



1 **Brief Communication: The reliability of gas extraction**
2 **techniques for analysing CH₄ and N₂O compositions in gas**
3 **trapped in permafrost ice-wedges**

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16

17 **Abstract.** Methane (CH₄) and nitrous oxide (N₂O) compositions in ground ice may provide
18 information on their production mechanisms in permafrost. However, existing gas extraction
19 methods has not been well tested. We test conventional wet and dry gas extraction methods
20 using ice-wedges from Alaska and Siberia. We find that both methods extract gas from the
21 easily extractable parts of the ice (e.g., gas bubbles), and yield similar results for CH₄ and N₂O
22 mixing ratios. We also find insignificant effects of microbial activity during wet extraction.
23 However, both techniques are unable to fully extract gas from the ice, presumably because gas
24 molecules adsorbed onto or enclosed in soil aggregates are not easily extractable. Estimation
25 of gas production in subfreezing environment of permafrost should consider the incomplete
26 gas extraction.

27

28 **1. Introduction**

29 Permafrost soils preserve large amounts of soil carbon and nitrogen in a frozen state



30 (e.g., Hugelius et al., 2014; Salmon et al., 2018), removing this frozen carbon (C) and nitrogen
31 (N) 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 remineralization of the buried soil C and N and their abrupt emission into the atmosphere in
34 the form of greenhouse gases (GHGs) – carbon dioxide (CO₂), methane (CH₄), and nitrous
35 oxide (N₂O), which in turn trigger positive feedbacks (e.g., Salmon et al., 2018). In addition,
36 the projected polar amplification (e.g., Masson-Delmotte et al., 2013) may strengthen these
37 positive feedbacks. However, the processes responsible for in-situ C and N remineralization
38 and GHG production in ground ice are poorly understood, despite the fact that ground ice
39 accounts for a substantial portion of the upper permafrost: up to approximately 40–90% by
40 volume of ice-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 respiration (e.g., Lacelle et al., 2011). Among others, the
43 GHGs in ground ice may provide detailed information on in-situ biogeochemical processes
44 responsible for GHG production (e.g., Boereboom et al., 2013; Kim et al., 2019). However,
45 analytical methods remain poorly scrutinized. Boereboom et al. (2013) utilized the
46 conventional melting-refreezing method (wet extraction) used in polar ice core analyses. In this
47 technique, the ice samples were melted under a vacuum to liberate the enclosed gases, then
48 refrozen to expel the dissolved gases present in the meltwater. Other studies conducted by
49 Russian scientists used an on-site melting method in which a large (1–3 kg) block of ground
50 ice sample was melted in a saturated sodium chloride (NaCl) solution, in order to minimize
51 microbial activity and gas dissolution (Cherbunina et al., 2018 and references therein). A recent
52 study instead used a dry extraction technique to prevent the microbial activity during wet
53 extraction (Kim et al., 2019), which employed a needle-crusher in a vacuum to crush
54 approximately 10 g of ice sample without melting (Shin, 2014).



55 In this study, for the first time we test the reliability of both wet and dry extraction
56 methods for CH₄ and N₂O mixing ratios and contents (volume or moles of gas in a unit mass
57 at standard temperature and pressure conditions (STP)) using permafrost ground ice samples.
58 Ice-wedge samples from Alaskan and Siberian permafrost were used because the ice-wedge is
59 one of the most abundant morphological features of massive ground ice, consisting of
60 approximately 5 to 50% by volume of the upper permafrost (Kanevskiy et al., 2013; Jorgenson
61 et al., 2015). More specifically, this study aims to address the following scientific questions: 1)
62 Do wet and dry extraction methods yield different results? 2) Are the melting-refreezing results
63 affected by microbial activity during gas extraction? 3) How effectively does the wet/dry
64 extraction extract gases from ice wedges? To address the first question, CH₄ and N₂O results
65 from dry and wet extractions were compared. For the second question, we applied the wet
66 extraction method to both biocide-treated and control samples. Finally, for the third question
67 we carried out tests with and without extended number of hitting ice with a needle system in a
68 crushing chamber, as well as additional dry extraction from ice samples that had been degassed
69 by our wet extraction method.

70

71 **2. Materials and Methods**

72 **2.1. Ice samples and sample preparation**

73 The ice-wedge samples used in this study were collected from Churapcha, Cyuie
74 (central Yakutia), and Zyryanka (north-eastern Yakutia) in Siberia, as well as from northern
75 Alaska. The Churapcha site (61.97°N, 132.61°E) is located approximately 180 km east of
76 Yakutsk. The Cyuie site (61.73°N, 130.42°E) is located approximately 30 km southeast of
77 Yakutsk. The Cyuie samples were collected from two outcrops (CYB and CYC) (Kim et al.,
78 2019). At each site, 30 cm long ice-wedge cores were drilled perpendicular to the outcrop
79 surface.



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

88 For the Alaskan sampling locations, Bluff03 (69.40°N, 150.95°W) and Bluff06
89 (69.14°N, 150.61°W) are located in the Alaska North Slope region, approximately 120 and 150
90 km from the Arctic Ocean, or 100 and 70 km northwest of the Toolik Field Station (68.63°N,
91 149.59°W), respectively. Samples from Bluff03 were collected from the bluff walls that had
92 developed by gully formations on a gentle slope of the Yedoma using a chainsaw. Samples of
93 Bluff06 were collected from outcrops within eroded frozen peatland in a thaw lake basin. All
94 the ice-wedge samples used in this study were stored in a chest freezer at $< -18^{\circ}\text{C}$ before
95 analysis.

