

## REVIEWER 1

The Cryosphere Discuss.,

<https://doi.org/10.5194/tc-2019-304-RC1>, 2020 © Author(s) 2020. This work is distributed under the Creative Commons Attribution 4.0 License.

Interactive comment on “Methane Pathways in Winter Ice of Thermokarst Lakes, Lagoons and Coastal Waters in North Siberia” by Ines

Spangenberg et al.

Pat Langhorne (Referee)

pat.langhorne@otago.ac.nz

Received and published: 1 June 2020

This paper describes ice on three distinct water bodies, in particular examining the methane within the ice and the physical properties associated with understanding the observed methane concentrations. I am expert in the growth of ice on water bodies, but not on the suite of chemical techniques involved in the study and my comments below need to be read with this in mind. I believe that the study is interesting and deserves publication but could be made easier for the reader to understand, especially those not already expert in every aspect of the work.

Comment 1: The paper deals with three distinct water bodies which are expected to show different characteristics. Yet there is nothing in their abbreviated names that helps the reader immediately recognize which water body is being described. Why not call the sites Bay, Lake, Lagoon, or some abbreviation that is easily recognizable, such as BY, LK, LG?

Response: We changed the abbreviated names to Tiksi Bay (BY), Polar Fox Lagoon (LG) and Goltsovoye Lake (LK) throughout the paper. We have also changed the names and numbers of the cores to reflect the water body and sequential geographic position of each core.

Comment 2: In addition a number of cores are taken at each site, and interesting behavior is shown in these data in Figures 3-5. However the naming of the cores could better reflect their position and make it easier for the reader to interpret this behavior– for example the TB cores could be labeled from N to S, while GL cores from E to W.

Response: we have relabeled the cores but used the abbreviations suggested in the previous comment (e.g. BY-1, BY-2, etc.) always in a uniform manner following compass direction.

This has been applied consistently to all figures, the text, online data, and tables. We added the compass directions to the bathymetric profiles as well, to help the reader assign order to direction.

Comment 3: In my opinion there was too much description of the shape of graphs etc at the expense of what the reader might expect to learn from that particular type of behavior in the graph. I understand that the paper is the work of a thesis, but while such description is appropriate for a thesis it extends the length of a journal article unnecessarily. For example, sections 4.2.2, 4.2.3, 4.2.4, 4.3.1 and 4.4.1 give detailed description of what can be seen by looking at Figs 3, 4 and 5, and Table 2. What I wanted to know was what can be scientifically deduced from the observed values of parameters, or form of graphs. I suggest that the authors replace these detailed descriptions with the scientific evidence provided by the particular behaviors.

Response: We have tried to be strict in separating the reporting of results from their interpretation. The interpretation of the results is therefore only found in the discussion section. We take this comment to mean that the results section is unnecessarily long and we have made numerous edits to shorten the sections mentioned (please see track changes section).

Comment 4: I felt that the authors tended to make rather grandiose statements that were not obviously dealt with in the paper e.g. statements regarding ice as a barrier to methane fluxes and the importance to warming in the Arctic. I suggest that authors carefully consider what can be deduced from their work and focus on the aims of their study.

We agree that there is definitely room for us to hone our objectives, discussion and conclusions in order to be more precise about what we did, why, and what its implications were. Please see our answers below regarding the objectives, discussion and conclusions, where we detail the deletions and editing we have undertaken. We feel the paper has been slimmed down and become more precise in its aim and conclusions.

Comment 5: I do not have the expertise to critically review the chemical techniques used in this paper and whether they are appropriate and carefully carried out. I'm afraid that the editors must seek advice another reviewer for that expertise.

#### Technical Corrections

p. 1: Abstract: Please rewrite, taking into consideration the Comments above.

Adopted, see track changes version.

p.1, line 3: “.. provide insights on methane pathways in winter ice cover..” But at the end of the paper I had not recognized what these insights were, nor could I find it in the Abstract.

We agree that this was imprecisely worded. We have replaced the 3<sup>rd</sup> and 4<sup>th</sup> sentences of the abstract:

*“The fate of methane in these waters and is poorly understood. We provide insights into the methane pathways in the winter ice cover on three different water bodies in a continuous permafrost region in Siberia.”*

with:

*“How methane concentrations and fluxes in these waters are affected by the presence of an ice cover is poorly understood. To relate water body morphology, ice formation, and methane, we studied the ice of three different water bodies in locations typical of the transition of permafrost from land to ocean in a continuous permafrost coastal region in Siberia.”*

p.1, line 10: “except for three”

Corrected.

p. 1, Line 14: Comment that “methane oxidation may decrease methane concentrations during winter” Where? In the ice? In the atmosphere? Both? Is this the evidence for the winter pathway but I have not recognized it?

Response: the sentence has been re-worded and we have added “...on the lower ice surface.”

p. 1, Line 14-16: I could not follow how methane pathways in freshwater systems led to the understanding of permafrost carbon feedbacks in global warming – this seemed to be a huge leap to me – but perhaps I show my lack of knowledge of permafrost.

This sentence was deleted.

p. 2, Line 27-28: This is not a sentence

Corrected.

p. 3, Line 20-23: Here the authors clearly outline the three aims of the paper. I am clear that they have achieved the first aim, but I am unclear regarding aims 2 and 3. I return to this comment in the Conclusions.

Response: we agree, and have made the following changes:

P 3 lines 18—22: we have changed the objectives of the study to be more precise and focussed, from

*“This study aims to clarify the role of a winter ice cover for methane cycles of three different stages in the lake-lagoon-shelf transition in a region of rapidly thawing permafrost in northeast Siberia. Our objective is to demonstrate how methane is distributed within seasonal ice from Tiksi bay (TB), Polar Fox Lagoon (PF), and Goltsovoye Lake (GL), to better understand 1) how freezing processes differ between the three water bodies, 2) what the relationships between freezing dynamics and methane concentration in the ice are, and 3) the potential importance of methane oxidation in different water bodies.”*

to:

“To improve our understanding of how water bodies function as CH<sub>4</sub> sources or sinks, this study aims to clarify the role of the winter ice cover for CH<sub>4</sub> in three different stages in the lake-lagoon-shelf transition in a region of thawing permafrost in 10 northeast Siberia. Our objective is to demonstrate how CH<sub>4</sub> is distributed within seasonal ice from Tiksi Bay (BY), Polar Fox Lagoon (LG), and Goltsovoye Lake (LK), to better understand 1) how freezing processes differ between the three water bodies, 2) how freezing affects CH<sub>4</sub> concentration in the ice, and 3) to gain an indication of which processes change CH<sub>4</sub> concentration during the ice cover season.”

p. 3, Line 20-23: “The Bykovsky..”

Corrected.

p. 4, Line 3: please give approximate depths

Added depth range in parentheses.

p. 5, Table 1: The Table implies that PF had a temperature constant to 0.01 °C over its 4 m depth. I found this unlikely. Please justify.

Response: you are correct. We changed this value to 0.8 °C, which is certainly all that the measuring device allows.

p. 5, Lines 10-16: I don't see the point in telling us about data collected that is not analysed in the article.

We removed references to other studies and their sample material.

p. 5, Lines 15: What does “res” mean?

Typographic error: corrected.

p. 6, Sect 3.2: I think information about transport and storage of the cores is missing (e.g. temperature) and seems as important as other details that are provided.

We added “...transport in the frozen state...”

p. 6, Line 11: Define EC first time used.

Adopted.

p. 6, Line 12: “as soon as possible” is not very specific

Adopted.

p. 7, Line 2: “Slope”

Adopted.

p. 7, Line 23: “100 ppm that were”

Adopted.

p. 7, Line 27: “from the same bottle”

Adopted.

p. 8, Line 14: What is the “ice-free transect area” and why was it needed as scale in the photos?

We apologize for that error, and changed the sentence from:

*“A measurement tape at the side of the ice-free transect area served as scale in the images”*

to

*“A measurement tape at the side of the cleared transect area served as scale in the images and to measure the sizes of seeps and bubble types.”*

which refers back to the clearing of snow from the ice transect.

p. 8, Line 22: What are “the cores of the water bodies”?

Changed to: “We compared variability of measured parameters within each ice core as a function of depth below the ice surface, and between sets of cores from each water body.”

p. 8, Line 27: “identified”

Corrected.

p. 8, Line 27: How is regelation ice from snow melt identified?

Added: “...based on the appearance of the ice during sampling.”

p. 8, Sect 4.1: Difficult to follow as the reader needs to keep referring to which core numbers are from which site. A sketch of the ice types would reduce the need for detailed description and give a better overall view of the structure of the ice covers.

We have renamed the cores to be explicit about which site they come from and simplified the language in this section.

p. 9, Figure 2: Why does PF look so small on this figure? On Figure 1 no dimension of PH seems to be less than GL? In addition it would be good to label geographic location on the transects, i.e. N, S, NW etc

We have added compass directions to the bathymetric profiles.

PF (LG) appeared so small, because we showed the ice AND water (i.e. most of PF was occupied by ice), but since the ice was shown in white, it sort of disappeared. We have represented the ice with a light gray tone to make this clearer. We also discovered a mistake in water depth for TB (BY) and have corrected this in the figure.

p. 9, Line 2: remove “on”

Adopted.

p. 10, section 4.2.4 & p. 15, 4.4.1: I suggest replacing “stable” with “constant”. “Stable” implies “firmly fixed” and I am not sure that this is what you wish to imply. If you do mean “stable” then I think you need to justify why you expect no change under any change in circumstances.

Adopted.

p. 10, Line 12: spelling “composition”

Adopted.

p. 12, Fig 3: It is very interesting that PF is colder than GL. Is this because it is shallower?

We have expanded the discussion of ice core temperature to explain the difference, adding: “In addition, temperature increased towards the bottom of the ice (Fig. 3). The bottom ice offers a protected environment with favourable conditions for microbial metabolism: relatively warm temperatures, contact with liquid water and permeable ice. The latter permits migration of gases and nutrients, similar to marine ice, where most bacteria are located in the lowest centimetres of the ice (Krembs and Engel, 2001). At LG, the bottom ice temperature decreases during the winter. This occurs because the temperature of the underlying water remains in equilibrium with a dynamic freezing point that decreases with increasing salinity when LG is cut off from Tiksi Bay. The ice surface temperature at the time of coring was primarily a function of snow cover and air temperature. The ice coring locations for LG exhibited colder ice surface temperatures and steeper gradients compared to ice coring locations at LK. Ice has a high thermal conductivity and is susceptible to quick temperature changes. Since ice temperatures were also observed for windswept areas at LK, decreasing air temperatures from 8 April 2017 (final LK coring day) to 11 April 2017 (LG coring day) could explain the generally colder ice temperature profiles at LG.”

p. 15, Fig 6 caption: “free”. Has the ice free area been marked on Fig 1?

Thank you for finding the error and for the suggestion regarding the overview figure. We also changed “ice-freed” the caption of Fig. 6 to “snow-cleared”. The scale in Fig. 1 is too small to allow proper representation; the position of the bubble transect is marked in Fig. 2, to show the overlap to the ice core sites.

p. 15, Line 13-14: Is this statement tested in the present article, or is this speculation to introduce the Discussion?

We have deleted:

“It may act not only as a barrier, but also as a source or sink for methane or as a habitat for microbes that facilitate methane consumption.”

p. 16, Line 10-11: It was not at all obvious to me how the data presented showed that the type of water body determines the circulation of methane. Please explain.

We have re-structured and re-written parts of the abstract and conclusions, and hope that we more clearly explain how the data show differences in methane pathways from sediment to ice.

p. 16, Line 15: Suggest replacing “impact” with “setting”

Adopted.

p. 16, Line 18: “. . .(2018), while in winter, when the connection..”

Adopted.

p. 16, Line 26: Why would the freezing velocity be approximately constant? It is likely to decrease as  $1/(\text{ice thickness})$ .

The poorly worded point here was that the fractionation primarily reflects the composition of the water beneath the ice, rather than the smaller effect of shifting freezing rate. We have changed the first 2 sentences from:

*"Firstly, in an open system such as TB, the water circulates freely beneath the ice cover, impeding the enrichment of lighter water isotopes in the remaining water. Therefore, the isotope composition of the initial ice should remain more or less constant, and hence also that of the ice with depth (Gibson and Prowse, 1999), assuming the freezing velocity is roughly constant."*

to:

*"Firstly, in an open system such as BY, the water circulates freely beneath the ice cover. The isotope composition of the ice should remain more or less constant over the winter (Gibson, 1999), and reflect the fractionation resulting from freezing of Tiksi Bay water."*

p. 16, Line 24-29: The authors note that they have not taken into account the freeze fractionation influences (e.g. see Toyota et al., 2013), based on the assumption that the freezing velocity is roughly constant. If this is not necessary please provide an order of magnitude calculation to convince the reader that this is a small effect.

Toyota, T., I.J. Smith, A.J. Gough, P.J. Langhorne, G.H. Leonard, R.J. Van Hale, A.R. Mahoney, and T.G. Haskell. (2013) Oxygen-isotope fractionation during the freezing of seawater. Journal of Glaciology. Vol. 59, No. 216, 2013 doi:10.3189/2013JoG12J163

Added text:

*"Oxygen isotope fractionation during the freezing of sea water has been addressed by Toyota et al., (2013), through laboratory experiments and field observations. These authors demonstrate a general dependency of increasing isotope fractionation with decreasing ice growth rate. Therefore, faster freezing induces less isotope fractionation as compared to slowly formed ice at a later stage of sea ice formation. The difference between both is within 1‰ for a large range of ice growth rates."*

p. 17, Fig 7: Very nice helpful sketches. They might be useful earlier in the manuscript.

*We consider these sketches to be part of the outcome of the study, which require the explanations given in the discussion. They are based on the results, and were not a priori knowledge of the site or the processes that we would discover.*

p. 18, Line 2: "alone"

Deleted.

p. 18, Line 5: "may capture"

Adopted.

p. 18, Line 5-7: Interesting observation that may be compared with the results of Smith et al., (2016). Smith, I.J., Eicken, H., Mahoney, A.R., Van Hale, R., Gough, A.J., Fukamachi, Y., Jones, J. (2016). Surface water mass composition changes captured by cores of Arctic land-fast sea ice. Continental Shelf Research, 118:154-164, doi:10.1016/j.csr.2016.02.008.

Added the text:

*"Episodic advection of meteoric water during the winter season was also detected in land-fast sea ice cores from Barrow, Alaska (Smith et al., 2016)."*

p. 18, Line 7: "indicative for the preceding freezing process (Souchez and Jouzel, 1984)." I'm not sure what this means? Does this mean that freeze fractionation should be taken into account?

Changed to: *"This is reflected in the regression lines of the  $d_{18}O-d_D$  plot for BY, which differ in slope for the two sections (Fig. 8) and indicate a shift in fractionation (Souchez and Jouzel, 1984)."*

p. 18, Line 9: "Tab ??". This is not at all obvious from Fig 8.

Corrected. We have added a table of regression line statistics to show the basis for distinguishing groups of lines.

p. 18, Line 18: "but with the carbon isotope signature". I could not see much change in the carbon isotope?

