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

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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 have not been well tested. We tested conventional wet and dry gas extraction methods using ice wedges from Alaska and Siberia, 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 found insignificant effects of microbial activity during wet extraction. However, both techniques 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 such incomplete gas extraction.

1. Introduction

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

30 (e.g., Hugelius et al., 2014; Salmon et al., 2018), temporarily removing this frozen C and N

31 from active global cycles. Therefore, future projections of permafrost stability are of great

32 interest, particularly because thawing permafrost may lead to decomposition and/or

33 remineralisation of the buried soil C and N and their abrupt emission into the atmosphere in

34 the form of greenhouse gases (GHGs) such as carbon dioxide (CO_2), methane (CH_4), and

35 nitrous oxide (N_2O), which in turn can trigger positive feedbacks (e.g., Salmon et al., 2018). In

36 addition, projected polar amplification (e.g., Masson-Delmotte et al., 2013) may strengthen

37 these positive feedbacks. However, the processes responsible for in-situ C and N

38 remineralisation and GHG production in ground ice are poorly understood, despite the fact that

39 ground ice accounts for a substantial portion (up to ~40–90% by volume) of Pleistocene ice-

40 rich permafrost, or Yedoma (e.g., Kanevskiy et al., 2013; Jorgenson et al., 2015).

41   The gases trapped in ground ice allow unique insights into the origin of ground ice and

42 evidence for in-situ microbial aerobic and anaerobic respiration (Boereboom et al., 2013; Kim

43 et al., 2019; Lacelle et al., 2011). Among others, the GHGs in ground ice may provide detailed

44 information on in-situ biogeochemical processes responsible for GHG production (i.e.,

45 methanogenesis, nitrification, and denitrification) (e.g., Boereboom et al., 2013; Kim et al.,

46 2019). However, the relevant analytical methods remain poorly scrutinised. Boereboom et al.

47 (2013) utilised the conventional melting-refreezing method (wet extraction) used in polar ice

48 core analyses, in which the ice samples were melted under a vacuum to liberate the enclosed

49 gases and then refrozen to expel the dissolved gases present in the meltwater. Other studies

50 conducted by Russian scientists used an on-site melting method, in which a large (1–3 kg)

51 block of ground ice sample was melted in a saturated sodium chloride (NaCl) solution in order

52 to minimise gas dissolution (Arkhangelov and Novgorodova, 1991). A recent study instead

53 used a dry extraction technique to prevent microbial activity during wet extraction (Kim et al.,

54 2019), which employed a needle crusher in a vacuum to crush approximately 10 g of ice sample

55   without melting (Shin, 2014).

56   In this study, for the first time, we tested the reliability of both wet and dry extraction

57   methods for CH_4 and N_2O mixing ratios and contents (volume or moles of gas in a unit mass

58   at standard temperature and pressure conditions (STP)) using permafrost ground ice samples.

59   Ice-wedge samples from Alaskan and Siberian permafrost were used because ice wedges are

60   one of the most abundant morphological features of massive ground ice, consisting of

61   approximately 5–50% by volume of the upper permafrost (Kanevskiy et al., 2013; Jorgenson

62   et al., 2015). More specifically, we aimed to address the following scientific questions: (1) Do

63   wet and dry extraction methods yield different results? (2) Are the melting-refreezing results

64   affected by microbial activity during gas extraction? (3) How effectively does the wet/dry

65   extraction extract gases from ice wedges? To address the first question, we compared CH_4 and

66   N_2O results from dry and wet extractions. For the second question, we applied the wet

67   extraction method to both biocide-treated and control samples. Finally, for the third question

68   we carried out tests with and without extended needle system hits in a crushing chamber, as

69   well as additional dry extraction from ice samples that had been degassed by our wet extraction

70   method.

71

72   **2. Materials and methods**

73   **2.1. Ice samples and sample preparation**

74   The ice-wedge samples used in this study were collected from Churapcha, Cyuie

75   (central Yakutia), and Zyryanka (north-eastern Yakutia) in Siberia, as well as from northern

76   Alaska (Supplementary Figure 1). The Churapcha site (61.97°N, 132.61°E) was located

77   approximately 180 km east of Yakutsk while the Cyuie site (61.73°N, 130.42°E) was located

78   approximately 30 km southeast of Yakutsk. The Cyuie samples were collected from two

79   outcrops (CYB and CYC) (Kim et al., 2019). At each site, 30 cm long ice-wedge cores were

80   drilled perpendicular to the outcrop surface (Supplementary Figures 2 and 3).

81   Zyryanka is located in the southern boreal region of the Kolyma River, at the junction

82   of the Chersky and Yukaghir Ranges, in a region affected by thermokarst development

83   (Fedorov et al., 1991). Site A (Zy-A) was located on a tributary of the Kolyma River, ~22 km

84   north of Zyryanka. Site B (Zy-B) was ~14 km west of the start of the Kolyma tributary, which

85   begins ~11 km north of Zyryanka. Site F (Zy-F) was located ~4 km west of the tributary that

86   leads to site B. The ground ice samples were collected from riverbank walls exposed by lateral

87   erosion using a chainsaw (Supplementary Figure 4). Most of the outcrops that were sampled

88   for ground ice were on the first (lowest) terrace of the river.

89   For the Alaskan sampling locations, Bluff03 (69.40°N, 150.95°W) and Bluff06

90   (69.14°N, 150.61°W) were located in the Alaska North Slope region, ~120 and ~150 km from

91   the Arctic Ocean, or ~100 and ~70 km northwest of the Toolik Field Station (68.63°N,

92   149.59°W), respectively. Samples from Bluff03 were collected by chainsaw from bluff walls

93   that had developed by gully formation on a gentle slope of the Yedoma. Samples from Bluff06

94   were collected from outcrops within eroded frozen peatland in a thaw lake basin

95   (Supplementary Figure 5). All ice-wedge samples used in this study were stored in a chest

96   freezer at < -18 °C before analysis.

