



Characterizing ecosystem-driven chemical composition differences in natural and drained Finnish bogs using pyrolysis-GC/MS

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ABSTRACT

Aerobic decomposition increases in drained peatlands; releasing stored organic matter (OM) and shifting greenhouse gas fluxes from sink to source. This study explored how drainage influenced peat OM chemical composition by investigating paired sites from a *Sphagnum*-dominated ombrotrophic Finnish bog undergoing contrasting hydrological management (natural and drained). Peat OM was investigated in replicate cores using analytical pyrolysis, compared with observed vegetation, elemental analysis (O:C, N:C), stable isotopes ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$), and fraction radiocarbon. Principal component analysis of quantified pyrolysis products separated four primary components: vascular plants vs *Sphagnum*, aerobic degradation of fresh plant biomass, anaerobic processes in water-saturated depths, and pine vs *Eriophorum*. The largest influence of drainage on peat chemistry was via aerobic decomposition (decreased abundance of *Sphagnum* phenols and simple polysaccharides; accumulation of macromolecular polysaccharides) ($p < 0.05$, 0–2 cm). Drainage-induced shifts in vegetation (from *Sphagnum* to *Pinus sylvestris*) ($p < 0.01$, 0–2 cm) were reflected by increased abundance in lignin, N-compounds, and lipids, and decreased abundance in phenols and polysaccharides. Anaerobic processes also differentiated the natural and drained sites and primarily affected polysaccharides ($p < 0.05$, 0–2, 8–10 cm). Vegetation shifts and aerobic decomposition similarly affected many of the same compounds upon drainage—demonstrating the simultaneous influence of different processes on the same OM. Pre-drainage inter-core variation illustrated the importance of replicate cores in disentangling anthropogenic changes from natural biodiversity. These findings suggest that even short-term and moderate alterations in peatland hydrology strongly influence the chemical composition of peat OM, and that its chemistry serves as an effective indicator to assess decomposition status.

1. Introduction

Due to the low rate of decomposition relative to net primary productivity (NPP), organic matter (OM) accumulates in intact peatlands, resulting in a carbon (C) store of approximately 600 gigatonnes (Gt) globally (Yu et al., 2010). Degradation stemming from drainage, agriculture, forestry, burning, and extraction have impacted roughly 10 percent of these fragile ecosystems worldwide (Joosten, 2009). As peatlands are degraded and exposed to increasingly oxic conditions, aerobic decomposition increases, releasing carbon dioxide estimated at two Gt annually (Leifeld and Menichetti, 2018), and shifting these C-dense ecosystems from C sink to source (IPCC, 2014; Humpenöder et al.,

2020). To restore their numerous vital ecosystem services, peatland restoration projects are increasingly employed (Andersen et al., 2017; Dohong et al., 2018). In terms of C sequestration, peatland restoration is considered a success when NPP exceeds decomposition (Andersen et al., 2010), which results in a net increase of C storage. In order to target ecosystems that will most benefit from restoration (i.e., ecosystems susceptible to high C emissions), it is vital to improve our understanding of the factors influencing peat OM decomposition and C mineralization.

In chemically complex matrices such as peat, gas chromatography-mass spectrometry techniques can be coupled with pyrolysis (Py-GC/MS) for the chemical characterization of OM. The pyrolysis process breaks up complex macromolecules into smaller, more easily analyzed

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fragments prior to GC/MS analysis, preventing discriminative loss of high molecular weight organic compounds and providing a “fingerprint” of the OM’s overall chemical composition (White et al., 2004; Klein et al., 2021). Peat OM composition analyzed via Py-GC/MS provides detailed molecular information on (past) peatland vegetation composition and decomposition processes. A number of source-specific pyrolysis products have been identified, such as the *Sphagnum* spp. biomarker *p*-isopropenylphenol (Stankiewicz et al., 1997; Van der Heijden et al., 1997; Schellekens et al., 2009; McClymont et al., 2011), and lignin from vascular plants (Hedges and Mann, 1979). Pyrolysis-GC/MS has large potential to identify different peat decomposition pathways. For example, degradation of lignocellulose in graminoid-dominated peat results in preferential loss of polysaccharides over lignin, while for *Sphagnum*-dominated peat the reverse is true and structural polysaccharides are preferentially preserved over phenols (Schellekens et al., 2015a). In addition, chemical classes (phenols, polysaccharides, N compounds, lipids, etc.) can be compared to investigate broader land-use shifts (Zhang et al., 2019). Due to its complexity, it is useful to compare peatland OM chemical composition with other complementary methods as part of a multi-proxy analysis. In example, molar ratios can be used as an overall measure of degradation, as carbon, hydrogen, nitrogen, and oxygen stoichiometric ratios vary in peat according to OM origin and decomposition (Wang et al., 2014; Moore et al., 2018; Leifeld et al., 2020). Further, radiocarbon ($F^{14}C$) measurements are generally used in calibrated peat age assessments (Trumbore, 2000; Wang et al., 2021), but can also be used in raw form as a rapid screening tool to assess the presence of subsidence (and thus whether depth comparisons are valid measurements).

Studies conducting depth-based comparisons of natural and drained sites within the same peatland ecosystem are relatively scarce. To study the effect of peatland drainage on OM composition, core samples have often been obtained from different peat locations (and sometimes ecosystems) out of necessity (Kuder et al., 1998; Heller et al., 2015; Harris et al., 2020), as few research sites offer an opportunity for paired comparisons from the same location due to the general worldwide long-term degradation of peat. To explore how drainage impacts the composition of peat OM, this study aimed to identify differences in the chemical composition of natural and drained peatland sites from the same ecosystem – both by hydrological management and with depth.

2. Materials and methods

2.1. Location and sampling

The Lakkasuo peatland (61°48'N, 24°19'E) is an ombrotrophic bog in Finland that has been accumulating peat for the past 3,000–6,000 years, with a maximum reported peat depth of 3.7 m (Laine et al., 2004). Mean annual air temperature in the study area is 3 °C and mean annual precipitation is 700 mm (Minkkinen et al., 1999). In 1961, ditches were installed (70 cm depth, with spacing of 40–60 m) for forestry purposes. Approximately 50 percent of the peatland was affected by this drainage (Minkkinen et al., 1999). An extensive survey of Lakkasuo ecology has been previously conducted (Laine et al., 2004).

