Editor Decision: Publish subject to minor revisions (review by editor) (13 Dec 2020) by Petra Heil
Comments to the Author:
tc-2019-304 Submitted on 12 Dec 2019
Methane Pathways in Winter Ice of Thermokarst Lake-Lagoon-Coastal Water Transect in North Siberia

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Editor's comments:
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Dear Ines, Paul and co-authors.

Thank you for providing a much improved ms to review. This revised version is much easier to follow.

General comments:
* Pls use SI units. For example: 5-14: Change "10 cm" to 0.1 m".
In most cases we have adopted this requirement, including in all tables and figures. For electrical conductivity, "µS/cm" are almost universally accepted, especially for snow and ice. To avoid rendering our data obscure, we have left these as is.
* All measurements, incl for example in 3.3 Hydrochemistry in ice:
Include full specifications or error characteristics for each sensor. **Done**
* Pls include some information and discussion on the statistical methods used in the manuscript.
See specific comments below.
* The prevalence and impacts of snowloading on the ice should be discussed in some more detail (p20). Can you speculate on this process in a changing climate?
Recent changes to solid precipitation in the Lena Delta suggest that it has been increasing over the past 20 years, and it is projected to do so; since we did not track the distribution of snow over the winter, only observed its thickness at the time and location of coring, and since we do not have a baseline of observations at this location, it is somewhat difficult to speculate using the results we show here on the effects of increased snow load. All coring locations are subject to snow redistribution by wind over the winter. In our study snow loading that resulted in snow integrated in the floating ice was only observed at the eroding bluff of the thermokarst lake, where the bluff acted as a wind-leeward trap for snow.
* Rewrite the Conclusions section to make more impactful.
We have changed the conclusions from:
"CH4 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 CH4 fluxes to the atmosphere. 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, CH4 concentrations were low but, as in all three water bodies, supersaturated with respect to atmospheric concentration.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. CH4 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 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 CH_4-oxidizing micro-organisms.In the third water body, a land-locked thermokarst lake surrounded by Yedoma landscapes, rather uniformδ18O andδDvalues 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_4 concentrations in the lake ice were spatially highly variable. High CH_4 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_4 production and DOC could be a source for CH_4 production in the water or the ice, sediment pore water $\delta^{13}C_{CH4}$ values, and CH_4 and DOCconcentrations should be included in future studies to understand CH_4pathways from their source in comparable water bodies.Furthermore, the comparison between brackish and freshwater water bodies may yield insights into the constraints on CH_4 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_4 oxidation, future studies should include relative proportions of both greenhouse gases."

to

"CH_4 concentrations in the seasonal ice cover of three types of Arctic water bodies (coastal marine, lagoon and lake) differed in ways related to the process of ice formation and its importance as mitigator of CH_4 fluxes to the atmosphere. In the ice of Tiksi Bay, open to the central Laptev Sea throughout the winter and underlain by permafrost, CH_4 concentrations were low but, as in all three water bodies, supersaturated with respect to atmospheric concentration. In the coastal Polar Fox Lagoon, a breached thermokarst lake, ice formation sealed the channel between the lagoon to the sea midway during ice cover development. The brackish water trapped beneath the thickening ice during the winter led to increasing salt content. The CH_4 concentrations and stable isotope signatures strongly suggested that bacterial oxidation takes place at the interface between ice and water, reducing the 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 CH_4-oxidizing micro-organisms. In the third water body, a land-locked thermokarst lake surrounded by Yedoma landscapes, CH_4 concentrations in the lake ice were spatially highly variable. High CH_4 concentrations were local and probably associated with ebullition and snow loading of the ice near an eroding shoreline. Winter ice on the water bodies studied here showed a transition from a brackish water coastal environment, to a basin isolated only by freezing in winter, in which the availability of salt water facilitates oxidation, and finally to an isolated basin in which methane is released at discrete locations in winter. Since CH_4 is produced in the sediment in this setting, and since DOC can be a source for CH_4 production in the water or the ice, future studies including sediment pore water $\delta^{13}C_{CH4}$ values and CH_4 and DOC concentrations should reveal CH_4 pathways from their source in comparable water bodies. Furthermore, our comparison of CH_4 concentrations in brackish and fresh water bodies shows differences between CH_4 oxidation in thermokarst lakes and Arctic lagoons. If CH_4 oxidation takes place at the lower ice surface, as we suggest, future shorter ice cover duration and fresher water below the ice will decrease the CH_4 flux mitigation by winter ice cover in some settings. As carbon dioxide is an important greenhouse gas and the product of CH_4 oxidation, future studies should include relative proportions of both greenhouse gases."