97   Ice-wedge ice is different from polar ice cores in that its gas mixing ratios are not

98   homogeneous (e.g., Kim et al., 2019), which may hinder exact comparison with results from

99   adjacent ice samples. We therefore randomly mixed sub-samples to reduce the effect of the

100   heterogeneous gas composition distribution (the "random cube" method, hereafter). ~100–200

101   g of an ice-wedge sample were cut into 25–50 cubes of 3–4 g each; for each experiment, ~10–

102   12 cubes were randomly chosen so that the total weight of the sub-sample was ~40 g.

103   **2.2. Gas extraction procedures**

104   *Dry extraction (needle crusher)*

105   For dry extraction, we used a needle-crusher system at Seoul National University (SNU,

106   Seoul, South Korea) (Shin, 2014). In brief, 8–13 g of ice sample were crushed in a cold vacuum

107   chamber (extraction chamber). The ice samples were usually hit five times by the needle set.

108   The temperature within the extraction chamber was maintained at -37 °C using a cold ethanol-

109   circulating chiller. The extracted gas was dried by passing it through a water vapour trap at -

110   85 °C and cryogenically trapping it in a stainless-steel tube (sample tube) at approximately -

111   257 °C using a helium closed-cycle refrigerator (He-CCR). Since the extraction chamber

112   cannot accommodate ~40 g of ice at once, the ~40 g of random cube sub-samples were

113   extracted using three sequential extractions and the gas liberated from each extraction was

114   trapped in a sample tube.

115   Following extraction, the sample tubes were detached from the He-CCR, warmed to

116   room temperature (~20 °C), and attached to a gas chromatograph (GC) equipped with an

117   electron capture detector (ECD) and a flame ionisation detector (FID) to determine the mixing

118   ratios of CH_4 and N_2O. Details of the GC system are given in Ryu et al. (2018). The daily

119   calibration curves were established using working standards of 15.6 ± 0.2 ppm CH_4, 10000 ±

120   30 ppm CH_4, 2960 ± 89 ppb N_2O, 29600 ± 888 ppb N_2O, and a modern air sample from a

121   surface firn at Styx Glacier, Antarctica (obtained in November 2016), which was calibrated as

122   1758.6 ± 0.6 ppb CH_4 and 324.7 ± 0.3 ppb N_2O by the National Oceanic and Atmospheric

123   Administration (NOAA).

124

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

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

127   extraction system at SNU was employed (Yang et al., 2017; Ryu et al., 2018). The gas

128   extraction procedure was identical to the procedure described in Yang et al. (2017) and Ryu et

129   al. (2018), except for the sample gas trapping procedure (see below). Ice-wedge sub-samples

130   of ~40 g (composed of 10–12 ice cubes for each) were placed in a glass container welded to a

131   stainless-steel flange (sample flask), and the laboratory air inside the sample flasks was

132   evacuated for 40 min. The sample flasks were then submerged in a warm (~50 °C) tap water

133   bath to melt the ice samples. After melting was complete, the meltwater was refrozen by

134   chilling the sample flasks with cold ethanol (below -70 °C). The sample gas in the headspace

135   of each sample flask was then expanded to the volume-calibrated vacuum line to estimate the

136   volume of extracted gas, and trapped in a stainless-steel sample tube by the He-CCR device.

137   We attached the He-CCR device to our wet extraction line and the gas samples in the flasks

138   were cryogenically trapped. There were two reasons for using He-CCR instead of direct

139   expansion to a GC: (1) to better compare the dry and wet extraction methods by applying the

140   same trapping procedure, and (2) to maximise the amount of sample gas for GC analysis,

141   because gas expansion from a large flask allows only a small fraction of gas to be measured by

142   the GC.

143   For biocide-treated tests, 1.84 mmol of mercuric chloride ($HgCl_2$) was applied per unit

144   kilogram of soil, following established procedures for soil sterilisation (Fletcher and Kaufman,

145   1980). We obtained the average dry soil mass (0.33 g) from the leftover meltwater samples of

146   the previous wet extractions, which were carried out for comparison between dry and wet

147   extractions. Taking this into account, we added 24 μL of saturated $HgCl_2$ solution (at 20 °C) to

148   the sample flasks. The flasks with $HgCl_2$ solution were then frozen in a deep freezer at < -45 °C

149   to prevent the dissolution of ambient air into the solution during ice sample loading. After the

150   wet extraction procedure was complete, the extracted gas was trapped in a sample tube and the

151   CH_4 and N_2O mixing ratios were determined using the same GC-ECD-FID system as the dry-

152   extracted gas. The resulting CH_4 and N_2O mixing ratios were not corrected for partial

153   dissolution in ice melt in the flasks, because CH_4 and N_2O trapped in refrozen ice were

154   negligible compared to the ranges of the systematic blanks (see Appendix).

155

2.3. Gas content

The analytical methods described previously were used to 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) required data regarding the amount of gas extracted. 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}), 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).

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2.4. Dry soil content

Dry soil content was measured using the leftover meltwater from the control-wet extraction tests. After these 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 ~100 °C for 24 hr. The weight of each individual evaporating dish was pre-measured before use. The dry soil content was calculated by subtracting the

180 weight of the evaporating dish from the total weight of the dried soil sample plus the

181 evaporating dish.