Three peat core replicates were collected in June 2017 from the ombrotrophic natural/un-drained (ON) and drainage-affected locations (OD) to a depth of 1 m, using a Russian peat corer (Eijkelkamp, Netherlands). The water table levels were based on measurements obtained in a previous study and were approximately 6–7 cm below ground surface (bgs) in ON, and 15 cm bgs in OD (Jaatinen et al., 2007). ON and OD sampling sites were separated by a distance of approximately 15 m, and hydrologically separated by a drainage ditch (Murphy et al., 2009). Lateral distance between the replicate cores was measured with GPS and was approximately 1.3 m. The sampling depth was based on findings by (Krüger et al., 2016), who reported that the main effects of management in these two sites were primarily found in the upper 40 cm of the core depth profiles.

Surface vegetation in the area surrounding the OD sample site was described during the onsite assessment as a combination of *Oxycocco quadripetali-Pinetum silvestris*. Vegetation surrounding the ON sample site (which was restricted to hollow system areas) was described as a moist association of an *Empetrum-Sphagnum fuscum* bog with adjacent *S. fuscum* hummocks. Plant macrofossil assessments were conducted on sample cores ON1 and OD2 in 2017 and are provided in (Supplementary Tables 4&5).

After collection, the cores were stored at 2 °C until sample processing, where they were sliced into 2 cm sections, oven-dried at 40 °C for 72 h, and then homogenized in a mixer mill (Retsch MM 400) for three minutes at 25 Hz. Each core was analyzed to a four cm resolution in two cm sections (0–2, 4–6, 8–10, etc.), down to a depth of 70 cm, for a total of 108 samples across the six cores. Samples were denoted by their site source (ON or OD), followed by core number (1–3), and profile section depth in cm (for example, ON1 0–2).

2.2. Py-GC/MS

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) was performed using a double shot pyrolyzer (Frontier Laboratories, model 2020i) operating in single shot mode, attached to an Agilent 7890 Series GC. As the focus of this study was to conduct a broad chromatographic survey where unintentional derivatization of the larger peat matrix could be disadvantageous, chemical pre-treatments (such as tetramethylammonium hydroxide) were not applied prior to analysis. Approximately one mg of sample was introduced for one minute into the preheated (600 °C) micro-furnace. Samples were flushed with Helium (He) for one minute prior to furnace introduction. The pyrolyzer interface with the GC unit was held at 320 °C. Pyrolyzed compounds were swept from the pyrolysis furnace to the GC column in inert He. Since the Py-GC/MS method was the same for all samples, it was assumed that any preferential pyrolytic efficiency for different compound classes was consistent (Klein et al., 2020).

The GC was equipped with a 30 m column (5xi-5sil, equivalent to HP-5 ms) X 240 μ m, 0.25 μ m film thickness. In order to improve the chromatographic separation of abundant low molecular weight compounds, the GC oven temperature was held at 40 °C for 1 min and 50 °C for one minute at the start of each run (with a ramped increase of 3 °C min^{-1} between each hold time). The oven temperature was then increased to 165 °C at 3 °C min^{-1} , followed by a second increase from 165 °C to 310 °C at 5 °C min^{-1} , and then stabilized at 310 °C for 10 min. The inlet was set to 280 °C in split mode (100:1). He was used as a carrier gas at a controlled flow of 1 ml min^{-1} . The GC was coupled to an Agilent 5977B series mass selective detector. Spectra were acquired at 70 eV ionizing energy in the 50–600 mass to charge ratio (m/z) range.

Pyrolysis product identification and integration were performed using Agilent ChemStation software. 108 compounds were selected as representative of the peat matrix (dominant peaks), and plant species and decomposition processes (specific compounds). These 108 compounds were quantified in all samples and assigned per their relative abundance using the peak area of their characteristic ion fragments (Supplementary Table 1). All peaks were checked manually to prevent mischaracterization stemming from slight shifts in retention times. For compound assignment, mass spectra were compared with published data as reported in the NIST 2014 mass spectral digital library, as well as to available literature. Results are provided in relative rather than absolute abundances. The sums of all peak areas were set as 100 percent, and individual peak abundance was calculated in relative proportion to the total quantified peak area (as relative percent abundance).

Assigned compounds were grouped by compound class and probable origin. These groupings were phenols, polysaccharides, lignin (guaiacyl-derived and syringyl-derived), benzenes, N compounds, and lipids (aliphatics, *n*-alkanes, methylketones, fatty acids, and terpenoids). The chemical classification groupings were further considered by their broader peatland ecological origin and/or association (Schellekens

et al., 2009; Schellekens and Buurman, 2011; Schellekens et al., 2015a; Kaal et al., 2017).

2.3. Elemental analysis

Elemental analysis was conducted on all samples and used for the calculation of molar ratios (N:C, O:C) and C and N stocks (Section 3.4). Bulk C, H and N analysis was conducted by dry combustion using a EuroEA3000 Elemental Analyzer, and for organic O by pyrolysis at 1000 °C followed by GC-TCD quantification (Hekatech, Germany). Samples measured for pH from both ON and OD were pH < 4.2, and were thus assumed to be free of carbonate. Therefore, bulk C concentrations were considered to be equivalent to organic C concentrations. In addition to elemental analysis data, bulk density measurements obtained from the University of Basel were also used to calculate C and N stocks (Groß-Schmolders et al., 2020).

2.4. Radiocarbon isotope analysis

Fraction ^{14}C (F^{14}C) abundances were determined for three depths in each of the six cores (8–10, 48–50, 80–82 cm) using accelerator mass spectrometry (Oeschger Centre for Climate Change Research, Department of Chemistry and Biochemistry, University of Bern) in order to match the cores by F^{14}C and not only by depth (Section 3.4).

2.5. Statistics

To separate the multi-dimensional influence of ecosystem-driven processes (i.e., hydrological status, vegetation type, decomposition processes, etc.) on chemical composition, principal component analysis (PCA) was applied to the 108 quantified pyrolysis products using a correlation matrix. PCA pyrolysis product loadings take into account the shared variation of all pyrolysis products, and were used to interpret the processes reflected by individual PCs. PCA scores reflect the relative effect of the processes in the samples and were used to evaluate the effects of drainage by assessing their variation with depth and between cores. Small compound abundances have the ability to introduce analytical error in PCA correlation matrices, and were encountered in some pyrolysis products in this study. However, such pyrolysis products can also be particularly informative about the processes they reflect; therefore, their inclusion was maintained. PCA loadings and scores show weight of variance, but are not quantitative metrics. Pyrolysis product depth profiles are presented as a quantitative measure of the processes reflected by individual PCs, and were selected based on their explained variance (>0.5 loadings on each PC) (Schellekens et al., 2015b; Lopes-Mazzetto et al., 2018).

