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Organic matter chemistry controls greenhouse gas emissions from permafrost peatlands

Running head: Carbon dynamics in permafrost peatlands

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Primary research article

Abstract

Large tracts of arctic and subarctic peatlands are underlain by permafrost. These peatlands store large quantities of carbon (C), and are currently under severe threat from climate change. The aim of this study was to determine the size and organic chemistry of the easily degradable C pool in permafrost peatlands and link the functional organic chemistry to temperature and moisture controls of greenhouse gas emissions. First, we used a combination of field measurements and laboratory experiments to assess the influence of increased temperature and flooding on CO_2 and CH_4 emissions from sixteen permafrost peatlands in subarctic Sweden and Canada. Second, we determined the variation in organic matter chemistry and the associated microbial community composition of the peat active layer with depth using quantitative ^{13}C solid-state NMR and molecular biomarkers respectively. We demonstrate that the peat organic chemistry strongly controls CO_2 release from peat and that ca. 35 and 26 % of the peat organic matter, at the Swedish and Canadian peatlands sites, respectively, is easily degradable by heterotrophic microorganisms. In contrast to CO_2, CH_4 emissions were decoupled from peat functional organic chemistry. Furthermore we found strong relationships between the microbial community structure and the peat organic chemistry suggesting that substrate type and abundance is an important driver of microbial composition in sub-arctic peatlands. Higher temperatures resulted in greater CO_2 production with comparable temperature sensitivity throughout the active layer despite considerable variation in peat chemistry and microbial community composition with depth. Our study shows that functional organic chemistry controls both soil respiration rates and the composition of the microbial community. Furthermore, if these peatlands collapse and flood on thawing, they are unlikely to become large emitters of CH_4 without additional input of labile substrates.

Introduction

Subarctic peatlands rich in carbon (C) account for ca. 20% of permafrost area across the arctic and store ca. 94.3 Gt-C (Tarnocai et al. 2009; Schuur et al., 2011). With current estimates of anthropogenic fossil fuel emissions at 11.8 Gt-C yr-1 (Friedlingstein et al., 2014), this represents a substantial C reservoir at risk with sever implication for future global climate (Schneider von Deimling et al., 2012). The arctic is predicted to undergo mean annual temperature increases of over 5 °C (IPCC 2014) leading to estimated C losses of 232-380 GtC by 2011 from permafrost soils (Schuur et al. 2011). These high C loss rates is supported by incubation and modelling studies suggest that within 50 years ca. 40 % of the soil organic material (ca. 60 Gt-C) currently held in organic permafrost soils could be mineralised and released to the atmosphere (Schädel et al., 2014).

While it is well established that the extensive C stores in permafrost peatlands are especially susceptible to losses through a combination of expected climate warming (Dorrepaal et al., 2009; Wang et al., 2010; Harden et al., 2012) and high concentrations of labile constituents (i.e. easily degraded by microorganisms) (Dorrepaal et al., 2009; Schuur et al., 2009; Schuur and Abbott 2011; Schädel et al., 2014), uncertainties remain about the functional composition of the permafrost peatland C pool (e.g. the proportion of alkyls, O-alkyls, aromatics in the peat matrix) and how this may control C losses in a warming arctic. Furthermore, permafrost thaw in this region will result in deeper active layers which may subside, flood and result in thermokarst formation as the ice rich core is lost (Osterkamp 2007; Åkerman and Johansson 2008). This increased water logging, with associated anoxic conditions, may increase CH_4 emissions and potentially lower heterotrophic CO_2 losses (Christensen et al., 2004; Schuur et al., 2008; Treat et al., 2014).

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The susceptibility of peat to decomposition by microbes is linked to its organic chemistry. Peat chemistry has been shown to influence potential CO_2 and CH_4 emissions from subarctic, temperate and tropical peats in short term incubations with higher CO_2 and CH_4 production resulting from peat high in carbohydrates (O-alkyls) and proteins (White et al., 2002; Andresen and White 2006; Reiche et al., 2010; Wright et al., 2011; Treat et al., 2014). However, anaerobic CH_4 production is both less efficient and more strongly limited by substrate quality (Ström et al., 2012) than aerobic CO_2 production.

One of the factors determining if a given exothermic reaction will occur is the activation energy (E_a) of the reaction (Atkin1994). For organic materials, such as peat and litter, the relationship between E_a and the structure of molecules are described by kinetic theory (e.g. Lloyd and Taylor 1994; Craine et al., 2010): Kinetic theory postulates that decomposition of recalcitrant, structurally complex, organic compounds, that have greater activation energies, puts higher energy demands on microorganisms. Recalcitrant organic compounds therefore have greater temperature sensitivity than more labile compounds with lower E_a (Fierer et al., 2005). In the context of permafrost peatlands, understanding the temperature response and E_a of peat decomposition in different peat layers provides information which can be used to assess peat lability and vulnerability to decomposition at higher temperatures. However, there exists a severe lack of data quantitatively linking functional organic chemistry of peat to its temperature sensitivity (but see Treat et al., 2014 who used a semi-quantitative pyrolysis-GCMS biomarker approach to link peat chemistry to temperature sensitivity). In the context of permafrost soils, the temperature sensitivity of the constituent organic material may regulate how climate warming affects C release to the atmosphere.

98 The microbial community, through use of carbon for respiration and growth ultimately
99 controls the release of stored carbon from organic soils, and its activity is dependent on
100 environmental conditions such as temperature, hydrology and pH (Bergman et al., 1999; Yu
101 et al., 2007) as well as the quality and quantity of resources as influenced by organic
102 chemistry and the nutrient status of the soils (Webster et al 2001; Basiliko et al., 2006).
103 Greater fungal abundance in peat has been associated with more efficient microbial
104 communities i.e. communities with low respiration rates relative to the microbial biomass and
105 lower respiration quotients (qCO_2, i.e. the respiration rate per unit biomass) (Basiliko et al.,
106 2006), although others have found less clear cut depth effects (Myers et al., 2012). Fungi are
107 limited to aerobic environments and lower O_2 levels in deeper peat layers are likely to inhibit
108 fungal growth, with implications for degradation of more complex organic molecules
109 (Freeman et al., 2004). For example, lignin degradation by lignolytic microorganisms (mainly
110 fungi) require O_2 to efficiently depolymerize and solubilize lignin (Zeikus, 1981) and is thus
111 likely to be hampered in deep and/or waterlogged peat layers.
112
113 To further our understanding the fate of permafrost peatland carbon and greenhouse gas
114 feedbacks under future climate change conditions, this study explored the overarching
115 hypothesis that organic matter chemistry is the primary driver of decomposition in permafrost
116 peatlands, through its influence on greenhouse gas production, the temperature sensitivity of
117 decomposition processes, and microbial community composition in sub-arctic peatlands. The
118 objectives of this study were therefore to determine the peat functional chemistry, microbial
119 community composition, and CO_2 and CH_4 release from permafrost peatlands under different
120 moisture and temperature treatments. The study focused on the seasonally thawed active
121 layer which stores ca. 500 Pg of C (mineral and peat soils combined) across the Pan arctic
122 (Hugelius et al., 2014).

To achieve our objectives we tested the following specific hypothesis relating to the vulnerability of the peatland carbon store to environmental change:

1. *Ex situ* experimental flooding of permafrost plateau peat will result in a shift from net CH_4 uptake under mesic conditions to CH_4 efflux throughout the active layer.
2. Peat organic chemistry, as determined by quantitative ^{13}C NMR MAS, are linked to CO_2 and CH_4 emissions rates from plateau peat with higher CO_2 and CH_4 emissions from peat with a greater proportion of labile peat.
3. Deeper and more degraded peat contains more recalcitrant organic matter (e.g. alkyls), have higher E_a and Q_{10} values, and its decomposition is hence more sensitive to increases in temperature than surface peat, provided that other limiting factors are controlled (e.g. optimal pH, moisture and nutrient conditions).
4. The composition of the microbial decomposer community is driven, at least in part, by peat organic chemistry.

Materials and Methods

Site description

Two study areas were investigated, the Torneträsk area, northern Sweden (68°12´N, 19°03´E, 351 m asl) and the Churchill area, north eastern Canada (58°44'N, 93°49'W, 25 m asl). These areas were chosen as they are currently undergoing permafrost thaw (Lawerence et al., 2008; Sannel and Kuhry 2011; Åkerman and Johansson 2008). The mean annual temperature (MAT) in the Torneträsk area ranged between 0.8 and 1.0 °C and the mean annual precipitation (MAP) ranged from 304 mm in the west to 424 mm in the east), in Churchill, MAT was -7 °C was and MAP was 414 mm. Both areas support peatlands with permafrost cores, so called palsas. The initiation of peat formation in the Torneträsk area is ca. 800-900

