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1 **Title:** Plant organic matter inputs exert a strong control on soil organic matter decomposition in a
2 thawing permafrost peatland

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19 **Abstract.** Peatlands are a climate critical carbon (C) reservoir that will likely 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, while 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
32 higher quality SOM. We explain this discrepancy as the result of low solubilization of bog SOM facilitated
33 by the low pH in the bog which makes the solid phase carbohydrates less available to microbial
34 decomposition. Plant-associated lignins and tannins declined in the unsaturated palsa peat indicating
35 decomposition, but accumulated in the bog and fen peat where decomposition was presumably
36 inhibited by the anaerobic conditions. A molecular-level comparison of the aboveground C sources and
37 peat SOM demonstrates that climate-associated vegetation shifts in peatlands are important controls on
38 the mechanisms underlying changing C gas emissions.

39 **Keywords:** peatland, climate change, greenhouse gas production, *Sphagnum*, soil organic matter,
40 decomposition

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41 Introduction

42 Climate-change induced warming, especially in the Arctic, will provoke a series of responses
43 including changes to the overall plant community composition, individual plant primary productivity,
44 microbial community, and individual microorganisms which culminate in the whole ecosystem response
45 (Wardle et al., 2004). These interactions are complex and their interpretation is, in turn, complicated by
46 the extreme complexity of the soil organic matter (SOM) that acts as the repository of plant derived
47 substrates, inhibitory compounds, and microbially derived metabolic products. Understanding such
48 interactions is critical because interactions between plants and the microbial community have a strong
49 effect on the net release of the microbial respiration products CO₂ and CH₄ (Sutton-Grier and Megonigal
50 2011).

51 Peatlands are a globally significant carbon (C) reservoir estimated at 530 ± 160 Pg (Hugelius et
52 al., 2020) up to 1055 Pg (Nichols and Peteet 2019), representing 35-70% of planetary soil organic carbon
53 (Lal 2010). Much of the high-latitude peatland C (277-800 Pg) is currently protected from decomposition
54 as peatland permafrost (Tarnocai et al., 2009; Hugelius et al., 2014). Due to climate change, northern
55 high latitudes are warming two to three times faster than the global average (Rintoul et al., 2018), which
56 is causing permafrost to thaw (Christensen, 2014). Once thawed, the soil organic C is susceptible to
57 microbial decomposition into the potent greenhouse gases (GHG) carbon dioxide (CO₂) and, under
58 water-logged anaerobic conditions, methane (CH₄) (Schaedel et al., 2016; Chang et al., 2021). Many
59 peatlands are active C sinks (Turetsky et al., 2007; Jones et al., 2013) or near-C neutral (Zoltai 1993,
60 Euskirchen et al., 2012). The source or sink potential of a peatland depends on the balance between net
61 C uptake by primary production and C loss via heterotrophic respiration, both of which can be affected
62 by climate change. C uptake increases under a longer growing season (Natali et al., 2012), warming,
63 drying (e.g., Malhotra et al., 2020) and changing plant community structure (e.g., Norby et al., 2019). C
64 release via microbial respiration can be impacted by soil moisture (Blanc-Betes et al., 2016; Natali et al.,
65 2015; Elberling et al., 2013), temperature (Hicks-Pries et al., 2013) and active layer depth (O'Donnell et
66 al., 2011), as well as shifts in the quantity and quality of available organic matter (Treat et al., 2014;
67 Hough et al., *in press*). Primary producers initially fix C and supply that C to the subsurface where it can
68 be reworked by subsurface microorganisms. As the ultimate source of organic inputs to the peat, plants
69 exert a strong control on SOM quantity and quality (Sutton-Grier and Megonigal 2011) which we
70 hypothesize controls GHG production rates and their variation across thaw habitat types. Connecting
71 the quality of aboveground C sources to differences in peat SOM is an essential step in testing the
72 hypothesis that climate-associated vegetation shifts in peatlands influence changing C gas emissions.

73 Four major vegetation types dominate in high-latitude peatlands: bryophytes (mosses),
74 graminoids (sedges), shrubs, and trees (Clymo 1987; Rodwell 1991). While warmer temperatures
75 accelerate C loss from peat (Hopple et al., 2020; Hanson et al., 2020), this loss is greater when
76 graminoids and shrubs dominate rather than *Sphagnum* mosses (Walker et al., 2016). *Sphagnum* is
77 thought to suppress decomposition rates and thus GHG production by supplying poor-quality SOM (van
78 Breeman 1995; Turetsky 2003), by microbial inhibition via acidification of the environment (Spearing
79 1972), and by production of inhibitory phenolic compounds (Rudolph and Samland 1985; Williams et al,
80 1998) and antimicrobial acids and sugar derivatives (Fudyma et al., 2019). Thus, environmental changes
81 causing *Sphagnum* declines and increasing dominance by shrubs or sedges (e.g. McPartland et al., 2020;
82 Norby et al., 2019; Walker et al., 2016; Johannson et al., 2006) is likely to result in more reactive and
83 bioavailable SOM (Chanton et al., 2008; Tfaily et al., 2013; Wilson et al., 2021a). However, evidence has

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84 also been presented that compounds associated with some shrubs inhibit SOM degradation (Wang et
85 al., 2021; 2015). Sedges, such as *Carex* and *Eriophorum*, have been correlated with higher CH₄
86 production (Hines et al., 2008) and greater SOM reactivity (Chanton et al., 2008), thought to occur
87 because sedges contain more cellulose, bioavailable N, and a higher proportion of labile compounds
88 compared to *Sphagnum* (AminiTabrizi et al., 2020; Hodgkins et al., 2014, 2016). Graminoids also contain
89 aerenchyma which are capable of transporting O₂ to the rhizosphere, potentially enhancing
90 decomposition. In contrast, *Sphagnum* lack such tissues, thus *Sphagnum*-dominated habitats generally
91 have lower O₂ availability providing a further thermodynamic constraint on SOM degradation in
92 *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. These analyses will be used to assess (1) the quality of plant organic matter inputs in each of
99 the three habitats, (2) which plant compounds accumulate as peat in each habitat type, and (3) the
100 pathways by which plant-derived compounds are decomposed and how these differ across habitat
101 types. Our assessments of organic matter quality will be used to determine how different plant types
102 contribute to changes in SOM quality and drive GHG production rates across the thaw gradient. This
103 information could be used to infer peatland-atmosphere feedback resulting from climate-driven shifts in
104 plant community composition.

105 **Methods**

106 *Site Description*

107 Stordalen Mire (68.35°N, 19.05°E) is located in northern Sweden just north of the Arctic circle
108 within the region of discontinuous permafrost. Climate change has accelerated thawing in the recent
109 few decades leading to changes in hydrology and vegetation cover which have resulted in a patterned
110 mosaic of habitat types within the mire (Johansson et al., 2006; Kokfelt et al., 2009); we focus here on
111 the three dominant habitat types at the site: palsas, bogs, and fens. Some areas of the mire are still
112 underlain by intact permafrost and elevated above the surroundings into relatively dry palsa plateaus.
113 Warming has caused thawing of the permafrost in some areas causing, e.g., palsas to collapse and flood,
114 producing wetter collapse features (Johansson et al., 2006). *Sphagnum* can infiltrate such pools,
115 eventually elevating the surface enough to form a bog, or in some cases, the insulating effects of the
116 *Sphagnum* are sufficient to allow the permafrost to refreeze. Alternatively, palsa can thaw completely
117 and subside to the level of the surrounding water table, causing flooding and creating a fully-inundated
118 fen. Fens are characterized by sedges and other aquatic vegetation (Zoltai 1993; Vitt et al., 1994;
119 Jorgenson et al., 2001; Malmer et al., 2005), high CO₂ uptake, and the highest CH₄ emissions of the three
120 habitat types (Hodgkins et al., 2014; McCalley et al., 2014). A bog, dominated by *Sphagnum*, can develop
121 if the thawing permafrost collapses but remains above the local water table.

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

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126 (Chanton et al., 2008; AminiTabrizi et al., 2020; Hodgkins et al., 2014, 2016; Tfamily et al., 2013), leading to
127 much higher overall CH₄ and CO₂ emission rates from fens as compared to bogs (Hodgkins et al., 2014)
128 and the even-drier palsas (McCalley et al., 2014). Since the 1970's, the areal coverage of *Sphagnum*
129 across the mire has declined significantly (Malmer et al., 2005), giving way to increased sedge cover as
130 wetter conditions across the mire have increased the areal coverage of fen habitats (Kokfelt et al., 2009;
131 Bäckstrand et al., 2010). This gradient in habitats across the mire creates a unique opportunity to
132 explore changes in SOM quality with habitat transition within the context of changing greenhouse gas
133 production rates.

134

135 *Plant Collection*

136 To explore differences in plant organic matter inputs across the three habitat types, samples of
137 the characteristic species from each habitat (Malmer 2005) were collected. Water extracts from the
138 whole plants and tissue types (leaves, stems, roots) were used to compare organic matter inputs
139 composition across the different plant types. Plant-associated compounds were then compared to the
140 peat from each habitat to understand what compounds were easily decomposed (i.e., which compounds
141 stimulated microbial activity) versus those compounds that were less bioavailable and that tended to
142 accumulate in the peat. Plants were collected during the peak of the growing season (early August) in
143 2014 resulting in the following samples for each habitat: palsa – *Rubus chamaemorus*, *Betula nana*,
144 *Empetrum nigrum*, *Andromeda polifolia*, *Dicranum elongatum*, *Eriophorum vaginatum*, fruticose lichen
145 of unknown species; bog – *Sphagnum spp.*; fen – *Eriophorum angustifolium*, *Carex rostrata*. Whole plant
146 samples were collected and separated by tissue type (roots, stems, and leaves), then immediately flash-
147 frozen in liquid N₂ and kept frozen at -20°C until processing in February 2015. Since mosses do not have
148 root, stem, and leaf differentiation, they were not separated and were processed as whole plants.
149 Additional plant samples for FT-IR analysis were collected in August 2015 and included *Sphagnum*
150 *fuscum*, *S. magellanicum*, *E. nigrum*, *A. polifolia*, and an unknown species of lichen. These samples were
151 similarly flash frozen in the field in liquid N₂ and then kept at -20°C until analysis.