Correlation analyses were conducted using regression analysis and Pearson correlation. Differences between ON and OD in mean relative abundance of pyrolysis products (i.e., for summed chemical classes and for pyrolysis products with PC loadings >|0.5|) were tested by independent T-test. Significance for all statistical tests was set at $p < 0.05$. Results presenting average values are given as mean \pm standard deviation of the mean. Statistical analyses and related depth plots were done using Python (version 3.8.2).

3. Results

3.1. General composition of peat pyrolysis products

A complete list of the pyrolysis products identified, including mean abundance of individual products, is provided in Supplementary Table 1. Across the investigated samples (all sites and depths), the contribution of primary chemical classes to all quantified pyrolysis products was: phenols 10.40%, lignin (guaiacyl- and syringyl-derived) 1.79%, benzenes 1.34%, N compounds 0.38%, polysaccharides 85.09%, and lipids (aliphatics and terpenoids) 1.00%. Depth profiles of

the relative abundance of summed chemical classes (%) are given in Fig. 1. Average and standard deviation of the relative abundance of each summed compound class is provided in Supplementary Table 2.

Depth profiles of the summed compound classes (Fig. 1(a-f)) demonstrated the largest differences in abundance in the surface peat (0–10 cm), with significantly higher abundances observed in OD for summed lignin (0–2 cm, $p < 0.01$), benzenes (0–2, 8–10, 12–14 cm, $p < 0.05$) and summed lipids (0–2 cm, $p < 0.01$). While not significantly different in surface samples (0–4 cm), summed N compound relative abundance increased rapidly through the acrotelm of OD, where it was significantly higher in OD from 8 to 14 cm ($p < 0.05$) – reaching maximum abundance between 4 and 10 cm before decreasing with depth and approaching similar abundance between sites at 16–18 cm. Summed phenols and polysaccharides were not significantly different in surface samples, but trended higher in ON than OD, with continued increased abundance in ON until approximately 8–10 cm. Levoglucosan was a highly dominant pyrolysis product (average 44% abundance across all cores and depths) in the summed polysaccharides, and demonstrated through its outsized influence on the polysaccharide depth profile that individual pyrolysis products do not contribute similar influence in terms of abundance to their respective summed compound class. When investigated separately from levoglucosan, the average relative abundance of the polysaccharides class was significantly higher in ON in surface samples (0–2 cm) ($p < 0.001$), and decreased from the surface before generally stabilizing with depth. Below 12–14 cm, the relative abundances of all summed compound classes followed generally similar trends; however, differences in individual core chemistry were apparent in certain depths (i.e., benzenes, N compounds, and lipids from 32 to 42 cm, and lignin from 36 to 52 cm).

3.2. Application of principal component analysis to quantified pyrolysis products

Principal components (PC) 1 to 4 explained 68.7% of the variance in all pyrolysis products. Pyrolysis product loadings for PC1–4 are provided in Supplementary Table 3. Depth profiles of scores for PC1–4 are shown in Fig. 2(a) and summed relative abundance of pyrolysis products (%) with loadings (>|0.5|) representative of each PC are shown in Fig. 2(b-c). Loading projections of PC1 vs PC2, and PC3 vs PC4, which were used to identify the processes (Section 4.1) are provided in Fig. 3.

PC1 scores (29.4% explained variance) were significantly different between ON and OD in surface samples, with high positive scores in OD and scores close to 0 in ON (0–2 cm) (Fig. 2(a), $p < 0.01$). With the exception of OD2, PC1 OD scores maximized at 4–6 cm before decreasing and approaching ON scores around 12–14 cm. Below 12–14 cm, both ON and OD scores remained near zero in PC1 - with the exception of OD1, which demonstrated mostly negative scores, and ON2, which demonstrated sustained positive scores - particularly in the depths between 40 and 52 cm. PC2 (19.0% explained variance) demonstrated high positive scores in both sites in surface samples (0–2 cm) that rapidly decreased with depth. OD scores approached zero at approximately 4–6 cm, whereas ON scores approached zero (with the exception of ON2) at approximately 8–10 cm. ON demonstrated significantly higher positive scores than OD at the surface (0–2 cm) ($p < 0.05$). Below 8–10 cm, PC2 scores remained near zero - with the exception of OD1, which demonstrated consistently positive scores with depth, and ON2, which demonstrated consistently negative scores. PC3 (12.2% explained variance) scores showed more variation through the depth profile, and were generally characterized by high positive scores in surface samples that decreased with depth; rapidly in the surface samples, then more gradually through the remainder of the cores. ON demonstrated significantly higher positive PC3 scores in surface samples (0–2, 8–10 cm) ($p < 0.05$). PC4 (8.5% explained variance) was separated by high positive scores in OD and low negative scores in ON in surface samples (0–2 cm) ($p < 0.05$). PC4 scores approached zero in all cores at approximately 8–10 cm. Below this depth, PC4 scores remained

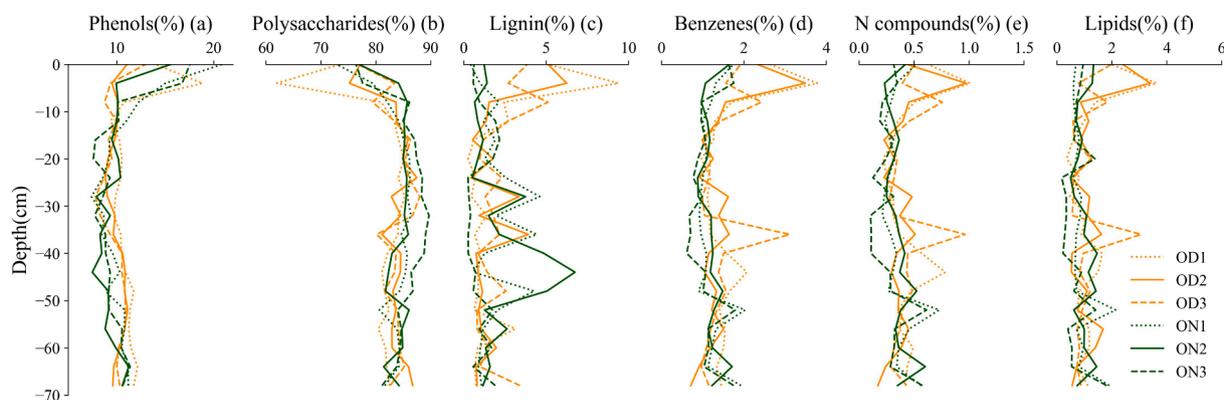


Fig. 1. (a-f) Relative abundance (%) of pyrolysis products summed by compound class for ON (green) and OD (orange).

near zero through the remainder of the profile, with the exception of ON1-2, which both demonstrated negative scores.