148 (Kokfelt et al., 2009) and ca. 3500-5200 years BP in the Churchill area (Hugelius et al.,
149 2010). Total peat depths, including the permanently frozen layer, range from 90 to 160 cm
150 with a maximum active (i.e. seasonally thawed) layer depth of 95 cm (Kuhry 2008; Åkerman
151 and Johansson 2008). The depth to the permafrost varies between wetter and drier areas with
152 a shallower active layer in drier areas. The sites were characterised by areas of raised peat
153 plateaus, supported by an ice-rich core, with relatively dry surface conditions (mesic),
154 dominated by bryophytes, lichens and evergreen dwarf shrub (Supplementary information 1).
155 At the Torneträsk sites *Sphagnum fuscum* was the dominant moss species while *Dicranum*
156 *elongatum* contributed to ground cover to a large extent at the Churchill sites. The main
157 evergreen shrubs species at both areas were *Empetrum nigrum* and *Ledum* sp. while *Betula*
158 *nana* was the dominant deciduous shrub. Lichens were more abundant at the Churchill
159 peatlands than in the Torneträsk area. The most common herbaceous species for both areas
160 was *Rubus chamaemorus*. The Torneträsk sites showed signs of small scale permafrost thaw
161 and areas of peat collapse, with collapsed areas ranging between tens to hundreds of meters
162 across). In Churchill, thermokarst areas were actively forming adjacent to plateau areas.
163 Marginal collapsed areas tended to be vegetated by graminoids mainly *Carex* and
164 *Eriophorum* species. See Supplementary information 1 for full species lists.
165
166 *Sampling strategy*
167 Eight mesic (i.e. moderately moist) peat plateau sampling sites were selected from discrete
168 peatlands within each region (i.e. n = 8; with a total of 16 peatlands sampled). Sampling
169 locations were distributed over a total distance of ca. 100 km at Torneträsk and ca. 15 km at
170 Churchill (Supplementary information 2). Site selection was based on vegetation type,
171 hydrology and an active layer consisting entirely of peat. The size of the sites varied from ca.
172 2 ha at the shore of lake Torneträsk to several kilometres across. Peat cores were collected at

the time of maximum permafrost thaw; the Torneträsk peat sampling performed in September 2008 and the Churchill sampling end of August 2009. Measurements of CO_2 and CH_4 exchange, soil temperature, active layer depth was assessed *in situ*, and vegetation turf samples were collected for above and below ground biomass determination at each site. Methods and data describing the *in situ* CO_2 and CH_4 flux data are presented in supplementary information 3.

From each site eleven peat monoliths were collected through the active layer in a 4m×4m plot a using a 7 cm × 7 cm Macaulay peat corer. From each monolith intact peat sections of 10 cm length were collected from three depths throughout the active layer at each site, corresponding to the top 0-10 cm peat layer (L1), the bottom 10 cm layer just above the permafrost table (L3), and an intermediate 10 cm sample (L2) half way between L1 and L3 (note that at one of the Churchill peatlands shallow active layer depth only allowed for two 10 cm samples to be collected, designated L1 and L3). Samples were placed in plastic bags and placed in sealed plastic containers at 4°C for transport and storage prior to analysis. In the laboratory a subset of 7 randomly selected cores were homogenised to provide a large pooled sample from each layer (seven of the eleven cores) which were used for the chemical and microbiological characterisation of the peat. The remaining monoliths were randomly assigned to either one of two experiments (a flooding experiment and a temperature response experiment).

Site properties

To determine total above and below ground plant biomass we harvested the biomass in three subplots 10 cm × 10 cm in area ca. 4 m apart at each peatland site. We determined root biomass at three depths from the peat surface to just above the permafrost table,

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198 corresponding to L1, L2 and L3 i.e. 7 cm × 7 cm ×10 cm samples, in each of the three
199 subplots harvested for above ground biomass. We separated the above ground biomass into
200 moss, deciduous shrubs, evergreen shrubs, graminoids, lichen and leaf litter and washed in
201 deionised water. The total root biomass was manually separated from the soil using tweezers
202 and gently washed in deionised water to remove any peat attached to the roots. Samples were
203 then dried at 50 °C for 48 hours and weighed to estimate root biomass.
204
205 Soil temperature and moisture was determined in parallel with the CO_2 flux measurements
206 using digital thermometers and a hand held Theta meter connected to a Theta probe (Delta-T
207 Devices, Cambridge UK). The maximum active layer depth was determined by measuring the
208 depth at which frozen peat was present at the base of the peat cores.
209
210 *Long term flooding experiment*
211 To investigate the impact of peat moisture status on CO_2 and CH_4 fluxes (hypotheses 1 and 2)
212 we used paired intact peat monoliths from each layer (L1, L2 and L3) and from each peatland
213 (six peat samples per peatland) in a flooding experiment whereby monoliths were randomly
214 allocated to either aerobic (field capacity) or anaerobic (flooded) moisture conditions. To
215 achieve the two treatments we saturated all of the peat cores by raising the water levels to 1
216 cm above the peat surface. For the anaerobic treatment the water levels were maintained at
217 this level for the duration of the experiment, while for the aerobic treatment the cores were
218 allowed to drain until field capacity were reached (ca. three days). The peat samples were
219 then loosely covered by parafilm and incubated at 15 °C, which reflected the summer soil
220 temperature at 10 cm depth (Table 1). CO_2 and CH_4 fluxes for each sample were determined
221 after 14 days incubation and 2-3 weeks thereafter over a period of four months (a total of five
222 sampling occasions). The samples moisture levels were maintained during the length of the

223 incubation experiment by regular addition of deionised water to target weight. For the
224 Torneträsk peats an additional sampling was made ca. 10 months after the initiation of the
225 flooding experiment to assess more long term effects of flooding on gas production. CO_2 and
226 CH_4 fluxes were determined from gas sampled taken at 0 and 30 minutes from each peat core
227 placed in air tight 1.5 L jars with sampling ports and analysed by gas chromotography (GC)
228 (Sjögersten et al., 2011).
229
230 This data, in conjunction with quantitative data on peat organic chemistry (see below), was
231 used to determine the lability of the soil organic carbon (SOC). We defined "labile SOC" as
232 functional organic groups associated with high heterotrophic CO_2 production and, based on
233 kinetic theory, low E_a's (see temperature response experiment below).
234
235 To quantify acetate concentrations (a precursor for anaerobic CH_4 production – Ström et al.,
236 2003) in the flooded treatment, 20 ml porewater samples were collected at the end of the
237 experiment using Rhizon samplers (Rhizosphere Research Products, UK) and analysed using
238 an anion HPLC system fitted with a Synergi Hydro-RP column for acetic acid detection. The
239 flow rate was 1 ml min^{-1}, detection was made using UV at 220 nm (photo-diode array
240 detection).
241
242 *Temperature response experiment*
243 Hypothesis 3 was assessed by determining the temperature sensitivity of CO_2 production and
244 peat lability down the peat profile, expressed both as E_a and Q_{10} (proportional increase in
245 CO_2 production per 10 °C rise in temperature) values, by measuring the potential CO_2 efflux
246 at different temperatures. Conditions for decomposition in the peat were optimized by
247 aerating the peat to avoid O_2 limitation of decomposition, adjusting peat moisture and

248 improving pH and N and P levels. We focused on N and P additions as these nutrients are
249 known to limit decomposition in northern peatlands (Gerdol et al., 2007; Moore et al., 2008;
250 Bragazza et al., 2012). For the experimental nutrient (N and P combined) and pH
251 amendments we used homogenised peat from each layer taken from two combined peat
252 monoliths after roots were removed. The pooled peat sample was then split into equal masses
253 (ranging between 150 and 330 g fresh weight in each container depending variation in the
254 original peat sample masses) and packed loosely into aluminium containers to ensure the
255 samples were fully aerated. The nutrient treatment involved addition of 0.5 mmol of NH_4NO_3
256 and 0.3 mmol of KH_2PO_4 per g dwt peat together with 0.12 mmol $Ca(OH)_2$ per gram fresh
257 peat to raise the pH to 6.5. Both control and optimised samples were adjusted to 300%
258 moisture content, to reflect field moisture conditions (Table 1). Optimized peat samples were
259 then incubated at four increasing temperatures for a week. On day one samples were placed
260 in an incubator (2 °C) equilibrated for 24 hours. On day two gas samples for flux
261 determination were collected (see above), after which the temperature was raised to 8°C for
262 24 hours. Gas collection (from the 8°C incubation) on day three and the temperature raised to
263 14°C and samples were again incubated for 24 hours followed by gas samples collection.
264 After this sampling the temperature was brought to 20 °C for 24 hours prior to the final gas
265 sampling.
266
267 Based on the short-term temperature response activation energies (E_a) were derived by
268 plotting the natural logarithm of *k* against the inverse of the temperature (T) according to the
269 following equation (Lloyd and Taylor 1994):
270
271 $\ln k = \ln A - E_a/(R \times T)$ (1)
272

where *k* is the respiration rate, A is the frequency factor, R is the gas constant and T is temperature. The slope of the Arrhenius curve gives –Ea/R and the intercept at 1/T = 0 gives lnA.

The Q_{10} value describes the increase in respiration rates with a 10°C increase in temperature (Hamdi et al., 2013) and was calculated using eq. 2

$$Q_{10} = e^{10k}. \quad (2)$$

where *k* is the rate coefficient from exponential relationship between temperature and respiration rates.

Peat organic chemistry

To address hypotheses 2, 3 and 4 we investigated the organic composition of the peat material in a fully quantitative way using solid state ^{13}C NMR MAS to determine the % of different chemical functional groups present (Preston et al., 1996). Quantitative ^{13}C NMR MAS spectra were recorded at ambient temperature using direct polarization, experimental details are described below: For the NMR measurements the soils were packed into 7.5 mm diameter MAS rotors aiming to maximise the amount of sample to improve the signal to noise ratio. ^{13}C MAS spectra were recorded on a Varian Infinity plus spectrometer operating at 75.47 MHz using a direct polarization experiment and a spinning rate of 7 kHz. Settings were optimized during test runs of peat samples. Specifically, continuous wave (CW) proton decoupling with a radio frequency (rf) amplitude of 65 kHz applied during the acquisition time which lasted 34.1 s. The spectral width was 300 kHz and 10240 points were collected. Background signals were suppressed by inserting a short spin echo prior to acquisition.

