



Sphagnum in *Sphagnum*-dominated peatlands: bioavailability and effects on organic matter stabilization

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Abstract The unique pectin-like carbohydrate “sphagnum” has been shown to protect organic matter from microbial decomposition in *Sphagnum*-dominated peatlands. However, the bioavailability of sphagnum has not been evaluated, and it is not known if it persists or continues to affect decomposition processes over the long timescales of peat formation. To address this, we assessed the connection between sphagnum content and organic matter decomposition rates in a temperate peatland near Fenville, MI, USA. We compared the effects of sphagnum over two timescales: (1) a short-term litter incubation assay using mosses from different peatland

microtopographies; and (2) oxic and anoxic incubation assays of peat collected from multiple depths within the peat profile, reflecting a natural long-term decomposition continuum. On both timescales, we hypothesized that higher sphagnum content would be associated with lower decomposition rates, and that sphagnum would be selectively preserved compared to bulk C and other carbohydrates. The litter decomposition experiment supported both hypotheses, as higher sphagnum content was associated with lower mass loss, and sphagnum content increased due to selective preservation. In the peat, we observed weak but significant correlations between the relative abundance of sphagnum (as a fraction of total non-cellulosic sugars) and both aerobic and anaerobic respiration rates. This relationship was stronger in cores collected from hollow microtopographies than those from hummocks. However, there was not a significant relationship between respiration rates and the total (C-normalized) sphagnum content. Sphagnum content increased with depth in the peat profile, indicating selective preservation compared to bulk C. Additionally, we observed the accumulation of non-cellulosic glucose in the deep peat, likely derived from microbial exopolysaccharides. Together, these results indicate that sphagnum persists in the catotelm and continues to contribute to the long-term stabilization of organic matter in *Sphagnum*-rich peatlands, although the weak relationship with respiration indicates that its influence is relatively minor.

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Introduction

Northern peatlands are a globally significant C sink, currently containing between 450 and 1,055 Pg C, despite only occupying 2–3% of the total land surface area of Earth (Gorham 1991; Nichols and Peteet 2019; Yu et al. 2010). C accumulation is driven by lower rates of organic matter decomposition than net primary production (Moore and Basiliko 2006). Several environmental factors, including persistent anoxia, low pH, and cool temperatures contribute to the stabilization of peat organic matter, but the apparent recalcitrance of *Sphagnum* (peat moss) also appears to play a role (van Breemen 1995). *Sphagnum* decays slower than vascular plants when exposed to the same wetland environments (Coulson and Butterfield 1978; Hobbie 1996; Moore et al. 2007). In addition, it maintains low decay rates when decomposing in mineral soil (Coulson and Butterfield 1978). These experiments demonstrate that the chemical composition or physical structure of *Sphagnum* contributes to the low rates of decomposition in peatlands, in addition to environmental factors.

The mechanisms responsible for the low quality of *Sphagnum* litter have been attributed to several compound classes, including specific phenols such as sphagnum acid (Verhoeven and Liefveld 1997; Zhao et al. 2021), lignin-like phenolics (Bengtsson et al. 2018; Zaccone et al. 2008), and structural carbohydrates (Ballance et al. 2007; Hájek et al. 2011; Stalheim et al. 2009). These three components tend to covary in *Sphagnum*, and together correlate well with the rate of *Sphagnum* litter decomposition (Bengtsson et al. 2018). Phenols and lignin-like phenolics located in *Sphagnum* cell walls have been shown to exhibit a “masking” effect, shielding structural carbohydrates from decomposition. However, they are preferentially degraded over polysaccharides in aerobic conditions due to phenol oxidase, enabling further microbial digestion of *Sphagnum* litter (Freeman et al. 2001; Schellekens et al. 2015; Tsuneda et al. 2001). Phenols are also hypothesized to play a key role in the long-term stabilization of peat due to the “enzymatic latch” mechanism, which refers to the inhibition of phenol

oxidase activity in the absence of oxygen (Freeman et al. 2004, 2001).

Among structural carbohydrates, the *Sphagnum*-specific molecule “sphagnum” has been shown to play a role in slowing *Sphagnum* decomposition, thereby aiding in C storage (Børsheim et al. 2001; Hájek et al. 2011; Maksimova et al. 2013). For example, experimentally removing sphagnum using a chemical treatment accelerated decomposition, while removing the *Sphagnum* phenols had no effect (Hájek et al. 2011). Sphagnum is a pectin-like polysaccharide comprised of an alternating galacturonic acid and rhamnose backbone (Ballance et al. 2007; Kremer et al. 2004). The mechanism by which sphagnum aids in peat preservation is debated, but is often attributed to its exceptionally high cation exchange capacity (CEC) (Painter 1991; Richter and Dainty 1989; Turetsky 2003). The high CEC of sphagnum results from the unesterified uronic acids present, and it has been demonstrated that this allows for the sequestration of N and metals, lowering nutrient availability for microbes (Painter 1991; Verhoeven and Liefveld 1997), decreasing the pH of the surrounding environment (Ballance et al. 2008; Stalheim et al. 2009), and the potential electrostatic immobilization of extracellular enzymes (Ballance et al. 2008; Painter 2003). Additionally, sphagnum fortification of cell walls, particularly in hyaline cells, may aid in the storage of water, helping to prevent decomposition (Kremer et al. 2004; Verhoeven and Liefveld 1997).

Sphagnum (along with other structural carbohydrates) has been shown to play an important role in slowing the decomposition of *Sphagnum* litter in litter bag studies. Sphagnum abundance is correlated with lower decay rates among different *Sphagnum* species (Bengtsson et al. 2018; Turetsky et al. 2008). Additionally, *Sphagnum* species that inhabit relatively dry microtopography (hummocks) generally have higher sphagnum and structural carbohydrate contents than those in lower and wetter microtopography (hollows) (Limpens et al. 2017; Turetsky et al. 2008). Several studies have demonstrated slower litter decay of hummock species despite a drier and more oxygen-rich habitat, indicating lower litter quality of the hummock species (Clymo 1965; Hájek 2009; Johnson et al. 1990; Johnson and Damman 1991).

Despite the demonstrated importance of sphagnum during the early stages of decomposition, it is not known if these short-term effects persist and

contribute to long-term stabilization of the peat. Most litter bag studies are only a few years in duration. In contrast, it takes several years for decaying litter to form surface peat, and decades to centuries for surface peat to be incorporated into the anoxic catotelm (the layer below the lowest annual position of the water table), whereupon it continues to experience anaerobic decomposition for millennia. It is not known if sphagnum persists over these longer timescales, and if so whether it continues to slow decomposition. Therefore, in this study we evaluated the bioreactivity of sphagnum over both short-term moss decomposition and long-term peat formation. Effects on short-term decomposition were evaluated using a 1-year laboratory incubation of moss tissue, and long-term effects were evaluated by comparing peat collected from different depths, with varying ages and decay histories. Sphagnum content was estimated in both moss tissues and peat by quantifying rhamnose, a sugar monomer that comprises nearly half of sphagnum (Ballance et al. 2007), but is relatively rare in other plant carbohydrates (Popper and Fry 2003; Thomas et al. 1987). Accordingly, *Sphagnum* biomass is enriched in rhamnose compared to vascular plants and other mosses (Jia et al. 2008; Philben et al. 2014a).

To evaluate the effects of sphagnum on short- and long-term organic matter preservation in peat, we evaluated two hypotheses: (1) higher sphagnum content is associated with lower decay rates over both short and long timescales (measured by mass loss for moss decomposition, and CO₂ production in peat); and (2) sphagnum accumulates with decomposition both during short-term decomposition and long-term peat formation due to selective preservation compared to other carbohydrates and bulk peat C. This would result in an increase in rhamnose concentrations over the course of the incubation experiments, and elevated concentration in deep peat compared to relatively fresh surface peat.

Materials and methods

Study site and sample collection

All moss and peat samples were collected from Miner Lake Bog in Allegan County, Michigan, USA (N 42.6074, W 86.0620). Miner Lake Bog is

a temperate peatland consisting of a small bog area (approximately 50 m²) dominated by *Sphagnum* mosses and leatherleaf (*Chamaedaphne calyculata*), and a sedge meadow dominated by *Eriophorum* spp. and *Carex* spp. sedges. *Sphagnum* samples were collected from three hollow and three hummock plots within the bog. The samples included both the green and senescent portions of the moss stems. Mosses collected from the hummocks were identified as *Sphagnum magellanicum*, and the mosses from the hollow as *Sphagnum cuspidatum*. Mosses were tentatively identified based on field observations and macroscopic examination with a dissection microscope, then confirmed using compound microscopy. Samples from each plot were processed independently and treated as replicates. Samples of a non-*Sphagnum* bryophyte (*Polytrichum* sp.) were also collected from three plots in the forest surrounding the bog for comparison.