3.3. Pyrolysis products reflective of processes (PCs)

PC1 was characterized by high positive loadings ($>|0.5|$) of pyrolysis products guaiacyl-derived lignin (19–27), catechols (10, 12) benzenes (1,2), C-29 sterols (59, 62, 63), sesquiterpenes (103–108), and N compounds (34, 36–39); and high negative loadings of phenols (17, 18) and polysaccharides (69, 71, 82, 86, 88, 90, 91) (Fig. 3). Pyrolysis products with positive loadings on PC1 were in significantly greater abundance in OD in surface samples (0–2 cm) ($p < 0.05$); whereas products with negative loadings were in significantly higher abundance in ON (0–2 cm) ($p < 0.05$) (Fig. 2 (b-c)). Below 8–10 cm depth, relative abundance stabilized in pyrolysis products with positive loadings - with the exception of ON2, which demonstrated higher relative abundances between 40 and 50 cm. While greater variability was observed in the pyrolysis products associated with negative PC1 loadings, abundances also stabilized below 8–10 cm - with the exception of OD1, which demonstrated consistently higher abundance through the remainder of the profile.

PC2 demonstrated high positive loadings of polysaccharides (68, 72, 76–81, 84, 89, 92, 93, 97), unsaturated aliphatics (55, 56) and phenols (3, 4, 6, 9, 13, 17, 18); and high negative loadings of levoglucosan (100), 1,6-anhydro- β -D-glucofuranose (101), and an unknown (likely polysaccharide) compound (83). Pyrolysis products with positive loadings on PC2 displayed significantly higher abundance in ON in surface samples (0–2 cm) ($p < 0.01$); whereupon all products rapidly decreased in relative abundance from the surface before stabilizing at approximately 8–10 cm. Products with negative loadings displayed significantly higher abundance in OD in surface samples (0–2 cm) ($p < 0.01$), and rapidly increased from the surface to the same depth as the compounds with positive loadings on PC2.

PC3 was characterized by high positive loadings of levogalactosan (98), 4-vinylphenol (11), 2-furanmethanol (72), and dihydro-6-methyl-2H-pyran-3(4H)-one (93); and negative loadings of polysaccharides (69, 70, 73, 74, 75, 78, 82, 85, 88, 96), the N compound 3-hydroxypyridine monoacetate (35), pristene (54), *p*-cresol (5), and the C-27 methylketone (47). PC3 associated pyrolysis products were in significantly higher abundance in ON in surface samples (0–2 cm) for both products with positive loadings ($p < 0.01$), and negative loadings ($p < 0.05$). Products associated with positive loadings on PC3 decreased rapidly in surface samples, and maintained a decreasing trend through the remainder of the profile. Products associated with negative loadings on PC3 demonstrated a slight increase in relative abundance with depth; however, the trend was less robust.

PC4 was characterized by positive loadings of levomannosan (99) and 4-vinylsyringol (30), as well as guaiacyl-derived lignin, C-29 sterols, catechols, and sesquiterpenoids; and negative loadings of *n*-alkanes and

n-alkenes (41, 43, 44), methylketones (46, 47), and the polysaccharide 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one (87). Syringyl-derived lignin also demonstrated almost exclusively negative loadings on PC4. Pyrolysis products with high positive loadings on PC4 displayed significantly higher abundance in OD (0–2 cm) ($p < 0.05$). Products with negative loadings were not significantly different in surface samples, but were significantly higher in ON at 4–6 cm ($p < 0.05$).

3.4. Elemental and radiocarbon analysis

Molar ratios were calculated from bulk peat samples for C, H, N, and O. Average O:C molar ratios were significantly higher in ON than OD in the upper 6 cm of the profile ($p < 0.05$) (Fig. 4). N:C molar ratios were significantly higher in OD than ON to the same depth. Differences between ON and OD were observed to approximately the same depth as those observed via Py-GC/MS analysis. Average C and N stocks were calculated to 82 cm depth in both ON and OD (kg/m^3). Average C and N stocks (respectively) were 17.97 ± 2.72 and 0.30 ± 0.05 in ON, and 28.33 ± 2.98 and 0.51 ± 0.07 in OD. C stocks were significantly higher in OD than ON ($p < 0.05$).

To improve the peat core depth correlations by identifying possible subsidence-caused depth shifts in the profile, drained and natural cores from the Lakkasuo site were matched by fraction radiocarbon abundance ($F^{14}\text{C}$) (Supplementary Table 6). No significant difference was observed in $F^{14}\text{C}$ abundance between ON and OD samples measured to 82 cm depth.

3.5. Correlation with complementary analyses (C/N ratios & bulk isotopes)

PC scores were correlated with bulk stable isotope values ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) measured in a study conducted on the same peat cores (Groß-Schmolders et al., 2020), as well as C/N ratios determined using elemental analysis data obtained in this study (Table 1, Supplementary Fig. 1). Significant moderate negative correlations were identified between PC1 and CN, and PC3 and $\delta^{15}\text{N}$ ($p < 0.01$), with significant relationships also observed between PC4 and $\delta^{13}\text{C}$ (negative correlation), and PC3 and C/N (positive correlation).