96 The ice-wedge ice is most different from polar ice cores, in that their gas mixing ratios
97 are not homogeneous (e.g., Kim et al., 2019), which may hinder exact comparison with results
98 from adjacent ice samples. We therefore randomly mixed sub-samples to reduce the effect of
99 the heterogeneous gas composition distribution (random cube method hereafter).
100 Approximately 100–200 g of an ice-wedge sample was cut into 25 to 50 cubes of 3–4 g each,
101 and for each experiment, ~10 to 12 cubes were randomly chosen so that the total weight of the
102 sub-sample was ~40 g.

103

104 **2.2. Gas extraction procedures**



105 ***Dry extraction (needle crusher)***

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

116 Following extraction, the sample tubes were detached from the He-CCR, warmed to
117 room temperature ($\sim 20^{\circ}\text{C}$), and attached to a gas chromatograph (GC) equipped with an
118 electron capture detector (ECD) and a flame ionization detector (FID) to determine the mixing
119 ratios of CH_4 and N_2O . Details of the GC system are given in Ryu et al. (2018). The daily
120 calibration curves were established using working standards of 15.6 ± 0.2 ppm CH_4 , $10000 \pm$
121 30 ppm CH_4 , 2960 ± 89 ppb N_2O , 29600 ± 888 ppb N_2O , and a modern air sample from a
122 surface firn at Styx Glacier, Antarctica, which was calibrated as 1758.6 ± 0.6 ppb CH_4 and
123 324.7 ± 0.3 ppb N_2O by the National Oceanic and Atmospheric 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 is identical to the procedure described in Yang et al. (2017) and Ryu et al.
129 (2018), except for the sample gas trapping procedure (see below). Ice-wedge sub-samples of



130 ~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 In this study, we attached the He-CCR device to our wet extraction line and the gas samples in
138 the flasks were cryogenically trapped. The reasons for using He-CCR instead of direct
139 expansion to a GC are twofold: 1) to better compare the dry and wet extraction methods by
140 applying the same trapping procedure, and 2) to maximize the amount of sample gas for GC
141 analysis, because the gas expansion from a large flask allows only a small fraction of gas to be
142 measured by 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 sterilization (Fletcher and Kaufman,
145 1980). Taking the dry soil mass of the analysed samples (0.33 g) into account, we added 24 μL
146 of saturated HgCl_2 solution (at 20°C) to the sample flasks. The flasks with HgCl_2 solution were
147 then frozen in a deep freezer at $< -45^\circ\text{C}$ to prevent the dissolution of ambient air into the
148 solution during ice sample loading. After the wet extraction procedure was complete, the
149 extracted gas was trapped in a sample tube and the CH_4 and N_2O mixing ratios were determined
150 using the same GC-ECD-FID system as the dry-extracted gas. The resulting CH_4 and N_2O
151 mixing ratios have not been corrected for partial dissolution in ice melt in the flasks, because
152 CH_4 and N_2O trapped in refrozen ice are negligible compared to the ranges of the systematic
153 blanks (see Appendix).

154



155 **2.3. Gas content**

156 The analytical methods described previously are for determining the mixing ratios of
157 CH₄ and N₂O in the extracted gas. To convert these mixing ratios into moles of CH₄ and N₂O
158 per unit mass of ice-wedge sample (CH₄ and N₂O content, respectively, hereafter) requires data
159 regarding the amount of gas extracted. The gas content is a measure of gas volume enclosed in
160 a unit mass of ice sample at STP (in mL kg_{ice}⁻¹). Thus, the CH₄ and N₂O contents can be
161 calculated using the gas content, the total mass of the random cube ice, and the gas mixing
162 ratio. The gas content in the control and HgCl₂-treated wet extraction experiments was
163 calculated from the temperature and pressure of the extracted gas and the internal volume of
164 the vacuum line. The details of the extraction system and correction methods used for
165 estimating gas content are described in Yang (2019). Similarly, the gas content of the dry
166 extraction samples was also inferred from the volume and pressure of gas inside the vacuum
167 line once the sample tube was attached to the line for GC analysis. The uncertainties of the
168 calculated CH₄ and N₂O contents were calculated by using error propagation of the blanks and
169 gas content uncertainties (see Appendix for uncertainty estimation of the blank corrections and
170 gas contents).