152 *Peat Collection*

153 Peat was collected in August 2014, from the same three habitats along the thaw gradient where
154 plants were collected, using a Wardenaar corer (Eijkelpamp, Raleigh, NC USA). The cores were sectioned
155 by depth, placed in Teflon coated vials, and frozen at -20°C before analysis. On returning to the lab, peat
156 samples were freeze dried and ground to a homogenous powder using a SPEX SamplePrep 5100
157 Mixer/Mill ball grinder. Porewater was also collected from the site using a perforated stainless-steel
158 tube inserted into the peat to the desired depth. Gentle suction was applied using a gas tight syringe
159 fitted to the tube using a three-way valve. Once 30 mL of porewater was obtained, it was placed in a
160 polycarbonate sample vial and frozen at -20°C prior to analysis. An additional 30 mL of porewater was
161 collected in three locations within 1 m of the core for replicate pH analysis immediately in the field.
162 Samples were collected from the shallowest depth it was possible to draw porewater: 10-14 cm in the
163 bog and 1-5 cm in the fen. We used the solid peat to compare the compounds present in the palsa,
164 where the conditions are not water saturated and no porewater could be collected, to the other sites
165 where water saturation has already effectively extracted dissolved compounds from the peat. A list of
166 sample types and the number of samples analyzed by each method are given in Supplemental Table 1.

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

168 To examine the bulk chemical characteristics of the plants and solid peat, the dried and ground
169 material were analyzed by Fourier Transform Infrared Spectroscopy (FT-IR). For FT-IR, only stems and
170 leaves from each plant were available for analysis (no roots). Recent advances in FT-IR analysis allow us
171 to quantitatively evaluate differences in carbohydrates and aromatic compounds among samples
172 (Hodgkins et al., 2018). FTIR spectra were collected using a PerkinElmer Spectrum 100 FTIR
173 spectrometer fitted with a Csi beam splitter and a deuterated triglycine sulfate detector. Transmission-
174 like spectra were obtained using a Universal ATR accessory with a zinc selenide/diamond composite
175 single-reflectance system. Each sample was placed directly on the ATR crystal, and force was applied so
176 that the sample came into good contact with the crystal. Spectra were acquired in % transmittance
177 mode between 4000 and 650 cm^{-1} (wavenumber) at a resolution of 4 cm^{-1} , and four scans were
178 averaged for each spectrum. The standard deviations of carbohydrate and aromatic carbon values were
179 within 5% of the mean values when 4 replicate samples were run and scanned four times. That is, if a
180 sample was found to be 30% carbohydrate, the analytical error on 4 aliquots that were each scanned 4
181 times was 1.5%. Spectra were ATR-corrected, baseline-corrected, and then converted to absorbance
182 mode using the instrument software. Area-normalized and baseline-corrected peak heights for common
183 classes of compounds observed in SOM were calculated using the methods and script described by
184 Hodgkins et al., (2018), expanded to include peak assignments by Palozzi and Lindo (2017).

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

186 We used Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS) to gain a
187 higher resolution view of the compounds present in the palsa peat, peat porewater from the bog and
188 fen, and the plant samples. Plant samples were thawed and each tissue type (roots, stems, and leaves
189 when available), in addition to whole plant samples for mosses, which lack leaf/stem/root
190 differentiation, were analyzed after water extraction in which 0.5 g of undried plant material was shaken
191 in 4 mL nanopure water and then allowed to sit for 2 hours, and the supernatant decanted. The
192 resulting extracts were mixed 1:2 with HPLC-grade methanol and immediately direct-injected into a 12 T
193 Bruker ESI-FTICR-MS spectrometer operating in negative mode. Solid peat samples (from an 8-18 cm
194 deep section at each site) were analyzed after water-extracting the dried and ground peat samples. For
195 this method, 0.5 g of the dried and ground peat, which is expected to yield 25 mg C, was added to 1 mL
196 of degassed deionized water and then placed on a shaker for 2 hours. The solutions were then
197 centrifuged to form a pellet and the supernatant was decanted. The supernatant and porewater
198 samples were then each mixed 1:2 (by volume) with HPLC grade methanol, and the resulting solutions
199 were injected through direct injection onto a 12 T Bruker ESI-FTICR-MS spectrometer operating in
200 negative mode. For each sample, ninety-six individual scans were averaged and then internally
201 calibrated using organic matter homologous series separated by 14 Da (i.e., CH_2 groups). The mass
202 measurement accuracy was <1 ppm for singly charged ions across a broad m/z range (i.e., $200 < m/z <$
203 1200). Chemical formula assignments were made using an in-house built software program following
204 the Compound Identification Algorithm, described by Kujawinski and Behn (2006) and modified by
205 Minor et al., (2008) and based on the following 'Golden Rules' criteria: signal/noise > 7, and mass
206 measurement error < 1 ppm, taking into consideration the presence of C, H, O, N, S and P and excluding
207 other elements. All observed ions in the spectra were singly charged based on identification of 1.0034
208 Da spacing found between carbon isotopologues of the same molecule (e.g., between $^{12}\text{C}_n$ and $^{12}\text{C}_{n-1}-$
209 $^{13}\text{C}_1$). Two technical replicates were collected for most samples and, when available, peaks present in

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210 either (or both) spectra were combined and the signal intensities were averaged for downstream
211 analysis.

212 Complex organic matter such as both the plant extracts and the peat are expected to result in
213 thousands, if not tens of thousands, of unique compounds by FTICR-MS. A number of approaches exist
214 to aid in visualizing such complex datasets. These include the use of van Krevelen diagrams that depict
215 the H/C vs. O/C ratios of individual compounds, which enables tentative inferences about general
216 compounds classes. For example, lipids are generally low O/C with high H/C, while carbohydrates
217 generally fall in the region near O/C = 1 and H/C = 2. In addition, the molecular formulae derived from
218 FTICR-MS analyses can be used to calculate the nominal oxidation state of the carbon (NOSC) in
219 individual compounds observed in the DOM. This is done through a simple calculation from the
220 molecular formula $NOSC = 4 - (4C + H - 3N - 2O + 5P - 2S)/C$ (Keiluweit et al., 2016), but provides
221 tremendous insight into the thermodynamic energy yield on oxidation of that C (La Rowe and van
222 Cappellin 2011), which is directly relevant to understanding organic matter quality (Wilson and Tfaily
223 2018).

224 *Chemical transformation Analysis*

225 Chemical transformation analysis of the chemical compounds identified by FTICR-MS involves
226 calculating the mass differences between individual compounds and matching those mass differences to
227 specific chemical moieties. By matching these results with known biochemical transformations
228 accomplished by microorganisms in the environment, it is possible to infer the decomposition pathways
229 by which individual compounds are degraded and produced (e.g., Stenson et al., 2003; Kujawinski et al.,
230 2016; Wilson et al., 2017). This process is possible because of the extremely high mass resolution of the
231 FTICR-MS technique which allows us to narrow down the possible matches within 1 ppm. The current
232 database of microbial transforms contains 186 unique transforms (Wilson et al., 2017), including
233 hydroxylation, methoxylation, and transamination reactions.

234

235 **Results**

236 The pH for the porewater at the bog surface averaged 4.2 ± 0.2 . In the fen, the porewater pH at the
237 surface averaged 5.6 ± 0.4 . No porewater was available in the surface palsa for collection.

238

239 *FT-IR*

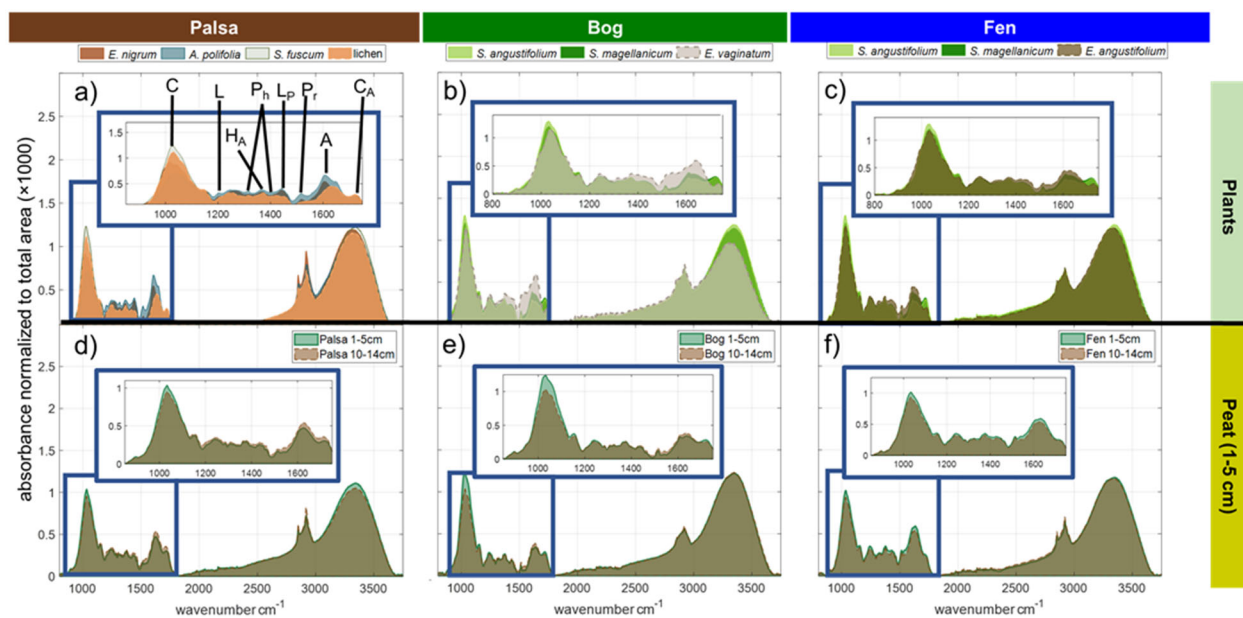
240 The leaf and stem FT-IR spectra were quite similar for both vascular plants (*E. nigrum*, *A.*
241 *polifolia*) in the palsa habitat, with the exception that *A. polifolia* leaves had lower carbohydrate content
242 and *E. nigrum* leaves had lower carboxylic acid content and aliphatic waxes compared to stems from the
243 same plant (Figure 1; Supplemental Table 2). Because of the similarity between leaf and stem spectra for
244 each plant and because of expected higher turnover of leaves compared with stems, we compared the
245 FT-IR spectra from the leaves of the dominant plants to the peat in each habitat type (Figure 1). High
246 peak intensities were observed at wavenumbers corresponding to carbohydrates (i.e., O-alkyls at 1030
247 cm^{-1}); lignin (1265 cm^{-1}); humic acids (1426 cm^{-1}); phenolic lignin-like structures (1515 cm^{-1}); protein-like
248 (1550 cm^{-1}); aromatics (1650 cm^{-1}); C=O stretching associated with carboxylic acids, aldehydes ketones