All moss samples were inspected by hand to remove soil and vascular plant debris. Subsamples of each moss sample were oven-dried (70 °C) until constant weight, and ground using a Wiley Mill (Thomas Scientific). C and N content were determined using an Elementar Isotope Cube elemental analyzer. Water holding capacity (WHC) was determined by saturating the moss with deionized water over filter paper and recording the mass after the moss stopped dripping. The remainder of the moss samples were kept at 4 °C and field moisture content in a sealed plastic bag until the start of the decomposition experiments.

Five peat cores (3 m in length) were collected from the site using a Russian peat borer (AMS, Idaho Falls, ID, USA). Two cores (Cores 1 and 2) were collected from hollows, two (Cores 3 and 5) were collected from hummocks, and one (Core 4) was collected from the sedge meadow adjacent to the bog. Cores were collected in 50 cm segments, wrapped in plastic wrap to minimize drying and air exposure, and stored in PVC tubes cut in half lengthwise. 8 cm sections were taken from each core every 20 cm and homogenized by hand. Subsamples were weighed and dried to determine water content, then ground as described above for chemical analysis. An additional subsample was mixed with CaCl₂ in a 1:10 (w/v) mixture and pH was measured using a Thermo Scientific Orion pH electrode (Thermo Scientific, Waltham, MA, USA).

Decomposition experiments

Moss decomposition microcosms were constructed by adding 8.5 g of moss to 70 mL glass serum bottles, which were wrapped in aluminum foil prior to incubation to prevent photosynthesis. A microbial inoculum was created by mixing a sample of surface peat with MilliQ (18.2 M Ω -cm) water until saturated. 0.5 mL of this slurry was added to each of the moss microcosms using a micropipette. The mosses were adjusted to 70% of their measured WHC and the bottles were capped with parafilm to reduce water losses. A total of 21 microcosms were constructed: three replicates of *Sphagnum* moss from each of the three hollow and hummock plots, and three replicate incubations of the *Polytrichum* sp. Approximately monthly, water was replaced based on the mass change of the microcosm, and the parafilm was replaced. After 323 days of incubation, samples were removed from incubation vials, weighed to determine mass remaining, and dried and ground for chemical analysis.

Peat incubation experiments were conducted on a total of 60 samples, representing 11–13 depths within each of the five cores (two hummock, two hollow, and one sedge meadow). Peat microcosms were constructed by adding 10 g of the field-moist homogenized peat to each of two 70 mL serum bottles, one each for aerobic and anaerobic incubation. The oxic microcosms were covered with parafilm with holes for gas exchange and pre-incubated at room temperature for 7 to 10 days. The microcosms were then capped with rubber septa and the concentration of CO₂ in the headspace was measured using an Agilent 6890 gas chromatograph with a flame ionization detector (GC-FID) equipped with a methanizer (Restek Corporation, Bellefonte, PA, USA). The headspace CO₂ concentration was measured again after 24 h to determine the rate of CO₂ production. Anoxic microcosms were immediately sealed with a rubber stopper and flushed with N₂ to remove air from the head space. Microcosms were incubated at room temperature for 20–24 days, after which CO₂ concentrations were measured by GC-FID. Reported rates of CO₂ production in both incubations include dissolved inorganic C species calculated using Henry's Law (Sander 2015) and the measured pH of each peat sample.

Carbohydrate analysis

Moss and peat samples were hydrolyzed, converted to trimethylsilyl-dithioacetal (TMSD) derivatives, and analyzed using gas chromatography/mass spectrometry (GC-MS) to determine their total non-cellulosic sugar content. 20 \pm 1 mg of dried sample material were weighed into a 2 mL gas chromatography vial. 1 mL of 2 M trifluoroacetic acid (TFA; De Ruiter et al. 1992; Rumpel and Dignac 2006) was then added to each sample. Vials were capped and vortexed for 10 s before heating at 100 °C for five hours (Garna et al. 2006). After hydrolysis, samples were transferred to 1.5 mL centrifuge tubes, and centrifuged for 5 min at 3000 RPM. A 400 μ L aliquot of the supernatant was transferred into a GC vial, then all liquid was evaporated under a gentle stream of N₂ gas at 50 °C using a Thermo-Scientific Reacti-Therm heating module. Any samples not immediately derivatized were stored in the freezer.

Samples were converted to TMSD derivatives following the method of Xia et al. (2018). Aliquots of peat hydrolysates were prepared for silylation with the addition of a 2:1 mixture of ethanethiol and 13 M TFA, prepared separately and vortexed for 10 s before addition (Xia et al. 2018). This prevented isomerization of sugars present, avoiding multiple peaks in the GC chromatograms (Pitthard and Finch 2001). 100 μ L of the ethanethiol and TFA mixture was added to each sample before vortexing for 10 s to ensure complete dissolution of all hydrolyzed materials. After allowing the reaction to proceed for ten minutes at ambient temperature, samples were vortexed again for 10 s, then silylated with 385 μ L of pyridine, 75 μ L of hexamethyldisilazane, and 40 μ L of chlorotrimethylsilane before capping and sealing vials with parafilm to prevent evaporation. The reaction was allowed to proceed for 30 min at 70 °C before vortexing and cooling.

Liquid–liquid extraction was used to isolate organic compounds for analysis. Derivatized samples were added to 10 mL separatory funnels by rinsing with 2 mL of MilliQ water in 1 mL increments, then extracted with 3 mL of chloroform in 1 mL increments. The aqueous phase remaining in separatory funnels was removed before washing organic components with 3 mL of NaCl brine. The remaining organic fraction was dried over MgSO₄ before filtering with quartz wool into a GC vial for analysis.

GC-MS analysis was performed on an Agilent 6890 GC with a Model 5973 Mass Selective Detector (Agilent Technologies, Santa Clara, CA, USA). The temperature profile and MS parameters utilized were in accordance with Xia et al. (2018). Sugar content of samples was calculated using calibration curves made from a mixed sugar standards using six sugar monomers (xylose, arabinose, rhamnose, galactose, glucose, and mannose).

The recovery of sugar monomers from acid hydrolysis of carbohydrates is highly dependent on the acid used and the reaction conditions (De Ruiter et al. 1992; Garna et al. 2006, 2004). Aggressive hydrolysis is necessary to achieve complete cleavage of glycosidic linkages, but different types of linkages have varying resistance to acid. Sugar monomers decompose in acid over time, again at different rates. Therefore, the hydrolysis conditions that optimize recovery varies by carbohydrate. We selected hydrolysis conditions (2 M TFA for 6 h; Wicks et al. 1991) that were reported in the literature to be optimal for the hydrolysis of pectin (Garna et al. 2006), as a close structural analogue for sphagnum.

Optimizing hydrolysis to maximize the total carbohydrate yield requires harsher conditions than is optimal for pectin hydrolysis (Cowie and Hedges 1984). Pre-treatment of samples with concentrated H_2SO_4 at room temperature for 2 h, followed by dilution to 1.2 M and heating for 3 h has been shown to maximize the recovery of cellulose (Pakulski and Benner 1992; Skoog and Benner 1997). Cellulose is typically the most abundant carbohydrate, so this method also maximizes the total hydrolysable sugar yield. As the TFA hydrolysis used herein does not efficiently hydrolyze cellulose, our reported yields should be interpreted as the total of the hemicellulose fraction, plus an unknown fraction of the cellulose. The total sugar yields measured in this study are correspondingly lower than those reported in studies using H_2SO_4 pretreatment and hydrolysis. For example, we measured that the sugar yield of *Sphagnum* biomass was approximately 9–12% of total C, compared to 35–40% using H_2SO_4 hydrolysis with pretreatment (Philben et al. 2015, 2014a). However, our approach in the present study maximized recovery of pectins, and is therefore ideal for assessing the abundance of sphagnum.

Data analysis

One-way ANOVA tests with post-hoc Tukey's Honest Significant Difference tests were used to determine significant differences in mass loss, sugar content and composition in the three moss types. Two-tailed t-tests were performed to determine significant changes in sugar composition before and after decomposition. Two-tailed t-tests were also used to determine significant differences in CO_2 production rates and sugar composition between peat samples from hollow and hummock cores. The relationship between sugar composition and CO_2 production rates was tested using linear regression. All statistics were performed in R version 3.6.1 (R Core Team, 2013), and figures were created using Origin 2019b.

Results

Moss decomposition experiments

Mass loss over 323 days of decomposition varied significantly among the moss types (ANOVA; $F=6.899$; degrees of freedom (df)=2; $p=0.007$). The non-*Sphagnum* moss, *Polytrichum* sp., averaged $37 \pm 2.3\%$ mass loss (mean ± 1 standard error), compared to $31.5 \pm 2.2\%$ in *Sphagnum cuspidatum* and $21.5 \pm 3\%$ in *Sphagnum magellanicum* (Fig. 1). Mass loss in the hollow species (*S. cuspidatum*) was significantly higher than in hummock species (*S. magellanicum*; Tukey's HSD; $p=0.0304$), and was significantly higher in *Polytrichum* sp. than in *S. magellanicum* ($p=0.0124$). However, the difference between *Polytrichum* sp. and *S. cuspidatum* was not significant ($p=0.4789$).

