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Limited contribution of permafrost carbon to methane release from thawing peatlands

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Models predict that thaw of permafrost soils at northern high-latitudes will release tens of billions of tonnes of carbon (C) to the atmosphere by 2100[1-3]. The effect on the Earth's climate depends strongly on the proportion of this C which is released as the more powerful greenhouse gas methane (CH_4), rather than carbon dioxide (CO_2)[1,4]; even if CH_4 emissions represent just 2% of the C release, they would contribute approximately one quarter of the climate forcing[5]. In northern peatlands, thaw of ice-rich permafrost causes surface subsidence (thermokarst) and water-logging[6], exposing substantial stores (10s of kg C m^{-2}, ref. 7) of previously-frozen organic matter to anaerobic conditions, and generating ideal conditions for permafrost-derived CH_4 release. Here we show that, contrary to expectations, although substantial CH_4 fluxes (>20 g CH_4 m^{-2} yr^{-1}) were recorded from thawing peatlands in northern Canada, only a small amount was derived from previously-frozen C (<2 g CH_4 m^{-2} yr^{-1}). Instead, fluxes were driven by anaerobic decomposition of recent C inputs. We conclude that thaw-induced changes in surface wetness and wetland area, rather than the anaerobic decomposition of previously-frozen C, may determine the effect of permafrost thaw on CH_4 emissions from northern peatlands.

Permafrost peatlands occupy more than 1 million km^2 (ref. 7), and could dominate the permafrost CH_4 feedback[3]. Although these peatlands only store approximately 20% of the total permafrost C stock which is predicted to thaw this century[8], potential decomposition rates associated with frozen organic soils are up to five times greater than for frozen mineral soils[9], and peats are disproportionately likely to be water-logged following thaw[3,10]. For these reasons, one modelling study assumed that all the CH_4 released as a result of permafrost thaw would be derived from currently-frozen peats (histels)[3]. The histels most vulnerable to thaw during this century are located in the southern permafrost zone[11], where the presence of permafrost raises the peat surface above the water table, forming plateaus dominated by tree, shrub, moss and lichen communities (see supplementary material)[12]. This results in the formation of a mixture of woody (sylvic) and Sphagnum-moss peat. Thaw of ice-rich permafrost within these peatland plateaus causes surface subsidence, resulting in the

formation of collapse wetlands with water-logging and vegetation change[6,12]. In collapse wetlands, there is then significant potential for CH_4 to be released from the decomposition of previously-frozen organic matter because: 1) thaw makes 10s of kg C m^{-2} vulnerable to microbial decomposition, and 2) water-logging produces oxygen-limited conditions throughout the soil profile and thus all newly-thawed organic matter will decompose under anaerobic conditions. However, despite the potential importance of these peatlands to the permafrost CH_4 feedback[3], to date, no study has quantified rates of CH_4 release from the decomposition of previously-frozen C in these systems.

Unlike in thermokarst lakes where there is no in situ vegetation[13], it is unclear to what extent any CH_4 emitted from collapse wetlands is derived from old, previously-frozen C (ref. 14) versus new C inputs from the hydrophilic vegetation communities that develop post thaw[6,15]. This is important because determining the source of the CH_4 is required for accurately simulating future fluxes, as the factors controlling emission rates differ fundamentally. While the total C stock and its decomposability are the main relevant predictors of CH_4 release from previously frozen C (ref. 3), the most important driver of CH_4 fluxes from new C inputs is the change in wetland area, together with the quantity and quality of new inputs[16]. Radiocarbon (^{14}C) measurements offer the potential to address this key uncertainty. Because permafrost C is typically thousands of years old, measuring the ^{14}C content of the CH_4 can determine whether previously-frozen, old C contributes substantially to CH_4 release post thaw. However, until recently such measurements were very challenging in remote locations.

Using new techniques that overcome previous limitations[17], we quantified the ^{14}C content of CH_4 produced within, and emitted from the surface, in contrasting collapse wetlands in both the sporadic discontinuous permafrost zone (near Teslin, Yukon Territory in 2013: 60°05'27.5"N, 132°22'06.4"W) and the extensive discontinuous permafrost zone (near Yellowknife, Northwest Territories in 2014: 62°27'25.7" N, 114°31'59.8 " W). The total depth of peat in the collapse wetlands was at least 160 cm in Teslin and 140 cm in Yellowknife. 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 CH_4 from 40 cm below the transition
92 depth at each site, and collected samples of CH_4 released from surface collars that either
93 included (full-profile collars) or physically excluded (near-surface collars) CH_4 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 CH_4 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 CH_4 up from depth[18] versus Sphagnum
100 moss-dominated communities).
101 Collapse wetlands released substantial amounts of CH_4, whereas, consistent with
102 previous observations[6,15], net CH_4 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 CH_4 emissions reached up to 400 mg CH_4 m^{-2} day^{-1} with an
105 estimated release of 21 g CH_4 m^{-2} during the growing season (Fig. 2a). We did not observe
106 differences in CH_4 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 years[19]. 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 CH_4 emissions were lower than in Teslin (Fig. 2a,b). We calculated that 3.2
113 g and 2 g CH_4 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.