182

183 **3. Results and discussion**

184 **3.1. Comparison between wet and dry extraction methods**

185   The results from the wet and dry extractions were compared using 23 CH_4 and 21 N_2O

186 ice-wedge samples from Alaska and Siberia. In both the CH_4 and N_2O mixing ratio analyses,

187 we found that the wet and dry extraction results did not differ significantly ($p > 0.1$), regardless

188 of sampling site or soil content (Figure 1a-d). We note that the heterogeneous distribution of

189 gas mixing ratios at the centimetre scale (Kim et al., 2019) may not have been completely

190 smoothed out by our sub-sample selection, although we randomly chose 8–12 ice cubes for

191 each measurement. Some previous studies have avoided using the wet extraction method

192 because of potential reactivation of microbial CH_4 and/or N_2O production in ice melt (e.g.,

193 Cherbunina et al., 2018; Kim et al., 2019). Assuming that activation of microbial metabolism

194 is unlikely during dry extraction at a temperature of -37 °C in the extraction chamber for < 1 h,

195 our findings may imply that wet extraction does not stimulate microbial reactivation to a

196 measurable extent.

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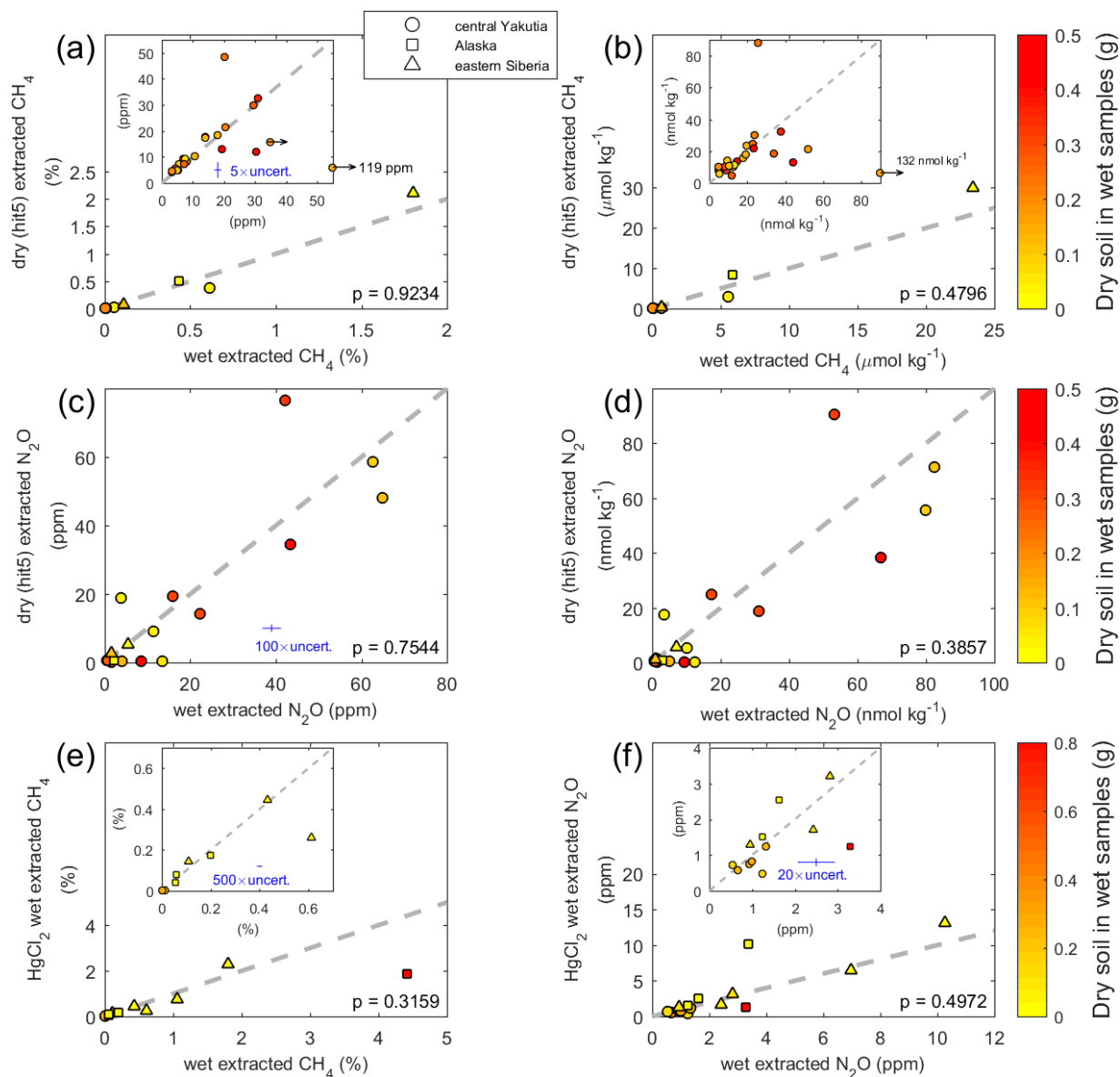
Figure 1. Comparison of CH_4 and N_2O mixing ratios and contents obtained by different extraction methods. Shown are scatter plots between wet- and dry (hit5) extraction results of CH_4 (a and b) and N_2O (c and d), and between control- and biocide-treated wet extraction results for CH_4 (e) and N_2O (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.

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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). 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 1e,f), indicating that the bias due to microbial activity during ~1 hr of the melting-refreezing procedure was not significant. This 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 indicated an insignificant difference between the two results ($p > 0.9$). Data from individual sampling sites also 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 production of CH_4 and N_2O.

3.3. Dry extraction efficiency and gas mixing ratios

One limitation of our needle crushing dry extraction technique was the inability to

224 completely extract gas from ice samples, because small ice particles and/or flakes placed in the

225 space between the needles were not fully crushed. The gas extraction efficiency of the SNU

226 needle-crusher system has been reported as ~80–90% for polar ice core samples (Shin, 2014).