Prior to the decomposition experiment, the three moss types had a similar yield of total non-cellulosic sugars, but differed in composition. The six quantified sugar monomers accounted for an average of $10.3 \pm 1.0\%$ of the total C in *S. cuspidatum*, $11.4 \pm 0.5\%$ in *S. magellanicum*, and $9.9 \pm 2.9\%$ in *Polytrichum* sp. (Fig. 2a). Differences in the total sugar content were not significantly different among the moss types ($F=2.868$; $df=2$; $p=0.0845$). However, the relative abundance of rhamnose (expressed as a mole % of the total sugars) was significantly different ($F=23.35$; $df=2$; $p<0.001$; Fig. 2b). Mole % rhamnose was significantly higher in both

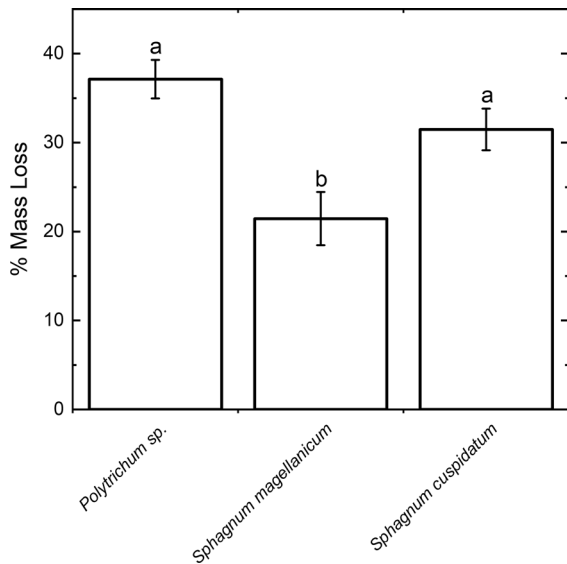


Fig. 1 Mass loss over the course of the moss decomposition experiment. Error bars indicate one standard error of the mean. Letters indicate significantly different groups ($p < 0.05$)

S. magellanicum and *S. cuspidatum* compared to the *Polytrichum* sp. ($15.5 \pm 0.4\%$, $13.8 \pm 0.5\%$, and $8.6 \pm 1.2\%$, respectively; $p < 0.001$). While the average mole % rhamnose in *S. magellanicum* was higher than in *S. cuspidatum*, the difference was not significant ($p = 0.2187$). The C-normalized yield of rhamnose also varied significantly by moss type ($F = 8.843$; $df = 2$; $p = 0.002$; Fig. 2c). Rhamnose content was significantly higher in *S. magellanicum* than in *S. cuspidatum* (1.8 ± 0.1 vs. $1.4 \pm 0.1\%$

of total C; $p = 0.0425$). The rhamnose content in *Polytrichum* sp. ($1.2 \pm 0.1\%$ of total C) was significantly lower than *S. magellanicum* ($p = 0.002$), but not significantly different than *S. cuspidatum* ($p = 0.2751$). The relatively higher rhamnose content of *S. magellanicum* was at the expense of xylose and mannose, which were more abundant in *S. cuspidatum* (Fig. 3). *Polytrichum* sp., in contrast, was dominated by mannose (46.5 ± 2.7 mol %), with correspondingly lower mole % of the other sugars.

Decomposition affected the relative abundance, but not the total yield of the analyzed sugars. The change in %C as total sugars did not vary significantly for either *Sphagnum* species when comparing the “initial” and “final” moss samples ($p = 0.160$ and 0.359 for *S. cuspidatum* and *S. magellanicum*, respectively; Fig. 3). However, rhamnose was selectively preserved, increasing from 13.8 to 15.9 mol % in *S. cuspidatum* and from 15.5 to 18.0% in *S. magellanicum*. The increase was significant in both *Sphagnum* species ($p = 0.037$ and 0.021 , respectively). The absolute abundance of rhamnose increased in both moss types (from 1.4 to 1.9% of total C in *S. cuspidatum* and from 1.8 to 1.9% in *S. magellanicum*), but the change was only significant for *S. cuspidatum* ($p = 0.008$). In *S. cuspidatum*, changes in the relative composition of the other sugars were subtle (Fig. 3). Mannose declined from 20.8 to 19.6 mol %, but no other sugar changed abundance by more than 1 mol %. In *S. magellanicum*, mole % xylose increased from 18.9 to 24.8% of the total sugars, while the abundance of arabinose, glucose, mannose, and galactose declined.

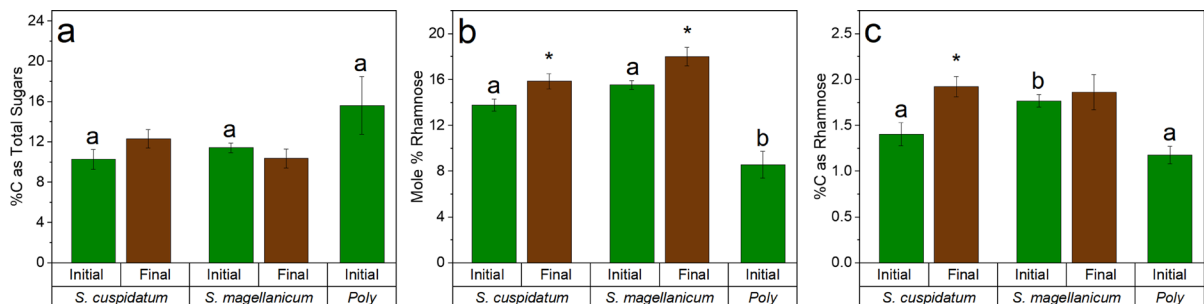


Fig. 2 Changes in %C as total sugars (a), mole % rhamnose (b), and %C as rhamnose (c) in the three moss types, before and after the moss decomposition experiment. “Poly” refers to *Polytrichum* sp., which was analyzed only prior to the decom-

position experiment. Error bars indicate one standard error. Letters indicate significantly different groups among the initial moss tissues. Asterisks (*) indicate a significant difference in composition between the initial and final moss tissues

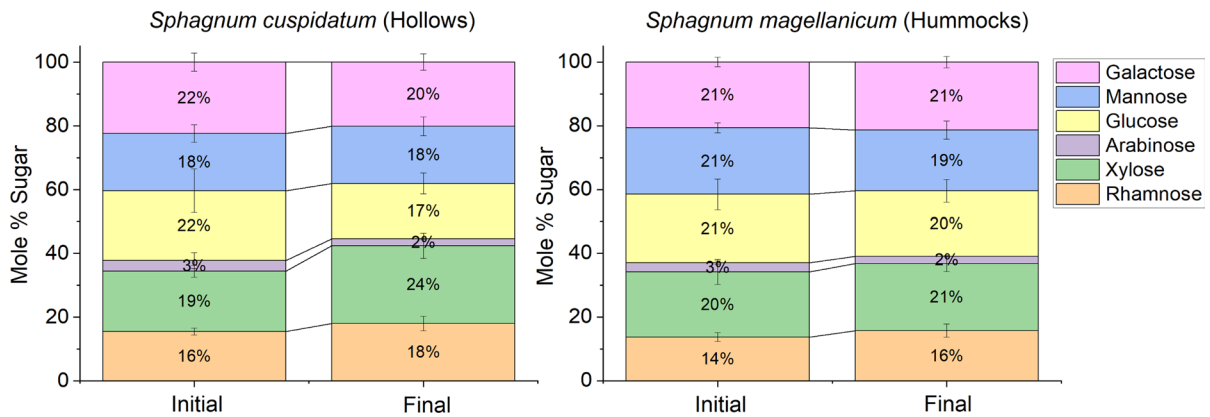


Fig. 3 Changes in the relative abundance of sugar monomers during the moss decomposition experiment. Error bars indicate one standard error

CO₂ production from peat incubation experiments

CO₂ production in peat microcosms was highly variable both within individual cores and among cores collected from different locations within the bog. Overall, peat collected from hollows produced significantly more CO₂ during the aerobic incubations ($p < 0.001$; Fig. 4). CO₂ production was $> 350 \mu\text{mol g dry weight}^{-1} \text{ day}^{-1}$ in the surface peat for both hollow cores, but was less than $150 \mu\text{mol g dry weight}^{-1} \text{ day}^{-1}$ throughout the hummock and sedge meadow cores. Aerobic CO₂ production generally declined with depth, but this was not apparent in all cores. For example, in peat from Cores 1 and 3, the surface peat had the highest respiration rate, but there was no apparent change with depth in the rest of the core.

Rates of anaerobic CO₂ production were approximately two orders of magnitude lower than in the aerobic incubations. Similar to the patterns for the aerobic incubations, the rate of CO₂ production tended to decline with depth in most of the cores, with the exception of Core 1. Unlike in the aerobic incubations, the difference between cores from hummocks and hollows was not significant ($p = 0.337$).