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249 and other oxygenated moieties (1720 cm^{-1}); and aliphatic fats (2920 cm^{-1} and 2850 cm^{-1})(Supplemental
 250 Table 2). In the palsa, the two depths of peat were very similar, with deeper peat having a slightly higher
 251 aromatic, carboxylic acid, and waxy lipid content relative to the shallower peat (Figure 1d). The
 252 carbohydrate content of the palsa peat was lower than the *S. fuscum* and lichens. The waxy lipids, peaks
 253 2850 cm^{-1} and 2920 cm^{-1} , were extremely well differentiated in the leaves of *E. nigrum* and *A. polifolia*
 254 compared to the leaves of *S. fuscum* and lichens (Figure 1a).

255 In the bog, *Sphagnum* mosses and *E. vaginatum* leaf and bog peat FT-IR spectra were compared
 256 (Figure 1b,e). The waxy lipid peaks at 2850 and 2920 cm^{-1} were slightly more differentiated in the *E.*
 257 *vaginatum* compared to the *Sphagnum*, consistent with higher waxy lipid content in *E. vaginatum*. The
 258 leaf carboxylic acid peak (1720 cm^{-1}) was stronger in the *Sphagnum* compared to the *E. vaginatum*. The
 259 bog peat had the highest humic acid content of any of the sites (Supplemental Table 2).

260 In the palsa, *E. vaginatum* had the highest leaf aromatic content (Supplemental Table 2). In the
 261 FT-IR spectra of the peat from the different habitats (Figure 1d, e, f) several absorption bands typical of
 262 humic materials were observed in our samples (Artz et al., 2008; Chapman et al., 2001; Leifeld et al.,
 263 2012). The bog peat had the highest carbohydrate content of any of the sites. The fen peat had a higher
 264 abundance of protein-like structures and lower abundance of carboxylic acids compared to the other
 265 sites. Aliphatics (2920 cm^{-1} and 2850 cm^{-1}) were much less well defined in the bog peat compared to the
 266 other sites, indicating fewer waxy lipids (Artz et al. 2008; Coccozza et al. 2003) compared to the other
 267 sites. Comparisons between the shallow and deep peat (Figure 1d,e,f) at each site indicated differences
 268 in decomposition among the habitats. Carbohydrates, protein-like structures, and aromatics became
 269 less pronounced with depth in the fen, while aliphatic waxes increased and humic acids decreased with
 270 depth in the bog.



271
 272 Figure 1: Layered FT-IR spectra comparing dominant plants (leaf material only) and peat in each habitat.
 273 All spectra are baseline-corrected and normalized to total peak area as described in Hodgkins et al.,
 274 (2018). Inset plots enlarge the $850\text{--}1750\text{ cm}^{-1}$ region where many chemical functional groups exist within
 275 a short span of wavenumbers. In the panel (a) inset, important peaks discussed in the text are marked: C

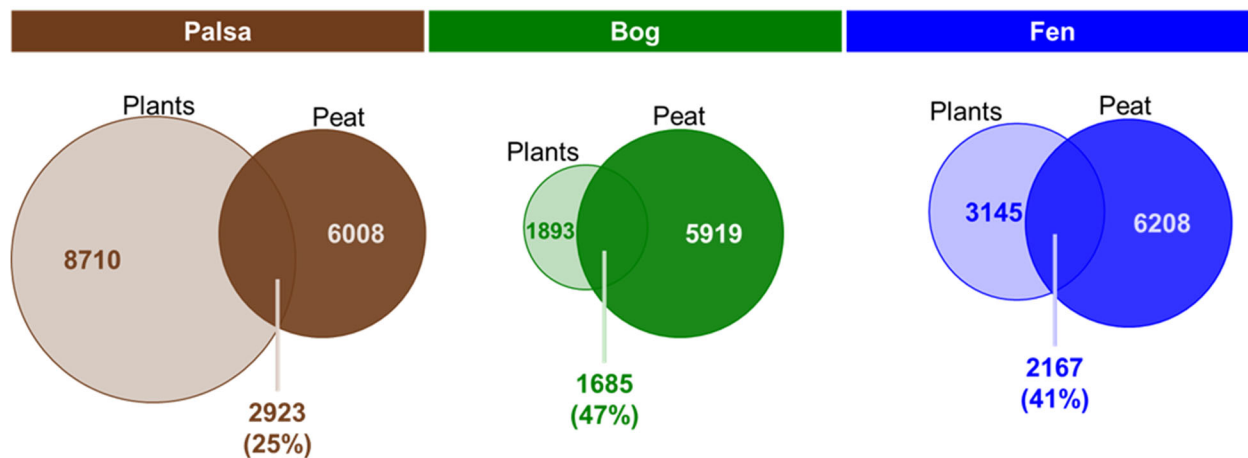
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276 = carbohydrates, L = lignin, H_A = humic acids, P_h = phenolic-lignin, L_p = lignin-like, P_r = proteinaceous, A =
277 aromatics, C_A = carboxylic acids. Panel (a) shows the overlaid spectra for lichens, *A. polifolia*, *E. nigrum*,
278 and *S. fuscum*, the dominant plant types in the palsa, while palsa peat spectra are shown in panel (d).
279 Panel (b) shows the overlaid spectra for the bog's dominant plants *S. angustifolium*, *S. magellanicum*,
280 and *E. vaginatum*, with the bog peat in panel (e). Panel (c) shows the fen's dominant plants, *E.*
281 *angustifolium*, *S. angustifolium*, and *S. magellanicum*, which are reflected in fen peat in panel (f).

282

283 FTICR-MS Results

284 Among all of the plant samples, leaves, stems, and roots combined we observed 19,072
285 compounds via FTICR-MS. Of those, we were able to assign a molecular formula to 14,260 compounds
286 (75%), which is a typical assignment rate for complex SOM. Across all habitats in the peat, we observed
287 15,198 unique compounds of which we were able to assign molecular formulae to 11,254 (74%). Palsa
288 plants had the highest diversity of compounds (n = 11,633, Figure 2). Of those, the majority of
289 compounds were not present in the peat (75%) suggesting that they were microbially decomposed
290 and/or processed. The remaining 25% were present in the peat, suggesting that they are resistant to
291 microbial decay and accumulate over time (Figure 2). The bog plants had the lowest diversity of
292 compounds (n = 3578) but they also appeared to be the most resistant to microbial decomposition as
293 47% were observed in the bog peat. The fen was intermediate between the palsa and bog with fen
294 plants having 5312 compounds of which 41% were observed to accumulate in the peat (Figure 2).



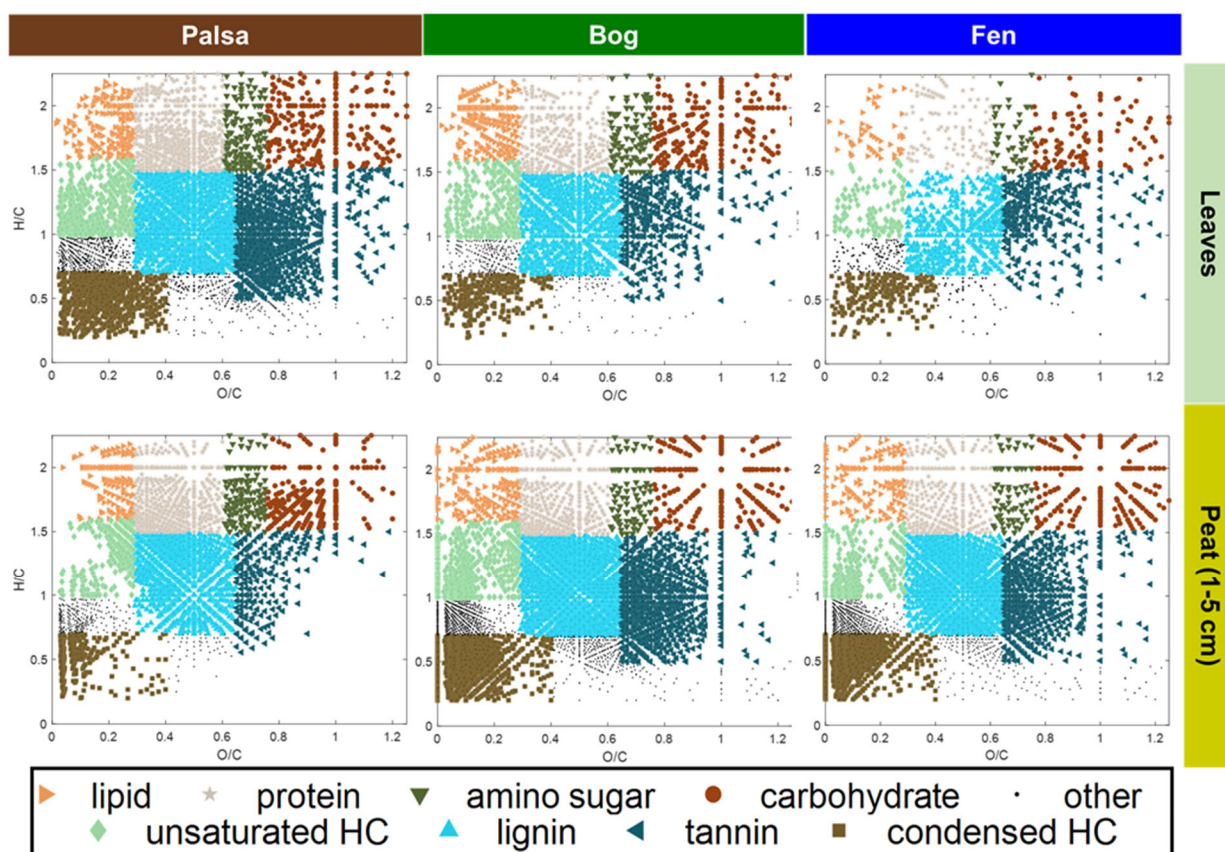
295

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

302 We compared the compounds observed in the composite plant extracts (leaves only, or whole
303 plants for lichens and mosses) to those in the shallow peat from each habitat type (Figure 3) (The
304 supplement contains comparisons of the stem extracts from the palsa, Supp. Fig. 1, and root extracts to
305 the peat for each habitat, Supp. Fig. 2). There were striking differences in the plant leaf compounds as

