We would like to thank again the reviewers and the Editor for their careful review of our major revision. Our point-by-point responses to all the comments and annotations are presented below. The comments from the reviewer are shown in black, and our responses in red. Where indicated, additions to the manuscript are shown in blue and deleted text is indicated by red strikethrough, and the pages and line numbers are based on our revised (non-track) manuscript. The English was further improved by a professional editing company.

==========

Comments from the reviewer #1 and our responses:

1) GENERAL COMMENTS

The authors made a notable effort to deal with all the comments and suggestions I made in my first review, and I thank them very much for that.

Re. general comments #2 (site map, field and lab protocol pictures) and #4 (statements not supportedby figures, data or references), the authors answered to the concerns I raised, and I have nothingmore to add.

➔ We thank the reviewer for his/her positive assessment of our revision.

Re. general comment #1 (broad-audience impact), I still think that this work is relevant for a rather specialized audience, but I understand the points brought by the authors. I'll let the final decision to the Editor and I'm OK with the acceptance of the manuscript (after minor revision, see below).

➔ As addressed in our major revision, we believe that our findings are important in broad community working on permafrost as well as climate sciences. We thank the reviewer for his/her understanding.

Re. general comment #3 (main text structure, methods vs. results sentences), I totally get it that thispaper mainly focuses on experimental/methodological aspects, as the authors say. In fact, themanuscript reads easily as is (as I already mentioned in my first review). Still, many sentencesappearing in the Results and Discussion section are indeed associated to the work conducted in thelab, i.e. methods. If the Editor agrees to accept this non-conventional structure, I am OK with that.

➔ We agree that the conventional structure is an effective way to organize scientific articles. However, each experiment has own rationale and our manuscript was written following the logical flow, which would be difficult to maintain in the conventional format. Thus, we believe that current structure is best for our manuscript.

I made a few (minor) specific comments, see below.

General question: What is the difference between 'Appendix' figures (included in the submittedmanuscript) and 'Supplementary' figures (appearing in a separate file)? Why not group them all in the same category?

➔ We prefer to put the methodological aspects (i.e., correction and uncertainty estimate) and the results of complementary experiments in Appendix rather than Supplement for readers to find them easily. Instead, we put the maps, pictures, and schematic diagrams in Supplement as a separate file to reduce the total length of main text, but the readers are still accessible if they are interested. We believe this criteria is not unreasonable, but certainly we will follow the Editor's decision.

A final, important remark: according to the journal's guidelines, the data availability question (P26,L467-468, see below) should be settled BEFORE publication, not after.

➔ We submitted our dataset to Zenodo data repository, and added citation following the journal's policy.

2) SPECIFIC COMMENTS AND EDITORIAL SUGGESTIONS

P= page number, L = line number.

P1, L18-19. « However, existing gas extraction methods HAVE not been well tested. »

➔ Done.
➔ However, existing gas extraction methods ~~has~~have not been well tested.

P2, L30-31. Carbon and nitrogen have just been mentioned in the line above, so I suggest using 'C'and 'N' from now on (« … temporarily removing this frozen C and N from active global cycles. »).

➔ Revised as suggested.
➔ Permafrost preserves large amounts of soil carbon (C) and nitrogen (N) in a frozen state (e.g., Hugelius et al., 2014; Salmon et al., 2018), temporarily removing this frozen ~~carbon~~C and ~~nitrogen~~N from active global cycles.

P4, L98. If we are talking about the gas mixing ratios of the ice-wedge ice, then we should read « … inthat ITS gas mixing ratios are not homogenous… ».

➔ Done.
➔ ~~The i~~Ice-wedge ice is ~~most~~ different from polar ice cores~~,~~ in that ~~their~~its gas mixing ratios are not homogeneous (e.g., Kim et al., 2019), which may hinder exact comparison with results from adjacent ice samples.

P8, L190-193. I don't understand this sentence. Maybe it's related to the phrase 'of in centimeter scales'. What does it mean, this 'OF IN' phrase? Is there a word missing here, or a word that should not appear?

➔ We revised the phrase as follows.
➔ We note that the heterogeneous distribution of gas mixing ratios ~~of in~~at the centimetre scale~~s~~ (Kim et al., 2019) may not have been completely smoothed out by our sub-sample selection, although we randomly chose 8–12 ice cubes for each measurement.

P11, L240-241. In my first review I suggested to display this information as a figure, rather than in abusy table (former manuscript version: P11, L236-237). The authors prefer to keep it as a table,arguing that the large ranges in CH4 and N2O mixing ratios make figures less readable. To me, the supplementary figure provided by the authors in their reply (same page, just below) looks great, andwe see the significant differences not only between sites (central Yakutia, eastern Siberia, Alaska), but also between extraction techniques ('hit5' vs. 'hit100'). I thus prefer by far a figure, compared to atable. However, if the Editor also favors a table, then I would suggest to at least add some basic stats (min-max-mean-SD) below each of the 3 sites, so that the reader can easily and efficiently have a 'bigpicture' view of these data.

➔ We replaced Table 1 with the figure we showed in our previous response, and the figure caption has been changed accordingly. Instead, we moved the original Table 1 to Appendix because our main text still refers to the Table, for example, the hit100/hit5 ratios.

P14, L311. « Even though a small of contamination does exist, … » (remove 'of').

➔ Done.

➔ Even though ~~a small of~~minor contamination ~~does exist~~did occur, its effects ~~have~~ had already been subtracted via blank correction and taken into account in the overall error estimation (see Appendix).

P17, L357-359. Please add a reference (re. solubility of N2O in water compared to CH4).

➔ We added below citation in the sentence as well as in the reference list.

➔ Fogg, P. G. T., and Sangster, J.: Chemicals in the Atmosphere: Solubility, Sources and Reactivity, John Wiley & Sons, Inc., 2003.

P20, L409. Repetition of the bullet point just above (« Our findings indicate… »). Suggestion: « These results indicate/suggest that… ».

➔ We agree with the reviewer, however, we revised the sentence as below because the previous phrasing had no add value and therefore was unnecessary. As this sentence is already a part of the conclusion section where we are already summarizing our results.

➔ ~~Our findings indicate that the s~~Saturated NaCl solution is unnecessary ~~to prevent~~for preventing microbial activity during melting, as employed by, e.g., Cherbunina et al. (2018).

P26, L467-468. Data availability: How to make sure that the data will indeed be uploaded in a publicrepository (e.g., Pangaea) only AFTER publication? For several journals now, including TC, thedatasets must be CITED within the text and included in the reference list (including an individual DOI):https://www.the-cryosphere.net/about/data_policy.htmlI thus suggest submitting the datasets to a public repository with the FAIR approach ('findable,accessible, interoperable, and reusable'), and launch the process BEFORE the manuscript isaccepted for publication. I let the Editor take the final decision about this.

➔ Please refer to our response above.

3) FIGURES AND TABLES

See general comment above: some figures are in the Appendix, and some others (map, field and labprotocol pictures) appear separately in the Supplementary document. Why?

➔ Please find our response to general comment.

Brief Communication: The reliability of gas extraction techniques for analysing CH_4 and N_2O compositions in gas trapped in permafrost ice -wedges

Ji-Woong Yang[1*], Jinho Ahn[1], Go Iwahana[2], Sangyoung Han[1], Kyungmin Kim[1] and Alexander Fedorov[3,4]**

[1]School of Earth and Environmental Sciences, Seoul National University, Seoul, South Korea
[2]International Arctic Research Center, University of Alaska, Fairbanks, USA
[3]Melnikov Permafrost Institute, Russian Academy of Science, Yakutsk, Russia
[4]North-Eastern Federal University, Yakutsk, Russia
*Now at: Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris-Saclay, Gif-sur-Yvette, France
**Now at: Division of Earth and Planetary Materials Science, Department of Earth Science, Graduate School of Science, Tohoku University, Sendai, Japan

Correspondence: Jinho Ahn (jinhoahn@snu.ac.kr)

Abstract. Methane (CH_4) and nitrous oxide (N_2O) compositions in ground ice may provide information on their production mechanisms in permafrost. However, existing gas extraction methods ~~has~~have not been well tested. We tested conventional wet and dry gas extraction methods using ice -wedges from Alaska and Siberia~~. We,~~ finding that both methods can extract gas from the easily extractable parts of the ice (e.g., gas bubbles), and yield similar results for CH_4 and N_2O mixing ratios. We also ~~find~~ found insignificant effects of microbial activity during wet extraction. However, both techniques ~~are~~ were unable to fully extract gas from the ground ice, presumably because gas molecules adsorbed onto or enclosed in soil aggregates are not easily extractable. Estimation of gas production in subfreezing environment of permafrost should consider ~~the~~ such incomplete gas extraction.

1. Introduction

Permafrost preserves large amounts of soil carbon (C) and nitrogen (N) in a frozen state

(e.g., Hugelius et al., 2014; Salmon et al., 2018), temporarily removing this frozen ~~carbon~~C and ~~nitrogen~~N from active global cycles. Therefore, future projections of permafrost stability are of great interest, particularly because thawing permafrost may lead to decomposition and/or remineralis~~z~~ation of the buried soil C and N and their abrupt emission into the atmosphere in the form of greenhouse gases (GHGs) ~~—~~such as carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), which in turn can trigger positive feedbacks (e.g., Salmon et al., 2018). In addition, ~~the~~ projected polar amplification (e.g., Masson-Delmotte et al., 2013) may strengthen these positive feedbacks. However, the processes responsible for in-situ C and N remineralis~~z~~ation and GHG production in ground ice are poorly understood, despite the fact that ground ice accounts for a substantial portion (up to ~~approximately~~ ~40–90% by volume) of Pleistocene ice-rich permafrost, or Yedoma (e.g., Kanevskiy et al., 2013; Jorgenson et al., 2015).