Sugar composition of the peat

There were no consistent trends in the total sugar content with depth in the peat profile. While the sugar content varied between 5.3 and 17.0 percent of the total C, only Core 2 exhibited a consistent decline

in the sugar yield with increasing depth (Fig. 5). Increases with depth in the relative abundance (mole %) of rhamnose were observed in Cores 2, 4, and 5, but not in the other two cores (Figure S1). This pattern was therefore not consistent across microtopographies. Although neither parameter exhibited consistent changes with depth, %C as sugars and mole % rhamnose were inversely correlated across all five cores ($r^2 = 0.44$; Fig. 6), indicating that lower sugar yields resulted in enrichment of rhamnose. The total rhamnose content (%C as rhamnose) consistently increased with depth in the peat profiles (Fig. 5). While the shapes of the profiles varied, the highest rhamnose content was found in the bottom half (below 1.5 m) in all five cores, and each core exhibited a trend toward higher rhamnose content with depth in the bottom meter. In addition, an increase in mole % glucose was consistently observed in all five cores (Figure S2). The relative increase in glucose abundance was at the expense of xylose and arabinose, both of which declined in abundance with depth.

The sugar composition of the peat significantly explained some of the variability in CO₂ production, but the relationship varied by microtopography (Fig. 7). The total sugar content was significantly correlated with CO₂ production only in the anaerobic incubations of the hollow cores ($p = 0.0288$; $r^2 = 0.208$; Fig. 7b)). Mole % rhamnose was the best predictor of respiration rates; it was significantly correlated with aerobic respiration in the hollows ($r^2 = 0.248$; $p = 0.015$; Fig. 7c),

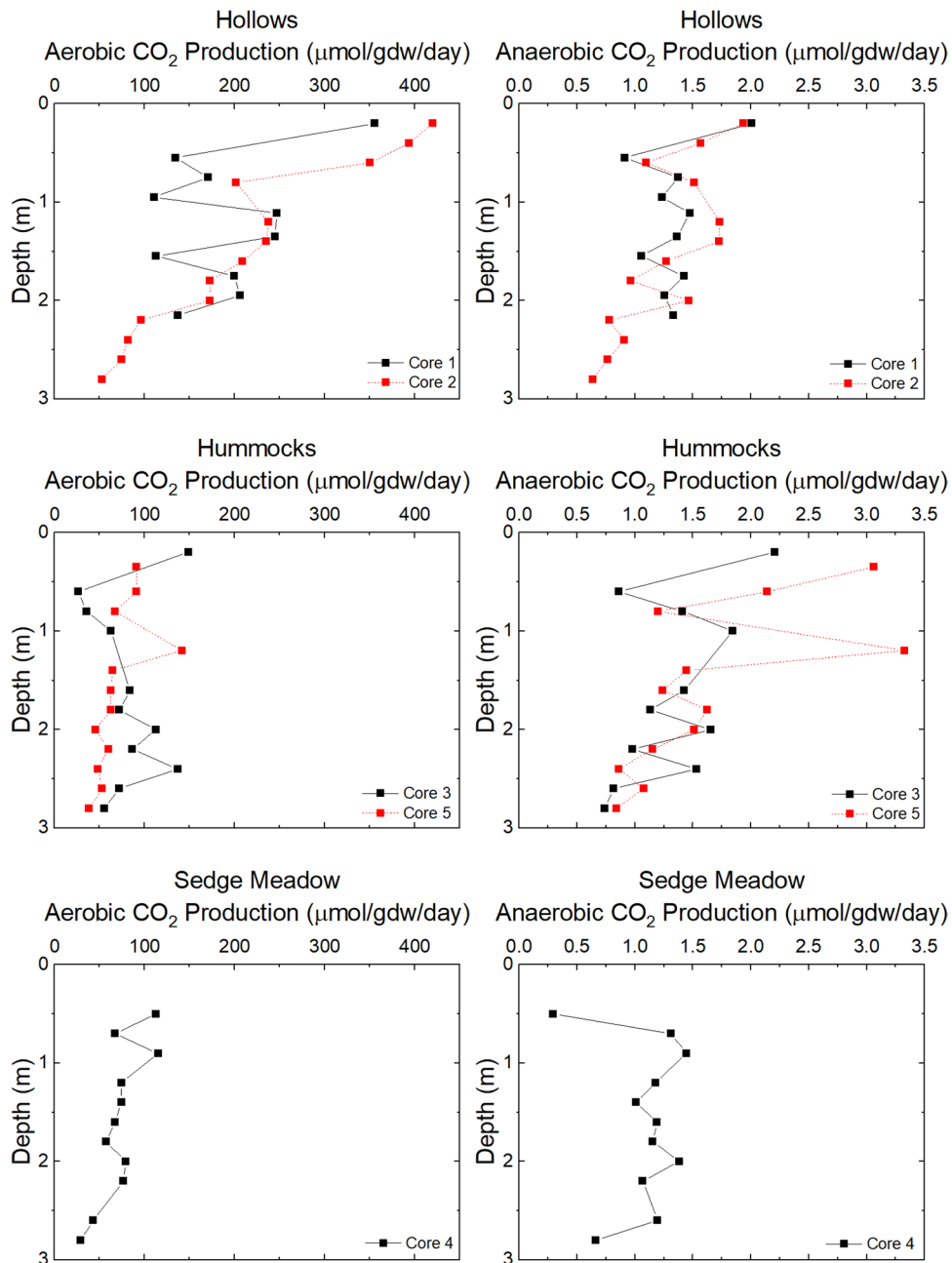
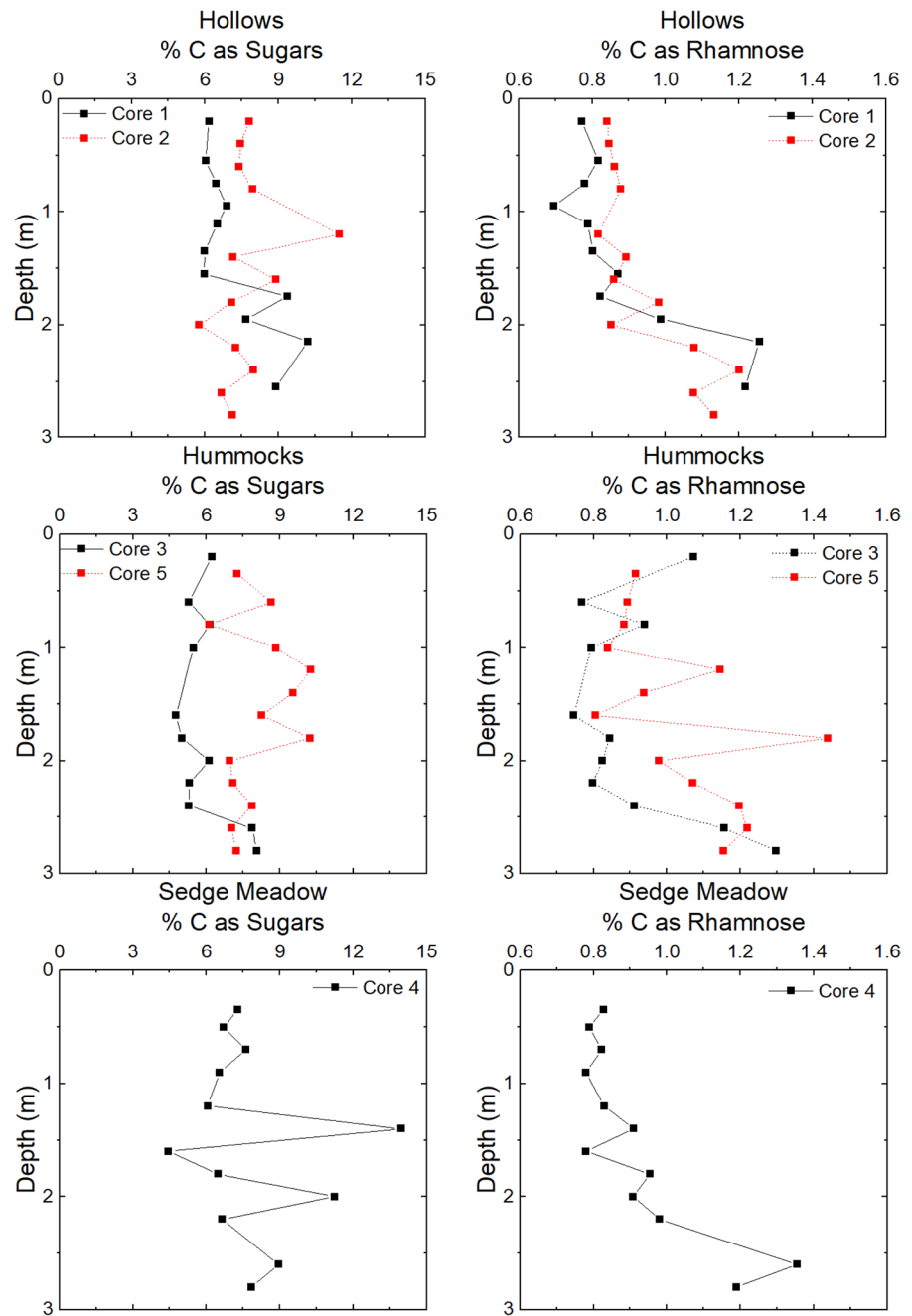


Fig. 4 Aerobic (left) and anaerobic (right) CO_2 production observed in peat microcosm incubation experiments. Units are $\mu\text{mol CO}_2$ produced per g dry weight of soil per day

anaerobic respiration in the hollows ($r^2=0.390$; $p=0.001$), and anaerobic respiration in the hummocks ($r^2=0.1724$; $p=0.0488$; Fig. 7d). The C-normalized yield of rhamnose did not significantly predict either aerobic or anaerobic CO_2 production in any of the three microtopographies, and

none of the measured parameters significantly correlated with either type of respiration in the sedge meadow core.