171

172 **2.4. Dry soil content**

173 Dry soil content was measured using the leftover meltwater from the control-wet
174 extraction tests. After the control-wet extractions were complete, the sample flasks were shaken
175 well and the meltwater samples were each poured into a 50 mL conical tube. The meltwater
176 and soils were separated by a centrifugal separator at 3000 rpm for 10 min. The separated wet
177 soils were wind-dried in evaporating dishes at approximately 100°C for 24 hours. The weight
178 of each individual evaporating dish was pre-measured before use. The dry soil content was
179 calculated by subtracting the weight of the evaporating dish from the total weight of the dried



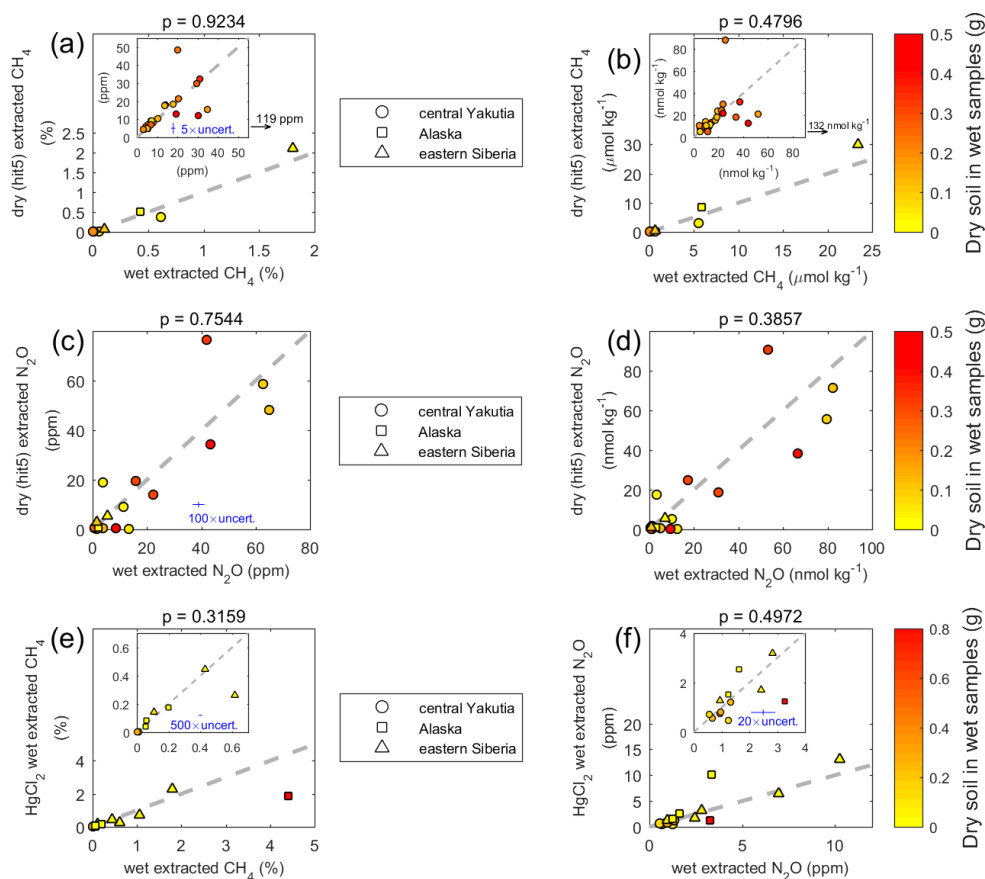
180 soil sample plus the evaporating dish.

181

182 **3. Results and Discussion**

183 **3.1. Comparison between wet and dry extraction methods**

184 The results from the wet and dry extractions were compared using 23 ice-wedge
185 samples (21 for N₂O) from Alaska and Siberia. In both the CH₄ and N₂O mixing ratio analyses,
186 we found that the wet and dry extraction results did not differ significantly ($p > 0.1$), regardless
187 of sampling site or soil content (Figure 1, a to d). We noted that the heterogeneous distribution
188 of gas mixing ratios may not have been completely smoothed out by our sub-sample selection,
189 although we randomly chose 8–12 ice cubes for each measurement. Some previous studies
190 have avoided using the wet extraction method because of potential reactivation of microbial
191 CH₄ and/or N₂O production in ice melt (e.g., Cherbunina et al., 2018; Kim et al., 2019).
192 Assuming that activation of microbial metabolism is unlikely during dry extraction at a
193 temperature of -37°C in the extraction chamber for < 1 h, our findings may imply that wet
194 extraction does not stimulate microbial reactivation to a measurable extent.



195

Figure 1. Comparison of CH₄ and N₂O mixing ratios and contents obtained by different extraction methods. Shown are scatter plots between wet- and dry (hit5) extraction results of CH₄ (a and b) and N₂O (c and d), and between control- and biocide-treated wet extraction results for CH₄ (e) and N₂O (f). 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 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 top of each plot.

196



197 **3.2. Testing microbial alteration during wet extraction**

198 To test the microbial production of CH₄ and N₂O during wet extraction more accurately,
199 we conducted wet extraction experiments on samples treated with HgCl₂, a commonly used
200 effective biocide (e.g., Torres et al., 2005), and compared the results with those of untreated
201 (control) wet extractions. We prepared 12 additional ice-wedge samples using the random cube
202 method for these tests (see Materials and Methods section). We found no significant differences
203 between the control and HgCl₂-treated wet extraction results for both CH₄ and N₂O mixing
204 ratios (Figures 1e and 1f), indicating that the bias due to microbial activity during
205 approximately an hour of the melting-refreezing procedure is not significant. This is further
206 supported by tests on an additional 12 ice-wedge samples (using the random cube protocol)
207 treated with 2-bromo-ethane-sulfonate (BES), a specific methanogenesis inhibitor (e.g., Nollet
208 et al., 1997) (Figure A3). Similar to the HgCl₂-treated experiments, 25 μL of a saturated BES
209 solution was added to each sample flask. These additional tests were carried out only for CH₄.
210 The two-sided t-test for the CH₄ data indicates an insignificant difference between the two
211 results ($p > 0.9$). Data from individual sampling sites also do not show significant differences
212 ($p > 0.9$ for the Alaskan samples and $p > 0.5$ for the central Yakutian samples).