The gases trapped in ground ice allow unique insights into the origin of ground ice and evidence for in-situ microbial aerobic and anaerobic respiration~~s~~ (Boereboom et al., 2013; Kim et al., 2019; Lacelle et al., 2011). Among others, the GHGs in ground ice may provide detailed information on in-situ biogeochemical processes responsible for GHG production (i.e., methanogenesis, nitrification, and denitrification) (e.g., Boereboom et al., 2013; Kim et al., 2019). However, the relevant analytical methods remain poorly scrutinis~~z~~ed. Boereboom et al. (2013) utilis~~z~~ed the conventional melting-refreezing method (wet extraction) used in polar ice core analyses~~. In this technique~~, in which the ice samples were melted under a vacuum to liberate the enclosed gases~~,~~ and then refrozen to expel the dissolved gases present in the meltwater. Other studies conducted by Russian scientists used an on-site melting method, in which a large (1–3 kg) block of ground ice sample was melted in a saturated sodium chloride (NaCl) solution~~,~~ in order to minimis~~z~~e gas dissolution (Arkhangelov and Novgorodova, 1991). A recent study instead used a dry extraction technique to prevent ~~the~~ microbial activity during

wet extraction (Kim et al., 2019), which employed a needle ~~-~~crusher in a vacuum to crush approximately 10 g of ice sample without melting (Shin, 2014).

In this study, for the first time, we tested the reliability of both wet and dry extraction methods for CH_4 and N_2O mixing ratios and contents (volume or moles of gas in a unit mass at standard temperature and pressure conditions (STP)) using permafrost ground ice samples. Ice-wedge samples from Alaskan and Siberian permafrost were used because ice wedges are one of the most abundant morphological features of massive ground ice, consisting of approximately 5~~ to -~~50% by volume of the upper permafrost (Kanevskiy et al., 2013; Jorgenson et al., 2015). More specifically, ~~this study~~we ~~aims~~ aimed to address the following scientific questions: (1) Do wet and dry extraction methods yield different results? (2) Are the melting-refreezing results affected by microbial activity during gas extraction? (3) How effectively does the wet/dry extraction extract gases from ice wedges? To address the first question, we compared CH_4 and N_2O results from dry and wet extractions ~~were compared~~. For the second question, we applied the wet extraction method to both biocide-treated and control samples. Finally, for the third question we carried out tests with and without extended ~~number of hitting ice with a~~ needle system hits in a crushing chamber, as well as additional dry extraction from ice samples that had been degassed by our wet extraction method.

2. Materials and ~~Methods~~methods

2.1. Ice samples and sample preparation

The ice-wedge samples used in this study were collected from Churapcha, Cyuie (central Yakutia), and Zyryanka (north-eastern Yakutia) in Siberia, as well as from northern Alaska (Supplementary Figure 1). The Churapcha site (61.97°N, 132.61°E) ~~is~~ was located approximately 180 km east of Yakutsk~~.~~ while ~~The~~ the Cyuie site (61.73°N, 130.42°E) ~~is~~ was located approximately 30 km southeast of Yakutsk. The Cyuie samples were collected from

two outcrops (CYB and CYC) (Kim et al., 2019). At each site, 30 cm long ice-wedge cores were drilled perpendicular to the outcrop surface (Supplementary Figures 2 and 3).

Zyryanka is located in the southern boreal region of the Kolyma River, at the junction of the Chersky and Yukaghir Ranges, in a region affected by thermokarst development (Fedorov et al., 1991). Site A (Zy-A) ~~is~~ was located on a tributary of the Kolyma River, ~~approximately~~ ~22 km north of Zyryanka. Site B (Zy-B) ~~is~~ was ~~approximately~~ ~14 km west of the start of the Kolyma tributary, which begins ~11 km north of Zyryanka. Site F (Zy-F) ~~is~~ was located ~~approximately~~ ~4 km west of the tributary that leads to site B. The ground ice samples were collected from riverbank walls exposed by lateral erosion using a chainsaw (Supplementary Figure 4). Most of the outcrops that were sampled for ground ice were on the first (lowest) terrace of the river.

For the Alaskan sampling locations, Bluff03 (69.40°N, 150.95°W) and Bluff06 (69.14°N, 150.61°W) ~~are~~ were located in the Alaska North Slope region, ~~approximately~~ ~120 and ~150 km from the Arctic Ocean, or ~100 and ~70 km northwest of the Toolik Field Station (68.63°N, 149.59°W), respectively. Samples from Bluff03 were collected by chainsaw from ~~the~~ bluff walls that had developed by gully formation~~s~~ on a gentle slope of the Yedoma ~~using a chainsaw~~. Samples ~~of~~ from Bluff06 were collected from outcrops within eroded frozen peatland in a thaw lake basin (Supplementary Figure 5). All ~~the~~ ice-wedge samples used in this study were stored in a chest freezer at < -18 °C before analysis.

~~The i~~Ice-wedge ice is ~~most~~ different from polar ice cores~~,~~ in that ~~their~~its gas mixing ratios are not homogeneous (e.g., Kim et al., 2019), which may hinder exact comparison with results from adjacent ice samples. We therefore randomly mixed sub-samples to reduce the effect of the heterogeneous gas composition distribution (the "random cube" method, hereafter). ~~Approximately~~ ~100–200 g of an ice-wedge ~~wedge~~ sample ~~was~~ were cut into 25 ~~to~~ 50 cubes of 3–4 g each~~, and;~~ for each experiment, ~10 ~~to~~ 12 cubes were randomly chosen so that the

105 total weight of the sub-sample was ~40 g.

106 **2.2. Gas extraction procedures**

107 ***Dry extraction (needle crusher)***

108 For dry extraction, we used a needle-crusher system at ~~the~~ Seoul National University
109 (SNU, Seoul, South Korea) (Shin, 2014). In brief, 8~~~~13 g of ice sample were crushed in a
110 cold vacuum chamber (extraction chamber). The ice samples were usually hit five times by the
111 needle set. The temperature within the extraction chamber was maintained at -37 °C ~~by~~ using
112 a cold ethanol-circulating chiller. The extracted gas was dried by passing it through a water
113 vapour~~r~~ trap at -85 °C and cryogenically trapping it in a stainless-steel~~-steel~~ tube (sample tube)
114 at approximately -257 °C using a helium closed-cycle refrigerator (He-CCR). Since the
115 extraction chamber cannot accommodate ~40 g of ice at once, the ~40 g of random cube sub-
116 samples were extracted using three sequential extractions and the gas liberated from each
117 extraction was trapped in a sample tube.

118 Following extraction, the sample tubes were detached from the He-CCR, warmed to
119 room temperature (~20 °C), and attached to a gas chromatograph (GC) equipped with an
120 electron capture detector (ECD) and a flame ionis~~z~~ation detector (FID) to determine the mixing
121 ratios of CH_4 and N_2O. Details of the GC system are given in Ryu et al. (2018). The daily
122 calibration curves were established using working standards of 15.6 ± 0.2 ppm CH_4, 10000 ±
123 30 ppm CH_4, 2960 ± 89 ppb N_2O, 29600 ± 888 ppb N_2O, and a modern air sample from a
124 surface firn at Styx Glacier, Antarctica (obtained in November 2016), which was calibrated as
125 1758.6 ± 0.6 ppb CH_4 and 324.7 ± 0.3 ppb N_2O by the National Oceanic and Atmospheric
126 Administration (NOAA).

127

128 ***Wet extraction (melt-refreeze)***

129 For the control and $HgCl_2$-treated wet extraction experiments, a melting-refreezing wet

extraction system at SNU was employed (Yang et al., 2017; Ryu et al., 2018). The gas extraction procedure ~~is~~ was identical to the procedure described in Yang et al. (2017) and Ryu et al. (2018), except for the sample gas trapping procedure (see below). Ice-wedge sub-samples of ~40 g (composed of 10–12 ice cubes for each) were placed in a glass container welded to a stainless-steel ~~steel~~ flange (sample flask), and the laboratory air inside the sample flasks was evacuated for 40 min. The sample flasks were then submerged in a warm (~50 °C) tap water bath to melt the ice samples. After melting was complete, the meltwater was refrozen by chilling the sample flasks with cold ethanol (below -70 °C). The sample gas in the headspace of each sample flask was then expanded to the volume-calibrated vacuum line to estimate the volume of extracted gas, and trapped in a stainless-steel sample tube by the He-CCR device. ~~In this study, w~~We attached the He-CCR device to our wet extraction line and the gas samples in the flasks were cryogenically trapped. There were two reasons for using He-CCR instead of direct expansion to a GC ~~are twofold~~: (1) to better compare the dry and wet extraction methods by applying the same trapping procedure, and (2) to maximis~~z~~e the amount of sample gas for GC analysis, because ~~the~~ gas expansion from a large flask allows only a small fraction of gas to be measured by the GC.

