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4 **Limited contribution of permafrost carbon to methane release from thawing**
5 **peatlands**

6

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33 **Models predict that thaw of permafrost soils at northern high-latitudes will release**
34 **tens of billions of tonnes of carbon (C) to the atmosphere by 2100¹⁻³. The effect on the**
35 **Earth's climate depends strongly on the proportion of this C which is released as the**
36 **more powerful greenhouse gas methane (CH₄), rather than carbon dioxide (CO₂)^{1,4};**
37 **even if CH₄ emissions represent just 2% of the C release, they would contribute**
38 **approximately one quarter of the climate forcing⁵. In northern peatlands, thaw of ice-**
39 **rich permafrost causes surface subsidence (thermokarst) and water-logging⁶,**
40 **exposing substantial stores (10s of kg C m⁻², ref. 7) of previously-frozen organic**
41 **matter to anaerobic conditions, and generating ideal conditions for permafrost-**
42 **derived CH₄ release. Here we show that, contrary to expectations, although**
43 **substantial CH₄ fluxes (>20 g CH₄ m⁻² yr⁻¹) were recorded from thawing peatlands in**
44 **northern Canada, only a small amount was derived from previously-frozen C (<2 g CH₄**
45 **m⁻² yr⁻¹). Instead, fluxes were driven by anaerobic decomposition of recent C inputs.**
46 **We conclude that thaw-induced changes in surface wetness and wetland area, rather**
47 **than the anaerobic decomposition of previously-frozen C, may determine the effect of**
48 **permafrost thaw on CH₄ emissions from northern peatlands.**

49 Permafrost peatlands occupy more than 1 million km² (ref. 7), and could dominate
50 the permafrost CH₄ feedback³. Although these peatlands only store approximately 20% of
51 the total permafrost C stock which is predicted to thaw this century⁸, potential decomposition
52 rates associated with frozen organic soils are up to five times greater than for frozen mineral
53 soils⁹, and peats are disproportionately likely to be water-logged following thaw^{3,10}. For these
54 reasons, one modelling study assumed that all the CH₄ released as a result of permafrost
55 thaw would be derived from currently-frozen peats (histels)³. The histels most vulnerable to
56 thaw during this century are located in the southern permafrost zone¹¹, where the presence
57 of permafrost raises the peat surface above the water table, forming plateaus dominated by
58 tree, shrub, moss and lichen communities (see supplementary material)¹². This results in the
59 formation of a mixture of woody (sylvic) and *Sphagnum*-moss peat. Thaw of ice-rich
60 permafrost within these peatland plateaus causes surface subsidence, resulting in the

61 formation of collapse wetlands with water-logging and vegetation change^{6,12}. In collapse
62 wetlands, there is then significant potential for CH₄ to be released from the decomposition of
63 previously-frozen organic matter because: 1) thaw makes 10s of kg C m⁻² vulnerable to
64 microbial decomposition, and 2) water-logging produces oxygen-limited conditions
65 throughout the soil profile and thus all newly-thawed organic matter will decompose under
66 anaerobic conditions. However, despite the potential importance of these peatlands to the
67 permafrost CH₄ feedback³, to date, no study has quantified rates of CH₄ release from the
68 decomposition of previously-frozen C in these systems.

69 Unlike in thermokarst lakes where there is no *in situ* vegetation¹³, it is unclear to what
70 extent any CH₄ emitted from collapse wetlands is derived from old, previously-frozen C (ref.
71 14) versus new C inputs from the hydrophilic vegetation communities that develop post
72 thaw^{6,15}. This is important because determining the source of the CH₄ is required for
73 accurately simulating future fluxes, as the factors controlling emission rates differ
74 fundamentally. While the total C stock and its decomposability are the main relevant
75 predictors of CH₄ release from previously frozen C (ref. 3), the most important driver of CH₄
76 fluxes from new C inputs is the change in wetland area, together with the quantity and
77 quality of new inputs¹⁶. Radiocarbon (¹⁴C) measurements offer the potential to address this
78 key uncertainty. Because permafrost C is typically thousands of years old, measuring the ¹⁴C
79 content of the CH₄ can determine whether previously-frozen, old C contributes substantially
80 to CH₄ release post thaw. However, until recently such measurements were very challenging
81 in remote locations.

82 Using new techniques that overcome previous limitations¹⁷, we quantified the ¹⁴C
83 content of CH₄ produced within, and emitted from the surface, in contrasting collapse
84 wetlands in both the sporadic discontinuous permafrost zone (near Teslin, Yukon Territory in
85 2013: 60°05'27.5"N, 132°22'06.4"W) and the extensive discontinuous permafrost zone (near
86 Yellowknife, Northwest Territories in 2014: 62°27'25.7" N, 114°31'59.8" W). The total depth
87 of peat in the collapse wetlands was at least 160 cm in Teslin and 140 cm in Yellowknife.
88 Peat cores extracted from the collapse wetlands revealed clear stratigraphic transitions from

89 relatively undecomposed sedge/moss peat accumulated post thaw to plateau peat. The
90 depths of this transition were ~60 cm at Teslin and ~25 cm at Yellowknife (see
91 supplementary material). We used probes to collect CH₄ from 40 cm below the transition
92 depth at each site, and collected samples of CH₄ released from surface collars that either
93 included (full-profile collars) or physically excluded (near-surface collars) CH₄ production
94 from peat layers deeper than 40 cm from the surface (Fig. S1). In addition, site differences
95 allowed us to 1) determine how the contributions of the different CH₄ sources changed with
96 time since peat plateau collapse from recent to ~60 years (Fig. 1a; at Teslin by sampling at
97 the collapse wetland Margin, 5m in, and at the wetland centre) and 2) investigate the
98 importance of the different types of post-thaw vegetation community (Fig. 1b; Yellowknife:
99 sedges with their potential for rapidly transporting CH₄ up from depth¹⁸ versus *Sphagnum*
100 moss-dominated communities).

101 Collapse wetlands released substantial amounts of CH₄, whereas, consistent with
102 previous observations^{6,15}, net CH₄ release was not detected from undisturbed peat plateaus.
103 In Teslin, the water table remained within 5 cm of the soil surface throughout the 2013
104 growing season (Fig S3) and CH₄ emissions reached up to 400 mg CH₄ m⁻² day⁻¹ with an
105 estimated release of 21 g CH₄ m⁻² during the growing season (Fig. 2a). We did not observe
106 differences in CH₄ fluxes across the gradient of time since collapse (up to an age of 60
107 years; P = 0.192). This demonstrates that high fluxes can persist for multiple decades
108 (Fig. 2a), although previous studies have identified lower fluxes in collapse wetlands with
109 ages older than 200 years¹⁹. In Yellowknife, an anomalously dry summer in 2014, with less
110 than 30 mm of rain in June and July, approximately 30% of the long-term average rainfall for
111 these months, resulted in the water table falling to a depth of 30 cm (Fig S3). As a result,
112 growing season CH₄ emissions were lower than in Teslin (Fig. 2a,b). We calculated that 3.2
113 g and 2 g CH₄ m⁻² were released from sedge- and moss-dominated collapse wetlands,
114 respectively. The difference between vegetation communities was not significant (P =
115 0.093), but there was some uncertainty in calculating growing season fluxes caused by
116 limited mid-season site access due to forest fire hazards.