Before recording quantitative data, similar spectra were obtained as a function of relaxation delay for a selection of samples in order to check for saturation. A relaxation delay of 64 s was found to be sufficient to provide quantitative spectra and this delay was used in all experiments. The resulting FIDs were digitally filtered to remove noise outside the central 20 % of the spectral width and reduced by a factor 5. Line broadening of 100 Hz was applied before Fourier transformation, which was followed by automatic phasing. No baseline correction was applied to the data. Spectra were referenced externally to solid adamantane (resonance at δ = 38.5 ppm) to provide a chemical shift scale relative to neat TMS (Morcombe and Zilm 2003). After processing, the spectra were integrated over chemical shift ranges corresponding to the major organic functional groups (Sjögersten et al., 2003).

The presence of spinning sidebands with significant intensity in MAS spectra results in errors in quantitative analysis by solid-state NMR. Efficient suppression of sidebands from a ^{13}C site with a given shift anisotropy $\zeta = \delta_{zz} - \delta_{iso}$ is achieved either by increasing the MAS rate or decreasing the magnetic field. Note that the MAS rate chosen was the maximum possible with the 7.5 mm MAS probe. Use of smaller MAS rotors with faster maximum spinning rates was precluded here by the unacceptable loss of sensitivity from smaller sample volumes. However, the relatively low B_0 field employed in this work ensures that spinning sideband intensities can be ignored during quantification. Experimentally, this assumption is shown to be justified by the lack of significant intensity in all spectra between 210 and 300 ppm (see Fig. 1 for examples). This region of the spectrum is where the most intense downfield sideband is expected for aromatic, phenolic and carbonyl ^{13}C sites which normally have δ_{iso} = 120 - 200 ppm and $\zeta \sim 100$ ppm. Other ^{13}C sites have $\zeta < 70$ ppm for which the theoretical intensity of the most intense sideband is always less than 5% of that of the isotropic line for ω_0 = 75.47 MHz and ω_r = 7 kHz.

To determine peat C content, a sub sample of the pooled samples from each layer from each peatland (total of 47 samples) was homogenised using a ball mill and analysed for C and N using a total element analyser (Flash EA 1112, CE Instruments, Wigan, UK).

Microbial community composition and biomass

To address hypothesis 4 we determined the microbial community composition using standard ELFA techniques (Frostegård & Bååth 1996; Zogg et al., 1997; Schutter and Dick 2000). Briefly, ester linked fatty acids (ELFA) were extracted from 0.5g of freeze dried peat using alkaline methanolysis (Frostegård & Bååth 1996). The resultant methyl esters were re-dissolved in isohexane and analysed by GC. Double bonds of the fatty acids were related to the methyl end (ω) of the molecule (Zogg et al., 1997). The fatty acid 23:0 was added as a known standard. The total biomass of bacteria included all fatty acids from the Gram negative and Gram positive bacteria and fatty acids 15:0 and 17:0. Fatty acid 18:2ω6,9 was used as an indicator for fungal biomass (Frostegård & Bååth 1996). Total microbial fatty acid biomass was estimated by adding together fungal and bacterial fatty acid biomarkers.

Data analysis and calculations

Differences between region and depth were analysed using mixed linear models with 'site' as the random effect and 'region' and 'depth' and their interaction as fixed effects. For the flooding experiment a repeated measures structure was applied with 'site' as the random effect and 'region', 'depth' and 'treatment' and their interactions as fixed effects. Regression analysis was used to investigate the relationship between of the CO_2 and CH_4 emissions, the microbial community structure and peat organic functional chemistry. Normality was assessed using residual plots. In the case of regression analysis, the % variance explained by

348 the relationship is reported as σ^2. All the statistical analysis was done using Genstat 13th
349 edition.
350
351 **Results**
352 *Site properties*
353 The plant biomass at the Torneträsk peatlands was strongly dominated by mosses. In
354 Churchill, lichens contributed the highest biomass followed by mosses and evergreen dwarf
355 shrubs (Table 1, Supplementary information 2). Root biomass was comparable with above
356 ground biomass. The maximum active layer depth in mesic areas of these peatlands was 49.9
357 ± 0.9 cm and 31.2 ± 1.4 cm, in Torneträsk and Churchill, respectively (Supplementary
358 information 1). During the sampling period the peatlands were net CO_2 sources and weak
359 CH_4 sinks *in situ* (methods and data are shown in Supplementary information 3 and 4), mean
360 soil temperatures were 8 and 5 °C and soil moisture content were ca. 540 and 450 % at the
361 time of the flux measurements in Torneträsk and Churchill, respectively.
362
363 *Long term flooding experiment*
364 *Ex situ* incubation of intact peat cores, both in flooded and non-flooded cores, showed that
365 surface peat produced more CO_2 than deeper layers on a mass basis (Fig. 2a). In contrast,
366 more CH_4 was produced at depth, while net CH_4 oxidation was found in the two layers
367 closest to the surface (Fig. 2b). Experimental flooding induced increased CH_4 emissions (with
368 170 % over 4 months) at both sites (Fig. 2b). In the surface layer, flooding reduced CH_4
369 oxidation but did not result in net CH_4 emission. Long term incubation of the peats from the
370 Torneträsk site, revealed no further increase in the CH_4 production 10 months after the
371 flooding treatment was applied (Time: $P > 0.05$; data not shown). In line with the low CH_4

fluxes, acetate concentrations in the pore water solution were below the detection limit (< 12.5 mg l^{-1}, data not shown).

Peat organic chemistry

The peat chemistry at the two areas differed with respect to their aromaticity, which was higher in Churchill peat, but the alkyl to O-alkyl ratios did not differ between areas (Fig. 3 a and b, Table 2). The most pronounced changes in peat chemistry with depth were a relative loss of carbohydrates (O-alkyls) with depth at the Torneträsk sites, and a relative reduction in aromatics with depth in Churchill (Fig. 3 c and d, Table 2). There were consistent shifts in concentrations of acetals (declining) and alkyls (increasing) with depth at both sites, while concentrations of phenolics decreased with depth in Churchill but not in Torneträsk (Fig. 3 c, d, e and f, Table 2). The peat functional organic chemistry was related to the composition of the vegetation: The ratio between cryptogams and vascular plants showed a positive relationship with both amounts of O-alkyls ($\sigma^2 = 18.4$; $F_{1,15} = 4.38$, $P = 0.055$), and overall carbohydrate type compounds (O-alkyls+n-alkyls+acetals) ($\sigma^2 = 27.9$, $F_{1,15} = 6.81$, $P < 0.05$) (Supplementary information 6), but not the aromatic or aliphatic fraction of the peat.

At each site the most abundant functional group (Fig. 3 a and c) was the strongest predictor of CO_2 efflux under non-flooded conditions (flooding experiment; Fig. 4a and b): There was a strong positive relationship between peat CO_2 efflux and the proportion of carbohydrates (O-alkyls) at the Torneträsk sites and a somewhat weaker regression between the amount of aromatics and the CO_2 efflux at the Churchill sites. Although the other functional groups present in the peat are, to a degree, likely to contribute to total CO_2 effluxes, no other functional groups were significantly related to the CO_2 efflux. Using the relationship between the CO_2 efflux and the concentration of carbohydrates and aromatics as a lability indicator,

we estimated the size of the labile C pool to 35 (O-alkyls only) and 26 % (O-alkyls + aromatics) of the peat organic matter content, i.e. mean concentrations of the respective functional groups through the active layer, at the peatland sites in the Torneträsk and Churchill areas, respectively (Figure 3 b-d). In contrast, the peat chemistry (as determined by ^{13}C solid state NMR) was not a significant predictor of CH_4 fluxes from flooded peat at either of the two sites.

Temperature response experiment

The potential release of CO_2 from optimized peat (aerated peat with adjusted moisture, pH and N and P levels) increased significantly as temperatures were raised experimentally from 2 to 20 °C (Supplementary information 5 a and b). For example, CO_2 release from L3 increased with 330 and 130 % in response to this temperature increase at Torneträsk and Churchill respectively. This demonstrates that the organic C decomposition *per se* is sensitive to increased temperature, even though low nutrient content and pH *in situ* can limit the temperature sensitivity of decomposition. The overall temperature response of the peat in the active layer from the two sites was exponential (Supplementary information 5 c).

The shifts in peat chemistry with depth did not significantly alter either the E_a, 48.3 ± 6.0 kJ mol^{-1} (range 5.5 to 125) or the Q_{10} values, mean 2.3 ± 0.2, with depth. However, the E_a showed a positive relationship with the phenolic content of the peat from the Torneträsk sites (Fig. 4c), while there was no relationship between E_a and the functional organic chemistry of Churchill peats.