Fig. 5 Depth profiles of the total sugar content and %C as rhamnose in the five peat cores



Discussion

Effect of sphagnum on moss decomposition

We found that a hummock *Sphagnum* species exhibited a lower rate of decomposition than a hollow species, and that both *Sphagnum* species decayed

slower than a non-*Sphagnum* moss (Fig. 1), consistent with previous literature (Bengtsson et al. 2016; Clymo 1965; Johnson and Damman 1991; Rydin et al. 2006). Also consistent with previous studies (Turetsky et al. 2008), this could not be explained by a difference in total carbohydrate content, which was not significantly different across the moss types. The

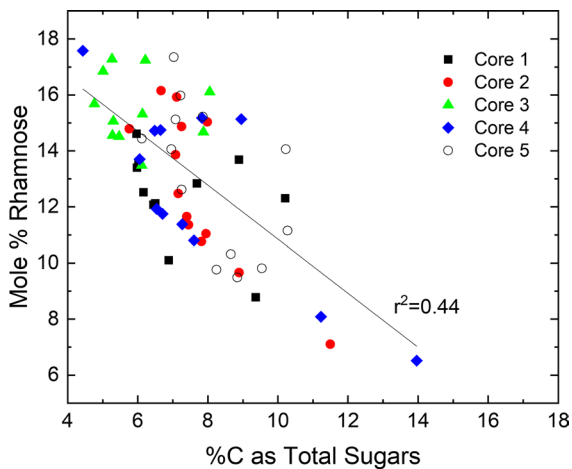


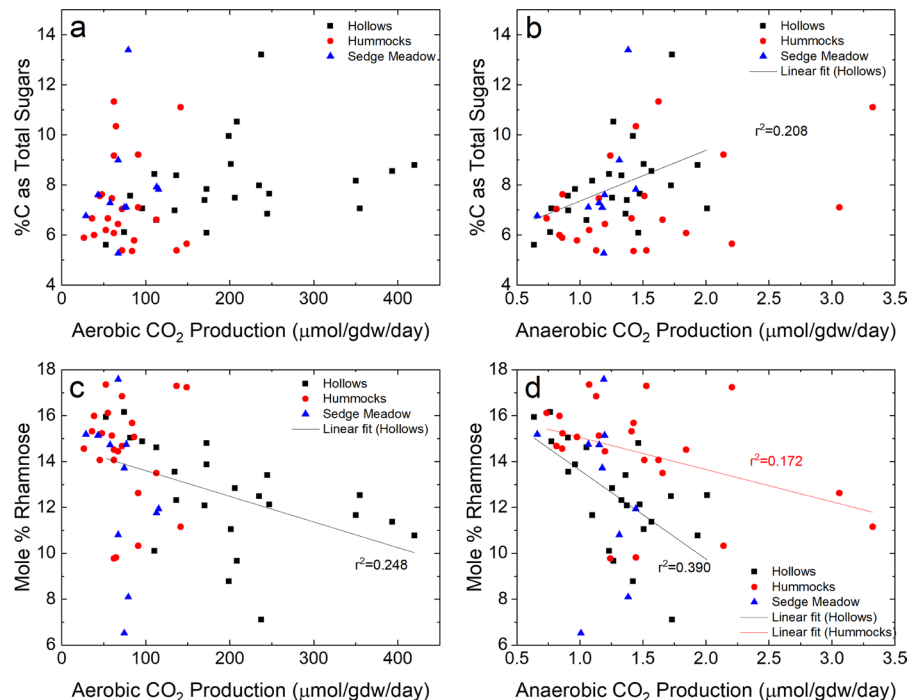
Fig. 6 Correlation between the total sugar content and mole % rhamnose in the analyzed peat samples

ranking of decomposition rates (*Polytrichum* sp. > *S. cuspidatum* > *S. magellanicum*) was the inverse of the ranking of sphagnum content (as measured by %C as rhamnose), which supports the hypothesis that sphagnum inhibits moss decomposition. However, sphagnum content co-varies with other relatively recalcitrant biomolecules such as amorphous and lignin-like

phenols in *Sphagnum* (Bengtsson et al. 2018). Our observed relationship therefore does not demonstrate that sphagnum itself is causing the difference in decay rates.

Selective preservation of sphagnum was observed during decomposition of both *Sphagnum* species. The increase in both mole % rhamnose and the abundance of rhamnose as a fraction of the total C indicates that sphagnum was degraded slower than either other carbohydrates or bulk C, respectively. In contrast, we did not observe selective decomposition of total non-cellulosic sugars, which remained a constant fraction of total C before and after the experiment. In previous studies, selective decomposition of carbohydrates is often observed due to their relative lability compared to other biomolecules (Kögel-Knabner 2002; Preston et al. 2009). However, the timing and trajectory can vary considerably. For example, in a litter bag study of cypress needle decomposition, the sugar yield declined by 54% within the first year (corresponding to 59% mass loss). In contrast, smooth cordgrass litter exhibited a decline in sugar yield only after four years of decomposition and >90% mass loss (Opsahl and Benner 1999). In another example, the carbohydrate content of spruce needles changed little during the first year of decomposition (up to 25% mass loss;

Fig. 7 Correlations between CO₂ production rates and total sugar content (a and b) or mole % rhamnose (c and d). Regression lines are displayed when the slope was significantly different from 0. Units for respiration rates are $\mu\text{mol CO}_2$ produced per g dry weight of soil per day



Lorenz et al. 2000), but declined significantly after six years (Preston et al. 2009). The observed lack of change in total sugar yield could therefore be attributed to the relatively low levels of mass loss in the moss decomposition experiment (<40%). This is supported by the generally lower sugar yields in the peat soils compared to in the moss tissues.

Overall, the moss decomposition experiment revealed that sphagnum accumulates due to selective preservation, and that higher sphagnum content is associated with lower decay rates in the three moss species. Both lines of evidence are consistent with sphagnum playing an important role in the stabilization of *Sphagnum* organic matter during the early stages of peat diagenesis.

Selective carbohydrate decomposition in the peat column

The peat column provides a natural extension of the diagenetic continuum to evaluate selective preservation of sugars over longer timescales. The surface peat represents a more advanced stage of decay than mosses from the experiment, having experienced at least several years of decomposition. The extent of decomposition is expected to increase with depth within the surface acrotelm, the layer above the lowest position of the water table, in which peat is exposed to oxygen at least part of the year. In the catotelm, below the lowest position of the water table, rates of organic matter decomposition are two to three orders of magnitude lower (Clymo 1984). Therefore, the extent of decomposition does not necessarily continue increasing with depth despite increasing age, and may also reflect differences in environmental conditions when that peat was still in the acrotelm (Philben et al. 2014b; Williams and Yavitt 2003).

The evidence for selective decomposition of carbohydrates was mixed. The total non-cellulosic sugar yield was lower in the peat than in the mean post-decomposition moss sample in all but three peat samples, consistent with selective decomposition of total carbohydrates compared to bulk C. However, there was little evidence for further declines with depth in the peat column. This suggests that selective loss of carbohydrates occurs mainly in the late stages of litter decay and the early stages of peat formation, so that surface peat is already depleted in easily degradable carbohydrates. This is consistent with Pipes and

Yavitt (2022), who also observed a large difference in composition between plant biomass and surface peat, but minimal changes with depth.

The abundance of rhamnose throughout the peat cores provides evidence that sphagnum persists in the catotelm. Pipes and Yavitt (2022) used sequential extraction to show that a pectin-like organic matter fraction (attributed to sphagnum) survives long-term decomposition and is found in the catotelm. This pectin-like fraction was defined functionally as the fraction extracted by cyclohexanediamine tetra acetic acid (CDTA), which is thought to release ionically-bound pectin through the removal of calcium, but the composition cannot be confirmed. In contrast, our approach specifically identifies a sugar monomer associated with sphagnum (rhamnose), but can provide no information regarding function. Together, these studies provide complementary support for the persistence of both the structure and function of sphagnum in the catotelm.

