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Publication Date

2022-05-01

DOI

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Peer reviewed

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19 **Abstract.** Peatlands are climate critical carbon (C) reservoirs that could become a C source under
20 continued warming. A strong relationship between plant tissue chemistry and the soil organic matter
21 (SOM) that fuels C gas emissions is inferred, but rarely examined at the molecular level. Here we
22 compared Fourier transform infrared (FT-IR) spectroscopy measurements of solid phase functionalities
23 in plants and SOM to ultra-high-resolution mass spectrometric analyses of plant and SOM water extracts
24 across a palsa-bog-fen thaw and moisture gradient in an Arctic peatland. From these analyses we
25 calculated the C oxidation state (NOSC), a measure which can be used to assess organic matter quality.
26 Palsa plant extracts had the highest NOSC, indicating high quality, whereas extracts of *Sphagnum*, which
27 dominated the bog, had the lowest NOSC. The percentage of plant compounds that are less bioavailable
28 and accumulate in the peat, increases from palsa (25%) to fen (41%) to bog (47 %), reflecting the pattern
29 of percent *Sphagnum* cover. The pattern of NOSC in the plant extracts was consistent with the high
30 number of consumed compounds in the palsa and low number of consumed compounds in the bog.
31 However, in the FT-IR analysis of the solid phase bog peat, carbohydrate content was high implying high
32 quality SOM. We explain this discrepancy as the result of low solubilization of bog SOM facilitated by the
33 low pH in the bog which makes the solid phase carbohydrates less available to microbial decomposition.
34 Plant-associated condensed aromatics, tannins, and lignin-like compounds declined in the unsaturated
35 palsa peat indicating decomposition, but lignin-like compounds accumulated in the bog and fen peat
36 where decomposition was presumably inhibited by the anaerobic conditions. A molecular-level
37 comparison of the aboveground C sources and peat SOM demonstrates that climate-associated
38 vegetation shifts in peatlands are important controls on the mechanisms underlying changing C gas
39 emissions.

Introduction

Climate-change induced warming, especially in the Arctic, will provoke a series of responses including changes to the community of plants and microorganisms as well as the physiology of each member, which culminate in the whole ecosystem response (Wardle et al., 2004). These interactions are complex and their interpretation is, in turn, complicated by the extreme complexity of the soil organic matter (SOM) that acts as the repository of plant derived substrates, inhibitory compounds, and microbially derived metabolic products. Understanding such interactions is critical because interactions between plants and the microbial community have a strong effect on the net release of the microbial respiration products CO_2 and CH_4 (Sutton-Grier and Megonigal 2011).

Peatlands are a globally significant carbon (C) reservoir estimated at 530 ± 160 Pg (Hugelius et al., 2020) up to 1055 Pg (Nichols and Peteet 2019), representing 35-70% of planetary soil organic carbon (Lal 2010). Much of the high-latitude peatland C (277-800 Pg) is currently protected from decomposition as peatland permafrost (Tarnocai et al., 2009; Hugelius et al., 2014). Due to climate change, northern high latitudes are warming two to three times faster than the global average (Rintoul et al., 2018), which is causing permafrost to thaw (Christensen, 2014). Once thawed, the soil organic C is susceptible to microbial decomposition into the potent greenhouse gases (GHG) carbon dioxide (CO_2) and, under water-logged anaerobic conditions, methane (CH_4) (Schaedel et al., 2016; Chang et al., 2021). Many peatlands are active C sinks (Turetsky et al., 2007; Jones et al., 2013) or near-C neutral (Zoltai 1993, Euskirchen et al., 2012). The source or sink potential of a peatland depends on the balance between net C uptake by primary production and C loss via heterotrophic respiration, both of which can be affected by climate change. C uptake increases under a longer growing season (Natali et al., 2012), warming, drying (e.g., Malhotra et al., 2020) and changing plant community structure (e.g., Norby et al., 2019). C release via microbial respiration can be impacted by soil moisture (Blanc-Betes et al., 2016; Natali et al., 2015; Elberling et al., 2013), temperature (Hicks-Pries et al., 2013), pH differences, and active layer depth (O'Donnell et al., 2011), as well as shifts in the quantity and quality of available organic matter (Treat et al., 2014; Hough et al., *in press*). Primary producers initially fix C and supply that C to the subsurface where it can be reworked by subsurface microorganisms. As the ultimate source of organic inputs to the peat, plants exert a strong control on SOM quantity and quality (Sutton-Grier and Megonigal 2011) which we hypothesize controls GHG production rates and their variation across thaw habitat types. Connecting the quality of aboveground C sources to differences in peat SOM is an essential step in testing the hypothesis that climate-associated vegetation shifts in peatlands influence changing C gas emissions.

Four major vegetation types dominate in high-latitude peatlands: bryophytes (mosses), graminoids (sedges), shrubs, and trees (Clymo 1987; Rodwell 1991). Whereas warmer temperatures accelerate C loss from peat (Hopple et al., 2020; Hanson et al., 2020), this loss is greater when graminoids and shrubs dominate rather than *Sphagnum* mosses (Walker et al., 2016). *Sphagnum* is thought to suppress decomposition rates and thus GHG production by supplying poor-quality SOM (van Breeman 1995; Turetsky 2003), by microbial inhibition via acidification of the environment (Spearing 1972), and by production of inhibitory phenolic compounds (Rudolph and Samland 1985; Williams et al, 1998) and antimicrobial acids and sugar derivatives (Fudyma et al., 2019). Thus, environmental changes causing *Sphagnum* declines and increasing dominance by shrubs or sedges (e.g. McPartland et al., 2020; Norby et al., 2019; Walker et al., 2016; Johannson et al., 2006) is likely to result in more reactive and bioavailable SOM (Chanton et al., 2008; Tfaily et al., 2013; Wilson et al., 2021a). However, compounds

2

85   associated with some shrubs may also inhibit SOM degradation (Wang et al., 2021; 2015). Sedges, such
86   as *Carex* and *Eriophorum*, have been correlated with higher CH_4 production (Hines et al., 2008) and
87   greater SOM reactivity (Chanton et al., 2008), thought to occur because sedges contain more
88   bioavailable N and a higher proportion of labile compounds compared to *Sphagnum* (AminiTabrizi et al.,
89   2020; Hodgkins et al., 2014, 2016). Graminoids also contain aerenchyma which are capable of
90   transporting O_2 to the rhizosphere, potentially enhancing decomposition. In contrast, *Sphagnum* lacks
91   such tissues, thus *Sphagnum*-dominated habitats generally have lower O_2 availability providing a further
92   thermodynamic constraint on SOM degradation in *Sphagnum*-dominated habitats.

93   Here, we investigate how permafrost thaw-driven changes in the quality of plant-derived
94   organic matter influence SOM properties and thereby microbial decomposition. In this study, we analyze
95   fresh plant material and peat collected from three habitat types across a thawing permafrost mire using
96   the complementary techniques of Fourier Transform Infrared Spectroscopy (FT-IR) of solid phase
97   material and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS) of water
98   extracts. We hypothesize that (1) the quality of plant organic matter inputs will vary according to
99   changes in vegetation type across the three habitats, (2) different plant compounds accumulate as peat
100   in each habitat type resulting in differences in the bioavailability of organic matter for microbial
101   decomposition, and that, therefore, (3) the pathways by which plant-derived compounds are
102   decomposed differ across habitat types. Our assessments of organic matter quality will be used to
103   determine how different plant types contribute to changes in SOM quality and drive GHG production
104   rates across the thaw gradient. This information could be used to infer peatland-atmosphere feedback
105   resulting from climate-driven shifts in plant community composition.

106   **Methods**

107   *Site Description*

108   Stordalen Mire (68.35°N, 19.05°E) is located in northern Sweden just north of the Arctic circle
109   within the region of discontinuous permafrost. Climate change has accelerated thawing in the recent
110   few decades leading to changes in hydrology and vegetation cover which have resulted in a patterned
111   mosaic of habitat types within the mire (Johansson et al., 2006; Kokfelt et al., 2009); we focus here on
112   the three dominant habitat types at the site: palsas, bogs, and fens. Some areas of the mire are still
113   underlain by intact permafrost and elevated above the surroundings into relatively dry palsa plateaus.
114   Warming has caused thawing of the permafrost in some areas causing, e.g., palsas to collapse and flood,
115   producing wetter collapse features (Johansson et al., 2006). *Sphagnum* can infiltrate such pools,
116   eventually elevating the surface enough to form a bog, or in some cases, the insulating effects of the
117   *Sphagnum* are sufficient to allow the permafrost to refreeze. Alternatively, palsa can thaw completely
118   and subside to the level of the surrounding water table, causing flooding and creating a fully-inundated
119   fen. Fens are characterized by sedges and other aquatic vegetation (Zoltai 1993; Vitt et al., 1994;
120   Jorgenson et al., 2001; Malmer et al., 2005), high CO_2 uptake, and the highest CH_4 emissions of the three
121   habitat types (Hodgkins et al., 2014; McCalley et al., 2014). A bog, dominated by *Sphagnum*, can develop
122   if the thawing permafrost collapses but remains above the local water table.

123   In addition to the hydrological differences, plant communities also change across this gradient
124   of habitat types, from tundra-type vegetation dominated by shrubs, mosses, lichens, and small sedges in
125   the dry palsa; to *Sphagnum* and small sedges in the bog; to tall sedges with some *Sphagnum* in the fen
126   (Malmer et al., 2005). These differing plant communities likely contribute to differing SOM quality

127 (Chanton et al., 2008; AminiTabrizi et al., 2020; Hodgkins et al., 2014, 2016; Tfaily et al., 2013), leading to
128 much higher overall CH_4 and CO_2 emission rates from fens as compared to bogs (Hodgkins et al., 2014)
129 and the even-drier palsas (McCalley et al., 2014). Since the 1970's, the areal coverage of *Sphagnum*
130 across the mire has declined significantly (Malmer et al., 2005), giving way to increased sedge cover as
131 wetter conditions across the mire have increased the areal coverage of fen habitats (Kokfelt et al., 2009;
132 Bäckstrand et al., 2010). This gradient in habitats across the mire creates a unique opportunity to
133 explore changes in SOM quality with habitat transition within the context of changing greenhouse gas
134 production rates.