213 According to microbial sequencing studies that have shown the presence of viable
214 microbes in permafrost and ground ice (e.g., Katayama et al., 2007), it is likely that culturable
215 microbes exist in the ice-wedge samples used in this study. However, considering that at least
216 14 days and up to 3 months of culturing was required to identify microbe colonies extracted
217 from ground ice (Katayama et al., 2007; Lacelle et al., 2011), our melt-refreeze time of an hour
218 was insufficient for microbial activity to resume and produce CH₄ and N₂O.

219

220 **3.3. Dry extraction efficiency and gas mixing ratios**

221 One limitation of our needle crushing dry-extraction technique is the inability to



222 completely extract gas from ice samples, because small ice particles and/or flakes placed in the
223 space between the needles are not fully crushed. The gas extraction efficiency of the SNU
224 needle crusher system has been reported as ~80–90% for polar ice core ice samples (Shin,
225 2014). However, the gas extraction efficiency has not been tested for ice-wedge samples.
226 Depending on the extraction efficiency, the needle crushing method could underestimate the
227 gas contents if the gas is not completely extracted. Another possible bias in the gas mixing
228 ratios arises if the CH₄ and N₂O compositions are different between the crushed and uncrushed
229 portions of the ice-wedge samples.

230 To estimate the biases arising from incomplete gas extraction, we designed a series of
231 tests to identify the differences of the CH₄ and N₂O mixing ratios and contents between the
232 crushed and uncrushed sample portions. Each ice-wedge sample that was randomly collected
233 was first crushed by the regular dry extraction procedure (by hitting it five times with the needle
234 system, ‘hit5’), and the gas liberated from the sample was trapped in a sample tube. Then we
235 performed an additional 100 hits on the leftover ice (‘hit100’), monitored the amount of
236 additional gas liberated, and trapped the additional gas in a separate sample tube. Comparisons
237 between the hit5 and hit100 results are summarized in Table 1.

238 Here we regard the ratio of gas content of hit100 to that of hit5 (hit100/hit5 ratio
239 hereafter) as a measure of the gas extraction efficiency of the needle crusher system. The results
240 demonstrate an average hit100/hit5 ratio of gas content of 0.40 ± 0.07 for the Zyryanka samples,
241 0.24 ± 0.07 for the Bluff samples, and 0.14 ± 0.11 for the Cyuie samples (Table 1). Despite the
242 fact that the number of samples was limited, the ice-wedge samples from the different sites
243 show distinct hit100/hit5 ratios of the amount of extracted gas. However, we observed that the
244 leftover ice from the Bluff and Zyryanka samples were not well-crushed, even after 100 hits
245 with the needle crusher. This was especially true if the ice sub-samples contained soil
246 aggregates: the frozen soil aggregates were barely crushed. In contrast, the Cyuie samples were



247 relatively well-crushed, and the leftover samples were apparently finer-sized ice flakes. We
248 also observed that the hit100/hit5 ratios of gas content are highly variable within samples from
249 a particular site, implying that the extraction efficiency of the needle crusher not only depends
250 on site characteristics, but also on the individual ice sample hardness. When compared with the
251 dry soil content measured from the sub-samples used for wet extraction, no relationship was
252 observed between the dry soil content and the extraction efficiency. In addition, in the case of
253 samples uncrushed by the hit100 test, it is difficult to estimate the extraction efficiency using
254 the hit100/hit5 ratio of gas content, as the hit100 tests liberated only a marginal portion of gas
255 from these samples. This is because the large-sized uncrushed soil aggregates or particles may
256 have prohibited the needle crusher from crushing the small-sized ice flakes or grains. The
257 needles move up and down together, as they are fixed to a pneumatic linear motion feedthrough
258 device, thus if there is a sizable soil clod that cannot be crushed, it blocks the needle crusher
259 from moving further down. Therefore, we do not recommend using a needle crusher system to
260 measure gas contents in ice-wedge samples.

261 The hardness of the ice samples may also affect the gas mixing ratio analysis in the hit5
262 and hit100 procedures. The hit100/hit5 ratio of CH₄ mixing ratio of Bluff and Zyryanka
263 samples are less than 1 in four out of six samples, yielding an average of 0.9 ± 0.5 . However,
264 all five samples from the Cyuie ice-wedges have ratios greater than 1, with an average of 4.7
265 ± 2.6 (Table 1). The higher hit100/hit5 ratio of CH₄ mixing ratios of Cyuie samples indicates
266 that the gases extracted via the hit100 procedure have higher CH₄ mixing ratios than the gases
267 extracted via the hit5 procedure. Considering these results with those discussed previously, we
268 speculate that there are three ways gas can be trapped in ice-wedge ice: enclosed in bubbles,
269 adsorbed on soil particles, and entrapped in soil aggregates. The better-crushed leftover ice
270 flakes in the Cyuie samples may have allowed most of the gas in bubbles and part of the CH₄
271 molecules adsorbed on soil particles and/or trapped in microsites within soil aggregates to be