117 In Teslin, the CH₄ collected at depth with probes had a depleted ¹⁴C signature,
118 demonstrating that organic matter with radiocarbon ages ranging from 700 to 2800 years
119 before present (y BP), was decomposing to produce CH₄ (see Table S1). Conversely, the
120 ¹⁴C content of CH₄ released at the collapse wetland surface was greater than that of the
121 current atmosphere²⁰ (Fig 3a), indicating that the flux was dominated by C fixed since
122 nuclear weapons testing enriched the atmosphere in ¹⁴C during the second half of the 20th
123 century. The ¹⁴C content of the CH₄ emitted from collars that included deeper peat layers
124 was significantly lower than from the collars that excluded fluxes from below 40 cm
125 (P = 0.022), identifying a measureable contribution from deeper peat (>40 cm). Given the
126 variation in the ages of CH₄ collected by the probes, a sensitivity analysis (Equation 1) was
127 used to estimate the potential maximum contribution of previously-frozen C to the surface
128 flux. Based on dating the organic matter at the base of the active layer (1200 y BP), a
129 maximum of 8.4 % (1.5 to 2 g CH₄ m⁻²) of the CH₄ emissions was calculated to be derived
130 from former permafrost peat, and did not change significantly with time since collapse
131 (Fig. 4; Supplementary Information and Equation 1).

132 The drier conditions in Yellowknife made the collection of probe CH₄ samples more
133 challenging, which may have contributed to the younger age of the CH₄ (150-800 y BP;
134 Table S1). However, the CH₄ released from the soil surface had a lower ¹⁴C content than in
135 Teslin and was also lower than that of the current atmosphere, indicating that relatively old C
136 was being released (Fig. 3b). The ¹⁴C content of the CH₄ emitted from near-surface collars
137 was higher than that from the full-profile collars again suggesting a contribution from deeper
138 soil layers, although the difference between collar treatments was not statistically significant
139 (P = 0.375). By carrying out the same sensitivity analysis based on the age of uppermost
140 permafrost C, it was estimated that previously-frozen organic matter could have contributed
141 a maximum of 30% to the CH₄ emissions (Fig. 4); this corresponds to 0.7-1.0 g CH₄ m⁻²
142 during the growing season. No significant difference in ¹⁴C between the moss and sedge-
143 dominated vegetation communities was detected (P = 0.982). It appears that by suppressing
144 near-surface CH₄ production, the dry conditions greatly reduced total CH₄ fluxes and thus

145 there was a greater proportional contribution of previously-frozen C. Regardless, the
146 absolute amount of CH₄ derived from previously-frozen C remained low.

147 The results from these two contrasting sites in different permafrost zones
148 demonstrate that, where substantial CH₄ fluxes occurred, they were dominated by anaerobic
149 decomposition of recent C inputs. Total rates of CH₄ release from previously-frozen C were
150 low irrespective of differences in time since thaw, vegetation community composition and/or
151 water-table depth. By calculating maximum potential contributions of previously-frozen C,
152 our calculations still likely represent an overestimation, adding to confidence to this overall
153 conclusion (see sensitivity analysis in Supplementary Information).

154 In both study sites, permafrost thaw exposed ~1 m of previously-frozen peat and >50
155 kg C m⁻² to anaerobic decay and yet maximum CH₄ release rates from this store during the
156 growing season were only 1-2 g C m⁻², or 0.02-0.04 g CH₄-C kg soil C⁻¹. Rates of CH₄
157 emitted from the decomposition of previously-frozen C in thermokarst lakes *in situ* (0.5 g
158 CH₄-C kg soil C⁻¹ yr⁻¹)¹³ and observed rates of CH₄ production in anaerobic incubations (1.2
159 g CH₄-C kg soil C⁻¹ yr⁻¹)²¹ are at least an order of magnitude greater than our *in situ* peatland
160 fluxes. The low rates of CH₄ release may be related to oxidation of the CH₄ to CO₂ during
161 transport within the peat, or slow rates of anaerobic decomposition of previously-frozen
162 SOM. We consider it unlikely that oxidation could explain the low rate of old CH₄ release, at
163 least at Teslin where the water table remained within 5 cm of the peat surface throughout the
164 growing season, and the sedge communities will have promoted rapid CH₄ transport from
165 depth¹⁸. Under long-term anaerobic conditions, the build-up of inhibitory compounds (e.g.
166 phenolics) within peats, may strongly suppress microbial activity and contribute to low rates
167 of anaerobic decomposition at depth²². Possibly reflecting this, warming of up to 9 °C did not
168 increase rates of decomposition in anaerobic peat layers below 20 cm in an ombrotrophic
169 bog in northern Minnesota²³. Thus, there may be little potential for CH₄ release from the
170 decomposition of deep peat C stores irrespective of whether or not these layers have been
171 frozen in the recent past. Given that histels are currently predicted to play a key role in the
172 permafrost CH₄ feedback³, the low rates of release we observed, suggest that anaerobic

173 decomposition of previously-frozen peat may not result in the release of 1-4 GT of CH₄ by
174 2100 that models and expert assessments predict^{3,5}.

175 On the other hand, CH₄ fluxes from thawing peatlands may still represent a key
176 component of the permafrost feedback. The differences between our field sites indicate that
177 CH₄ fluxes vary with water table depth post thaw, which may be linked to the magnitude of
178 surface subsidence, local hydrological conditions and climate variability²⁴. In our wetter field
179 site at Teslin, despite the low contribution of previously-frozen C, substantial amounts (21 g
180 CH₄ m⁻²) of CH₄ were released during the growing season. The fact that high CH₄ fluxes
181 were observed from areas that had thawed several decades ago suggests that permafrost
182 thaw at this site could have promoted the release up to 1 kg of CH₄-C m⁻² over the last 50
183 years. Therefore, where there is deep subsidence and near-surface water-logging, CH₄
184 fluxes from thawing permafrost peatlands can still produce a positive feedback to climate
185 change; the CH₄ is just not primarily derived from previously-frozen C. There is evidence that
186 the endpoint for permafrost thaw in boreal peatlands is inundated fens¹⁰ and studies have
187 identified an expansion of this type of wetland in parts of northern Canada²⁵. The
188 subsequent CH₄ release could lead to substantial increases in regional CH₄ fluxes¹⁶.
189 However, considerable observational^{26,27} and modelling^{16,28} uncertainty remains regarding
190 whether permafrost thaw will increase or decrease wetland extent in different regions.
191 Remote sensing techniques that can directly detect the spatial extent of wetlands and their
192 vegetation communities, especially sedges^{25,29,30}, may prove invaluable for quantifying the
193 effect of permafrost thaw on high-latitude CH₄ fluxes.

194 In conclusion, our study demonstrates that anaerobic decomposition of new C inputs
195 drive CH₄ emissions in contrasting thawed permafrost peatlands in northern Canada. These
196 results may have major implications for modelling the permafrost feedback, suggesting that,
197 to simulate future fluxes, efforts should be focused on accurately predicting the effects of
198 permafrost thaw on the spatial extent of wetlands, rather than rates of anaerobic
199 decomposition of previously-frozen peat.