- Here the word “same” was missing and has been added.
- p. 18, Line 29: “(Lacelle, 2011)”  
Adopted.
- p. 18, Line 29: Again, this is not at all obvious from Fig 8.  
We have added a table of regression line statistics to show the basis for distinguishing groups of lines.
- p. 20, Line 29: “was”  
Adopted.
- p. 21, Fig 8: The changes in slope appear to be important but cannot be seen on the plots as currently displayed. Please consider how to display this information to match the Discussion. Why is global rather than local meteoric line used?  
To make the data less ambiguous, we have added a table with regression line coefficients (Table 3).
- p. 22, Fig 9: Is it not possible to write down the equation of the model displayed?  
The equation is in the methods section (Eq. 1). We have added a cross-reference to it in the figure caption. All parameters used for the Rayleigh model are given in the figure caption, i.e. the reader is provided with all information used to generate the plot.
- p. 22, Conclusions: Please return to the aims of the study here, and show how they have been moved forward.  
We have considerably changed the conclusions, please see track changes version.
- p. 23, Line 8: It is not obvious to me how the data provided has shown that the ice examined “acts primarily as a barrier to methane fluxes to the atmosphere, a barrier that is effective for most of the year but also will be effected by rapid changes due to Arctic warming and associated ice thinning.” Please make this clearer in the Discussion and/or Conclusion.  
We have deleted this sentence.
- p. 23, Line 8: What does “providing a habitat for methane oxidation” mean? Again this needs to have been explained earlier in the paper.  
Changed to “...providing a habitat for methane oxidizing microorganisms.” This is also described in an expanded form in the discussion on Page 19, lines 13-16:  
“In addition, temperature increased towards the bottom of the ice (Fig. 4). The bottom ice offers a protected environment with favourable conditions for microbial metabolism: relatively warm temperatures, contact with liquid water and permeable ice. The latter permits migration of gases and nutrients, similar to marine ice, where most bacteria are located in the lowest 15 centimetres of the ice (Krembs and Engel, 2001). At LG, the bottom ice temperature decreases during the winter. This occurs because the temperature of the underlying water remains in equilibrium with a dynamic freezing point that decreases with increasing salinity when LG is cut off from Tiksi Bay.”  
and lines 25-26:  
“During freezing of the ice cover, its growth rate decreases (cf. Anderson, 1961), providing more time and space for bacterial metabolism. CH<sub>4</sub> uptake from the water into the bottom of the ice and its oxidation there may have continued over the winter until the ice break-up. CH<sub>4</sub> oxidation ceases when concentrations are too low for oxidation to be efficient (Cowen et al., 2002; Valentine et al., 2001), at values ranging from 0.6 nM to 10 nM. CH<sub>4</sub> concentrations in the ice above 130 cm (Fig. 6) were less than 10 nM, suggesting that ice is an effective sink for CH<sub>4</sub> in this type of water body during winter.”

## REVIEWER 2

The Cryosphere Discuss.,

<https://doi.org/10.5194/tc-2019-304-RC2>, 2020 © Author(s) 2020. This work is distributed under the Creative Commons Attribution 4.0 License.

Interactive comment on “Methane Pathways in Winter Ice of Thermokarst Lakes, Lagoons and Coastal Waters in North Siberia” by Ines Spangenberg et al.

Blaize Denfeld (Referee)

[bdenfeld@gmail.com](mailto:bdenfeld@gmail.com)

Received and published: 13 July 2020

This study attempts to improve our understanding of CH<sub>4</sub> pathways in ice covered water bodies by focusing on ice and inland water continuum from lake to coast, both seldom included in the limited winter CH<sub>4</sub> inland water studies. In doing so, the study highlights varying CH<sub>4</sub> concentrations explained by the geomorphological differences between the aquatic systems. This is an interesting study with a unique data set and with revisions could be a nice addition to the scientific community.

### General Comments:

1) The studies focus is on Arctic waterbodies underlain by permafrost. However, the introduction covers a broader range, i.e. when referring to Arctic and Northern lakes not all are in continuous permafrost zones. I think this broad perspective of northern lakes is appropriate but think the introduction could be better structured to go from a broad approach (Northern ice-covered lakes) to lakes in a continuous permafrost landscape. In particular Paragraph 2 of the introduction would benefit from this restructuring.

We have substantially re-written the introduction, slimming it down, and removing the tacit differentiation between ebullition and diffusive fluxes of methane.

2) Additional details needed to be clarified in the methods, particularly on CH<sub>4</sub> lab sampling. See specific comments below.

Answered below.

3) The discussion is sorted into the three different water bodies, which works but it would be helpful to also have an overview of how the values calculated for these water bodies compare with values in the same system (lakes/coastal permafrost areas). Perhaps reporting a range for all 11 ice cores and discussing how it compares to other ice-covered inland water values. This could be done in the initial discussion paragraph before diving into the specifics of the three water body types.

We compare ranges in the results table but have not added comparisons to other values.

These are simply not available for all three water body types covered in this paper, nor are their seasonal variabilities characterized. This is part of what makes our paper unique.

4) In the conclusion, in addition to returning to the aims of the study it would be nice to know how these findings fit into understanding the lake-lagoon-coast transition in the arctic region. Although I appreciate that caution should be taken in making large upscaling statements given the limited sample size and snapshot in time.

We are trying to strike a balance between restricting ourselves to the conclusions permitted by our results, and explicit statements of what we feel are the implications of these findings.

5) Much of cited literature focuses on findings from lakes. Are there any studies that have looked at CH<sub>4</sub> concentrations below ice in coastal areas? If so, it would strength the paper to include them in the introduction and discussion (see general point 3).

We agree, but are not aware of any additional studies from coastal ice.

### Specific Comments:

Title: Since the study only investigates one lake, lagoon and bay perhaps the title would better represent the actually study as, “Methane Pathways in Winter Ice of Thermokarst Lake-Lagoon-Coastal Water Transect in North Siberia”

Yes, corrected.

P1, L 7-9: Could use a tie in sentence and possible move this information after L 5-6 as it is continuing to point out differences between the system, e.g. "In addition the three water bodies had different freezing systems. In TB. . ."

We have moved the sentence.

P1, L 12: is "above the ice-water interface" referring to in the ice? If so please clarify.

Clarified by including "in the ice".

P 2, L 7-9: This sentence should be rewritten. Is the idea that CH<sub>4</sub> can continue to accumulate in lakes over the ice-covered period whereas in soils the active layer freezes during winter and CH<sub>4</sub> is not produced? A reference showing that CH<sub>4</sub> production in the active layer of permafrost is mainly during summer would help support this statement. CH<sub>4</sub> has been found to accumulate in shallow lakes over winter, so the authors may need to think about the definition of "certain circumstances".

As part of revision of the introduction, these sentences have been removed. We do not seek to compare aquatic and soil environments.

P2, L 23-25: I assume these two sentences are referring to lake sediments? Please clarify.

This sentence has also been deleted.

P2, L 25: a third pathway, plant mediation, should be included.

This sentence has also been deleted.

P3, L 1-4: Are these the only two studies looking at CO<sub>2</sub> and CH<sub>4</sub> in ice? Perhaps these sentences could be simplified as one, "Of the limited studies, accumulation of CH<sub>4</sub> in and under the ice during winter were realized for shallow ice-covered lakes in Alaska (Phelps et al. 1998) and four lakes in discontinuous permafrost area (Boereboom et al. 2012)." Or something like that.

Adopted.

Pg 3, L6, "However, methane oxidation. . ."

Adopted.

P3, L10: change to, "methane has been found to oxidize at temperatures as low as "C."

Adopted.

## Material and Methods:

P5, L 15: typo "res"

Corrected.

P6, L 1-9: How were the ice samples stored, in -15C? Could there have been CH<sub>4</sub> oxidation? How effective was the vacuum pump at removing O<sub>2</sub>?

We describe that the ice cores were stored in sealed plastic tubes and in thermally insulated boxes for transport. We have added: "..., which effectively sealed the inner bag surface to the ice." We did look at our data critically and consider potential or plausible roles played by oxidation after sampling. The observed methane concentrations and isotope concentrations are not consistent with oxidation during transport.

Pg 6, L 22-25: How many samples were considered high salinity and low salinity?

Now specified in text (7 were "high").

Pg 7, L 14: Remove Global Meteoric Water Line, already abbreviated above.

Adopted.

Pg 7, L 19-20: More details needed here. When the N<sub>2</sub> was added did it create an overpressure in the vial or was 5 mL of water removed? How was the water sample equilibrated with the N<sub>2</sub>, shaken?

Was the equilibrated air then removed from the vial and injected into the GC?

Added: "For methane concentration, 5 ml N<sub>2</sub> was added and 5 ml of water simultaneously removed from the vials. Afterwards, the water sample was equilibrated with the N<sub>2</sub> by being shaken for 1 hour at room temperature. Then, 1.5 ml of the equilibrated air was removed from the vial and injected into a gas chromatograph (GC; Agilent 8900) with a flame ionization detector (FID)."

Pg 8, 10-19: Was the bubble transect done before or after the ice coring, i.e. were the ice core samples taken from the targeted plot area or were they randomly selected?



The bubble transect and coring happened during the same time period but were independent of each other, i.e. cores were not taken from the bubble transect.

P 18, L 9: typo, "(Tab. ??)"

Corrected.

P 18, L 10: typo, "admixture"

Corrected.

P 19, L 12-16: Could it also be because less is being produced?

This would not explain the shift in isotope composition.

P 20, L 29: typo, "lwas"

Corrected.

Table 1: In the legend add "Water" at the start of the second sentence. For the electrical conductivity column could you report Salinity [PSU] /EC [mS/cm] since salinity is known for all three water bodies. Or have two sperate columns for salinity and EC.

We have created two columns with a conversion to salinity.

Table 2: For PF replace Lake with Lagoon in the Sampling Site header.

Corrected.

Figure 4: GL has different scales for the first two rows

This is necessary, since the values for one core (LK-5) are so extreme and using the same scale would mask any variation at the other 2 sites. We have added to caption: "Note that the isotope concentration scales for Goltsovoye Lake (LK, at right) differ from the other 2 sites to accommodate the values observed in core LK-5."

Technical Comments:

1) There are many places where Methane is written out, since it is abbreviated to CH<sub>4</sub> on P1 L19 it should be changed to CH<sub>4</sub> thereafter.

Corrected, also in figure captions.

2) Keywords: remove . . . at end of list

Corrected.

Interactive comment on The Cryosphere Discuss., <https://doi.org/10.5194/tc-2019-304>, 2020.

# Compare Results

Old File:

**tc-2019-304-manuscript.pdf**

**28 pages (16.65 MB)**

2020-02-19 3:03:33 PM

versus

New File:

**tc-2019-304-manuscript\_revised\_20200907.pdf**

**30 pages (24.14 MB)**

2020-09-07 8:39:30 PM

## Total Changes

**525**

Text only comparison

## Content

**307** Replacements

**112** Insertions

**106** Deletions

## Styling and Annotations

**0** Styling

**0** Annotations

[Go to First Change \(page 1\)](#)

# Methane Pathways in Winter Ice of a Thermokarst Lake-Lagoon-Coastal Water Transect in North Siberia

Ines Spangenberg<sup>2,1</sup>, Pier Paul Overduin<sup>2</sup>, Ellen Damm<sup>2</sup>, Ingeborg Bussmann<sup>3</sup>, Hanno Meyer<sup>2</sup>, Susanne Liebner<sup>4,1</sup>, Michael Angelopoulos<sup>1,2</sup>, Boris K. Biskaborn<sup>2</sup>, Mikhail N. Grigoriev<sup>5</sup>, and Guido Grosse<sup>2,1</sup>

<sup>1</sup>Institute of Geosciences, University of Potsdam, Potsdam, Germany

<sup>2</sup>Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Potsdam, Germany

<sup>3</sup>Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Helgoland, Germany

<sup>4</sup>Section of Geomicrobiology, Helmholtz Centre Potsdam - GFZ German Research Centre for Geosciences, Potsdam, Germany

<sup>5</sup>Mel'nikov Permafrost Institute, Siberian Branch, Russian Academy of Sciences, Yakutsk, Russia

**Correspondence:** Paul Overduin (paul.overduin@awi.de)

**Abstract.** The thermokarst lakes of permafrost regions play a major role in the global carbon cycle. These lakes are sources of methane to the atmosphere although the methane flux is restricted by an ice cover for most of the year. How methane concentrations and fluxes in these waters are affected by the presence of an ice cover is poorly understood. To relate water body morphology, ice formation, and methane, we studied the ice of three different water bodies in locations typical of the transition of permafrost from land to ocean in a continuous permafrost coastal region in Siberia. In total, 11 ice cores were analyzed as records of the freezing process and methane composition during the winter season. The three water bodies differed in terms of connectivity to the sea, which affected fall freezing. The first was a bay underlain by submarine permafrost (Tiksi Bay, BY), the second a shallow thermokarst lagoon cut off from the sea in winter (Polar Fox Lagoon, LG) and the third a land-locked, freshwater thermokarst lake (Goltsovoye Lake, LK). Ice on all water bodies was mostly methane-supersaturated with respect to atmospheric equilibrium concentration, except for three cores from the isolated lake. In the isolated thermokarst lake, ebullition from actively thawing basin slopes resulted in the localized integration of methane into winter ice. Stable  $\delta^{13}\text{C}_{\text{CH}_4}$  isotope signatures indicated that methane in the lagoon ice was oxidized to concentrations close to or below the calculated atmospheric equilibrium concentration. Increasing salinity during winter freezing may lead to a micro-environment and methane oxidation in the lagoon ice, functioned as a methane sink. In contrast, the ice of the coastal marine environment was slightly supersaturated with methane, consistent with the brackish water below. Our interdisciplinary process study shows how water body morphology affects ice formation which mitigates methane fluxes to the atmosphere.

**Keywords:** permafrost, lake ice, methane oxidation, carbon fluxes, stable isotopes

## 1 Introduction

As a large reservoir of organic carbon, permafrost holds a potential positive feedback to climate warming (Strauss et al., 2013; Hugelius et al., 2014; Schuur et al., 2015). Amplified warming of the atmosphere in the Arctic is increasing ground temperatures and thawing permafrost (Biskaborn et al., 2019). As a consequence organic carbon stored in permafrost becomes available for microbial decomposition, leading to the release of greenhouse gases (Koven et al., 2011; Knoblauch et al., 2018). Therefore, these regions play an important role in the global carbon cycle and contribute to global warming (Schuur et al., 2015; Turetsky et al., 2019; Walter Anthony et al., 2018).

Arctic aquatic systems in permafrost regions are sources of atmospheric methane. CH<sub>4</sub> is produced mainly in carbon-bearing sediments under anoxic conditions (e.g. Conrad, 2009) and transported from sediment layers into the water column by diffusion and ebullition (Bastviken et al., 2008). Generally, the amount of CH<sub>4</sub> emitted from Arctic water bodies to the atmosphere is uncertain but is expected to increase as a result of Arctic warming (Bastviken et al., 2004; Boereboom et al., 2012; Cole et al., 2007; Walter et al., 2006). Northern high latitude lakes, i.e. thermokarst lakes, are suggested to act as CH<sub>4</sub> sources throughout the entire annual cycle (Wik et al., 2016) and may have particularly high CH<sub>4</sub> emissions if organic-rich permafrost deposits underneath are actively thawing and microbial decomposition results in CH<sub>4</sub> production (Walter et al., 2007). Recent studies have illustrated the importance of the winter period for annual CH<sub>4</sub> and CO<sub>2</sub> emission budgets of northern lakes (Denfeld et al., 2018; Powers and Hampton, 2016; Zimov et al., 2006); however, processes controlling CH<sub>4</sub> and CO<sub>2</sub> dynamics in the frozen period are still poorly understood. While gas may easily escape to the atmosphere in summer, an ice cover forms a barrier for 9 to 10 months in winter and traps bubbles under and eventually within the ice (Walter et al., 2008). Production of CH<sub>4</sub> is temperature-dependent (Kelly and Chynoweth, 1981; Zeikus and Winfrey, 1976), but CH<sub>4</sub> ebullition and accumulation under the ice suggest that CH<sub>4</sub> production continues during winter (Walter Anthony et al., 2010). Waters that are deep enough do not freeze to the bottom in winter and are therefore underlain with unfrozen sediment (talik) (Arp et al., 2016) in which microbes may produce methane in winter. Since seasonally ice-covered lakes dominate permafrost landscapes, they are expected to play a major role in changing the global carbon cycle (Grosse et al., 2013; Wik et al., 2016; Bartsch et al., 2017).

Previous work has focused mostly on the occurrence and spatial variability of CH<sub>4</sub> bubbles within lake ice (Walter et al., 2006; Wik et al., 2011; Sasaki et al., 2009; Walter Anthony et al., 2010) and CH<sub>4</sub> accumulation underneath lake ice (Boereboom et al., 2012; Langer et al., 2015). Of the few studies, CH<sub>4</sub> distribution in ice cores and under ice were analysed in shallow ice-covered tundra lakes in Alaska (Phelps et al., 1998) and in the ice covering four lakes in a discontinuous permafrost area (Boereboom et al., 2012). In both studies the accumulation of CH<sub>4</sub> in and under the ice during winter is observed. Their findings are corroborated by other studies, which also show a high CH<sub>4</sub> emission rate during ice melt in spring of high latitude lakes (Karlsson et al., 2013; Michmerhuizen et al., 1996). CH<sub>4</sub> may be oxidized at the ice-water interface (Canelhas et al., 2016; Rudd and Hamilton, 1978), but the conditions required are poorly understood (Canelhas et al., 2016; Winkel et al., 2019). While Phelps et al. (1998) suggest that methanotrophic activity is generally inhibited in cold waters, CH<sub>4</sub> has been found to oxidize at temperatures as low as 2°C (Canelhas et al., 2016).