For biocide-treated tests, 1.84 mmol of mercuric chloride ($HgCl_2$) was applied per unit kilogram of soil, following established procedures for soil steriliszation (Fletcher and Kaufman, 1980). We obtained the average dry soil mass (0.33 g) from the leftover meltwater samples of the previous wet extractions, which were carried out for comparison between dry- and wet extractions. Taking ~~the average dry soil mass (0.33 g)~~this into account, we added 24 µL of saturated $HgCl_2$ solution (at 20 °C) to the sample flasks. The flasks with $HgCl_2$ solution were then frozen in a deep freezer at < -45 °C to prevent the dissolution of ambient air into the solution during ice sample loading. After the wet extraction procedure was complete, the extracted gas was trapped in a sample tube and the CH_4 and N_2O mixing ratios were determined

using the same GC-ECD-FID system as the dry-extracted gas. The resulting CH_4 and N_2O mixing ratios ~~have~~ were~~not~~ not ~~been~~ corrected for partial dissolution in ice melt in the flasks, because CH_4 and N_2O trapped in refrozen ice ~~are~~ were negligible compared to the ranges of the systematic blanks (see Appendix).

2.3. Gas content

The analytical methods described previously ~~are~~ were used ~~for~~ to ~~determining~~ determine the mixing ratios of CH_4 and N_2O in the extracted gas. To convert these mixing ratios into moles of CH_4 and N_2O per unit mass of ice-wedge sample (CH_4 and N_2O content, respectively, hereafter) ~~requires~~ required data regarding the amount of gas extracted. ~~The~~ As the gas content is a measure of gas volume enclosed in a unit mass of ice sample at STP (in mL kg_{ice}^{-1})~~. Thus~~, the CH_4 and N_2O contents can be calculated using the gas content, the total mass of the random cube ice, and the gas mixing ratio. The gas content in the control and $HgCl_2$-treated wet extraction experiments was calculated from the temperature and pressure of the extracted gas and the internal volume of the vacuum line. The details of the extraction system and correction methods used for estimating gas content are described in Yang (2019). Similarly, the gas content of the dry extraction samples was also inferred from the volume and pressure of gas inside the vacuum line once the sample tube was attached to the line for GC analysis. The uncertainties of the calculated CH_4 and N_2O contents were calculated by using the error propagation of the blanks and gas content uncertainties (see Appendix for uncertainty estimation of the blank corrections and gas contents).

2.4. Dry soil content

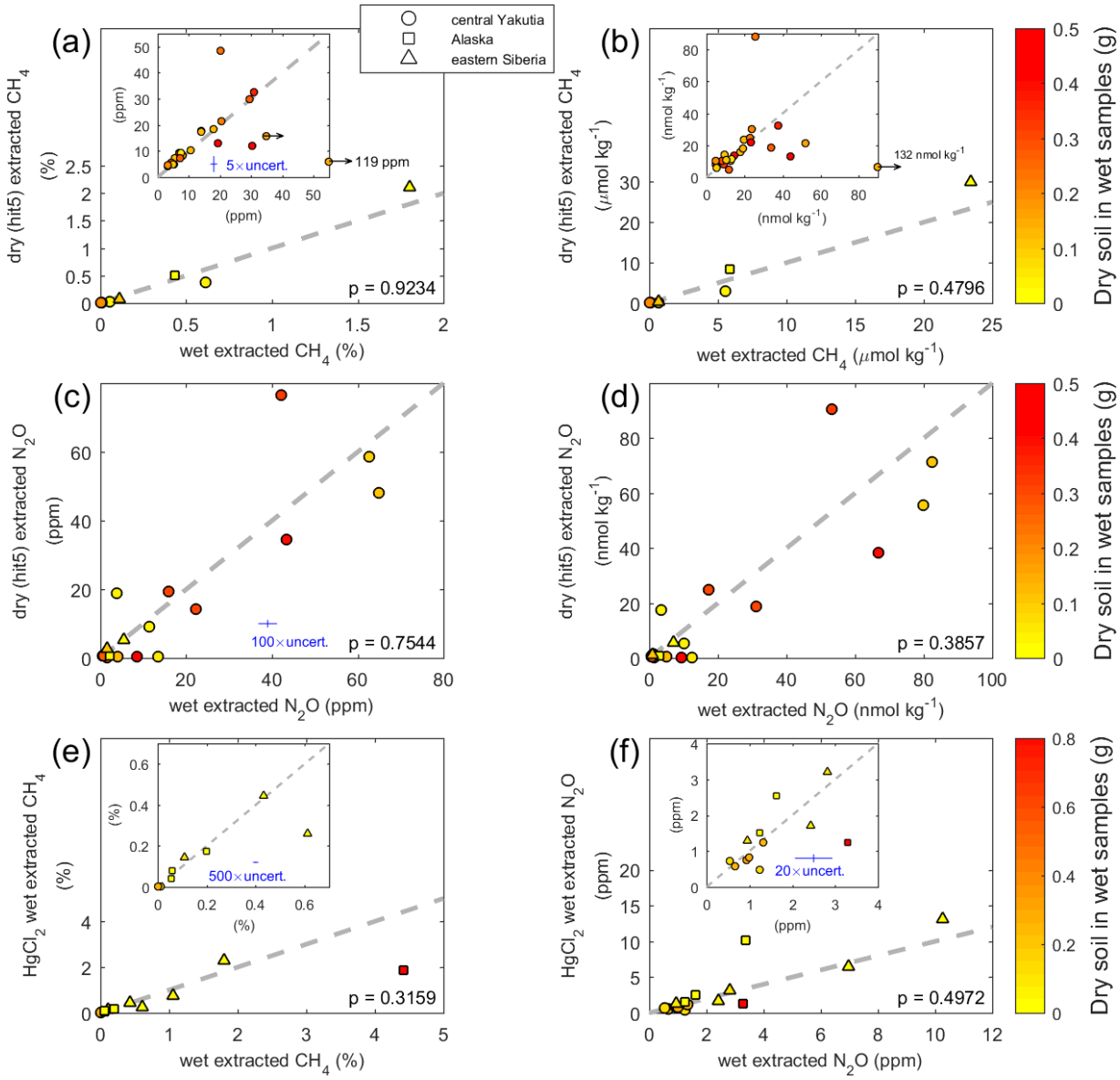
Dry soil content was measured using the leftover meltwater from the control-wet extraction tests. After these ~~control-wet extractions~~ were complete, the sample flasks were

shaken thoroughly and the meltwater samples were each poured into a 50 mL conical tube. The meltwater and soils were separated by a centrifugal separator at 3000 rpm for 10 min. The separated wet soils were wind-dried in evaporating dishes at ~~approximately ~~100 °C for 24 ~~hours~~hr. The weight of each individual evaporating dish was pre-measured before use. The dry soil content was calculated by subtracting the weight of the evaporating dish from the total weight of the dried soil sample plus the evaporating dish.

3. Results and ~~Discussion~~discussion

3.1. Comparison between wet and dry extraction methods

The results from the wet and dry extractions were compared using 23 CH_4 and 21 N_2O ice-wedge samples ~~(21 for N_2O)~~ from Alaska and Siberia. In both the CH_4 ~~CH_4~~ and N_2O mixing ratio analyses, we found that the wet and dry extraction results did not differ significantly ($p > 0.1$), regardless of sampling site or soil content (Figure 1~~, a to~~ d). We note that the heterogeneous distribution of gas mixing ratios ~~in~~ at the centimetre scale~~s~~ (Kim et al., 2019) may not have been completely smoothed out by our sub-sample selection, although we randomly chose 8–12 ice cubes for each measurement. Some previous studies have avoided using the wet extraction method because of potential reactivation of microbial CH_4 and/or N_2O production in ice melt (e.g., Cherbunina et al., 2018; Kim et al., 2019). Assuming that activation of microbial metabolism is unlikely during dry extraction at a temperature of -37 °C in the extraction chamber for < 1 h, our findings may imply that wet extraction does not stimulate microbial reactivation to a measurable extent.



201

Figure 1. Comparison of CH_4 and N_2O mixing ratios and contents obtained by different extraction methods. Shown are scatter plots between wet- and dry (hit5) extraction results of CH_4 (a and b) and N_2O (c and d), and between control- and biocide-treated wet extraction results for CH_4 (e) and N_2O (f). The 'hit5' denotes the dry extraction with five times hitting (see Section 3.3). Left panels (a, c, and e) and (f) present in mixing ratios of gas in bubbles, while right (b) and (d) panels in moles of gas in a unit mass of ice (gas content). The sampling locations are indicated by different symbols. The color of each data point indicates the dry soil weight in the subsamples used in control wet extraction. The 1-sigma uncertainties of the mixing ratios (a, c, e, and f) are magnified by 5x, 20x, 100x, and 500x as denoted as blue error bars (see Appendix). The error bars are not visible where the error bars are smaller than markers. The grey dashed lines are 1:1 reference line. Note that the units of the axes of the insets in (e) and (f) are identical to the original plots. The p-value of two-sided Students' t-test of each comparison is denoted at the bottom right corner of each plot.

202

3.2. Testing microbial alteration during wet extraction

To test the microbial production of CH_4 and N_2O during wet extraction more accurately, we conducted wet extraction experiments on samples treated with $HgCl_2$, a commonly used effective biocide (e.g., Torres et al., 2005), and compared the results with those of untreated (control) wet extractions. We prepared 12 additional ice-wedge samples using the random cube method for these tests (see Section 2~~Materials and Methods section~~). We found no significant differences between the control and $HgCl_2$-treated wet extraction results for both CH_4 and N_2O mixing ratios (Figure~~s~~ 1e ~~and 1,~~f), indicating that the bias due to microbial activity during ~~approximately an hour~~~1 hr of the melting-refreezing procedure ~~is~~ was not significant. This ~~is~~ was further supported by tests on an additional 12 ice-wedge samples (using the random cube protocol) treated with 2-bromo-ethane-sulfonate (BES), a specific methanogenesis inhibitor (e.g., Nollet et al., 1997) (Figure A3). Similar to the $HgCl_2$-treated experiments, 25 µL of a saturated BES solution was added to each sample flask. These additional tests were carried out only for CH_4. The two-sided t-test for the CH_4 data ~~indicates~~ indicated an insignificant difference between the two results ($p > 0.9$). Data from individual sampling sites also ~~do~~ did not show significant differences ($p > 0.9$ for the Alaskan samples and $p > 0.5$ for the central Yakutian samples).

