenland Analog Project (GAP) were provided by the Geological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

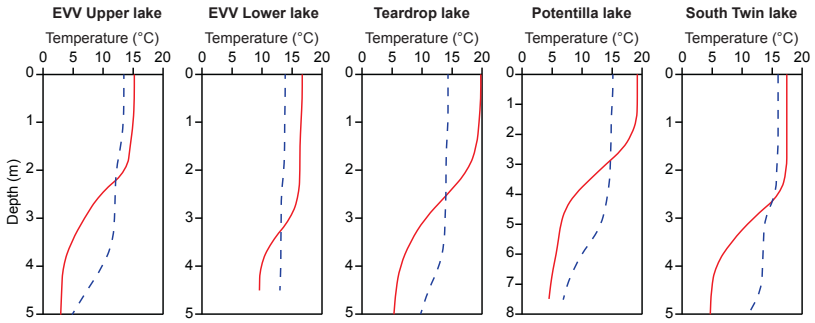

Figure 4. Profiles of temperature under open-water conditions in 2012 (red solid line) and 2013 (blue dashed line).

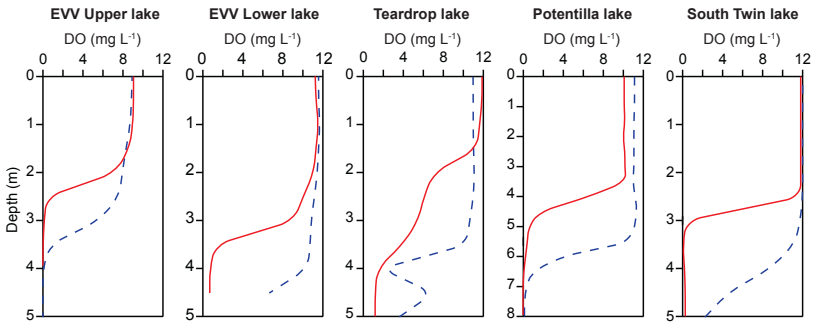

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Figure 5. Profiles of DO under open-water conditions in 2012 (red solid line) and 2013 (blue dashed line).

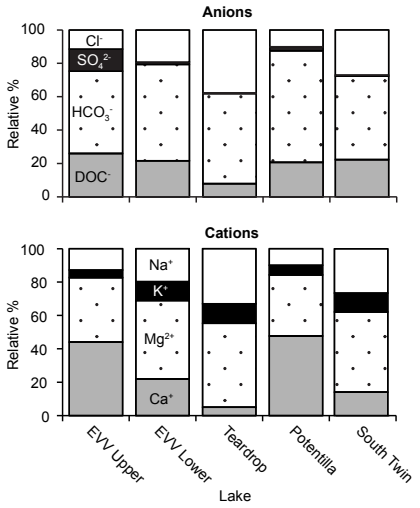
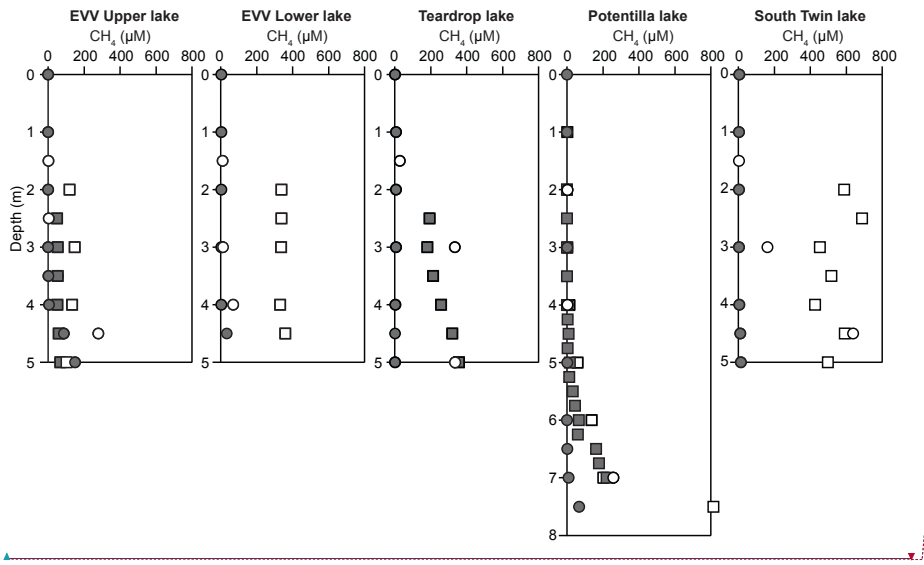


Figure 6. Relative percentages of median total charge associated with anions and cations in water samples from each of the study lakes. We assign the equivalents of missing anionic charge to DOC (Driscoll and Newton, 1985). In all study lakes, HCO_3^- was the dominant anion. SO_4^{2-} was the least abundant anion in all lakes except EVV Upper lake. There was no dominant cation from lake-to-lake.