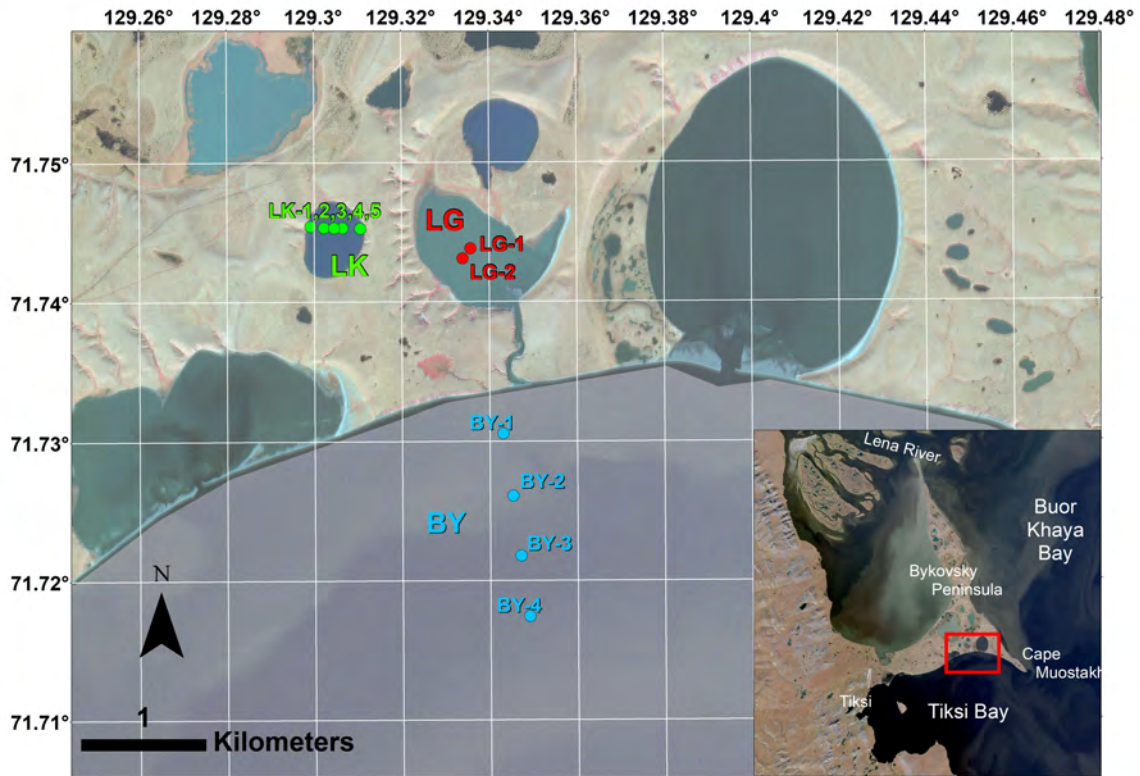
Few studies compare ice from different types of Arctic water bodies, crossing freshwater to saline gradients. CH<sub>4</sub> oxidation observed in Arctic shelf waters (Damm et al., 2005; Mau et al., 2013; Bussmann et al., 2017), and sediments (Overduin et al., 2015; Winkel et al., 2018), as well as in lake water (Bastviken et al., 2002; Lidstrom and Somers, 1984), and at the water-ice interface (Martinez-Cruz et al., 2015; Canelhas et al., 2016) may limit the emissions of CH<sub>4</sub> during spring ice melt (Canelhas et al., 2016). The transition from lakes to lagoons and further to bay waters via sea level rise and permafrost coastal erosion (e.g. Romanovskii et al., 2000) may substantially change the CH<sub>4</sub> budget of aquatic systems in permafrost regions, since CH<sub>4</sub> fluxes in lake systems are coupled to the lake's limnological and geomorphological characteristics (Bastviken et al., 2008, 2004; Boereboom et al., 2012; Denfeld et al., 2018).

To improve our understanding of how water bodies function as CH<sub>4</sub> sources or sinks, this study aims to clarify the role of the winter ice cover for CH<sub>4</sub> in three different stages in the lake-lagoon-shelf transition in a region of thawing permafrost in northeast Siberia. Our objective is to demonstrate how CH<sub>4</sub> is distributed within seasonal ice from Tiksi Bay (BY), Polar Fox Lagoon (LG), and Goltsovoye Lake (LK), to better understand 1) how freezing processes differ between the three water bodies, 2) how freezing affects CH<sub>4</sub> concentration in the ice, and 3) to gain an indication of which processes change CH<sub>4</sub> concentration during the ice cover season.

## 2 Study Area

This study was conducted on the southern coast of the Bykovsky Peninsula at 71° 40' - 71° 80' N and 129° 00' - 129° 30' E, in northeastern Siberia. The Bykovsky Peninsula is located northeast of the harbor town of Tiksi and approximately 20 km southeast of the Lena River Delta, central Laptev Sea (Grosse et al., 2007). This area offers a rich variety of water body types in the continuous permafrost zone, with ice-rich Yedoma permafrost, a widespread, organic-rich and syngenetic fine-grained deposit that accumulated during the glacial age in the unglaciated regions of Siberia and Central Alaska (Zimov et al., 2006; Schirrmeister et al., 2011). Most thermokarst lakes in the region originated in the early Holocene, when surficial permafrost thawed. Their sediments typically have total organic carbon (TOC) contents of about 5-30 % by weight (Biskaborn et al., 2012, 2013a, b, 2016; Schleusner et al., 2015). The southern coastline erodes at mean rates of between 0.25 and 0.60 m per year and can intersect these water bodies, draining them or leading to the formation of thermokarst lagoons (Lantuit et al., 2011; Schirrmeister et al., 2018). For our study, we selected three water bodies at the southern coast of Bykovsky Peninsula: Tiksi Bay (BY), Polar Fox Lagoon (LG) and Goltsovoye Lake (LK) (Fig. 1, Tab. 1).

BY is a relatively shallow bay (less than 11 m in general, and less than 5 m below our ice core transect) underlain by submarine permafrost (Overduin et al., 2016), at least close to the coast. The bay is located southeast of the Bykovskaya Channel, which is the major outlet of the Lena River through which about 25 % of the Lena's spring discharge exits the delta (Fedorova et al., 2015). The mixing of freshwater from the Lena River with saline water from the Laptev Sea results in brackish conditions in the bay (Lantuit et al., 2011). BY belongs to the Buor Khaya Bay region, where the water column is usually stratified, with a colder, more saline water layer underlying the brackish surface layer (Overduin et al., 2016). The depth of the pycnocline varies between 4 and 10 m and the stratification can be disturbed by storm events. Storm surges also



**Figure 1.** Study design on the Bykovsky Peninsula, NE Yakutia, Arctic Russia. Ice cores were recovered from three water bodies on the southern shore of Bykovsky Peninsula: Tiksi Bay (BY: blue), Polar Fox Lagoon (LG: red), and Goltsovoye Lake (LK: green dots). Imagery in the main map is Worldview-3 from Sep. 2, 2016 ((c) DigitalGlobe).

influence sea level at BY, with maximum wave heights of about 1.1 m. Tidally-based sea-level oscillations have little influence on the height of storm surges and the Bykovsky Peninsula region is characterized by a micro-tidal regime (Lantuit et al., 2011). LG is connected to BY by a shallow channel (Fig. 1) and therefore dominated by brackish water. LG represents a transitional stage between a land-bound thermokarst lake and a bay: a thermokarst lagoon. Its morphology suggests that it has been formed in a thermokarst depression. The lower extent of ice-rich sediments and the thermokarst lake beds can lie below sea level (Günther et al., 2015). LK is a slightly oval-shaped thermokarst lake about 0.5 km in diameter, surrounded by Yedoma uplands at various stages of degradation. Tab. 1 lists characteristics of the studied water bodies.

**Table 1.** Hydrological characteristics of water bodies of the southern Bykovsky Peninsula from which ice cores were taken for this study in spring 2017 (Strauss et al., 2018). Water temperatures and electrical conductivity for LG and LK were measured in the field below the ice; temperature and salinity for BY are from Charkin et al. (2017).

Water Body	Diameter [km]	Max. Depth [m]	Water temperature [°C]	Electrical Cond. [mS/cm]	Salinity [PSU]	Number of Ice Cores	Mean Ice Thickness [cm]
Tiksi Bay (BY)	10 – 26	11	–1 to 0		8.5–12.5	4	144
Polar Fox Lagoon (LG)	0.61 – 1.1	3.4	–0.8	11	approx. 12.5	2	166
Goltsovoye Lake (LK)	0.46 – 0.62	11.5	0 to 1.8	0.3	approx. 0.1	5	160

### 3 Methods

#### 3.1 Sampling in the field

Ice cores were collected from BY in a transect roughly perpendicular to the shore (Fig. 1). For LG, two cores were drilled near the center of the lagoon. The sites of the five cores from LK were located along an approximately west-east transect across the lake. Tab. 1 lists the mean ice thicknesses of the sampled ice core for the locations.

The ice cores were taken with a Kovacs Mark II ice coring system (9 cm diameter), between Apr. 5 and 12, 2017. Cores were collected in triplicate from each sampling site. One core was only used for temperature measurements. Immediately after sampling, temperature was measured by drilling small holes every 10 cm, at the boundaries between sample sections, and inserting a digital thermometer. Average temperature values were calculated for each section from the top and bottom depths. The other cores were wrapped in sealed plastic tubes and packed in thermally insulated boxes for the transport in the frozen state to Germany. Water column temperature and electrical conductivity were measured with a CTD (SonTek CastAway) at each coring site. Further details on field work and sampling can be found in the expedition report (Strauss et al., 2018).

#### 3.2 Sample processing

The ice cores were cut with a band saw in a cold room in Potsdam at –15 °C. Cores were cut at 10 cm intervals and samples were stored for melting in gas-tight TEDLAR bags at 4 to 7 °C (over 1-2 days). The closed bags were evacuated with a vacuum pump prior to melting, which effectively sealed the inner bag surface to the ice. After melting, the water was gently mixed and poured through tubing, without producing bubbles, into 100 mL glass bottles for the analysis of CH<sub>4</sub> concentrations and  $\delta^{13}\text{C}$  in CH<sub>4</sub>. The remaining water was distributed into other sample bottles for hydrochemical measurements of pH, electrical conductivity (EC), dissolved organic carbon (DOC),  $\delta^{18}\text{O}$  and  $\delta\text{D}$  isotopes of water, as well as major anion and cation concentrations. Data points in the graphs of variation against core depth thus represent a mean value for a section of usually 10 cm within an ice core.

### 3.3 Hydrochemistry in ice

EC and temperature of LK and LG were measured in the field. EC and pH of ice core samples were measured with a WTW Multilab 540 device directly after bottling. The salinity was calculated from the values of the EC referenced to 25 °C after McDougall and Barker (2011). The samples for DOC were filtered with 0.7 µm pore size glass fiber filters (the filters were first rinsed with 20 mL of the sample), filled in 20 mL glass-headspace vials and closed with aluminum crimp caps. For preservation, 50 µL of 30 % supra-pure HCl were added to the sample before closing the vials, which were stored at 4 °C until measurement. DOC was measured with a Shimadzu Total Organic Carbon Analyzer (TOC-VCPH). An average of three to five injections per sample was used as the measured value. The detection limit for the DOC measurement is 0.25 mg L<sup>-1</sup> and the uncertainty of the measurement was ±10 % for values higher than 1.5 mg L<sup>-1</sup>, and for values lower than 1.5 mg L<sup>-1</sup> the uncertainty was ±15-20 %.

### 3.4 Stable water isotopes

To measure stable water isotopes ( $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ), 10 mL of the untreated water sample was filled in 10 mL PE narrow-neck bottles. Seven samples with salinity higher 3 mS cm<sup>-1</sup> were measured with an Isotope Ratio Mass Spectrometer (IRMS: Finnigan Delta-S), using equilibration techniques (Meyer et al., 2000). All other samples had lower salinity and were measured with an Ultra High-Precision Isotopic Water Analyzer (PICARRO L2130-i, coupled with an autosampler and vaporizer using Cavity Ringdown Spectroscopy). The internal precision of the H and O isotope measurements is better than ±0.8 ‰ and ±0.10 ‰, respectively. The oxygen and hydrogen isotopic compositions are given relative to Standard Mean Ocean Water (VSMOW) using the conventional  $\delta$ -notation.

Stable water isotopes have been widely used in palaeoclimate and palaeohydrological research as isotope fractionation is temperature-dependent. The mean annual  $\delta^{18}\text{O}$  of precipitation is positively correlated with the mean annual air temperature, and hence snow typically has a strong isotope variability as well as relatively low (or light) values, particularly at high latitudes (Dansgaard, 1964). Stable water isotopes can be also used to trace water phase changes, i.e. during freezing as these are accompanied by kinetic isotope fractionation processes (Souchez and Jouzel, 1984; Lacelle, 2011). An  $\delta^{18}\text{O}$ - $\delta\text{D}$  plot gives valuable information about the freezing characteristics, as the regression line (freezing line) is usually lower than that of the Global Meteoric Water Line (GMWL, slope = 8). Slope values in the range of 6 to 7.3 can be interpreted as freezing under equilibrium conditions (Lacelle, 2011). The extent of fractionation in the system water-ice critically depends on the velocity and rate of freezing (Gibson and Prowse, 1999; Tranter, 2011) which in turn is directly connected to the thermal conditions and the water availability of a given system. Isotopic fractionation during freezing is accompanied by heavier isotope composition for the first ice and lighter isotope composition for the last ice formed (Gibson and Prowse, 1999, 2002). In this study, we differentiate between open and closed system freezing. In an open system, the water source under the ice and hence the isotope composition of the ice formed both remain largely constant, differing from closed-system freezing where the isotopic composition of the water pool changes prior to freezing. Furthermore, the water isotopic signature may be indicative for the mixing of different water masses (endmembers) i.e. precipitation with surface water. The isotopic signature is then indicative



for the relative contribution of each endmember and preceding natural isotopic fractionation processes, which changes if the endmembers' specific isotope composition differs. The  $\delta^{18}\text{O}$ - $\delta\text{D}$  values in ice may also be directly influenced by precipitation, if liquid or solid precipitation falls on the ice layer and freezes to a part of the ice. In a co-isotope plot,  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of precipitation generally have values that lie on or near to the GMWL (Craig, 1961).

### 5 3.5 Dissolved $\text{CH}_4$ concentration

Meltwater from the TEDLAR bags was filled until overflowing into 100 mL glass bottles, sealed with butyl stoppers and crimped with aluminum plugs. The samples were kept cold ( $4^\circ\text{C}$ ) and dark until the measurements in the lab (max. 2 months between sampling and measurement). For  $\text{CH}_4$  concentration, 5 mL of  $\text{N}_2$  was added into the vials, whereby 5 mL of water was removed from the vials. Afterwards, the water sample equilibrated with the  $\text{N}_2$  by shaken for 1 hour at room temperature.

10 Then, 1.5 mL of the equilibrated air was removed from the vial and injected into a gas chromatograph (GC; Agilent 8900) with a flame ionization detector (FID). For gas chromatographic separation, a packed column (Porapac Q 80/100 mesh) was used. The GC was operated isothermally ( $60^\circ\text{C}$ ) and the FID was held at  $250^\circ\text{C}$ . Standards of different gas mixtures between 1.665 and 100 ppm that were used for calibration, yielded standard deviations of  $<0.3$  ppm. The GC precision had an error of 1 %. 46 % ( $n = 74$ ) of the samples had  $\text{CH}_4$  concentrations below the lowest standard of 1.665 ppm (ranging from 0.7 ppm to 1.6

15 ppm), while 11 % ( $n = 18$ ) had concentrations exceeding the highest standard (ranging from 105 ppm to 2723 ppm).

### 3.6 Carbon isotopes of $\text{CH}_4$

The carbon isotopic composition of  $\text{CH}_4$  ( $\delta^{13}\text{C}_{\text{CH}_4}$ ) was measured on the same day and from the same bottle as the  $\text{CH}_4$  concentrations, to assure comparability of the data. After measuring the  $\text{CH}_4$  concentration, 20 mL of  $\text{N}_2$  were added to the sample bottle to increase the headspace of the bottle for stable carbon isotope measurements. The bottle was shaken for at least

20 30 minutes. 20 mL of gas were removed with a glass syringe by adding 20 mL of Milli-Q water at the same time to equilibrate pressure.  $\delta^{13}\text{C}_{\text{CH}_4}$  was determined using a Delta XP plus Finnigan mass spectrometer. The extracted gas was purged and trapped with PreCon equipment (Finnigan) to pre-concentrate the sample. The carbon isotopic ratios are given relative to the Vienna Pee Dee Belemnite (VPDB) standard using the conventional  $\delta$ -notation. The analytical error of the analyses is  $\pm 1.5$  ‰ for  $\delta^{13}\text{C}_{\text{CH}_4}$  values.  $\text{CH}_4$  concentration in nanomolar (nM) was calculated with the Bunsen solubility coefficient of Wiesenburg

25 and Guinasso Jr (1979).