According to microbial sequencing studies that have shown the presence of viable microbes in permafrost and ground ice (e.g., Katayama et al., 2007), it is likely that culturable microbes exist in the ice-wedge samples used in this study. However, considering that at least 14 days and up to 3 months of culturing was required to identify microbe colonies extracted from ground ice (Katayama et al., 2007; Lacelle et al., 2011), our melt-refreeze time of an hour was insufficient for microbial activity to resume ~~and~~ produc~~e~~tion of CH_4 and N_2O.

3.3. Dry extraction efficiency and gas mixing ratios

One limitation of our needle crushing dry ~~-~~extraction technique ~~is~~ was the inability to completely extract gas from ice samples, because small ice particles and/or flakes placed in the space between the needles ~~are~~ were not fully crushed. The gas extraction efficiency of the SNU needle~~-~~crusher system has been reported as ~80–90% for polar ice core samples (Shin, 2014). However, the gas extraction efficiency has not been tested for ice-wedge samples. Depending on the extraction efficiency, the needle crushing method could underestimate the gas contents if the gas is not completely extracted. Another possible bias in the gas mixing ratios arises if the CH_4 and N_2O compositions are different between the crushed and uncrushed portions of the ice-wedge samples.

To estimate the biases arising from incomplete gas extraction, we designed a series of tests to identify the differences of the CH_4 and N_2O mixing ratios and contents between the crushed and uncrushed sample portions. Each randomly collected ice-wedge sample ~~that was randomly collected~~ was first crushed by the regular dry extraction procedure (by hitting it five times with the needle system, 'hit5'), and the gas liberated from the sample was trapped in a sample tube. ~~Then we~~We then performed an additional 100 hits on the leftover ice ('hit100'), monitored the amount of additional gas liberated, and trapped the additional gas in a separate sample tube. Comparisons between the hit5 and hit100 results are summari~~s~~z~~z~~ed in Figure 2 and Table A1.

~~Here we~~We regarded the ratio of gas content of hit100 to that of hit5 (hit100/hit5 ratio, hereafter) as a measure of the gas extraction efficiency of the needle~~-~~crusher system. The results demonstrate an average hit100/hit5 ratio of gas content of 0.40 ± 0.07 for the Zyryanka samples, 0.24 ± 0.07 for the Bluff samples, and 0.14 ± 0.11 for the Cyuie samples (Table A1). Despite the fact that the number of samples was limited, the ice-wedge samples from the different sites showed distinct hit100/hit5 ratios of the amount of extracted gas. However, we observed that the leftover ice from the Bluff and Zyryanka samples were not well-crushed,

even after 100 hits with the needle crusher. This was especially true if the ice sub-samples contained soil aggregates: in these cases the frozen soil aggregates were barely crushed. In contrast, the Cyuie samples were relatively well-crushed, and the leftover samples were apparently finer-sized ice flakes. We also observed that the hit100/hit5 ratios of gas content ~~are~~ were highly variable within samples from a particular site, implying that the extraction efficiency of the needle crusher not only ~~depends~~ depended on ~~-~~site characteristics, but also on the individual ice sample hardness. When compared with the dry soil content measured from the sub-samples used for wet extraction, no relationship was observed between the dry soil content and the extraction efficiency (Figures 1 and A3). In addition, in the case of samples uncrushed by the hit100 test, it ~~is~~ was difficult to estimate the extraction efficiency using the hit100/hit5 ratio of gas content, as the hit100 tests liberated only a marginal portion of gas from these samples. This ~~is~~ was because the large-sized uncrushed soil aggregates or particles may have prohibited the needle crusher from crushing the small-sized ice flakes or grains. The needles move up and down together~~,~~ as they are fixed to a pneumatic linear motion feedthrough device~~,~~, so~~thus~~ if there is a sizeable~~able~~ soil clod that cannot be crushed, it blocks the needle crusher from moving further down. Therefore, we do not recommend using a needle~~-~~crusher system to measure gas contents in ice-wedge samples.

The hardness of the ice samples may also affect the gas mixing ratio analysis in the hit5 and hit100 procedures. The hit100/hit5 ratios of the CH_4 mixing ratio of the Bluff and Zyryanka samples ~~are~~ were less than 1~~1~~ in ~~four~~ 4 out of six samples, yielding an average of 0.9 ± 0.5. However, all five samples from the Cyuie ice ~~-~~wedges ~~have~~ had ratios greater than 1, with an average of 4.7 ± 2.6 (Table A1). The higher hit100/hit5 ratio of CH_4 mixing ratios of Cyuie samples ~~indicates~~ indicated that the gases extracted via the hit100 procedure ~~have~~ had higher CH_4 mixing ratios than the gases extracted via the hit5 procedure. Considering these results with those discussed previously, we speculate that there are three ways gas can be trapped in

ice-wedge ice: enclosed in bubbles, adsorbed on soil particles, and entrapped in soil aggregates. The better-crushed leftover ice flakes in the Cyuie samples may have allowed most of the gas in bubbles and part of the CH_4 molecules adsorbed on soil particles and/or trapped in microsites within soil aggregates to be liberated. Thus, the hit5 CH_4 mixing ratios of the Cyuie samples may ~~more~~ have better reflected the gas mixing ratios in bubbles, while the hit100 results reflected more of the contribution from gas adsorbed on soil and trapped within soil aggregates ~~than the hit5 results~~ because the ice sample containing larger-sized aggregates ~~has~~ had greater hardness than those with smaller aggregates or fine particles. If this ~~is~~ was the case for the Cyuie samples, we can infer that CH_4 is more concentrated in soil particles and in microsites within soil aggregates, compared to in bubbles in the ice. This is partly supported by evidence that ice-wedge layers exhibit relatively trace amounts of CH_4 compared to the surrounding permafrost soil layers (Rivkina et al., 2007); however, this needs to be further evaluated by detailed microbial and chemical analyses. ~~In the m~~Meanwhile, in the Bluff and Zyryanka samples, the hit5 results reflected the mixing ratios of the gases from the crushed portions, regardless of their origin: bubbles, particle adsorption, or microsites in aggregates (Figure 2 and Table A1). Given that some of the Bluff and Zyryanka ice-wedge samples were not fully crushed by the hit100 tests, ~~it may require~~ additional hits or another extraction technique may have been required. Unlike CH_4, the N_2O mixing ratios from the hit100 extractions ~~are~~ were higher than the hit5 in ~~ten~~ 10 ~~out~~ of ~~eleven~~ 11 samples, regardless of the sampling site. The hit100/hit5 ratios of N_2O mixing ratios of the Bluff and Zyryanka samples (1.9 ± 0.8 on average) ~~are~~ were not significantly different ($p = 0.32$) from those of the Cyuie samples (2.9 ± 1.8 on average). This can probably be explained by the fact that the N_2O mixing ratio is not necessarily higher in soil-rich ice because N_2O is an intermediate product of denitrification, while CH_4 is produced as the final product of methanogenesis.

~~One may expect that a~~Although a different crushing technique might be more suitable

for ice-wedge samples. However, none of the existing dry extraction techniques – centrifugal ice microtome (Bereiter et al., 2013), mechanical grater (Etheridge et al., 1988), or ball-mill crusher (Schaefer et al., 2011) – is more advantageous for ice-wedge analysis compared to the needle–crusher system used in this study. The hard portion of ice wedges (e.g., frozen soil aggregates, large soil particles) could easily damage the metal blades of the centrifugal ice microtome and mechanical grater devices, or block the space within the ball-mill chamber, limiting the movement of the milling balls.

It is worth noting that friction between stainless-steel steels surfaces could produce CH_4 with carbon from the damaged stainless steel surface and hydrogen gas (Higaki et al., 2006). If needle crushing causes contamination in this way, the dry extraction results should be affected by the number of hits. To check the impact of the needle crushing procedure on ice-wedge CH_4 and N_2O measurements, we carried out blank tests by changing the numbers of hits from 5 to 100. The results of these tests showed no systematic offset among the experiments with different numbers of hits (Figure A2), which implies implying that the crushing procedure does did not affect the dry extraction results for CH_4 and N_2O. Even though a small minor contamination does did exist occur, its effects have had already been subtracted via blank correction and taken into account in the overall error estimation (see Appendix). Therefore, we consider concluded that our findings are were not artefacts of metal friction during crushing.

To summarisze, from the hit5 and hit100 comparison tests, we found that (1) the needle-crusher method is was not able to fully crush the ice-wedge ice samples and thus is was unsuitable for measuring gas contents in a unit mass of ice, and that (2) weak crushing (e.g., a small number of hits by the needle–crusher system) may better reflect gas mixing ratios of in the soft parts of the samples (such as air bubbles) than strong crushing (e.g., a greater number of hits).