In Teslin, the CH_4 collected at depth with probes had a depleted ^{14}C signature, demonstrating that organic matter with radiocarbon ages ranging from 700 to 2800 years before present (y BP), was decomposing to produce CH_4 (see Table S1). Conversely, the ^{14}C content of CH_4 released at the collapse wetland surface was greater than that of the current atmosphere[20] (Fig 3a), indicating that the flux was dominated by C fixed since nuclear weapons testing enriched the atmosphere in ^{14}C during the second half of the 20th century. The ^{14}C content of the CH_4 emitted from collars that included deeper peat layers was significantly lower than from the collars that excluded fluxes from below 40 cm ($P = 0.022$), identifying a measureable contribution from deeper peat (>40 cm). Given the variation in the ages of CH_4 collected by the probes, a sensitivity analysis (Equation 1) was used to estimate the potential maximum contribution of previously-frozen C to the surface flux. Based on dating the organic matter at the base of the active layer (1200 y BP), a maximum of 8.4 % (1.5 to 2 g CH_4 m^{-2}) of the CH_4 emissions was calculated to be derived from former permafrost peat, and did not change significantly with time since collapse (Fig. 4; Supplementary Information and Equation 1).

The drier conditions in Yellowknife made the collection of probe CH_4 samples more challenging, which may have contributed to the younger age of the CH_4 (150-800 y BP; Table S1). However, the CH_4 released from the soil surface had a lower ^{14}C content than in Teslin and was also lower than that of the current atmosphere, indicating that relatively old C was being released (Fig. 3b). The ^{14}C content of the CH_4 emitted from near-surface collars was higher than that from the full-profile collars again suggesting a contribution from deeper soil layers, although the difference between collar treatments was not statistically significant ($P = 0.375$). By carrying out the same sensitivity analysis based on the age of uppermost permafrost C, it was estimated that previously-frozen organic matter could have contributed a maximum of 30% to the CH_4 emissions (Fig. 4); this corresponds to 0.7-1.0 g CH_4 m^{-2} during the growing season. No significant difference in ^{14}C between the moss and sedge-dominated vegetation communities was detected ($P = 0.982$). It appears that by suppressing near-surface CH_4 production, the dry conditions greatly reduced total CH_4 fluxes and thus

there was a greater proportional contribution of previously-frozen C. Regardless, the absolute amount of CH_4 derived from previously-frozen C remained low.

The results from these two contrasting sites in different permafrost zones demonstrate that, where substantial CH_4 fluxes occurred, they were dominated by anaerobic decomposition of recent C inputs. Total rates of CH_4 release from previously-frozen C were low irrespective of differences in time since thaw, vegetation community composition and/or water-table depth. By calculating maximum potential contributions of previously-frozen C, our calculations still likely represent an overestimation, adding to confidence to this overall conclusion (see sensitivity analysis in Supplementary Information).

In both study sites, permafrost thaw exposed ~1 m of previously-frozen peat and >50 kg C m^{-2} to anaerobic decay and yet maximum CH_4 release rates from this store during the growing season were only 1-2 g C m^{-2}, or 0.02-0.04 g CH_4-C kg soil C^{-1}. Rates of CH_4 emitted from the decomposition of previously-frozen C in thermokarst lakes in situ (0.5 g CH_4-C kg soil C^{-1} yr^{-1})[13] and observed rates of CH_4 production in anaerobic incubations (1.2 g CH_4-C kg soil C^{-1} yr^{-1})[21] are at least an order of magnitude greater than our in situ peatland fluxes. The low rates of CH_4 release may be related to oxidation of the CH_4 to CO_2 during transport within the peat, or slow rates of anaerobic decomposition of previously-frozen SOM. We consider it unlikely that oxidation could explain the low rate of old CH_4 release, at least at Teslin where the water table remained within 5 cm of the peat surface throughout the growing season, and the sedge communities will have promoted rapid CH_4 transport from depth[18]. Under long-term anaerobic conditions, the build-up of inhibitory compounds (e.g. phenolics) within peats, may strongly suppress microbial activity and contribute to low rates of anaerobic decomposition at depth[22]. Possibly reflecting this, warming of up to 9 ^{o}C did not increase rates of decomposition in anaerobic peat layers below 20 cm in an ombrotrophic bog in northern Minnesota[23]. Thus, there may be little potential for CH_4 release from the decomposition of deep peat C stores irrespective of whether or not these layers have been frozen in the recent past. Given that histels are currently predicted to play a key role in the permafrost CH_4 feedback[3], the low rates of release we observed, suggest that anaerobic

decomposition of previously-frozen peat may not result in the release of 1-4 GT of CH_4 by 2100 that models and expert assessments predict[3,5].