Microbial community composition

The total microbial biomass differed between areas and with depth (Fig. 5a). The changes with depth were driven by a strong decline in fungal biomass and a more modest decrease in gram negative bacteria, while gram positive bacteria did not change in abundance with depth or site (Fig. 5b - d). These shifts in microbial community resulted in a pronounced decline in the fungal to bacterial ratio with depth, 8.4 ± 2.0, 3.7 ± 1.7, 0.3 ± 0.1 for L1, L2 and L3, respectively in Churchill and 4.3 ± 0.7, 1.1± 0.4, 0.2 ± 0.0 for L1, L2 and L3, respectively, in Torneträsk (overall depth effect: $F_{2,26} = 13.65$, $P < 0.001$). Fungal to bacterial ratios was greater in Churchill than Torneträsk, 4.5 ± 1.1 and 1.9 ± 0.5, respectively ($F_{1,13} = 6.34$, $P < 0.05$). In addition to variation in microbial communities with area and depth, peat organic chemistry was a strong driver of the microbial community composition (Fig. 6). Specifically, the fungal to bacterial ratio declined in response to higher concentrations of alkyls in the peat, while fungal biomass became relatively more abundant in response to higher concentrations of aromatics (Fig. 6 a and b). Total bacterial fatty acid biomarkers increased significantly in response to increasing amounts of carboxyls in the peat, while greater biomass of gram positive bacteria was found in peat with higher concentration of phenolics (Fig. 6 c and d). Note that these relationships remained highly significant also after area and depth was fitted in the statistical model indicating that the relationships were independent of area and depth.

Discussion

Variation in soil organic chemistry with depth and across geographic areas

The difference in the dominant organic functional groups in peat among areas (Fig. 3 and Table 2) is likely due to a combination of contrasting litter inputs and decomposition environment (Turetsky 2004). With regards to litter inputs, peat from Churchill, where the vegetation was more lichen dominated, contained more aromatics, likely from aromatic lichen litter (Yoshikawa et al., 2008) than peat from the Torneträsk region (Table 1 and 2). In

446 contrast, the peat from Torneträsk, where the vegetation was moss dominated (predominantly
447 by *Sphagnum* species) which have high concentrations of carbohydrates and generally low
448 amonts of lignin (Maksimova et al., 2013), contained more O-alkyls.
449
450 The changes in peat functional chemistry with depth at the Torneträsk sites (Table 2) reflect
451 the decline in carbohydrates (O-alkyls) found with depth in moss peat (Treat et al., 2014 and
452 Reice et al., 2010) and are likely linked to preferential decomposition of these functional
453 groups. At the Churchill sites the preferential loss of aromatics with depth (Table 2) clearly
454 suggests that this component of the peat material, which generally is considered recalcitrant,
455 is degradable in line with findings by Reice et al., (2010). The contrasting litter inputs from
456 the vegetation, together with the lower fungal biomass at the Churchill sites, may be
457 responsible for the different depth profiles in peat chemistry between the study areas (Table 1
458 and 2; Fig 5b). It is also plausible that the change in the microbial community structure
459 contributes to the changes in peat chemistry with depth through both preferential degradation,
460 as fungi and bacteria are able to degrade different functional groups, and have different cell
461 wall composition (Strickland and Rousk 2010).
462
463 *Impacts of experimental flooding on greenhouse gas emissions*
464 Flooded CH_4 emissions were several orders of magnitude lower than CO_2 emissions under
465 non-flooded conditions throughout the peat profile (Fig. 3), highlighting the lower efficiency
466 of anaerobic decomposition processes found in a range of different peatlands (Moore and
467 Dalva 1997; Inglett et al., 2012; Treat et al., 2014). In support of our first hypothesis, we
468 found that flooding increased overall CH_4 emissions (Fig. 3). However, the CH_4 emission
469 induced by experimental flooding of mesic peat was small compared to CH_4 emissions from
470 old areas of collapsed peat colonised by graminoids (Bubier et al., 1995). The small increase

in CH_4 emissions following flooding in deeper peats indicate that although present, the activity of the methanogenic community remained low over the time frame of the experiment.

Relationship between peat organic chemistry and greenhouse gas emissions

Our data supported our second hypothesis that functional organic chemistry controls CO_2 emissions from drained peatlands, but we found no link between the bulk peat organic chemistry and CH_4 emissions under either non-flooded or flooded conditions. The lack of relationship between peat organic chemistry and CH_4 production is important as it suggests that peat chemistry may not influence CH_4 emissions in the shorter term, should these peatland plateaus subside and flood. We speculate that CH_4 production following flooding of plateau peat is limited by the availability of the specific substrates i.e. sugars and low molecular weight organic acids which are fermented to acetate, the precursor for CH_4 production (Joabsson et al., 1999; Ström et al., 2003; Ström et al., 2012), together with slow establishment of a functioning methanogenic community (Treat et al., 2015). It is plausible that the peat at our study sites supports limited, or no, acetate production due to low plant litter, low root exudate inputs from the low productivity vegetation, and high decomposition rates under the relatively dry conditions found on peat plateaus. Indeed, acetate levels in flooded peats were very low, which suggests either that hydrogenotrophic methane production was driving the weak increases in CH_4 production observed in the deeper peat layers in response to flooding or simply that low acetate levels indicate rapid consumption. Similarly low CH_4 production and low substrate quality of the dissolved organic matter has been reported for recently collapsed palsas in northern Sweden (Hodgkins et al., 2013). Therefore, collapsed peat plateaus may only become substantial CH_4 sources after the establishment of a more productive plant community and associated release of root exudates and plant litter into the peat (Ström et al., 2003, Prater et al., 2007; Koelbener et al., 2010;

Ström et al., 2012; Hodgkin et al., 2013). This time-lag, prior to conditions that allow for a substantial increase in CH_4 emissions following peatland collapse (Jackowicz-Korczynski et al., 2010), has implications for the net radiative forcing resulting from rapid thawing.

The strong positive relationship between peat CO_2 emissions and peat composition (Fig. 4a and b), particularly O-alkyl and aromatics content at the two sites respectively, demonstrates the potential for rapid degradation of these functional groups under optimal conditions in line with findings from the boreal forest in Canada (Preston et al., 2014). Indeed, the higher concentrations of these functional groups in surface peats (Fig. 3) may, in part, explain the higher CO_2 production in this layer (Fig. 2 a). Comparable strong relationships between peat quality and CO_2 emissions have been shown in peatlands at high latitude (Turetsky 2004; Wickland and Neff 2008; Hodgkins et al., 2014; Treat et al., 2014) as well as in temperate and tropical regions (Reiche et al., 2010; Wright et al., 2011). Together, our study and those of Wickland and Neff (2008) and Treat et al., (2014) shows that the large pool of carbohydrates (up to 35 % of the peat at the Torneträsk sites; Table 2) in permafrost peatlands are easily converted to CO_2 and released to the atmosphere.

Temperature sensitivity of decomposition

The high potential CO_2 loss rates in response to increased temperature demonstrated in this study compare with CO_2 loss rates following permafrost thaw in arctic tundra (Dorrepaal et al., 2009; Schuur et al 2009; Paulter et al., 2010). Specifically, our study indicated a ca. 20 % increases in potential CO_2 release when comparing current temperatures to temperature predictions for 2100 (Fig. 4f; IPCC 2014). Our data did not fully support our third hypothesis which postulated that deeper, more degraded peat is more sensitive to increases in temperature than surface peat. In our study we did not see a significant shift in the E_a and Q_{10}

521 with depth while the positive relationship between E_a and the content of phenolics (Fig. 4e)
522 found at the Torneträsk sites lend some support to the C quality – temperature hypothesis.
523 The lack of a clear change in E_a or Q_{10} with depth suggests that the shifts in peat chemistry
524 with depth are not large enough to substantially alter the energy demand of decomposition
525 organisms, or that an Arrhenius temperature relationship does not apply. This contrasts with
526 studies in boreal peatlands where Q_{10} values increase from 3.5-4.5 in surface peat (0-20 cm)
527 to 4.5-6 in deeper peat (26-32 cm) containing more recalcitrant carbon (Hilasvuori et al.,
528 2013). However, in the study by Hilasvuori et al. (2013), the change in the soil organic matter
529 chemistry with depth was not quantified, making comparisons difficult.
530
531 *Microbial community structure and functioning*
532 The strong decline in fungal biomass with depth (Fig. 5b), is most likely due to reduced peat
533 O_2 levels in deeper layers (Freeman et al., 2004; Jaatinen et al., 2007), in agreement with
534 findings in boreal peatlands (Golovchenko et al., 2002). The relative shift in the bacterial
535 community (Fig. 5c and d) with depth is also likely related to the more anoxic conditions
536 and/or colder temperatures and more decomposed organic material (Andersen et al., 2013). It
537 is plausible that the large decline in CO_2 production with depth (Fig. 3) is linked, at least in
538 part, to microbial community composition and/or size (Coolen et al., 2011). The decline in
539 fungi and their oxidative enzymatic systems in lower layers, together with changes in peat
540 chemistry, may explain of the decline in the CO_2 production (Basilko et al., 2006; Bragazza
541 et al., 2013). The strong relationships between substrate type and microbial community
542 composition suggest that the abundance of particular microbial groups is governed, at least in
543 part, by substrate type (Dimitriu et al., 2010). The relatively high abundance of bacterial
544 biomass in alkyl rich peat may suggest that bacterial groups are the main degraders of alkyl
545 functional groups. In parallel, the positive relationships between total bacteria and gram

positive bacteria and carboxyl and phenolics, respectively, suggest that these peat functional groups promote bacterial decomposition. The greater fungi to bacteria ratio found in peats with high concentrations of aromatics may reflect the greater enzymatic capacity of fungi with regards to decomposition of large complex aromatic compounds in soil (Strickland and Rousk 2010). Taken together, is it clear that the microbial community respond strongly both to the changes in the abiotic environment, associated with the peat depth, and substrate availability and may drive differences in peat chemistry.