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306 well as the peat across the different habitats (Figure 3). The plant composite in the fen (including
 307 extracts of *E. angustifolium*, and *C. rostrata*) had low numbers of lipid-like (fatty acids) and protein-like
 308 compounds relative to the dominant plants from the palsa (lichens, *A. polifolia*, and *E. nigrum*) and bog
 309 (*Sphagnum* and *E. vaginatum*) and habitats (Figure 3). Both the bog and fen peat had relatively more
 310 tannin-like compounds compared to the palsa peat despite having lower abundances of these
 311 compounds in their plant composites relative to the palsa.

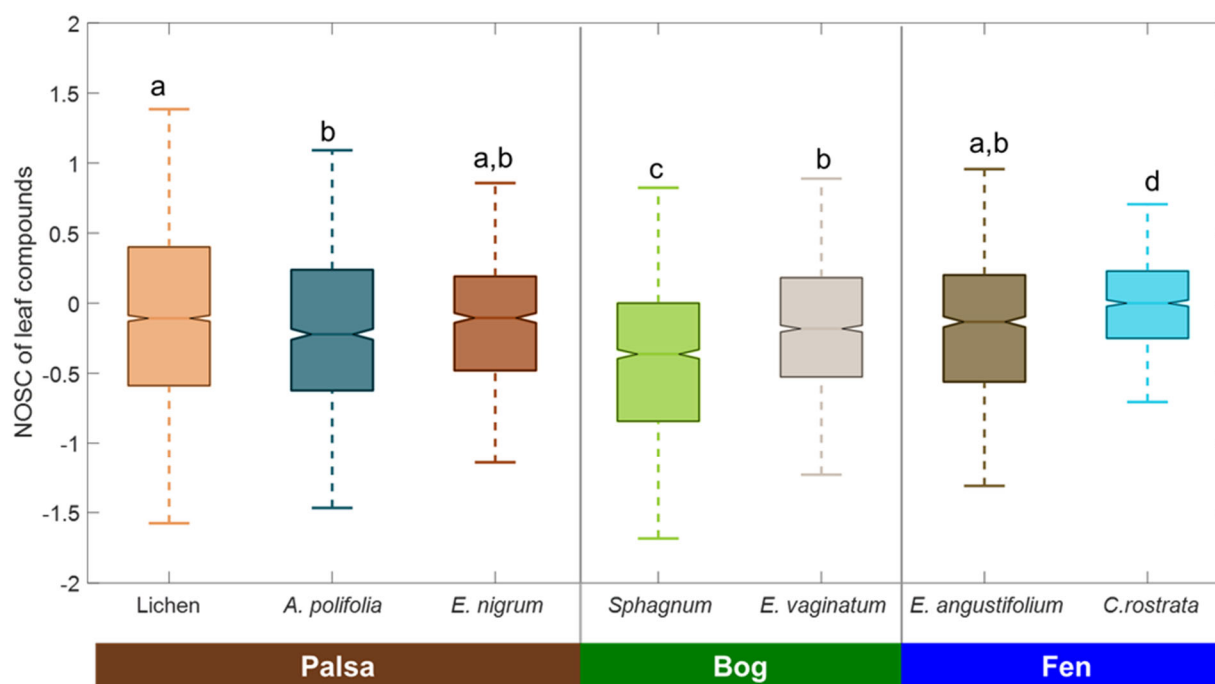


312
 313 Figure 3: The combined FTICR-MS of the dominant plant species' leaves (or for mosses and lichens, the
 314 entire plant) and near-surface (1-5 cm) peat extracts from each habitat. Dominant plants for the palsa
 315 were lichens, *A. polifolia*, and *E. nigrum*; for the bog *Sphagnum* and *E. vaginatum*; and for the fen *E.*
 316 *angustifolium* and *C. rostrata*. Each point represents an observed molecular formula, and is categorized
 317 by color and symbol according to inferred compound classes.

318
 319 We calculated the nominal oxidation state of the carbon (NOSC) in the water extracts of the
 320 dominant plant leaves (whole plants for lichens, *Sphagnum*) from each habitat (Figure 4) as a metric for
 321 determining organic matter quality (Wilson and Tfaily 2018). Lichens, *A. polifolia*, and *E. nigrum*
 322 together comprise 31% of the aboveground leaf, 95% of aboveground stem, and 22% of the
 323 belowground (root) biomass in the palsa. *Sphagnum* accounts for 74% of the biomass in the bog overall,
 324 with *E. vaginatum* contributing 13% of the bog's aboveground and 20% of the belowground biomass. In
 325 the fen, *E. angustifolium* is 63% of the aboveground and 81% of the belowground biomass, while *C.*
 326 *rostrata* contributes approximately 5% of the above and belowground biomass. *Sphagnum* had the

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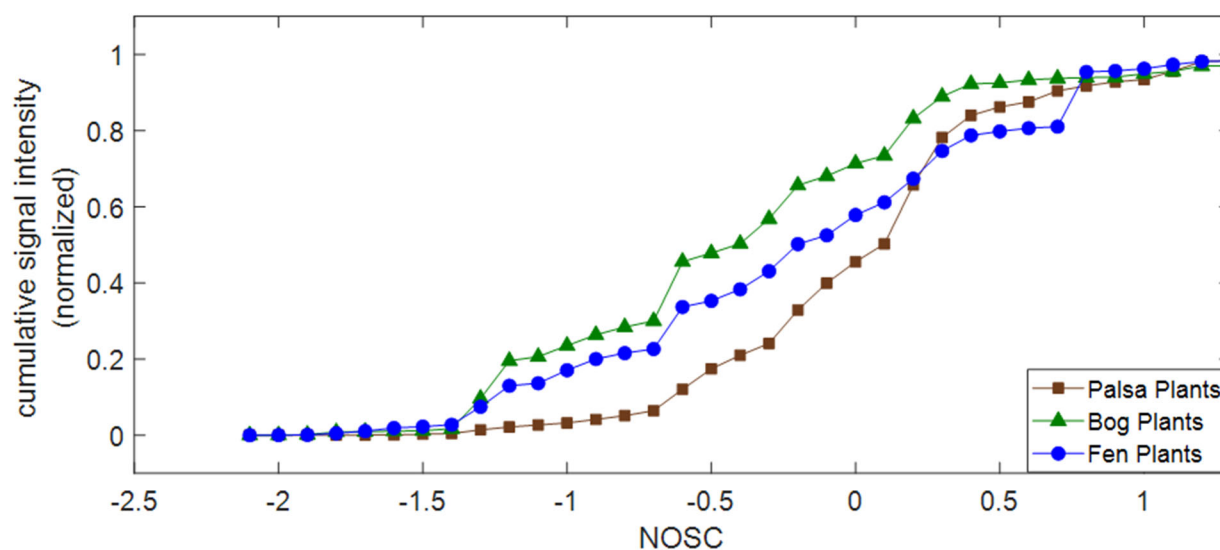
327 lowest NOSC of any of the habitat-dominant plants (Figure 4). *E. angustifolium*, in the fen, had
328 intermediate NOSC values that were nevertheless significantly higher than those found in *Sphagnum*.
329 The palsa plant community was more diverse, lichens had the highest NOSC values and *E. nigrum* and *A.*
330 *polifolia* had significantly higher NOSC values than *Sphagnum*.



331
332 Figure 4: Nominal oxidation state of carbon (NOSC) for dominant plant leaf extracts (whole plants for
333 lichens, *Sphagnum*) from each habitat. Different lowercase letters above bars indicate significant
334 differences by ANOVA followed by pairwise comparison (Tukey's Honestly Significant Difference).

335 It is possible that the average NOSC was being disproportionately influenced by a large number
336 of compounds with extreme NOSC values, but that were present at overall low concentration. To
337 determine whether this was the case, we calculated the normalized signal intensity for each compound
338 in the composite of all plant parts (leaves, stems, and roots combined) from all plants collected in each
339 habitat. We plotted the cumulative normalized signal intensity against the NOSC of the compounds
340 (Figure 5) and found that compounds with NOSC < 0 accounted for 46% of the signal intensity in the
341 palsa, 71% of the signal intensity in the bog, and 58% of the signal intensity in the fen. Although not
342 strictly quantitative within similar sample types, signal intensity roughly follows concentration in
343 samples with similar overall matrices.