135

136 *Plant Collection*

137   To explore differences in plant organic matter inputs across the three habitat types, samples of
138 the characteristic species from each habitat (Malmer 2005) were collected. Water extracts from the
139 whole plants and tissue types (leaves, stems, roots) were used to compare organic matter inputs
140 composition across the different plant types. Plant-associated compounds were then compared to the
141 peat from each habitat to understand what compounds were easily decomposed (i.e., which compounds
142 stimulated microbial activity) versus those compounds that were less bioavailable and that tended to
143 accumulate in the peat. Plants were collected during the peak of the growing season (early August) in
144 2014 resulting in the following samples for each habitat: palsa – *Rubus chamaemorus, Betula nana,*
145 *Empetrum nigrum, Andromeda polifolia, Dicranum elongatum, Eriophorum vaginatum,* fruticose lichen
146 of unknown species; bog – *Sphagnum magellanicum.*; fen – *Eriophorum angustifolium, Carex rostrata*.
147 Whole plant samples were collected and separated by tissue type (roots, stems, and leaves), then
148 immediately flash-frozen in liquid N_2 and kept frozen at -20°C until processing in February 2015. Since
149 mosses do not have root, stem, and leaf differentiation, they were not separated and were processed as
150 whole plants. Additional plant samples for FT-IR analysis were collected in August 2015 and included
151 *Sphagnum fuscum, S. magellanicum, E. nigrum, A. polifolia,* and an unknown species of lichen. These
152 samples were similarly flash frozen in the field in liquid N_2 and then kept at -20°C until analysis.

153 *Soil Organic Matter Collection*

154   Peat was collected from the same three habitats along the thaw gradient where plants were
155 collected, using a Wardenaar corer (Eijkelkamp, Raleigh, NC USA). The cores were sectioned by depth
156 and the 1-5 cm section from each core was placed in a Teflon coated vial, and frozen at -20°C before
157 analysis. On returning to the lab, visible roots were removed and the remaining peat samples were
158 freeze dried and ground to a homogenous powder using a SPEX SamplePrep 5100 Mixer/Mill ball
159 grinder. Although smaller fine roots were likely present in the surface peat, they make up a small
160 fraction of the overall mass of the sample. Porewater was also collected from the site using a perforated
161 stainless-steel tube inserted into the peat to the desired depth. Gentle suction was applied using a gas
162 tight syringe fitted to the tube using a three-way valve. Once 30 mL of porewater was obtained, it was
163 placed in a polycarbonate sample vial and frozen at -20°C prior to analysis. An additional 30 mL of
164 porewater was collected in three locations within 1 m of the core for replicate pH analysis immediately
165 in the field. Porewater samples were collected from the shallowest depth it was possible to draw
166 porewater: 10-14 cm in the bog and 1-5 cm in the fen. We used the solid peat to compare the
167 compounds present in the palsa, where the conditions are not water saturated and no porewater could
168 be collected, to the other sites where water saturation has already effectively extracted dissolved

169 compounds from the peat. The dissolved organic carbon (DOC) and nitrogen (N) concentration of
170 porewater samples, reported as mmol-C L^{-1} were measured simultaneously by high-temperature
171 catalytic oxidation using a Shimadzu Total Organic Carbon analyzer equipped with a non-dispersive
172 infrared detector and a Total Nitrogen Measuring unit. Triplicate measurements were done for each
173 sample, and the coefficient of variance was always <2%.

174 *Fourier Transform Infrared Spectroscopy (FT-IR)*

175 To examine the bulk chemical characteristics of the plants and solid peat, the dried and ground
176 material were analyzed by Fourier Transform Infrared Spectroscopy (FT-IR). For FT-IR, only stems and
177 leaves from each plant were available for analysis (no roots). Recent advances in FT-IR analysis allow us
178 to quantitatively evaluate differences in carbohydrates and aromatic compounds among samples
179 (Hodgkins et al., 2018). FTIR spectra were collected using a PerkinElmer Spectrum 100 FTIR
180 spectrometer fitted with a CsI beam splitter and a deuterated triglycine sulfate detector. Transmission-
181 like spectra were obtained using a Universal ATR accessory with a zinc selenide/diamond composite
182 single-reflectance system. Each sample was placed directly on the ATR crystal, and force was applied so
183 that the sample came into good contact with the crystal. Spectra were acquired in % transmittance
184 mode between 4000 and 650 cm^{-1} (wavenumber) at a resolution of 4 cm^{-1}, and four scans were
185 averaged for each spectrum. The standard deviations of carbohydrate and aromatic carbon values were
186 within 5% of the mean values when 4 replicate samples were run and scanned four times. That is, if a
187 sample was found to be 30% carbohydrate, the analytical error on 4 aliquots that were each scanned 4
188 times was 1.5%. Spectra were ATR-corrected, baseline-corrected, and then converted to absorbance
189 mode using the instrument software. Area-normalized and baseline-corrected peak heights for common
190 classes of compounds observed in SOM were calculated using the methods and script described by
191 Hodgkins et al., (2018), expanded to include peak assignments by Palozzi and Lindo (2017). Briefly, the
192 baseline before and after each peak (corresponding to a known functional group) is determined by
193 finding the local minimum of the spectrum within the expected region of each endpoint. A linear
194 regression between the two identified end-points then represents the local baseline for the desired
195 peak. This baseline is subtracted from the peak height and the resulting baseline-corrected absorbances
196 are calculated. Peak locations are then defined as the maximum of the base-line corrected absorbance
197 within the identified region. The height of the peak location is divided by the total integrated area of
198 the entire spectrum to yield a normalized peak height. Using a variety of materials, Hodgkins et al.,
199 (2018) showed a strong correlation between these normalized peak heights and the percent of
200 compound classes comprising each sample measured using more laborious wet chemistry techniques.

201 *Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS)*

202 We used Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS) to gain a
203 higher resolution view of the compounds present in the palsa peat, peat porewater from the bog and
204 fen, and the plant samples. Plant samples were thawed and each tissue type (roots, stems, and leaves
205 when available), in addition to whole plant samples for mosses, which lack leaf/stem/root
206 differentiation, were analyzed after water extraction in which 0.5 g of undried plant material was shaken
207 in 4 mL nanopure water and then allowed to sit for 2 hours, and the supernatant decanted. The
208 resulting extracts were mixed 1:2 with HPLC-grade methanol and immediately direct-injected into a 12 T
209 Bruker ESI-FTICR-MS spectrometer operating in negative mode. Solid peat samples (from the 1-5cm
210 deep section at each site) were analyzed after water-extracting the dried and ground peat samples. For

211   this method, 0.5 g of the dried and ground peat, which is expected to yield 25 mg C, was added to 1 mL
212   of degassed deionized water and then placed on a shaker for 2 hours. The solutions were then
213   centrifuged to form a pellet and the supernatant was decanted. The supernatant and porewater
214   samples were then each mixed 1:2 (by volume) with HPLC grade methanol, and the resulting solutions
215   were injected through direct injection onto a 12 T Bruker ESI-FTICR-MS spectrometer operating in
216   negative mode. To adjust for variations in carbon concentration among samples, the ion accumulation
217   time for each sample is adjusted, typically from 0.1 to 0.3 s (Tfaily et al., 2019). For each sample, ninety-
218   six individual scans were averaged and then internally calibrated using organic matter homologous
219   series separated by 14 Da (i.e., CH_2 groups). The mass measurement accuracy was <1 ppm for singly
220   charged ions across a broad m/z range (i.e., 200 < m/z < 1200). Chemical formula assignments were
221   made using an in-house built software program following the Compound Identification Algorithm,
222   described by Kujawinski and Behn (2006) and modified by Minor et al., (2008) and based on the
223   following 'Golden Rules' criteria: signal/noise > 7, and mass measurement error < 1 ppm, taking into
224   consideration the presence of C, H, O, N, S and P and excluding other elements. All observed ions in the
225   spectra were singly charged based on identification of 1.0034 Da spacing found between carbon
226   isotopologues of the same molecule (e.g., between $^{12}C_n$ and $^{12}C_{n-1}$–$^{13}C_1$). Two technical replicates were
227   collected for most samples and, when available, peaks present in either (or both) spectra were
228   combined and the signal intensities were averaged for downstream analysis.

229   Complex organic matter such as both the plant extracts and the peat are expected to result in
230   thousands, if not tens of thousands, of unique compounds by FTICR-MS. A number of approaches exist
231   to aid in visualizing such complex datasets. These include the use of van Krevelen diagrams that depict
232   the H/C vs. O/C ratios of individual compounds, which enables tentative inferences about general
233   compounds classes. For example, lipids are generally low O/C with high H/C, Whereas carbohydrates
234   generally fall in the region near O/C = 1 and H/C = 2. In addition, the molecular formulae derived from
235   FTICR-MS analyses can be used to calculate the nominal oxidation state of the carbon (NOSC) in
236   individual compounds observed in the DOM. This is done through a simple calculation from the
237   molecular formula NOSC = 4 − (4C + H − 3N − 2O + 5P − 2S)/C (Keiluweit et al., 2016), but provides
238   tremendous insight into the thermodynamic energy yield on oxidation of that C (La Rowe and van
239   Cappellin 2011), which is directly relevant to understanding organic matter quality which is a measure of
240   the ability of microorganisms to degrade that organic matter under the environmental conditions
241   (Wilson and Tfaily 2018). Average NOSC for each plant sample was calculated and then analysis of
242   variance (ANOVA) was used to assess whether the mean NOSC of plant species were different. To
243   compare plants across habitats and account for differences in biomass coverage of the different species
244   across the habitats we created a series of composite plant samples for each habitat. These composites
245   were created by first multiplying the signal intensity of each peak in a plant sample by the total signal
246   intensity of each spectrum to get the relative signal intensity for each mass (%SI). We then multiplied
247   that result by the proportional biomass coverage of that plant in the given habitat. Then we summed
248   one replicate from each plant species across all species present to create one composite plant sample.
249   This was done repeatedly until all combinations of replicates were used and we had generated a number
250   of plant composites for each habitat that could be used in downstream comparisons to changes in the
251   peat composition.