On the other hand, CH_4 fluxes from thawing peatlands may still represent a key component of the permafrost feedback. The differences between our field sites indicate that CH_4 fluxes vary with water table depth post thaw, which may be linked to the magnitude of surface subsidence, local hydrological conditions and climate variability[24]. In our wetter field site at Teslin, despite the low contribution of previously-frozen C, substantial amounts (21 g CH_4 m^{-2}) of CH_4 were released during the growing season. The fact that high CH_4 fluxes were observed from areas that had thawed several decades ago suggests that permafrost thaw at this site could have promoted the release up to 1 kg of CH_4-C m^{-2} over the last 50 years. Therefore, where there is deep subsidence and near-surface water-logging, CH_4 fluxes from thawing permafrost peatlands can still produce a positive feedback to climate change; the CH_4 is just not primarily derived from previously-frozen C. There is evidence that the endpoint for permafrost thaw in boreal peatlands is inundated fens[10] and studies have identified an expansion of this type of wetland in parts of northern Canada[25]. The subsequent CH_4 release could lead to substantial increases in regional CH_4 fluxes[16]. However, considerable observational[26,27] and modelling[16,28] uncertainty remains regarding whether permafrost thaw will increase or decrease wetland extent in different regions. Remote sensing techniques that can directly detect the spatial extent of wetlands and their vegetation communities, especially sedges[25,29,30], may prove invaluable for quantifying the effect of permafrost thaw on high-latitude CH_4 fluxes.

In conclusion, our study demonstrates that anaerobic decomposition of new C inputs drive CH_4 emissions in contrasting thawed permafrost peatlands in northern Canada. These results may have major implications for modelling the permafrost feedback, suggesting that, to simulate future fluxes, efforts should be focused on accurately predicting the effects of permafrost thaw on the spatial extent of wetlands, rather than rates of anaerobic decomposition of previously-frozen peat.

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Figure legends

Figure 1| Schematic diagram of the site-specific sampling designs. Panel **a** shows the Teslin sampling locations, which were established at three separate positions across a gradient of time since thaw of a peat plateau, from (i) recent thaw at the edge of the collapse wetland (Margin); to (ii) 5 m into the wetland where there were still standing dead trees (5 m); and in the wetland centre where collapse occurred approximately 60 years ago (centre). Panel **b** shows the Yellowknife sampling locations in Moss and Sedge-dominated collapse wetlands. Three replicate collapse features colonized by each vegetation type were studied. The average ages of the collapse features are presented below the figures and the deeper water table in Yellowknife is indicated (water table depths are identified with the black upside-down triangles). The arrows indicate the locations at which CH_4 fluxes were measured. The smaller arrows indicate that, although measurements were made on the plateaus, no net release of CH_4 was detected.

Figure 2| Seasonal CH_4 fluxes in the collapse wetlands. Panel **a**. Teslin and **b**. Yellowknife (mean ± s.e.m; n=3 for measurements at each time point). It was not possible to visit the Yellowknife site during the middle of the growing season because of forest fires. During this time there was no rainfall and thus the water table would have remained at least as deep within the peat profile, making it extremely unlikely that we missed any peaks in CH_4 release. Note the difference in the y-axes scales in panels a and b. We did not detect net CH_4 emissions on the undisturbed peat plateaus.

Figure 3| Mean ^{14}C content of CH_4 collected from full-profile collars, near-surface collars and the probes located 40 cm below the moss/sedge peat and plateau peat transitions in the different thermokarst wetlands. Panel **a** shows the results for Teslin and panel **b** the results from Yellowknife collapse wetlands. The dashed lines indicates the

estimated ^{14}C content of the atmosphere in the respective sampling years[20]. Error bars represent ± s.e.m. (n=3).

Figure 4 | Sensitivity analysis to estimate the contribution of previously-frozen C to surface CH_4 fluxes. The difference in the ^{14}C contents of the CH_4 released from near-surface and full-profile collars was used and the age of previously-frozen C (Page in Equation 1) was varied between 600 and 1800 y BP to create the sensitivity analysis curve. The presence of white river ash tephra at the base of the active layer in the plateaus indicates the age of the permafrost peat on the plateaus to be at least 1200 yr BP. Using the $^{14}CH_4$ data and assuming Page to equal 1200 yr BP, the maximum possible contribution from previously-frozen carbon can be calculated (thin dashed lines).

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Author Contributions

I.P.H., D.C., and C.E.A. designed the study; M.D.A.C. led the CH_4 flux measurements with the support of C.E.A., J.P.F. and R.T. and carried out the sampling and initial processing of the CH_4 samples under the supervision of M.H.G.; Site selection and set-up was carried out 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 the overall project. The manuscript was drafted by M.D.A.C., C.E.A. and I.P.H. and all authors contributed to the final version.

Competing Financial Interests

The authors declare no competing financial interests

Methods

Field-site description

Research was undertaken in two study sites: near Teslin, Yukon Territory in 2013 (sporadic discontinuous permafrost zone) and near Yellowknife, Northwest Territories (extensive discontinuous permafrost zone) in 2014. The mean annual air temperature (MAAT) (1981 – 2010) for Teslin was -0.6℃, with monthly averages ranging from -17.1℃ in January to 14.1℃ in July and the mean annual precipitation (MAP) was 346 mm[31]. For Yellowknife, the MAAT (1981 – 2010) was -4.3℃, with monthly averages ranging from -25.6℃ in January to 17.0℃ in July. The MAP for Yellowknife was 289 m m.