4. Discussion

4.1. Interpretation of the main processes by PCA loadings

The positive loadings on PC1 for guaiacyl-derived lignin, benzenes, C-29 sterols, sesquiterpenes, and N compounds are indicative of vascular plant growth, whereas negative loadings of phenols and polysaccharides are indicative of *Sphagnum* (Fig. 3). PC1 therefore reflects vegetation origin. The negative loadings for most phenol pyrolysis products (with the exception of the catechols (10, 12)) are in agreement with the

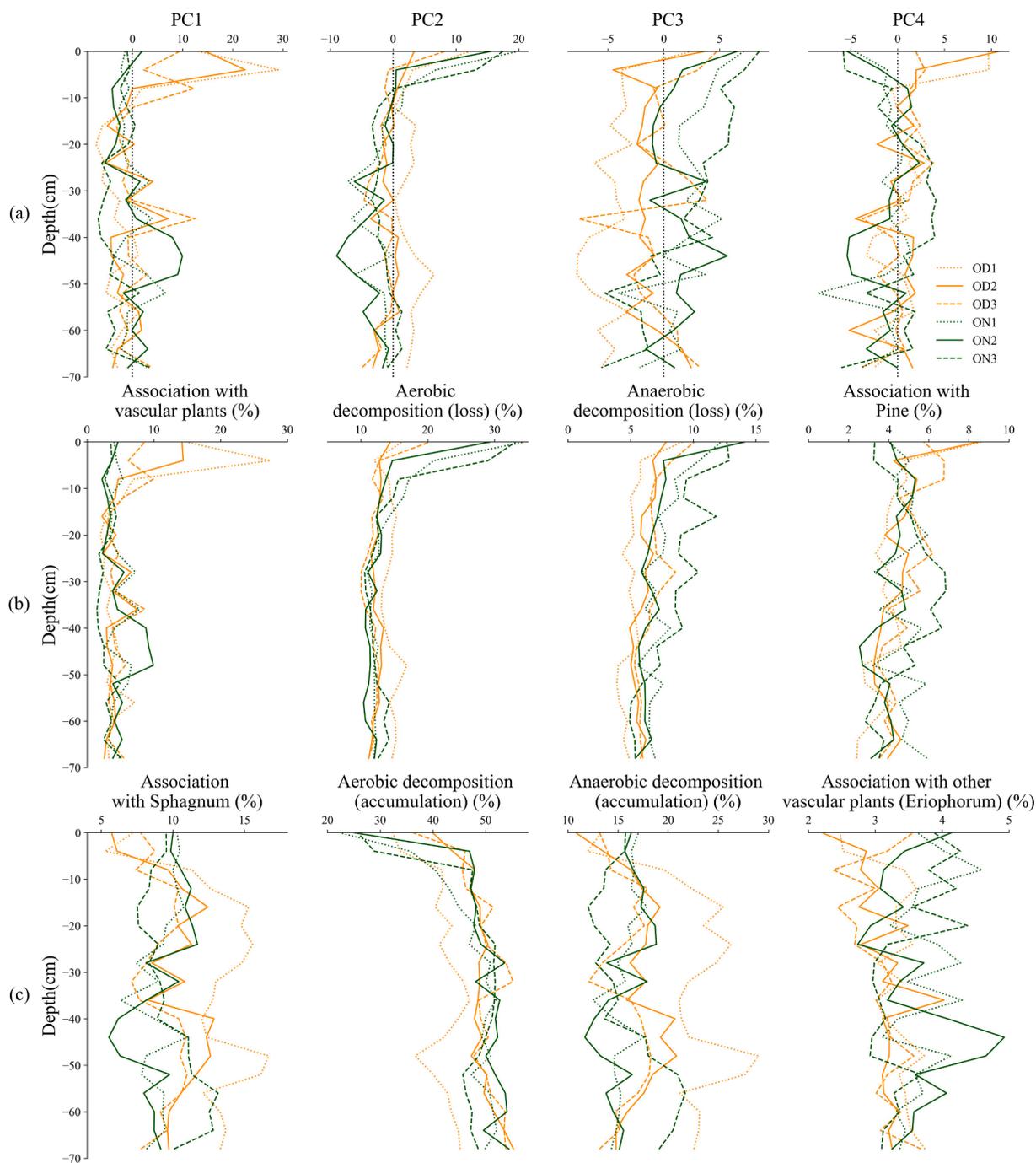


Fig. 2. (a-c) Interpretation of environmental processes driving chemical differences in Lakkasuo OM as reflected by PC1-PC4 (from left to right); demonstrated by (a) score projections with depth, (b) relative abundance (%) of associated pyrolysis products with PC positive loadings (>0.5), and (c) relative abundance (%) of associated pyrolysis products with PC negative loadings (<-0.5). ON is depicted in green, OD is depicted in orange.

negative loadings of the *Sphagnum* biomarker *p*-isopropenylphenol (13), and suggest that at the studied sites, most phenols can be primarily attributed to *Sphagnum*-derived OM rather than lignin-derived OM regardless of hydrological conditions (Zeh et al., 2020). *Sphagnum* spp. produce a pectin-like structural polysaccharide (sphagnan) in their cell walls that is the most likely source of the majority of the polysaccharides with negative loadings on PC1 (Hájek et al., 2011). The highest negative loadings on PC1 were observed for the polysaccharide α -acetobutyrolactone (86), which is associated with “fresh” plant material in peat (Tolu et al., 2015). In contrast, the high positive loadings of guaiacyl-derived lignin (relative to syringyl) are consistent with contribution from gymnosperms (Hedges and Mann, 1979). The high positive

loadings of N are in agreement with the higher rhizospheric nutrient demand of vascular plants compared to *Sphagnum*; who have been shown to thrive in nutrient-poor ombrotrophic conditions such as those occurring in this bog (Limpens et al., 2003; Malmer et al., 2003). Further, while both mosses and higher plants contain C-29 sterols, vascular plants generally display higher abundance (Ronkainen et al., 2013), and their positive loadings on PC1 support the argument that they can largely be attributed to pine litter in this ecosystem.