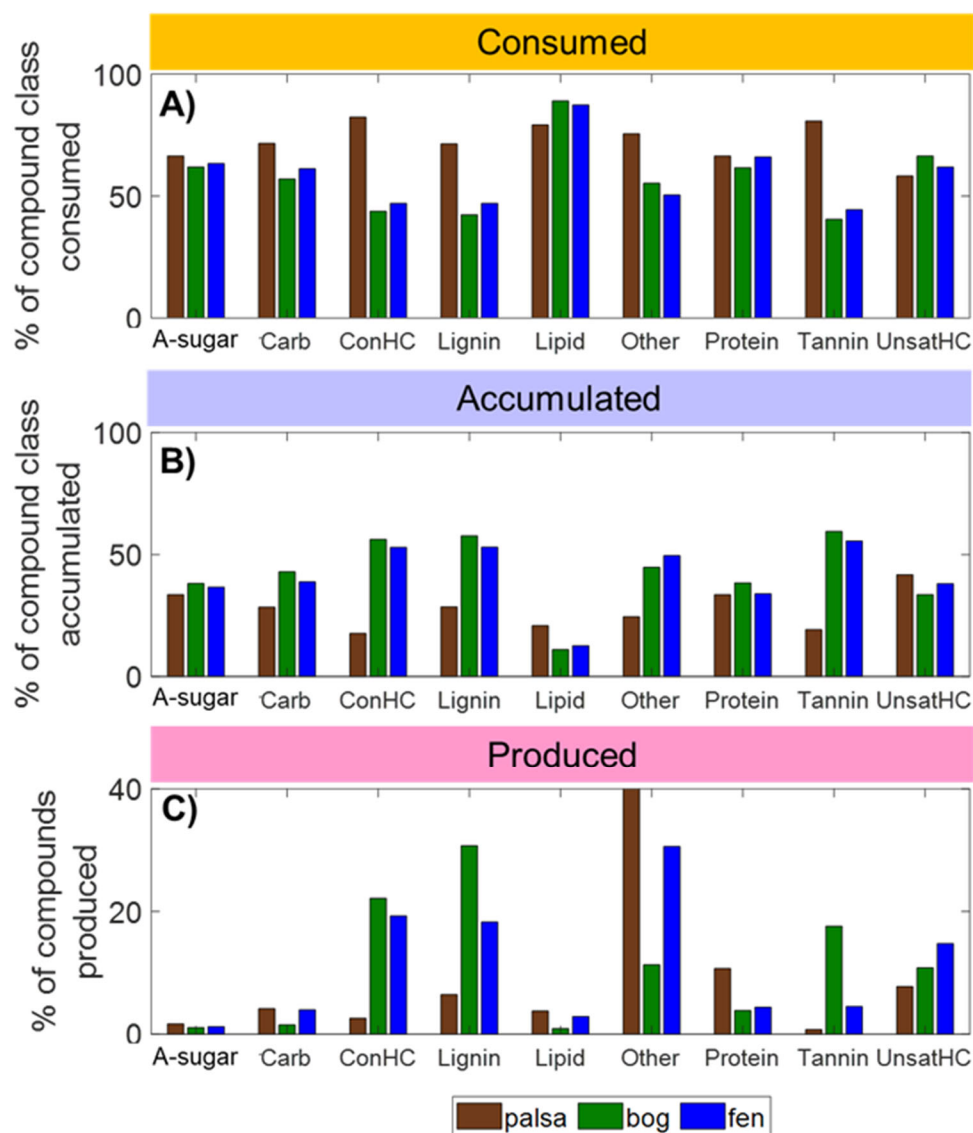
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344
345 Figure 5: Cumulative signal intensity normalized to total intensity as a function of NOSC in the composite
346 plant samples from each habitat.

347 We then examined the characteristics of the plant-associated compounds that were either (1)
348 consumed or that (2) accumulated in the peat as well as the compounds in the peat that were not
349 present in the original plant material and were therefore assumed to be (3) microbially produced (Figure
350 6). Consumed compounds are those that appear in the plant extracts but not in the peat suggesting that
351 they were decomposed. Accumulated compounds appear in both the plants and the peat, apparently
352 resistant to decay. Some compounds appear only in the peat suggesting that they were produced during
353 decomposition presumably by microbial processes, although abiotic production is also possible (Fudyma
354 et al., 2020). This comparison is sensitive to even minor abundance plant compounds, for example,
355 compounds could appear to be produced if they came from a minor species that was not included in the
356 plant mixture. To minimize this effect, we included all plant parts (leaves, stems, and roots) from all
357 plant species sampled at a given habitat (regardless of abundance) to compare against the peat
358 compounds. In the palsa, this included: lichens, *A. polifolia*, *E. nigrum*, *D. elongatum*, *R. chamaemorus*,
359 and *B. nana*. In the bog this included *Sphagnum*, *E. vaginatum*, and *E. angustifolium*. In the fen this
360 included *E. angustifolium*, *C. rostrata*, and *Sphagnum*. In the palsa, tannins, lignins, condensed
361 hydrocarbons, and carbohydrates were more readily consumed compared to the bog and fen. In
362 contrast, a higher percentage of the total lipid content was consumed in the bog and fen compared to
363 the palsa. In the palsa a lower percentage of the lignins, tannins, and condensed hydrocarbons
364 accumulated in the peat (Figure 6) suggesting that the higher redox in the palsa facilitated the
365 decomposition of these types of compounds. Compared to palsa, a high proportion of condensed
366 hydrocarbons, tannins, and lignins appeared in the bog and fen (Figure 6 c) peat. In addition to
367 unclassified ('other') compounds, a high proportion of protein-like compounds were produced in the
368 palsa compared to the other sites (Figure 6 c).

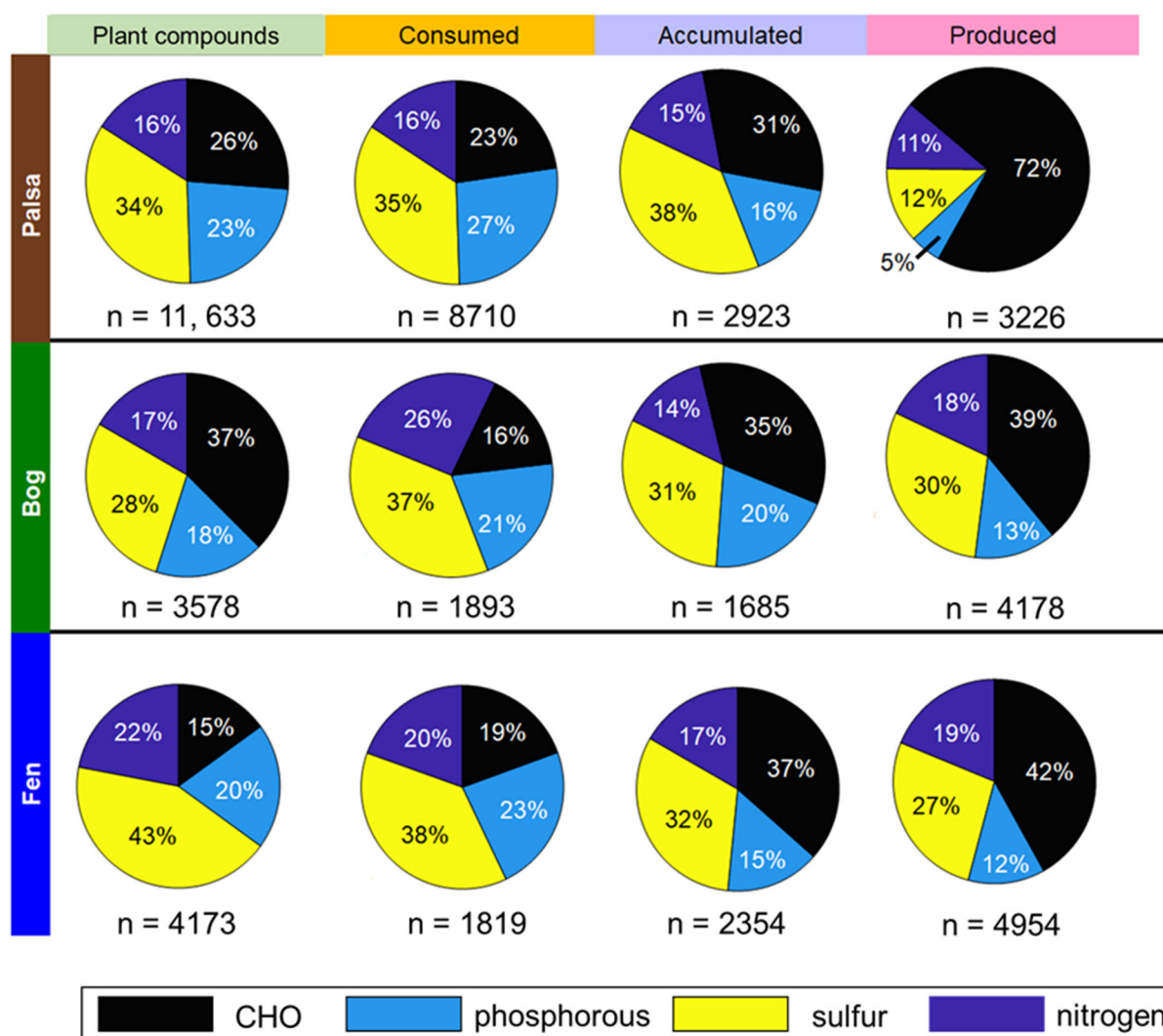
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369
 370 Figure 6: Inferred percentages of consumed, accumulated, and produced compounds within the peat
 371 extracts, by chemical class (inferred from the molecular formulae from FT-ICR MS, per Figure 3), for each
 372 habitat. (A) Percentage of consumed compounds, calculated as the number of consumed compounds in
 373 each class divided by the total number of compounds in that class originally present in the plant
 374 extracts. (B) Percentage of accumulated compounds, calculated as the number of plant compounds of
 375 each class that were also present in the peat, divided by the total number of compounds in that class
 376 originally present in the plant extracts. (C) Percentage of produced compounds, calculated as
 377 compounds present in the peat but absent from the plant material, and are inferred to be microbially
 378 produced, divided by the total number of compounds in the peat. Note that the maximum y-axis value
 379 in (C) was set to 40% to improve visualization of differences; the only produced class that exceeded 40%
 380 was the unclassified “other” compounds at 62.5% in the palsa.