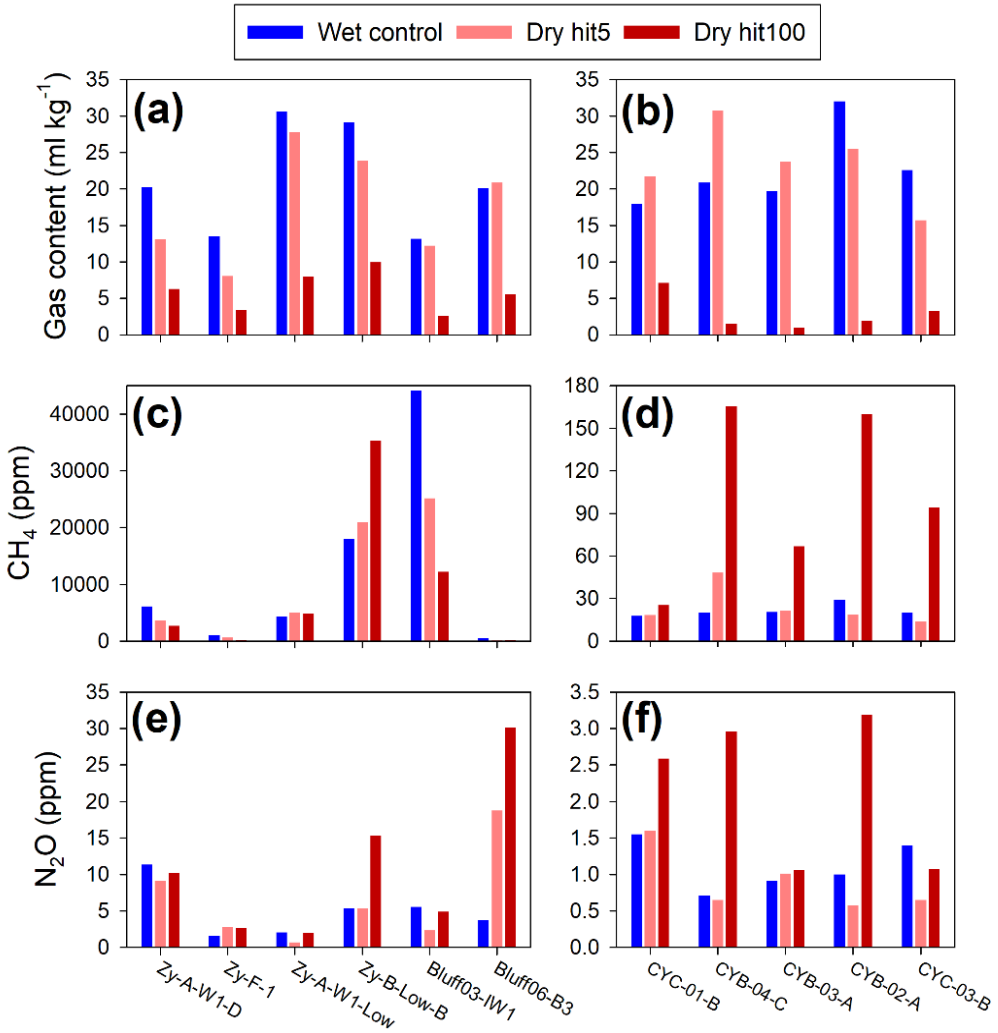


Figure 2. Results of dry extraction tests with 5- and additional 100 times hitting ice-wedge samples, denoted as 'hit5' and 'hit100', respectively (c to f). Also plotted are gas content results from both experiments, where the hit100 values are given in the unit of ml kg^{-1} at STP conditions (a and b). It should be noted that the 'hit100' gas content results indicate the additional amount of gas extracted after 'hit5' crushing and evacuation.

3.4. Residual gas mixing ratios and content~~s~~ after wet extraction

To examine how well the gas ~~is~~ was extracted by wet extraction, we applied the dry extraction method to refrozen ice-wedge samples after wet extraction. We first prepared degassed ice-wedge samples that had undergone repetitive wet extractions (wet-degassed ice, hereafter). Once the wet extraction experiments were completed, we repeated two cycles of melting-refreezing and evacuation procedures to degas the ice melt. After degassing by a total

of three cycles of wet extraction and evacuation, the outermost surfaces (~2 mm) of the wet-degassed ice were trimmed away in the walk-in freezer at SNU on the morning of experiments. The wet-degassed ice was then inserted into the needle crusher ~~and,~~ the crusher chamber was evacuated~~., a~~A specific amount of standard air was injected~~. Then~~, and the wet-degassed ice samples were hit 20 or 60 times by the needle crusher. The amount of gas and the gas mixing ratio of the additionally extracted gas from the wet-degassed ice are ~~shown~~ given in Figure 3 and Table A2~~1~~.

These tests using the wet-degassed ice showed an additional gas extraction of ~12~~ to ~~20 ml kg_{ice}^{-1}, which ~~is~~ Was ~43~~ to ~~88% of the amount of gas extracted during the initial wet extraction. The additionally extracted gas from the dry extraction is referred to as residual gas hereafter. This ~~is~~ was in ~~remarkably~~ remarkable~~in~~ contrast to the ~~less than~~≤ 1% residual fraction of the SNU wet extraction system for ice from polar ice sheets. If such a considerable amount of gas ~~is~~ was left intact by repeated wet extractions, the composition of the additional gas ~~is~~ must be important ~~to~~ for understand~~ing~~ ~~how much~~ the extent of bias for conventional wet extraction results ~~are biased~~.

Figure 3 and Table A~~1~~2 show the mixing ratios and contents of CH_4 and N_2O in the residual gas. The mixing ratios of the residual gas were estimated using mass balance calculations with observed mixing ratios and the amounts of the injected standard and extracted residual gas. The CH_4 mixing ratios of the residual gas ranged from 10.37~~ to ~~23.78 ppm, ~~which~~ ~~is~~ similar to the range of the wet extracted gas~~. This evidence~~, ~~indicates~~ indicating that CH_4 in ice ~~-~~wedges cannot be fully extracted by a melting-refreezing procedure. We suspect two possible reasons for this: (1) ~~During~~ during wet extraction, the ice-wedge samples melted and the soil particles settled at the bottom of the sample flask without any physical impact to the soil particles, causing the adsorbed CH_4 molecules on the soil particles to remain adsorbed~~.~~, and (2) ~~During~~ during refreezing, the soils accumulated at the bottom of the flasks ~~are~~ crumpled

around the centre of the refrozen ice~~,~~ because the sample flasks ~~are~~ were chilled from outside, which facilitated gas entrapment within the frozen soil aggregate. In contrast, the N_2O mixing ratios of the residual gas exhibited very low values compared to those from the initial wet extraction (Figure 3 and Table A2~~1~~). These results ~~imply~~ implied that most of the N_2O in ice wedges ~~is~~ was extracted by three melting-refreezing cycles, such that only a small amount of N_2O ~~is~~ was left adsorbed or entrapped in ice-wedge soils. ~~The authors posit~~We therefore suggest that this might be attributed to the high solubility of N_2O to water compared to CH_4 (Fogg and Sangster, 2003). However, ~~it needs~~ further investigation is needed to better understand this.

~~In this section~~In summary, we found that a certain amount of gas remained in ice wedges, even after three cycles of wet extraction, and that it was~~which is~~ extractable instead by needle crushing. This implies that, unlike polar ice cores, wet extraction of ice ~~-~~wedges does not guarantee near-complete gas extraction, and therefore, precise measurements of the gas content of ice wedges are difficult to obtain. ~~The~~ This difficulty in measuring gas content imposes a large uncertainty ~~in~~ when estimating CH_4 and N_2O contents. Furthermore, we found that the residual gas ~~has~~ had a similar order CH_4 mixing ratio as the gas extracted by initial melting-refreezing, indicating that a comparable amount of CH_4 still ~~remains~~ remained unextracted in ice ~~-~~wedges. Hence, a novel extraction method is required to produce reliable gas content and gas mixing ratios in ice wedges. In contrast, our results show that the N_2O content of the residual gas ~~is~~ was at trace levels, ~~which may~~ suggesting that most of the N_2O in ice ~~-~~wedges is extractable during initial melting-refreezing. Therefore, wet extraction could be applicable for estimating the N_2O content of ice wedges. However, given that the above evidence resulted from three consecutive cycles of melting-refreezing and evacuation, it is unclear how many melting-refreezing cycles are required to extract most ~~of the~~ N_2O from ice wedges. It should be noted that combination of repetitive wet extractions with dry extraction

does not guarantee reliable estimation of N_2O mixing ratio, because extraction efficiency of the other gas components may be different from that of N_2O. Our findings imply that previous estimates of CH_4 budgets in ground ice based on wet extraction principle (e.g., Boereboom et al., 2013; Cherbunina et al., 2018) might have been underestimated, and that ~~the~~ CH_4 production within subfreezing permafrost environments could be larger than previously estimated. Future study should be devoted to a novel extraction method ~~which is easy to~~able to easily and effectively extract gas molecules from ice ~~effectively~~.