Conclusion

In conclusion, we demonstrate that peat functional organic chemistry is strongly related to CO_2 but not CH_4 emissions. With regards to E_a and Q_{10} – values, only the relationship between phenolic concentrations and E_a supported the notion of higher E_a's being found in peat with higher concentrations of recalcitrant, complex organic molecules and that such relationship may only be noticeable when differences on the soil organic chemistry e.g. with depth, is more pronounced than in our study. Finally, the strong relationships between the microbial community structure and substrate type suggests that peat functional organic chemistry modifies the decomposer community with implications for decomposition processes.

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883 **Tables**

884 Table 1. Site characteristics of the peatlands in the Torneträsk and Churchill areas. Above ground and root biomass is expressed in g m^{-2}, the root

885 biomass is shown for each of 10 cm three peat layers (L) sampled, i.e. L1, L2 and L3, with L1 being surface peat and L3 being from just above

886 the permafrost table. Soil temperature was measured at 10 cm depth, the soil moisture content (0-10 cm depth) is expressed on a dry weight

887 basis. Mean ± SE are shown, n =8.

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	Torneträsk		Churchill	
Moss	743.5	± 78.0	475.4	± 195.5
Deciduous shrub	8.0	± 3.5	13.6	± 5.6
Herbaceous	5.0	± 0.9	19.1	± 7.3
Evergreen shrub	70.5	± 20.2	311.7	± 57.6
Graminoids	1.2	± 0.8	2.8	± 1.8
Lichen	9.3	± 1.4	771.0	± 202.6
Leaf litter	41.4	± 7.0	465.0	± 82.0
Total above ground biomass	837.4	± 77.9	1593.5	± 188.1
Roots L1	505.7	± 78.7	439.9	± 147.7
Roots L2	207.1	± 38.0	77.2	± 13.7
Roots L3	71.0	± 12.5	99.3	± 34.1
Soil moisture (%)	537.4	± 63.4	449.4	± 93.1
Air temperature (°C)	14.5	± 0.6	16.4	± 0.5
Soil temperature (°C)	8.0	± 0.1	5.0	± 0.4
Permafrost depth (cm)	50.1	± 0.7	31.2	± 1.4

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893 Table 2. Significant differences for NMR derived C belonging to different functional groups among layer, area and their interactions is shown, n

894 = 8, ns denotes no significant difference. To enable comparison of differences between layers in Fig. 3 the standard error of the difference (SED)

895 for layer is included in the table.

	Significance of fixed effects		
	Area	Layer (SED)	Area*Layer
Acetals	$F_{1,13}$= 3410.58***	$F_{2,28}$=10.01***, (0.5)	ns
Alkyl	$F_{1,41}$= 24.49 ***	$F_{2,41}$=9.84***, (0.9)	ns
Aromatics	$F_{1,14}$= 172.24***	$F_{2,27}$=9.16***, (0.8)	ns
Carboxyls	$F_{1,14}$= 5.46*	$F_{2,27}$=4.24*, (0.5)	ns
N-alkyls	$F_{1,13}$= 6.76*	$F_{2,27}$=8.93***, (0.2)	$F_{2,27}$=10.43***
O-alkyls	$F_{1,13}$= 60.38***	ns, (1.0)	$F_{2,27}$=8.52***
Phenolics	$F_{1,14}$= 13.41**	$F_{2,27}$=8.16**, (0.3)	$F_{2,27}$ = 7.46**
Alkyl to O-alkyl	ns	$F_{2,28}$=9.97***, (0.03)	ns
Aromaticity	$F_{1,13}$= 230.8**	$F_{2,27}$=10.01**, (0.9)	$F_{2,27}$ = 4.00*

Figure captions

Figure 1. Solid-state ^{13}C NMR spectra recorded as described in the text of representative samples of peat from (left) the Torneträsk area and (right) the Churchill area collected from three depths (top spectrum corresponds to upper level).

Figure 2. a) CO_2 fluxes from peat collected throughout the active layer from the surface at Torneträsk and Churchill (L1-3) incubated at field capacity at 15°C for four months (means are based on five repeat sampling events) in the laboratory in Nottingham (Site: $P > 0.05$; Layer: $F_{2,426} = 110.06$, $P < 0.001$, means, standard error of the mean (SE) and the standard error of the differences (SED) are shown, b) CH_4 fluxes measured from peat cores from L1-3 incubated at field capacity or flooded conditions at 15 ºC for four month (five repeat sampling events) (Flooding treatment: $F_{1,101} = 3.99$, $P < 0.05$; means, SE and SED are shown). Note that CO_2 and CH_4 fluxes did not vary significantly ($P > 0.05$) over time over the four months.

Figure 3. Concentration (%) of NMR derived C into different functional groups in peat cores collected from three depths (peat layers 1-3) in the Torneträsk area, Sweden and the Churchill area, Canada. a) Variation in of alkyls, N-alkyls, O-alkyls, acetals, aromatics, phenolics, and carboxyls with depth at the Torneträsk sites. b) Variation in the alkyl to O-alkyl and the aromaticity ratio with depth at the Torneträsk sites. c) Variation in alkyls, N-alkyls, O-alkyls, acetals, aromatics, phenolics, and carboxyls with depth at the at the Churchill sites. d) Variation in the alkyl to O-alkyl and the aromaticity ratio with depth at the Churchill sites. Chemical shifts for different functional groups were: aliphatics $\delta = 0 – 47$ ppm, N-alkyls $\delta = 47 – 59$ ppm, O-alkyls $\delta = 59 – 92$ ppm, acetals $\delta = 92 – 112$ ppm, aromatics $\delta = 112 – 139$

ppm, phenolics δ = 139 – 162 ppm, carboxyls δ = 162 – 220 ppm. Mean and ± SE are shown. Statistics for differences among depths and areas are shown in Table 2.

Figure 4. Relationship between mean CO_2 emissions from peat L1, L2 and L3, white, grey and dark grey circles, respectively, incubated at 15 °C, at field capacity and the dominant peat functional groups in a) Torneträsk ($F_{1,18} = 24.47$, $P < 0.001$, $\sigma^2 = 57$) and b) Churchill ($F_{1,22} = 6.70$, $P < 0.05$, $\sigma^2 = 21$). c) Relationship between activation energy (log E_a) and the phenolic content of the peat from the Torneträsk region ($F_{1,16} = 6.99$, $P < 0.05$, $\sigma^2 = 27$).

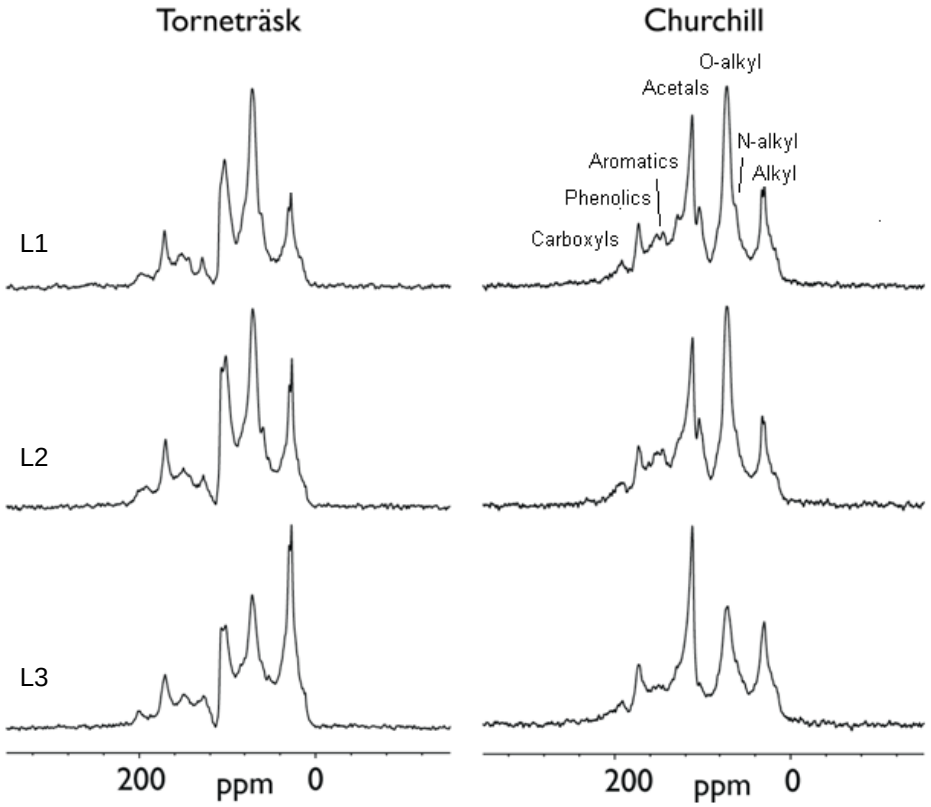
Figure 5. Microbial biomass markers determined through the active layer (L1-3) of a) total microbial biomass (Depth: $F_{2,27} = 15.54$, $P < 0.001$, Site: $F_{1,13} = 8.33$, $P < 0.05$, Depth×Site: F2,27 = 3.48, $P < 0.05$) b) fungi (Depth: $F_{2,27} = 14.36$ $P < 0.001$, Site: F1,13 = 8.11, $P < 0.05$, Depth×Site: $F_{2,27} = 3.49$, P , $P < 0.05$) c) gram negative bacteria (Depth: $F_{2,27} = 11.33$ $P <$ 0.001, Site: F1,14 = 3.66, P = 0.077, Depth×Site: P > 0.6) d) gram positive bacteria (Depth: $F_{2,28} = 0.71$, $P > 0.5$, Site: F1,14 = 2.06, P >0.1, Depth×Site: P > 0.2). Mean and SE is shown, n = 8.