272 liberated. Thus, the hit5 CH₄ mixing ratios of the Cyuie samples may more reflect the gas
273 mixing ratios in bubbles, while the hit100 results reflect more of the contribution from gas
274 adsorbed on soil and trapped within soil aggregates than the hit5 results because soil-rich ice
275 has greater hardness than the soil-poor ice. If this is the case for the Cyuie samples, we can
276 infer that CH₄ is more concentrated in soil particles and in microsites within soil aggregates,
277 compared to in bubbles in the ice. This is partly supported by evidence that ice-wedge layers
278 exhibit relatively trace amounts of CH₄ compared to the surrounding permafrost soil layers
279 (Rivkina et al., 2007); however, this needs to be further evaluated by detailed microbial and
280 chemical analyses. In the meanwhile, in the Bluff and Zyryanka samples, the hit5 results reflect
281 the mixing ratios of the gases from the crushed portions, regardless of their origin: bubbles,
282 particle adsorption, or microsites in aggregates. Given that some of the Bluff and Zyryanka ice-
283 wedge samples were not fully crushed by the hit100 tests, it may require additional hits or
284 another extraction technique. Unlike CH₄, the N₂O mixing ratios from the hit100 extractions
285 are higher than the hit5 in ten out of eleven samples, regardless of the sampling site. The
286 hit100/hit5 ratios of N₂O mixing ratios of the Bluff and Zyryanka samples (1.9 ± 0.8 on average)
287 are not significantly different ($p = 0.32$) from those of the Cyuie samples (2.9 ± 1.8 on average).
288 This can probably be explained by the fact that the N₂O mixing ratio is not necessarily higher
289 in soil-rich ice because N₂O is an intermediate product in relatively oxic conditions, while CH₄
290 is produced strictly in anoxic conditions.

291 One may expect that a different crushing technique might be more suitable for ice-
292 wedge samples. However, none of the existing dry extraction techniques - centrifugal ice
293 microtome (Bereiter et al., 2013), mechanical grater (Etheridge et al., 1988), or ball-mill
294 crusher (Schaefer et al., 2011) is more advantageous for ice-wedge analysis compared to the
295 needle crusher system used in this study. The hard portion of ice wedges (e.g., frozen soil
296 aggregates, large soil particles) could easily damage the metal blades of the centrifugal ice



297 microtome and mechanical grater devices, or block the space within the ball-mill chamber,
298 limiting the movement of the milling balls.

299 It is worth noting that friction between stainless steels could produce CH₄ with carbon
300 from the damaged stainless-steel surface and hydrogen gas (Higaki et al., 2006). If needle
301 crushing causes contamination in this way, the dry extraction results should be affected by the
302 number of hits. To check the impact of the needle crushing procedure on ice-wedge CH₄ and
303 N₂O measurements, we carried out blank tests by changing the numbers of hits from 5 to 100.
304 The results of these tests show no systematic offset among the experiments with different
305 numbers of hits (Figure A2), which implies that the crushing procedure does not affect the dry
306 extraction results for CH₄ and N₂O. Even though a small of contamination does exist, its effects
307 have already been subtracted via blank correction and taken into account in the overall error
308 estimation (see Appendix). Therefore, we consider that our findings are not artefacts of metal
309 friction during crushing.

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



315 **Table 1.** Results of dry extraction tests with 5- and additional 100 times hitting ice-wedge samples, denoted as ‘hit5’ and ‘hit100’, respectively. ‘hit100/hit5’
 316 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
 317 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
 318 additional amount of gas extracted after ‘hit5’ crushing and evacuation.

Site Location	Sample	gas content				CH ₄ mixing ratio				N ₂ O mixing ratio			
		Wet control		Dry hit100		Wet control		Dry hit100		Wet control		Dry hit100	
		ml/kg	ml/kg	ml/kg	ml/kg	hit100/hit5	ppm	ppm	ppm	ppm	hit100/hit5	ppm	ppm
Zyryanka, Northeastern Siberia	Zy-A-W1-D	20.2	13.1	6.3	0.48	6138	3713	2721	0.7329	11.37	9.10	10.15	1.12
	Zy-F-1	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	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	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	13.2	12.2	2.6	0.21	44160	25230	12240	0.4851	5.58	2.36	4.93	2.09
	Bluff06-B3	20.1	20.9	5.6	0.27	558.7	164.2	219.5	1.337	3.74	18.78	30.14	1.605
	CYC-01-B	18.0	21.7	7.1	0.33	18.0	18.3	25.4	1.39	1.55	1.60	2.59	1.62
Cyuie, Central Yakutia	CYB-04-C	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	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	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	22.6	15.7	3.3	0.21	20.3	13.9	94.5	6.80	1.40	0.65	1.08	1.7



319 **3.4. Residual gas mixing ratios and contents after wet extraction**

320 To examine how well the gas is extracted by wet extraction, we applied the dry
321 extraction method to refrozen ice-wedge samples after wet extraction. We first prepared
322 degassed ice-wedge samples that had undergone repetitive wet extractions (wet-degassed ice
323 hereafter). Once the wet extraction experiments were completed, we repeated two cycles of
324 melting-refreezing and evacuation procedures to degas the ice melt. After degassing by a total
325 of three cycles of wet extraction and evacuation, the outermost surfaces (~2 mm) of the wet-
326 degassed ice were trimmed away in the walk-in freezer at SNU on the morning of experiments.
327 The wet-degassed ice was then inserted into the needle crusher and the crusher chamber was
328 evacuated. A specific amount of standard air was injected. Then, the wet-degassed ice samples
329 were hit 20 or 60 times by the needle crusher. The amount of gas and gas mixing ratio of the
330 additionally extracted gas from the wet-degassed ice are shown in Figure 2 and Table A1.