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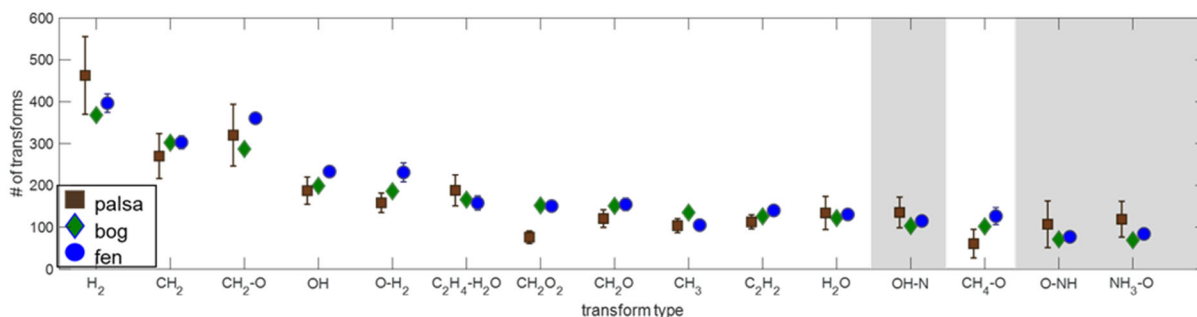
381 We also examined the nitrogen (N), sulfur (S), and phosphorus (P) content of the various
 382 compounds (Figure 7). Overall, the plants in the fen had a higher proportion of both nitrogen and sulfur
 383 containing compounds compared to the plants in either the bog or palsa. In the bog, a higher
 384 percentage of nitrogen-containing compounds was consumed relative to either the fen or the palsa
 385 (Figure 7). Additionally, when compared to the proportions present originally in the plants, a higher
 386 percentage of N- and S-containing compounds were consumed in the bog. A higher percentage of CHO-
 387 only compounds accumulated in the fen compared to the starting plant material suggesting that N-, S-,
 388 and P-containing compounds were preferentially consumed. A high percentage of the produced
 389 compounds in the palsa were CHO-only compounds and very few phosphorus or sulfur containing
 390 compounds were produced. This result contrasts with the bog and fen where phosphorus and sulfur
 391 containing compounds were ~40% of the total compounds produced.



392
 393 Figure 7: The proportion of compounds that were exclusively CHO or that contained N, S, or P, in each
 394 habitat, for total plant compounds (for leaves, stems, and roots of the plants collected in each habitat),
 395 and those inferred to have been consumed, accumulated, or produced in the peat. Percentages the
 396 number of compounds in each category, divided by the total number of compounds in the group (n)
 397 indicated under each chart.

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398 To understand potential differences in the decomposition pathways among the three habitats
399 that have contributed to the differences observed in the produced compounds, we calculated the
400 number of times each transform (i.e., chemical transformation pathways by which SOM decomposes)
401 occurred within a sample in the peat and plotted the most frequently observed transforms from each
402 site (Figure 8). Hydrogenation (H_2) was the most frequent transform for all of the habitat types.
403 Demethylation followed by oxidation (CH_2-O) was the second most frequent for the palsa and fen, but
404 side-chain (de)methylation (CH_2) was second for the bog. Transformations involving changes of N (OH-N,
405 O-NH, and NH_3-O) were highest in the palsa.



406
407 Figure 8: Top transforms for each habitat's peat given as the molecular differences among compounds
408 (i.e., H_2 refers to a difference of 2 hydrogen atoms). Points are plotted as averages \pm 1 s.d. for 3 samples
409 of palsa, and for 2 samples of fen; one sample was available for bog. Transforms involving nitrogen are
410 highlighted in gray.

411

412 Discussion

413 In our investigation of changes in plant and soil organic material (SOM) composition along a
414 permafrost thaw gradient, we observed a strong relationship between the plant-derived organic
415 compounds and SOM compounds suggesting that aboveground vegetation and roots shape
416 belowground processes and subsequent SOM decomposition in this peatland. Across the thaw gradient,
417 there were significant changes in CO_2 and CH_4 production potential (Hodgkins et al., 2014) and emissions
418 (McCalley et al., 2014). The palsa was associated with net CO_2 emission and little, or no, CH_4 production,
419 the bog and fen both exhibit net CO_2 uptake, and CH_4 emissions from the fen were the highest of the
420 three habitat types (Bäckstrand et al., 2010; McCalley et al., 2012). $CO_2:CH_4$ ratio production potentials,
421 clearly indicated that the fen was the most methanogenic of the three sites (Hodgkins et al., 2014).

422 Hodgkins et al. (2014) found that differences in the major SOM classes drove variability in
423 greenhouse gas (GHG) emissions across the mire. In particular, they ascribed increasing GHG emissions
424 across the thaw gradient to increasing SOM lability as inferred from decreasing C/N ratios and lower
425 molecular weight, aromaticity, organic acid, and organic oxygen contents. Our results support that
426 conclusion and further show that differences in SOM are driven by changes in the plant community,
427 confirming the central role of plants in controlling SOM quality. The plant community is the initial source
428 of the organic matter to the subsurface (Sutton-Grier and Megonigal, 2011). Microbial decomposition
429 then removes some chemical species while creating others, thereby modifying the inputs in a way that is
430 partially dependent on oxygen availability within each habitat. *Sphagnum* plays a particularly strong role
431 in habitats where this species dominates. Organic matter in *Sphagnum* extracts has significantly lower

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432 NOSC than other abundant plant species (Figure 4). Such low NOSC is consistent with low organic matter
433 quality (Wilson and Tfaily 2018) suggesting a mechanism for suppressed SOM decomposition in the bog,
434 especially as compared to the fen. In addition, *Sphagnum* produces many compounds that are
435 potentially inhibitory to microbial activity (Fudyma et al. 2020) including organic acids which result in
436 lower pH in the bog relative to the fen habitat. All of these factors work synergistically to facilitate C
437 storage in *Sphagnum*-dominated environments. The percentage of plant compounds that accumulate in
438 the peat, and are therefore less bioavailable, increases from palsa (25%) to fen (41%) to bog (47%)
439 (Figure 2), which is opposite to the trend in plant species diversity across the habitats. *Sphagnum* limits
440 decomposition rates by producing low NOSC compounds (Figure 4), producing microbially inhibitory
441 compounds (Fudyma et al., 2020), but it appears that these effects of *Sphagnum* can be attenuated by
442 increasing proportional cover of other plant species.

443 The high carbohydrate peak in the FT-IR analysis of the bog peat relative to the other habitats
444 (Figure 1) was unexpected, particularly since CO₂ production potential is low in the bog (Hodgkins et al.,
445 2014) and carbohydrates are a highly bioavailable C source that should stimulate production. However,
446 the high carbohydrate content of the bog peat is consistent with other observations that sugars tend to
447 accumulate in *Sphagnum*-dominated peat (AminiTabrizi et al., 2020), and that the hydrolytic enzymes
448 responsible for the initial breakdown of carbohydrates are less active in bog peat relative to the other
449 habitat types (Woodcroft et al., 2018). Analysis of the solid phase (FT-IR) bog peat revealed high
450 abundance of bioavailable carbohydrates, however, the FTICR-MS analysis revealed low quality organic
451 matter in the water-soluble fraction. This implies that the availability of labile C in the bog is, in part,
452 limited by solubilization of the cell walls, likely due to the low pH in the bog (pH = 4.2) which is known to
453 inhibit DOM hydrolysis (Curtin et al., 2016). The high relative abundance of the carboxylic acid peak in
454 the solid *Sphagnum* (Figure 1) is consistent with the high abundance of carboxylated sugars and uronic
455 acids that comprise the structural components of *Sphagnum* cell walls (Painter 1991; Ballance et al.,
456 2007) which could explain the relatively high carbohydrate peak in the solid bog peat as well as the
457 lower pH in the bog relative to the fen.

458 In the fen, FT-IR results show a greater reduction in the intensities of nearly all of the important
459 functionalities with depth of the peat compared to any of the other habitats (Figure 1f) which we
460 conclude reflects higher decomposition rates. In both the palsa and fen it appears that decomposition
461 rapidly follows organic matter deposition, based on the low abundance of carbohydrates even in the
462 shallow peat relative to the available plants. In contrast, the bog peat intensities are quite similar to
463 those of the *Sphagnum*, suggesting that the organic matter has changed (decomposed) little following
464 deposition. This result is consistent with the lower GHG emissions in the bog relative to fen (McCalley et
465 al., 2014; Hodgkins et al., 2014) and the supposition that bog SOM is less bioavailable than fen SOM.

466 We found a high abundance of waxy lipids in the leaves of *E. nigrum* and *A. polifolia* from the
467 palsa (as seen in the strong differentiation between the 2850 cm⁻¹ and 2920 cm⁻¹ FT-IR peaks; Figure 1a)
468 (Artz et al. 2008; Coccozza et al. 2003). While these compounds are frequently thought to be refractory,
469 they do not appear as strongly even in the shallow peat, suggesting that they are at least partially
470 degraded following deposition. Alternatively, because the leaves of *E. nigrum* and *A. polifolia* are very
471 small and evergreen, they are likely underrepresented in the peat since they don't all drop in the fall
472 (unlike the deciduous plants in the habitat). The low differentiation between these peaks in the lichen is
473 consistent with lichens lacking the waxy cuticle that coats plant leaves. The low relative abundance of

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474 carbohydrates in the palsa peat relative to the abundant plant species is consistent with fast
475 decomposition in the surface depleting highly bioavailable compounds soon after deposition.

476 While FT-IR is practical for looking at overall changes of functional groups in the bulk solid-phase
477 SOM, FTICR-MS provides finer-resolution detail of the water-extractable compounds, down to the
478 individual molecular level. Overall, we observed fewer unique compounds in peat samples relative to
479 the plant sample set as determined by FTICR-MS (15,198 vs 19,072 respectively). This result is consistent
480 with loss of compounds with decomposition of the plant material following deposition. The percent of
481 plant compounds that were also found in the peat increased from palsa (25%) to fen (41%) to bog (47%)
482 (Figure 2). This pattern suggests that a higher percentage of plant compounds were decomposed in the
483 palsa so that they are no longer detectable. The apparently higher decomposition in the palsa occurs
484 even though the palsa also has the greatest number of different compounds of all the sites. The richness
485 (i.e., number) of compounds observed in the plants across the different habitat types (Figure 2) follows
486 the same pattern as the plant species diversity changes across the sites: palsa > fen > bog (Hough et al.,
487 2020; Johansson et al., 2006). Interestingly, this trend is opposite that observed in the diversity of the
488 plant-associated microbial communities across these sites (Hough et al., 2020; Wilson et al., 2021b).
489 Nevertheless, the richness of compounds in the peat is similar across the different habitats, which
490 suggests that a high diversity of microbial pathways in the bog and fen is responsible for transforming
491 the less diverse plant matter into more diverse peat.