Sphagnum content was also lower in the surface peat compared to the decomposed moss litter. This could be interpreted as selective decomposition of sphagnum during peat formation, but is more likely due to mixing with vascular plants that lack sphagnum. Vascular plants have lower rhamnose content but are rich in arabinose and xylose due to arabinoxylan hemicelluloses (Comont et al. 2006; Cowie and Hedges 1984; Wicks et al. 1991). In contrast, both mole % rhamnose and the %C as rhamnose increased with depth in most of the cores. This is unlikely to result from vegetation change over time; while a detailed paleoecological reconstruction has not been conducted at this site, the succession at a nearby site (DeVries-Zimmerman et al. 2014) and at other Michigan kettle lake bogs (Booth et al. 2004) has proceeded from lake sediments to fen to bog communities. In our cores, we observed a transition from fibrous peat at the top, to sapric peat between two and three meters depth, based on macroscopic visual inspection. Previous coring at this site shows the fen (characterized by marl deposits) to bog transition occurring at deeper depths than those utilized for this study (DeVries-Zimmerman personal communication 2024). Thus, the deeper sapric peat would be expected to have lower *Sphagnum* content. Furthermore, there was no increase in arabinose or xylose abundance with depth, as would be expected for a vascular plant source. The observed increase in sphagnum content is therefore

most likely to result from selective preservation rather than shifts in the botanical sources of the peat.

The increase in mole % glucose with depth was the most consistent trend observed, occurring in all five cores (Fig. 5). Although cellulose is a glucose polymer, this pattern cannot be attributed to cellulose preservation because our method does not efficiently hydrolyze cellulose. Two processes could contribute to the accumulation of glucose with depth. First, it could be attributed to accumulation of microbial exopolysaccharides, many of which are enriched in glucose (Andrew and Jayaraman 2020; Decho 1990; Leppard et al. 1977). Second, it could result from the partial breakdown of cellulose, such that its glycosidic bonds are labile to hydrolysis under more mild conditions (Comont et al. 2006). Both interpretations indicate that the extent of decomposition in the peat cores increased with depth below 1 m.

This is consistent with an increase in the relative abundance of non-cellulosic glucose with depth observed in a French peatland (Comont et al. 2006). However, the cores used in this study were 50 cm in length and therefore reflected mostly transformations within the acrotelm. Our observation of increasing glucose abundance below 1 m indicates that selective decomposition continued in the catotelm under anaerobic conditions. Despite the apparently advancing state of decomposition, our results indicate that microbial remains and cellulose, rather than sphagnum, were selectively preserved during this phase of decomposition.

Relationship between respiration rates and sugar composition

Overall rates of CO₂ production in the anoxic microcosms were on the low end of the range reported in previous studies. For example, Moore and Dalva (1997) reported a range of 1.6 to 42.7 μmol g⁻¹ day⁻¹ in incubations of 140 peat samples, compared to a range of 0.5 to 3.5 μmol g⁻¹ day⁻¹ observed in the present study. In contrast, the rates observed in the oxic microcosms were much higher, and on the upper end of the range of observed rates (Moore and Dalva 1997; Scanlon and Moore 2000; Yavitt et al. 2005). This discrepancy may be due to the relatively long pre-incubation period used in the oxic experiments, likely allowing microbial biomass to increase before the measurement of CO₂ production rates.

Peat in cores collected from hollows appeared to have higher organic matter quality than the hummock cores, as indicated by higher rates of aerobic CO₂ production. This is consistent with moss decomposition results attributed to greater investment in structural carbohydrates by hummock-dwelling species (Turetsky et al. 2008; this study). Our results suggest that the difference in organic matter quality between microtopographies extends into the peat, as hollow samples from as deep as 2 m exhibited aerobic CO₂ production higher than any in the two hummock cores (Fig. 4). However, the difference in quality only affected aerobic decomposition; there was no difference in anaerobic CO₂ production between the microtopographies.

CO₂ production generally declined with depth in the cores, with the exception of aerobic production in the hummock cores and anaerobic production in Site 5 (the sedge meadow). This reflects declining organic matter quality as the extent of decomposition increases with depth in the peat column. Additionally, a declining supply of dissolved organic C (DOC) derived from leaching from surface sources could also contribute to this trend, as such leachates have been demonstrated to be important substrates even deep in the peat profile (Chanton et al. 2008, 1995).

There was a correlation between the respiration rates and the relative abundance of rhamnose (sphagnum as a percentage of the total sugars), but not the C-normalized yield of rhamnose (reflecting total sphagnum content). As non-cellulosic carbohydrates are among the most bioavailable organic matter fractions, this relationship suggests that the composition of this pool can play an important role in determining its overall bioavailability. In contrast, the lack of a relationship between the C-normalized rhamnose yield and respiration rates suggests that a higher relative abundance of sphagnum could be offset by a higher total non-cellulosic sugar yield in some samples. These results indicate a continuing significant, but relatively subtle, influence of sphagnum on organic matter stabilization in peat profiles, in partial support of our first hypothesis. The weak relationship is consistent with other co-occurring mechanisms for organic matter stabilization in the catotelm such as the enzymatic latch (Freeman et al. 2004, 2001).

We also observed important differences in the relationship between organic matter quality and CO₂ production among different microtopographies, as

sphagnum relative abundance better predicted respiration in the hollows compared to in the hummocks (Fig. 7). The correlation was not significant in the sedge meadow core, consistent with lower abundance of *Sphagnum* remains. This pattern, along with the overall lower CO₂ production in the hummock compared to the hollow peat, indicates that the chemical composition has a larger impact on the bioavailability of hollow peat. We suggest that this could result from greater structural stability of hyaline cells in hummock mosses (Turetsky et al. 2008), which can provide a physical barrier against microbial attachment, but is not apparent in chemical signatures (Philben et al. 2018; Tsuneda et al. 2001). The physical structure of *Sphagnum* stems has been observed to persist deeper into the peat in hummocks than in hollows (Johnson et al. 1990), which may contribute to the persistent disparity in respiration rates between the microtopographies below the surface.

Overall, it appears that sphagnum has a measurable but limited effect on decomposition rates during long-term peat formation. The inverse correlation between %C as sugars and mole % rhamnose indicates that sphagnum is selectively preserved compared to other sugars, and constitutes a significant fraction of the total carbohydrates in highly degraded peats. The correlation between sphagnum relative abundance and respiration supported the hypothesis that sphagnum continues to inhibit microbial activity, even in highly decomposed deep peat soils. However, the relatively weak correlation indicates that less than 40% of the variability in respiration is explained by the sugar composition, and that other environmental factors play an important role in determining organic matter quality in the peat.

Conclusions

We hypothesized that higher sphagnum content reduces the rate of organic matter decomposition and that sphagnum is selectively preserved, both during short-term litter decomposition and long-term peat formation. Both hypotheses were at least partially supported. In the moss decomposition experiment, we found that higher sphagnum content was associated with lower decay rates, consistent with previous studies. In addition, the relative abundance of sphagnum increased during decomposition, indicating selective

preservation. In the peat, sphagnum content increased with depth, indicating its persistence and selective preservation over the longer timescales associated with peat formation. The relative abundance of sphagnum as a fraction of total sugars was generally associated with lower CO₂ production, although there was no relationship between respiration and the total sphagnum content (normalized to total C). These results indicate that sphagnum continues to play a role in the stabilization of organic matter during the slow process of anaerobic decomposition in the catotelm, although the relatively weak relationships suggest that it is one of many processes contributing to the inhibition of decomposition under these conditions.

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Author contributions Lauren Bryan and Michael Philben contributed to study conception and design. Lauren Bryan and Erik Schoonover adapted the carbohydrate method and performed the analysis. Rachel Shaw and Alexis Koehl conducted the incubation experiments. Suzanne DeVries-Zimmerman contributed to field sampling and identified the moss species. Lauren Bryan analyzed the data and wrote the first draft of the manuscript, with input from Michael Philben, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability All data used in the manuscript are available in the supplementary information.

Declarations

Competing interests The authors have no relevant financial or non-financial interests to disclose.