252 *Chemical transformation Analysis*

253   Chemical transformation analysis of the chemical compounds identified by FTICR-MS involves
254 calculating the mass differences between individual compounds and matching those mass differences to
255 specific chemical moieties. By matching these results with known biochemical transformations
256 accomplished by microorganisms in the environment, it is possible to infer the decomposition pathways
257 by which individual compounds are degraded and produced (e.g., Stenson et al., 2003; Kujawinski et al.,
258 2016; Wilson et al., 2017). This process is possible because of the extremely high mass resolution of the
259 FTICR-MS technique which allows us to narrow down the possible matches within 1 ppm. The current
260 database of microbial transforms contains 186 unique transforms (Wilson et al., 2017), including
261 hydroxylation, methoxylation, and transamination reactions.

262

263 **Results**

264 The pH for the porewater at the bog surface averaged 4.2 ± 0.2. In the fen, the porewater pH at the
265 surface averaged 5.6 ± 0.4. The DOC and DON concentrations in the bog (surface 5 cm) was 4.1 ± 1.2
266 mmol C L^{-1} and 0.1 ± 0.01 mmol C L^{-1} respectively. The DOC and DON in the fen were 0.1 ± 0.1 mmol C L^{-1}
267 ^{1} and 0.03 ± 0.01 mmol C L^{-1} respectively. No porewater was available in the surface palsa for collection.

268

269 *FT-IR*

270   The leaf and stem FT-IR spectra were quite similar for both vascular plants (*E. nigrum, A.*
271 *polifolia*) in the palsa habitat, with the exception that *A. polifolia* leaves had lower carbohydrate content
272 and *E. nigrum* leaves had lower carboxylic acid content and aliphatic waxes compared to stems from the
273 same plant (Supplemental Table 1). Because of the similarity between leaf and stem spectra for each
274 plant and because of expected higher turnover of leaves compared with stems, we compared the FT-IR
275 spectra from the leaves of the dominant plants to the peat in each habitat type (Figure 1).

276   In the FT-IR spectra of the peat from the different habitats (Figure 1) several absorption bands
277 typical of humic materials were observed in our samples (Artz et al., 2008; Chapman et al., 2001; Leifeld
278 et al., 2012). High peak intensities were observed at wavenumbers corresponding to carbohydrates (i.e.,
279 O-alkyls at 1030 cm^{-1}); C-O stretch of phenols consistent with lignin (1265 cm^{-1}); humic acids (1426 cm^{-1});
280 phenolic lignin-like structures (1515 cm^{-1}); protein-like (1550 cm^{-1}); aromatics (1650 cm^{-1}); C=O
281 stretching associated with carboxylic acids, aldehydes ketones and other oxygenated moieties (1720 cm^{-1}
282 ^{1}); and aliphatic fats (2920 cm^{-1} and 2850 cm^{-1})(Supplemental Table 1).
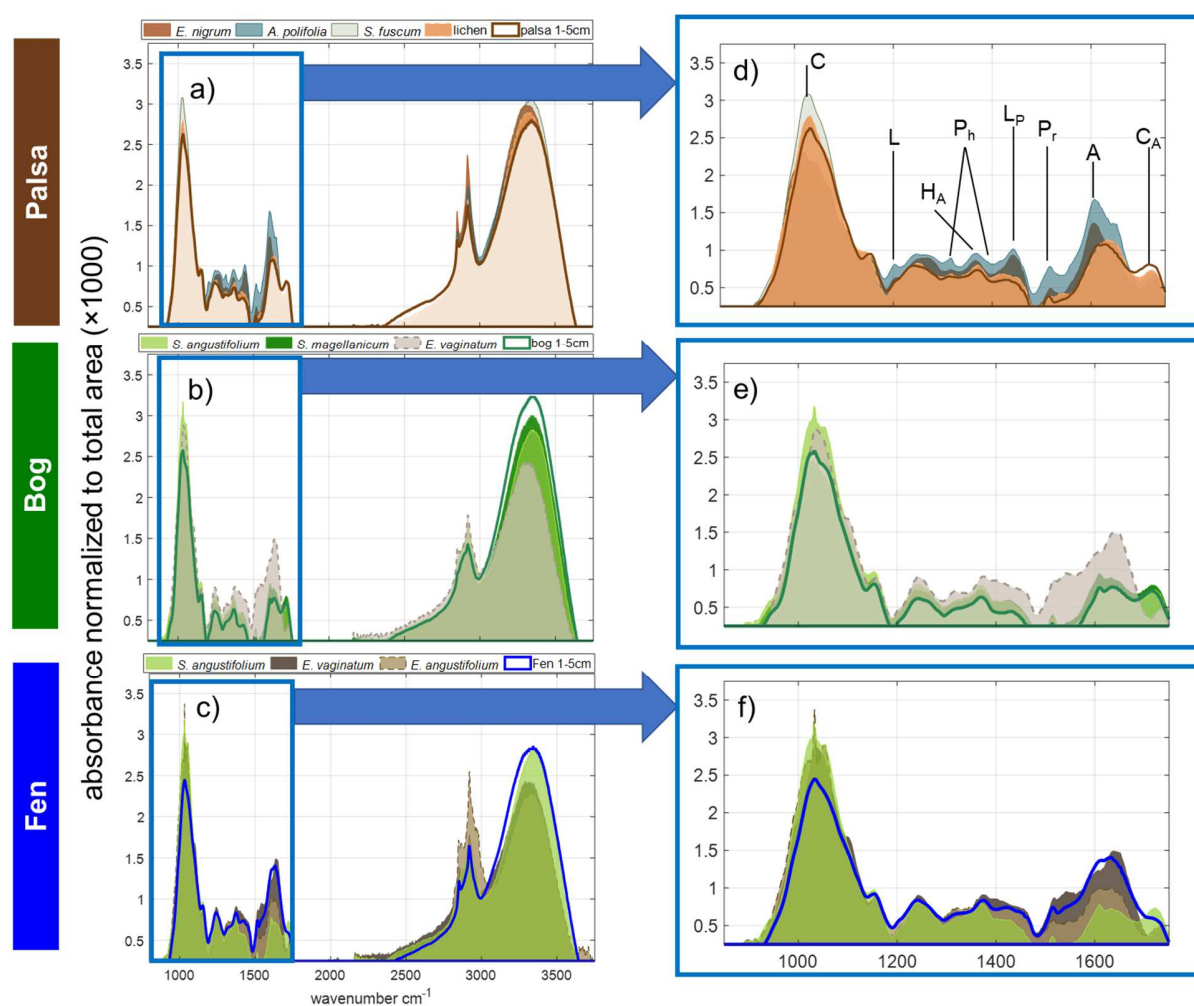
Figure 1: Layered FT-IR spectra comparing the average spectra for dominant plants and peat in each habitat. All spectra are baseline-corrected and normalized to total peak area as described in Hodgkins et al., (2018). Panel (a) shows the overlaid spectra for the 1.5 cm palsa peat and lichens, A. *polifolia, E. nigrum,* and *S. fuscum*, the dominant plant types in the palsa. Panel (b) shows the overlaid spectra for the bog 1-5cm peat and bog's dominant plants *S. angustifolium*, *S. magellanicum*, and *E. vaginatum*. Panel (c) shows the fen 1-5cm with the fen's dominant plants, *E. angustifolium, E. vaginatum,* and *S. angustifolium.* Panels d-f enlarge the 850-1750 cm^{-1} region for the palsa, bog, and fen spectra (respectively) where many chemical functional groups exist within a short span of wavenumbers. In panel (d), important peaks discussed in the text are marked: C = carbohydrates, L = lignin-like, H_A = humic acids, P_h = phenolic-lignin, L_P = lignin-like, P_r = proteinaceous, A = aromatics, C_A = carboxylic acids.

The bog peat had a high carbohydrate peak compared to the other sites (Supplemental Figure 1). The fen peat had a higher abundance of aromatic and protein-like structures and a lower abundance of carboxylic acids compared to the other sites (Supplemental Figure 1). Aliphatics (2920 cm^{-1} and 2850 cm^{-1}) were much less well defined in the bog peat compared to the other sites (Figure 1b), indicating fewer waxy lipids (Artz et al. 2008; Cocozza et al. 2003) compared to the other sites.

300   The overall spectra for peat were similar to the dominant plants in the particular habitat. For
301   example, palsa peat was overall most similar to lichen (Figure 1a,d), bog peat was overall most similar to
302   *Sphagnum* (Figure 1b,e), and fen peat was most similar to the *Eriophorum* species (Figure 1c,f).
303   Nevertheless, there were some differences. In the palsa, the carbohydrate content of the palsa peat was
304   lower than the S. fuscum and lichens, but higher than that in *E. nigrum*. The waxy lipids, peaks 2850 cm^{-1}
305   and 2920 cm^{-1}, were extremely well differentiated in the leaves of *E*. *nigrum* and *A*. *polifolia* compared
306   to the leaves of *S. fuscum* and lichens (Figure 1a). *A. polifolia* and *E. nigrum*, the two vascular plants, had
307   higher aromatic, protein and lignin-like content relative to the other plant species in the palsa (Figure
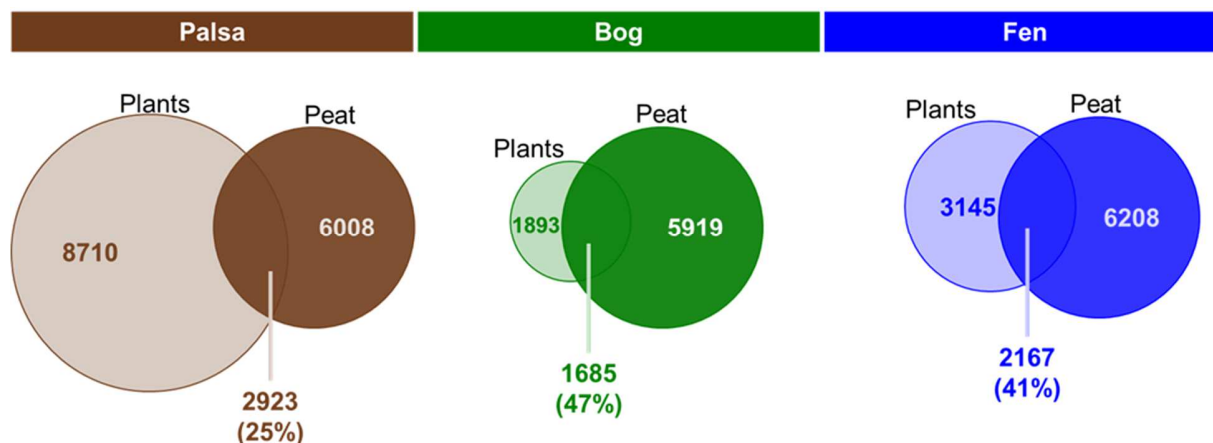308   1d).