200 **References**

- 201 1 Ciais, P. *et al.* in *Climate Change 2013: The Physical Science Basis. Contribution of*
202 *Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on*
203 *Climate Change* (eds T.F. Stocker *et al.*) Ch. 6, 465-570 (Cambridge University
204 Press, 2013).
- 205 2 Schaefer, K., Lantuit, H., Romanovsky, V. E., Schuur, E. A. G. & Witt, R. The impact
206 of the permafrost carbon feedback on global climate. *Environ. Res. Lett.* **9**, 085003,
207 (2014).
- 208 3 Koven, C. D. *et al.* A simplified, data-constrained approach to estimate the
209 permafrost carbon-climate feedback. *Phil. Trans. R. Soc. A.* **373**, 20140423, (2015).
- 210 4 Schuur, E. A. G. *et al.* Climate change and the permafrost carbon feedback. *Nature*
211 **520**, 171-179, (2015).
- 212 5 Schuur, E. A. G. *et al.* Expert assessment of vulnerability of permafrost carbon to
213 climate change. *Clim. Change* **119**, 359-374, (2013).
- 214 6 Turetsky, M. R., Wieder, R. K., Vitt, D. H., Evans, R. J. & Scott, K. D. The
215 disappearance of relict permafrost in boreal north America: Effects on peatland
216 carbon storage and fluxes. *Glob. Change Biol.* **13**, 1922-1934, (2007).
- 217 7 Hugelius, G. *et al.* Estimated stocks of circumpolar permafrost carbon with quantified
218 uncertainty ranges and identified data gaps. *Biogeosciences* **11**, 6573-6593, (2014).
- 219 8 Harden, J. W. *et al.* Field information links permafrost carbon to physical
220 vulnerabilities of thawing. *Geophys. Res. Lett.* **39**, L15704, (2012).
- 221 9 Schadel, C. *et al.* Circumpolar assessment of permafrost C quality and its
222 vulnerability over time using long-term incubation data. *Glob. Change Biol.* **20**, 641-
223 652, (2014).
- 224 10 Swindles, G. T. *et al.* The long-term fate of permafrost peatlands under rapid climate
225 warming. *Sci. Rep.* **5**, 17951, (2015).
- 226 11 McGuire, A. D. *et al.* Sensitivity of the carbon cycle in the Arctic to climate change.
227 *Ecol. Monogr.* **79**, 523-555, (2009).

- 228 12 Treat, C. C. *et al.* Effects of permafrost aggradation on peat properties as determined
229 from a pan-Arctic synthesis of plant macrofossils. *J. Geophys. Res. Biogeosci.* **121**,
230 78-94, (2016).
- 231 13 Walter Anthony, K. M. *et al.* Methane emissions proportional to permafrost carbon
232 thawed in Arctic lakes since the 1950s. *Nat. Geosci.* **9**, 679-682, (2016).
- 233 14 Miao, Y. *et al.* Growing season methane emission from a boreal peatland in the
234 continuous permafrost zone of Northeast China: effects of active layer depth and
235 vegetation. *Biogeosciences* **9**, 4455-4464, (2012).
- 236 15 Wickland, K. P., Striegl, R. G., Neff, J. C. & Sachs, T. Effects of permafrost melting
237 on CO₂ and CH₄ exchange of a poorly drained black spruce lowland. *J. Geophys.*
238 *Res. Biogeosci.* **111**, G02011, (2006).
- 239 16 Gao, X. *et al.* Permafrost degradation and methane: low risk of biogeochemical
240 climate-warming feedback. *Environ. Res. Lett.* **8**, 035014, (2013).
- 241 17 Garnett, M. H., Hardie, S. M. L. & Murray, C. Radiocarbon analysis of methane
242 emitted from the surface of a raised peat bog. *Soil Biol. Biochem.* **50**, 158-163,
243 (2012).
- 244 18 Knoblauch, C., Spott, O., Evgrafova, S., Kutzbach, L. & Pfeiffer, E. M. Regulation of
245 methane production, oxidation, and emission by vascular plants and bryophytes in
246 ponds of the northeast Siberian polygonal tundra. *J. Geophys. Res. Biogeosci.* **120**,
247 2525-2541, (2015).
- 248 19 Johnston, C. E. *et al.* Effect of permafrost thaw on CO₂ and CH₄ exchange in a
249 western Alaska peatland chronosequence (vol 9, 085004, 2013). *Environ. Res. Lett.*
250 **9**, 109601 (2014).
- 251 20 Levin, I., Kromer, B. & Hammer, S. Atmospheric $\Delta^{14}\text{CO}_2$ trend in Western European
252 background air from 2000 to 2012. *Tellus B* **65**, (2013).
- 253 21 Treat, C. C. *et al.* A pan-Arctic synthesis of CH₄ and CO₂ production from anoxic soil
254 incubations. *Glob. Change Biol.* **21**, 2787-2803, (2015).

255 22 Freeman, C., Ostle, N. & Kang, H. An enzymic 'latch' on a global carbon store - A
256 shortage of oxygen locks up carbon in peatlands by restraining a single enzyme.
257 *Nature* **409**, 149-149, (2001).

258 23 Wilson, R. M. *et al.* Stability of peatland carbon to rising temperatures. *Nat. Commun.*
259 **7**, (2016).

260 24 Olefeldt, D., Turetsky, M. R., Crill, P. M. & McGuire, A. D. Environmental and
261 physical controls on northern terrestrial methane emissions across permafrost zones.
262 *Glob. Change Biol.* **19**, (2013).

263 25 Baltzer, J. L., Veness, T., Chasmer, L. E., Sniderhan, A. E. & Quinton, W. L. Forests
264 on thawing permafrost: fragmentation, edge effects, and net forest loss. *Glob.*
265 *Change Biol.* **20**, 824-834 (2014).

266 26 Smith, L. C., Sheng, Y., MacDonald, G. M. & Hinzman, L. D. Disappearing Arctic
267 lakes. *Science* **308**, 1429-1429, (2005).

268 27 Watts, J. D., Kimball, J. S., Bartsch, A. & McDonald, K. C. Surface water inundation
269 in the boreal-Arctic: potential impacts on regional methane emissions. *Environ. Res.*
270 *Lett.* **9**, 075001, (2014).

271 28 Lawrence, D. M., Koven, C. D., Swenson, S. C., Riley, W. J. & Slater, A. G.
272 Permafrost thaw and resulting soil moisture changes regulate projected high-latitude
273 CO₂ and CH₄ emissions. *Environ. Res. Lett.* **10**, 094011, (2015).

274 29 Fraser, R. H. *et al.* Detecting Landscape Changes in High Latitude Environments
275 Using Landsat Trend Analysis: 1. Visualization. *Remote Sens.* **6**, 11533-11557,
276 (2014).

277 30 Hartley, I. P. *et al.* Quantifying landscape-level methane fluxes in subarctic Finland
278 using a multiscale approach. *Glob. Change Biol.* **21**, 3712-3725, (2015).

279

280 **Figure legends**

281

282 **Figure 1| Schematic diagram of the site-specific sampling designs.** Panel **a** shows the
283 Teslin sampling locations, which were established at three separate positions across a
284 gradient of time since thaw of a peat plateau, from (i) recent thaw at the edge of the collapse
285 wetland (Margin); to (ii) 5 m into the wetland where there were still standing dead trees (5
286 m); and in the wetland centre where collapse occurred approximately 60 years ago (centre).
287 Panel **b** shows the Yellowknife sampling locations in Moss and Sedge-dominated collapse
288 wetlands. Three replicate collapse features colonized by each vegetation type were studied.
289 The average ages of the collapse features are presented below the figures and the deeper
290 water table in Yellowknife is indicated (water table depths are identified with the black
291 upside-down triangles). The arrows indicate the locations at which CH₄ fluxes were
292 measured. The smaller arrows indicate that, although measurements were made on the
293 plateaus, no net release of CH₄ was detected.