492 While there is considerable overlap in common compounds between the peat and the dominant
493 plant types found within each habitat, many of the plant compounds were not found in the peat, while
494 the peat also had many unique compounds not found in the plants. These results indicate both loss and
495 production of novel compounds following plant organic matter deposition, presumably through the
496 metabolic action of microorganisms. Only 25% of compounds from the palsa plant composite were also
497 observed in the shallow peat (Figure 2), indicating that 75% of plant compounds were either consumed
498 or metabolically processed into other molecules and that the plants in the palsa were largely
499 bioavailable and susceptible to decomposition. It is likely that the higher lability (as inferred from NOSC)
500 of the dominant plant compounds (Figure 4) contributes to the greater decomposition of organic matter
501 from palsa plants. Additionally, the higher availability of oxygen as a terminal electron acceptor (TEA) in
502 the palsa compared to the other sites could catalyze the decomposition of a range of bioavailable
503 compounds in the palsa relative to the other habitats. The higher oxygen content could explain why
504 hard to decompose chemical classes such as tannins, lignins, and condensed hydrocarbons, which
505 accumulate in the bog and fen, are more readily consumed in the palsa (Figure 6).

506 In highly oxygenated environments, production of CO₂ is thermodynamically favored, but in
507 anoxic, TEA-depleted, waterlogged environments, CO₂ is sometimes the only available TEA, resulting in
508 CH₄ production. Plants exert a strong influence on the CO₂:CH₄ ratio by being the prime source of
509 organic substrates (i.e., electron donors) in the subsurface (Meronigal et al., 2004; Sutton-Grier and
510 Meronigal 2011), and by controlling the availability of TEAs used in decomposing that organic matter.
511 There is a strong relationship between NOSC calculated from the molecular formula and the
512 thermodynamic catabolic energy yield on oxidation of that C (LaRowe and van Cappellin 2011;
513 Keiluweit et al., 2016), and that energy yield is a measure of organic matter quality (Wilson and Tfaily
514 2018). Natural organic matter typically has NOSC values ranging from -4 to +4 with corresponding ΔG°_{c}
515 ΔG°_{ox} ranging from -54 to +174 kJ (mol C)⁻¹, which suggests that most organic matter oxidation must be
516 coupled to an energy yielding reduction in order to become thermodynamically feasible. Oxygen is

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517 capable of oxidizing compounds along the full range of NOSC values with enough energy to produce
518 ATP. Thus, OM decomposition in the aerobic palsa is unlikely to be thermodynamically inhibited,
519 although some evidence suggests that NOSC influences decomposability in aerobic environments as well
520 (Graham et al., 2017). However, in the bog and fen where inundation creates anaerobic conditions and
521 where the availability of other alternative terminal electron acceptors (such as Fe(III) or sulfate) is low,
522 decomposition becomes thermodynamically limited, resulting in the accumulation of compounds with
523 lower NOSC values such as fatty acids, waxes, and lignin.

524 While the palsa has higher oxygen availability than the other two sites, which could contribute
525 to higher decomposition rates, the higher NOSC values of the dominant palsa plant compounds (Figure
526 4) are consistent with the palsa plant material also being inherently easier to decompose, regardless of
527 the available TEAs (Keiluweit et al., 2016). The high bioavailability of palsa plants, particularly lichens
528 (Figure 4) is contrary to generally accepted ideas that the sedges, abundant in the fen, should be the
529 most easily biodegradable (Malmer et al 2005). The rate of litter input in the fen is highest of any of the
530 habitats and could be faster than the microbial community can process, leading to a build-up of
531 otherwise biologically attractive substrates (Malmer et al 2005). Similar classes of compounds
532 accumulate in the bog and fen and both habitats have high production of condensed hydrocarbons,
533 lignins and tannins compared to the palsa (Figure 6 B). These compounds are unlikely to be produced
534 microbially, but are more probably due to increased (abiotic) leaching in the waterlogged bog and fen
535 sites.

536 Nutrient limitation is a possible control of SOM decomposition in peatlands. While it has been
537 shown that *Sphagnum*-dominated peatlands are nitrogen-limited (Bragganza et al., 2006), we also found
538 evidence that dominant plants in the bog habitat are also lower in S relative to the plants from other
539 habitats (Figure 7). This result is consistent with measurements of bulk S in the litter (Hough et al., in
540 review) and suggests that S is limiting. In support of this hypothesis, the consumed compounds in the
541 bog were disproportionately S-containing compounds (37% vs. 28% S in the original plant material;
542 Figure 7). Consistent with the understanding of N limitation, the consumed compounds in the bog were
543 also disproportionately N-containing compounds (26% vs. 17% in the original plant material; Figure 7). In
544 contrast to the palsa, where the majority (72%) of putatively microbially produced compounds did not
545 contain either N, S, or P (i.e., produced compounds were largely CHO-only), both the bog and fen peats
546 had relatively large percentages of produced compounds containing these critical heteroatoms. The
547 correlation among N and S containing compounds would be consistent with the production of microbial
548 proteins. In other peatlands, climate effects such as warming have been associated with increases in
549 microbial peatland cycling (Wilson et al., 2021a). Increases in the nitrogen content of decomposing peat
550 have been observed in other studies from enhanced C losses during decomposition (Leifeld et al., 2020).
551 The large percentages of produced compounds with N, S, and P suggest potential organic S and P cycling
552 occurring in the anaerobic habitats.

553 We examined the mechanisms by which compounds are decomposed, and found that palsa has
554 the highest overall number of transforms (i.e., potential mechanisms by which the SOM is being
555 degraded), probably reflecting the diversity of aerobic pathways, but the fen also has a higher number
556 of transforms compared to the bog (Figure 8). Higher numbers of transforms in the fen relative to the
557 bog are consistent with the higher diversity of compounds in the fen plant litter stimulating microbial
558 activity and creating a more active system. Additionally, inhibitory compounds in the bog could limit
559 microbial activity, thereby suppressing the number of transforms utilized. In particular, the fen has a

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560 higher frequency of (de)hydrogenation (H₂), hydroxylation (OH), demethylation followed by oxygenation
561 (CH₂-O), and dehydrogenation followed by oxidation (O-H₂). Dehydrogenation and demethylation
562 followed by oxidation (net transform: CH₄-O) are common mechanisms of lignin decomposition (Stenson
563 et al., 2003). Finding that these reactions are more prevalent in the fen than in the bog is consistent with
564 the low lignin content of bog plants (i.e., *Sphagnum*) compared with the dominant fen plants
565 (*Eriophorum*). Surprisingly, CH₄-O is less prevalent in the palsa, where we would expect high rates of
566 lignin decomposition due to the abundance of lignin-rich woody vegetation. Additionally, the palsa had
567 the most diverse consumption of lignin-like compounds (Figure 6) and, in contrast to the other habitats
568 studied, the palsa is well-oxygenated in the surface layer, which should promote the activity of the
569 lignin-degrading enzyme phenol oxidase (Freeman et al., 2001; Sinsabaugh 2010). The FT-IR results also
570 suggest more lignin content in the palsa plants relative to the dominant plants in the fen (Figure 1 a,c),
571 but lower lignin content in the palsa peat relative to the fen peat, which also suggests decomposition of
572 lignin is occurring in the fen. To reconcile these apparently conflicting results, we hypothesize that in the
573 palsa, the greater oxygen availability allows faster, multi-step decomposition of lignin in the plant litter,
574 such that the surface peat had already lost much of the lignin or its decomposition products; whereas in
575 the fen, lignin decomposition is occurring (as inferred from the number of transforms), but is slowed by
576 oxygen limitation. An alternate explanation is that although the plants are woody, litter input in any year
577 comes mostly from the leaves, so the woody biomass has less effect on the peat.

578 Several transforms involving exchanges with N were important, particularly in the palsa,
579 including oxygen or hydroxyl exchange with N, NH, or NH₃ (Figure 8). These sorts of transforms are
580 expected to occur when intermediates of N-fixation interact with SOM (Thorn et al., 1992, 2016; Thorn
581 and Mikita 2000). The higher frequency of these N-involving transforms in the palsa could be related to
582 the abundance of lichens, which are significant nitrogen-fixers in locations where herbaceous nitrogen-
583 fixing plants are less abundant (Gunther 1989). In contrast, the mechanisms of decomposition as
584 inferred from transform abundance in the wetter anaerobic habitats seem to be more similar to each
585 other than either is to the drier palsa.

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

597

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602 Biology Integration Institute, NSF Award # 2022070. All data published in this manuscript is publicly
 603 accessible via the IsoGenie database <https://isogenie-db.asc.ohio-state.edu/>. We have no conflicts of
 604 interest to declare.