309   In the bog, *Sphagnum* mosses and *E. vaginatum* leaf and bog peat FT-IR spectra were compared
310   (Figure 1 b,e). The waxy lipid peaks at 2850 and 2920 cm^{-1} were slightly more differentiated in the *E.*
311   *vaginatum* compared to the *Sphagnum,* consistent with higher waxy lipid content in *E. vaginatum*. The
312   leaf carboxylic acid peak (1720 cm^{-1}) was stronger in the *Sphagnum* compared to *E. vaginatum*. *E.*
313   *vaginatum* had the highest humic acid, lignin-like, protein and aromatic peaks in the bog (Figure 2 b,e).

314   The fen peat had higher protein-like, lignin-like, phenolic and aromatic peaks relative to the
315   other sites consistent with the higher abundance of these peaks in the *Eriophorum* species at that site
316   (Figure 1f). These peaks were relatively smaller in the peat from the bog and the phenolic and lignin like
317   peaks were larger in the fen relative to the palsa. The carbohydrate peak in the fen was lower than in
318   the bog.

319

320   *FTICR-MS Results*

321   Among all of the plant samples, leaves, stems, and roots combined we observed 19,072
322   molecular ions via FTICR-MS. Of those, we were able to assign a molecular formula to 14,260 peaks
323   (75%), which is a typical assignment rate for complex SOM. Across all habitats in the peat, we observed
324   15,198 unique compounds of which we were able to assign molecular formulae to 11,254 (74%). Palsa
325   plants had the highest diversity of compounds (n = 11,633, Figure 2). Of those, the majority of
326   compounds were not present in the peat (75%) suggesting that they were microbially decomposed
327   and/or processed. The remaining 25% were present in the peat, suggesting that they are resistant to
328   microbial decay and accumulate over time (Figure 2). The bog plants had the lowest diversity of
329   compounds (n = 3578) but they also appeared to be the most resistant to microbial decomposition as
330   47% were observed in the bog peat. The fen was intermediate between the palsa and bog with fen
331   plants having 5312 compounds of which 41% were observed to accumulate in the peat (Figure 2).

Palsa **Bog** **Fen**

Plants — Peat
8710 — 6008
2923 (25%)

Plants — Peat
1893 — 5919
1685 (47%)

Plants — Peat
3145 — 6208
2167 (41%)

332

333 Figure 2: Comparison of compounds in plant extracts (leaf, roots, stems, and whole mosses combined)
334 and in the shallow peat. Numbers in each circle indicate the number of different compounds identified
335 by FTICR-MS that are unique to either the plants or peat collected from each habitat, whereas shared
336 compounds are indicated by the overlapping regions (with numbers directly below, and the percentage
337 of plant compounds these represent). We refer to these overlap-region compounds as "accumulated"
338 because they are plant-derived and appear resistant to microbial decomposition, persisting in the peat.

339   We show the nominal oxidation state of the carbon (NOSC) in the water extracts of the
340 dominant plant leaves (whole plants for lichens, *Sphagnum*) from each habitat (Figure 3) as a metric for
341 determining organic matter quality (Wilson and Tfaily 2018). Lichens, *A. polifolia,* and *E. nigrum*
342 together comprise 31% of the aboveground leaf, 95% of aboveground stem, and 22% of the
343 belowground (root) biomass in the palsa. *Sphagnum* accounts for 74% of the biomass in the bog overall,
344 with *E. vaginatum* contributing 13% of the bog's aboveground and 20% of the belowground biomass. In
345 the fen, *E. angustifolium* is 63% of the aboveground and 81% of the belowground biomass, Whereas *C.*
346 *rostrata* contributes approximately 5% of the above and belowground biomass. Sphagnum had the
347 lowest NOSC of any of the habitat-dominant plants (Figure 3). *E. angustifolium*, in the fen, had
348 intermediate NOSC values that were nevertheless significantly higher than those found in *Sphagnum*.
349 The palsa plant community was more diverse, lichens had the highest NOSC values and *E. nigrum* and *A.*
350 *polifolia* had significantly higher NOSC values than *Sphagnum*.
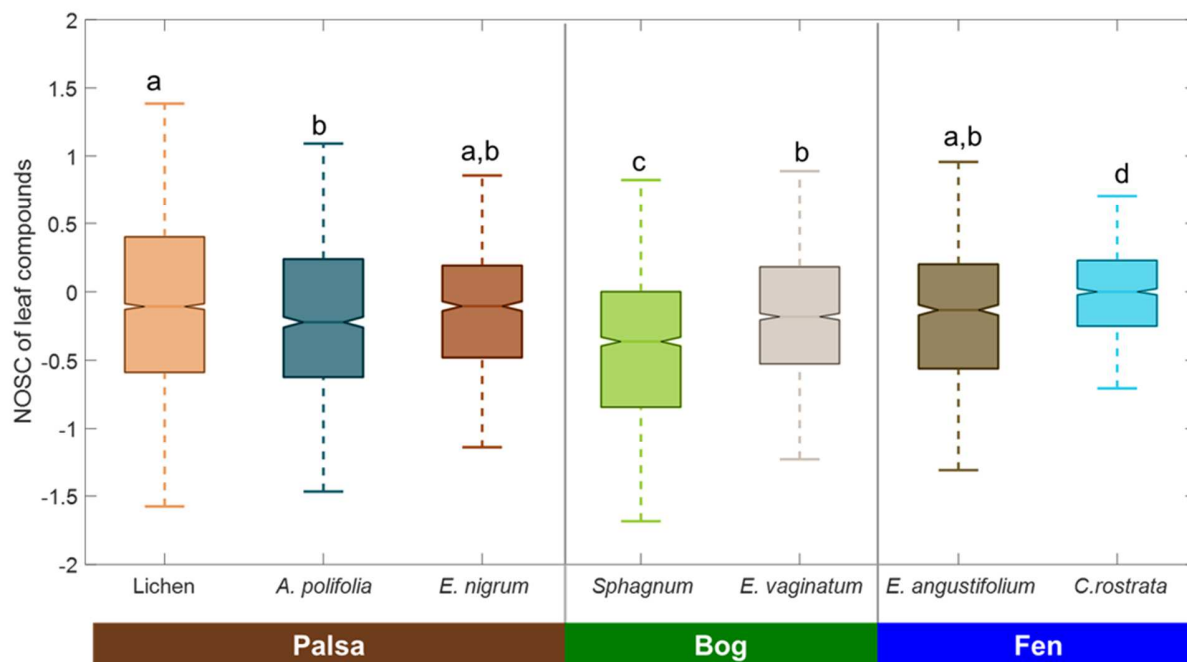
Figure 3: Nominal oxidation state of carbon (NOSC) for dominant plant leaf extracts (whole plants for lichens, *Sphagnum*) from each habitat. *E. vaginatum* are present in the bog as well as the fen, but at higher abundance. Different lowercase letters above bars indicate significant differences by ANOVA followed by pairwise comparison (Tukey's Honestly Significant Difference).

It is possible that the average NOSC was being disproportionately influenced by a large number of compounds with extreme NOSC values, but that were present at overall low concentration. To determine whether this was the case, we calculated the normalized signal intensity for each compound in the composite of all plant parts (leaves, stems, and roots combined) from all plants collected in each habitat. We plotted the cumulative normalized signal intensity against the NOSC of the compounds (Figure 4) and found that compounds with NOSC < 0 accounted for 46% of the signal intensity in the palsa, 71% of the signal intensity in the bog, and 58% of the signal intensity in the fen. Although not strictly quantitative within similar sample types, signal intensity roughly follows concentration in samples with similar overall matrices.

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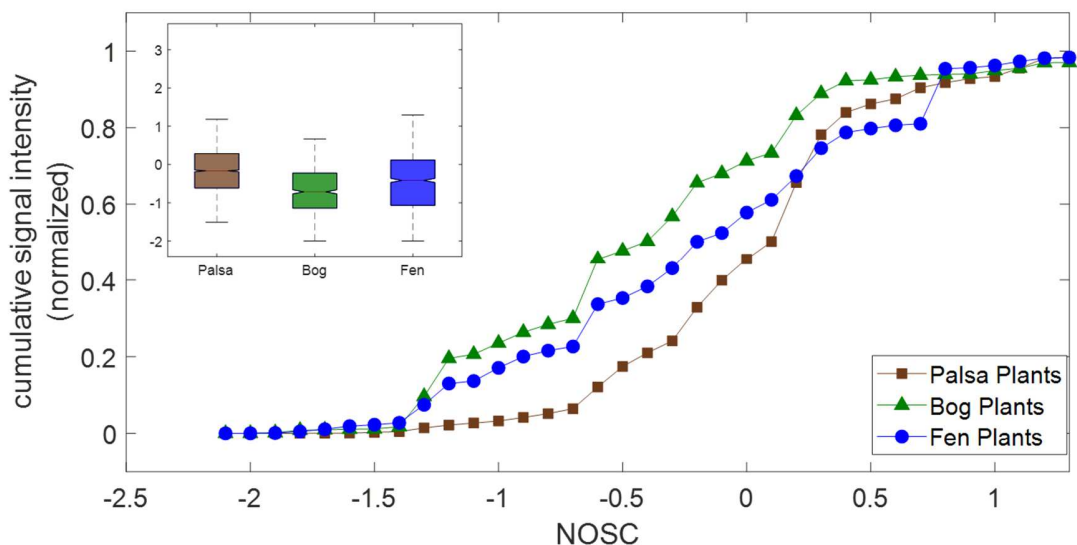
Figure 4: Cumulative signal intensity normalized to total intensity as a function of NOSC in the unique
compounds from the plant samples in each habitat. The small inset boxplots compare the overall means
for the unique compounds from the palsa, bog and fen plants, all habitats were significantly different
(ANOVA, p < 0.0001).