Minor comments:
Throughout manuscript:
Pls change "e.g." to "e.g.," and "i.e." to "i.e.,". **Changed**

2-10: Remove "Generally, ". **Done**
2-17: "Escape" from where? -- I would also prefer to be specific and refer to "ice- and snow-free environments" rather than "in summer".
Changed to: " While gas may easily escape from thermokarst lakes to the atmosphere in ice- and snow-free periods, an ice cover forms a barrier for 9 to 10 months in winter. During the wintertime, gas bubbles are trapped under and eventually within the ice."
3-16: Instead of "71° 40' - 71° 80' N and 129° 00' - 129° 30'E" decimal lat and lon would be more contemporary. **Corrected**
3-27: Change "less than 11 m in general" to "largely less than 11 m deep". **Changed**
3-28: Change "is located southeast" to "is located to the southeast". **Changed**
3-28: Remove "the" from "the Bykovskaya Channel". **Removed**
3-33: Correct "can be disturbed by storm events" to "may be disturbed by storm events". **Changed**
4-Cap1: What does "(c)" in "((c) DigitalGlobe)." mean? **Corrected**
4-1: Correct "Tidally-based sea-level oscillations" to "Sea-level oscillations driven by tides" **Changed**
4-7: Would you turn "Tab. 1 lists characteristics of the studied water bodies." into an active statement about the water bodies or their characteristics please? **Changed**
5-3: Correct "cores were drilled" to "cores were recovered". **Changed**
5-5: Pls make the statement "Tab. 1 lists the mean ice thicknesses of the sampled ice core for the locations." an active one about the ice cores and their thickness. **Changed**
5-8: Correct "temperature was measured" to "vertical temperature profiles were obtained". **Corrected**
5-8: Correct "every 10 cm," to "every 0.1 m,". **Corrected**
5-12: Can you pls provide the specifications of the sensors used in this study? E.g., resolution and accuracy of the CTD sensors? **Added "The accuracy and resolution of the devices were ±0.05 and 0.01 ◦C, respectively, for temperature and ±5 and 1 µS/cm−1 for electrical conductivity. "**
5-15: Change "(over 1-2 days)." to "for 1 -- 2 days." **Changed**
6-23: Correct "An δ 18 O-δD plot gives" to "The comparison of δ 18 O to -δD provides". **Corrected**
6-26: Clarify "equilibrium conditions": Equilibrium of what? **changed to "equilibrium freezing conditions."**
6-29: Change "for the first ice" to "for new ice". **As it stands, "first ice" refers to the first ice formed and not to new ice or ice that formed at a later date - this is an important distinction.**
7-7: Correct "kept cold" to "kept cool". **Corrected**
8-7: Correct "The photos were rectified" to "The images were orthorectified". **Corrected**
8-11: Provide info on "R environment". --> I.e., that is is a software based on xxx to do yyy or similar. See your info on AGISoft. --
Added "(a free software environment with interpreted computer language for statistical computing and graphics, www.r-project.org)"
Provide info on the 14 distance classes and how they affect the kernel calculations. (So there are no surprises to the reader when "class A seeps" etc. are noted further down in the ms.)
We agree and added information on how we calculated 14 distance classes. The classes do not affect the density function that is based on the original data distribution. To explain better we added the following text: "We chose 14 distance classes in a Kernel density estimation guided by two criteria: 1) only allow bin size in which each bin is represented by seep data, and 2) maximize visualization of the density trend over the profile."
8-15: Remove "densely". **Removed.**