For all water bodies, a Rayleigh distillation model of the type discussed by Coleman et al. (1981) and used by Damm et al. (2005, 2015) was calculated:

$$\delta^{13}\text{C}_{\text{CH}_4} = 1000 \left( \frac{1}{\alpha} - 1 \right) \ln f + (\delta^{13}\text{C}_{\text{CH}_4})_0 \quad (1)$$

where  $\alpha$  is the isotope fractionation factor,  $f$  is the fraction of the  $\text{CH}_4$  remaining and  $(\delta^{13}\text{C}_{\text{CH}_4})_0$  is the initial isotopic

30 composition. For the Rayleigh model, bacterial oxidation was assumed to be the only  $\text{CH}_4$  sink, with no further inputs or mixing that would affect the isotopic composition of  $\text{CH}_4$  (Mook, 1994).

### 3.7 Bubble transect

To gain insight into the type and spatial distribution of  $\text{CH}_4$  bubbles trapped in the ice of LK, a  $\text{CH}_4$  bubble transect was mapped. Snow was cleared from a lake ice transect of 70 m length and 1.4 m width, starting 30 m from the northwest shoreline aiming towards the lake centre (Fig. 3). A GoPro Hero 7 camera was used to take densely overlapping photos of the transect from approx. 1.7 m vertical height along the entire transect to photographically record the  $\text{CH}_4$  bubble patches captured in the lake ice that are associated with seep types. A measurement tape at the side of the cleared transect area served as scale in the images and to measure the sizes of seeps and bubble types. The photos were rectified and mosaicked in the image rectification software AGISoft Professional and the georeferenced mosaic was imported to a desktop geographical information system (ArcGIS, version 10.4).  $\text{CH}_4$  seep types were classified and mapped following Walter Anthony and Anthony (2013). The distance to the shoreline of seep classes was calculated in ArcGIS using the “near” function. The Kernel density estimation in 14 distance classes was calculated in the R environment.

## 4 Results

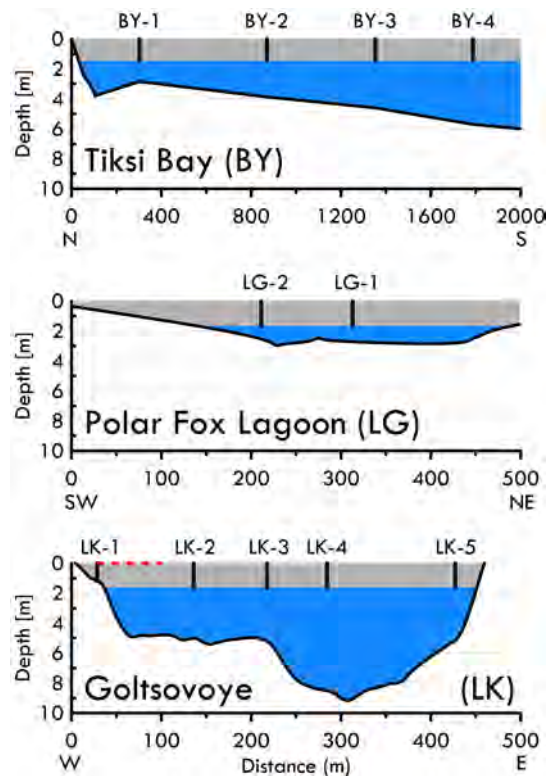
### 4.1 Ice morphology

We compared variability of measured parameters within each ice core as a function of depth below the ice surface, and between sets of cores from each water body. For a simple comparison between ice cores and the three water bodies, mean values and the range (min., max. values) were calculated for every location (Tab. 2). The length of the ice cores ranged from 110 to 197 cm, corresponding to total ice thicknesses. Mean lengths were 144 cm in BY, 166 cm in LG, and 160 cm in LK. The ice of all cores from BY was nontransparent, with a high concentration of enclosed gas bubbles. The uppermost 3 cm (BY-4) to 10 cm (BY-2) was identified as regelation ice from snow melt based on the appearance of the ice during sampling.

The snow thickness ranged from 11 cm (BY-4) to 32 cm (BY-2). For LG, the ice of the two cores was clear and contained inclusions of elongated gas bubbles. The uppermost 3 cm of core LG-1 appeared milky-white. The difference in snow thickness above the two cores was quite large with 8 cm (LG-2) and 20 cm (LG-1). For LK, the ice morphology was heterogeneous. LK-2 appeared transparent-white, while LK-1 included small, elongated air bubbles and the uppermost 5 cm was regelation ice from snow melt. The ice of core LK-4 appeared whiter below a depth of 111 cm, while LK-5 was milky-white from the surface until the depth of about 112 to 114 cm. The snow cover was generally solid and characterized by different melt forms. The thickness of the snow-layer ranged from 0 cm in snow-free cores LK-2 and LK-3 to max. 92 cm in LK-5. For all cores, no algae inclusions were visible (Strauss et al., 2018).

### 4.2 Spatial bubble distribution

In the total snow-cleared transect area of  $89.2 \text{ m}^2$  we found 29 seeps of class A and five seeps of class B (Fig.3), but none of larger classes C or hot spots (Walter Anthony and Anthony, 2013). The average density of class A seeps in the observed area was  $0.33 \text{ seeps/m}^2$ . Seep density of class B was more than 6 times lower ( $0.05 \text{ seeps/m}^2$ ) and the total seep density



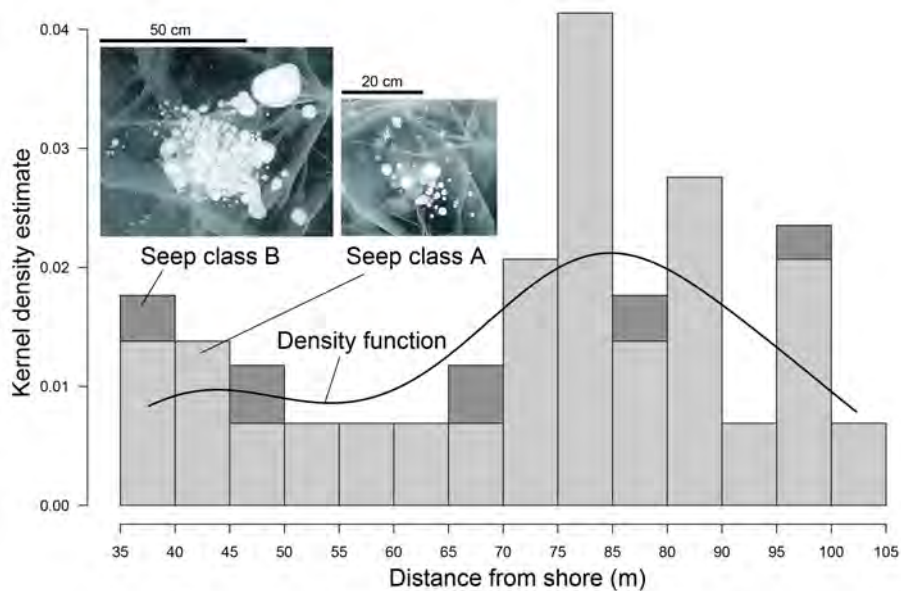
**Figure 2.** Cross-sections of the bathymetry of the Tiksi Bay (BY) profile (N to S), Polar Fox Lagoon (LG) from southwest to northeast, and Goltsovoye Lake (LK) along the coring transect (W to E). Positions of the ice cores are indicated as numbered vertical lines in the grey ice layer. The position of the bubble transect at Goltsovoye Lake is represented with a dashed red line.

over the transect (classes A+B) was  $0.39 \text{ seeps/m}^2$ . The distribution of seep density along the transect showed no linear or homogeneous pattern.

### 4.3 Hydrochemistry of the ice

#### 4.3.1 Electrical conductivity (EC)

- 5 The four cores of the bay (BY) had EC values ranging from  $340$  to  $2065 \mu\text{S cm}^{-1}$  (Tab. 2) and similar vertical trends: the EC increased with depth in the upper portion (until approximately 80-90 cm), and then decreased in the lower portion of the cores (>80-90 cm) (Fig. 4). For the two lagoon cores (LG), the EC ranged from  $101$  to  $3630 \mu\text{S cm}^{-1}$  (Tab. 2). In both cores, EC showed a similar increase with depth (Fig. 4): the EC was lower in the upper portion of the ice and highest at the bottom. In the lake (LK), EC was uniformly distributed with depth, and values ranged from  $2.10 \mu\text{S cm}^{-1}$  to  $150 \mu\text{S cm}^{-1}$ . EC measured
- 10 in the ice of the freshwater LK was low compared to the other two marine-influenced locations.



**Figure 3.** Distribution of CH<sub>4</sub> seeps class A and B (Walter Anthony and Anthony, 2013) in Goltsovoye Lake (LK) perpendicular to the northwestern shore in a snow-cleared area of 70 x 1.4 m. Bars represent the frequency of seeps A and B given as probability. The black line shows the Kernel density function (Gaussian Kernel performed on distances to shore, width is 34 data points).

### 4.3.2 Temperature

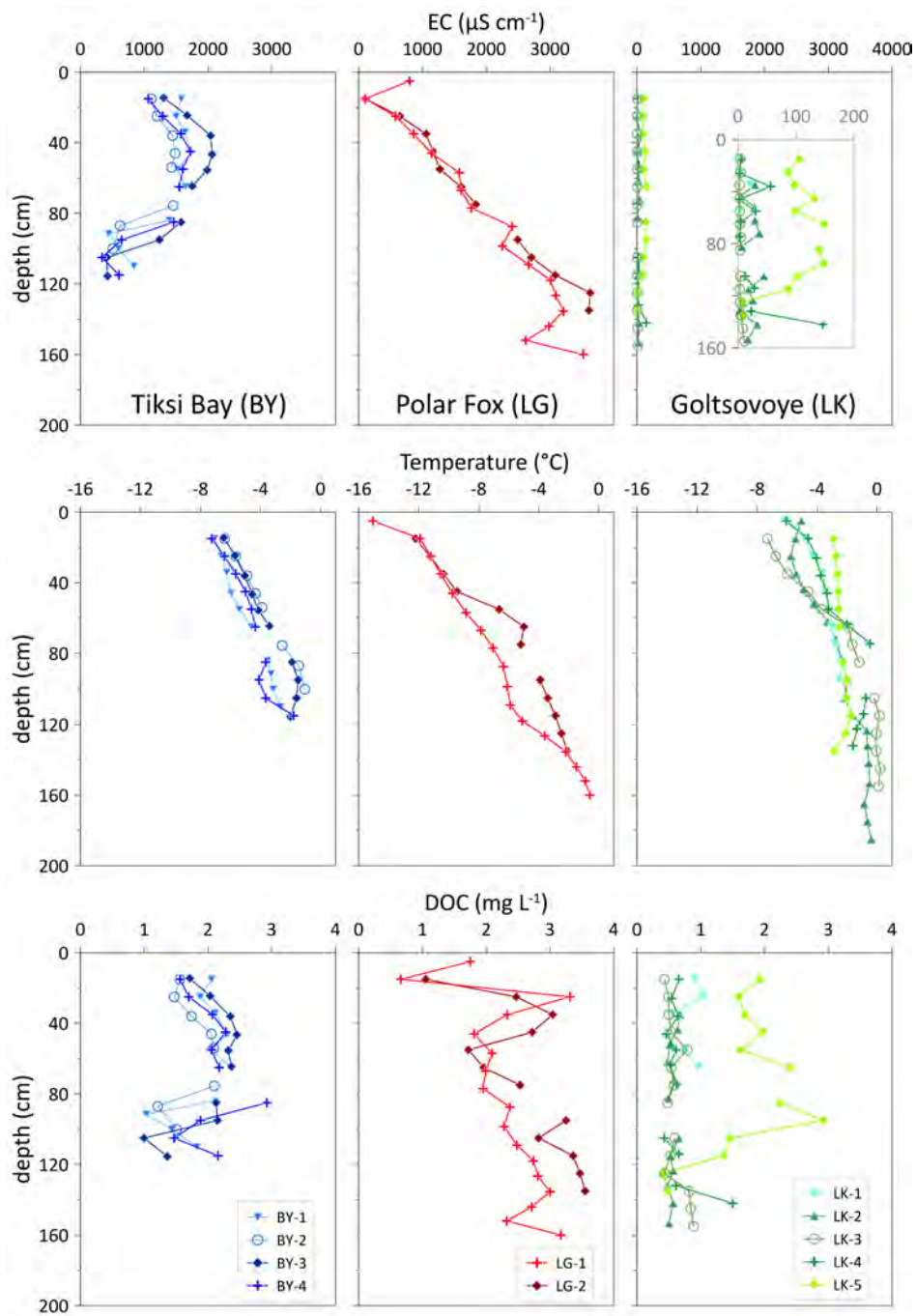
Fig. 4 shows the ice temperatures measured in the field. Overall, the temperature for all ice cores increased with depth (Fig. 4), a reflection of the temperature offset between air and water at the end of winter. Ice temperatures for BY ranged from  $-7.3^{\circ}\text{C}$  at the surface to  $-1.1^{\circ}\text{C}$  at the bottom (Tab. 2). For both cores in LG, the temperature ranged from  $-15.1^{\circ}\text{C}$  (first 10 cm) to  $-0.6^{\circ}\text{C}$  (bottom depths) (Tab. 2). The temperature of the four cores of LK was in the range from  $-7.3$  to  $0.20^{\circ}\text{C}$  (Tab. 2).

### 4.3.3 Dissolved organic carbon (DOC)

For BY, the DOC concentration ranged from  $1.0$  to  $2.9\text{ mg L}^{-1}$  (Tab. 2, Fig. 4). For the cores of LG, DOC concentrations increased with depth, with values up to  $3.6\text{ mg L}^{-1}$  in the lower ice. In the upper ice, DOC concentrations were highly variable and range from  $0.7\text{ mg L}^{-1}$  to  $3.3\text{ mg L}^{-1}$  (0-60 cm) (Fig. 4). DOC concentrations were between  $0.7\text{ mg L}^{-1}$  and  $3.6\text{ mg L}^{-1}$  for both cores, with a mean value of  $2.5 \pm 0.7\text{ mg L}^{-1}$  (Tab. 2). The lowest DOC concentrations ( $0.4\text{ mg L}^{-1}$ ) of the three locations were observed at LK, where the mean concentration of all samples was  $0.9 \pm 0.6\text{ mg L}^{-1}$  (Tab. 2).

### 4.3.4 Stable water isotopes

For the four cores of the BY transect,  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values ranged from  $-16.7\text{‰}$  to  $-14.7\text{‰}$  and  $-129\text{‰}$  to  $-114\text{‰}$ , respectively (Tab. 2). However, changes of the stable isotope composition with depth in the ice cores of BY were relatively



**Figure 4.** Vertical distribution of the electrical conductivity (EC), temperature, and dissolved organic carbon (DOC) in ice cores with depth.

**Table 2.** The mean  $\pm$ SD values and ranges (in parentheses) of measured parameters for all ice core samples for each site are shown.

