Key Points:
- Changes in vegetation and water table position directly and interactively mediate peat redox environment and the redox-activity of DOM
- Phenolic character consisted of increased molecular weight in more oxidized peat occurring with a lower water table and presence of sedges
- Plant functional groups have stratified effects on unique compounds, with more aromatics accumulating in mixed species rhizospheres

Reduction-Oxidation Potential and Dissolved Organic Matter Composition in Northern Peat Soil: Interactive Controls of Water Table Position and Plant Functional Groups

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Abstract Globally important carbon (C) stores in northern peatlands are vulnerable to oxidation in a changing climate. A growing body of literature draws attention to the importance of dissolved organic matter (DOM) in governing anaerobic metabolism in organic soil, but exactly how the reduction-oxidation (redox) activities of DOM, and particularly the phenolic fraction, are likely to change in an altered climate remain unclear. We used large mesocosms in the PEATcosm experiment to assess changes in peatland DOM and redox potential in response to experimental manipulations of water table (WT) position and plant functional groups (PFGs). WT position and PFGs interacted in their effects on redox potential and quantity and quality of DOM. Phenolics were generally of higher molecular weight and more oxidized with sedges in lowered WTs. Altered DOM character included changes in dissolved nitrogen (N), with higher N: [phenolics] with higher E4:E6 (absorbance ratio $\lambda = 465:665$) DOM in the lowered WT and sedge PFG treatments. Conversely, biomolecular assignments to amino-sugars were largely absent from low-WT treatments. Low WT resulted in the creation of unique N compounds, which were more condensed (lower H:C), that changed with depth and PFG. The accumulation of oxidized compounds with low WT and in sedge rhizospheres could be very important pools of electron acceptors beneath the WT, and their mechanisms of formation are discussed. This work suggests the effects of changes in vegetation communities can be as great as WT position in directly and interactively mediating peat redox environment and the redox-activity of DOM.

Plain Language Summary Peatlands are important ecosystems in both the global carbon (C) cycle and the Earth's climate system owing to their ability to store vast quantities of C taken from the atmosphere. Peat C stays locked up in these ecosystems largely owing to cool and wet conditions, and as such, these C stores are vulnerable to release back to the atmosphere if the climate or water levels change. Water table level and plant species composition have a combined effect on C and nitrogen (N) cycling in peatlands. We manipulated both factors in an experimental setting composed of 24 large bins into which we put intact peatland miniecosystems. Sedges play a big role in producing N compounds below the peat surface, and this work suggests these compounds can actually be synthesized into larger, less accessible compounds. In addition, activities of sedge roots and other dominant plant communities (such as shrubs in the heath family of plants) may interact in the synthesis of oxidized, larger molecules. These molecules can allow microbes to continue to decompose peat even in the absence of oxygen. This could increase the release of greenhouse gas carbon dioxide to the atmosphere, while reducing inputs of the stronger greenhouse gas methane.

1. Introduction

While peatlands are widely appreciated for their high density of soil organic carbon (Kolka et al., 2018), there are still gaps in our mechanistic understanding of the vulnerability of this tremendous carbon store to

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mineralization (Bridgham et al., 2008; Waddington et al., 2015). Peat decomposition is largely arrested in the hypoxic and anoxic environments occurring in saturated soils (Blodau, 2002). However, abiotic and biotic factors responding to climate change can alter water table (WT) position and reduction-oxidation (redox) conditions in peatlands (Roulet et al., 1992). Trends and climate models predict a general pattern of decreased water availability in the summer (Thomson et al., 2005), with precipitation patterns becoming more variable in recent decades (Easterling et al., 2000; Kunkel et al., 2003; Wuebbles et al., 2019). In turn, these changes in climate can lead to increased WT variation at the local scale, including large midsummer declines in WT height (Hilbert et al., 2000). The net effects of decreased water availability in peatlands could drive important increases in peat oxidation and alter the physical and chemical properties of peat (Laiho, 2006). In turn, these factors influence plant community composition (Churchill et al., 2015; Dieleman et al., 2015; Weltzin et al., 2000) and net primary production in peatlands (Chimner et al., 2017; Chivers et al., 2009; Radu & Duval, 2018; Strack & Waddington, 2007). Exactly how plant communities change in response to climate change drivers will likely affect the carbon sink-strength of these ecosystems.