294

295 **Figure 2| Seasonal CH₄ fluxes in the collapse wetlands.** Panel **a.** Teslin and **b.**
296 Yellowknife (mean ± s.e.m; n=3 for measurements at each time point). It was not possible to
297 visit the Yellowknife site during the middle of the growing season because of forest fires.
298 During this time there was no rainfall and thus the water table would have remained at least
299 as deep within the peat profile, making it extremely unlikely that we missed any peaks in CH₄
300 release. Note the difference in the y-axes scales in panels a and b. We did not detect net
301 CH₄ emissions on the undisturbed peat plateaus.

302

303 **Figure 3| Mean ¹⁴C content of CH₄ collected from full-profile collars, near-surface**
304 **collars and the probes located 40 cm below the moss/sedge peat and plateau peat**
305 **transitions in the different thermokarst wetlands.** Panel **a** shows the results for Teslin
306 and panel **b** the results from Yellowknife collapse wetlands. The dashed lines indicates the

307 estimated ^{14}C content of the atmosphere in the respective sampling years²⁰. Error bars
308 represent \pm s.e.m. (n=3).

309

310 **Figure 4 | Sensitivity analysis to estimate the contribution of previously-frozen C to**

311 **surface CH_4 fluxes.** The difference in the ^{14}C contents of the CH_4 released from near-

312 surface and full-profile collars was used and the age of previously-frozen C (Page in

313 Equation 1) was varied between 600 and 1800 y BP to create the sensitivity analysis curve.

314 The presence of white river ash tephra at the base of the active layer in the plateaus

315 indicates the age of the permafrost peat on the plateaus to be at least 1200 yr BP. Using the

316 $^{14}\text{CH}_4$ data and assuming Page to equal 1200 yr BP, the maximum possible contribution

317 from previously-frozen carbon can be calculated (thin dashed lines).

318

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329

330 **Author Contributions**

331 I.P.H., D.C., and C.E.A. designed the study; M.D.A.C. led the CH₄ flux measurements with
332 the support of C.E.A., J.P.F. and R.T. and carried out the sampling and initial processing of
333 the CH₄ samples under the supervision of M.H.G.; Site selection and set-up was carried out
334 by A.G.L, S.A.W., S.V.K., I.P.H., C.E.A., D.C., J.B.M., G.K.P., A.T., and M.W., who also led
335 the overall project. The manuscript was drafted by M.D.A.C., C.E.A. and I.P.H. and all
336 authors contributed to the final version.

337

338 **Competing Financial Interests**

339 The authors declare no competing financial interests

340

341

342 **Methods**

343

344 Field-site description

345

346 Research was undertaken in two study sites: near Teslin, Yukon Territory in 2013
347 (sporadic discontinuous permafrost zone) and near Yellowknife, Northwest Territories
348 (extensive discontinuous permafrost zone) in 2014. The mean annual air temperature
349 (MAAT) (1981 – 2010) for Teslin was -0.6°C, with monthly averages ranging from -17.1°C in
350 January to 14.1°C in July and the mean annual precipitation (MAP) was 346 mm³¹. For
351 Yellowknife, the MAAT (1981 – 2010) was -4.3°C, with monthly averages ranging
352 from -25.6°C in January to 17.0°C in July. The MAP for Yellowknife was 289 mm.

353 The Yukon study site contains an isolated permafrost peat plateau fringed by a
354 collapse wetland (Fig 1a) located near MP788 (Alaskan Highway Milepost), approximately
355 20 km southeast of Teslin in the Yukon Territory (60°05'27.5"N, 132°22'06.4"W). The mean
356 thaw depth in 2013 on peat plateau was 49 cm, while thaw depths exceeded 120 cm in the
357 wetland³². The peat plateau was elevated up to 1.5 m above the surrounding wetland, with
358 resistivity probe measurements suggesting that permafrost thickness was between 15 and
359 18 m in the higher parts of the plateau³². A layer of tephra identified as White River Ash
360 present near the bottom of the active layer in the peat plateau indicates that the minimum
361 age of the organic matter at the top of the current permafrost layer was ~1200 BP³³. The
362 unfrozen wetland was dominated by hydrophilic sedges (*Carex rostrata* Stokes).

363 The second study site was a peat plateau, collapse wetland complex approximately
364 8 km west of Yellowknife, Great Slave Lake region in the Northwest Territories (62°27'25.7"
365 N, 114°31'59.8" W). Approximately 65% of the Great Slave Lake region is underlain by thin
366 permafrost exhibiting widespread signs of degradation³⁴. The underlying bedrock constitutes
367 part of the Canadian Shield consisting of Precambrian granites. At the end of the last glacial
368 maximum, the whole Yellowknife region was submerged by glacial Lake McConnell. During
369 the Holocene, the lake recessed resulting in permafrost aggradation within lacustrine

370 sediments and peat mound formation in the newly exposed land³⁵. The site contains an
371 intact peat plateau surrounded by multiple collapse wetlands characterised by two distinct
372 vegetation communities: 1) sedge-dominated (*Carex rostrata*) with isolated moss patches,
373 and 2) *Sphagnum spp* moss carpet with little vascular plant cover (Fig 1b). Maximum active-
374 layer thickness on the peat plateau during the year of study was ~50 cm, with no ice being
375 detected within the collapse wetlands during the middle of the growing season. Access to
376 the study site was limited at times during the middle of the 2014 summer due to road closure
377 from nearby wildfires. This reduced the amount of flux data that was collected but did not
378 interfere with the ¹⁴CH₄ sample collection.

379

380 Sampling design

381

382 In 2013, at the Teslin study site, three sampling areas were established across a
383 gradient from the actively subsiding edge of the permafrost plateau to the centre of the
384 collapse wetland, to investigate how time since initial thaw affected the ¹⁴C content and
385 source of CH₄ released. The first sampling area was located adjacent to the intact plateau
386 (representing recent thaw), the second area was 5 m into the collapse wetland (representing
387 an intermediate time since thaw with dead trees still standing) and the third sampling
388 location was established at the centre of the wetland (representing the longest time since
389 thaw and with no standing trees). In 2014, in Yellowknife, sampling locations were
390 established in three replicate collapse wetlands dominated by either moss or sedge, to
391 assess how contributions of previously-frozen C depended on vegetation type. Radiocarbon
392 analysis of the peat transition (plateau to sedge/moss peat) indicated that permafrost thaw
393 had started ~60 years ago in Teslin, and in Yellowknife, on average 18 and 42 years ago in
394 the moss and sedge dominated collapse wetlands, respectively (Fig. 1b).

395

396 Chamber flux measurements

397

398 CH₄ flux measurements using the static chamber method³⁶ were carried out twice
399 monthly (July –October) in Teslin, but were more limited in Yellowknife due to forest fires. In
400 each sampling location, three replicate PVC collars, 10 cm deep and 30 cm in diameter,
401 were inserted 5 cm into the wetland soil surface, with 5 cm of the collar projecting above the
402 water or peat surface, and all vegetation being maintained intact inside the chamber. The
403 chamber lids were attached to sampling collars using a rubber inner tube creating an internal
404 headspace volume of 11 L during chamber enclosure. Each chamber lid contained CPC
405 quick connect auto-shutoff couplings (Colder Products Company, USA) which allowed a
406 closed loop to be set up between the chamber headspace and a CH₄ analyser [Detecto Pak
407 Infrared CH₄ analyser (DP-IR), Heath Consultants Inc, USA]. CH₄ concentrations were
408 measured five times at hourly intervals. The flux was calculated from the time series of CH₄
409 concentrations within the chamber using linear regression and all R² values were greater
410 than 0.9. The overall annual (growing season) CH₄ flux estimates were calculated by linear
411 interpolation between measured fluxes. An intercomparison between the DP-IR measured
412 CH₄ concentrations and Gas chromatography confirmed the suitability of the approach (see
413 Fig S2 and Supplementary materials).