227 However, the gas extraction efficiency has not been tested for ice-wedge samples. Depending

228 on the extraction efficiency, the needle crushing method could underestimate the gas contents

229 if the gas is not completely extracted. Another possible bias in the gas mixing ratios arises if

230 the CH_4 and N_2O compositions are different between the crushed and uncrushed portions of

231 the ice-wedge samples.

232   To estimate the biases arising from incomplete gas extraction, we designed a series of

233 tests to identify the differences of the CH_4 and N_2O mixing ratios and contents between the

234 crushed and uncrushed sample portions. Each randomly collected ice-wedge sample was first

235 crushed by the regular dry extraction procedure (by hitting it five times with the needle system,

236 'hit5'), and the gas liberated from the sample was trapped in a sample tube. We then performed

237 an additional 100 hits on the leftover ice ('hit100'), monitored the amount of additional gas

238 liberated, and trapped the additional gas in a separate sample tube. Comparisons between the

239 hit5 and hit100 results are summarised in Figure 2 and Table A1.

240   We regarded the ratio of gas content of hit100 to that of hit5 (hit100/hit5 ratio, hereafter)

241 as a measure of the gas extraction efficiency of the needle-crusher system. The results

242 demonstrate an average hit100/hit5 ratio of gas content of 0.40 ± 0.07 for the Zyryanka samples,

243 0.24 ± 0.07 for the Bluff samples, and 0.14 ± 0.11 for the Cyuie samples (Table A1). Despite

244 the fact that the number of samples was limited, the ice-wedge samples from the different sites

245 showed distinct hit100/hit5 ratios of the amount of extracted gas. However, we observed that

246 the leftover ice from the Bluff and Zyryanka samples were not well-crushed, even after 100

247 hits with the needle crusher. This was especially true if the ice sub-samples contained soil

248 aggregates: in these cases the frozen soil aggregates were barely crushed. In contrast, the Cyuie

249   samples were relatively well-crushed, and the leftover samples were apparently finer-sized ice

250   flakes. We also observed that the hit100/hit5 ratios of gas content were highly variable within

251   samples from a particular site, implying that the extraction efficiency of the needle crusher not

252   only depended on-site characteristics, but also on the individual ice sample hardness. When

253   compared with the dry soil content measured from the sub-samples used for wet extraction, no

254   relationship was observed between the dry soil content and the extraction efficiency (Figures

255   1 and A3). In addition, in the case of samples uncrushed by the hit100 test, it was difficult to

256   estimate the extraction efficiency using the hit100/hit5 ratio of gas content, as the hit100 tests

257   liberated only a marginal portion of gas from these samples. This was because the large-sized

258   uncrushed soil aggregates or particles may have prohibited the needle crusher from crushing

259   the small-sized ice flakes or grains. The needles move up and down together as they are fixed

260   to a pneumatic linear motion feedthrough device, so if there is a sizeable soil clod that cannot

261   be crushed, it blocks the needle crusher from moving further down. Therefore, we do not

262   recommend using a needle-crusher system to measure gas contents in ice-wedge samples.

263   The hardness of the ice samples may also affect the gas mixing ratio analysis in the hit5

264   and hit100 procedures. The hit100/hit5 ratios of the CH_4 mixing ratio of the Bluff and Zyryanka

265   samples were less than 1 in 4 out of six samples, yielding an average of 0.9 ± 0.5. However, all

266   five samples from the Cyuie ice wedges had ratios greater than 1, with an average of 4.7 ± 2.6

267   (Table A1). The higher hit100/hit5 ratio of CH_4 mixing ratios of Cyuie samples indicated that

268   the gases extracted via the hit100 procedure had higher CH_4 mixing ratios than the gases

269   extracted via the hit5 procedure. Considering these results with those discussed previously, we

270   speculate that there are three ways gas can be trapped in ice-wedge ice: enclosed in bubbles,

271   adsorbed on soil particles, and entrapped in soil aggregates. The better-crushed leftover ice

272   flakes in the Cyuie samples may have allowed most of the gas in bubbles and part of the CH_4

273   molecules adsorbed on soil particles and/or trapped in microsites within soil aggregates to be

274   liberated. Thus, the hit5 CH_4 mixing ratios of the Cyuie samples may have better reflected the

275   gas mixing ratios in bubbles, while the hit100 results reflected more of the contribution from

276   gas adsorbed on soil and trapped within soil aggregates because the ice sample containing

277   larger-sized aggregates had greater hardness than those with smaller aggregates or fine particles.

278   If this was the case for the Cyuie samples, we can infer that CH_4 is more concentrated in soil

279   particles and in microsites within soil aggregates, compared to in bubbles in the ice. This is

280   partly supported by evidence that ice-wedge layers exhibit relatively trace amounts of CH_4

281   compared to the surrounding permafrost soil layers (Rivkina et al., 2007); however, this needs

282   to be further evaluated by detailed microbial and chemical analyses. Meanwhile, in the Bluff

283   and Zyryanka samples, the hit5 results reflected the mixing ratios of the gases from the crushed

284   portions, regardless of their origin: bubbles, particle adsorption, or microsites in aggregates

285   (Figure 2 and Table A1). Given that some of the Bluff and Zyryanka ice-wedge samples were

286   not fully crushed by the hit100 tests, additional hits or another extraction technique may have

287   been required. Unlike CH_4, the N_2O mixing ratios from the hit100 extractions were higher than

288   the hit5 in 10 of 11 samples, regardless of the sampling site. The hit100/hit5 ratios of N_2O

289   mixing ratios of the Bluff and Zyryanka samples (1.9 ± 0.8 on average) were not significantly

290   different ($p = 0.32$) from those of the Cyuie samples (2.9 ± 1.8 on average). This can probably

291   be explained by the fact that the N_2O mixing ratio is not necessarily higher in soil-rich ice

292   because N_2O is an intermediate product of denitrification, while CH_4 is produced as the final

293   product of methanogenesis.