Figure 6. Relationship between peat functional organic chemistry and microbial biomarkers relating to fungal and bacterial biomass at the two study areas and across the three peat depths. a) Relationship between alkyl concentrations and fungal to bacterial ratios in the peat ($F_{2,44} = 10.27$, $P < 0.001$, $\sigma^2 = 30$), b) relationship between aromatic concentrations and fungal to bacterial ratios in the peat ($F_{2,44} = 6.84$, $P < 0.001$, $\sigma^2 = 24$), c) relationship between carboxyl concentrations and bacterial biomass in the peat ($F_{1,22} = 6.70$, $P < 0.05$, $\sigma^2 = 21$) and d) relationship between phenolics concentrations and gram positive bacterial biomass in the peat ($F_{2,46} = 6.84$, $P < 0.01$, $\sigma^2 = 20$).

946 **Figures 1-6**

947

948 Figure 1



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951 Figure 2

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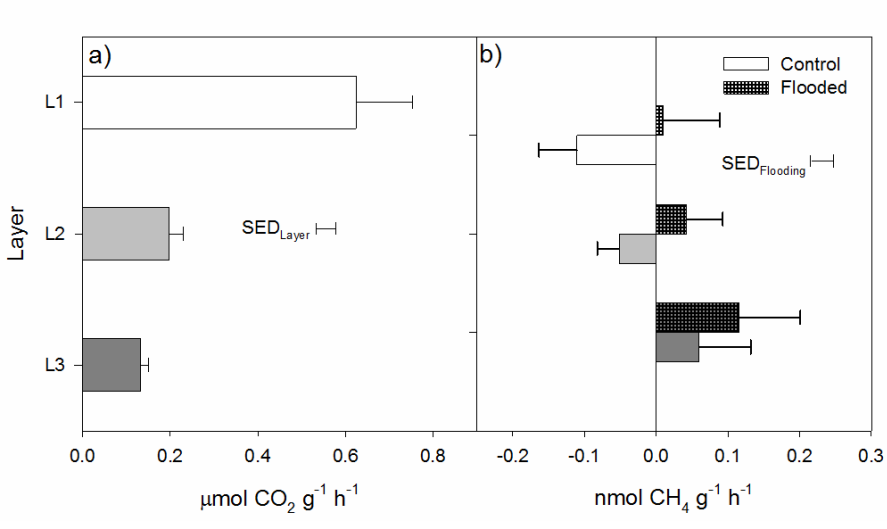

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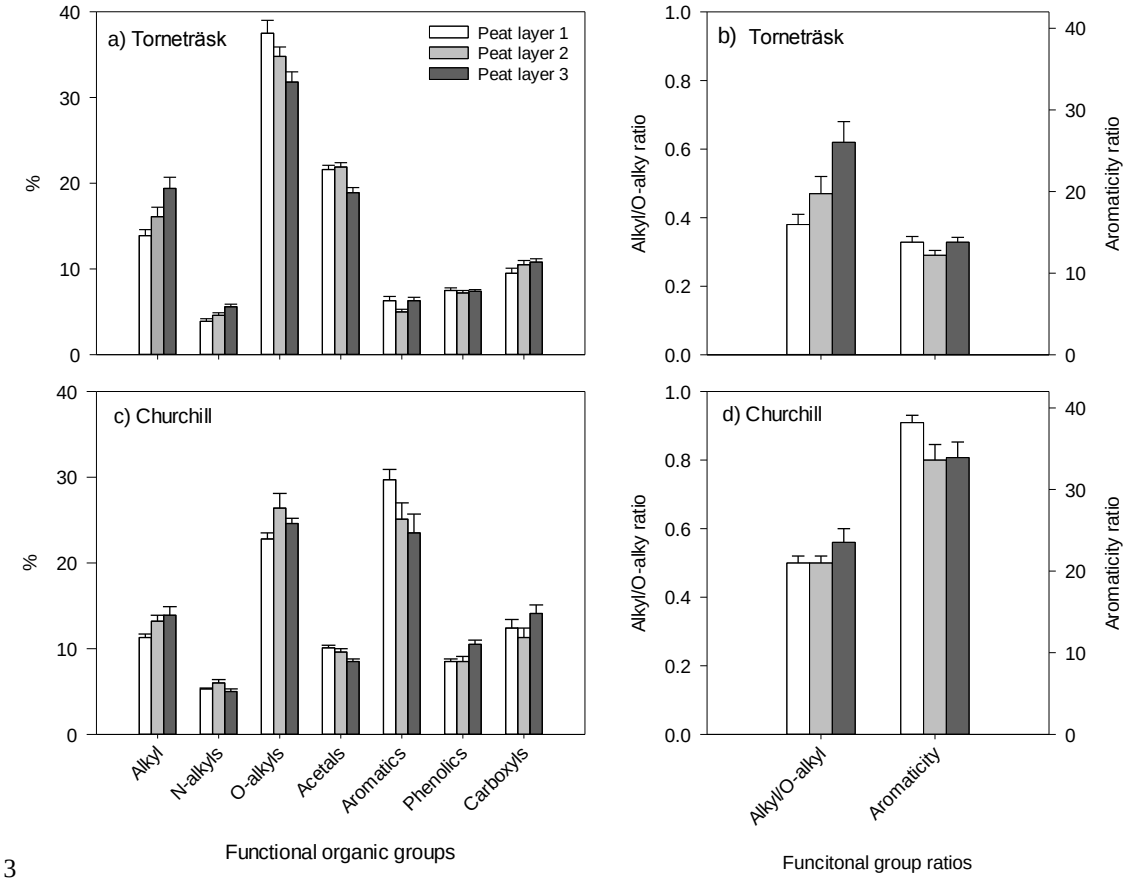

956 Figure 3

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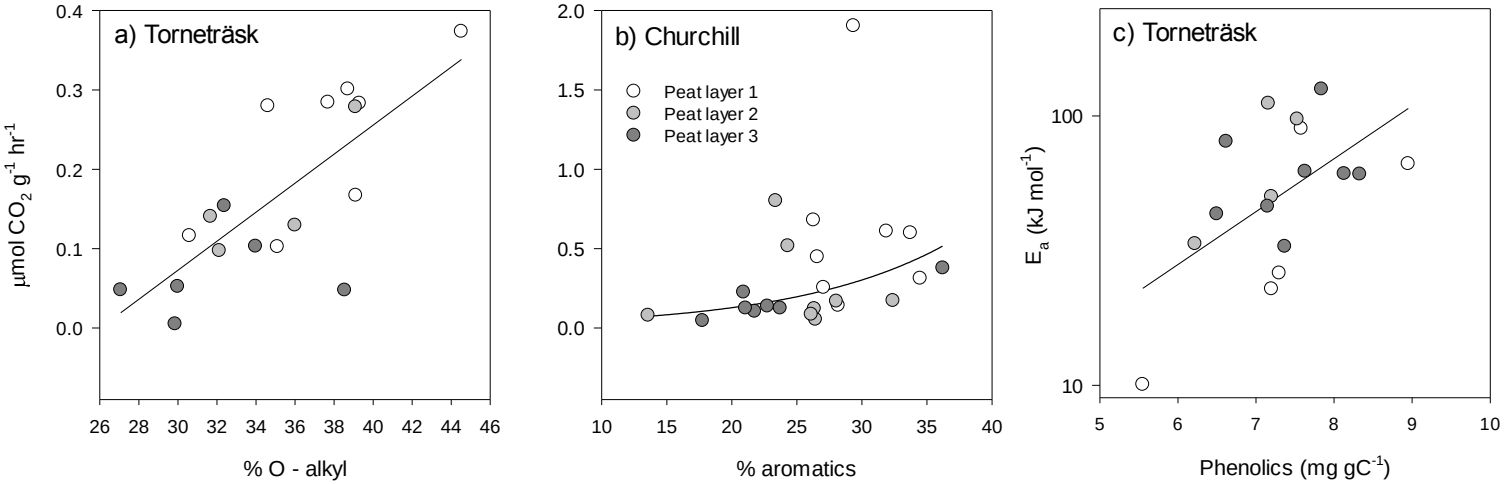
a) Torneträsk
µmol CO_2 g^{-1} hr^{-1}
% O - alkyl
b) Churchill
Peat layer 1
Peat layer 2
Peat layer 3
% aromatics
c) Torneträsk
E_a (kJ mol^{-1})
Phenolics (mg gC^{-1})