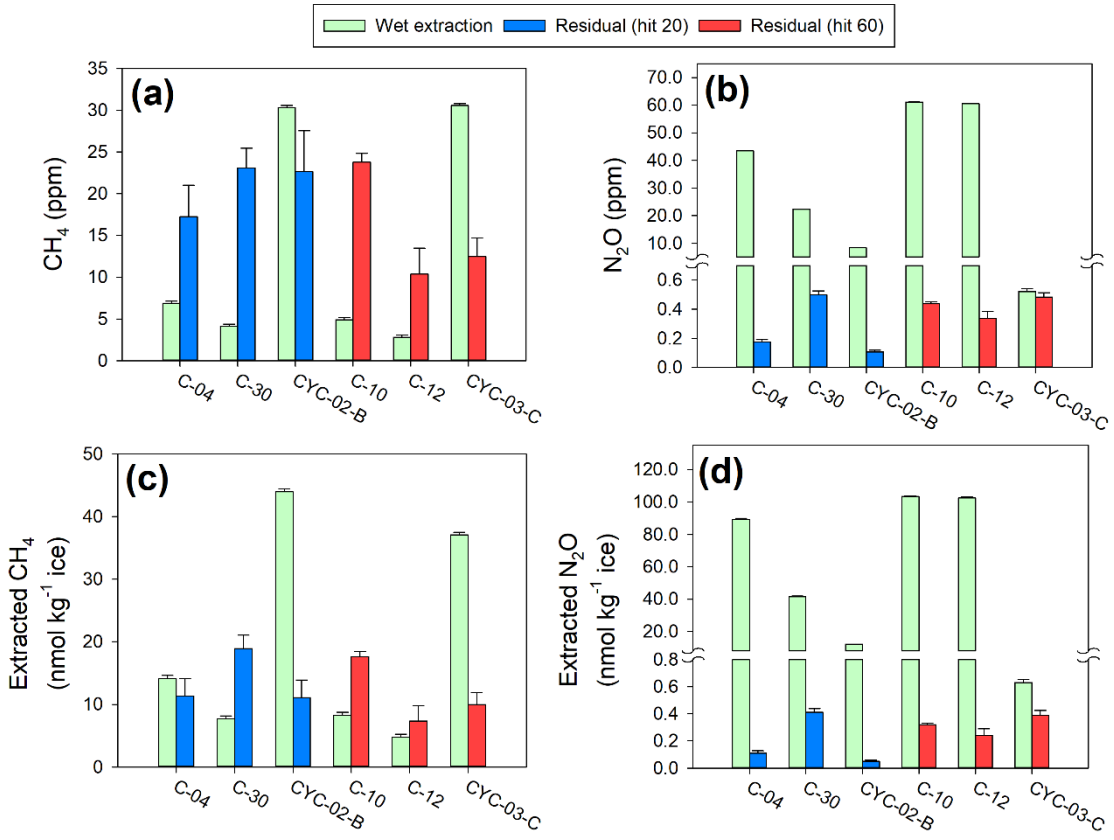


Figure 3. Comparison of wet-extracted gas and residual gas for CH_4 and N_2O mixing ratios (a and b) and contents (c and d). The residual gas was extracted from the dry extraction method using the wet-degassed ice samples. The light green bars show the results of initial wet extraction, and the blue and red bars indicate the dry extraction of wet-degassed ice with 20- and 60-times hitting, respectively. The Cyuie samples are denoted as 'CYC', while 'C' indicates the Churapcha samples.

4. Conclusions

In this study we carried out comparisons between (1) wet and dry extractions, between (2) untreated and biocide-treated wet extractions, and (3) gas extraction from the easyily to extract and difficult to extract parts of ice-wedge ice in order to better understand the characteristics of each extraction method, in order to and adequately analyse CH_4 and N_2O mixing ratios and gas contents from permafrost ice wedges. Based on these comparisons, our major findings are can be summariszed as follows:

1) Existing wet and dry extraction methods allow gas extraction from the soft parts of ice (e.g., ice bubbles) and show insignificant differences in CH_4 and N_2O mixing ratios.
2) Wet extraction results are unlikely to be affected by microbial production of CH_4 and N_2O during the melting-refreeze procedure.
3) Both dry and wet extraction methods are not able to fully extract gas from ice-wedge samples, presumably due to gas adsorbed on soil particles or enclosed within soil aggregates, which may have different gas mixing ratios compared to the gas in bubbles. Further research is required to develop a proper method to quantify and extract adsorbed and enclosed gases. In the meantime, we propose that both existing techniques may be suitable for gas mixing ratio measurements for bubbles in relatively soft ice wedges (i.e., easily crushed ice wedges by hit5 extraction, e.g., Cyuie ice wedges in this study). ExceptionallyAlthough, the N_2O content in ice wedges may be measured by using repeated wet extractions, but this is not the case for determining the N_2O mixing ratio.
4) Our findings indicate that pPrevious estimates of ground ice CH_4 and N_2O budget might may be underestimated, implying that the greenhouse gas production in subfreezing environment of permafrost environments is larger than our the current

understanding.

5) ~~Our findings indicate that the s~~Saturated NaCl solution is unnecessary ~~to~~ for preventing microbial activity during melting, as employed by, e.g., Cherbunina et al. (2018). However, it remains ~~as~~ an open question as to how effectively the adsorbed gas molecules can be extracted by ~~the~~ this method.

Appendix. Systematic blank correction and uncertainty estimation

Since the SNU dry extraction systems, including the sample tubes, were originally designed for CO_2 measurements from polar ice cores, these systems have not been tested for CH_4 and N_2O analysis. We therefore carried out a series of tests to estimate the systematic blank, which is defined here as blanks.

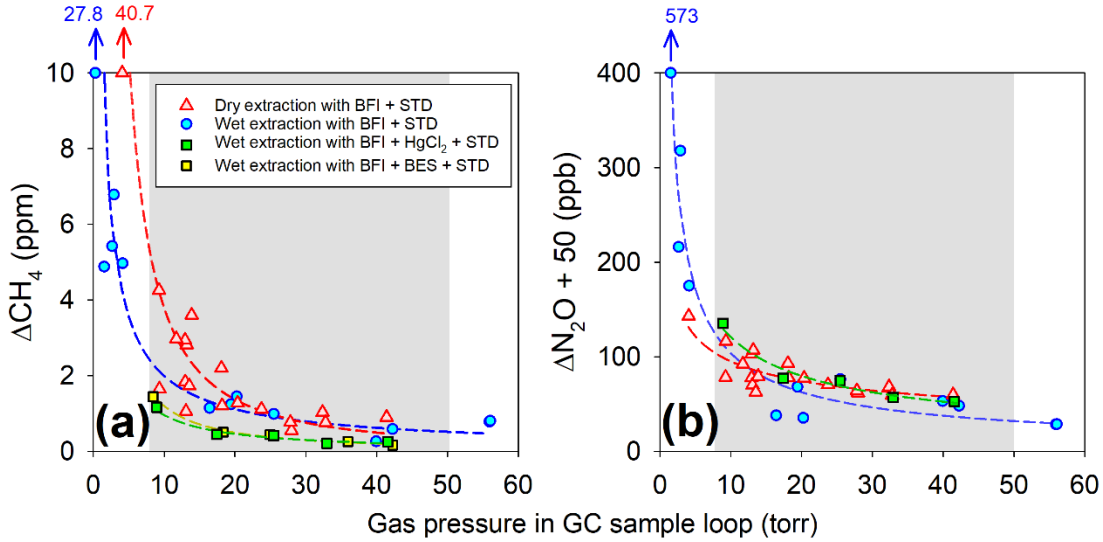
The systematic blanks were tested with bubble-free ice (BFI) and standard air in a cylinder calibrated by NOAA. The BFIs were was prepared as described in Yang et al. (2017).), other than cutting. A major difference is that the BFI block was cut into small BFI pieces of 3–4 g, to mimic the random cube sampling protocol (see Materials and Methods section in the main text Section 2). The systematic blanks for the dry extraction method were tested as follows. A total of ~45 g of BFI cubes was were placed into the crushing chamber, which was sealed with a copper gasket, and evacuated until the interior gas pressure inside the chamber dropped lower than ~60 mTorr, because of the vapour pressure formed by sublimation of the BFI. After evacuation was completed, standard gas was injected into the crushing chamber. The amount of standard injected was controlled by a volume- -calibrated vacuum line in the dry extraction system. Then the BFI samples were hit with the needle system 5 to – 100 times, and the gases in the chamber were passed through a water trap and cryogenically pumped into the sample tubes, using the He-CCR. The number of hits did not significantly affect the systematic blank (Figure A2) and the regression curve for blank correction was fitted to the entire set of data points (red dashed curve in Figure A1).

For the wet extraction, a total of ~45 g of BFI cubes was were placed into each sample flask. The flasks were connected to the wet extraction line and sealed with a copper gasket, then evacuated. Once a vacuum was established, a known amount of standard gas was injected into each flask and the flasks were submerged into a warm water bath for ~40 min to melt completely. The flasks were then submerged into the a cold ethanol bath, which was (chilled

to -80°C~~,~~ ~~)~~ to refreeze. For the $HgCl_2$ and Sodium 2-bromo-ethane-sulfonate (BES) treated experiments, we first prepared ~~the~~ saturated solutions of $HgCl_2$ and BES at room temperature (20 °C) and added 24 µL of $HgCl_2$ or 20 µL of BES solution into the empty flasks in a fume hood. Then we placed the flasks in a deep freezer~~,~~ ~~(maintained~~ at -45 °C for 20 min~~,)~~ to freeze the solutions before the BFI pieces were placed.

The results of the blank experiments are shown in Figure A1. The systematic blanks appeared to be inversely correlated with the gas pressure in the sample tube. The systematic blank test results were fitted using exponential regression curves (dashed lines in Figure A1), and these regression curves were then used for systematic blank correction in our ice-wedge sample analyses.