294   Although a different crushing technique might be more suitable for ice-wedge samples,

295   none of the existing dry extraction techniques – centrifugal ice microtome (Bereiter et al., 2013),

296   mechanical grater (Etheridge et al., 1988), or ball-mill crusher (Schaefer et al., 2011) – is more

297   advantageous for ice-wedge analysis compared to the needle-crusher system used in this study.

298   The hard portion of ice wedges (e.g., frozen soil aggregates, large soil particles) could easily

299 damage the metal blades of the centrifugal ice microtome and mechanical grater devices, or

300 block the space within the ball-mill chamber, limiting the movement of the milling balls.

301 It is worth noting that friction between stainless-steel surfaces could produce CH_4 with

302 carbon from the damaged surface and hydrogen gas (Higaki et al., 2006). If needle crushing

303 causes contamination in this way, the dry extraction results should be affected by the number

304 of hits. To check the impact of the needle crushing procedure on ice-wedge CH_4 and N_2O

305 measurements, we carried out blank tests by changing the number of hits from 5 to 100. The

306 results of these tests showed no systematic offset among the experiments with different

307 numbers of hits (Figure A2), implying that the crushing procedure did not affect the dry

308 extraction results for CH_4 and N_2O. Even though minor contamination did occur, its effects had

309 already been subtracted via blank correction and taken into account in the overall error

310 estimation (see Appendix). Therefore, we concluded that our findings were not artefacts of

311 metal friction during crushing.

312 To summarise, from the hit5 and hit100 comparison tests, we found that (1) the needle-

313 crusher method was not able to fully crush the ice-wedge ice samples and thus was unsuitable

314 for measuring gas content in a unit mass of ice, and (2) weak crushing (e.g., a small number of

315 hits by the needle-crusher system) may better reflect gas mixing ratios in the soft parts of the

316 samples (such as air bubbles) than strong crushing (e.g., a greater number of hits).
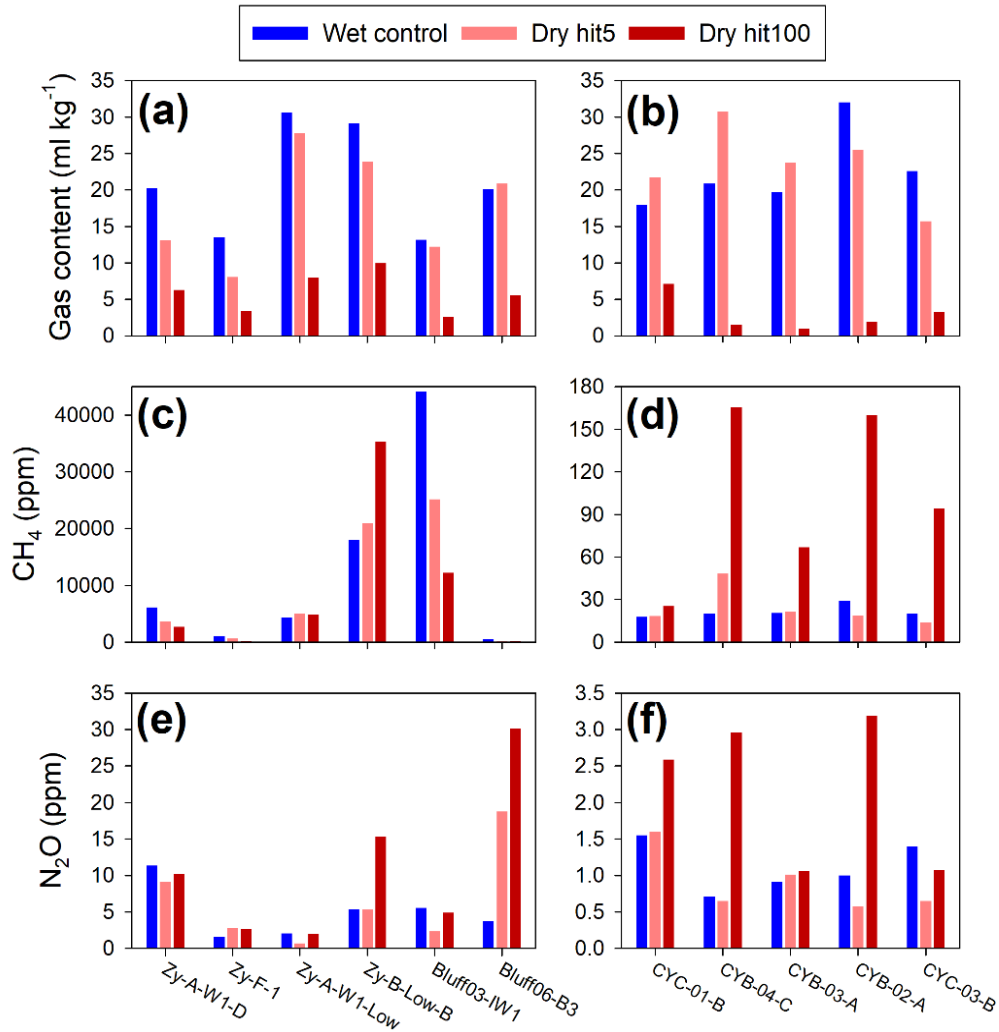
Figure 2. Results of dry extraction tests with 5- and additional 100 times hitting ice-wedge samples, denoted as 'hit5' and 'hit100', respectively (c to f). Also plotted are gas content results from both experiments, where the hit100 values are given in the unit of ml kg^{-1} at STP conditions (a and 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 after wet extraction

To examine how well the gas 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

329   of three cycles of wet extraction and evacuation, the outermost surfaces (~2 mm) of the wet-

330   degassed ice were trimmed away in the walk-in freezer at SNU on the morning of experiments.