605

606 **Competing Interests Statement**

607 The authors have no competing interests to declare.

608

609

	GPS Coordinates	FT-IR	FTICR-MS
Plants			
<i>E. angustifolium</i> roots			2
<i>E. angustifolium</i> leaf			2
<i>E. angustifolium</i> (whole)		1	
<i>A. polifolia</i> . roots			2
<i>A. polifolia</i> . leaf		1	1
<i>A. polifolia</i> . stem		1	1
<i>R. chamaemorus</i> . leaf		1	2
<i>R. chamaemorus</i> . stem		1	1
<i>R. chamaemorus</i> . roots			2
<i>E. nigrum</i> . roots		1	2
<i>E. nigrum</i> . leaf		1	1
<i>E. nigrum</i> . stem		1	1
<i>B. nana</i> . leaf			1
<i>B. nana</i> . stem		1	1
<i>B. nana</i> . roots			2
<i>S. fuscum</i>		1	
<i>S. angustifolium</i>		1	
<i>S. magellanicum</i>		1	
<i>Sphagnum</i> spp			1
<i>E. vaginatum</i> roots			2
<i>E. vaginatum</i> leaf			2
<i>E. vaginatum</i> (whole)		1	
Lichen		1	2
Peat			
Palsa 1-5cm	N 68 21.1959 E 019 02.7974	1	3
Palsa 10-14cm	N 68 21.1959 E 019 02.7974	1	
Bog 1-5cm	N 68 21.1973 E 019 02.8537	1	
Bog 10-14cm	N 68 21.1973 E 019 02.8537	1	1
Fen 1-5cm	N 68 21.1992 E 019 02.8063	1	1
Fen 10-14cm	N 68 21.1992 E 019 02.8063	1	1

610

611 Supplemental Table 1: List of Samples. Numbers indicate the number of samples analyzed by the
 612 indicated method.

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613

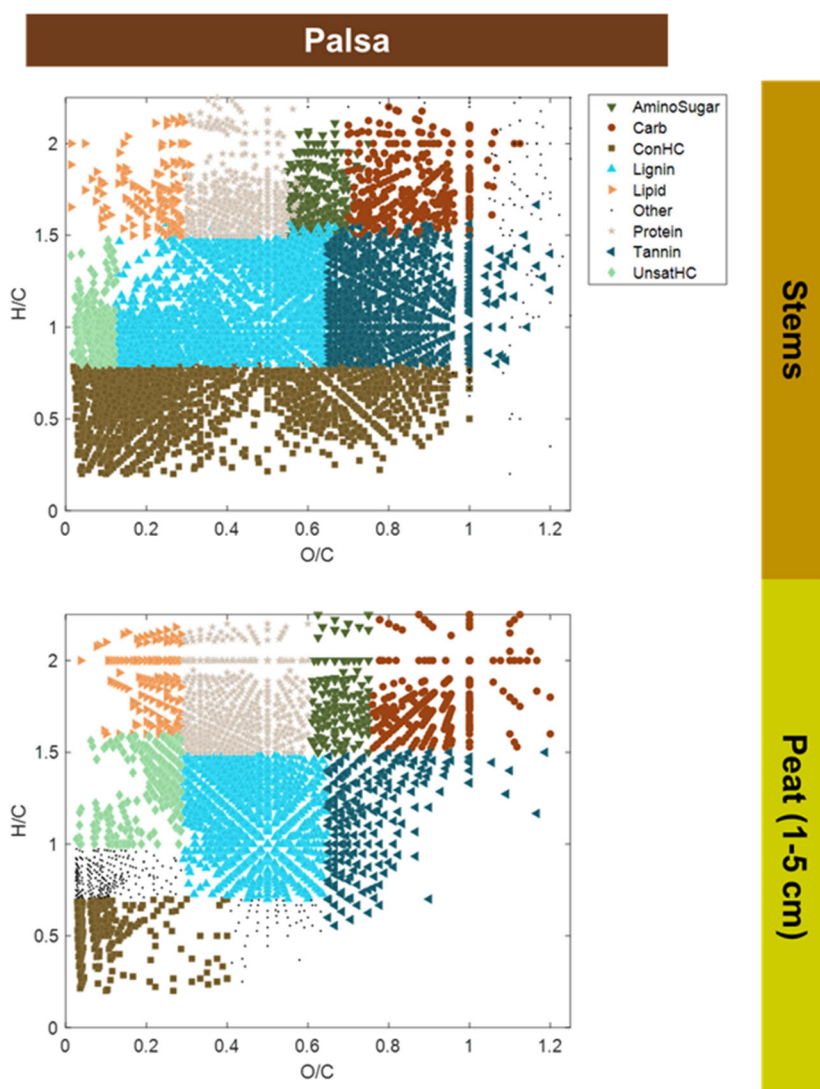
	carbohydrates (1030 cm ⁻¹)	aromatics (1650 cm ⁻¹)	lignin (1265 cm ⁻¹)	aliphatic wax ² (2850 cm ⁻¹)	aliphatic wax ¹ (2920 cm ⁻¹)	lignin-like (1515 cm ⁻¹)	phenolic lignin (1371 cm ⁻¹)	carboxylic acids (1720 cm ⁻¹)	phenolics (1440 cm ⁻¹)	humic acids (1426 cm ⁻¹)	proteinaceous (1550 cm ⁻¹)	organic acids (1700 cm ⁻¹)
Plants												
<i>E. angustifolium</i>	1.05	0.24	0.15	0.12	0.07	0.06	0.06	0.09	0.02	0.01	0.00	0.00
<i>A. polifolia. leaf</i>	0.56	0.30	0.08	0.19	0.12	0.08	0.06	0.12	0.11	0.02	0.00	0.00
<i>A. polifolia. stem</i>	1.01	0.26	0.20	0.21	0.13	0.09	0.08	0.17	0.03	0.02	0.00	0.00
<i>R. chamaemorus. leaf</i>	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>R. chamaemorus. stem</i>	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>E. nigrum. leaf</i>	0.82	0.27	0.10	0.28	0.20	0.05	0.07	0.11	0.12	0.03	0.00	0.00
<i>E. nigrum. stem</i>	0.92	0.27	0.23	0.53	0.43	0.09	0.10	0.31	0.03	0.02	0.00	0.00
<i>B. nana. stem</i>	0.88	0.29	0.23	0.11	0.05	0.09	0.08	0.15	0.04	0.02	0.00	0.01
<i>S. fuscum</i>	1.12	0.18	0.11	0.13	0.06	0.04	0.05	0.10	0.02	0.02	0.00	0.00
<i>S. angustifolium</i>	1.18	0.15	0.15	0.10	0.04	0.07	0.06	0.11	0.02	0.02	-0.01	0.00
<i>S. magellanicum</i>	1.08	0.19	0.14	0.11	0.06	0.08	0.06	0.10	0.04	0.02	-0.01	0.00
<i>E. vaginatum</i>	1.04	0.35	0.17	0.13	0.08	0.05	0.05	0.08	0.00	0.00	0.01	0.01
Lichen	0.99	0.23	0.11	0.16	0.08	0.01	0.06	0.10	0.02	0.01	0.00	0.00
Peat												
Palsa 1-5cm	0.90	0.25	0.11	0.16	0.10	0.04	0.07	0.09	0.05	0.02	0.00	0.00
Palsa 10-14cm	0.80	0.25	0.10	0.24	0.17	0.03	0.06	0.09	0.04	0.02	0.00	0.00
Bag 1-5cm	1.14	0.18	0.15	0.07	0.02	0.08	0.08	0.08	0.06	0.06	0.00	0.00
Bag 10-14cm	0.93	0.18	0.12	0.10	0.05	0.08	0.08	0.07	0.06	0.03	0.00	0.00
Fen 1-5cm	0.91	0.28	0.16	0.15	0.09	0.08	0.07	0.06	0.04	0.02	0.00	0.00
Fen 10-14cm	0.83	0.27	0.14	0.17	0.11	0.08	0.07	0.06	0.05	0.02	0.00	0.00

614 Supplemental Table 2: Normalized, baseline-corrected peak heights of major functionalities in the FT-IR
 615 spectra of the plants and peat from the different habitats. Peak heights are calculated according to
 616 modifications of Hodgkins et al., (2018) and reported as absorbance × 10³. Wavenumber assignment of
 617 functionalities is based on that given in Palozzi and Lindo (2017).
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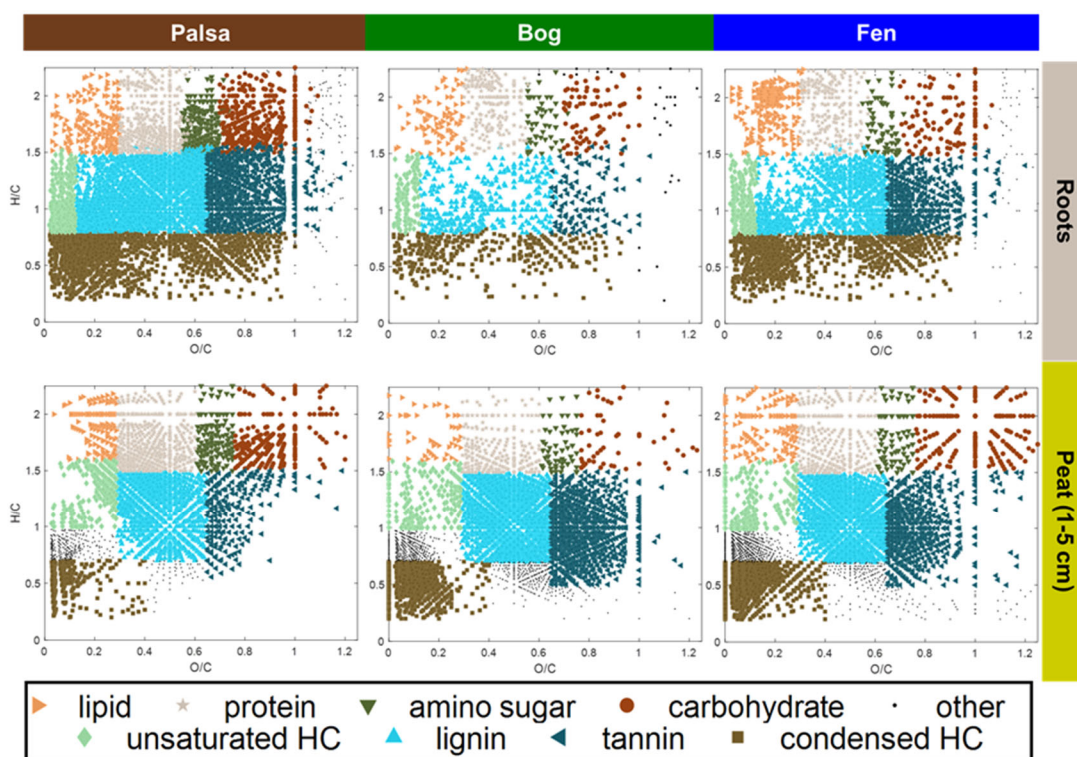


621

622 Supplemental Figure 1: Comparing compounds observed in the plant stem extracts from palsa to those
623 in the palsa peat. Symbols are color-coded according to major chemical classes as inferred from the
624 FTICR-MS-derived molecular formulae. Stems were only analyzed in the palsa so bog and fen are not
625 included.

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