To calculate uncertainties of the blank corrections, the blank test data were fitted with exponential regression curves (Figure A1). The root-mean-square-deviations (RMSD) of the data from the regression curves ~~are~~ were taken as the uncertainties of blank corrections (Figure 1). Since the ice-wedge data used in this study showed the pressure in GC sample loop of about 8~~~~~~ ~~–~~50 torr, the RMSD were estimated from the blank test data within this pressure range. The uncertainty of the gas content measurement ~~is~~ was calculated by error propagation from those of pressure, line volume, and mass of ice samples.



473

Figure A1. Systematic blank of the needle crushing (dry extraction) and melting-refreezing (wet extraction) methods for (a) CH_4 and (b) N_2O measurements in control and biocide ($HgCl_2$) treated experiments. Also plotted are the CH_4 blanks of BES-treated wet extractions. The dashed lines represent exponential regression curve fittings. Note that all data are plotted against the amount of gas trapped in the sample tube, presented here as the pressure in the GC sample loop when the sample gas is expanded. The grey shaded areas indicate the range of ice-wedge samples used in this study (see main text). The big-delta (Δ) notion in the y-axes indicate the offset from the values of the standard used.

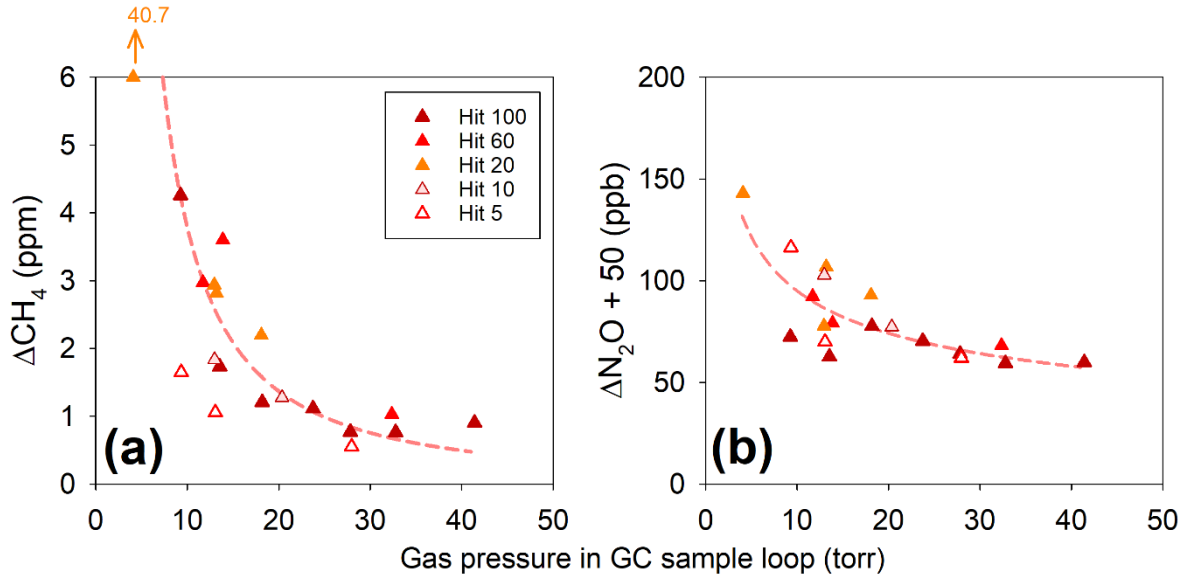


Figure A2. Influence of different number of hitting on the systematic blank of the needle crushing (dry extraction) system for (a) CH_4 and (b) N_2O measurements. Note that all data are plotted against the amount of gas trapped in the sample tube, presented here as the pressure in the GC sample loop when the sample gas is expanded (see main text). The big-delta (Δ) notion in the y-axes indicate the offset from the values of the standard used.

474

475

476

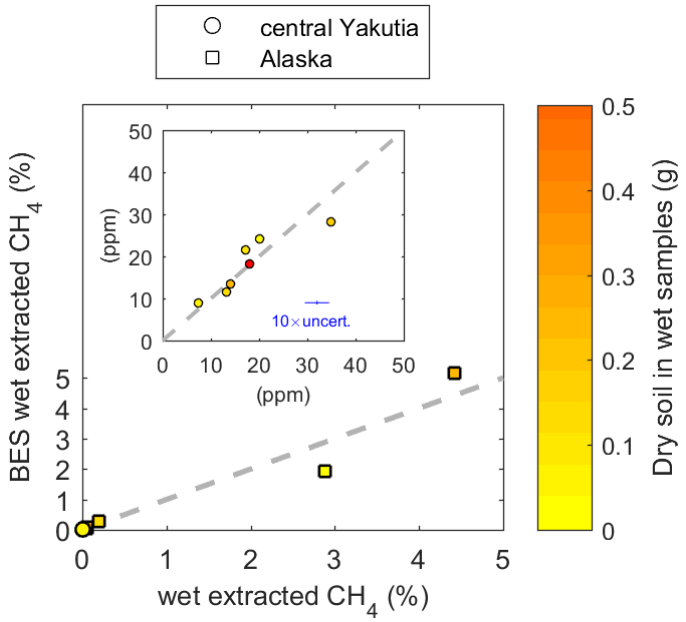


Figure A3. Comparison between control- and BES-treated wet extraction results for CH_4. The sampling area is indicated by different symbols. The color of each data point indicates the dry soil weight in the subsamples used in control wet extraction. The grey dashed lines are 1:1 reference line. The blue error bar indicates the 1-sigma uncertainty of mixing ratios magnified by 10x.

477

478

Table A1. Results of dry extraction tests with 5- and additional 100 times hitting ice-wedge samples, denoted as 'hit5' and 'hit100', respectively. 'hit100/hit5' is the ratio in extracted gas content or gas mixing ratio of 'hit100' to 'hit5' cases. Also shown are gas content results from both experiments, where the hit100 values are given both in the unit of ml kg^{-1} at STP conditions and µmol/kg (in parenthesis). It should be noted that the 'hit100' gas content results indicate the additional amount of gas extracted after 'hit5' crushing and evacuation.

Site Location	Sample	soil content	gas content				CH_4 mixing ratio				N_2O mixing ratio			
			Wet control	Dry hit5	Dry hit100	hit100/hit5	Wet control	Dry hit5	Dry hit100	hit100/hit5	Wet control	Dry hit5	Dry hit100	hit100/hit5
		wt. %	ml/kg	ml/kg	ml/kg		ppm	ppm	ppm		ppm	ppm	ppm	
Zyryanka, Northeastern Siberia	Zy-A-W1-D	0.155	20.2	13.1	6.3	0.48	6138	3713	2721	0.7329	11.37	9.10	10.15	1.12
	Zy-F-1	0.618	13.5	8.1	3.4	0.42	1080	655.6	173.5	0.2646	1.57	2.81	2.65	0.942
	Zy-A-W1-Low	0.049	30.6	27.8	8.0	0.29	4309	5073	4818	0.9497	2.07	0.69	2.02	2.9
	Zy-B-Low-B	0.107	29.1	23.9	10.0	0.418	18030	21010	35290	1.680	5.37	5.32	15.36	2.89
Northern Alaska	Bluff03-IW1	2.07	13.2	12.2	2.6	0.21	44160	25230	12240	0.4851	5.58	2.36	4.93	2.09
	Bluff06-B3	0.078	20.1	20.9	5.6	0.27	558.7	164.2	219.5	1.337	3.74	18.78	30.14	1.605
Cyuie, Central Yakutia	CYC-01-B	0.252	18.0	21.7	7.1	0.33	18.0	18.3	25.4	1.39	1.55	1.60	2.59	1.62
	CYB-04-C	0.498	20.9	30.7	1.5	0.049	20.2	48.4	165.6	3.42	0.71	0.65	2.96	4.5
	CYB-03-A	0.420	19.7	23.7	1.0	0.041	20.5	21.5	67.1	3.12	0.91	1.01	1.06	1.05
	CYB-02-A	0.403	32.0	25.5	1.9	0.073	29.1	18.7	159.8	8.55	1.00	0.58	3.19	5.5
	CYC-03-B	0.830	22.6	15.7	3.3	0.21	20.3	13.9	94.5	6.80	1.40	0.65	1.08	1.7

Table A2~~1~~. Comparison of results from extracted gas from the conventional wet extraction method and the residual gas in ice after 3-times wet extraction. The residual gas was extracted by a needle crusher (see section 3.4 for details of the mehtods)

Site location	Sample	soil content	Wet extraction					Residual gas				
			gas content	CH_4 mixing ratio	N_2O mixing ratio	CH_4 content	N_2O content	gas content	CH_4 mixing ratio	N_2O mixing ratio	CH_4 content	N_2O content
		wt. %	ml/kg	ppm	ppm	nmol/kg	nmol/kg	ml/kg	ppm	ppm	nmol/kg	nmol/kg
Churapcha, central Yakutia	C-10	0.524	37.9	4.9	61.13	8.3	103	16.6	23.8	0.437	17.6	0.324
Churapcha, central Yakutia	C-30	1.03	41.7	4.1	22.28	7.7	41.5	18.4	23	0.50	19	0.41
Cyuie, central Yakutia	CYC-03-C	1.09	27.2	30.5	0.52	37.1	0.63	17.9	12.5	0.48	10.0	0.39
Churapcha, central Yakutia	C-04	1.38	46.0	6.9	43.46	14	89.2	14.7	17	0.17	11	0.11
Cyuie, central Yakutia	CYC-02-B	1.12	32.5	30.3	8.34	44.0	12.1	11.0	23	0.11	11	0.053
Churapcha, central Yakutia	C-12	0.370	38.0	2.8	60.47	4.8	103	15.9	10	0.34	7.3	0.24

Data availability

~~The data will be uploaded on the public data repository of Pangaea after publication.~~All data used in this study are available at Zenodo repository (Yang et al., 2020).