370   We compared the compounds observed in composite plant extracts (described in the methods)
to those in the shallow peat from each habitat type (Figure 5). There were significant differences in the
plant compounds as well as the peat across the different habitats (Figure 5). The bog and fen peat had
relatively more tannin-like, lignin-like and condensed aromatic compounds (TLC) as well as more
protein-like and lipid-like (unsaturated hydrocarbons + lipids) compared to the palsa peat (ANOVA p <
0.05 for all comparisons, Figure 5a,b,c respectively). These differences were reflected in the composite
plant samples for each site (Figure 5a,b,c) which showed a similar trend of higher protein-like, TLC, and
lipid-like compounds relative to the palsa. The palsa plants had higher average NOSC relative to the bog
and fen, which was also reflected in higher NOSC in the palsa peat (ANOVA p < 0.05; Figure 5d).
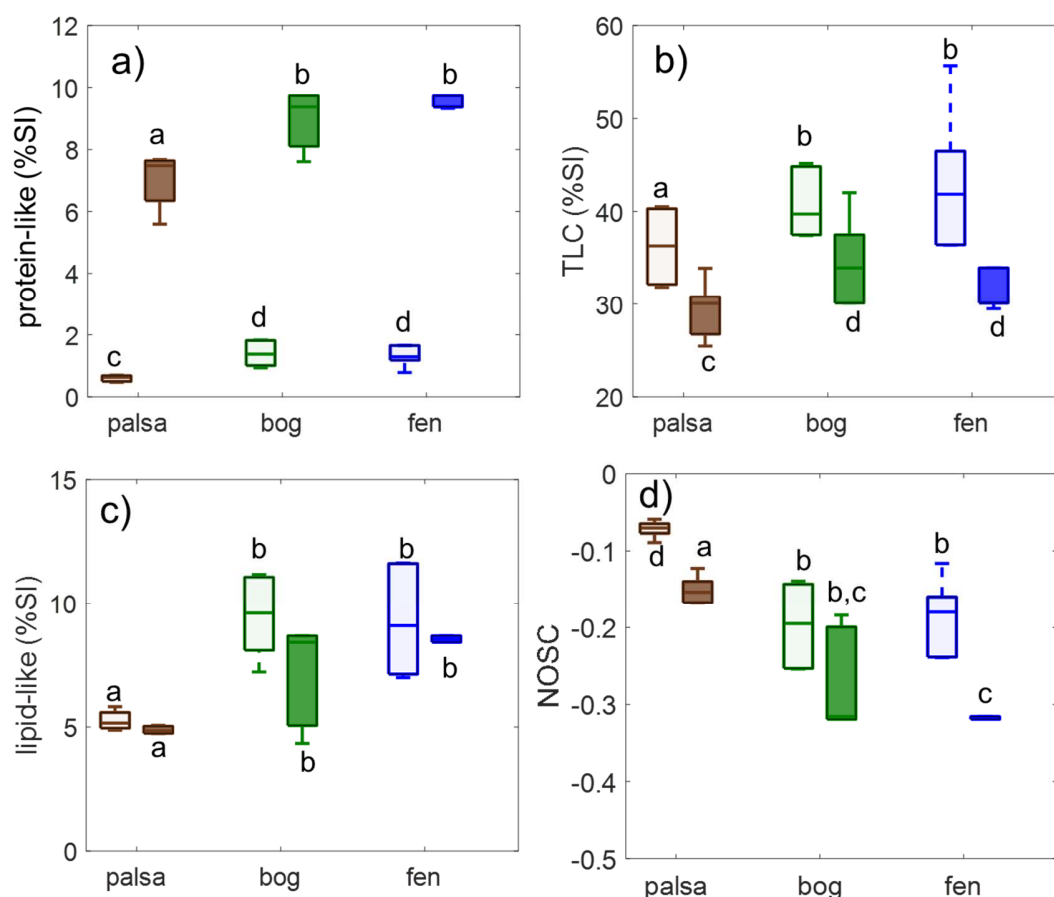
Figure 5: FTICR-MS-based compound classes compared for plant composites (as described in the methods and indicated here by the light-shaded boxes) and near surface (1-5cm) peat extracts across habitats. ANOVA was used to compare the means of groups; significant results are indicated by small lower-case letters next to each box. Panel (a) protein-like compounds are plotted as the sum of the signal intensities of all protein-like compounds normalized to the sum of signal intensities across the whole spectrum (%SI). Panel (b) presents the %SI calculated similarly for condensed aromatics + lignin-like + tannin-like (TLC) compounds. Panel (c) presents the %SI for unsaturated hydrocarbons and lipid-like compounds. Panel (d) presents the average signal intensity normalized NOSC. Boxes for plant samples were taken from a series of composite plant samples for each habitat (as described in the methods).

We then examined the characteristics of the plant-associated compounds that were either (1) consumed or that (2) accumulated in the peat as well as the compounds in the peat that were not present in the original plant material and were therefore assumed to be (3) either microbially produced or modified from their original form (Figure 6), either biotically or abiotically (e.g. Fudyma et al., 2020). Some of the newly observed compounds are identified as lignins (or at least lignin-like) which are produced by plants. Since these lignin-like compounds do not appear in the plant data, but do appear in the peat, those compounds must have been modified from their original structure such as via hydrolysis

398   or hydrogenation (e.g. Wilson et al., 2017). The comparison between samples to identify consumed or
399   newly observed compounds is sensitive to even minor abundance plant compounds, for example,
400   compounds could appear to be produced if they came from a minor species that was not included in the
401   plant mixture. To minimize this effect, we included all plant parts (leaves, stems, and roots) from all
402   plant species sampled at a given habitat (regardless of abundance) to compare against the peat
403   compounds. In the palsa, this included: lichens, *A polifolia, E. nigrum, D. elongatum, R. chamaemorus*,
404   and *B. nana.* In the bog this included *Sphagnum*, *E. vaginatum*, and *E. angustifolium*. In the fen this
405   included *E. angustifolium, C. rostrata*, and *Sphagnum*. Condensed aromatics ($p < 0.05$), tannins (n.s.),
406   and lignins (n.s.) made up a greater proportion of consumed compounds in the palsa compared to the
407   bog and fen (Figure 6a). In contrast, lipids made up a higher percentage of consumed compounds in the
408   bog ($p < 0.01$) and fen (n.s.) compared to the palsa. In the palsa a lower percentage of the lignin-like,
409   proteins, and lipids accumulated in the peat (Figure 6b) suggesting that the higher redox in the palsa
410   facilitated the decomposition of these types of compounds. Carbohydrates and amino sugars made up a
411   higher proportion of newly observed compounds in palsa compared to the bog and fen (Figure 6c).
412   Newly observed compounds in the fen were more lignin-like (n.s.) and lipid-like ($p < 0.05$), but had a
413   lower proportion of condensed aromatics ($p < 0.05$) and tannins (n.s.) compared to the newly observed
414   compounds in the palsa.

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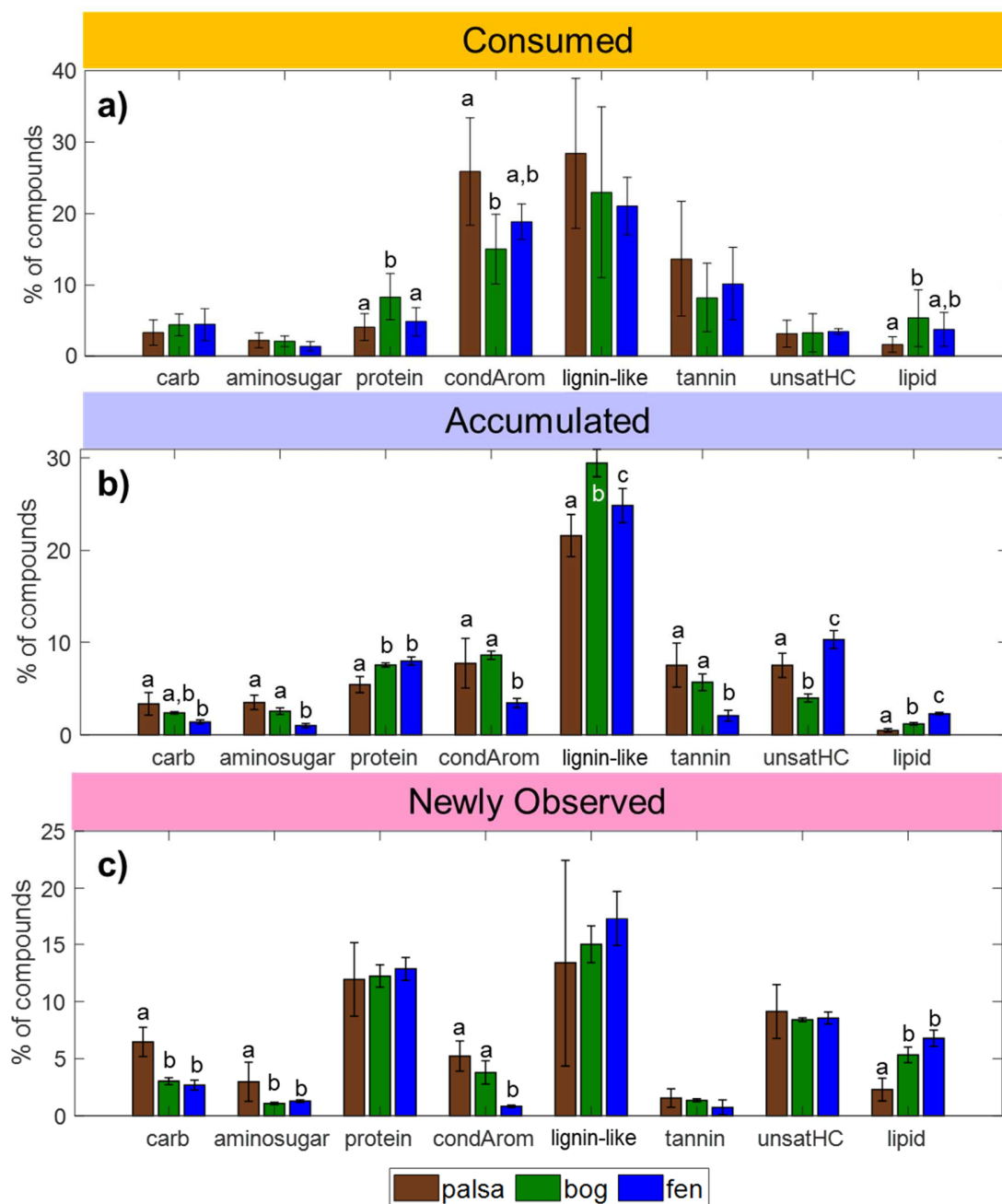
Figure 6: Inferred percentages of consumed, accumulated, and newly observed compounds, by chemical
class (inferred from the molecular formulae from FT-ICR MS, per Figure 3), for each habitat. Chemical
classes are carbohydrate-like (carb), amino sugars, proteins, condensed aromatics (condArom), lignin-
like, tannin, unsaturated hydrocarbons (unsatHC) and lipids. (A) Percentage of consumed compounds,
calculated as the number of consumed compounds in each class divided by the total number of
compounds that were present in the plants but not observed in the peat extracts. (B) Percentage of
accumulated compounds, calculated as the number of plant compounds of each class that were also
present in the peat, divided by the total number of accumulated compounds. (C) Percentage of newly