8-19: Correct "was identified" to "were identified". **Corrected**
8-25: Correct "until the depth of about 112 to 114 cm." to "down to a depth of ca 1.12 to 1.14 m." **Corrected**
8-25: What is a "solid" snow cover. This is not a technical term. Change to something like "The snow cover generally had a hard surface and was characterized...".
Changed to: "The snow cover was hard-packed and characterized by different melt forms."
8-26: Rewrite "thickness of the snow-layer ranged from 0 cm": The thickness cannot be Zero. Instead there is an absence of snow.
Changed to: "Snow was either absent (LK-2 and LK-3) or 0.15 m (LK-4), 0.23 m (LK-1) and 0.92 m (LK-5) thick."
8-26: Change "For all cores, no algae inclusions were visible (Strauss et al., 2018)." to "In none of the cores algae inclusions were detected (Strauss et al., 2018)." **Changed**
9-Fig2: Explain the blue and grey shading. I assume they are for the water and the ice. - It appears that the ice thickness is constant for each profile. Pls correct.
That is correct. The grey colour shows the mean ice thickness for each water body, since we did not measure ice thickness between boreholes. Changed caption to: "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 ice layer (grey shading shows mean water body ice thickness) and the water column below the ice is indicated in blue. The position of the bubble transect at Goltsovoye Lake is represented with a dashed red line."
12-Tab2: Rename "site" or "sampling site" to "transect". **Changed**
12-7: Add close bracket to read "(Fig. 5)." **Changed**
14-14: Remove "values" from "values ranged". **Changed**
14-14: Change "The values" to "These values". **Changed**
14-14: Correct "smaller" to "lower". **Corrected**
14-15: Correct "for the other" to "of the other". **Corrected to "of the cores of the other locations"**
14-15: Remove "values" twice and "the" from "In LG, the". **Removed**
14-17: Remove "The" and "values". **Removed**
14-17: Change "The pattern is similar but inverse to the CH 4 concentrations." to "The pattern is inverse to that of the CH 4 concentrations." **Changed**
14-20: Correct "is quite constant." to "is relative constant." **Corrected**
14-25: Change "A seasonal ice cover is" to "The seasonal ice cover forms". **Changed**
14-26: Correct "covered by ice for 9 months of the year" to "typically ice covered for about 9 months every year". **Corrected**
14-28: Correct "all increase," to "all increased,". **Corrected**
14-30: Correct "shortens" to "will shorten". **Corrected**
16-21: Correct "whens" to "when". **Corrected**
17-Fig7: Change "studied in this paper" to "under investigation". **Changed**
18-26: Correct brackets: One more closing than opening brackets. **Changed to "(4.8 m to 8.3 m below the sediment surface, Angelopoulos et al., 2020)".**
18-27/28: Not a sentence. Pls rewrite. **Changed to "For ice that formed before the lagoon was separated from the sea (above 0.6 m), the isotopic signature indicates freezing under equilibrium conditions (Lacelle, 2011), with a slope of 8.2 between δ18O and δD (Fig. 8, Tab. 3)."**
18-last para: The use of "later (deeper)" and "earlier (upper)" and similar is confusing. Pls rewrite.
We have simplified by removing references to "earlier/later" ice and by referencing to ice core position (upper vs lower, relative to specific depth).
19-6: Use SI units: "60 cm". -- Throughout manuscript. **Changed**
19-31: Correct "euqilibrium" to "equilibrium". **Changed**

20-12: Replace "This circumstance clearly shows" with "Our data demonstrate". **Changed**
20-16: Rewrite "involvement of snow". **Changed to "indicate snow as a source".**
20-32: Correct "Fi. 6" to "Fig. 6". **Corrected**
29-22: Should "Walter Anthony, K.," read "Walter Anthony, K.M.,"? - not least for consistency?
We agree, but this is not how the different journals have cited the same author. Katey's surname has changed with marriage and both are used in citations, and some journals neglect to use her middle initial. To make the papers findable, we follow the citation provided by the journals.
References: Not checked, nor cross searched.