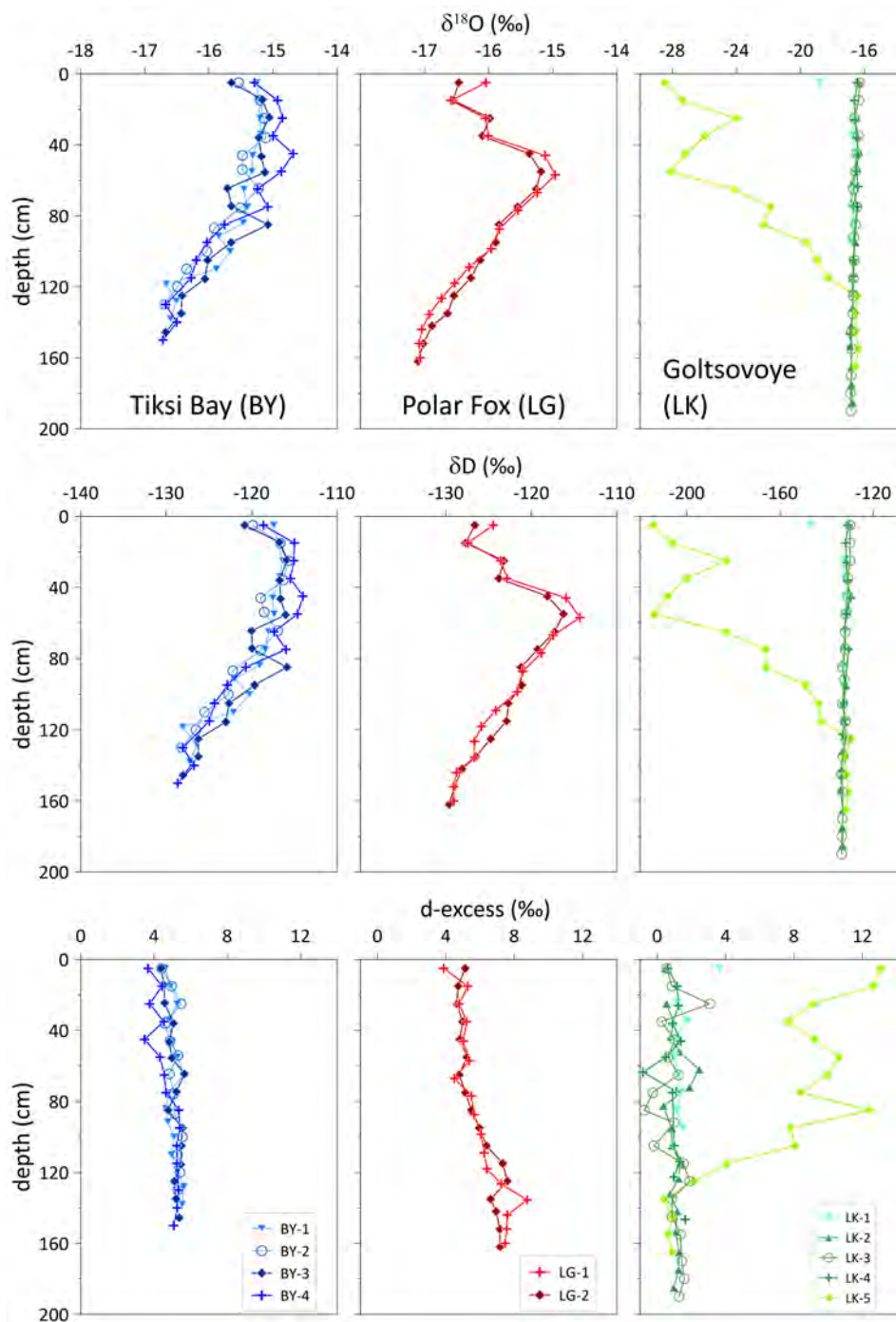
Parameter	Sampling Site					
	Tiksi Bay (BY)		Polar Fox Lagoon (LG)		Goltsovoye Lake (LK)	
Salinity	<b>0.64</b> $\pm$ 0.26	(0.16–1.05)	<b>1.02</b> $\pm$ 0.57	(0.05–1.91)	<b>0.02</b> $\pm$ 0.02	(0.00–0.07)
EC [ $\mu$ S cm <sup>-1</sup> ]	<b>1276</b> $\pm$ 498	(340–2065)	<b>1979</b> $\pm$ 1075	(101–3630)	<b>34.4</b> $\pm$ 45.6	(2.10–150)
pH	<b>7.03</b> $\pm$ 0.25	(6.43–7.66)	<b>7.06</b> $\pm$ 0.28	(6.63–7.69)	<b>6.15</b> $\pm$ 0.95	(4.89–8.45)
Temperature [°C]	<b>-4.25</b> $\pm$ 1.74	(-7.25 – -1.05)	<b>-6.53</b> $\pm$ 3.90	(-15.0 – -0.60)	<b>-2.68</b> $\pm$ 1.86	(-7.30 – 0.20)
DOC [mg L <sup>-1</sup> ]	<b>1.92</b> $\pm$ 0.42	(1.00–2.93)	<b>2.47</b> $\pm$ 0.70	(0.66–3.55)	<b>0.86</b> $\pm$ 0.58	(0.41–2.92)
CH <sub>4</sub> [nM]	<b>6.03</b> $\pm$ 1.22	(3.48 – 8.44)	<b>54.7</b> $\pm$ 109	(2.59–539)	<b>645</b> $\pm$ 2282	(0.02–14817)
$\delta^{13}\text{C}_{\text{CH}_4}$ [‰]	<b>-46.0</b> $\pm$ 3.76	(-51.9 – -36.9)	<b>-51.0</b> $\pm$ 14.2	(-79.7 – -31.8)	<b>-50.0</b> $\pm$ 15.9	(-91.6 – -12.3)
$\delta^{18}\text{O}$ [‰]	<b>-15.7</b> $\pm$ 0.58	(-16.7 – -14.7)	<b>-16.2</b> $\pm$ 0.64	(-17.1 – -15.0)	<b>-17.8</b> $\pm$ 3.00	(-28.4 – -16.3)
$\delta\text{D}$ [‰]	<b>-120</b> $\pm$ 4.33	(-129 – -114)	<b>-123</b> $\pm$ 4.33	(-130 – -114)	<b>-140</b> $\pm$ 21.0	(-214 – -129)
d-excess	<b>5.0</b> $\pm$ 0.5	(3.5 – 5.7)	<b>6.0</b> $\pm$ 1.2	(3.9 – 8.8)	<b>2.4</b> $\pm$ 3.3	(-0.8 – 13.1)

similar to each other. While the values in the upper portion (to approximately 80–90 cm) were quite constant, except for the top of the ice, values decreased in the lower portion (below 80–90 cm) (Fig. 5). The values were lowest at the bottom of the ice cores in each case. The d-excess (d-excess =  $\delta\text{D} - 8 \delta^{18}\text{O}$  (Dansgaard, 1964)) was quite uniform with a range from 3.5‰ to 5.7‰ for all four cores of BY (Tab. 2).

5 For LG, the stable water isotope composition ranges between  $-17.1$ ‰ to  $-15.0$ ‰ for  $\delta^{18}\text{O}$  and  $-130$ ‰ to  $-114$ ‰ for  $\delta\text{D}$  (Tab. 2). The d-excess values were constant from 10 to 20 cm until 90 cm, followed by an increase near the bottom of the cores (Fig. 5).

For LK, the values of the stable water isotopes range from  $-28.4$  to  $-16.3$ ‰ for  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values from  $-215$  to  $-129$ ‰ (Tab. 2). Both  $\delta\text{D}$  and  $\delta^{18}\text{O}$  in the LK cores did not vary with depth and were similar to the isotope signatures of BY and LG.

10 LK-5 differed, with much lower  $\delta$ -values (Fig. 5). Values for the d-excess were between  $-0.8$ ‰ and  $13.1$ ‰ (Tab. 2). For all LK cores except LK-5, d-excess values range from  $-0.8$  to  $3.6$ ‰ (Fig. 5).



**Figure 5.** Vertical distribution of the stable water isotopic compositions ( $\delta^{18}\text{O}$ ,  $\delta\text{D}$  and d-excess) in ice cores with depth. Note that the isotope composition scales for Goltsovoye Lake (LK, at right) differ from the other 2 sites to accommodate the values observed in core LK-5.

## 4.4 CH<sub>4</sub> in the ice

### 4.4.1 Dissolved CH<sub>4</sub> concentrations

In the ice cores from BY, CH<sub>4</sub> concentrations were generally very low (3.48-8.44 nM, mean: 6.03±1.22 nM) (Tab. 2) compared to the other locations and showed no variations with depth (Fig. 6). The dissolved CH<sub>4</sub> concentrations in the water beneath the ice cores were 51 nM and 154 nM (BY-1 and BY-2). In the ice cores from LG, we observed high CH<sub>4</sub> concentrations in the upper ice (up to 193.7 nM), followed by a decrease at depths from 60 to 100 cm and a final increase towards 539 nM at the bottom of LG-1. In LG ice CH<sub>4</sub> concentrations covered a wide range, with values from 2.59 nM to 539 nM (Tab. 2, Fig. 6). In the ice cores of LG, we observed high CH<sub>4</sub> concentrations in the upper ice (up to 194 nM), followed by a decrease at depths from 60 to 100 cm and a final increase at the bottom of LG-1. Concentrations of 1768 nM and 3394 nM (LG-2 and LG-1, respectively) were measured for the dissolved CH<sub>4</sub> concentrations in the water beneath the ice cores. In the ice cores of LK, CH<sub>4</sub> concentrations were low and uniform with depth in the LK-1, LK-2 and LK-4. Very high and very variable concentrations (maximum 14817 nM in LK-3) were observed in the LK-3 and LK-5, which both contained bubbles.

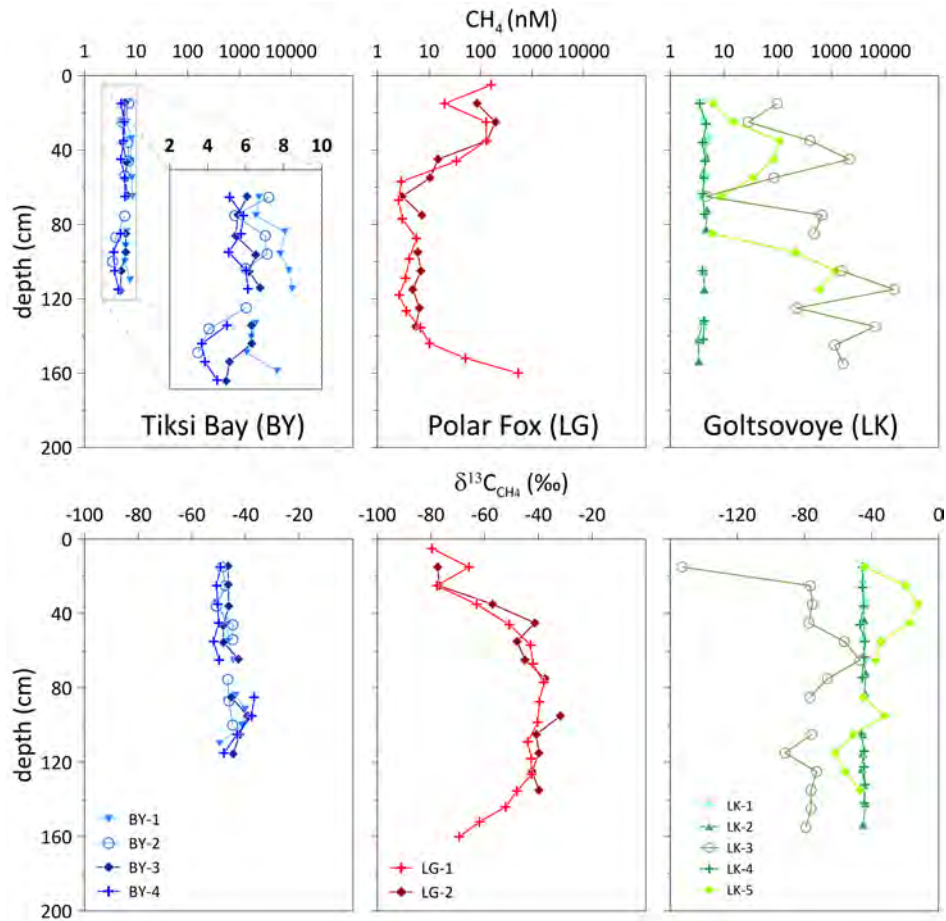
### 4.4.2 Stable carbon isotopes

In the ice cores from BY,  $\delta^{13}\text{C}_{\text{CH}_4}$  values ranged from -51.9‰ to -36.9‰. The values are in a smaller range than the  $\delta^{13}\text{C}_{\text{CH}_4}$  values for the cores of the other locations (Tab. 2). In LG, the  $\delta^{13}\text{C}_{\text{CH}_4}$  values range from -79.7 to -31.8‰ for both cores (Tab. 2). The cores indicate a similar pattern, with carbon isotopes more enriched in  $\delta^{13}\text{C}_{\text{CH}_4}$  in the lower portion of the cores than in the upper portion (Fig. 6). The stable  $\delta^{13}\text{C}_{\text{CH}_4}$  values decrease in the bottom depths of LG-1. The pattern is similar but inverse to the CH<sub>4</sub> concentrations. In LK, the  $\delta^{13}\text{C}_{\text{CH}_4}$  values range from -91.6 to -12.3‰ (Tab. 2). The highest and lowest values occurred in LK-3 and LK-5. These two cores show changes in the  $\delta^{13}\text{C}_{\text{CH}_4}$  values with depths, whereas the stable carbon isotopic signal of the other cores (LK-1, LK-2 and LK-4) varies between -46.8 to -43.3‰ and is quite constant. In LK-1, LK-2 and LK-4, the  $\delta^{13}\text{C}_{\text{CH}_4}$  values had a mean of -43.3‰ and were uniform ( $\pm 2.2\%$ ) with depth, in contrast to LK-3 and LK-5, where values ranged from -91.6 to -12.3‰, with a strong variability within and between the two cores. Greater variability was observed for CH<sub>4</sub> concentrations.

## 5 Discussion

A seasonal ice cover is a barrier to gas exchange between water and the atmosphere. The coastal water bodies studied here are covered by ice for 9 months of the year, a period that is shortening for both lake and marine ice (e. g. Günther et al., 2015). At the same time, air temperatures (Boike et al., 2013), sea level rise rates (Nerem et al., 2018), and coastal thermo-erosion rates (Günther et al., 2013) all increase, indicating a rapidly shifting regime for aquatic environments in the region. The importance of the persistence and duration of the seasonal ice cover in all of these processes is poorly understood. As further warming of the Arctic shortens the duration of ice cover, pathways to CH<sub>4</sub> emissions will probably shift.





**Figure 6.** Vertical distribution of the  $\text{CH}_4$  concentration (on a logarithmic scale) and  $\delta^{13}\text{C}_{\text{CH}_4}$  with depth for the three locations.

The three water bodies in this study represent 1) the marine shoreface, in a setting where ice-rich Yedoma permafrost is undergoing thermo-erosion (BY), 2) a thermokarst lake that has become a coastal lagoon via thermo-erosion (LG) and, 3) a terrestrial thermokarst lake (LK). Although the ice cover sampled from all three settings was largely clear ice, we observed systematic differences in ice hydrochemistry and  $\text{CH}_4$  concentration. As observed in Harris et al. (2017), the degree of connectivity to the sea is important in determining the composition of the water for coastal lagoons. In the LG setting, thickening of the ice cover eventually plugged the shallow connection of the brackish basin to the sea, at which point freezing concentrated the remaining brine beneath the ice for the rest of the winter (**semi-closed system**), a typical situation in lagoons, behind barrier islands or on gently inclined shorefaces. Landfast ice on the shoreface does not close off the water basin, which continues to undergo exchange with the central Laptev Sea and Lena River inflow (**open system**). The thermokarst lake had neither outlets nor significant inlets, and the ice effectively closed off the water body (**closed system**), isolating the freshwater basin and its talik. Based on our data, we suggest that the type of water body also determines the circulation of  $\text{CH}_4$ . In the following we

examine in detail how the water body type affected ice growth, CH<sub>4</sub> concentrations and composition and discuss the processes involved.

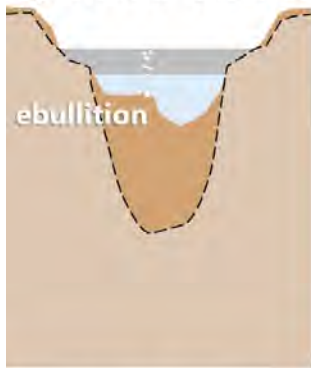
## 5.1 Tiksi Bay (BY) – the open system

BY is part of Buor Khaya Bay and via the central Laptev Sea perennially connected to the Arctic Ocean. The marine setting delays the onset of ice formation compared to the terrestrial aquatic system shown by satellite images from ESA Sentinel-1 and -2. In addition to sea water, snowmelt in spring, small coastal catchments and the Lena River enter into BY between Cape Muostakh and around the southern end of Muostakh Island. Lena River discharge follows a nival discharge regime, with very high discharge in the spring and early summer months (Magritsky et al., 2018), while in winter, when the connection between Buor Khaya Bay and BY is restricted by sea ice, the contribution of Lena discharge must be much smaller. When BY freezes, it is supposed to be a continuously open system, i.e. water exchange is ongoing during winter below the ice. Both aspects (open system and the mixing of fresh and brackish water) are corroborated in the stable water isotopes composition of the ice cores. A mean  $\delta^{18}\text{O}$  value of  $-15\text{‰}$  for BY is well below full marine conditions and displays the continuous and strong influence of freshwater supply through the Lena River to the Laptev Sea.