425 observed compounds, calculated as compounds present in the peat but absent from the plant material,
426 and are inferred to be either microbially produced or modified from their original form in the source
427 plants, divided by the total number of newly observed compounds. Lowercase letters above bars
428 indicate comparisons among palsa, bog and fen for the compound class, only significant differences are
429 indicated (ANOVA, followed by TukeyHSD, $p < 0.05$).

430   We also examined the nitrogen (N), sulfur (S), and phosphorus (P) content of the various
431 compounds. Overall, the plants in the fen had a higher proportion of nitrogen and sulfur containing
432 compounds compared to the plants in the bog and a higher proportion of nitrogen containing
433 compounds compared to the palsa ($p < 0.05$, ANOVA followed by Tukey HSD, see Supplemental Table 2
434 for full statistical results). When compared to the proportions present originally in the plants, a high
435 percentage of N-, S-, and P-containing compounds were consumed in the bog. A high percentage of the
436 newly observed compounds in the palsa were CHO-only compounds and comparatively few phosphorus
437 or sulfur containing compounds were newly observed. This result contrasts with the bog and fen where
438 phosphorus and sulfur containing compounds were ~40% of the total newly observed compounds.
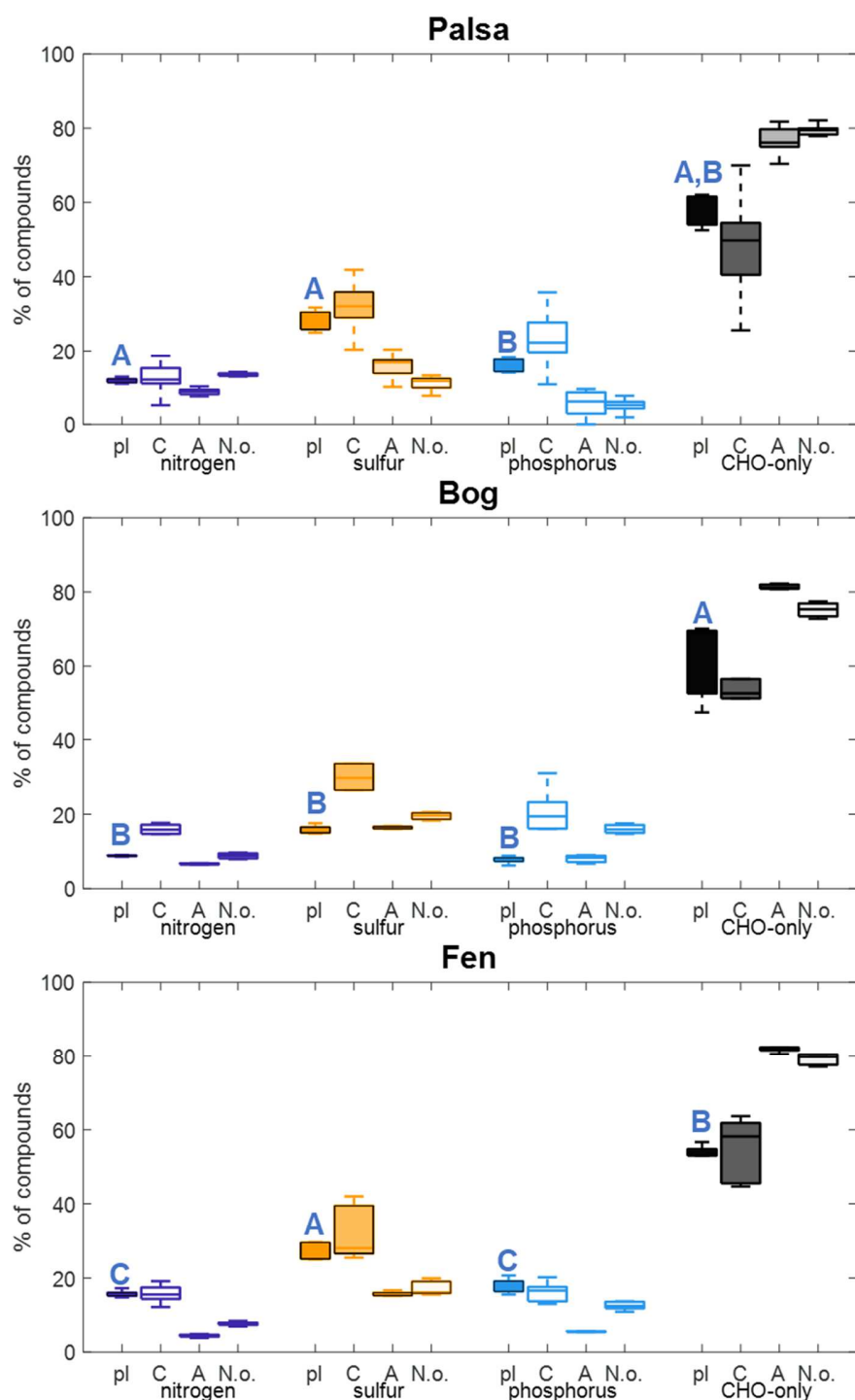
Figure 7: The proportion of compounds that were exclusively CHO or that contained N, S, or P, in each habitat, for composite plant samples (as described in methods), and those inferred to have been consumed (C), accumulated (A), or newly observed (N.o.) in the peat. Percentages indicate what percentage of the total number of compounds contain N, S, P or are CHO-only compounds. Some compounds contain multiple heteroatoms (e.g. N and S or N and P) thus the percentage may not sum to

445   100%. Significant results for ANOVA comparisons of the plant composites among habitats are indicated
446   by different blue capital letters just above each box. (See Supplemental Table 2 for all statistical results).

447   To understand potential differences in the decomposition pathways among the three habitats
448   that have contributed to the differences observed in the produced compounds, we calculated the
449   number of times each transform (i.e., chemical transformation pathways by which SOM decomposes)
450   occurred within a sample in the peat and plotted the most frequently observed transforms from each
451   site (Figure 8). Hydrogenation (H_2) was the most frequent transform for all of the habitat types.
452   Demethylation followed by oxidation (CH_2-O) was the second most frequent for the palsa and fen, but
453   side-chain (de)methylation (CH_2) was second for the bog. Transformations involving changes of N (OH-N,
454   O-NH, and NH_3-O) were highest in the palsa.
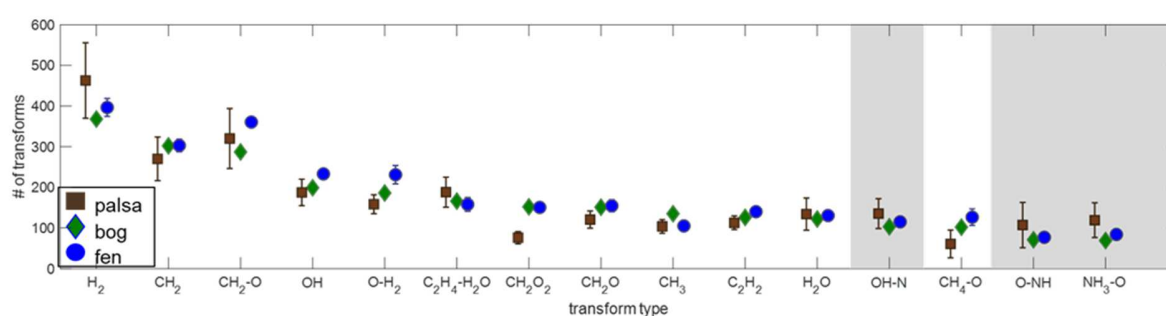
455
456   Figure 8: Top transforms for each habitat's peat given as the molecular differences among compounds
457   (i.e., H_2 refers to a difference of 2 hydrogen atoms). Points are plotted as averages ± 1 s.d. for 3 samples
458   of palsa, and for 2 samples of fen; one sample was available for bog. Transforms involving nitrogen are
459   highlighted in gray.