331   The wet-degassed ice was then inserted into the needle crusher, the crusher chamber was

332   evacuated, a specific amount of standard air was injected, and the wet-degassed ice samples

333   were hit 20 or 60 times by the needle crusher. The amount of gas and the gas mixing ratio of

334   the additionally extracted gas from the wet-degassed ice are given in Figure 3 and Table A2.

335   These tests using the wet-degassed ice showed an additional gas extraction of ~12–20

336   ml kg_{ice}^{-1}, which Was ~43–88% of the amount of gas extracted during the initial wet extraction.

337   The additionally extracted gas from the dry extraction is referred to as residual gas hereafter.

338   This was in remarkable contrast to the < 1% residual fraction of the SNU wet extraction system

339   for ice from polar ice sheets. If such a considerable amount of gas was left intact by repeated

340   wet extractions, the composition of the additional gas must be important for understanding the

341   extent of bias for conventional wet extraction results.

342   Figure 3 and Table A2 show the mixing ratios and contents of CH_4 and N_2O in the

343   residual gas. The mixing ratios of the residual gas were estimated using mass balance

344   calculations with observed mixing ratios and the amounts of the injected standard and extracted

345   residual gas. The CH_4 mixing ratios of the residual gas ranged from 10.37–23.78 ppm, similar

346   to the range of the wet extracted gas, indicating that CH_4 in ice wedges cannot be fully extracted

347   by a melting-refreezing procedure. We suspect two possible reasons for this: (1) during wet

348   extraction, the ice-wedge samples melted and the soil particles settled at the bottom of the

349   sample flask without any physical impact to the soil particles, causing the adsorbed CH_4

350   molecules on the soil particles to remain adsorbed, and (2) during refreezing, the soils

351   accumulated at the bottom of the flasks crumpled around the centre of the refrozen ice because

352   the sample flasks were chilled from outside, which facilitated gas entrapment within the frozen

353   soil aggregate. In contrast, the N_2O mixing ratios of the residual gas exhibited very low values

354   compared to those from the initial wet extraction (Figure 3 and Table A2). These results implied

355   that most of the N_2O in ice wedges was extracted by three melting-refreezing cycles, such that

356   only a small amount of N_2O was left adsorbed or entrapped in ice-wedge soils. We therefore

357   suggest that this might be attributed to the high solubility of N_2O to water compared to CH_4

358   (Fogg and Sangster, 2003). However, further investigation is needed to better understand this.

359   In summary, we found that a certain amount of gas remained in ice wedges, even after

360   three cycles of wet extraction, and that it was extractable instead by needle crushing. This

361   implies that, unlike polar ice cores, wet extraction of ice wedges does not guarantee near-

362   complete gas extraction, and therefore, precise measurements of the gas content of ice wedges

363   are difficult to obtain. This difficulty in measuring gas content imposes a large uncertainty

364   when estimating CH_4 and N_2O contents. Furthermore, we found that the residual gas had a

365   similar order CH_4 mixing ratio as the gas extracted by initial melting-refreezing, indicating that

366   a comparable amount of CH_4 still remained unextracted in ice wedges. Hence, a novel

367   extraction method is required to produce reliable gas content and gas mixing ratios in ice

368   wedges. In contrast, our results show that the N_2O content of the residual gas was at trace levels,

369   suggesting that most of the N_2O in ice wedges is extractable during initial melting-refreezing.

370   Therefore, wet extraction could be applicable for estimating the N_2O content of ice wedges.

371   However, given that the above evidence resulted from three consecutive cycles of melting-

372   refreezing and evacuation, it is unclear how many melting-refreezing cycles are required to

373   extract most N_2O from ice wedges. It should be noted that combination of repetitive wet

374   extractions with dry extraction does not guarantee reliable estimation of N_2O mixing ratio,

375   because extraction efficiency of the other gas components may be different from that of N_2O.

376   Our findings imply that previous estimates of CH_4 budgets in ground ice based on wet

377   extraction principle (e.g., Boereboom et al., 2013; Cherbunina et al., 2018) might have been

378   underestimated, and that CH_4 production within subfreezing permafrost environments could be

379   larger than previously estimated. Future study should be devoted to a novel extraction method

380   able to easily and effectively extract gas molecules from ice.