For PC2, the decrease in relative abundance of *Sphagnum* phenols (positive loadings), corresponding with increasing relative abundance of levoglucosan and 1,6-anhydro- β -D-glucofuranose (negative loadings) is consistent with preferential aerobic degradation of phenols over

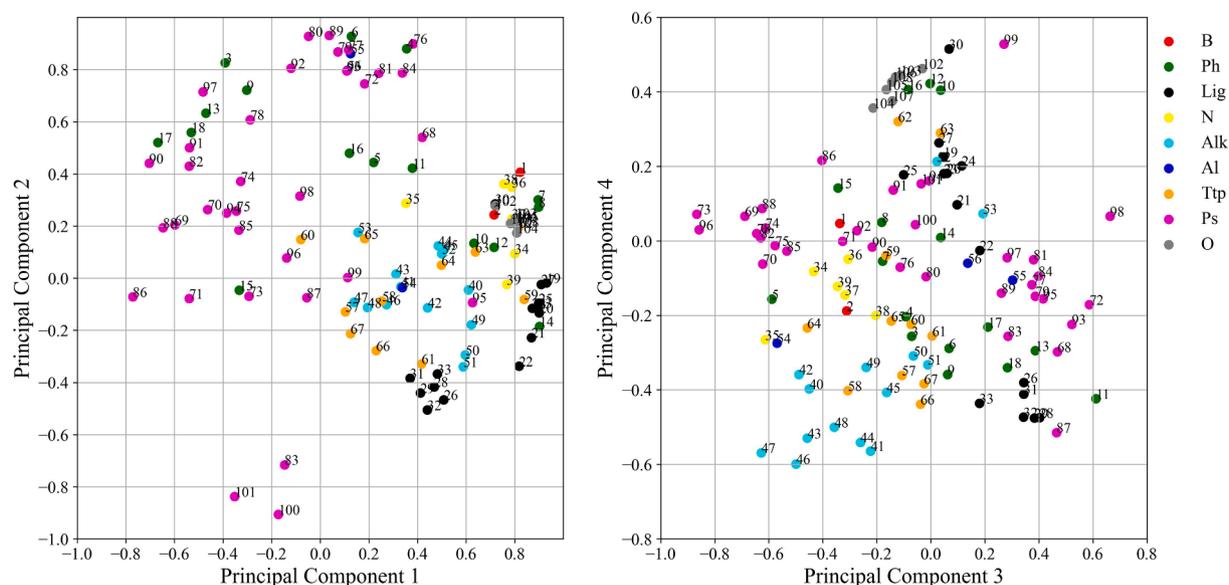


Fig. 3. Principal component loadings of (left) PC1-PC2 projections, and (right) PC3-PC4 projections. PC1-4 explained 68.7% of the variance in all pyrolysis products (PC1 = 29.4%, PC2 = 19.0%, PC3 = 12.2%, PC4 = 8.5%). B, benzenes; Ph, phenols; Lig, lignin (all); N, nitrogen compounds; Alk, *n*-alkanes, *n*-alkenes, and *n*-methylketones; Al, other aliphatic hydrocarbons; Ttp, triterpenoids; Ps, polysaccharides; O, other terpenoids (mono- and sesquiterpenes).

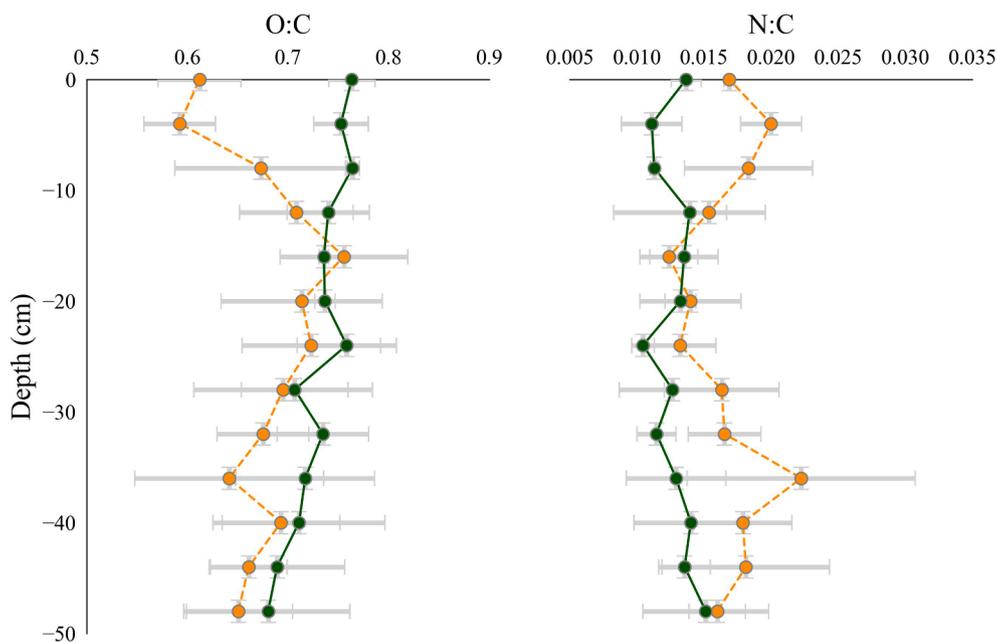


Fig. 4. O:C (left) and N:C (right) depth profile molar ratios in ON and OD. Solid green lines indicate ON, and dashed orange lines indicate OD. Standard deviation was calculated through the average molar ratios of the three replicate cores.

polysaccharides in *Sphagnum* peat (Schellekens et al., 2015a), resulting in the relative accumulation of more “recalcitrant” compounds associated with cellulose (such as levoglucosan). PC2 thus reflects aerobic decomposition. The high positive loadings of phenols and polysaccharides that also had positive loadings on PC1 (associated with vascular plant material) likely indicate “fresh” plant material, and reflect preferential loss of polysaccharides over lignin in peat (Schellekens and Burman, 2011).

PC3 separates polysaccharide pyrolysis products by positive and negative loadings, which combined with the observed decrease in relative abundance over the entire depth profile (PC3, Fig. 2(b)), (suggesting “palatability” of these compounds) is consistent with anaerobic processes in the deeper water-saturated depths. 2-Furanmethanol has

been previously proposed as a potential pyrolysate biomarker for bacteria (Eudy et al., 1985; Klein et al., 2021), and its high positive loadings here combined with its rapid decrease in abundance from the surface in both sites support this argument. 1,4:3,6-Dianhydro-D-glucopyranose and the phenol *p*-cresol (negative loadings) are both ubiquitous pyrolysis products in peat (Hatcher et al., 1988), and are likely artifacts of poorly decomposed OM preserved in anaerobic conditions. Further, the negative loadings of the polysaccharides here likely indicate inhibited decomposition of the sphagnum polysaccharide complex, as it is resistant to degradation in anaerobic conditions (Painter, 1991; Hájek et al., 2011). The particularly high negative loadings of the small polysaccharide 2-propylfuran (73) on PC3 are also notable, as its similarity in abundance between sites in surface samples together with its increase

Table 1

Correlation of PC scores 1–4 with corresponding $\delta^{15}\text{N}$, $\delta^{13}\text{C}$, C/N ratios, and a summary of the processes reflected by each PC. Bold indicates significance at $p < 0.01$. Signs (\pm) depict the direction of influence of the processes, interpreted by the loadings on each PC.