885 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.

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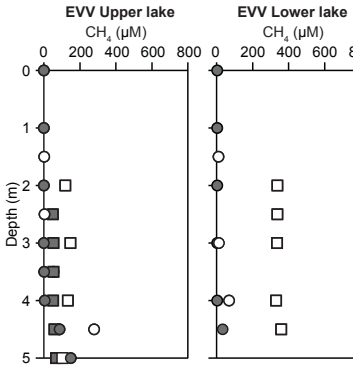

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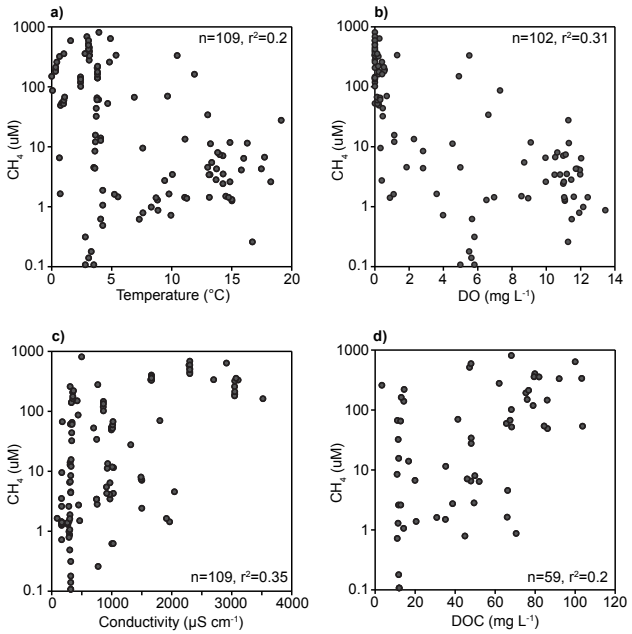

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Figure 8. Relationships between dissolved CH_4 concentrations from 2012-2014 and **a)** temperature, **b)** DO, **c)** conductivity, and **d)** DOC.

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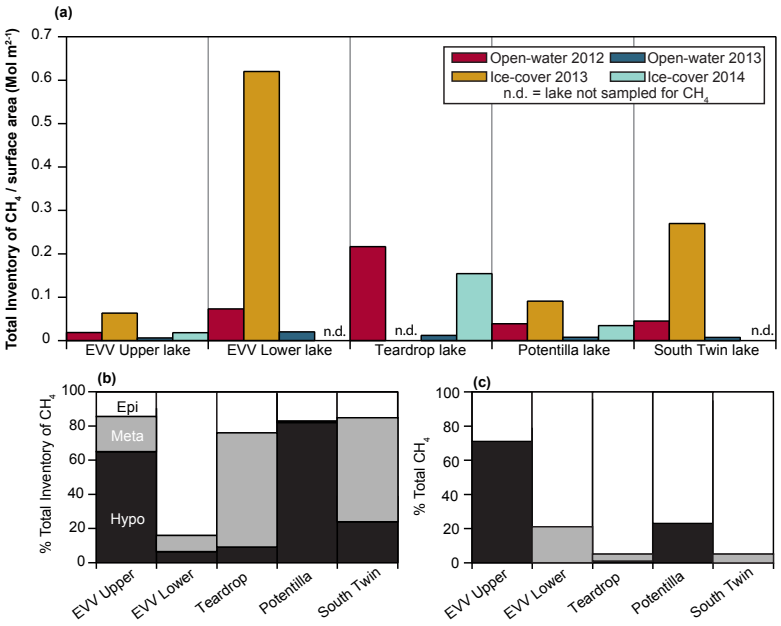

Figure 9. **a)** Total inventory (moles) of CH_4 in the water column of each lake under both open-water conditions in July 2012 (black) and July 2013 (grey) and ice-covered conditions in April 2013 (white) and April 2014 (hashed-lines). For seasons where the inventory was low, total moles are written 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

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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

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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)

n.d. refers to seasons when a given lake was not measured
sample size is in parentheses

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	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)

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