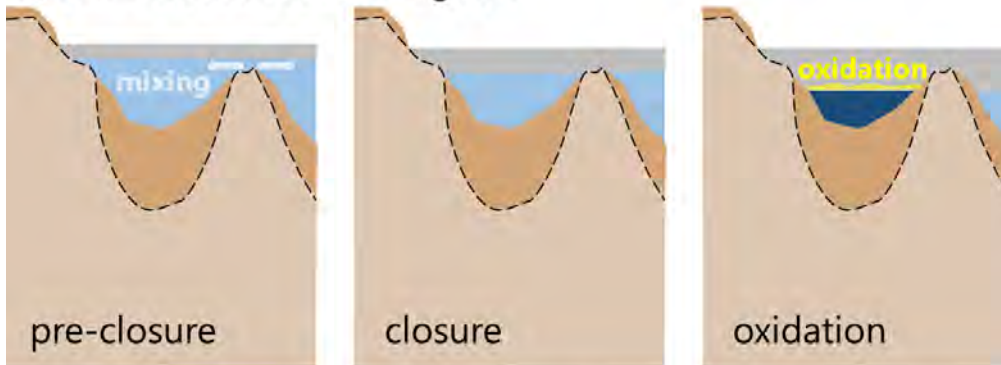
Firstly, in an open system such as BY, the water circulates freely beneath the ice cover. The isotope composition of the ice should remain more or less constant over the winter (Gibson and Prowse, 1999), and reflect the fractionation resulting from freezing of Tiksi Bay water. Accordingly, the water isotopic composition and salinity values are constant until the ice is approximately 80-90 cm thick (Fig. 4,5). The small variation at the top might be due to variability in isotopic fractionation, i.e. related to a change of the freezing rate after ice formation started. Oxygen isotope fractionation during the freezing of sea water has been addressed by Toyota et al. (2013), through laboratory experiments and field observations. These authors demonstrate a general dependency of increasing isotope fractionation with decreasing ice growth rate. Therefore, faster freezing induces less isotope fractionation when compared to slowly formed ice at a later stage of sea ice formation. The difference between both is within 1‰ for a large range of ice growth rates.

Secondly, BY is influenced by marine and river water, and a change in this ratio may change the isotopic composition of  $\delta^{18}\text{O}$  and  $\delta\text{D}$ . The exchange of the water below the ice might have disturbed an equilibrium freezing process. Hence, water mixing is likely reflected in the small shift towards  $-17\text{‰}$  in  $\delta^{18}\text{O}$  and  $-130\text{‰}$  in  $\delta\text{D}$  in the lower part of the ice (>90 cm) (Figs. 4, 5, and 6), even though the  $\delta^{18}\text{O}$ - $\delta\text{D}$  data behave like isotopic fractionation in a closed system, where the last ice formed displays lightest isotope composition. The change of the water isotope composition without a change in the d-excess, as well as changing EC and DOC, suggest a substantial contribution of another water mass and indicate the reduction of marine influence or an increased river water impact in the lower part of the ice compared to the upper part. Reduced salinity and lower EC concentrations corroborated the enhanced freshwater content in the bottom segments of the ice cores, further substantiated by lower  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values. Overall, the upper part of the BY ice cores indicate freezing from brackish water whereas the lower part may capture a slightly higher proportion of river water probably reflecting changes to the isotopic and hydrochemical composition of BY. This is reflected in the regression lines of the  $\delta^{18}\text{O}$ - $\delta\text{D}$  plot for BY, which differ in slope for the two sections (Fig. 8) and indicate a shift in fractionation (Souchez and Jouzel, 1984). Episodic advection of meteoric water

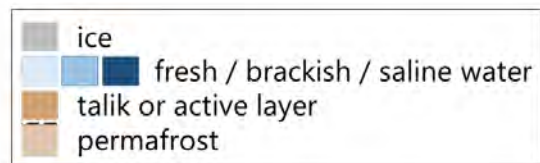
**a) closed: thermokarst lake**



**b) semi-closed: coastal lagoon**



**c) open: marine shoreface**



**Figure 7.** Schematics of geomorphological differences between the three aquatic systems studied in this paper: a) the closed system represents a typical thermokarst lake, such as LK, with a closed talik and a complete winter ice cover over freshwater; b) the semi-closed system is a brackish to highly saline water body (LG), whose ice cover separates it from the marine system at some point during the winter and for which continued ice growth results in hypersalinity; and c) the open system (BY), where ice cover growth does not prevent mixing with marine and or fluvial waters beneath the ice.

during the winter season was also detected in land-fast sea ice cores from Barrow, Alaska (Smith et al., 2016). The samples of the upper portion of the ice plot along a regression slope of 6.9, demonstrating open system freezing under equilibrium conditions (Lacelle, 2011). In contrast, the lower portion of the ice plots along a regression line of 7.9 (Tab. 3), close to the slope of the GMWL of 8. Hence, we assumed this portion of the ice to be mixed with water of meteoric origin. The change in the water isotopes between the upper and lower ice was not related to closed system freezing, as this would also be indicated by a deviation from the GMWL and a change in the d-excess.

CH<sub>4</sub> concentrations in BY ice are small but still supersaturated relative to the atmospheric background concentration and probably the result of freezing of CH<sub>4</sub>-supersaturated brackish water in BY. CH<sub>4</sub> supersaturation has been reported for the Buor Khaya Bay (Bussmann, 2013) and large amounts of CH<sub>4</sub> are stored in sediments of this region (Overduin et al., 2015). Supersaturation in the shallow water of BY is probably caused by CH<sub>4</sub> release from sediments (Bussmann et al., 2017), which likely occurs in the fall when cooling induces convection and resuspension events (Damm et al., 2007). In comparison, during calm sub-ice winter conditions resuspension events cease and methane concentration decreases in the brackish water from which the ice forms, shown by the slightly reduced concentration in the lower part of the ice (>90 cm) (Fig. 5). The slight decrease in concentration with increasing distance from shore and a homogeneous carbon isotopic signature also points to calm water conditions during freezing and a local source of CH<sub>4</sub>. Very similar processes during freezing for all BY cores are corroborated by the homogeneous ( $\delta^{13}\text{C}_{\text{CH}_4}$ ) carbon isotopic signature along the onshore-offshore gradient.

## 5.2 Polar Fox Lagoon (LG) – the semi-closed system

LG is connected to BY through a wide, shallow and winding channel. Storm surges and high water events in the summer force sea water, driftwood and sediment into LG. ESA Sentinel-1 and -2 imagery indicate that the ice on LG started to form in mid-October, and hence earlier than at BY. During the early freezing period, the connecting channel allowed water exchange between LG and BY, until the growing ice reached the channel bed (less than 0.5 m deep) where it exits LG in 2017. At that point, LG changed from a connected to an isolated system, affecting water chemistry below the ice. The timing of closure, interpreted from the change of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values with depth, corresponds to an ice thickness of 60 cm. At the time of coring the ice thickness on LG was about 1.6 m; consequently the outer lake area, more than 75 % of the lagoon area, was assumed to be frozen to the bed (Angelopoulos et al., 2020). In the lagoon centre, ice was floating and the lagoon had a talik, although it contained a thin ice-bearing layer (4.8 m to 8.3 m below the sediment surface) Angelopoulos et al. (2020).

Ice that formed before the lagoon was separated from the sea (above 60 cm), the isotopic signature indicates freezing under equilibrium conditions (Lacelle, 2011), with a slope of 8.2 between  $\delta^{18}\text{O}$  and  $\delta\text{D}$  (Fig. 8, Tab. 3). Below this depth, however, isotopic values decrease, indicating freezing under closed conditions. Freezing leads to a lighter isotope signature of the remaining water, as the heavy isotopes are preferentially incorporated into the ice (slope: 6.5 Gibson and Prowse, 1999, 2002). This results in lighter isotope composition in later (deeper) ice and an increase of d-excess compared to earlier (upper) ice. The concentrations of dissolved constituents (indicated by EC and DOC) also increase with increasing ice thickness (Fig. 4), corroborating this interpretation. Thermokarst lake basins that are transformed into thermokarst lagoons are increasingly affected by seawater, at least intermittently, during high water events such as storm surges, resulting in changes to their temperature and

salinity regimes (Romanovskii et al., 2000). Increasing salinity in turn also affects subsurface permafrost thaw dynamics and may therefore result in different CH<sub>4</sub> production rates (Angelopoulos et al., 2019, 2020).

In the uppermost ice, i.e. when freezing started, CH<sub>4</sub> concentration in LG water was more than ten times higher than in BY. The isotopic signature was in the range of microbially produced CH<sub>4</sub> (−70 to −80‰) (Whiticar, 1999). This large excess of δ<sup>13</sup>C-depleted CH<sub>4</sub> clearly points to CH<sub>4</sub> from the unfrozen talik, released into the water body and stored therein during the ice-free season. When LG switched from a connected to a closed system at around 60 cm ice thickness, ongoing CH<sub>4</sub> oxidation beneath the ice lowered the CH<sub>4</sub> concentration captured in the ice to ≤10 nM, comparable to those in BY ice. At the same time, the CH<sub>4</sub> isotopic signature became comparably enriched in δ<sup>13</sup>C (Fig. 6, 9). Ongoing ice formation under closed system conditions (below 60 cm), as indicated by stable water isotopes, induced a continuous increase in ice salinity (Fig. 4) which in turn favoured the shift of the horizon where CH<sub>4</sub> oxidation could occur from the water to the bottom of the ice. This is corroborated by the Rayleigh fractionation curves calculated for ice that grew under closed conditions, using as initial CH<sub>4</sub> isotopic signature the uppermost value, i.e. the signature when freezing began (Fig. 6, 9).

In addition, temperature increased towards the bottom of the ice (Fig. 4). The bottom ice offers a protected environment with favourable conditions for microbial metabolism: relatively warm temperatures, contact with liquid water and permeable ice. The latter permits migration of gases and nutrients, similar to marine ice, where most bacteria are located in the lowest centimetres of the ice (Krembs and Engel, 2001). At LG, the bottom ice temperature decreases during the winter. This occurs because the temperature of the underlying water remains in equilibrium with a dynamic freezing point that decreases with increasing salinity when LG is cut off from Tiksi Bay. The ice surface temperature at the time of coring was primarily a function of snow cover and air temperature. The ice coring locations for LG exhibited colder ice surface temperatures and steeper gradients compared to ice coring locations at LK. Ice has a high thermal conductivity and is susceptible to quick temperature changes. Since ice temperatures were also observed for windswept areas at LK, decreasing air temperatures from 8 April 2017 (final LK coring day) to 11 April 2017 (LG coring day) explain the generally colder ice temperature profiles at LG. How salty the sub-ice water becomes is probably highly variable from year to year and will depend on how much sea water is forced into the lagoon during the fall storm season.

During freezing of the ice cover, its growth rate decreases (cf. Anderson, 1961), providing more time and space for bacterial metabolism. CH<sub>4</sub> uptake from the water into the bottom of the ice and its oxidation there may have continued over the winter until the ice break-up. CH<sub>4</sub> oxidation ceases when concentrations are too low for oxidation to be efficient (Cowen et al., 2002; Valentine et al., 2001), at values ranging from 0.6 nM to 10 nM. CH<sub>4</sub> concentrations in the ice above 130 cm (Fig. 6) were less than 10 nM, suggesting that ice is an effective sink for CH<sub>4</sub> in this type of water body during winter.

### 5.3 Goltsovoye Lake (LK) – the closed system

The ice core hydrochemistry from LK reflected a water body that froze in equilibrium with atmospheric CH<sub>4</sub> concentrations, with two cores that showed the influence of snow loading and of ebullition.

LK is an isolated thermokarst basin surrounded by ice-rich Yedoma uplands to the west and east and partially degraded Yedoma uplands to the north and south. The lake is underlain by continuous permafrost some hundreds of meters deep, and has

a thaw bulb (talik) beneath its bed due to the positive temperatures at the lake bottom. Water in LK derives from precipitation, most of which falls as snow, overland flow and perhaps as groundwater flow through the shallow active layer. Thus, the concentration of dissolved constituents remains small in lake water and ice, as reflected in very low electrical conductivities of less than  $50 \mu\text{S cm}^{-1}$  (Fig. 4).

5 Water depths range from  $< 1\text{ m}$  to about  $8.5\text{ m}$  from the western to eastern shore, respectively (Fig. 2). This asymmetric shape influences the progress of ice growth in winter. Ice formation typically starts from the lake shore, most likely at the very shallow west shore, and leads to bedfast ice formation at the position of LK-1, i. e. lake ice frozen to the lake bed. Hence, it is likely that LK-1 began to form earlier in the season, and that the upper ice in this core, and probably also in LK-4, reflected the chemistry of the summer/autumn lake water. All cores except LK-5 had similar  $\delta^{18}\text{O}$  (around  $-16.5\text{‰}$ ) and  $\delta\text{D}$  ( $-140\text{‰}$ ) values, and with a regression slope of 6.6 (Fig. 8, Tab. 3), pointing to freezing under equilibrium conditions (Lacelle, 2011). At this location both, the  $\text{CH}_4$  concentrations and the uniform  $\delta^{13}\text{C}$  signature indicate equilibrated values with respect to the atmospheric background values (Fig. 6). This circumstance clearly shows that lake water was not supersaturated during the ice-free season. The other two cores show clear differences and are described in the following.

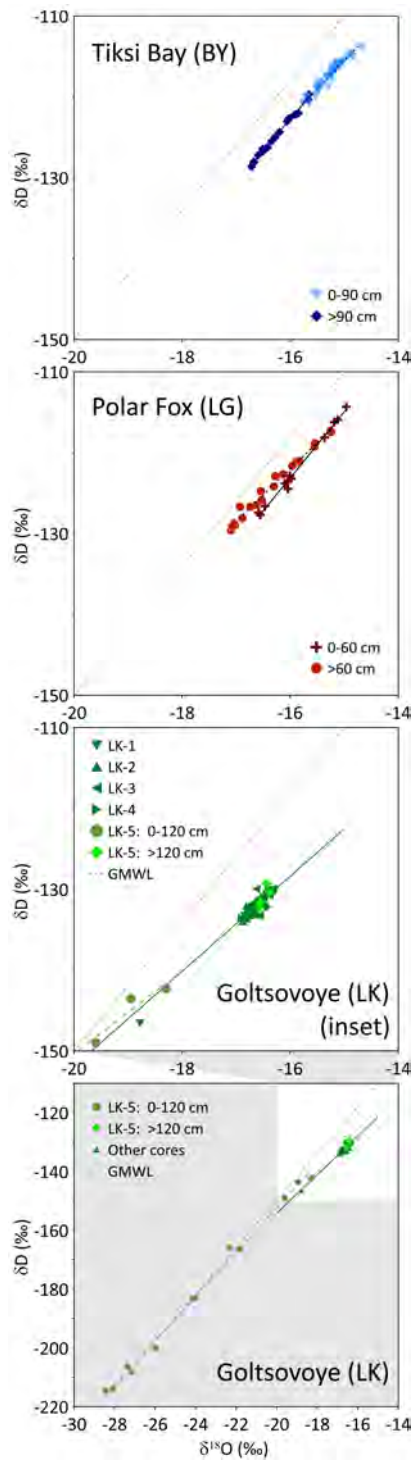
For LK-5 stable water isotopes in the upper 120 cm follow the GMWL (Fig. 8), indicating equilibrium fractionation (in the system vapour-water, as snow is involved) due to different precipitation sources.  $\delta^{18}\text{O}$  values as low as  $-28\text{‰}$  indicate the involvement of snow. The proximity of snow samples to the GMWL is typical for Northern Siberia and has been also found at snow patches on the Bykovsky Peninsula (Meyer et al., 2002). LK-5 lay close to LK's steepest shoreline, where active thermo-erosion results in shoreline retreat, and that lies in the lee of prevailing winds (Günther et al., 2015), where deep snow is expected to accumulate and load the lake ice. 92 cm thick snow lay on the ice at this location at the time of drilling and water streamed out of the hole after coring (Strauss et al., 2018), indicating an ice cover under positive hydrostatic pressure. The ice of LK-5 was milky-white from the surface to about 112 to 114 cm depth consistent with a mixture of snow and water. Thus, we conclude a snow signal evident from the stable isotope composition in the upper 120 cm of LK-5. The higher EC and DOC in the same interval (relative to lower ice and to the other LK cores) are unlikely to have derived from snow, however, and imply heterogeneous ice development above 120 cm. These may be the result of mixing of uprising lake water with snow within ice cracks. Adams and Lasenby (1985) describe the formation of white ice (or snow ice) by water percolation through thermally-induced cracks to the surface of the ice, where the water mixes with snow and forms another ice layer above the former ice. This was observed by Adams and Lasenby (1985) when a snow load depressed the surface of the ice cover below the hydrostatic water level. The high and highly variable  $\text{CH}_4$  concentrations over this interval, together with the high EC and DOC, suggest that resuspension events, for example slope failure, occurred during ice formation. The carbon stable isotope signature in LK-5 may reflect microbial  $\text{CH}_4$  oxidation in the sediment rather than oxidation in or beneath the ice.