The Yukon study site contains an isolated permafrost peat plateau fringed by a collapse wetland (Fig 1a) located near MP788 (Alaskan Highway Milepost), approximately 20 km southeast of Teslin in the Yukon Territory (60°05'27.5"N, 132°22'06 .4"W). The mean thaw depth in 2013 on peat plateau was 49 cm, while thaw depths exceeded 120 cm in the wetland[32]. The peat plateau was elevated up to 1.5 m above the surrounding wetland, with resistivity probe measurements suggesting that permafrost thickness was between 15 and 18 m in the higher parts of the plateau[32]. A layer of tephra identified as White River Ash present near the bottom of the active layer in the peat plateau indicates that the minimum age of the organic matter at the top of the current permafrost layer was ~1200 BP[33]. The unfrozen wetland was dominated by hydrophilic sedges (Carex rostrata Stokes).

The second study site was a peat plateau, collapse wetland complex approximately 8 km west of Yellowknife, Great Slave Lake region in the Northwest Territories (62°27'25.7" N, 114°31'59.8" W). Approximately 65% of the Great Slave Lake region is underlain by thin permafrost exhibiting widespread signs of degradation[34]. The underlying bedrock constitutes part of the Canadian Shield consisting of Precambrian granites. At the end of the last glacial maximum, the whole Yellowknife region was submerged by glacial Lake McConnell. During the Holocene, the lake recessed resulting in permafrost aggradation within lacustrine

sediments and peat mound formation in the newly exposed land[35]. The site contains an intact peat plateau surrounded by multiple collapse wetlands characterised by two distinct vegetation communities: 1) sedge-dominated (Carex rostrata) with isolated moss patches, and 2) Sphagnum spp moss carpet with little vascular plant cover (Fig 1b). Maximum active-layer thickness on the peat plateau during the year of study was ~50 cm, with no ice being detected within the collapse wetlands during the middle of the growing season. Access to the study site was limited at times during the middle of the 2014 summer due to road closure from nearby wildfires. This reduced the amount of flux data that was collected but did not interfere with the $^{14}CH_4$ sample collection.

Sampling design

In 2013, at the Teslin study site, three sampling areas were established across a gradient from the actively subsiding edge of the permafrost plateau to the centre of the collapse wetland, to investigate how time since initial thaw affected the ^{14}C content and source of CH_4 released. The first sampling area was located adjacent to the intact plateau (representing recent thaw), the second area was 5 m into the collapse wetland (representing an intermediate time since thaw with dead trees still standing) and the third sampling location was established at the centre of the wetland (representing the longest time since thaw and with no standing trees). In 2014, in Yellowknife, sampling locations were established in three replicate collapse wetlands dominated by either moss or sedge, to assess how contributions of previously-frozen C depended on vegetation type. Radiocarbon analysis of the peat transition (plateau to sedge/moss peat) indicated that permafrost thaw had started ~60 years ago in Teslin, and in Yellowknife, on average 18 and 42 years ago in the moss and sedge dominated collapse wetlands, respectively (Fig. 1b).

Chamber flux measurements

CH_4 flux measurements using the static chamber method[36] were carried out twice monthly (July –October) in Teslin, but were more limited in Yellowknife due to forest fires. In each sampling location, three replicate PVC collars, 10 cm deep and 30 cm in diameter, were inserted 5 cm into the wetland soil surface, with 5 cm of the collar projecting above the water or peat surface, and all vegetation being maintained intact inside the chamber. The chamber lids were attached to sampling collars using a rubber inner tube creating an internal headspace volume of 11 L during chamber enclosure. Each chamber lid contained CPC quick connect auto-shutoff couplings (Colder Products Company, USA) which allowed a closed loop to be set up between the chamber headspace and a CH_4 analyser [Detecto Pak Infrared CH4 analyser (DP-IR), Heath Consultants Inc, USA]. CH_4 concentrations were measured five times at hourly intervals. The flux was calculated from the time series of CH_4 concentrations within the chamber using linear regression and all R^2 values were greater than 0.9. The overall annual (growing season) CH_4 flux estimates were calculated by linear interpolation between measured fluxes. An intercomparison between the DP-IR measured CH_4 concentrations and Gas chromatography confirmed the suitability of the approach (see Fig S2 and Supplementary materials).