Interactions of hydrology and plant functional groups could create feedbacks to oxidation and decomposition dynamics in peat (Waddington et al., 2015). Bogs are dominated by three major functional groups of plants: *Sphagnum* mosses, ericaceous shrubs (e.g., heath plants), and sedges. While these broad groups often coexist, changes in hydrology alter their abundances (Potvin et al., 2015). In sedges, the presence of aerenchyma tissue, resultant deep rooting, and lack of mycorrhizae promote oxidation hotspots occupied by consortia of aerobic and anaerobic free-living heterotrophs in the rhizosphere. Under conditions of WT drawdown, this sedge-mediated mineralization generally increases peat subsidence and colonization of hollows by less recalcitrant *Sphagnum* species (Potvin et al., 2015). In contrast, Ericaceae lack aerenchyma and are shallow rooted and therefore dominate in hummock microsites or in relatively drier conditions. The Ericaceae produce recalcitrant litter (Cornelissen, 1996) and have mycorrhizal fungi, which possess some oxidative extracellular enzymes but lack peroxidase enzyme activity (Cairney & Burke, 1998; Cairney & Meharg, 2003); these factors have an inhibitory effect on peat decomposition (Read et al., 2004) thus promoting hummock formation and creation of microsites that are more likely to be above the WT (Belyea & Malmer, 2004; Ohlson & Dahlberg, 1991). As such, there are interactive effects between altered hydrology and plant functional groups, which have been shown to influence decomposition dynamics in peat (Wiedermann, Kane, Potvin, et al., 2017). However, the interactive effects of changes in peat saturation or vegetation community on oxygen supply and redox environment remain to be elucidated.

The redox status of wetland environments can theoretically be represented in the sequential reduction chain of the terminal electron acceptors (TEAs) present (Megonigal et al., 2004). However, several studies have demonstrated relatively high rates of decomposition in peat (as heterotrophic production of CO_2) when the thermodynamic yield indicated by inorganic TEAs would suggest otherwise (Deppe et al., 2010; Dettling et al., 2006; Kane et al., 2013; Keller & Bridgham, 2007; Vile et al., 2003). A growing body of literature draws attention to the importance of humic substances and organometallic complexes in governing anaerobic metabolism in organic soil (Gao et al., 2019; Heitmann et al., 2007; Klüpfel et al., 2014; Lipson et al., 2010). Humic substances are rapid scavengers of oxidants (Bauer et al., 2007; Brouns et al., 2014) and as such would be expected to be particularly effective electron acceptors in peatlands with a fluctuating WT or with increased colonization of sedges (cf. Agethen et al., 2018). However, to date, little has been done to evaluate the redox activities of humic substances specifically in response to climate change drivers in peatlands.

While the exact roles humic substances play in terminal metabolism of hydric soils remain largely conceptual (Boye et al., 2017; Keller & Bridgham, 2007; Wüst et al., 2009), quinone or quinone-like moieties in dissolved organic matter (DOM) are likely driving redox dynamics (Nurmi & Tratnyek, 2002; Schwarzenbach et al., 1990). The electron accepting capacity of humic substances has been shown to increase with the relative quinone content of the total pool of phenolic DOM in laboratory experiments (Aeschbacher et al., 2012; Sharpless et al., 2014). The diagenesis and oxidation of fulvic acids (which contain phenols) also generally result in higher molecular weight DOM (Visser, 1983a). Collectively, this work suggests that an increase in the overall shift in the phenolic pool to quinone moieties or higher molecular weight DOM should influence the redox potential of peat soil pore water. However, exactly how phenolic

content and its character within the DOM pool are likely to change with an altered climate in peatlands are still debated in the literature (Brouns et al., 2014; Pinsonneault et al., 2016; Wang et al., 2015; Wiedermann, Kane, Veverica, et al., 2017).