For final publication, the manuscript should be
accepted as is
accepted subject to **technical corrections**
accepted subject to **minor revisions**
reconsidered after **major revisions**
I am willing to review the revised paper.
I am **not** willing to review the revised paper.
rejected

Suggestions for revision or reasons for rejection (will be published if the paper is accepted for final publication)
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. The authors have taken considerable care to respond to the comments of the reviewers and (in my opinion) the revised version is much improved. The authors are much clearer about the aims of their study, and the description of the science and conclusions is clarified. The paper is now easy to read and almost without typographic error.

As before I alert the editor to the fact that I am not expert on the suite of chemical techniques involved in the study.

I have a few remaining minor comments.

Comment 1: The title of the study (and I do prefer the new title) and the focus of the Introduction and Discussion is on winter ice. However the ice is sampled in spring. I would like some discussion regarding why the authors believe that the measurements are representative of winter. For example is the sampled ice thickness close to the maximum seasonal ice thickness? Is the ice still growing at the time of sampling? For those readers not familiar with the progress of the seasons in this geographic area, it would be useful to relate the seasons to the dates of the year. It would be very useful if the dates of sampling were given in Table 1.
Added:
"Ice growth ceases when heat flux to the atmosphere slows, and is negligible by the end of April at our study site. Ice was cored at close to its maximum thickness to include almost the entire winter record of freezing. Ice cores were drilled on April 8, 2017 (LK), April 10, 2017 (LG) and April 11, 2017 (BY)."

Comment 2: I would still like more information about transport and storage of the cores (for example on p. 5, Sect 3.2). What was the approximate temperature during transport; how long between taking cores and performing the analyses? It is important for the reader to be convinced that there have not been irreversible changes during transport.
Added:
"Cores were stored in freezers after drilling, in a permafrost tunnel (*lednik*) while waiting for transport and then transported by refrigerated truck at freezer temperatures (-18°C). We did not record temperature during transport, but based on a comparison of photos of the cores after drilling and in the laboratory, the structure and ice morphology of the cores were preserved during transport. We are therefore confident that not even surficial melting took place. "
We had included the timing of sampling and analyses, but the other reviewer asked that it be removed.

Comment 3: Could snow cover be added to Fig. 2 to help the reader understand the temperature measurements and the snow loading described in section 5.3?
Snow cover is in general not thick enough to be distinguishable in Figure 2, we do not have data beyond depths at drilling locations and snow is redistributed throughout the winter. We fell that portraying the thickness at the time of sampling would be misleading. The importance of snow at our sites is captured in the ice record as described in the discussion. We therefore prefer not to include it in Fig. 2.

Technical Corrections
p. 1: Abstract: Abstract is now much clearer.
Thank you.

p. 5, Table 1: In relation to statement that winter ice, please could you put dates of sampling in the Table.
Dates have been added to Section 3.2

p. 5, Sect 3.1: We are told the ice was sampled between Apr 5 and 12. But how is April related to winter ice?
See above added text.

p. 6, Line 32: "prior to freezing" or "during freezing"?
Changed from "changes prior to freezing" to "changes as freezing progresses."

p. 7, Line 7: "2 months between sampling and measurement" Thank you – this is the sort of information that I consider important. But I was not sure whether "sampling" meant taking the core or filling the glass bottles.
Replaced "sampling" with "filling the sample bottles".

p. 7, Line 9: replace "shaken" with "shaking"
Done

p. 8, Line 4: Fig. 2 (rather than Fig. 3). Fig. 3 is cited before Fig. 2.
Changed to "(Fig. 2 & 3)".

p. 8, Line 19-21: Paragraph break seems to have been placed part way through the description of BY ice. Please check.
Checked and changed

p. 8, Line 20: Begin sentence "On the ice of Tiksi Bay, the snow thickness…"
Done

p. 12, Lines 1-2: A rather strange sentence "While the …. (below 80-90 cm)" I think this sentence is unnecessary but I leave this as a decision of the authors.
We have deleted the sentence.