414

415 ¹⁴CH₄ sample collection and analysis

416

417 In order to estimate the proportion of CH₄ flux derived from previously-frozen organic
418 material, we measured the ¹⁴C content of CH₄ released using two types of sampling collars
419 made from PVC pipe with an internal diameter of 30 cm. The first collar type was a full-
420 profile collar inserted 40 cm into the wetland profile. For the second collar type, 40 cm cores
421 were extracted using a serrated knife, transferred into cylinders with sealed bottoms (near-
422 surface collars), and then inserted back into the wetland to exclude any CH₄ contributions
423 from depth (Fig. S1). All vegetation was maintained within the two collar types. Extracted
424 cores were retained intact during the transfer to the near-surface collars. Some root damage

425 will have occurred during installation, but there was no die back or visible effect on growth of
426 surface vegetation within the sampling collar and therefore it appears that the impacts were
427 minimal. Water-table depths rarely differed between the full-profile and near-surface collars
428 but when they did, water was added to the near-surface collars from the surrounding
429 wetland.

430 To establish whether anaerobic decomposition of former permafrost was taking
431 place, probes were inserted into the peat profiles. Consistent with previous observations^{6,37},
432 peat cores extracted from collapse wetlands at both study sites, revealed a clear and sharp
433 transition between a relatively undecomposed layer of sedge or *Sphagnum* moss peat that
434 had accumulated vertically since the initiation of collapse, and the underlying plateau peat.
435 This was observed at a depth of on average 60 cm in Teslin and 25 cm in Yellowknife.
436 Probes were inserted 40 cm below these transition zones at 100 and 65 cm depth for Teslin
437 and Yellowknife, respectively. Given that the active layer thickness was ~50 cm on the
438 plateau and some peat compaction will have taken place following collapse, by installing the
439 probes at these depths we were able to sample from approximately where the top of the
440 permafrost was before thaw took place. Each probe was sealed at the bottom to prevent
441 blockages during installation, and the bottom 10 cm of the probe was perforated to allow
442 water to enter. The emergent component of the probe contained a tygon tubing attachment
443 which was sealed using WeLoc clips to prevent gas exchange with the atmosphere. Three
444 replicates of each collar type and the probes were established in each sampling location.

445 CH₄ sampling for radiocarbon analysis was carried out in mid-August in both years to
446 ensure that seasonal ice had thawed completely. As with the flux measurements, chambers
447 were attached to the collars, with rubber tubes used to create an airtight seal between collar
448 and chamber. The total headspace volume was ~11 L. During enclosure, changes in CH₄
449 concentration within the chamber headspace were monitored by connecting the DP-IR
450 analyser to the chambers through the same tubes and connectors as used for the flux
451 monitoring. When sufficient concentrations had accumulated within the chamber headspace,
452 samples were collected by attaching a 10 L foil gas sample bag (SKC, UK) to the exhaust of

453 the DP-IR (via CPC couplings). To prevent the creation of a vacuum, chamber pressure was
454 equilibrated to the atmosphere during sample collection through a vent in the lid. Dilution by
455 ingress of atmospheric air caused chamber CH₄ concentration to fall during sampling; this
456 was monitored using the DP-IR. In Teslin, given the high concentrations of CH₄ in the
457 chambers, and the low concentration of CH₄ in the atmosphere, contamination will have
458 been < 2% of the CH₄ collected and will not have had a measureable effect on the ¹⁴C
459 contents. Due to lower rates of CH₄ release in Yellowknife, multiple sample bags were
460 extracted and then bulked for radiocarbon processing, increasing potential contamination to
461 around 5% but still within measurement error for ¹⁴CH₄.

462 For the probe sampling, 1 L of soil water was extracted using 60ml syringes then
463 transferred in a 10 L collapsible water carrier ['Accordion Water Carrier' (AWC); Highlander,
464 Livingston, UK]. The first syringe of water was discarded to remove any experimental error
465 associated with water standing within the probe. The headspace of the water carrier was
466 inflated with atmospheric air. Given that the target CH₄ concentration required for
467 radiocarbon analysis were > 350 ppm, CH₄ concentrations of 1.8 ppm present in ambient air
468 represented a contamination of < 0.5 %. In order to equilibrate CH₄ from water, the water
469 carrier was shaken for 3 minutes; previous testing had demonstrated that 3 minutes are
470 sufficient to equilibrate and transfer CH₄ from the water without influencing the isotopic
471 composition³⁸. CH₄ concentrations in the water carrier headspace were monitored using the
472 DP-IR. By squeezing the water carrier, the headspace was transferred to a foil bag, attached
473 through CPC couplings, but care was taken to ensure that water did not enter the foil bag.

474 New techniques have recently been developed at the UK Natural Environment
475 Research Council Radiocarbon Facility that overcome previous obstacles for radiocarbon
476 analysis of CH₄ from remote locations¹⁷. These include i) improved gas collection methods
477 that allow samples to be reliably ¹⁴C dated even at CH₄ concentrations well below the lower
478 explosive limit, and ii) conversion of CH₄ samples to CO₂ followed by collection on zeolite
479 molecular sieves prior to transportation. The first stage of laboratory processing was to
480 remove any CO₂ from the field sample. This was carried out by passing the field sample

481 through a soda lime cartridge (dimensions diameter 20mm, length 250mm) into a cleaned
482 (CO₂ free) foil bag. Verification of CO₂ removal was confirmed using an infra-red gas
483 analyser (EGM-4; PP-systems UK) and the process was repeated if necessary. Next, the
484 CO₂-free sample was transferred through another soda lime cartridge to remove any final
485 traces of CO₂ from the sample, after which the CH₄ was converted to CO₂ through
486 combustion at 950°C using a platinum-alumina bead catalyst. This CO₂ was transferred
487 through a cartridge containing magnesium perchlorate to absorb any water vapour produced
488 during combustion, and then trapped on a molecular sieve cartridge containing Type 13X
489 zeolite³⁹ to enable safe transportation to the Radiocarbon facility in the UK. Back in the UK,
490 CH₄-derived CO₂ was desorbed by heating, cryogenically purified and aliquoted into
491 separate samples for ¹⁴C and δ¹³C analysis. Following convention, radiocarbon results were
492 expressed as conventional radiocarbon years before present (BP; where 0 BP = AD 1950)
493 and %modern⁴⁰.

494

495 Calculations and data analysis.

496

497 Probe samples yielded highly variable ¹⁴C contents, and contemporary signatures
498 were observed in Yellowknife, perhaps reflecting the fact that it was difficult to reliably
499 sample deep water from the 65 cm probes given the water table was at 30 cm (Table S1).
500 For these reasons, we used a sensitivity analysis approach to calculate the maximum
501 possible contribution of CH₄ derived from previously-frozen peat (Equation 1; Fig. 4), varying
502 the age of this CH₄ between 600 and 1800 y BP. These ages were chosen because
503 radiocarbon and tephra dating indicated that the age of the organic matter at the top of the
504 permafrost in the peat plateaus was approximately 1200 y BP. In addition, although variable,
505 the average age of the CH₄ collected from the 1 m probes in Teslin was 1216 ± 213 y BP
506 (mean ± 1SE, N=9).