Author contributions

JWY and JA conceived the research and designed the experiments. GI, JA, KK, and AF drilled the ice-wedge ice samples from Alaska and Siberia. JWY, JA, SH, and KK conducted the laboratory experiments. JWY and JA led the manuscript preparation with inputs from all other co-authors.

Competing interests

The authors declare no conflict interest.

Acknowledgements

The authors greatly acknowledge those who contributed to collect ice-wedge ice samples. We thank Gwangjin Lim and Jaeyoung Park for their help in sample preparations and gas extraction experiments, and Min Sub Sim for kind advice on inhibition experiments for methanogen.

Financial support

This project was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) (NRF-2018R1A2B3003256 and NRF-2018R1A5A1024958) and the NASA ABoVE (Arctic Boreal and Vulnerability Experiment; grant no. NNX17AC57A).

References

Arkhangelov, A. A., and Novgorodova, E. V.: Genesis of massive ice at 'Ice Mountains', Yenesei River, Western Siberia, according to results of gas analyses, Permafrost Periglac. Proc., 2, 167-170, http://doi.org/10.1002/ppp.3430020210, 1991.

Bereiter, B., Stocker, T. F., and Fischer, H.: A centrifugal ice microtome for measurements of atmospheric CO_2 on air trapped in polar ice cores, Atmos. Meas. Tech., 6, 251-262, http://doi.org/10.5194/amt-6-251-2013, 2013.

Boereboom, T., Samyn, D., Meyer, H., and Tison, J. -L.: Stable isotope and gas properties of two climatically contrasting (Pleistocene and Holocene) ice wedges from Cape Mamontov Klyk, Laptev Sea, northern Siberia, The Cryosphere, 7, 31-46, http://doi.org/10.5194/tc-7-31-2013, 2013.

Brown, J., Ferrians Jr., O. J., Heginbottom, J. A., and Melnikov, E.: Circum-Arctic map of permafrost and ground-ice conditions, version 2, National Snow and Ice Data Center, Boulder, CO, 2002.

Cherbunina, M. Y., Shmelev, D. G., Brouchkov, A. V., Kazancev, V. S., and Argunov, R. N.: Patterns of spatial methane distribution in the upper layers of the permafrost in central Yakutia, Mosc. Univ. Geol. Bull., 73, 100-108, 2018.

Fedorov, A. N., Botulu, T. A., Vasiliev, I. S., Varlamov, S. P., Gribanova, S. P., Dorofeev, I. V.: Permafrost-landscape map of the Yakut ASSR, Gosgeodezia, Moscow, Russia, Map, 1991 (In Russian).

Fogg, P. G. T., and Sangster, J.: Chemicals in the Atmosphere: Solubility, Sources and Reactivity, John Wiley & Sons, Inc., 2003.

Higaki, S., Oya, Y., and Makide, Y.: Emission of methane from stainless steel surface investigated by using tritium as a radioactive tracer, Chem. Lett., 35, 292-293, https://doi.org/10.1246/cl.2006.292, 2006.

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, https://doi.org/10.5194/bg-11-6573-2014, 2014.

Jorgenson, M. T., Kanevskiy, M., Shur Y, Moskalenko, N., Brown, D. R. N., Wickland, K., Striegl, R., and Koch, J.: Role of ground ice dynamics and ecological feedbacks in recent ice wedge degradation and stabilization, J. Geophys. Res., 120, 2280-2297, https://doi.org/10.1002/2015JF003602, 2015.

Kanevskiy, M., Shur, Y., Jorgenson, M. T., Ping, C. -L., Michaelson, G. J., Fortier, D., Stephani, E., Dillon, M., and Tumskoy, V.: Ground ice in the upper permafrost of the Beaufort Sea coast of Alaska, Cold Reg. Sci. Technol., 85, 56-70, https://doi.org/10.1016/j.coldregions.2012.08.002, 2013.

Katayama, T., Tanaka, M., Moriizumi, J., Nakamura, T., Brouchkov, A., Douglas, T. A., Fukuda, M., Tomita, F., and Asano, K.: Phylogenetic analysis of bacteria preserved in a permafrost ice wedge for 25,000 years, Appl. Environ. Microbiol., 73, 2360-2363, https://doi.org/10.1128/AEM.01715-06, 2007.

Kim, K., Yang, J. -W., Yoon, H., Byun, E., Fedorov, A., Ryu, Y., and Ahn, J.: Greenhouse gas formation in ice wedges at Cyuie, central Yakutia, Permafrost Periglac. Process., 30, 48-57, http://doi.org/10.1002/ppp.1994, 2019.

Lacelle, D., Radtke, K., Clark, I. D., Fisher, D., Lauriol, B., Utting, N., and Whyte, L. G.: Geomicrobiology and occluded O_2-CO_2-Ar gas analyses provide evidence of microbial respiration in ancient terrestrial ground ice, Earth Planet. Sci. Lett., 306, 46-54, https://doi.org/10.1016/j.epsl.2011.03.023, 2011.

Masson-Delmotte, V., Schulz, M., Abe-Ouchi, A., Beer, J., Ganopolski, A., Rouco, J. F. G., Jansen, E., Lambeck, K., Luterbacher, J., Naish, T., Osborn, T., Otto-Bliesner, B., Quinn, T., Ramesh, R., Rojas, M., Shao, X., and Timmerman, A.: Information from paleoclimatic archives, Climate change 2013: The Physical science basis, Contribution of working group I to the fifth assessment report of the Intergovernmental Panel on Climate Change, 383-464, https://doi.org/10.1017/CBO9781107415324.013, 2013.

Nollet, L., Demeyer, D., and Verstraete, W.: Effect of 2-bromoethanesulfonic acid and Peptostreptococcus products ATCC 35244 addition on stimulation of reductive acetogenesis in the ruminal ecosystem by selective inhibition of methanogenesis, Appl. Environ. Microbiol., 63, 194-200, 1997.

Rivkina, E., Shcherbakova, V., Laurinavichius, K., Petrovskaya, L., Krivushin, K., Kraev, G., Pecheritsina, S., and Gilichinsky, D.: Biogeochemistry of methane and methanogenic

archaea in permafrost, FEMS Microbiol. Ecol., 61, 1-15, https://doi.org/10.1111/j.1574-6941.2007.00315.x, 2007.

Ryu, Y., Ahn, J., and Yang, J. -W.: High-precision measurement of N_2O concentration in ice cores, Environ. Sci. Technol., 52, 731-738, https://doi.org/10.1021/acs.est.7b05250, 2018.

Salmon, V. G., Schadel, C., Bracho, R., Pegoraro, E., Celis, G., Mauritz, M., Mack, M. C., and Schuur, E. A. G.: Adding depth to our understanding of nitrogen dynamics in permafrost soils, J. Geophys. Res., 123, 2497-2512, https://doi.org/10.1029/2018JG004518, 2018.

Schaefer, H., Lourantou, A., Chappellaz, J., Luthi, D., Bereiter, B., and Barnola, J. -M.: On the stability of partially clathrated ice for analysis of concentration and $\delta^{13}C$ of palaeo-atmospheric CO_2, Earth Planet. Sci. Lett., 307, 334-340, https://doi.org/10.1016/j.epsl.2011.05.007, 2011.

Shin, J.: Atmospheric CO_2 variations on millennial time scales during the early Holocene, Master thesis, School of Earth and Environmental Sciences, Seoul National University, South Korea, 58 pp., 2014.

Strauss, J., Laboor, S., Fedorov, A. N., Fortier, D., Froese, D., Fuchs, M., Grosse, G., Günther, F., Harden, J. W., Hugelius, G., Kanevskiy, M. Z., Kholodov, A. L., Kunitsky, V. V., Kraev, G., Lapointe-Elmrabti, L., Lozhkin, A. V., Rivkina, E., Robinson, J., Schirrmeister, L.., Shmelev, D., Shur, Y., Siegert, C., Spektor, V., Ulrich, M., Vartanyan, S. L., Veremeeva, A., Walter Anthony, K. M., and Zimov, S. A.: Database of Ice-Rich Yedoma Permafrost (IRYP), PANGAEA, https://doi.org/10.1594/PANGAEA.861733, 2016.

Torres, M. E., Mix, A. C., and Rugh, W. D.: Precise $\delta^{13}C$ analysis of dissolved inorganic carbon in natural waters using automated headspace sampling and continuous-flow mass spectrometry, Limnol. Oceanogr.: Methods, 3, 349-360, 2005.

Yang, J. -W., Ahn, J., Brook, E. J., and Ryu, Y.: Atmospheric methane control mechanisms during the early Holocene, Clim. Past, 13, 1227-1242, https://doi.org/10.5194/cp-13-1227-2017, 2017.

Yang, J. -W.: Paleoclimate reconstructions from greenhouse gas and borehole temperature of polar ice cores, and study on the origin of greenhouse gas in permafrost ice wedges, Ph.D. thesis, School of Earth and Environmental Sciences, Seoul National University, Seoul, 188 pp., 2019.

Yang, J. -W., Ahn, J., Iwahana, G., Han, S., Kim, K., and Fedorov, A.: Comparison of different gas

extraction techniques to analyze CH_4 and N_2O compositions in gas trapped in permafrost ice wedges, Zonodo, https://doi.org/10.5281/zenodo.3701243, 2020.