There are complex interactions among the persistence of phenolic compounds, redox conditions, and extracellular enzyme activities, which all are affected by changes in peatland hydrology and plant composition. A proposed mechanism for the persistence and accumulation of phenolic DOM is the enzymic latch hypothesis (Freeman et al., 2001), in which there is suppression of phenol oxidase activity in anoxic conditions, which occur with a high WT. In this conceptual model, the accumulation of phenolics further stabilizes peat by inhibiting hydrolytic enzyme activity. However, subsequent study has observed mixed evidence for this hypothesis and has shown higher phenolics with declines in WT position in peat mesocosm experiments controlling for plant functional groups and WT position (Dieleman et al., 2016; Romanowicz et al., 2015). In this same experimental framework, the highest phenolic concentrations were observed in treatments with lowered WT positions and sedge vegetation (Haynes et al., 2017). The accumulation of phenolics can further complicate decomposition dynamics through the occlusion of necessary nutrients, particularly nitrogen (e.g., Northup et al., 1995; Schnitzer, 1985). More work investigating the mechanisms driving changes in phenolic or redox-active DOM, in the context of altered hydrology or change in vegetation community in peatlands, is needed to elucidate these decomposition dynamics.

It is possible that varying reports on the preservation of phenolic or redox-active DOM with changes in redox conditions are due to changes in DOM composition and the energetics of its decomposition (LaRowe & Van Cappellen, 2011). Recent work has demonstrated that the nominal oxidation state of carbon (NOSC) influences the decomposability of DOM in anaerobic environments (Boye et al., 2017). The activation of different functional groups in DOM depend on overall redox potential (Bauer et al., 2007; Helburn & MacCarthy, 1994). As such, in reducing environments with low-NOSC DOM, the amount of energy required to fully oxidize DOM increases (Keiluweit et al., 2016). Perhaps counterintuitively, it is more thermodynamically favorable to oxidize compounds with a high NOSC in reducing environments (LaRowe & Van Cappellen, 2011; Pracht et al., 2018), which has been nominated as a preservation mechanism for low-NOSC DOM in anoxic environments (Boye et al., 2017). Therefore, changes in NOSC have important implications for the fates of different pools or types of peatland DOM, which can exhibit a wide range of carbon oxidation states depending on source of plant material (Worrall et al., 2016, 2017). The preservation of these different compounds likely depends on how the intrinsic oxidation state varies in relation to redox oscillations within the peat, such as occurs at the WT interface (Tfaily et al., 2018) or within sedge rhizospheres (Askaer et al., 2010). Taken together, these studies suggest a complex and yet poorly resolved interplay among changes in redox conditions, plant functional groups, and the character of leachates, exudates, or water-soluble products of the decomposition of different plant tissues in determining the fates of phenolic or redox-active DOM in peatlands.

In this study we investigated the consequences of altered precipitation and peatland plant functional groups (PFGs) on peatland redox status and the resulting effects on pore water composition. A peatland mesocosm experiment manipulated WT and plant community composition to simulate potential effects of climate change on key peatland ecosystem functions (Potvin et al., 2015). The mesocosm approach enabled the investigation of interactive effects among WT position (relatively high and stable vs. low and more variable) and PFGs (removal of ericaceous shrub, removal of sedges, and an unmanipulated mixed community) on peat redox status and DOM character over 3 years. Because the activation of different functional groups in DOM depend on overall redox potential, we hypothesized that changes in PFGs and altered hydrology resulted in changes not only in the total pool of phenolics but also in the character of the phenolics in response to changes in redox conditions. Specifically, we hypothesized (H1) there would be more redox-active DOM, with higher NOSC, and molecular weight, in the low-WT and sedge treatments. We expected (H2) that the more oxidized DOM, in having been broken down by aerobic heterotrophs, would exhibit lower aromaticity and have a lower N content. We investigated changes in the molecular mass of DOM, and biomolecular indicators unique to our treatments, to understand the degree to which our treatments influenced DOM oxidation and degradation versus polymerization and macromolecular transformation. Finally, we hypothesized (H3) the effects of increased oxidation on DOM properties to be manifest deeper in the peat profile with the presence of sedges. To address these overarching questions, we measured changes in electrochemistry, anions, dissolved organic carbon, and absorbance and fluorescence spectroscopy of the

peat pore water at three different strata approximately biweekly for 3 years at our mesocosm facility. We used Fourier-transform ion-cyclotron-resonance mass spectrometry (FT-ICR MS) on one complete suite of samples to investigate changes in peat pore water molecular composition and DOM redox activity (NOSC) and compared these analyses with complementary absorption and fluorescence spectroscopic approaches. With these data, we evaluated changes in DOM molecular weight, NOSC, and the presence of unique compounds in response to our treatments.