PC	$\delta^{15}\text{N}$	$\delta^{13}\text{C}$	C/N	Process
PC1	0.09	-0.16	-0.55	Vegetation shift: vascular plants (Pine) (+) vs <i>Sphagnum</i> (-)
PC2	-0.17	-0.27	-0.05	Aerobic decomposition processes: “fresh” plant material (+) vs increasing aerobic decomposition (-)
PC3	-0.50	0.24	0.33	Anaerobic decomposition processes: degradation of “palatable” compounds (+) vs relative accumulation (-)
PC4	0.06	-0.43	0.21	Vegetation shift: Pine (+) vs other vascular plants (<i>Eriophorum</i>) (-)

in relative abundance in the water-saturated depths in all cores suggests a possible origin from microbial residue.

The separation of lignin compounds on PC4 – with guaiacyl-derived compounds generally displaying positive loadings and syringyl-derived compounds displaying negative loadings – suggest that PC4 reflects the separation of pine from the contribution of another vascular (likely angiosperm-derived) source. The positive loadings of C-29 sterols, catechols, and sesquiterpenoids further indicate the influence of pine; whereas the 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one (negative loadings) is a pyrolysis product of xylose, a hemicellulose-derived compound highly abundant in grass and sedge species (Pouwels et al., 1989; Schellekens et al., 2015b). While the compound is also abundant in wood, its high negative loadings in association with syringyl-derived lignin suggest that 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one is likely contributed by *Eriophorum* spp. in this bog, which corresponds with findings from macrofossil assessments conducted on two of the cores in 2017 (Supplementary Tables 4&5). Debate exists over whether *n*-alkane-2-ones are contributed directly by peat-forming vegetation (Nichols and Huang, 2007; Zhang et al., 2020) or by microbial sources via oxidation of *n*-alkanes or *n*-fatty acids (Lopez-Dias et al., 2013). The high positive loadings of the methylketones on PC4 combined with their negative loadings on PC3 in association with anaerobic processes suggest a multiple-source origin.

4.2. Effects of drainage on OM chemistry in Lakkasuo by PCA scores

In PC1, the clear separation of scores (Fig. 2(a)) in ON and OD demonstrate the difference in chemical composition between *Sphagnum* and vascular plants in the surface peat. The higher positive scores observed in OD surface samples for PC1 (associated with vascular plants) is consistent with the positive higher scores in OD surface samples for PC4 (associated with Pine), and indicates that the majority of the vascular plant OM contribution in the upper acrotelm depths can be attributed to the *Pinus silvestris* onsite. The convergence of PC1 scores between 8 and 12 cm suggests that beneath these depths, the overall ecosystem was not substantially different between the two sites (however, see Section 4.3). PC1 scores suggest that prior to the drainage activities onsite, OD1 and ON3 maintained the most consistent *Sphagnum* cover, whereas ON1 and ON2 experienced intermittent periods with more vascular plant growth.

The PC2 scores trace the shift in chemistry occurring via aerobic decomposition processes with depth. In surface samples, the higher positive scores in ON (as well as the slower decreases with depth in ON1 and ON3) is consistent with “fresh” *Sphagnum*, in contrast to the more rapidly degraded OM deposited in the drained horizons of OD. The convergence of the scores between 8 and 10 cm coincide with the convergence in PC1 scores reflecting changes in botanical composition, and suggest that both sites were generally water-saturated prior to drainage. Individually, ON2’s rapid decrease (compared to the other two

ON cores) in surface samples is consistent with observations from PC1 indicating increased vascular plant abundance in that core, and suggest that while it may be water-saturated presently, ON2 experienced the most consistent aerobic conditions of the six cores prior to the drainage activities. In contrast, OD1’s consistently positive PC2 scores with depth suggest that before drainage activities, it was likely the most water-saturated of the six core sampling sites.

PC3 reflects anaerobic degradation in the deeper water saturated zone – particularly by the separation of source-dependent polysaccharides. Positive scores on PC3 likely show “fresh” plant material, whereas negative scores indicate increasingly anaerobically processed OM. While more variability was observed with depth in the PC3 scores, they generally trend higher in ON than OD through the entire profile depths, and suggest that ON experienced less microbial activity under anaerobic conditions compared to OD. In contrast, OD1 demonstrated the lowest PC3 scores of the six cores with depth, in addition to its scores consistent with increased *Sphagnum* cover (PC1) and water-saturated conditions (PC2). This suggests that OD1 may have experienced the most consistent anaerobic conditions of the six cores prior to the drainage activities.

The shift from high positive scores to low or negative scores observed in PC4 below 8–10 cm shows that before the drainage and forestry activities, *Pinus sylvestris* played little to no role in the ecosystem. However, the intermittent negative scores observed, particularly in the case of ON1 and ON2, indicate previous abundance of *Eriophorum* in addition to *Sphagnum* cover (as indicated by PC1 scores). Moreover, the vacillating shifts between zero and negative scores observed in each core with depth suggest that dominant vegetative cover may also have been somewhat cyclical – perhaps with regular transitions from wet hollows and *Sphagnum* to drier hummocks and *Eriophorum*.

4.3. Representation of environmental processes

PCA illustrated that peat OM in the profile was often influenced by multiple processes (PCs) simultaneously. In example, many of the same pyrolysis products (i.e., polysaccharides and phenols) with high negative loadings on PC1 (Fig. 2(c), *Sphagnum*-associated) also demonstrated high positive loadings on PC2 (Fig. 2(b), association with OM loss via aerobic decomposition). This demonstrates the simultaneous influence of multiple environmental processes on the same OM, and indicates the presence of multiple concurrent chemical signals driven by *Sphagnum*, vascular plants, and aerobic (and to a lesser degree, anaerobic) decomposition processes that must be disentangled.

While the PC scores best reflect the processes demonstrating the net effect of drainage (Fig. 2(a)), the pyrolysis product depth profiles provide a quantitative approach that permits visualization of the relative amount of OM affected by each process (Fig. 2(b-c)). Moreover, comparison of pyrolysis products allows for targeted abundance-driven comparisons as a method of clarifying unclear origins in peat OM.