The highest concentrations of  $\text{CH}_4$  were found in LK-3 (up to  $15\,000\text{ nM}$ ), with the lowest  $\delta^{13}\text{C}$  signatures (down to  $-150\text{‰}$ , Fi. 6). LK-3 was drilled above the steepest portion of the lake bed, where ebullition may be a by product of thermokarst processes beneath the bed. The  $^{12}\text{C}$ -enriched signal is consistent with  $\text{CH}_4$  that has not been oxidized in the sediment and is released in gas bubbles. The earlier release of the lightest  $\text{CH}_4$  may be the result of fractionation during migration in the

sediment and may be an indication the ebullition and ice formation are related, i.e. that ebullition was initiated as a result of pressure changes owing to the onset of freezing.

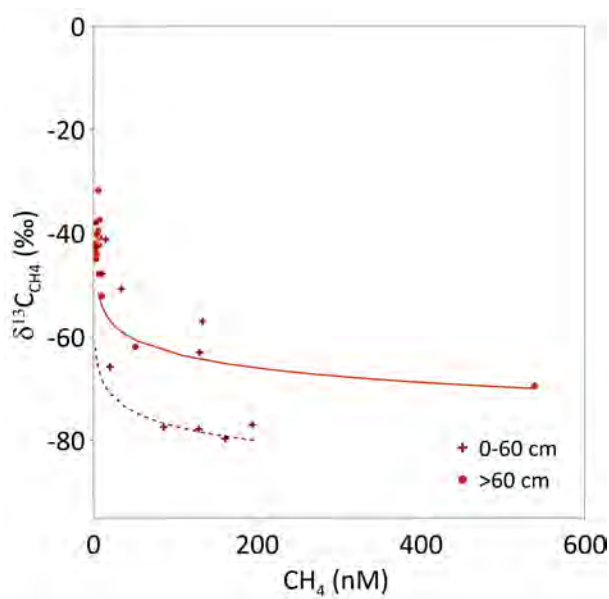
**Table 3.** Regression lines of the  $\delta^{18}\text{O}$  versus  $\delta\text{D}$  plot for the three systems (Fig. 8).

SYSTEM	REGRESSION LINE
Tiksi Bay (0-90 cm)	$\delta\text{D} = 6.9 \delta^{18}\text{O} - 12.7$ ( $r^2=0.95$ , $n=35$ )
Tiksi Bay (>90 cm)	$\delta\text{D} = 7.9 \delta^{18}\text{O} + 3.5$ ( $r^2=0.99$ , $n=23$ )
Polar Fox (LG) (0-60 cm)	$\delta\text{D} = 8.2 \delta^{18}\text{O} + 7.5$ ( $r^2=0.99$ , $n=12$ )
Polar Fox (LG) (>60 cm)	$\delta\text{D} = 6.5 \delta^{18}\text{O} - 18.8$ ( $r^2=0.99$ , $n=22$ )
Goltsovoye (LK) (LK-5)	$\delta\text{D} = 7.5 \delta^{18}\text{O} - 2.0$ ( $r^2=0.995$ , $n=12$ )
Goltsovoye (LK) (other LK cores)	$\delta\text{D} = 6.6 \delta^{18}\text{O} - 22.5$ ( $r^2=0.93$ , $n=59$ )



**Figure 8.** Isotope composition and linear regressions for Tiksi Bay (BY, top), Polar Fox Lagoon (LG, middle) and Goltsovoye Lake (LK, bottom) ice cores. For comparison, the global meteoric water line (GMWL,  $\delta D = 8 * \delta^{18}O + 10$ ; (Craig, 1961), grey dotted line) is shown. The axes limits of the lowest graph differ from those above.





**Figure 9.** Observed  $\delta^{13}\text{C}_{\text{CH}_4}$  and  $\text{CH}_4$  concentrations in the ice of Polar Fox Lagoon (LG) for shallow and deep ice (above and below 60 cm). The lines show  $\delta^{13}\text{C}_{\text{CH}_4}$  calculated based on Rayleigh fractionation during oxidation (Eq. 1).  $\text{CH}_4$  oxidation was calculated with  $\alpha = 1.004$ . Initial concentrations were taken from surface ice: 195 nM (0 to 60 cm, dotted line) and 450 nM (>60 cm, solid line) and the initial isotopic signatures were  $-80\text{‰}$  and  $-70\text{‰}$ , respectively.

## 6 Conclusions

$\text{CH}_4$  concentrations in the seasonal ice cover of three types of Arctic water bodies, representing three different stages of permafrost degradation, revealed differences related to the process of ice formation and its importance as mitigator of  $\text{CH}_4$  fluxes to the atmosphere.

- 5 In the ice of Tiksi Bay, open to the central Laptev Sea throughout the winter and underlain by permafrost, the signatures of the stable isotopes of water and electrical conductivity reflected the composition of the upper layer of brackish water throughout the winter, with an increasing proportion riverine waters during winter. In this setting,  $\text{CH}_4$  concentrations were low but, as in all three water bodies, supersaturated with respect to atmospheric concentration.

- 10 In the coastal Polar Fox Lagoon, a breached thermokarst lake, ice formation sealed the channel between the lagoon to the sea. This isolated and concentrated the remaining brackish water beneath the thickening ice during the winter.  $\text{CH}_4$  was present at variable concentrations, but the concentration profile over depth and the stable isotope signatures strongly suggest that bacterial oxidation takes place at the interface between ice and water, reducing the  $\text{CH}_4$  concentration preserved in the ice. We interpret this as evidence that the ice cover may act as a sink, providing a habitat for  $\text{CH}_4$ -oxidizing micro-organisms.

- 15 In the third water body, a land-locked thermokarst lake surrounded by Yedoma landscapes, rather uniform  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values and very low electrical conductivity in all lake ice cores (except for one) indicate either subsurface contributions to the

lake in winter or a lake deep enough not to behave like a closed system. CH<sub>4</sub> concentrations in the lake ice were spatially highly variable. High CH<sub>4</sub> concentrations were local and probably associated with ebullition and snow loading of the ice near an eroding shoreline.

Thus winter ice on the water bodies studied here showed a transition from isolated basins in which methane is released at discrete locations in winter, to a basin isolated only by freezing in winter, in which the availability of salt water facilitates oxidation, and finally to a brackish water coastal environment. As the sediment is a known environment for CH<sub>4</sub> production and DOC could be a source for CH<sub>4</sub> production in the water or the ice, sediment pore water  $\delta^{13}\text{C}_{\text{CH}_4}$  values, and CH<sub>4</sub> and DOC concentrations should be included in future studies to understand CH<sub>4</sub> pathways from their source in comparable water bodies. Furthermore, the comparison between brackish and freshwater water bodies may yield insights into the constraints on CH<sub>4</sub> oxidation in thermokarst lakes and Arctic lagoons. That methane oxidation can take place at the lower ice surface means that projected changes to ice cover duration and coastal water composition may affect methane flux mitigation by winter ice cover. As carbon dioxide is an important greenhouse gas and the product of CH<sub>4</sub> oxidation, future studies should include relative proportions of both greenhouse gases.





*Data availability.* Concentration data are available on PANGAEA (insert doi here).

**15** *Author Contributions* IS, PPO, ED, SL and IB conceptualized the study. Field investigations and/or laboratory analyses were carried out by IS, BKB, ED, GG, HM, IB, MA, MNG, PPO and SL. IS and PPO prepared the manuscript with contributions from all co-authors. The authors declare that they have no conflict of interest.

**20** *Acknowledgements.* This study was funded in part by the project PETA-CARB (ERC #338335). The Russian Foundation for Basic research supported this work via projects awarded to Mikhail N. Grigoriev (18-05-70091, 18-45-140057). Logistical support for the fieldwork was provided by the Russian Hydrographic Service (HydroBase Tiksi). We thank Hoang Vu Tuyen for rectifying and mosaicking images for the CH<sub>4</sub> bubble transect and Ilsetraut Stölting for help with CH<sub>4</sub> measurements.

## References

- Adams, W. and Lasenby, D.: The roles of snow, lake ice and lake water in the distribution of major ions in the ice cover of a lake, *Annals of Glaciology*, 7, 202–207, 1985.
- Anderson, D. L.: Growth rate of sea ice, *Journal of Glaciology*, 3, 1170–1172, 1961.
- 5 Angelopoulos, M., Westermann, S., Overduin, P., Faguet, A., Olenchenko, V., Grosse, G., and Grigoriev, M. N.: Heat and salt flow in subsea permafrost modeled with CryoGRID2, *Journal of Geophysical Research: Earth Surface*, 124, 920–937, <https://doi.org/10.1029/2018JF004823>, 2019.
- Angelopoulos, M., Overduin, P., Westermann, S., Tronicke, J., Strauss, J., Schirrmeister, L., Biskaborn, B. K., Liebner, S., Maximov, G., Grigoriev, M. N., et al.: Thermokarst lake to lagoon transitions in eastern Siberia: Do submerged taliks refreeze?, *Journal of Geophysical Research: Earth Surface*, p. e2019JF005424, <https://doi.org/10.1029/2019JF005424>, 2020.
- 10 Arp, C. D., Jones, B. M., Grosse, G., Bondurant, A. C., Romanovsky, V. E., Hinkel, K. M., and Parsekian, A. D.: Threshold sensitivity of shallow Arctic lakes and sublake permafrost to changing winter climate, *Geophysical Research Letters*, 43, 6358–6365, 2016.
- Bartsch, A., Pointner, G., Leibman, M. O., Dvornikov, Y. A., Khomutov, A. V., and Trofaier, A. M.: Circumpolar mapping of ground-fast lake ice, *Frontiers in Earth Science*, 5, 12, 2017.
- 15 Bastviken, D., Ejlertsson, J., and Tranvik, L.: Measurement of methane oxidation in lakes: a comparison of methods, *Environmental science & technology*, 36, 3354–3361, 2002.
- 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 biogeochemical cycles*, 18, 2004.
- 20 Bastviken, D., Cole, J. J., Pace, M. L., and Van de Bogert, M. C.: Fates of methane from different lake habitats: Connecting whole-lake budgets and CH<sub>4</sub> emissions, *Journal of Geophysical Research: Biogeosciences*, 113, 2008.
- Biskaborn, B. K., Herzsuh, U., Bolshiyarov, D., Savelieva, L., and Diekmann, B.: Environmental variability in northeastern Siberia during the last ~ 13,300 yr inferred from lake diatoms and sediment–geochemical parameters, *Palaeogeography, Palaeoclimatology, Palaeoecology*, 329, 22–36, 2012.
- 25 Biskaborn, B. K., Herzsuh, U., Bolshiyarov, D., Savelieva, L., Zibulski, R., and Diekmann, B.: Late Holocene thermokarst variability inferred from diatoms in a lake sediment record from the Lena Delta, Siberian Arctic, *Journal of paleolimnology*, 49, 155–170, 2013a.
- Biskaborn, B. K., Herzsuh, U., Bolshiyarov, D. Y., Schwamborn, G., and Diekmann, B.: Thermokarst processes and depositional events in a tundra lake, northeastern Siberia, *Permafrost and Periglacial Processes*, 24, 160–174, 2013b.
- Biskaborn, B. K., Subetto, D., Savelieva, L. A., Vakhrameeva, P. S., Hansche, A., Herzsuh, U., Klemm, J., Heinecke, L., Pstryakova, L., Meyer, H., et al.: Late Quaternary vegetation and lake system dynamics in north-eastern Siberia: implications for seasonal climate variability, *Quaternary Science Reviews*, 147, 406–421, 2016.
- 30 Biskaborn, B. K., Smith, S. L., Noetzli, J., Matthes, H., Vieira, G., Streletskiy, D. A., Schoeneich, P., Romanovsky, V. E., Lewkowicz, A. G., Abramov, A., et al.: Permafrost is warming at a global scale, *Nature communications*, 10, 264, 2019.
- Boereboom, T., Depoorter, M., Coppens, S., and Tison, J.-L.: Gas properties of winter lake ice in Northern Sweden: implication for carbon gas release, *Biogeosciences*, 9, 827–838, 2012.
- 35 Boike, J., Kattenstroth, B., Abramova, K., Bornemann, N., Chetverova, A., Fedorova, I., Fröb, K., Grigoriev, M., Grüber, M., Kutzbach, L., Langer, M., Minke, M., Muster, S., Piel, K., Pfeiffer, E.-M., Stoof, G., Westermann, S., Wischnewski, K., Wille, C., and Hubberten,

- H.-W.: Baseline characteristics of climate, permafrost and land cover from a new permafrost observatory in the Lena River Delta, Siberia (1998–2011), *Biogeosciences*, 10, 2105–2128, 2013.
-  Bussmann, I.: Distribution of methane in the Lena Delta and Buor-Khaya Bay, Russia, *Biogeosciences*, 10, 4641–4652, 2013.
- 5 Bussmann, I., Hackbusch, S., Schaal, P., and Wichels, A.: Methane distribution and oxidation around the Lena Delta in summer 2013, *Biogeosciences*, 14, 4985–5002, 2017.
- Canelhas, M. R., Denfeld, B. A., Weyhenmeyer, G. A., Bastviken, D., and Bertilsson, S.: Methane oxidation at the water-ice interface of an ice-covered lake, *Limnology and Oceanography*, 61, S78–S90, 2016.
- Charkin, A. N., Rutgers van der Loeff, M., Shakhova, N. E., Gustafsson, Ö., Dudarev, O. V., Cherepnev, M. S., Salyuk, A. N., Koshurnikov, A. V., Spivak, E. A., Gunar, A. Y., et al.: Discovery and characterization of submarine groundwater discharge in the Siberian Arctic seas: a case study in the Buor-Khaya Gulf, Laptev Sea, *The Cryosphere*, 11, 2305–2327, 2017.
- 10 Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J., et al.: Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget, *Ecosystems*, 10, 172–185, 2007.
- Coleman, D. D., Risatti, J. B., and Schoell, M.: Fractionation of carbon and hydrogen isotopes by methane-oxidizing bacteria, *Geochimica et Cosmochimica Acta*, 45, 1033–1037, 1981.
- 15 Conrad, R.: The global methane cycle: recent advances in understanding the microbial processes involved, *Environmental microbiology reports*, 1, 285–292, 2009.
- Cowen, J. P., Wen, X., and Popp, B. N.: Methane in aging hydrothermal plumes, *Geochimica et Cosmochimica Acta*, 66, 3563–3571, 2002.
- Craig, H.: Isotopic variations in meteoric waters, *Science*, 133, 1702–1703, 1961.
- 20 Damm, E., Mackensen, A., Budéus, G., Faber, E., and Hanfland, C.: Pathways of methane in seawater: Plume spreading in an Arctic shelf environment (SW-Spitsbergen), *Continental Shelf Research*, 25, 1453–1472, 2005.
- Damm, E., Schauer, U., Rudels, B., and Haas, C.: Excess of bottom-released methane in an Arctic shelf sea polynya in winter, *Continental Shelf Research*, 27, 1692–1701, 2007.
- Damm, E., Rudels, B., Schauer, U., Mau, S., and Dieckmann, G.: Methane excess in Arctic surface water-triggered by sea ice formation and melting, *Scientific reports*, 5, 16 179, 2015.
- 25 Dansgaard, W.: Stable isotopes in precipitation, *Tellus*, 16, 436–468, 1964.
-  Denfeld, B. A., Baulch, H. M., del Giorgio, P. A., Hampton, S. E., and Karlsson, J.: A synthesis of carbon dioxide and methane dynamics during the ice-covered period of northern lakes, *Limnology and Oceanography Letters*, 3, 117–131, 2018.
- Fedorova, I., Chetverova, A., Bolshiyarov, D., Makarov, A., Boike, J., Heim, B., Morgenstern, A., Overduin, P. P., Wegner, C., Kashina, V., et al.: Lena Delta hydrology and geochemistry: long-term hydrological data and recent field observations, *Biogeosciences*, 12, 345–363, 2015.
- 30  Gibson, J. and Prowse, T.: Isotopic characteristics of ice cover in a large northern river basin, *Hydrological Processes*, 13, 2537–2548, 1999.
- Gibson, J. and Prowse, T.: Stable isotopes in river ice: identifying primary over-winter streamflow signals and their hydrological significance, *Hydrological Processes*, 16, 873–890, 2002.
- 35 Grosse, G., Schirmermeister, L., Siebert, C., Kunitsky, V. V., Slogoda, E. A., Andreev, A. A., and Dereviagyn, A. Y.: Geological and geomorphological evolution of a sedimentary periglacial landscape in Northeast Siberia during the Late Quaternary, *Geomorphology*, 86, 25–51, 2007.
- 