2. Materials and Methods

2.1. Mesocosm Experiment

The mesocosm experiment known as PEATcosm (Peatland Experiment at the Houghton Mesocosm Facility) was an outdoor, controlled experiment that manipulated WT positions and vascular plant functional groups in peat mesocosms to simulate potential climate change impacts as previously described in detail (Haynes et al., 2017; Potvin et al., 2015). Briefly, 24 1 m^3 (1 m × 1 m × 1 m) peat monoliths were extracted intact from an ombrotrophic peatland located in Meadowlands, Minnesota, USA in the summer of 2010. Monoliths were transferred intact and uncompacted into individual mesocosm bins in the field and transported to the U.S. Forest Service Northern Research Station mesocosm facility in Houghton, Michigan, USA. The stainless-steel interior of each bin was Teflon-coated to prevent metal transfer between the bin and the peat. The top of each bin was open, exposing the peat to ambient climate conditions. The mesocosm bins were inserted into a climate-controlled tunnel and insulated on the sides, which established vertical temperature gradients as would be observed in a natural peatland profile.

The PEATcosm study was a 2 × 3 full-factorial experimental design with two WT treatments crossed with three vascular PFG treatments in a randomized complete block design, with four replicates per treatment combination, resulting in a total of 24 experimental units. Plant functional group treatments were initiated in 2010, and WT treatments were initiated in the summer of 2012. The PFG treatments were designed to distinguish between effects of Ericaceae (non-aerenchymatous shallowly rooted shrubs with enzymatically competent mycorrhizal root symbionts) and sedges (aerenchymatous herbaceous graminoids with nonmycorrhizal roots that penetrate deeper into the saturated peat). As such, there were three vegetation treatments: 1) all Ericaceae removed ("sedge" or "S" treatment), 2) all sedge removed ("Ericaceae" or "E" treatment), and 3) no vegetation removed ("unmanipulated" or "U" treatment). The WT treatments were based on long-term data from the Marcell Experimental Forest in north-central Minnesota (Sebestyen et al., 2011), located near the peat monolith harvest site. The two target WT profiles were modeled after typical variability, average-WT years ("high WT") and high variability, low-WT years ("low WT"). The mean difference between the high and low-WT positions was approximately 20 cm throughout the experiment (2012–2014; *see* Potvin et al., 2015 *and* Haynes et al., 2017 *for hydrograph data*). These target WT profiles were maintained by a combination of artificial precipitation additions, translucent rain-exclusion covers, and regulated outflow (spring-only, from ~25 cm depth, roughly at the acrotelm-catotelm boundary) from each of the bins.

Data monitoring, logging, and systems control were conducted by National Instruments (NI) LabVIEW software (LabVIEW; Austin, TX, USA) as previously described in detail (Potvin et al., 2015). Temperature, water level, and dissolved oxygen were logged every 10 min by a NI Controller (CompactRIO 9074) linked to the LabVIEW monitoring software. Water level was monitored using submersible vented pressure transducers (Grainger 2HMC7) deployed in PVC well pipe in the center of each mesocosm bin. To examine the direct effects of PFG on peat redox prior to the initiation of WT drawdown experiments (May–June 2012), dissolved oxygen was continuously measured using In-Situ RDO Pro optical sensors (In-Situ Corporation; Ft. Collins, CO, USA) deployed in the pressure transducer wells to a depth of 10 cm beneath the WT surface in each bin.

2.2. Pore Water Sampling and Analysis

Pore water was collected from a micropiezometer nest (ultra-high-density polyethylene casing with inner Teflon tubing) installed in each of the 24 mesocosms. Piezometers had compartmentalized 10-cm slotted regions covered with Nitex nylon mesh (37 m) centered at three depths—20 cm, 40 cm, and 70 cm below the peat surface. The compartmentalized regions within these three depths effectively acted as oxygen

diffusion chambers for assessing pore water redox potential (Megonigal & Rabenhorst, 2013). Pore water was harvested by purging the lines through a three-way stopcock prior to sampling with a syringe. Approximately biweekly throughout the growing seasons of 2012–2014, samples were drawn from the three depths for a suite of analyses. A small amount of pore water was drawn with a syringe as a prerinse for sample collection in high-density polyethylene Nalgene bottles. Approximately 100 ml of sample was collected and then filtered through 0.45-m nylon membrane filters (within 3 hr; stored in a cooler). Approximately 30 ml of sample was acidified (HCl) and refrigerated for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) analyses, 30-ml refrigerated and reserved for absorption and fluorescence spectroscopy (within 1–2 days), and approximately 40 ml of sample was frozen prior to anion analyses.