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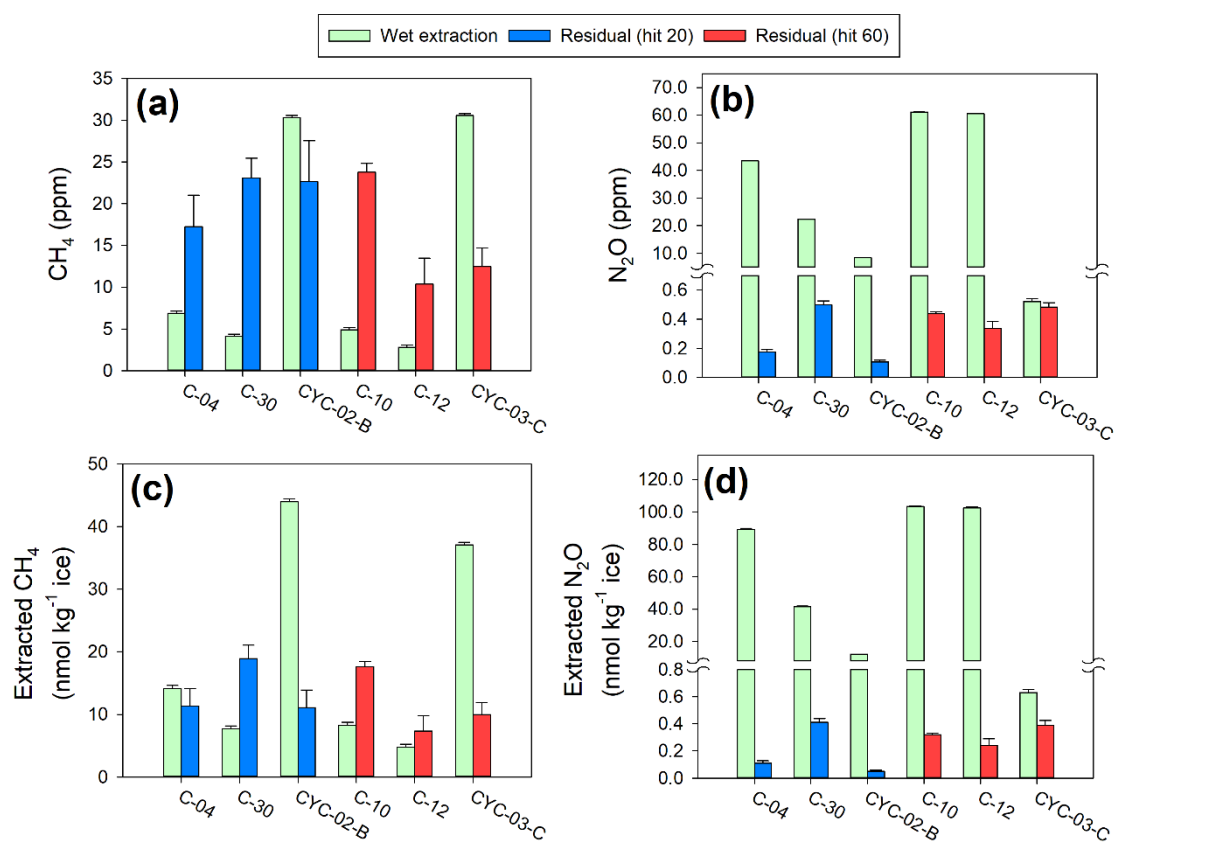
Figure 3. Comparison of wet-extracted gas and residual gas for CH₄ and N₂O mixing ratios (a and b) and contents (c and d). The residual gas was extracted from the dry extraction method using the wet-degassed ice samples. The light green bars show the results of initial wet extraction, and the blue and 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 extraction, (2) untreated and biocide-treated wet extraction, and (3) gas extraction from the easy to extract and difficult to extract parts of ice-wedge ice in order to better understand the characteristics of each extraction method and adequately analyse CH_4 and N_2O mixing ratios and gas contents from permafrost ice wedges. Based on these comparisons, our major findings can be summarised 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). Although the N_2O content in ice wedges may be measured by using repeated wet extractions, this is not the case for determining the N_2O mixing ratio.

4) Previous estimates of ground ice CH_4 and N_2O budget may be underestimated, implying that the greenhouse gas production in subfreezing permafrost environments is larger than the current understanding.

408 5) Saturated NaCl solution is unnecessary for preventing microbial activity during

409   melting, as employed by, e.g., Cherbunina et al. (2018). However, it remains an

410   open question as to how effectively the adsorbed gas molecules can be extracted by

411   this method.

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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 BFI was prepared as described in Yang et al. (2017), other than cutting the BFI block into small pieces of 3–4 g to mimic the random cube sampling protocol (see Section 2). The systematic blanks for the dry extraction method were tested as follows. A total of ~45 g of BFI cubes were placed into the crushing chamber, which was sealed with a copper gasket and evacuated until the interior gas pressure 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 5–100 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 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 a cold ethanol bath (chilled to -80°C) to refreeze. For the $HgCl_2$ and Sodium 2-bromo-ethane-sulfonate (BES) treated experiments, we

439 first prepared saturated solutions of $HgCl_2$ and BES at room temperature (20 °C) and added 24

440 μL of $HgCl_2$ or 20 μL of BES solution into the empty flasks in a fume hood. Then we placed

441 the flasks in a deep freezer (at -45 °C for 20 min) to freeze the solutions before the BFI pieces

442 were placed.

443   The results of the blank experiments are shown in Figure A1. The systematic blanks

444 appeared to be inversely correlated with the gas pressure in the sample tube. The systematic

445 blank test results were fitted using exponential regression curves (dashed lines in Figure A1),

446 and these regression curves were then used for systematic blank correction in our ice-wedge

447 sample analyses.

448   To calculate uncertainties of the blank corrections, the blank test data were fitted with

449 exponential regression curves (Figure A1). The root-mean-square-deviations (RMSD) of the

450 data from the regression curves were taken as the uncertainties of blank corrections (Figure 1).

451 Since the ice-wedge data used in this study showed the pressure in GC sample loop of about

452 8–50 torr, the RMSD were estimated from the blank test data within this pressure range. The

453 uncertainty of the gas content measurement was calculated by error propagation from those of

454 pressure, line volume, and mass of ice samples.