460

461   **Discussion**

462   In our investigation of changes in plant and soil organic material (SOM) composition along a
463   permafrost thaw gradient, we observed a strong relationship between the plant-derived organic
464   compounds and SOM compounds suggesting that aboveground vegetation and roots shape
465   belowground processes and subsequent SOM decomposition in this peatland (Figure 1,5). Across the
466   thaw gradient at Stordalen, there are well-documented significant changes in CO_2 and CH_4 production
467   potential (Hodgkins et al., 2014; Wilson et al., 2019) and emissions (McCalley et al., 2014). The palsa is
468   associated with net CO_2 emission and little, or no, CH_4 production, the bog and fen both exhibit net CO_2
469   uptake, and CH_4 emissions from the fen are the highest of the three habitat types (Bäckstrand et al.,
470   2010; McCalley et al., 2014). CO_2:CH_4 ratio production potentials, clearly indicate that the fen is the most
471   methanogenic of the three sites (Hodgkins et al., 2014; Wilson et al., 2019). Hodgkins et al. (2014)
472   hypothesized that differences in the major SOM classes drove variability in greenhouse gas (GHG)
473   emissions across the mire and ascribed increasing GHG emissions across the thaw gradient to increasing
474   SOM lability as inferred from decreasing C/N ratios and lower molecular weight, aromaticity, organic
475   acid, and organic oxygen contents suggesting low inputs of labile organic C are limiting CO_2 and CH_4
476   production in the bog. The FT-IR analysis shows that the carbohydrate peak, a highly bioavailable C
477   source that should stimulate production, was much higher in the bog peat relative to the other habitats
478   (Figure 1). This high carbohydrate content of the bog peat is consistent with other observations that

18

479   sugars tend to accumulate in *Sphagnum*-dominated peat (AminiTabrizi et al., 2020), and that the

480   hydrolytic enzymes responsible for the initial breakdown of carbohydrates are less active in Stordalen

481   bog peat relative to the other habitat types (Woodcroft et al., 2018). Additionally, the total dissolved

482   organic carbon and nitrogen contents were much higher in the bog relative to the fen. Whereas analysis

483   of the solid phase (FT-IR) bog peat revealed high abundance of bioavailable carbohydrates, the FTICR-

484   MS analysis revealed low quality organic matter in the water-soluble fraction (Figure 5d) and little

485   accumulation of carbohydrates or amino sugars in the bog (Figure 6b). Cumulatively, these results are

486   consistent with the hypothesis that low CO_2 production in the bog is not due solely to lower availability

487   of labile compounds, but to some process that inhibits the breakdown of larger carbohydrates into

488   easier to assimilate monomers. This implies that the availability of labile C in the bog is, in part, limited

489   by solubilization of the cell walls, likely due to the low pH in the bog (pH = 4.2) which is known to inhibit

490   DOM hydrolysis (Curtin et al., 2016). The high relative abundance of the carboxylic acid peak in the solid

491   *Sphagnum* (Figure 1) is consistent with the high abundance of carboxylated sugars and uronic acids that

492   comprise the structural components of Sphagnum cell walls (Painter 1991; Ballance et al., 2007) which

493   could explain the relatively high carbohydrate peak in the solid bog peat as well as the lower pH in the

494   bog relative to the fen.

495

496   Whereas the plant community is the initial source of the organic matter to the subsurface

497   (Sutton-Grier and Megonigal, 2011) subsequent microbial decomposition removes some chemical

498   species and creates others, thereby modifying the inputs in a way that is partially dependent on oxygen

499   availability within each habitat. *Sphagnum* plays a particularly strong role in habitats where this species

500   dominates. Organic matter in *Sphagnum* extracts has significantly lower NOSC than other abundant

501   plant species (Figure 3). Such low NOSC is consistent with low organic matter quality (Wilson and Tfaily

502   2018) suggesting a mechanism for suppressed SOM decomposition in the bog, especially as compared to

503   the fen. In addition, *Sphagnum* produces many compounds that are potentially inhibitory to microbial

504   activity (Fudyma et al. 2020) including organic acids which result in lower pH in the bog relative to the

505   fen habitat. All of these factors work synergistically to facilitate C storage in *Sphagnum*-dominated

506   environments. The percentage of plant compounds that accumulate in the peat, and are therefore less

507   bioavailable, increases from palsa (25%) to fen (41%) to bog (47%) (Figure 2), which is opposite to the

508   trend in plant species diversity across the habitats. *Sphagnum* limits decomposition rates by producing

509   low NOSC compounds (Figure 3) and producing microbially inhibitory compounds (Fudyma et al., 2020),

510   but it appears that these effects of *Sphagnum* can be attenuated by increasing proportional cover of

511   other plant species.

512   We found a high abundance of waxy lipids in the leaves of *E. nigrum* and *A. polifolia* from the

513   palsa (as seen in the strong differentiation between the 2850 cm^{-1} and 2920 cm^{-1} FT-IR peaks; Figure 1a)

514   (Artz et al. 2008; Cocozza et al. 2003). Whereas these compounds are frequently thought to be

515   refractory, they do not appear as strongly in the palsa peat, suggesting that they are at least partially

516   degraded following deposition. Alternatively, because the leaves of *E. nigrum* and *A. polifolia* are very

517   small and evergreen, they are likely underrepresented in the peat since they don't all drop in the fall

518   (unlike the deciduous plants in the habitat). The low differentiation between these peaks in the lichen is

519   consistent with lichens lacking the waxy cuticle that coats plant leaves.

520   Whereas FT-IR is practical for looking at overall changes of functional groups in the bulk solid-
521   phase SOM, FTICR-MS provides finer-resolution detail of the water-extractable compounds, down to the
522   individual molecular level. Overall, we observed fewer unique molecular formulae in peat samples
523   relative to the plant sample set as determined by FTICR-MS (15,198 vs 19,072 respectively). This result is
524   consistent with loss of compounds with decomposition of the plant material following deposition. The
525   percent of plant compounds that were also found in the peat increased from palsa (25%) to fen (41%) to
526   bog (47%) (Figure 2). This pattern suggests that a higher percentage of plant compounds were
527   decomposed in the palsa so that they are no longer detectable. The apparently higher decomposition in
528   the palsa occurs even though the palsa also has the greatest number of different compounds of all the
529   sites. The richness (i.e., number) of compounds observed in the plants across the different habitat types
530   (Figure 2) follows the same pattern as the plant species diversity changes across the sites: palsa > fen >
531   bog (Hough et al., 2020; Johansson et al., 2006). Interestingly, this trend is opposite that observed in the
532   diversity of the plant-associated microbial communities across these sites (Hough et al., 2020; Wilson et
533   al., 2021b). Nevertheless, the richness of compounds in the peat is similar across the different habitats,
534   which suggests that a high diversity of microbial pathways in the bog and fen is responsible for
535   transforming the less diverse plant matter into more diverse peat.

536   Whereas there is considerable overlap in compounds between the peat and the dominant plant
537   types found within each habitat, many of the plant compounds were not found in the peat and the peat
538   also had many unique compounds not found in the plants. These results indicate both loss and
539   production of novel compounds following plant organic matter deposition, presumably through the
540   metabolic action of microorganisms. Only 25% of compounds from the palsa plant composite were also
541   observed in the surface (1-5cm) peat (Figure 2), indicating that 75% of plant compounds were either
542   consumed or metabolically processed into other molecules and that the compounds produced by plants
543   in the palsa were largely bioavailable and susceptible to decomposition. It is likely that the higher lability
544   (as inferred from NOSC) of the dominant plant compounds (Figure 3,4) contributes to the greater
545   decomposition of organic matter from palsa plants. Additionally, the higher availability of oxygen as a
546   terminal electron acceptor (TEA) in the palsa compared to the other sites could catalyze the
547   decomposition of a range of bioavailable compounds in the palsa relative to the other habitats. The
548   higher oxygen content could explain why hard to decompose chemical classes such as tannins, lignins,
549   and condensed hydrocarbons are more readily consumed in the palsa than in the bog and fen (Figure
550   6a).

551   In highly oxygenated environments, production of CO_2 is thermodynamically favored, but in
552   anoxic, TEA-depleted, waterlogged environments, CO_2 is sometimes the only available TEA, resulting in
553   CH_4 production. Plants exert a strong influence on the CO_2:CH_4 ratio by being the prime source of
554   organic substrates (i.e., electron donors) in the subsurface (Megonigal et al., 2004; Sutton-Grier and
555   Megonigal 2011), and by controlling the availability of TEAs used in decomposing that organic matter.
556   There is a strong relationship between NOSC calculated from the molecular formula and the
557   thermodynamic catabolic energy yield on oxidation of that C (LaRowe and van Cappellin 2011; Keiluweit
558   et al., 2016), and that energy yield is a measure of organic matter quality (Wilson and Tfaily 2018).
559   Natural organic matter typically has NOSC values ranging from -4 to +4 with corresponding ΔG°_{C-ox}
560   ranging from -54 to +174 kJ (mol C)$^{-1}$, which suggests that most organic matter oxidation must be
561   coupled to an energy yielding reduction in order to become thermodynamically feasible. Oxygen is
562   capable of oxidizing compounds along the full range of NOSC values with enough energy to produce

563 ATP. Thus, OM decomposition in the aerobic palsa is unlikely to be thermodynamically inhibited,
564 although some evidence suggests that NOSC influences decomposability in aerobic environments as well
565 (Graham et al., 2017). However, in the bog and fen where inundation creates anaerobic conditions and
566 where the availability of other alternative terminal electron acceptors (such as Fe(III) or sulfate) is low,
567 decomposition becomes thermodynamically limited, resulting in the accumulation of compounds with
568 lower NOSC values such as unsaturated lignin, lipids, and unsaturated hydrocarbons (Figure 6b).

569 Whereas the palsa has higher oxygen availability than the other two sites, which could
570 contribute to higher decomposition rates, the higher NOSC values of the dominant palsa plant
571 compounds (Figure 3) are consistent with the palsa plant material also being inherently easier to
572 decompose, regardless of the available TEAs (Keiluweit et al., 2016). The high bioavailability of palsa
573 plants, particularly lichens (Figure 3) is contrary to generally accepted idea that the sedges, abundant in
574 the fen, should be the most easily biodegradable (Malmer et al 2005). The rate of litter input in the fen
575 is highest of any of the habitats and could be faster than the microbial community can process, leading
576 to a build-up of otherwise biologically attractive substrates (Malmer et al 2005). Both bog and fen
577 habitats have higher occurrences of newly observed lignin-like compounds relative to the palsa (Figure 6
578 c). These compounds are unlikely to be produced microbially, but are more probably due to microbial
579 modification of plant-derived compounds and increased (abiotic) leaching in the waterlogged bog and
580 fen sites.