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References

- Andrew M, Jayaraman G (2020) Structural features of microbial exopolysaccharides in relation to their antioxidant activity. *Carbohydr Res* 487:107881. <https://doi.org/10.1016/j.carres.2019.107881>
- Ballance S, Børsheim KY, Inngjerdingen K, Paulsen BS, Christensen BE (2007) A re-examination and partial characterisation of polysaccharides released by mild acid hydrolysis from the chlorite-treated leaves of *Sphagnum papillosum*. *Carbohydr Polym* 67:104–115. <https://doi.org/10.1016/j.carbpol.2006.04.020>
- Ballance S, Kristiansen KA, Holt J, Christensen BE (2008) Interactions of polysaccharides extracted by mild acid hydrolysis from the leaves of *Sphagnum papillosum* with either phenylhydrazine, o-phenylenediamine and its oxidation products or collagen. *Carbohydr Polym* 71:550–558. <https://doi.org/10.1016/j.carbpol.2007.06.025>
- Bengtsson F, Granath G, Rydin H (2016) Photosynthesis, growth, and decay traits in *Sphagnum*—a multispecies comparison. *Ecol Evol* 6:3325–3341. <https://doi.org/10.1002/ece3.2119>
- Bengtsson F, Rydin H, Hájek T (2018) Biochemical determinants of litter quality in 15 species of *Sphagnum*. *Plant Soil* 425:161–176. <https://doi.org/10.1007/s11104-018-3579-8>
- Booth RK, Jackson ST, Gray CE (2004) Paleocology and high-resolution paleohydrology of a kettle peatland in upper Michigan. *Quatern Res* 61:1–13. <https://doi.org/10.1016/j.yqres.2003.07.013>
- Børsheim KY, Christensen BE, Painter TJ (2001) Preservation of fish by embedment in *Sphagnum* moss, peat or holocellulose: experimental proof of the oxopolysaccharidic nature of the preservative substance and of its antimicrobial and tanning action. *Innov Food Sci Emerg Technol* 2:63–74. [https://doi.org/10.1016/S1466-8564\(00\)00029-1](https://doi.org/10.1016/S1466-8564(00)00029-1)
- Chanton JP, Bauer JE, Glaser PA, Siegel DI, Kelley CA, Tyler SC, Romanowicz EH, Lazrus A (1995) Radiocarbon evidence for the substrates supporting methane formation within northern Minnesota peatlands. *Geochim Cosmochim Acta* 59:3663–3668. [https://doi.org/10.1016/0016-7037\(95\)00240-Z](https://doi.org/10.1016/0016-7037(95)00240-Z)
- Chanton JP, Glaser PH, Chasar LS, Burdige DJ, Hines ME, Siegel DI, Tremblay LB, Cooper WT (2008) Radiocarbon evidence for the importance of surface vegetation on fermentation and methanogenesis in contrasting types of boreal peatlands. *Global Biogeochem Cycles*. <https://doi.org/10.1029/2008GB003274>
- Clymo RS (1965) Experiments on breakdown of sphagnum in two bogs. *J Ecol* 53:747–758. <https://doi.org/10.2307/2257633>
- Clymo RS (1984) The limits to peat bog growth. *philosophical transactions of the royal society of London. B, Biol Sci* 303:605–654. <https://doi.org/10.1098/rstb.1984.0002>
- Comont L, Laggoun-Défarge F, Disnar J-R (2006) Evolution of organic matter indicators in response to major environmental changes: the case of a formerly cut-over peat bog (Le Russey, Jura Mountains, France). *Org Geochem* 37:1736–1751. <https://doi.org/10.1016/j.orggeochem.2006.08.005>
- Coulson JC, Butterfield J (1978) An investigation of the biotic factors determining the rates of plant decomposition on blanket bog. *J Ecol*. <https://doi.org/10.2307/2259155>
- Cowie GL, Hedges JI (1984) Carbohydrate sources in a coastal marine environment. *Geochim Cosmochim Acta* 48:2075–2087. [https://doi.org/10.1016/0016-7037\(84\)90388-0](https://doi.org/10.1016/0016-7037(84)90388-0)
- De Ruiter GA, Schols HA, Voragen AG, Rombouts FM (1992) Carbohydrate analysis of water-soluble uronic acid-containing polysaccharides with high-performance anion-exchange chromatography using methanolysis combined with TFA hydrolysis is superior to four other methods. *Anal Biochem* 207:176–185. [https://doi.org/10.1016/0003-2697\(92\)90520-H](https://doi.org/10.1016/0003-2697(92)90520-H)
- Decho AW (1990) Microbial exopolymer secretions in ocean environments: their role (s) in food webs and marine processes. *Oceanogr Mar Biol Annu Rev* 28:73–153
- DeVries-Zimmerman S, Fisher TG, Hansen EC, Dean S, Björck S (2014) Sand in lakes and bogs in Allegan County, Michigan, as a proxy for eolian sand transport. *Geol Soc Am Spec Pap* 508:111–131. [https://doi.org/10.1130/2014.2508\(07\)](https://doi.org/10.1130/2014.2508(07))
- Freeman C, Ostle N, Kang H (2001) An enzymic 'latch' on a global carbon store. *Nature* 409:149–149. <https://doi.org/10.1038/35051650>
- Freeman C, Ostle NJ, Fenner N, Kang H (2004) A regulatory role for phenol oxidase during decomposition in peatlands. *Soil Biol Biochem* 36:1663–1667. <https://doi.org/10.1016/j.soilbio.2004.07.012>
- Garna H, Mabon N, Wathelet B, Paquot M (2004) New method for a two-step hydrolysis and chromatographic analysis of pectin neutral sugar chains. *J Agric Food Chem* 52:4652–4659. <https://doi.org/10.1021/jf049647j>
- Garna H, Mabon N, Nott K, Wathelet B, Paquot M (2006) Kinetic of the hydrolysis of pectin galacturonic acid chains and quantification by ionic chromatography. *Food Chem* 96:477–484. <https://doi.org/10.1016/j.foodchem.2005.03.002>
- Gorham E (1991) Northern Peatlands: role in the carbon cycle and probable responses to climatic warming. *Ecol Appl* 1:182–195. <https://doi.org/10.2307/1941811>
- Hájek T (2009) Habitat and species controls on *Sphagnum* production and decomposition in a mountain raised bog. *Boreal Environ Res* 14:947–958
- Hájek T, Ballance S, Limpens J, Zijlstra M, Verhoeven JTA (2011) Cell-wall polysaccharides play an important role in decay resistance of *Sphagnum* and actively depressed