507

508

$$\text{PF CH}_4 (\%) = \left(\frac{\text{FP}^{14}\text{CH}_4 - \text{NS}^{14}\text{CH}_4}{\text{Page} - \text{NS}^{14}\text{CH}_4} \right) * 100 \quad (\text{Equation 1})$$

509

510 Where PF CH₄ (%) is the % contribution of previously-frozen C to the total CH₄ efflux,
511 FP¹⁴CH₄ is the ¹⁴C content of the CH₄ collected from the Full-profile collars, NS¹⁴CH₄ is the
512 ¹⁴C content of the CH₄ collected from the Near-surface collars, and Page is the ¹⁴C content
513 of previously-frozen C, which was varied between ¹⁴C contents equivalent to radiocarbon
514 ages of 600 and 1800 y BP (see Supplementary materials for more information).

515 Statistical analyses were carried out using SPSS (Version 22, SPSS Science) and
516 data were checked for suitability for parametric analysis. Repeated measures two-way
517 ANOVAs were used to determine whether CH₄ fluxes changed over time (within-subject
518 factor) or differed across the gradient of time since thaw (Fig. 1a) or between vegetation
519 communities (Fig. 1b; between-subject factors). Repeated-measures two-way ANOVAs were
520 also used to examine the effects of collar type (within-subject factor) and either time since
521 thaw or vegetation community (between-subject factors) on the ¹⁴C content of the CH₄
522 released.

523

524 Data availability

525

526 All of the radiocarbon data are presented in the supplementary information (Table S1). The
527 CH₄ flux data and environmental monitoring data are available from the corresponding
528 author upon request.

529

530

531 **References in methods only:**

- 532 31 Environment Canada, Climate Data Online. at
533 [<http://climate.weather.gc.ca/climate_normals>](http://climate.weather.gc.ca/climate_normals)
- 534 32 Lewkowicz, A. G., Etzelmuller, B. & Smith, S. L. Characteristics of Discontinuous
535 Permafrost based on Ground Temperature Measurements and Electrical Resistivity
536 Tomography, Southern Yukon, Canada. *Permafrost Periglac.* **22**, 320-342, (2011).
- 537 33 Clague, J. J., Evans, S. G., Rampton, V. N. & Woodsworth, G. J. Improved age
538 estimates for the white-river and bridge-river tephtras, western Canada. *Can. J. Earth*
539 *Sci.* **32**, 1172-1179, (1995).
- 540 34 Morse, P. D., Wolfe, S. A., Kokelj, S. V. & Gaanderse, A. J. R. The Occurrence and
541 Thermal Disequilibrium State of Permafrost in Forest Ecotopes of the Great Slave
542 Region, Northwest Territories, Canada. *Permafrost Periglac.* **27**, 145-162, (2016).
- 543 35 Wolfe, S. A. & Morse, P. D. Lithalsa Formation and Holocene Lake-Level Recession,
544 Great Slave Lowland, Northwest Territories. *Permafrost Periglac.* doi:DOI:
545 10.1002/ppp.1901 (2016).
- 546 36 Livingston, G. & G, H. in *Biogenic trace gases: measuring emissions from soil and*
547 *water* (eds P.A. Matson & R.C Harriss) 14-51 (Blackwell Publishing, 1995).
- 548 37 Myers-Smith, I. H. *et al.* Wetland succession in a permafrost collapse: interactions
549 between fire and thermokarst. *Biogeosciences* **5**, 1273-1286 (2008).
- 550 38 Garnett, M. H., Gulliver, P. & Billett, M. F. A rapid method to collect methane from
551 peatland streams for radiocarbon analysis. *Ecohydrology* **9**, 113-121, (2016).
- 552 39 Hardie, S. M. L., Garnett, M. H., Fallick, A. E., Rowland, A. P. & Ostle, N. J. Carbon
553 dioxide capture using a zeolite molecular sieve sampling system for isotopic studies
554 (¹³C and ¹⁴C) of respiration. *Radiocarbon* **47**, 441-451 (2005).
- 555 40 Stuiver, M. & Polach, H. A. Reporting of ¹⁴C data - discussion. *Radiocarbon* **19**, 355-
556 363 (1977).