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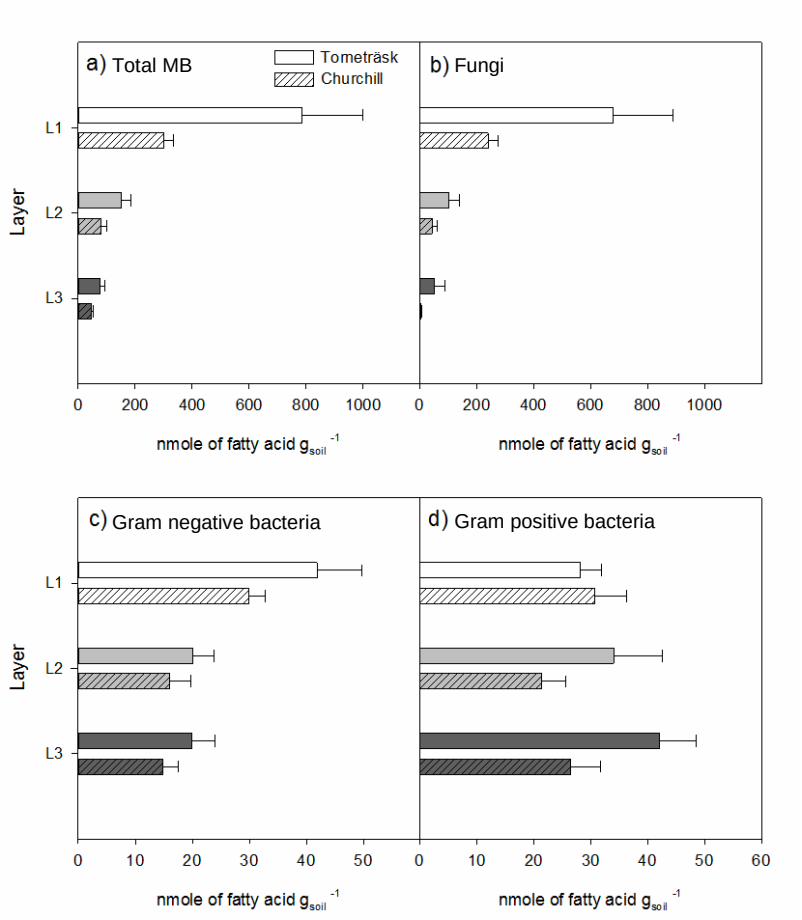
960 Figure 5



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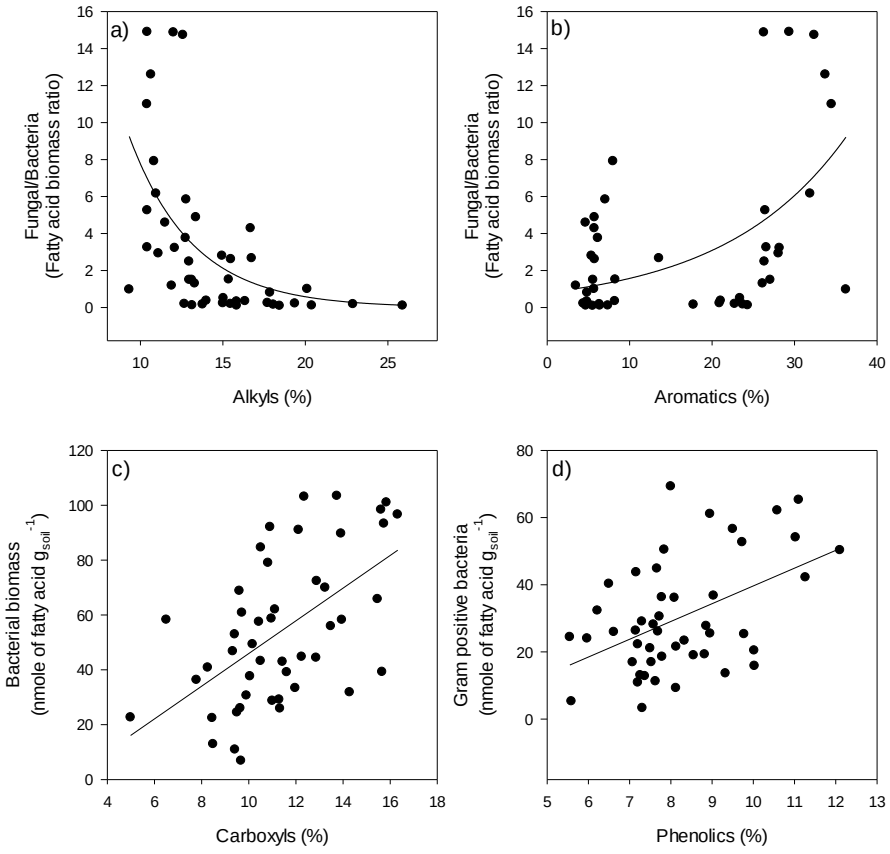
963 Figure 6



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Supplementary information 1. Dominant plant species at the Torneträsk and Churchill peatlands. Species found in wetter areas are *italicised*.

Area	Moss	Deciduous shrub	Herbaceous	Evergreen shrub	Graminoids	Lichen
Torneträsk	Sphagnum fuscum Polytricum sp. Scorpidium scorpioides Racomitrium lanuginosum *Sphagnum cuspidatum* *Sphagnum auriculatum* *Sphagnum palustre*	Betula nana *Salix lanata* *Salix phylicifolia*	Rubus chamaemorus Pinguicula vulgaris	Empetrum nigrum Ledum palustre Andromeda polifolia Vaccinium vitis-ideae Vaccinium uliginosum Vaccinium oxycoccus	*Eriophorum angustifolium* *Carex acutiformis* *Eriophorum vaginatum*	Cladonia rangiferina Cladonia coccifera Cladonia pontentosa Cladonia cervicornis
Churchill	Dicranum elongatum Sphagnum fuscum	Betula gladulosa Salix arctophila Salix lanata	Rubus chameomorus Pinguicula vulgaris Saxifraga aizodies *Potentilla palustris* Tofieldia pusilla	Empetrum nigrum Ledum decumbens Andromeda polyfolia Vaccinium vitis-ideae Rhododendron lapponica Picea glauca Arctostophalus sp.	Deschampsia flexuosa Calamagrostis sp. *Carex scirpoidea* *Carex vaginatum* *Carex capillaris*	Cladina stellaria Cladina rangifera Flavocetraria nivalis Flavocetraria cuculata Bryoria nitidula

968 Supplementary information 2. Peatland locations and peat properties

Area	Site no	Site name	Easting[a]	Northing[a]	Elevation (m absl)	Active layer depth (cm)	Layer[b]	Bulk density (g cm^{-3})	C (mg g^{-1})	N (mg g^{-1})	C:N	Moisture content (% dry weight)
Torneträsk	1	Abisko Research station	7588331	1623701	343	49.3	1	0.03	44.0	0.6	75.1	777.2
							2	0.06	46.4	1.1	43.9	594.4
							3	0.09	48.6	1.6	30.0	372.6
	2	Kursflaket (Abisko östra)	7587485	1626340	350	46.5	1	0.05	48.5	0.8	62.2	474.7
							2	0.05	47.4	1.3	36.0	495.2
							3	0.09	46.9	1.8	26.6	456.7
	3	Kärtosape (Mellanflaket)	7586903	1628129	390	51.3	1	0.06	48.9	1.3	37.8	287.6
							2	0.11	50.1	1.3	37.5	247.2
							3	0.14	41.8	1.4	29.1	227.5
	4	Storflaket	7588147	1633139	350	49.0	1	0.07	48.7	0.9	51.4	358.7
							2	0.08	46.8	1.9	24.0	390.2
							3	0.07	48.5	1.6	30.9	526.3
	5	Stordalen väst	7588147	1633139	350	50.0	1	0.03	47.6	0.6	77.2	519.8
							2	0.08	49.6	1.9	25.8	421.9
							3	0.12	46.9	2.3	20.4	350.5
	6	Stordalen IBP	7588605	1633727	354	51.9	1	0.04	47.4	0.6	82.3	449.5
							2	0.06	53.1	1.0	50.6	439.8
							3	0.08	49.2	1.9	25.9	416.5
	7	Narkervare (Torneträsk st.)	7575403	1663072	355	49.8	1	0.04	50.2	1.0	49.8	396.0
							2	0.07	49.4	1.2	42.6	426.3
							3	0.09	54.2	1.5	37.3	348.2
	8	Stenbacken	7572484	1664837	411	53.1	1	0.06	47.4	0.8	62.4	385.4

							2	0.06	48.0	1.3	36.8	449.5
							3	0.09	49.5	1.8	28.1	356.9
Churchill	1	PPD	15V 0453504	UTM 6510605	15.9	37.3	1	0.07	44.2	1.2	35.4	275.3
							2	0.11	44.0	1.6	27.7	286.1
							3	0.13	33.0	3.6	9.2	226.7
	2		15V 0451568	UTM 6510026	15.9	25.3	1	0.06	40.0	1.0	39.2	387.0
							2	0.09	42.5	1.2	35.2	401.0
							*	*	*	*	*	*
	3		15V 0451423	UTM 6509167	20.1	31.0	1	0.05	40.4	0.7	58.1	479.9
							2	0.09	40.1	1.9	21.0	509.8
							3	0.08	40.8	2.5	16.5	453.3
	4		15V 0451423	UTM 6509167	20.1	30.2	1	0.06	43.2	1.3	34.1	284.3
							2	0.08	40.5	2.0	20.0	380.8
							3	0.08	40.3	2.0	20.4	396.6
	6		15V 0451283	UTM 6508919	22	30.0	1	0.06	40.4	0.7	58.6	325.8
							2	0.10	43.0	1.0	42.8	324.3
							3	0.08	41.9	2.2	18.9	390.8
	8		15V 0452519	UTM 6499496	33	29.3	1	0.02	38.3	0.4	99.7	1079.1
							2	0.04	36.8	0.3	128.8	1121.2
							3	0.03	39.2	0.4	107.9	1113.9
	9		15V 0452544	UTM 6499323	33.3	29.7	1	0.04	41.4	1.1	38.8	350.7
							2	0.07	43.0	1.0	42.8	393.7
							3	0.10	31.5	1.4	22.9	223.5
	10	Twin lakes	15V 0451736	UTM 6498165	35.4	37.3	1	0.06	40.6	0.6	70.0	413.1
							2	0.06	30.6	0.6	52.3	485.3

	3	0.11	40.9	1.3	32.2	410.2

969 [a]The coordinates for the Torneträsk site are in RT 90 (Swedish grid), while the coordinates for the Churchill sites are in UTM

970 [b]The peat layers are 1) surface peat, 2) half way through the active layer, 3) just above the permafrost table.