581 Nutrient limitation is a possible control of SOM decomposition in peatlands. Whereas it has
582 been shown that *Sphagnum*-dominated peatlands are nitrogen-limited (Braggazza et al., 2006), we
583 found evidence that dominant plants in the bog habitat are also lower in S relative to the plants from
584 other habitats (Figure 7). This result is consistent with measurements of bulk S in the litter (Hough et al.,
585 2021) and suggests that S is limiting in the bog habitat. In support of this hypothesis, the consumed
586 compounds in the bog were disproportionately S-containing compounds relative to the amount of S
587 initially present in the plants (Figure 7). Consistent with the understanding of N limitation, the consumed
588 compounds in the bog were also disproportionately N-containing compounds compared to N
589 compounds present initially in the bog plants (Figure 7). The correlation among N and S containing
590 compounds would be consistent with the production of microbial proteins. In other peatlands, climate
591 effects such as warming have been associated with increases in microbial peatland cycling (Wilson et al.,
592 2021a). Increases in the nitrogen content of decomposing peat have been observed in other studies
593 from enhanced C losses during decomposition (Leifeld et al., 2020). The large percentages of produced
594 compounds with S, and P suggest potential organic S and P cycling occurring in the anaerobic habitats.

595 We examined the mechanisms by which compounds are decomposed, and found that palsa has
596 the highest overall number of transforms (i.e., potential mechanisms by which the SOM is being
597 degraded), probably reflecting the diversity of aerobic pathways, but the fen also has a higher number
598 of transforms compared to the bog (Figure 8). Higher numbers of transforms in the fen relative to the
599 bog are consistent with the higher diversity of compounds in the fen plant litter stimulating microbial
600 activity and creating a more active system. Additionally, inhibitory compounds in the bog could limit
601 microbial activity, thereby suppressing the number of transforms utilized. In particular, the fen has a
602 higher frequency of (de)hydrogenation (H_2), hydroxylation (OH), demethylation followed by oxygenation
603 (CH_2-O), and dehydrogenation followed by oxidation (O-H_2). Dehydrogenation and demethylation
604 followed by oxidation (net transform: CH_4-O) are common mechanisms of lignin decomposition (Stenson
605 et al., 2003). Finding that these reactions are more prevalent in the fen than in the bog is consistent with

21

the low true lignin content of bog plants (i.e., *Sphagnum*) compared with the dominant fen plants (*Eriophorum*). Surprisingly, CH_4-O is less prevalent in the palsa, where we would expect high rates of lignin decomposition due to the abundance of lignin-rich woody vegetation. Additionally, the palsa had the most diverse consumption of lignin-like compounds (Figure 6a) and, in contrast to the other habitats studied, the palsa is well-oxygenated in the surface layer, which should promote the activity of the lignin-degrading enzyme phenol oxidase (Freeman et al., 2001; Sinsabaugh 2010). The FT-IR results also suggest more lignin content in the palsa plants relative to the dominant plants in the fen (Figure 1 a,c), but lower lignin content in the palsa peat relative to the fen peat, which also suggests decomposition of lignin is occurring in the palsa. We hypothesize that in the palsa, the greater oxygen availability allows faster, multi-step decomposition of lignin in the plant litter, such that the surface peat had already lost much of the lignin or its decomposition products; whereas in the fen, lignin decomposition is occurring (as inferred from the number of transforms), but is slowed by oxygen limitation. An alternate explanation is that although the plants are woody, litter input in any year comes mostly from the leaves, so the woody biomass has less effect on the peat.

Several transforms involving exchanges with N were important, particularly in the palsa, including oxygen or hydroxyl exchange with N, NH, or NH_3 (Figure 8). These sorts of transforms are expected to occur when intermediates of N-fixation interact with SOM (Thorn et al., 1992, 2016; Thorn and Mikita 2000). The higher frequency of these N-involving transforms in the palsa could be related to the abundance of lichens, which are significant nitrogen-fixers in locations where herbaceous nitrogen-fixing plants are less abundant (Gunther 1989). In contrast, the mechanisms of decomposition as inferred from transform abundance in the wetter anaerobic habitats seem to be more similar to each other than either is to the drier palsa.

Mechanisms of organic matter decomposition differed between the palsa and the other habitats, but were similar between the two inundated sites suggesting that the quality of plant-derived inputs to the soil in permafrost systems influences SOM accumulation and decomposition below ground, as modified by environmental factors such as pH and oxygen availability. Shifts in plant communities in response to climate change have a profound effect on SOM composition through changing inputs. This composition in turn shapes decomposition, ultimately influencing GHG production. Nevertheless, peatlands are unique habitats in that they have a rich abundance of C but low abundance of terminal electron acceptors meaning that they are thermodynamically, yet not C, limited. Other climate forcings such as drought, which have the potential to alter the availability of TEAs, will therefore have a disproportionate influence in peatlands where an abundance of low-quality C is available for decomposition if the correct thermodynamic requirements are met.

Acknowledgments

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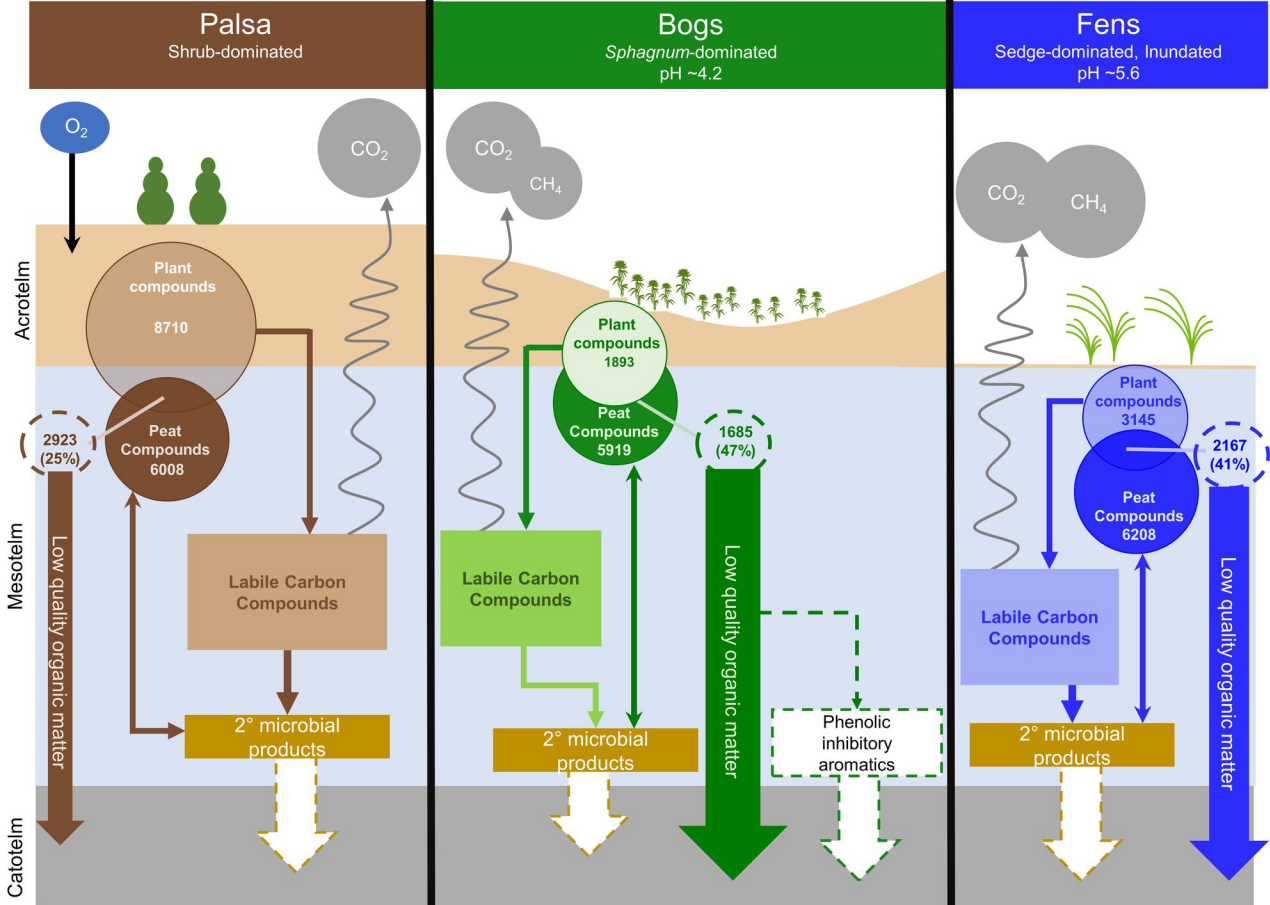891   decomposition. Organic Geochemistry, 112, 22-32.

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Palsa	Bogs	Fens
Shrub-dominated	*Sphagnum*-dominated pH ~4.2	Sedge-dominated, Inundated pH ~5.6

Palsa
- O_2
- CO_2
- Plant compounds 8710
- Peat Compounds 6008
- 2923 (25%)
- Labile Carbon Compounds
- 2° microbial products
- Low quality organic matter

Bogs
- CO_2
- CH_4
- Plant compounds 1893
- Peat Compounds 5919
- 1685 (47%)
- Labile Carbon Compounds
- 2° microbial products
- Phenolic inhibitory aromatics
- Low quality organic matter

Fens
- CO_2
- CH_4
- Plant compounds 3145
- Peat Compounds 6208
- 2167 (41%)
- Labile Carbon Compounds
- 2° microbial products
- Low quality organic matter

Acrotelm / Mesotelm / Catotelm

Organic compounds present in the dominant plants as well as peat soil organic matter from each of the habitats were detected using ultra high resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. The number of different compounds for the plants and the soil organic matter are given in Venn Diagrams for each of the three habitats. The overlap between the two pools is indicated as a number as well as a percent of the initial plant compounds input to the system. These plant compounds appear resistant to microbial decomposition as they persist in the peat. Plant compounds that were not found in the peat were assumed to have been microbially decomposed. We infer that these are labile compounds which were either decomposed into secondary microbial products or respired to CO_2 and, in the case of the bog and fen, CH_4. Differences in CO_2 and CH_4 emissions across the different habitats are inferred to result from changes in the quality of the initial plant organic matter that is input at each habitat. As the plant community changes across habitats as well as with changing climate, we expect subsequent alteration in CO_2 and CH_4 emissions.