557

Figure 1

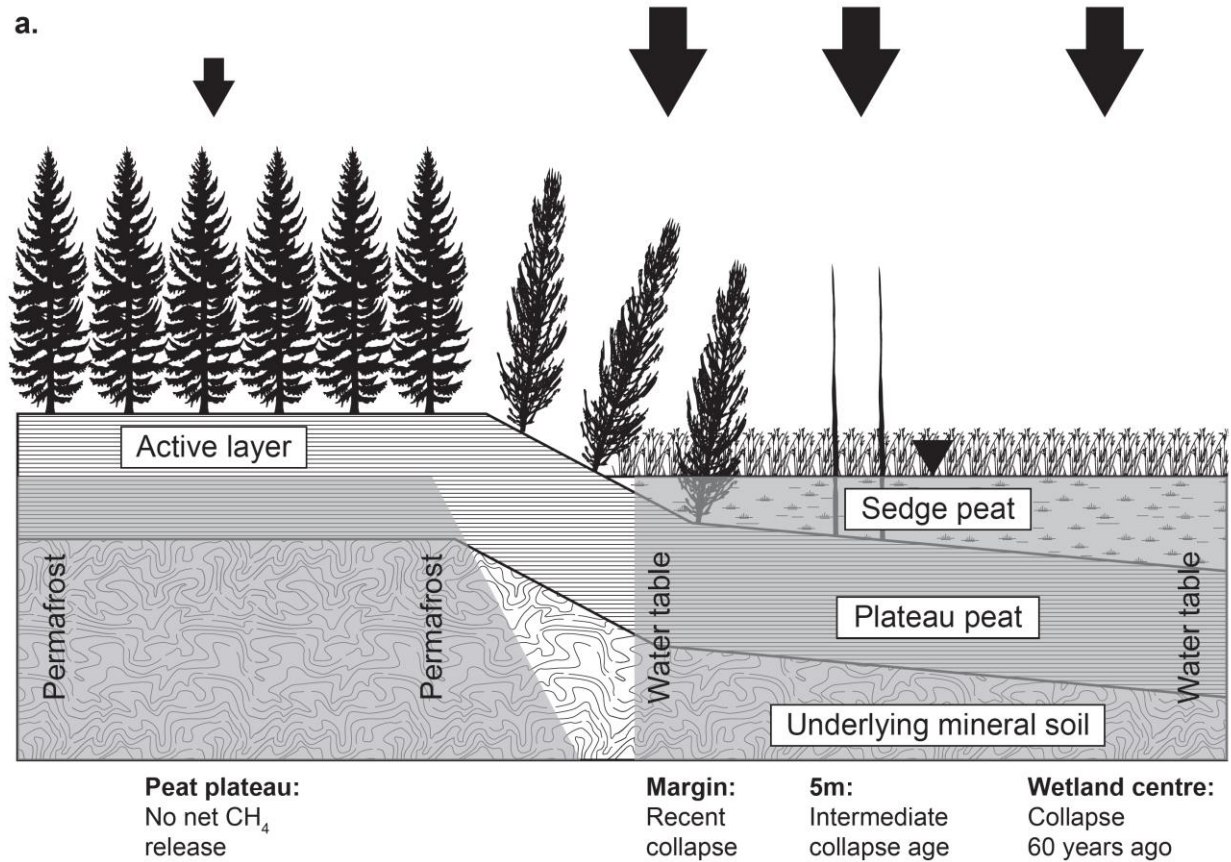
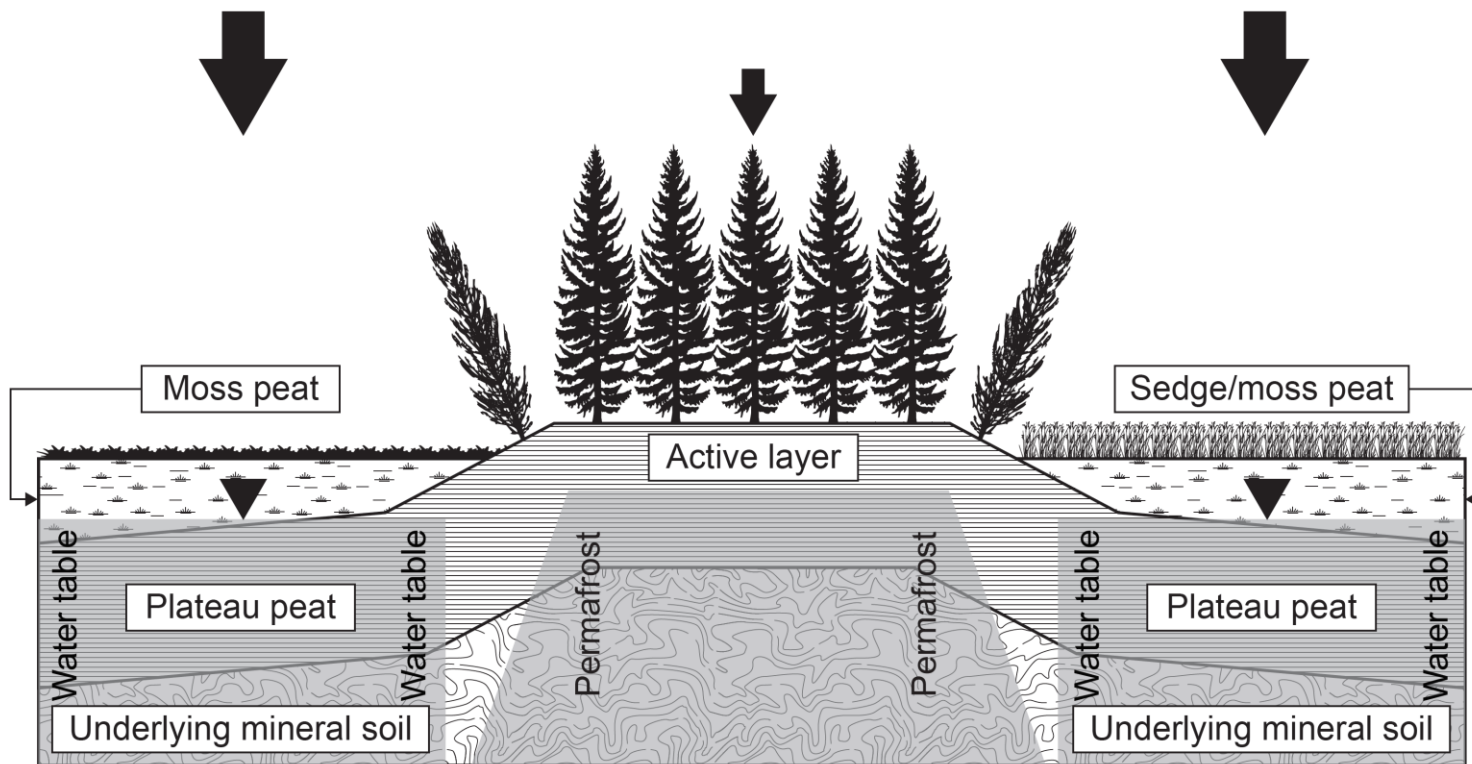


Figure 1

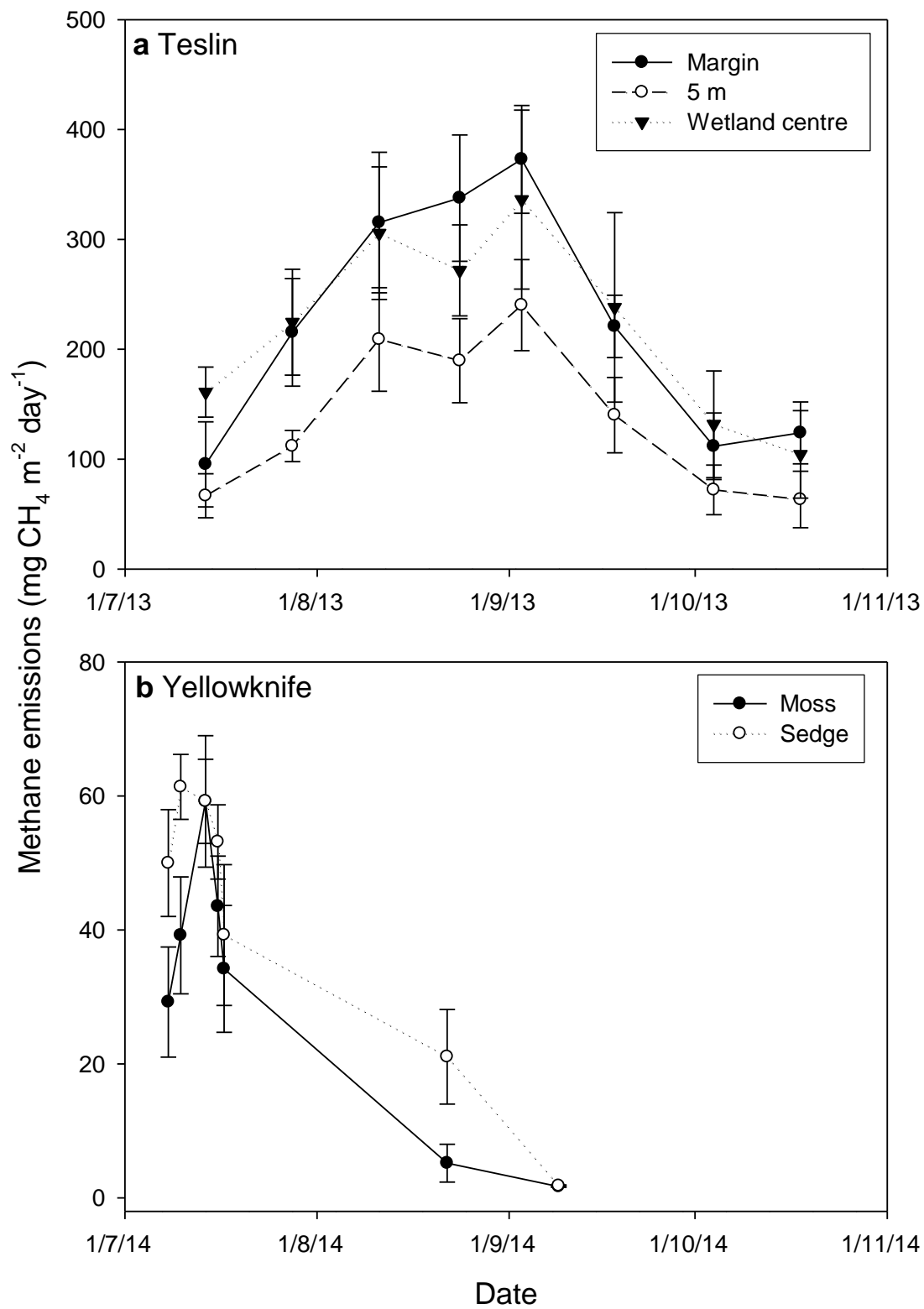
b.