331 The tests using the wet-degassed ice show an additional gas extraction of ~12 to 20 ml
332 $\text{kg}_{\text{ice}}^{-1}$, which is ~43 to 88% of the amount of gas extracted during the initial wet extraction.
333 The additionally extracted gas from the dry extraction is referred to as residual gas hereafter.
334 This is remarkably in contrast to the less than 1% residual fraction of the SNU wet extraction
335 system for ice from polar ice sheets. If such a considerable amount of gas is left intact by
336 repeated wet extractions, the composition of the additional gas is important to understand how
337 much the conventional wet extraction results are biased.

338 Figure 2 and Table A1 show the mixing ratios and contents of CH_4 and N_2O in the
339 residual gas. The mixing ratios of the residual gas were estimated using mass balance
340 calculations with observed mixing ratios and the amounts of the injected standard and extracted
341 residual gas. The CH_4 mixing ratios of the residual gas range from 10.37 to 23.78 ppm, which
342 is similar to the range of the wet extracted gas. This evidence indicates that CH_4 in ice-wedges
343 cannot be fully extracted by a melting-refreezing procedure. We suspect two possible reasons



344 for this: (1) During wet extraction, the ice-wedge samples melted and the soil particles settled
345 at the bottom of the sample flask without any physical impact to the soil particles, causing the
346 adsorbed CH₄ molecules on the soil particles to remain adsorbed. (2) During refreezing, the
347 soils accumulated at the bottom of the flasks are crumpled around the centre of the refrozen
348 ice, because the sample flasks are chilled from outside, which facilitated gas entrapment within
349 the frozen soil aggregate. In contrast, the N₂O mixing ratios of the residual gas exhibit very
350 low values compared to those from the initial wet extraction (Figure 2 and Table A1). These
351 results imply that most of the N₂O in ice wedges is extracted by three melting-refreezing cycles,
352 such that only a small amount of N₂O is left adsorbed or entrapped in ice-wedge soils.

353 In this section, we found that a certain amount of gas remained in ice wedges, even after
354 three cycles of wet extraction, which is extractable instead by needle crushing. This implies
355 that, unlike polar ice cores, wet extraction of ice-wedges does not guarantee near-complete gas
356 extraction, and therefore, precise measurements of the gas content of ice wedges are difficult
357 to obtain. The difficulty in measuring gas content imposes a large uncertainty in estimating
358 CH₄ and N₂O contents. Furthermore, we found that the residual gas has a similar order CH₄
359 mixing ratio as the gas extracted by initial melting-refreezing, indicating that a comparable
360 amount of CH₄ still remains unextracted in ice-wedges. Hence, a novel extraction method is
361 required to produce reliable gas content and gas mixing ratios in ice wedges. In contrast, our
362 results show that the N₂O content of the residual gas is at trace levels, which may suggest that
363 most of the N₂O in ice-wedges is extractable during initial melting-refreezing. Therefore, wet
364 extraction could be applicable for estimating the N₂O content of ice wedges. However, given
365 that the above evidence resulted from three consecutive cycles of melting-refreezing and
366 evacuation, it is unclear how many melting-refreezing cycles are required to extract most of
367 the N₂O from ice wedges. Our findings imply that previous estimates of CH₄ budget in ground
368 ice based on wet extraction principle (e.g., Boereboom et al., 2013; Cherbunina et al., 2018)



369 might have been underestimated, and that the CH₄ production within subfreezing permafrost
 370 environment could be larger than previously estimated. Future study should be devoted to a
 371 novel extraction method which is able to extract gas molecules from ice effectively.