p. 12, Line 7: "(Fig. 5)"
Changed

p. 14, Lines 7-9: This is a repetition of Lines 5-7.
Deleted

p. 14, Lines 19-21: This could be written more concisely and without repetition.
Changed from:
"In LK, the δ13C-CH4 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 δ13C-CH4 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 20 constant. In LK-1, LK-2 and LK-4, the δ13C-CH4 values had a mean of −43.3 ‰ and were uniform (±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 4 concentrations."
to:
"In LK-1, LK-2 and LK-4, the δ13C-CH4 values had a mean of −43.3 ‰ and were uniform (±2.2 ‰) with depth, whereas values in LK-3 and LK-5 ranged from −91.6 to −12.3 ‰, with a strong variability within and between the two cores (Tab. 2). A greater variability was observed for CH 4 concentrations."

p. 14, Lines 25-26: Please tell us which months and how these months relate to winter and spring (see Comment 1).
See above text.

p. 16, Line 6: Please tell us when the onset of ice formation took place on BY.
Fall cloud cover and storm events make it difficult to say when the lasting ice cover initiated at any location.

p. 16, Line 7: Please mark Muostakh Island on Fig. 1.
Muostakh Island is not shown on Fig. 1. Changed to "...south of Cape Muostakh.", which is inclusive.

p. 16, Line 21: delete "s" from "whens"
Done.

p. 16, Line 21-22: "The difference between both is within 1‰ for a large range of ice growth rates." I don't know what is meant by "both". Please clarify.
This sentence has been deleted. The previous sentence makes the actual point.

p. 16, Line 35: I could not find a reference to Fig. 7 in the text. I think Fig. 8 is referred to before Fig. 7.
Corrected.

p. 18, Line 1-4: Why should there be mixing of saline water with additional water of meteoric origin when the ice was 90 cm thick? At what approximate time of year did this occur? Why would it take place if additional river outflow was unlikely at that time? Please speculate on a physical reason for your observations.
Added: "Lena River water from much further south is carried into Tiksi Bay throughout the year and plots close to the Local Meteoric Water Line (slope 7.3, Juhls et al., 2020). In April this flux is still at base flow levels but contributes to the least dense surface water layer beneath the ice. "

p. 18, Line 26: Formatting of Angelopoulos et al

Done.

p. 19, Line 20-23: "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."
I am not convinced by this explanation because the temperature of the ice at depths greater than 100 cm are higher for LK than LG and the air temperature takes some time to propagate to this depth. I suspect that the thickness of the snow cover is much more important since ice has a higher thermal conductivity than snow. More detail on dates of sampling (Comment 1) and a description of the snow cover (Comment 3) may help explain these observations.
Please consider the primary argument that we make, which is that the water in LG is colder than in LK, due to cooling below 0°C as freezing progresses. This most likely drives temperatures deeper in the ice, for example at 100 cm as you point out, which reflect conditions prior to drilling, not air temperature changes between drilling dates. The snow thickness on LK ranged from 0 to 0.92 m, but all of the ice temperature profiles are grouped closely together when compared to LG (0.08 to 0.23 m), so that the water body, rather than the local snow thickness, is dominant in explaining the observed temperature profiles. We have added all of the snow thicknesses to the ice morphology description.

p. 19, Line 31: "equilibrium"
Changed.

p. 19, Line 31 & p. 20, Line 14-30: Snow loading discussion is very interesting. Please see Comment 3.
Please see above answer. We must restrict ourselves to the evidence of snow loading and inclusion in the ice record.

p. 23, Fig 9: I am surprised that the dashed line is the fit to the plus markers. This figure might be clearer and the fit more obvious if you plotted a linear fit of (™13CCH4-(™13CCH4)0) versus lnf
To be clear, the line is not a fit to the symbols nor an indication of correlation. The lines show the modelled Rayleigh fractionation using only the values for initial d13C-CH4 and the alpha value described in the text. To make this clearer, we have increased the length of the modelled values to lower fractions and changed the caption to: "Figure 9. Observed δ13C-CH4 and CH4 concentrations in the ice of Polar Fox Lagoon (LG) for shallow and deep ice (above and below 0.6 m, respectively, shown as symbols). The lines show δ13C-CH4 calculated based on Rayleigh fractionation during oxidation (Eq. 1). For these modelled values, α was set to 1.004 and the initial δ13C-CH4 values were 195 nM (0 to 0.6 m, dotted line) and 450 nM (>0.6 m, solid line) with initial isotopic signatures of −80‰ and−70‰, respectively."