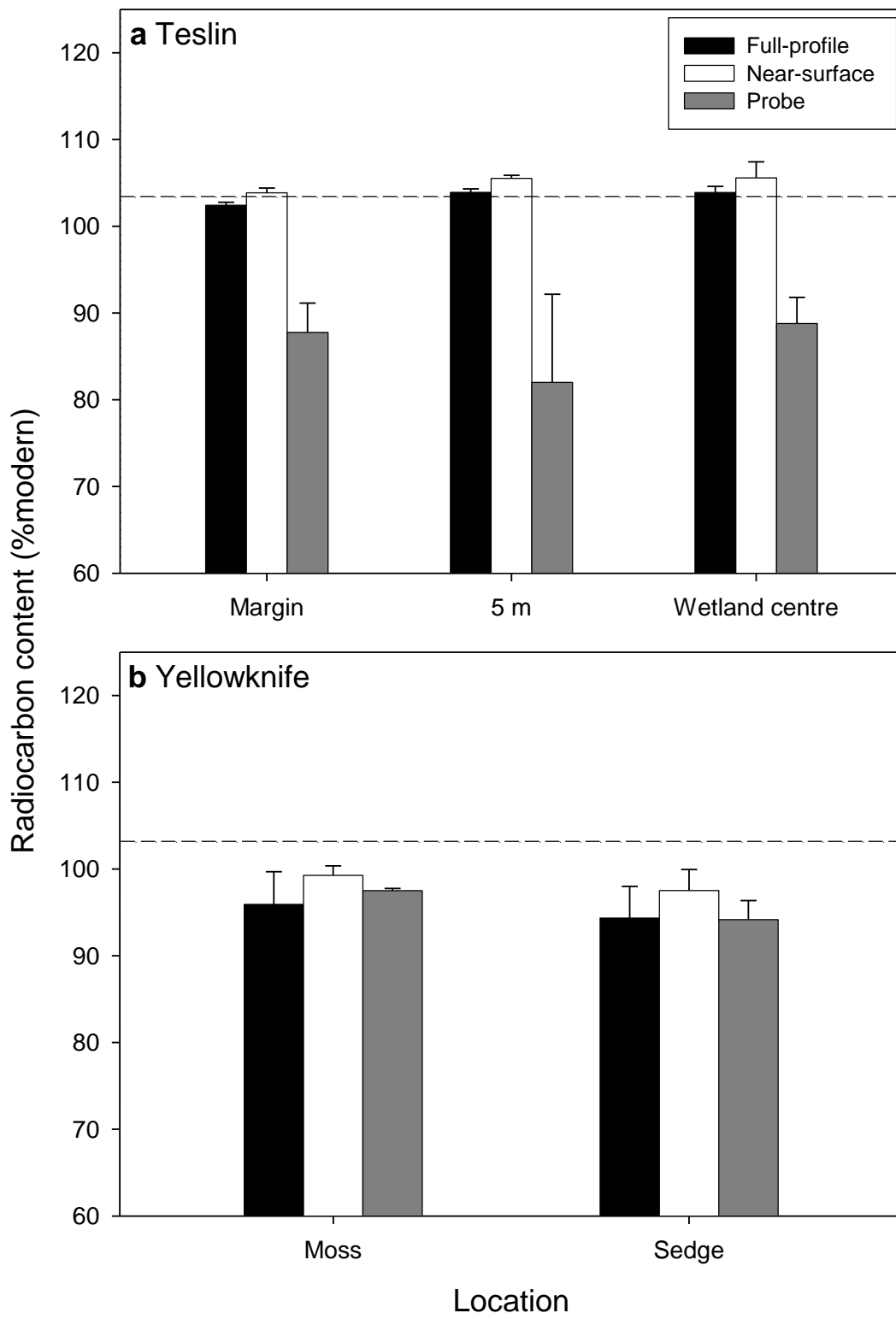


Moss wetland centre:
Collapse 18 years ago

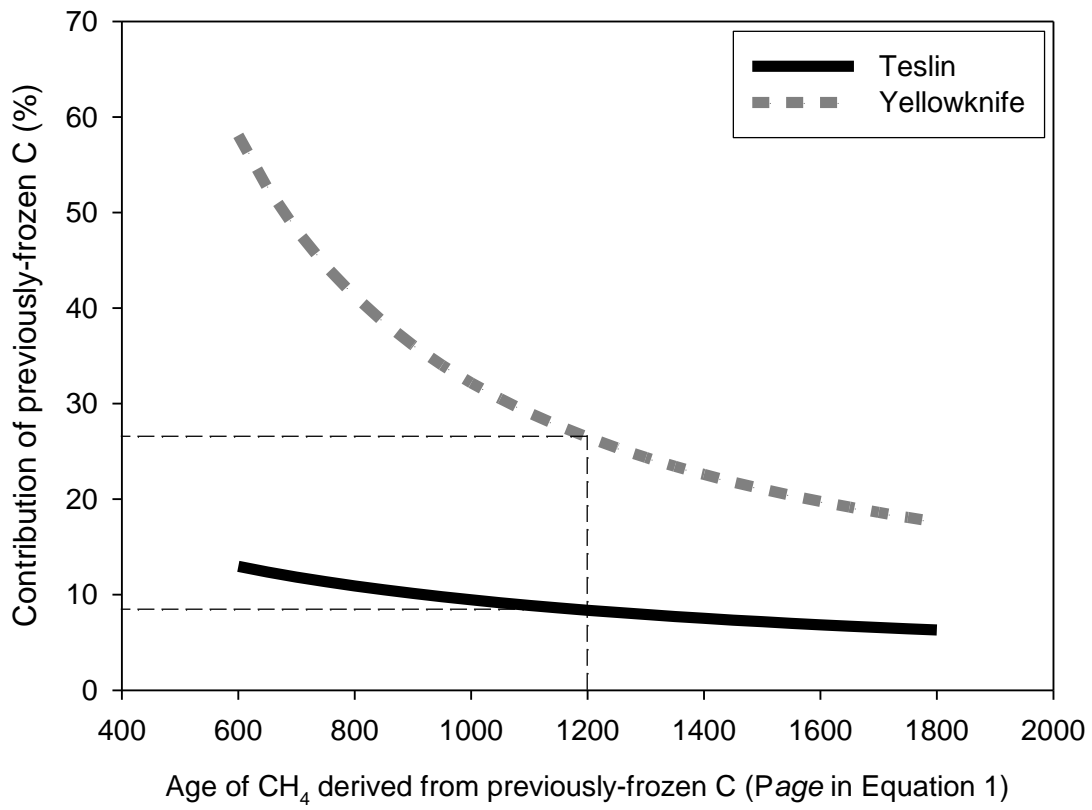
Peat plateau:
No net CH₄
release

Sedge wetland centre:
Collapse 42 years ago





571 **Figure 4**



572

573