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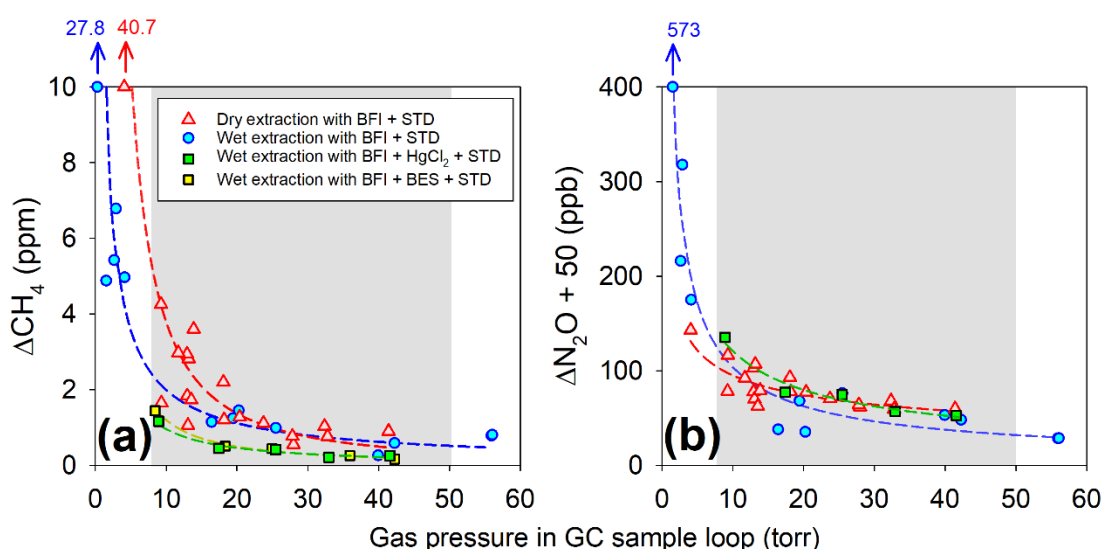
Figure A1. Systematic blank of the needle crushing (dry extraction) and melting-refreezing (wet extraction) methods for (a) CH$_4$ and (b) N$_2$O measurements in control and biocide (HgCl$_2$) treated experiments. Also plotted are the CH$_4$ blanks of BES-treated wet extractions. The dashed lines represent 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.
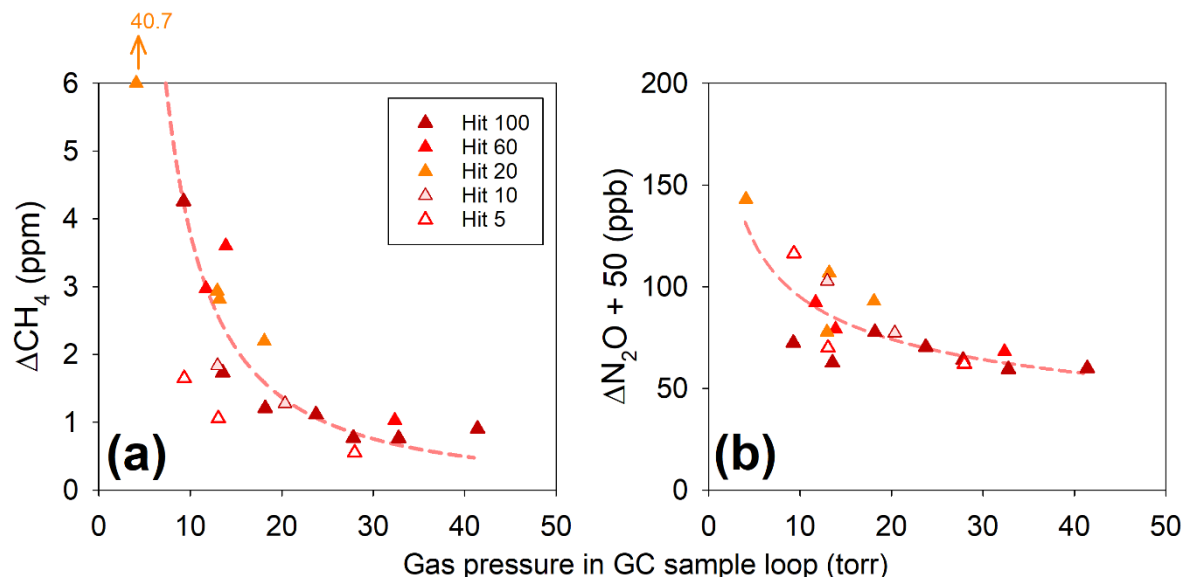
Figure A2. Influence of different number of hitting on the systematic blank of the needle crushing (dry extraction) system for (a) CH$_4$ and (b) N$_2$O measurements. Note that all data are plotted against the amount of gas trapped in the sample tube, presented here as the pressure in the GC sample loop 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.
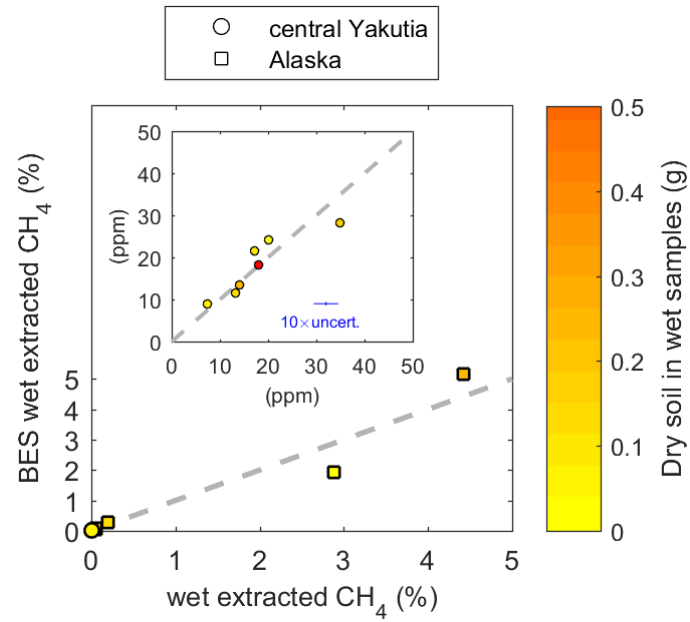
Figure A3. Comparison between control- and BES-treated wet extraction results for CH₄. The sampling area is indicated by different symbols. The color of each data point indicates the dry soil weight in the subsamples used in control wet extraction. The grey dashed lines are 1:1 reference line. The blue error bar indicates the 1-sigma uncertainty of mixing ratios magnified by 10x.

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462 **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'
463 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
464 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
465 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

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467

468   Table A2. Comparison of results from extracted gas from the conventional wet extraction method and the residual gas in ice after 3-times wet extraction. The
469   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

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Data availability

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.

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