$^{14}CH_4$ sample collection and analysis

In order to estimate the proportion of CH_4 flux derived from previously-frozen organic material, we measured the ^{14}C content of CH_4 released using two types of sampling collars made from PVC pipe with an internal diameter of 30 cm. The first collar type was a full-profile collar inserted 40 cm into the wetland profile. For the second collar type, 40 cm cores were extracted using a serrated knife, transferred into cylinders with sealed bottoms (near-surface collars), and then inserted back into the wetland to exclude any CH_4 contributions from depth (Fig. S1). All vegetation was maintained within the two collar types. Extracted 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 CH_4 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 CH_4
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 CH_4 concentration to fall during sampling; this
456 was monitored using the DP-IR. In Teslin, given the high concentrations of CH_4 in the
457 chambers, and the low concentration of CH_4 in the atmosphere, contamination will have
458 been < 2% of the CH_4 collected and will not have had a measureable effect on the ^{14}C
459 contents. Due to lower rates of CH_4 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 $^{14}CH_4$.
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 CH_4 concentration required for
467 radiocarbon analysis were > 350 ppm, CH_4 concentrations of 1.8 ppm present in ambient air
468 represented a contamination of < 0.5 %. In order to equilibrate CH_4 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 CH_4 from the water without influencing the isotopic
471 composition[38]. CH_4 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 CH_4 from remote locations[17]. These include i) improved gas collection methods
477 that allow samples to be reliably ^{14}C dated even at CH_4 concentrations well below the lower
478 explosive limit, and ii) conversion of CH_4 samples to CO_2 followed by collection on zeolite
479 molecular sieves prior to transportation. The first stage of laboratory processing was to
480 remove any CO_2 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 (CO_2 free) foil bag. Verification of CO_2 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 CO_2-free sample was transferred through another soda lime cartridge to remove any final
485 traces of CO_2 from the sample, after which the CH_4 was converted to CO_2 through
486 combustion at 950^{o}C using a platinum-alumina bead catalyst. This CO_2 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 zeolite[39] to enable safe transportation to the Radiocarbon facility in the UK. Back in the UK,
490 CH_4-derived CO_2 was desorbed by heating, cryogenically purified and aliquoted into
491 separate samples for ^{14}C and $\delta^{13}C$ analysis. Following convention, radiocarbon results were
492 expressed as conventional radiocarbon years before present (BP; where 0 BP = AD 1950)
493 and %modern[40].
494
495 Calculations and data analysis.
496
497 Probe samples yielded highly variable ^{14}C 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 CH_4 derived from previously-frozen peat (Equation 1; Fig. 4), varying
502 the age of this CH_4 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 CH_4 collected from the 1 m probes in Teslin was 1216 ± 213 y BP
506 (mean ± 1SE, N=9).
507
508

$$PF\ CH_4\ (\%) = \left(\frac{FP^{14}CH_4 - NS^{14}CH_4}{Page - NS^{14}CH_4} \right) * 100 \qquad \text{(Equation 1)}$$

Where PF CH_4 (%) is the % contribution of previously-frozen C to the total CH_4 efflux, $FP^{14}CH_4$ is the ^{14}C content of the CH_4 collected from the Full-profile collars, $NS^{14}CH_4$ is the ^{14}C content of the CH_4 collected from the Near-surface collars, and Page is the ^{14}C content of previously-frozen C, which was varied between ^{14}C contents equivalent to radiocarbon ages of 600 and 1800 y BP (see Supplementary materials for more information).

Statistical analyses were carried out using SPSS (Version 22, SPSS Science) and data were checked for suitability for parametric analysis. Repeated measures two-way ANOVAs were used to determine whether CH_4 fluxes changed over time (within-subject factor) or differed across the gradient of time since thaw (Fig. 1a) or between vegetation communities (Fig. 1b; between-subject factors). Repeated-measures two-way ANOVAs were also used to examine the effects of collar type (within-subject factor) and either time since thaw or vegetation community (between-subject factors) on the ^{14}C content of the CH_4 released.

Data availability

All of the radiocarbon data are presented in the supplementary information (Table S1). The CH_4 flux data and environmental monitoring data are available from the corresponding author upon request.

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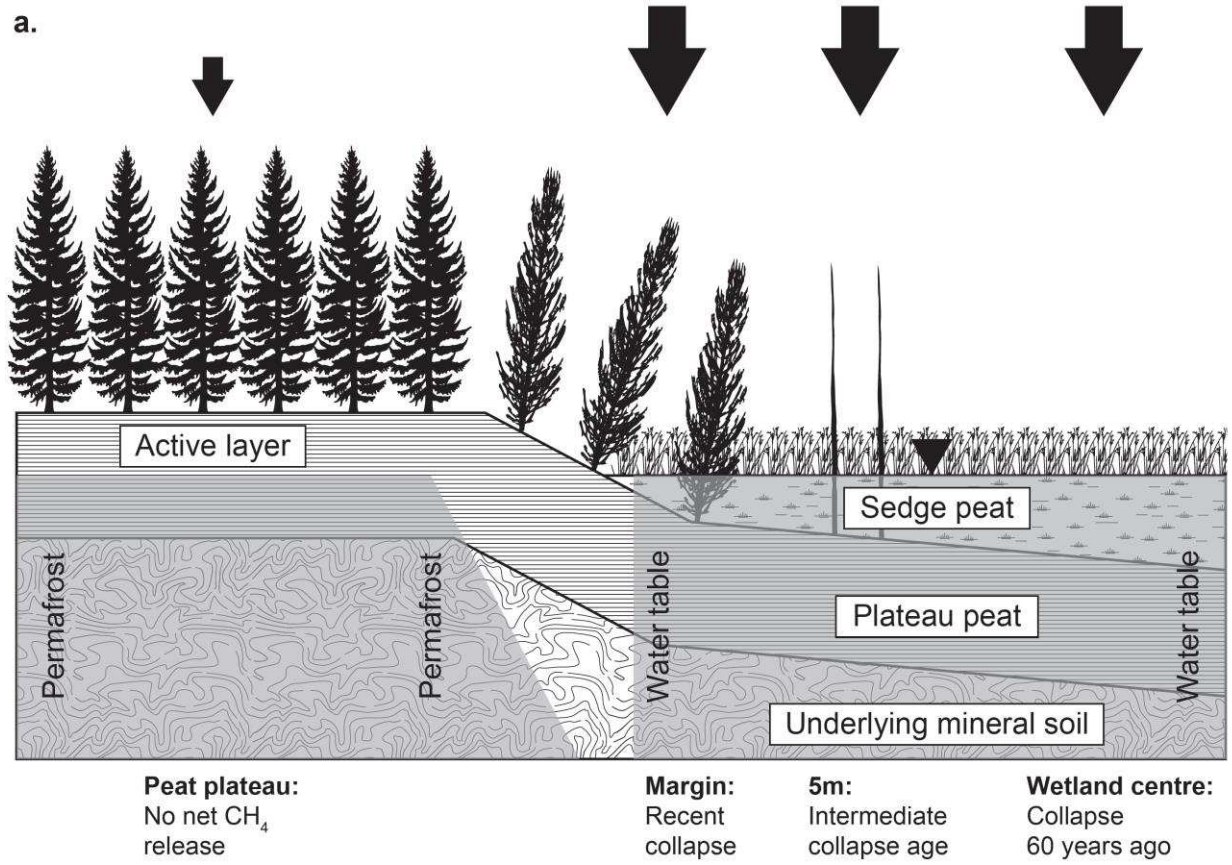
559 **Figure 1a.**