- decomposition in vitro. *Biogeochemistry* 103:45–57. <https://doi.org/10.1007/s10533-010-9444-3>
- Hobbie SE (1996) Temperature and plant species control over litter decomposition in alaskan tundra. *Ecol Monogr* 66:503–522. <https://doi.org/10.2307/2963492>
- Jia G, Dungait JAJ, Bingham EM, Valiranta M, Korhola A, Evershed RP (2008) Neutral monosaccharides as biomarker proxies for bog-forming plants for application to palaeovegetation reconstruction in ombrotrophic peat deposits. *Organic Geochem Stable Isotopes in Biogeochem* (II) 39:1790–1799. <https://doi.org/10.1016/j.orggeochem.2008.07.002>
- Johnson LC, Damman AW (1991) Species-controlled Sphagnum decay on a south Swedish raised bog. *Oikos*. <https://doi.org/10.2307/3545341>
- Johnson LC, Damman AW, Malmer N (1990) Sphagnum macrostructure as an indicator of decay and compaction in peat cores from an ombrotrophic south Swedish peat-bog. *J Ecol*. <https://doi.org/10.2307/2260889>
- Kögel-Knabner I (2002) The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter. *Soil Biol Biochem* 34:139–162. [https://doi.org/10.1016/S0038-0717\(01\)00158-4](https://doi.org/10.1016/S0038-0717(01)00158-4)
- Kremer C, Pettolino F, Bacic A, Drinnan A (2004) Distribution of cell wall components in Sphagnum hyaline cells and in liverwort and hornwort elaters. *Planta* 219:1023–1035
- Leppard GG, Massalski A, Lean DRS (1977) Electron-opaque microscopic fibrils in lakes: their demonstration, their biological derivation and their potential significance in the redistribution of cations. *Protoplasm* 92:289–309. <https://doi.org/10.1007/BF01279466>
- Limpens J, Bohlin E, Nilsson MB (2017) Phylogenetic or environmental control on the elemental and organo-chemical composition of Sphagnum mosses? *Plant Soil* 417:69–85. <https://doi.org/10.1007/s11104-017-3239-4>
- Lorenz K, Preston CM, Raspe S, Morrison IK, Feger KH (2000) Litter decomposition and humus characteristics in Canadian and German spruce ecosystems: information from tannin analysis and ¹³C CPMAS NMR. *Soil Biol Biochem* 32:779–792. [https://doi.org/10.1016/S0038-0717\(99\)00201-1](https://doi.org/10.1016/S0038-0717(99)00201-1)
- Maksimova V, Klavina L, Bikovens O, Zicmanis A, Purmalis O (2013) Structural characterization and chemical classification of some bryophytes found in Latvia. *Chem Biodivers* 10:1284–1294
- Moore T, Basiliko N (2006) Decomposition in Boreal Peatlands. In: Wieder RK, Vitt DH (eds) *Boreal Peatland Ecosystems, Ecological Studies*. Springer, Berlin Heidelberg, Berlin, Heidelberg
- Moore TR, Dalva M (1997) Methane and carbon dioxide exchange potentials of peat soils in aerobic and anaerobic laboratory incubations. *Soil Biol Biochem* 29:1157–1164. [https://doi.org/10.1016/S0038-0717\(97\)00037-0](https://doi.org/10.1016/S0038-0717(97)00037-0)
- Moore TR, Bubier JL, Bledzki L (2007) Litter decomposition in temperate peatland ecosystems: the effect of substrate and site. *Ecosystems* 10:949–963. <https://doi.org/10.1007/s10021-007-9064-5>
- Nichols JE, Peteet DM (2019) Rapid expansion of northern peatlands and doubled estimate of carbon storage. *Nat Geosci*. <https://doi.org/10.1038/s41561-019-0454-z>
- Opsahl S, Benner R (1999) Characterization of carbohydrates during early diagenesis of five vascular plant tissues. *Org Geochem* 30:83–94. [https://doi.org/10.1016/S0146-6380\(98\)00195-8](https://doi.org/10.1016/S0146-6380(98)00195-8)
- Painter TJ (1991) Lindow man, tollund man and other peat-bog bodies: the preservative and antimicrobial action of Sphagnum, a reactive glycuronoglycan with tanning and sequestering properties. *Carbohydr Polym* 15:123–142. [https://doi.org/10.1016/0144-8617\(91\)90028-B](https://doi.org/10.1016/0144-8617(91)90028-B)
- Painter TJ (2003) Concerning the wound-healing properties of Sphagnum holocellulose: the maillard reaction in pharmacology. *J Ethnopharmacol* 88:145–148. [https://doi.org/10.1016/S0378-8741\(03\)00189-2](https://doi.org/10.1016/S0378-8741(03)00189-2)
- Pakulski JD, Benner R (1992) An improved method for the hydrolysis and MBTH analysis of dissolved and particulate carbohydrates in seawater. *Mar Chem* 40:143–160. [https://doi.org/10.1016/0304-4203\(92\)90020-B](https://doi.org/10.1016/0304-4203(92)90020-B)
- Philben M, Kaiser K, Benner R (2014) Biochemical evidence for minimal vegetation change in peatlands of the west siberian lowland during the medieval climate anomaly and little ice age. *J Geophys Res Biogeosci*. <https://doi.org/10.1002/2013JG002396>
- Philben M, Kaiser K, Benner R (2014) Does oxygen exposure time control the extent of organic matter decomposition in peatlands? *J Geophys Res Biogeosci*. <https://doi.org/10.1002/2013JG002573>
- Philben M, Holmquist J, MacDonald G, Duan D, Kaiser K, Benner R (2015) Temperature, oxygen, and vegetation controls on decomposition in a James Bay peatland. *Global Biogeochem Cycles*. <https://doi.org/10.1002/2014GB004989>
- MPhilbenSButlerSABillingsRBennerKAEwardsSEZiegler-2018Biochemical and structural controls on the decomposition dynamics of boreal upland forest moss tissues *Biogeochemistry* 10.5194/bg-15-6731-2018Philben M, Butler S, Billings SA, Benner R, Edwards KA, Ziegler SE (2018) Biochemical and structural controls on the decomposition dynamics of boreal upland forest moss tissues. *Biogeochemistry*. <https://doi.org/10.5194/bg-15-6731-2018>
- Pipes GT, Yavitt JB (2022) Biochemical components of Sphagnum and persistence in peat soil. *Can J Soil Sci* 102:785–795. <https://doi.org/10.1139/cjss-2021-0137>
- Pitthard V, Finch P (2001) GC-MS analysis of monosaccharide mixtures as their diethylthioacetal derivatives: application to plant gums used in art works. *Chromatographia* 53:S317–S321. <https://doi.org/10.1007/BF02490349>
- Popper ZA, Fry SC (2003) Primary cell wall composition of bryophytes and charophytes. *Ann Bot* 91:1–12. <https://doi.org/10.1093/aob/mcg013>
- Preston CM, Nault JR, Trofymow JA (2009) Chemical changes during 6 years of decomposition of 11 litters in Some canadian forest sites. part 2. ¹³C abundance, solid-state ¹³C NMR spectroscopy and the meaning of “Lignin.” *Ecosystems* 12:1078–1102. <https://doi.org/10.1007/s10021-009-9267-z>
- R Core Team, R.C., 2013. R: A language and environment for statistical computing.
- Richter C, Dainty J (1989) Ion behavior in plant cell walls. I. characterization of the Sphagnum russowii cell wall ion exchanger. *Can J Bot* 67:451–459. <https://doi.org/10.1139/b89-063>

- Rumpel C, Dignac M-F (2006) Gas chromatographic analysis of monosaccharides in a forest soil profile: analysis by gas chromatography after trifluoroacetic acid hydrolysis and reduction–acetylation. *Soil Biol Biochem* 38:1478–1481. <https://doi.org/10.1016/j.soilbio.2005.09.017>
- Rydin H, Gunnarsson U, Sundberg S (2006) The Role of Sphagnum in Peatland Development and Persistence. In: Wieder RK, Vitt DH (eds) *Boreal Peatland Ecosystems, Ecological Studies*. Springer, Berlin, Heidelberg
- Sander R (2015) Compilation of Henry’s law constants (version 4.0) for water as solvent. *Atmos Chem Phys* 15:4399–4981. <https://doi.org/10.5194/acp-15-4399-2015>
- Scanlon D, Moore T (2000) Carbon dioxide production from peatland soil profiles: the influence of temperature, oxic/anoxic conditions and substrate. *Soil Sci* 165:153
- Schellekens J, Buurman P, Kuyper TW, Abbott GD, Pontevedra-Pombal X, Martínez-Cortizas A (2015) Influence of source vegetation and redox conditions on lignin-based decomposition proxies in graminoid-dominated ombrotrophic peat (Penido Vello, NW Spain). *Geoderma* 237–238:270–282. <https://doi.org/10.1016/j.geoderma.2014.09.012>
- Skoog A, Benner R (1997) Aldoses in various size fractions of marine organic matter: implications for carbon cycling. *Limnol Oceanogr* 42:1803–1813. <https://doi.org/10.4319/lo.1997.42.8.1803>
- Stalheim T, Ballance S, Christensen BE, Granum PE (2009) Sphagnan—a pectin-like polymer isolated from Sphagnum moss can inhibit the growth of some typical food spoilage and food poisoning bacteria by lowering the pH. *J Appl Microbiol* 106:967–976. <https://doi.org/10.1111/j.1365-2672.2008.04057.x>
- Thomas JR, McNeil M, Darvill AG, Albersheim P (1987) Structure of plant cell walls 1: XIX. isolation and characterization of wall polysaccharides from suspension-cultured douglas fir cells. *Plant Physiol* 83:659–671. <https://doi.org/10.1104/pp.83.3.659>
- Tsuneda A, Thormann MN, Currah RS (2001) Modes of cell-wall degradation of Sphagnum fuscum by Acremonium cf. curvulum and Oidiodendron maius. *Can J Bot* 79:93–100. <https://doi.org/10.1139/b00-149>
- Turetsky MR (2003) The role of bryophytes in carbon and nitrogen cycling. *The Bryologist* 106:395–409
- Turetsky MR, Crow SE, Evans RJ, Vitt DH, Wieder RK (2008) Trade-offs in resource allocation among moss species control decomposition in boreal peatlands. *J Ecol* 96:1297–1305
- van Breemen N (1995) How Sphagnum bogs down other plants. *Trends Ecol Evol* 10:270–275. [https://doi.org/10.1016/0169-5347\(95\)90007-1](https://doi.org/10.1016/0169-5347(95)90007-1)
- Verhoeven JTA, Liefveld WM (1997) The ecological significance of organochemical compounds in Sphagnum. *Acta Botanica Neerlandica* 46:117–130
- Wicks RJ, Moran MA, Pittman LJ, Hodson RE (1991) Carbohydrate signatures of aquatic macrophytes and their dissolved degradation products as determined by a sensitive high-performance ion chromatography method. *Appl Environ Microbiol* 57:3135–3143. <https://doi.org/10.1128/aem.57.11.3135-3143.1991>
- Williams CJ, Yavitt JB (2003) Botanical composition of peat and degree of peat decomposition in three temperate peatlands. *Ecoscience* 10:85–95. <https://doi.org/10.1080/11956860.2003.11682755>
- Xia Y-G, Sun H-M, Wang T-L, Liang J, Yang B-Y, Kuang H-X (2018) A modified GC-MS analytical procedure for separation and detection of multiple classes of carbohydrates. *Molecules* 23:1284. <https://doi.org/10.3390/molecules23061284>
- Yavitt JB, Williams CJ, Wieder RK (2005) Soil chemistry versus environmental controls on production of CH₄ and CO₂ in northern peatlands. *Eur J Soil Sci* 56:169–178. <https://doi.org/10.1111/j.1365-2389.2004.00657.x>
- Yu Z, Loisel J, Brosseau DP, Beilman DW, Hunt SJ (2010) Global peatland dynamics since the last glacial maximum. *Geophys Res Lett* 37:L13402. <https://doi.org/10.1029/2010GL043584>
- Zaccone C, Said-Pullicino D, Gigliotti G, Miano TM (2008) Diagenetic trends in the phenolic constituents of Sphagnum-dominated peat and its corresponding humic acid fraction. *Org Geochem* 39:830–838. <https://doi.org/10.1016/j.orggeochem.2008.04.018>
- Zhao Y, Liu C, Wang S, Wang Y, Liu X, Luo W, Feng X (2021) “Triple locks” on soil organic carbon exerted by sphagnum acid in wetlands. *Geochim Cosmochim Acta* 315:24–37. <https://doi.org/10.1016/j.gca.2021.09.028>

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