4.4. Other proxies (molar ratios, C stocks, stable isotopes)

In stoichiometric assessments, higher O:C molar ratios tend to indicate less decomposed material, whereas higher N:C ratios suggest a greater abundance of proteinaceous material (Leifeld et al., 2020). In the surface sample depths, the lower O:C and higher N:C molar ratios in OD compared to ON are in agreement with these expectations and overall findings from the Py-GC/MS analysis.

In Table 1, the negative correlation between PC1 scores and C/N ratios was in agreement with higher positive loadings of N compounds on PC1. The negative correlations between PC2 and both stable isotopes are consistent with enrichment of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ with increased aerobic decomposition, due to preferential microbial utilization of ^{12}C and ^{14}N during the decomposition process (Ågren et al., 1996; Nadelhoffer et al., 1996; Alewell et al., 2011; Krüger et al., 2015). However, the weak correlations also suggest that they have been influenced by other factors

in this peat. For PC3, the positive correlation with C/N combined with the negative correlation to $\delta^{15}\text{N}$ suggested links to increasingly anaerobic microbial processes with depth (Krüger et al., 2015). The stronger $\delta^{15}\text{N}$ trend is not necessarily unique to anaerobic decomposition, as relative $\delta^{15}\text{N}$ enrichment with depth is also typical in peat horizons governed by aerobic decomposition (Drollinger et al., 2019). However, our findings also correspond with data obtained from a bulk stable isotope study on the same peat cores, where initially depleted $\delta^{15}\text{N}$ values became more enriched with depth through the acrotelm and mesotelm before stabilizing in the catotelm, reflecting increased microbial contribution and transitioning decomposition communities in shallower peat regions (Krüger et al., 2015; Groß-Schmolders et al., 2020). For PC4, the increasing enrichment of $\delta^{13}\text{C}$ as scores are increasingly associated with *Eriophorum* is likely due to increased plant input in the historical samples where *Eriophorum* was more abundant (Section 4.2). The observed weak positive relationship between PC4 scores and C/N ratios also suggests a difference in the “quality” of deposited OM, depending on the dominant contributing vascular source. The lower C/N ratios and enriched ^{13}C ratios in samples associated with *Eriophorum* are consistent with other studies that reported lower C/N and enriched ^{13}C ratios for sedge species compared to woody shrubs (Biester et al., 2014; Zeh et al., 2020).

The lack of difference in F^{14}C abundance with depth between the sites suggests either that OD OM has been compensated somewhat by higher litter inputs, or that subsidence has not yet played a large role at the sampling site. As the drainage activities at Lakkasuo were both non-intensive and comparatively recent (<60 years), insufficient time may have passed to permit substantial peat subsidence. Cross-referencing of cores by depth were thus considered to be valid comparisons.

The higher C stocks in OD compared to ON correspond with findings of previous researchers that pine tree stands can play an important role in bulk C density and C stocks of drained peat - due to an increase in primary productivity through input of new C from fine tree root material (Minkinen and Laine, 1998; Minkinen et al., 1999; Hommeltenberg et al., 2014; Minkinen et al., 2018). The potentially outsized role of pine tree stands is also consistent with the higher abundance of guaiacyl-derived lignin observed in OD surface peat. Higher C stocks in OD were therefore considered evidence of increased contribution from pine-derived biomass, rather than subsidence stemming from peat oxidation.

4.5. Spatial variability

The depth profiles in Lakkasuo indicate that the changes in hydrology in the “modern” peatland (and its drainage activities) are preserved in the upper 10 cm of the cores. Below this depth, there is evidence of preservation of previous ecosystem conditions that were present prior to the drainage. Individual deviations from overall trends can be observed in single cores indicative of small-scale spatial biodiversity typical of hummock-hollow ecosystems and representative of natural variation in the peatland environment. Due to the close proximity of the Lakkasuo drained and natural sites and the similarity in ^{14}C abundance, it was assumed that the ecosystem was not significantly different between the two sampling locations prior to the drainage activities. The intra-site spatial variation apparent in the replicate cores partially overrides inter-site differences and thereby clearly demonstrates the effect of natural biodiversity on peat chemical composition. The effect of biodiversity can also be observed through the separation of PC4 scores between sample cores with depth, and provides some information about the history of the Lakkasuo sample site through the increased abundance in pyrolysis products reflective of *Eriophorum* cover – particularly in the ON1-2 cores. This seems to provide some evidence that historically, ON may generally have been the “drier” of the two sites prior to the drainage activities (relatively speaking in the context of an intact peat ecosystem), and underscores the importance that wherever possible, peatland OM comparisons should ideally be based on more than one field replicate.

5. Conclusions

Our findings confirm that peat hydrology is a strong driver for changes in peat chemical composition. PCA applied to a high resolution Py-GC/MS analysis of natural and drained peat core replicates from the same ecosystem allowed separation of concurrent environmental processes into individual components (changes in vegetation (PC1, PC4), aerobic decomposition processes (PC2), and anaerobic decomposition processes (PC3)). Aerobic conditions displayed the strongest drainage-induced influence on peat chemistry in terms of the relative percentage of OM affected, through large reductions in phenols and simple polysaccharides and relative accumulation of macromolecular polysaccharides levoglucosan and 1,6-anhydro- β -D-glucofuranose. The influence of drainage was also reflected by the changing botanical composition, through large reductions in phenols and polysaccharides indicative of the decreased *Sphagnum* cover at OD, and increased abundance of guaiacyl-derived lignin, benzenes, C-29 sterols, and sesquiterpenes representing the contribution from the onsite *Pinus silvestris*. Changing botanical composition (*Sphagnum* vs Pine) influenced the abundance of many of the same pyrolysis products that were also influenced by aerobic conditions, suggesting that concurrent chemical signals (*Sphagnum*, vascular plants, degradative processes) were present and distinguishable in the same OM - particularly in peat polysaccharides, but also in the phenol compound class. Anaerobic decomposition played a comparatively minor role in overall degradative processes; however, its effects were increasingly visible in the cores with depth.

Overall, these results indicate that even “short-term” (<60 years) and “moderate” (<30 cm decrease in water table in OD) changes in peat hydrology result in directly traceable changes in chemical composition. Moreover, OM chemical composition can be used as an effective tool to assess degradative status with depth in peatlands, particularly when core replicates can be taken. As land use shifts have recently been shown to have long-term impacts on peat OM composition and its overall susceptibility to degradation (Schimmel et al., 2021), the extent to which degradation-driven changes in OM composition are reflective of changes in C emissions is an area urgently requiring further study.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary Material

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