Figure 1



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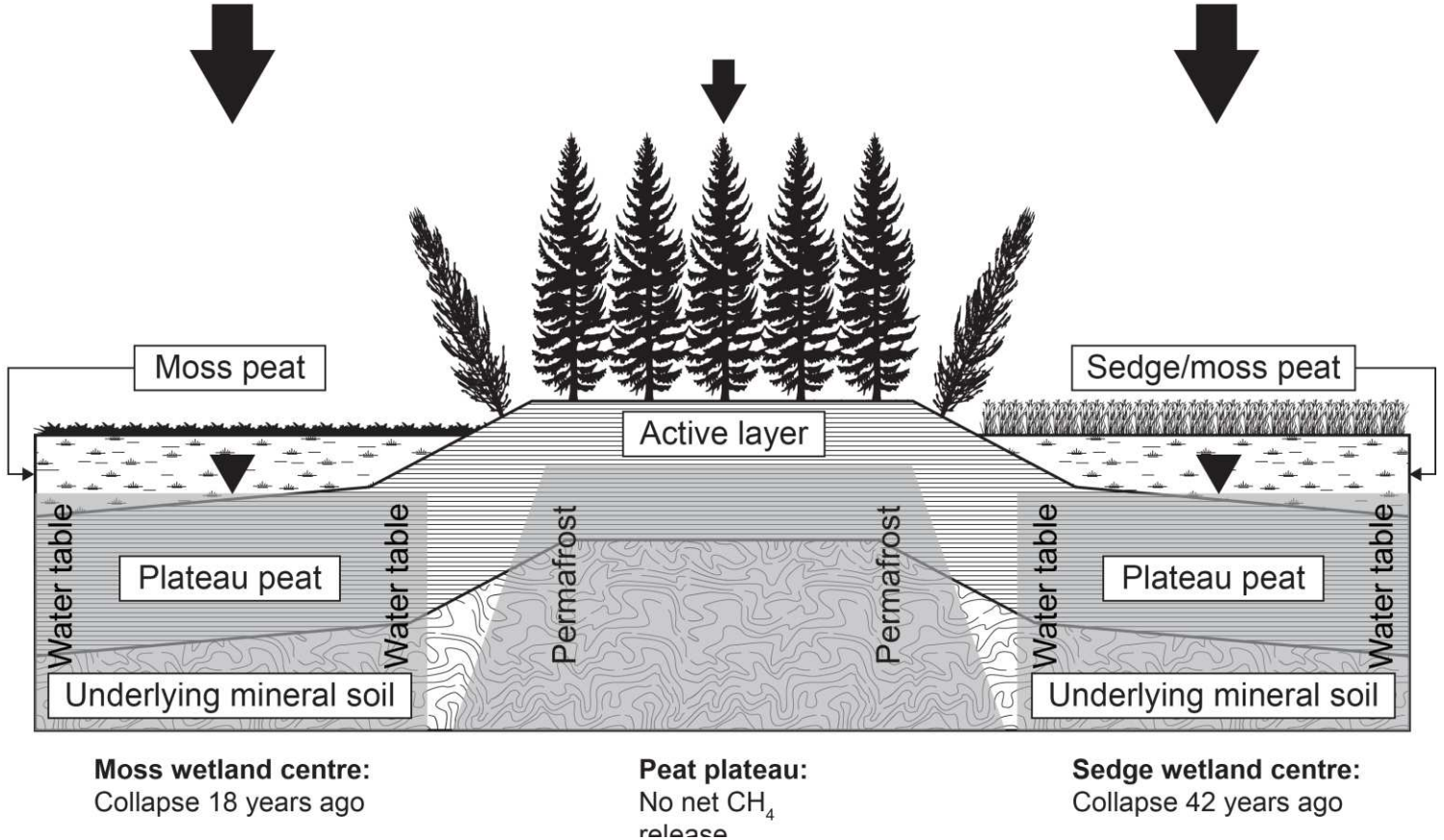
562 **Figure 1b**

Figure 1

b.