We measured DOC and TDN using a Shimadzu TOC-V Combustion Analyzer with a nitrogen module (Shimadzu Scientific Instruments, Columbia, MD, USA). Anions (nitrate, sulfate, chloride, and phosphate) and organic acids (acetate, propionate, formate, and oxalate) were quantified with an ICS-2000 ion chromatograph with an IonPac AS11 separator column, using suppressed conductivity detection and a KOH eluent gradient (Dionex Corporation, Bannockburn, IL, USA). Total phenolics (tannin and lignin) were analyzed using Hach (Loveland, CO, USA) reagents scaled to a microplate technique and standardized to tannic acid as previously described in detail (Romanowicz et al., 2015). Total and ferrous iron were measured in peat pore water using the *o*-phenanthroline method (Hach Co.; Methods 8146 and 8008, respectively) employing a correction factor for matrix interference effects as previously described in detail (Veverica et al., 2016). Pore water redox potential (Eh) was measured within 5 min of collection on samples collected as previously described with a platinum electrode (Hach Co., Intellical MTC301) connected to a sealed and sample-purged flow-through cell (Romanowicz et al., 2015). The probe was calibrated daily with an ampoule of Light's solution (Hach Co., no. 2612520) and conditioned with reducing solution (Hach Co., no. 2965349). All Eh values were normalized to a pH of 7 (Eh7), based on pH-Eh relationships for Quinhydrone (Bier, 2009).

From 2012–2014, pore water spectrophotometry (absorbance at $\lambda = 254$, 365, 465, and 665 nm) was conducted using a microplate spectrophotometer (Spectra-Max M2; Molecular Devices Corp., Sunnyvale,CA, USA). All data collected using microplates were normalized to data collected with quartz cuvettes (1-cm pathlength). Absorbance indexes used were E2:E3 ($\lambda = 254{:}365$ nm)—an inverse index of both molecular size (De Haan & De Boer, 1987; Helms et al., 2008; Zhang & He, 2015) and electron acceptor capacity (Sharpless et al., 2014)—and E4:E6 ($\lambda = 465{:}665$ nm)—an index of molecular size and/or quinone conjugation (Chen et al., 1977; Senesi et al., 1989; Helms et al., 2008) and fulvic acid content (Blodau & Siems, 2012; Wallage et al., 2006). An increase in E4:E6 is thought to be indicative of DOM containing higher concentrations of carboxylic and ketonic bonds (C=O) in addition to aromatic bonds linked and substituted primarily by oxygen (Chen et al., 2010), because these bonds readily absorb light at $\lambda = 46\ 5$ nm (E4; Uyguner & Bekbolet, 2005; Chen et al., 2010; Hribljan et al., 2014). We measured DOC specific absorbance at $\lambda = 254$ (SUVA254), which is an index of aromaticity (Weishaar et al., 2003). Starting in 2013, absorbance and fluorescence (Excitation-Emission Matrices, EEMs) were both measured simultaneously with a Horiba-Jobin Yvon Aqualog C (HORIBA, Ltd.; Kyoto, Japan) using a 1-cm quartz cell with a 0.1-s integration time, on samples within an hour of collection. Samples were diluted to absorbance <0.6 at $\lambda = 254$ nm to assure measurements fell within the linear range of the instrument. Run parameters and absorbance, excitation, and emission corrections were performed as previously described in detail (Veverica et al., 2016), with EEMs preprocessing steps following the schemes presented in Lawaetz and Stedmon (2009) and Singh et al. (2013). We normalized fluorescence intensities to an external, ultrapure Raman peak water standard (Starna Cells; Atascadero, CA, USA), integrated similarly to the sample Raman peak and collected daily.