- Grosse, G., Jones, B., and Arp, C.: Thermokarst Lakes, Drainage, and Drained Basins, in: *Treatise on Geomorphology*, edited by Shroder, J. F., pp. 325 – 353, Academic Press, San Diego, 2013.
- Günther, F., Overduin, P. P., Sandakov, A. V., Grosse, G., and Grigoriev, M. N.: Short-and long-term thermo-erosion of ice-rich permafrost coasts in the Laptev Sea region, *Biogeosciences*, 10, 4297–4318, 2013.
- 5 Günther, F., Overduin, P. P., Yakshina, I. A., Opel, T., Baranskaya, A. V., and Grigoriev, M. N.: Observing Muostakh disappear: permafrost thaw subsidence and erosion of a ground-ice-rich island in response to arctic summer warming and sea ice reduction, *The Cryosphere*, 9, 151–178, 2015.
- Harris, C. M., McClelland, J. W., Connelly, T. L., Crump, B. C., and Dunton, K. H.: Salinity and Temperature Regimes in Eastern Alaskan Beaufort Sea Lagoons in Relation to Source Water Contributions, *Estuaries and Coasts*, 40, 50–62, <https://doi.org/10.1007/s12237-016-0123-z>, 2017.
- 10 Hugelius, G., Strauss, J., Zubrzycki, S., Harden, J. W., Schuur, E. A. G., Ping, C.-L., Schirrmeister, L., Grosse, G., Michaelson, G. J., Koven, C. D., O'Donnell, J. A., Elberling, B., Mishra, U., Camill, P., Yu, Z., Palmtag, J., and Kuhry, P.: Estimated stocks of circumpolar permafrost carbon with quantified uncertainty ranges and identified data gaps, *Biogeosciences*, 11, 6573–6593, 2014.
- Karlsson, J., Giesler, R., Persson, J., and Lundin, E.: High emission of carbon dioxide and methane during ice thaw in high latitude lakes, *Geophysical research letters*, 40, 1123–1127, 2013.
- 15 Kelly, C. A. and Chynoweth, D. P.: The contributions of temperature and of the input of organic matter in controlling rates of sediment methanogenesis, *Limnology and Oceanography*, 26, 891–897, 1981.
- Knoblauch, C., Beer, C., Liebner, S., Grigoriev, M. N., and Pfeiffer, E.-M.: Methane production as key to the greenhouse gas budget of thawing permafrost, *Nature Climate Change*, 8, 309, 2018.
- 20 Koven, C. D., Ringeval, B., Friedlingstein, P., Ciais, P., Cadule, P., Khvorostyanov, D., Krinner, G., and Tarnocai, C.: Permafrost carbon-climate feedbacks accelerate global warming, *Proceedings of the National Academy of Sciences*, 108, 14769–14774, 2011.
- Krembs, C. and Engel, A.: Abundance and variability of microorganisms and transparent exopolymer particles across the ice–water interface of melting first-year sea ice in the Laptev Sea (Arctic), *Marine Biology*, 138, 173–185, 2001.
- Lacelle, D.: On the  $\delta^{18}\text{O}$ ,  $\delta\text{D}$  and D-excess relations in meteoric precipitation and during equilibrium freezing: theoretical approach and field examples, *Permafrost and Periglacial Processes*, 22, 13–25, 2011.
- 25 Langer, M., Westermann, S., Walter Anthony, K., Wischniewski, K., and Boike, J.: Frozen ponds: production and storage of methane during the Arctic winter in a lowland tundra landscape in northern Siberia, Lena River delta, *Biogeosciences*, 12, 977–990, 2015.
- Lantuit, H., Atkinson, D., Paul Overduin, P., Grigoriev, M., Rachold, V., Grosse, G., and Hubberten, H.-W.: Coastal erosion dynamics on the permafrost-dominated Bykovsky Peninsula, north Siberia, 1951–2006, *Polar Research*, 30, 7341, 2011.
- 30 Lidstrom, M. E. and Somers, L.: Seasonal study of methane oxidation in Lake Washington, *Appl. Environ. Microbiol.*, 47, 1255–1260, 1984.
- Magritsky, D., Aibulatov, D., and Gorelkin, A.: Regularities in the Space and Time Flow Variations in the Near-Mouth Reach and Delta of the Lena R., *Water Resources*, 45, 12–26, 2018.
- 35 Martinez-Cruz, K., Sepulveda-Jauregui, A., Walter Anthony, K., and Thalasso, F.: Geographic and seasonal variation of dissolved methane and aerobic methane oxidation in Alaskan lakes, *Biogeosciences*, 12, 4595–4606, 2015.
- Mau, S., Blee, J., Helmke, E., Niemann, H., and Damm, E.: Vertical distribution of methane oxidation and methanotrophic response to elevated methane concentrations in stratified waters of the Arctic fjord Storfjorden (Svalbard, Norway), *Biogeosciences*, 10, 6267–6278, 2013.

- McDougall, T. J. and Barker, P. M.: Getting started with TEOS-10 and the Gibbs Seawater (GSW) oceanographic toolbox, SCOR/IAPSO WG, 127, 1–28, 2011.
- Meyer, H., Schönicke, L., Wand, U., Hubberten, H.-W., and Friedrichsen, H.: Isotope studies of hydrogen and oxygen in ground ice-experiences with the equilibration technique, *Isotopes in Environmental and Health Studies*, 36, 133–149, 2000.
- 5 Meyer, H., Derevyagin, A. Y., Siegert, C., and Hubberten, H.-W.: Paleoclimate studies on Bykovsky Peninsula, North Siberia-hydrogen and oxygen isotopes in ground ice, *Polarforschung*, 70, 37–51, 2002.
- Michmerhuizen, C. M., Striegl, R. G., and McDonald, M. E.: Potential methane emission from north-temperate lakes following ice melt, *Limnology and Oceanography*, 41, 985–991, 1996.
- Mook, W.: Principles of isotope hydrology. Introductory course on Isotope Hydrology, Dep. Hydrogeol. Geogr. Hydrol., VU Amsterdam, Amsterdam, 1994.
- 10 Nerem, R. S., Beckley, B. D., Fasullo, J. T., Hamlington, B. D., Masters, D., and Mitchum, G. T.: Climate-change-driven accelerated sea-level rise detected in the altimeter era, *Proceedings of the National Academy of Sciences*, 115, 2022–2025, 2018.
- Overduin, P., Wetterich, S., Günther, F., Grigoriev, M. N., Grosse, G., Schirrmeister, L., Hubberten, H.-W., and Makarov, A. S.: Coastal dynamics and submarine permafrost in shallow water of the central Laptev Sea, East Siberia, *Cryosphere*, 10, 1449–1462, 2016.
- 15 Overduin, P. P., Liebner, S., Knoblauch, C., Günther, F., Wetterich, S., Schirrmeister, L., Hubberten, H.-W., and Grigoriev, M. N.: Methane oxidation following submarine permafrost degradation: Measurements from a central Laptev Sea shelf borehole, *Journal of Geophysical Research: Biogeosciences*, 120, 965–978, 2015.
- Phelps, A. R., Peterson, K. M., and Jeffries, M. O.: Methane efflux from high-latitude lakes during spring ice melt, *Journal of Geophysical Research: Atmospheres*, 103, 29 029–29 036, 1998.
- 20 Powers, S. M. and Hampton, S. E.: Winter limnology as a new frontier, *Limnology and Oceanography Bulletin*, 25, 103–108, 2016.
- Romanovskii, N., Hubberten, H.-W., Gavrilov, A., Tumskey, V., Tipenko, G., Grigoriev, M., and Siegert, C.: Thermokarst and land–ocean interactions, Laptev Sea region, Russia, *Permafrost and Periglacial Processes*, 11, 137–152, 2000.
- Rudd, J. W. and Hamilton, R.: Methane cycling in a cutrophic shield lake and its effects on whole lake metabolism I, *Limnology and oceanography*, 23, 337–348, 1978.
- 25 Sasaki, M., Imura, S., Kudoh, S., Yamanouchi, T., Morimoto, S., and Hashida, G.: Methane efflux from bubbles suspended in ice-covered lakes in Syowa Oasis, East Antarctica, *Journal of Geophysical Research: Atmospheres*, 114, 2009.
- Schirrmeister, L., Kunitsky, V., Grosse, G., Wetterich, S., Meyer, H., Schwamborn, G., Babiy, O., Derevyagin, A., and Siegert, C.: Sedimentary characteristics and origin of the Late Pleistocene Ice Complex on north-east Siberian Arctic coastal lowlands and islands—A review, *Quaternary international*, 241, 3–25, 2011.
- 30 Schirrmeister, L., Grigoriev, M. N., Strauss, J., Grosse, G., Overduin, P. P., Kholodov, A., Guenther, F., and Hubberten, H.-W.: Sediment characteristics of a thermokarst lagoon in the northeastern Siberian Arctic (Ivashkina Lagoon, Bykovsky Peninsula), *arktos*, 4, 13, 2018.
- Schleusner, P., Biskaborn, B. K., Kienast, F., Wolter, J., Subetto, D., and Diekmann, B.: Basin evolution and palaeoenvironmental variability of the thermokarst lake El'gene-K yuele, Arctic Siberia, *Boreas*, 44, 216–229, 2015.
- Schuur, E. A., McGuire, A. D., Schädel, C., Grosse, G., Harden, J., Hayes, D. J., Hugelius, G., Koven, C., Kuhry, P., Lawrence, D. M., et al.: Climate change and the permafrost carbon feedback, *Nature*, 520, 171, 2015.
- 35 Smith, I., Eicken, H., Mahoney, A., Van Hale, R., Gough, A., Fukamachi, Y., and Jones, J.: Surface water mass composition changes captured by cores of Arctic land-fast sea ice, *Continental Shelf Research*, 118, 154–164, <https://doi.org/10.1016/j.csr.2016.02.008>, 2016.

- Souchez, R. and Jouzel, J.: On the isotopic composition in  $\delta D$  and  $\delta^{18}O$  of water and ice during freezing, *Journal of Glaciology*, 30, 369–372, 1984.
- ✖ Strauss, J., Schirrmeister, L., Grosse, G., Wetterich, S., Ulrich, M., Herzschuh, U., and Hubberten, H.-W.: The deep permafrost carbon pool of the Yedoma region in Siberia and Alaska, *Geophysical Research Letters*, 40, 6165–6170, 2013.
- 5 Strauss, J., Boike, J., Bolshiyakov, D. Y., Grigoriev, M. N., El-Hajj, H., Morgenstern, A., Overduin, P. P., and Udke, A.: Russian-German Cooperation: Expeditions to Siberia in 2017, *Berichte zur Polar-und Meeresforschung= Reports on polar and marine research*, 725, 2018.
- Toyota, T., Smith, I. J., Gough, A. J., Langhorne, P. J., Leonard, G. H., Hale, R. J. V., Mahoney, A. R., and Haskell, T. G.: Oxygen-isotope fractionation during the freezing of seawater, *Journal of Glaciology*, 59, <https://doi.org/10.3189/2013JG12J16>, 2013.
- Tranter, M.: Isotopic Fractionation of Freezing Water, pp. 668–669, Springer Netherlands, Dordrecht, [https://doi.org/10.1007/978-90-481-](https://doi.org/10.1007/978-90-481-2642-2_310)
- 10 [2642-2\\_310](https://doi.org/10.1007/978-90-481-2642-2_310), 2011.
- Turetsky, M. R., Abbott, B. W., Jones, M. C., Anthony, K. W., Olefeldt, D., Schuur, E. A., Koven, C., McGuire, A. D., Grosse, G., Kuhry, P., et al.: Permafrost collapse is accelerating carbon release, 2019.
- Valentine, D. L., Blanton, D. C., Reeburgh, W. S., and Kastner, M.: Water column methane oxidation adjacent to an area of active hydrate dissociation, Eel River Basin, *Geochimica et Cosmochimica Acta*, 65, 2633–2640, 2001.
- 15 Walter, K., Chanton, J., Chapin, F., Schuur, E., and Zimov, S.: Methane production and bubble emissions from arctic lakes: Isotopic implications for source pathways and ages, *Journal of Geophysical Research: Biogeosciences*, 113, 2008.
- ✖ Walter, K. M., Zimov, S. A., Chanton, J. P., Verbyla, D., and Chapin III, F.: Methane bubbling from Siberian thaw lakes as a positive feedback to climate warming, *Nature*, 443, 71, 2006.
- Walter, K. M., Smith, L. C., and Stuart Chapin III, F.: Methane bubbling from northern lakes: present and future contributions to the global
- 20 methane budget, *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 365, 1657–1676, 2007.
- Walter Anthony, K., Schneider von Deimling, T., Nitze, I., Frolking, S., Emond, A., Daanen, R., Anthony, P., Lindgren, P., Jones, B., and Grosse, G.: 21st-century modeled permafrost carbon emissions accelerated by abrupt thaw beneath lakes, *Nature Communications*, 9, 3262, <https://doi.org/10.1038/s41467-018-05738-9>, 2018.
- 25 Walter Anthony, K. M. and Anthony, P.: Constraining spatial variability of methane ebullition seeps in thermokarst lakes using point process models, *Journal of Geophysical Research–Biogeosciences*, 118, 1015–1034, <https://doi.org/10.1002/jgrg.20087>, 2013.
- Walter Anthony, K. M., Vas, D. A., Brosius, L., Chapin, F. S., Zimov, S. A., and Zhuang, Q.: Estimating methane emissions from northern lakes using ice-bubble surveys, *Limnology and Oceanography: Methods*, 8, 592–609, 2010.
- Whiticar, M. J.: Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane, *Chemical Geology*, 161, 291–314,
- 30 1999.
- Wiesenburg, D. A. and Guinasso Jr, N. L.: Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and sea water, *Journal of chemical and engineering data*, 24, 356–360, 1979.
- Wik, M., Crill, P. M., Bastviken, D., Danielsson, Å., and Norbäck, E.: Bubbles trapped in arctic lake ice: Potential implications for methane emissions, *Journal of Geophysical Research: Biogeosciences*, 116, 2011.
- 35 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, *Nature Geoscience*, 9, 99, 2016.
- Winkel, M., Mitzscherling, J., Overduin, P. P., Horn, F., Winterfeld, M., Rijkers, R., Grigoriev, M. N., Knoblauch, C., Mangelsdorf, K., Wagner, D., et al.: Anaerobic methanotrophic communities thrive in deep submarine permafrost, *Scientific reports*, 8, 1291, 2018.

Winkel, M., Sepulveda-Jauregui, A., Martinez-Cruz, K., Heslop, J. K., Rijkers, R., Horn, F., Liebner, S., and Anthony, K. M. W.: First evidence for cold-adapted anaerobic oxidation of methane in deep sediments of thermokarst lakes, *Environmental Research Communications*, 1, 021 002, <https://doi.org/10.1088/2515-7620/ab1042>, 2019.

Zeikus, J. and Winfrey, M.: Temperature limitation of methanogenesis in aquatic sediments., *Appl. Environ. Microbiol.*, 31, 99–107, 1976.

5 Zimov, S. A., Schuur, E. A., and Chapin, F. S.: Permafrost and the global carbon budget, *Science*, 312, 1612–1613, 2006.