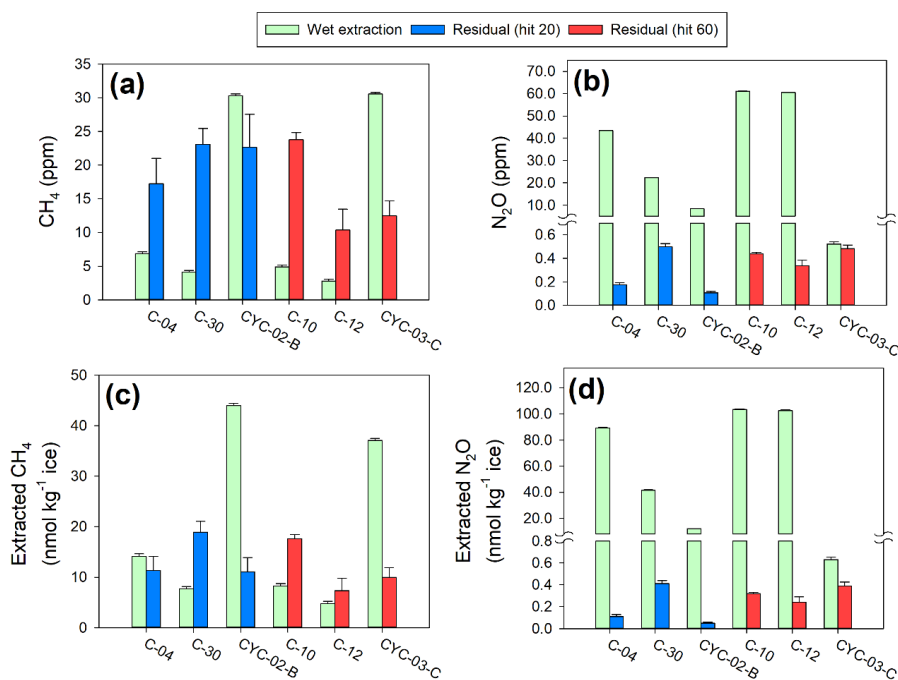


Figure 2. Comparison of wet-extracted gas and residual gas for CH₄ and N₂O mixing ratios (a and b) and contents (c and d). The residual gas was extracted from the dry extraction method using the wet-degassed ice samples. The light green bars show the results of initial wet extraction, and the blue and red bars indicate the dry extraction of wet-degassed ice with 20- and 60-times hitting, respectively.

372

373 4. Conclusions

374 In this study we carried out comparisons between wet and dry extractions, between
 375 untreated and biocide-treated wet extractions, and gas extraction from the easily to extract and
 376 difficult to extract parts of ice-wedge ice to better understand the characteristics of each
 377 extraction method, in order to adequately analyse CH₄ and N₂O mixing ratios and gas contents
 378 from permafrost ice wedges. Based on these comparisons, our major findings are summarized
 379 as follows:



- 380 1) Existing wet and dry extraction methods allow gas extraction from the soft parts of
381 ice (e.g., ice bubbles) and show insignificant differences in CH₄ and N₂O mixing
382 ratios.
- 383 2) Wet extraction results are unlikely to be affected by microbial production of CH₄
384 and N₂O during the melting-refreeze procedure.
- 385 3) Both dry and wet extraction methods are not able to fully extract gas from ice wedge
386 samples, presumably due to gas adsorbed on soil particles or enclosed within soil
387 aggregates, which may have different gas mixing ratios compared to the gas in
388 bubbles. Further research is required to develop a proper method to quantify and
389 extract adsorbed and enclosed gases. In the meantime, we propose that both existing
390 techniques may be suitable for gas mixing ratio measurements for bubbles in
391 relatively soft ice wedges. Exceptionally, the N₂O content in ice wedges may be
392 measured by using repeated wet extractions, but this is not the case for determining
393 the N₂O mixing ratio.
- 394 4) Our results indicate that previous estimates of ground ice CH₄ and N₂O budget
395 might be underestimated, implying that the greenhouse gas production in
396 subfreezing environment of permafrost is larger than our current understanding.
- 397 5) Our finding indicates that the saturated NaCl solution is unnecessary to prevent
398 microbial activity during melting, as employed by, e.g., Cherbunina et al. (2018).
399 However, it remains as an open question how effectively the adsorbed gas
400 molecules can be extracted by the method.
- 401
- 402



403 **Appendix. Systematic blank correction and uncertainty estimation**

404 Since the SNU dry extraction systems, including the sample tubes, were originally
405 designed for CO₂ measurements from polar ice cores, these systems have not been tested for
406 CH₄ and N₂O analysis. We therefore carried out a series of tests to estimate the systematic
407 blank, which is defined here as blanks.

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

422 For the wet extraction, a total of ~45 g of BFI cubes was placed into each sample flask.
423 The flasks were connected to the wet extraction line and sealed with a copper gasket, then
424 evacuated. Once a vacuum was established, a known amount of standard gas was injected into
425 each flask and the flasks were submerged into a warm water bath for ~40 min to melt
426 completely. The flasks were then submerged into the cold ethanol bath, which was chilled to -
427 80°C, to refreeze. For the HgCl₂ and Sodium 2-bromo-ethane-sulfonate (BES) treated