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Supplementary information 3.

CO_2 and CH_4 flux measurement in the field

At each peatland *in situ* gas exchange of CO_2 in three subplots ca. 4 m apart was measured on three separate days over a two week period in July 2008 and Aug 2009, in Torneträsk and Churchill, respectively. CO_2 fluxes were measured over 10 minutes using an EGM-4 Infra Red Gas Analyzer with a 30 cm diameter cuvette (PP Systems, Hitchin, UK - see Sjögersten et al. (2010) for details) between 10:00 and 17:00. At a subset of peatlands (n =3) in Churchill we recorded CO_2 measurement over one 24 h period collecting reading each hour. Methane fluxes from each plot were estimated in parallel with CO_2 measurements (i.e. sampling on three separate days from each peatland in between 10:00 and 17:00) using the closed chamber technique with four samples taken at 15 minute intervals and injected into evacuated glass vials for later analysis of CH_4 in the lab using a Gas Chromatograph (GC) (Sjögersten et al., 2011). Positive values of CO_2 and CH_4 fluxes represent an efflux to the atmosphere.

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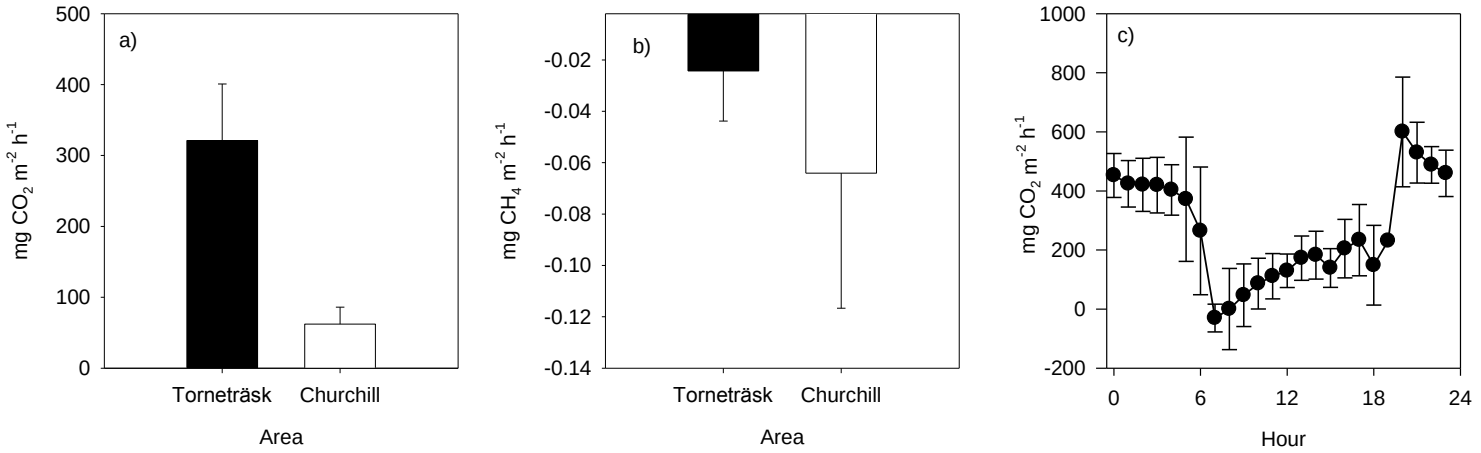
Supplementary information 4



Supplementary information 4. a) CO_2 and (b) CH_4 fluxes *in situ* at Torneträsk and Churchill, respectively. Mean and SE are shown, each data point is based on three sub samples per site, n = 8, collected at three occasions in July and August, at Torneträsk and Churchill, respectively. Additionally diurnal variation in CO_2 fluxes c) were recorded at three sites in August in Churchill. CO_2 fluxes (a) differed between Torneträsk and Churchill, $F_{1,38} = 15.16$, $P < 0.001$) but not for the CH_4 fluxes (b) $F_{1,28} = 0.58$, $P < 0.4$).

997 Supplementary information 5

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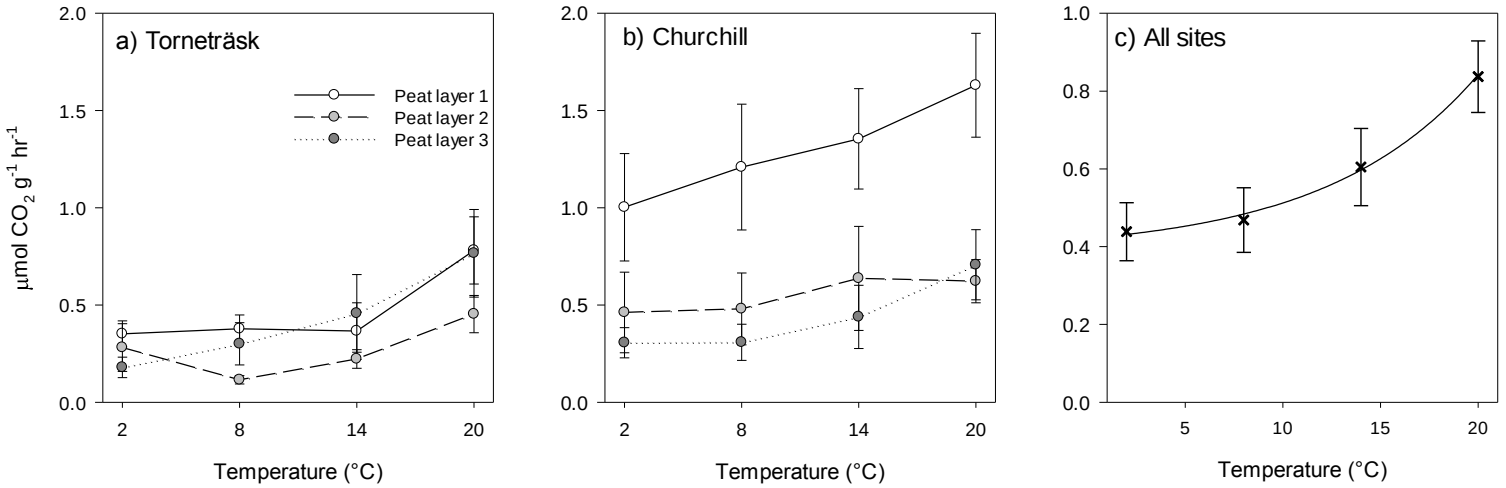

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1001 Supplementary information 5. Temperature response curves of optimised peat from three layers (L1-3) in the active layer in a) Torneträsk and b)

1002 Churchill (means ± SE are shown, n = 8; overall temperature effect for all layers: $F_{3,159} = 6.02$, $P < 0.001$; difference between areas: $F_{1,14} = 7.00$,

1003 $P < 0.05$), c) modelled overall relationship between temperature and CO_2 release ($CO_2 = 0.386+0.035\times(1.137^{T})$; $F_{2,179}= 6.68$ $P < 0.01$) for all

1004 sites (i.e. both Churchill and Torneträsk) and peat depth combined.

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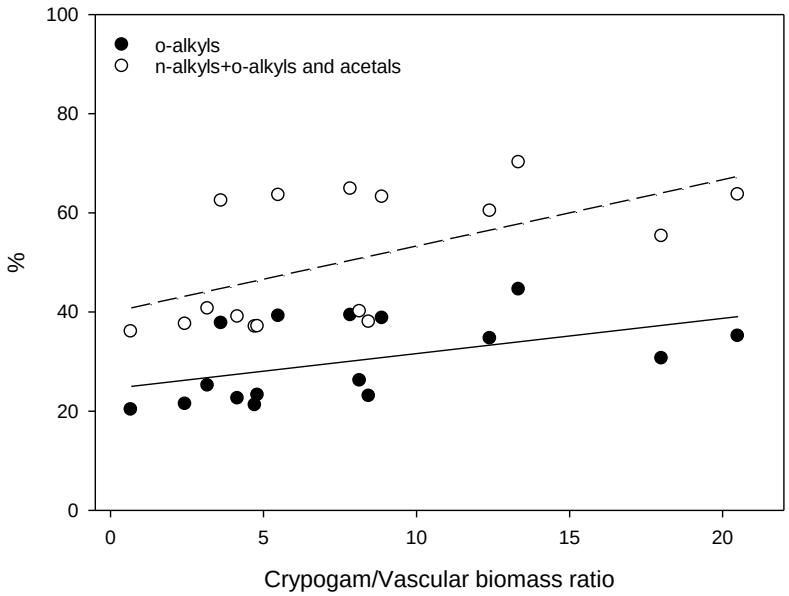

Supplementary information 6. Relationships between the crypogam/vascular biomass ratio and concentration of o-alkyls (%) and combined carbohydrate type compounds (n-alkyls+o-alkyls and acetals). Statistics are reported in the result section.

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