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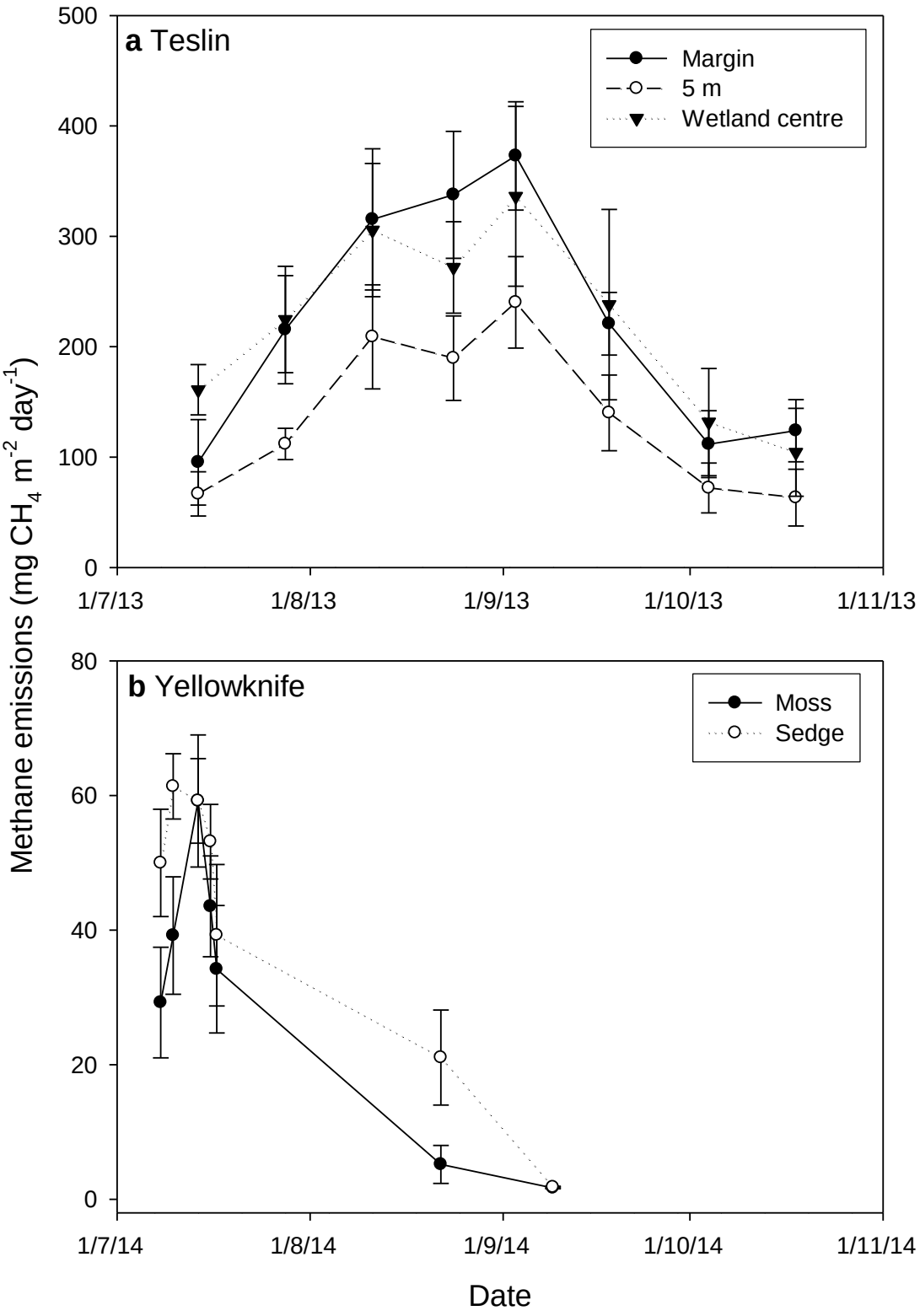
564 **Figure 2**