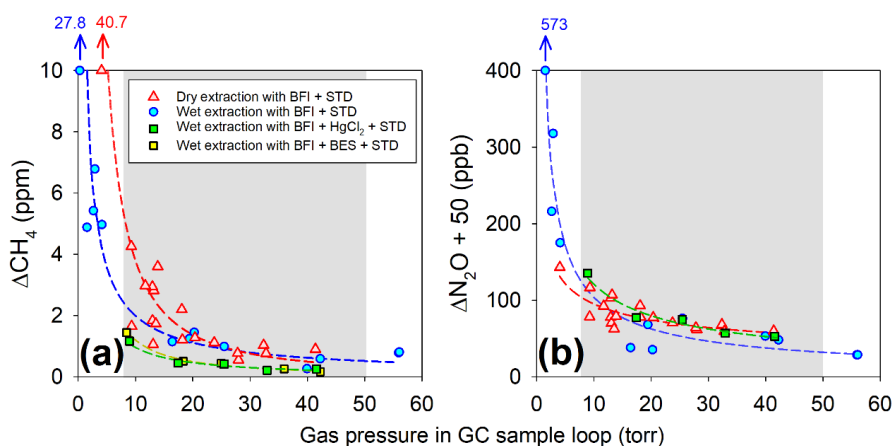


428 experiments, we first prepared the saturated solutions of HgCl_2 and BES at room temperature
429 (20°C) and added $24\ \mu\text{L}$ of HgCl_2 or $20\ \mu\text{L}$ of BES solution into the empty flasks in a fume
430 hood. Then we placed the flasks in a deep freezer, maintained at -45°C for 20 min, to freeze
431 the solutions before the BFI pieces were placed.

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

437 To calculate uncertainties of the blank corrections, the blank test data were fitted with
438 exponential regression curves (Figure A1). The root-mean-square-deviations (RMSD) of the
439 data from the regression curves are taken as the uncertainties of blank corrections (Figure 1).
440 Since the ice-wedge data used in this study showed the pressure in GC sample loop of about 8
441 ~ 50 torr, the RMSD were estimated from the blank test data within this pressure range. The
442 uncertainty of the gas content measurement is calculated by error propagation from those of
443 pressure, line volume, and mass of ice samples.

444



445

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.

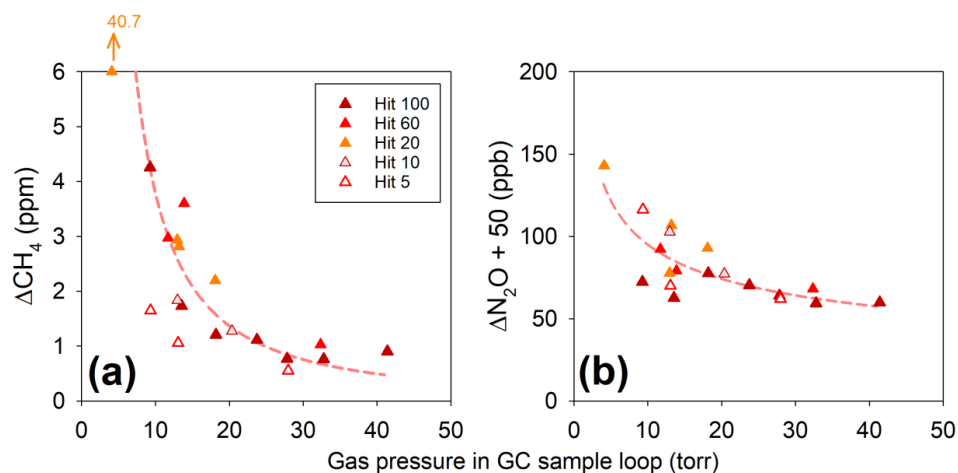


Figure A2. Influence of different number of hitting on the systematic blank of the needle crushing (dry extraction) system for (a) CH_4 and (b) N_2O measurements. Note that all data are plotted against the amount of gas trapped in the sample tube, presented here as the pressure in the GC sample loop 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.

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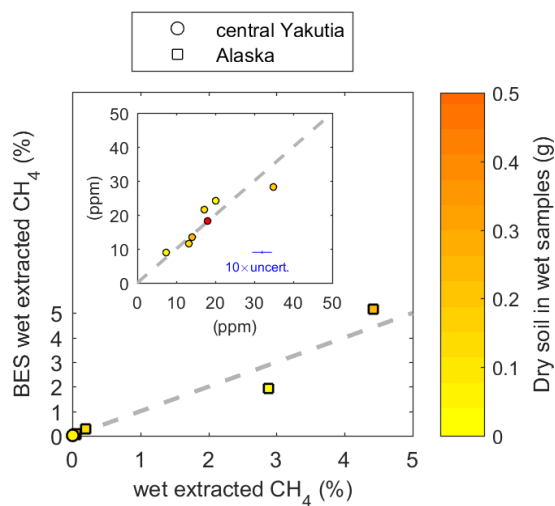


Figure A3. Comparison between control- and BES-treated wet extraction results for CH₄. The sampling area is indicated by different symbols. The color of each data point indicates the dry soil weight in the subsamples used in control wet extraction. The grey dashed lines are 1:1 reference line.

449

450



451 **Table A1.** Comparison of results from extracted gas from the conventional wet extraction method and the residual gas in ice after 3-times wet extraction. The
 452 residual gas was extracted by a needle crusher (see section 3.4 for details of the methods)

Site location	Sample	soil content	Wet extraction				Residual gas						
			gas content	CH ₄ mixing ratio	N ₂ O mixing ratio	CH ₄ content	N ₂ O content	gas content	CH ₄ mixing ratio	N ₂ O mixing ratio	CH ₄ content	N ₂ O content	
		wt. %	ml/kg	ppm	ppm	nmol/kg	nmol/kg	ml/kg	ppm	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	
Cyuié, 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	
Cyuié, 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	



455 **Data availability**

456 The data will be uploaded on the public data repository of Pangaea after publication.

457

458 **Author contributions**

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

462

463 **Competing interests**

464 The authors declare no conflict interest.

465

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470

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