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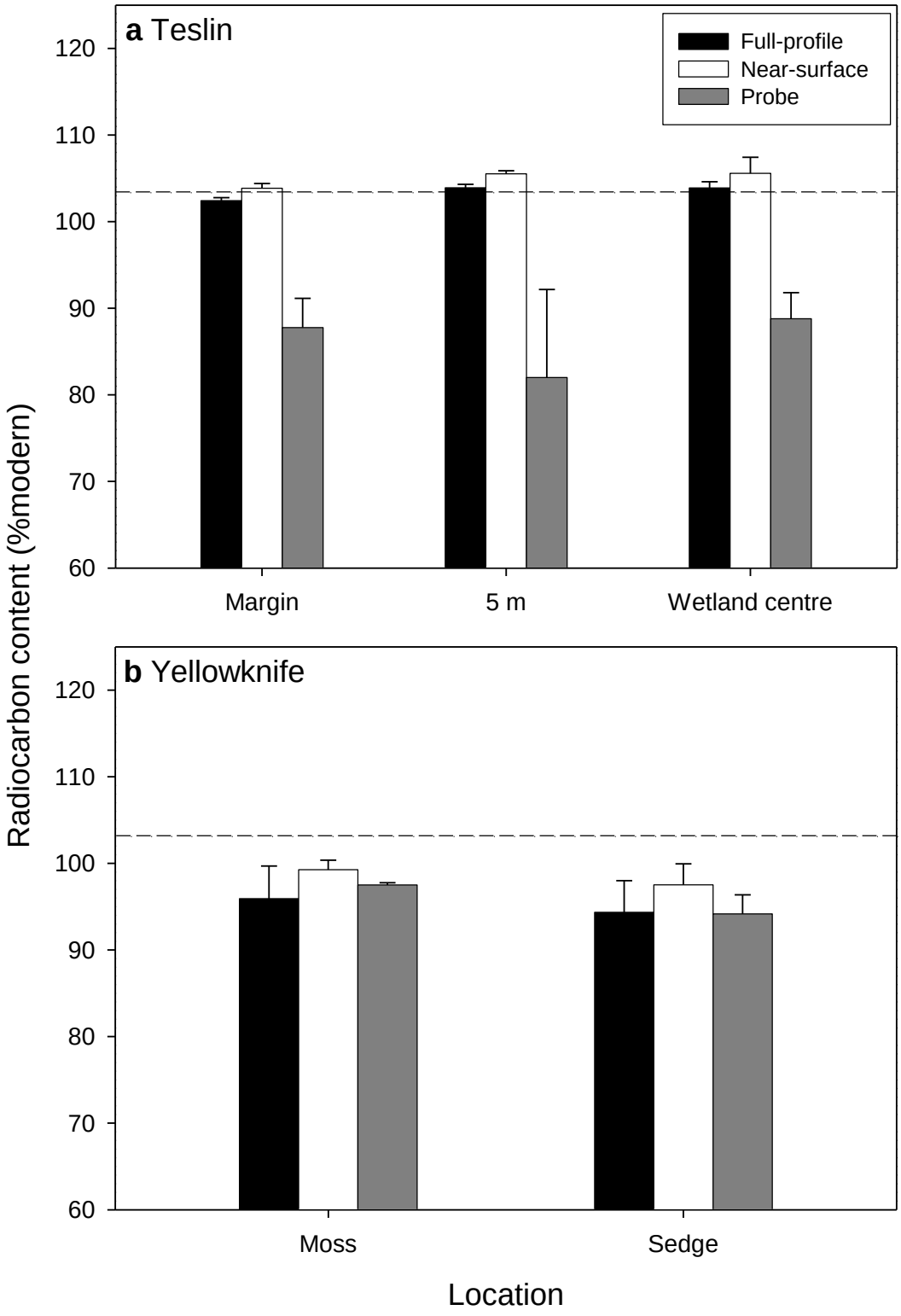
567 **Figure 3**



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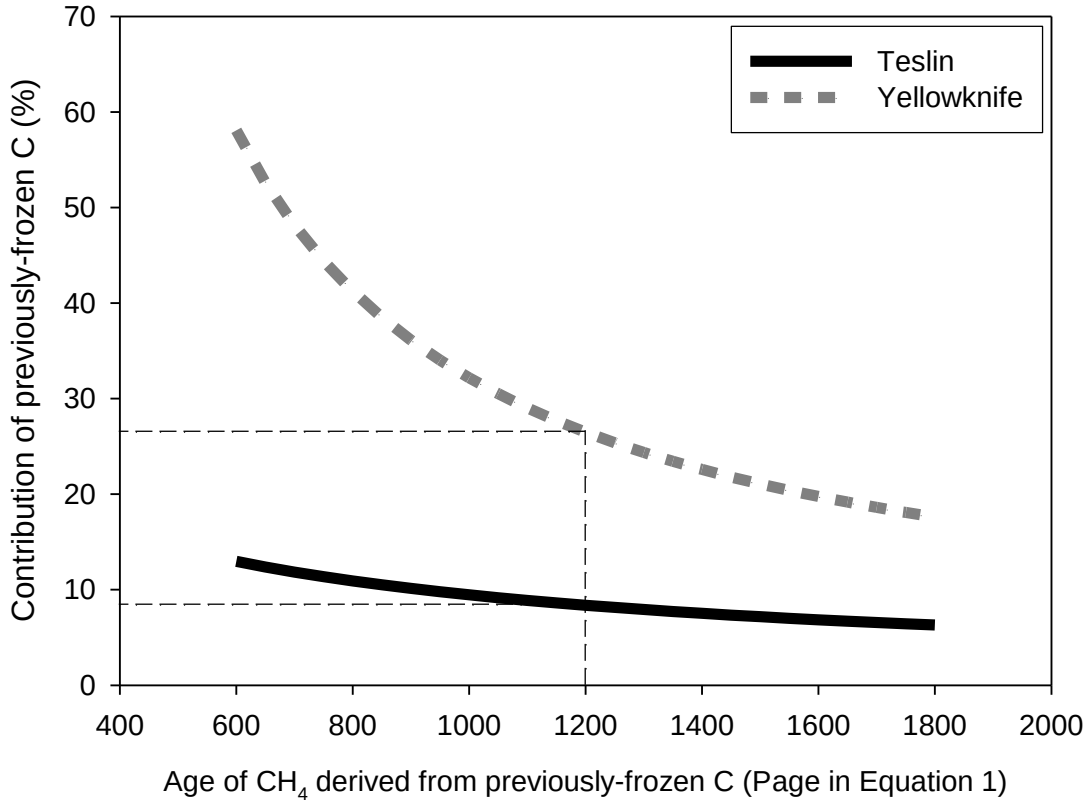
571 **Figure 4**



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