2.3. FT-ICR MS Measurements

A complete suite of pore water samples was collected for FT-ICR MS analyses in July of 2014 as an independent test of the absorption and fluorescence spectrophotometric assays of molecular weight and oxidation described above. A 12 Tesla Bruker SolariX FTICR spectrometer located at EMSL, a DOE-BER national user facility located in Richland, WA, was used to collect high-resolution mass spectra of the DOM in pore water samples as previously described in detail (Boye et al., 2017; *see supplemental methods for additional details*). Putative chemical formulas were assigned using Formularity software (Tolić et al., 2017; *see supplemental methods*).

Van Krevelen diagrams provide a means to visualize and compare the average properties of organic matter and assign compounds to the major biochemical classes (*i.e.*, lipid-, protein-, lignin-, unsaturated hydrocarbon-, and condensed hydrocarbon-like). In this study, biochemical compound classes are reported as relative abundance values based on counts of C, H, and O for the following O/C and H/C ranges; lipids (0 < O/C ≤ 0.3, 1.5 ≤ H/C ≤ 2.5), unsaturated hydrocarbons (0 ≤ O/C ≤ 0.125, 0.8 ≤ H/C < 2.5), proteins (0.3 < O/C ≤ 0.55, 1.5 ≤ H/C ≤ 2.3), amino sugars (0.55 < O/C ≤ 0.7, 1.5 ≤ H/C ≤ 2.2), lignin (0.125 < O/C ≤ 0.65, 0.8 ≤ H/C < 1.5), tannins (0.65 < O/C ≤ 1.1, 0.8 ≤ H/C < 1.5), and condensed hydrocarbons (0 ≤ 200 O/C ≤ 0.95, 0.2 ≤ H/C< 0.8). In this study, labile compounds refer to compounds that are readily utilized by microbial communities such as sugars and proteins, while the recalcitrant fraction is utilized with the aid of extracellular enzymes (Brookshire et al., 2005).

NOSC was calculated from the number of electrons transferred in organic carbon oxidation half reactions and is defined by the equation

$$\text{NOSC} = -((Z + 4a + b - 3c - 2d + 5e - 2f)/a) + 4$$

where a, b, c, d, e, and f are the stoichiometric numbers of elements C, H, N, O, P, S in organic material and Z is net charge of organic compound.

2.4. Statistics and Analysis

In our 3-year dataset, we examined changes in pore water Eh, DOC, TDN, and phenolic content in response to environmental (WT position, growing season) and biological (vegetation composition and biomass) variables and tested for interactive effects. We used a general linear mixed model approach, which enables statistical models to be fit to data where the response is not necessarily normally distributed (PROC GLIMMIX; SAS version 9.4, SAS Institute, Cary, North Carolina, USA). To account for repeated measures at multiple depths per mesocosm bin, sampling campaign was treated as a random effect, with the subject being sampling depth nested within each mesocosm bin (three depths, 24 bins). The distributions of response variables were evaluated in Kolmogorov-Smirnov tests using the UNIVARIATE procedure. The appropriate data distributions were assigned in the mixed-effects models (with distribution [dist] assigned as normal, lognormal, or beta as appropriate; link = log function). Type-3 tests of fixed effects and post hoc comparisons of least-squared means tests across treatments were considered significant at $\alpha = 0.05$. Least-squared mean value comparisons employed the Tukey-Kramer adjustment. All data are available in the public domain (https://doi.pangaea.de/10.1594/PANGAEA.902313).

Multivariate approaches were used to characterize pore water composition. We employed parallel factor analysis of all fluorescence EEMs as previously described (Veverica et al., 2016; *following* Stedmon & Bro, 2008; *and* Kothawala et al., 2014). This model identified five component classes describing >99% of fluorescence in all EEMs, with different regions of excitation (ex.) and emission (em.) as previously described (Veverica et al., 2016). Component 1 (C1 ex. 240, 325; em. 440) has been described as fulvic DOM (Kothawala et al., 2014). Components 2 and 3 (C2 ex. 250; em. 450; C3 ex. 255, 375; em. 450) have been described as terrestrial or less-condensed humic and fulvic materials (Kothawala et al., 2014; Olefeldt et al., 2013). Component 4 (C4 ex. 240, 325; em. 525) has been described as condensed aromatic and high molecular weight humic DOM, and Component 5 (C5 ex. 275; em. 328) has been described as lower molecular weight tyrosine and/or tryptophan-like DOM (free or bound in protein; Cory & Kaplan, 2012; Olefeldt et al., 2013; Kothawala et al., 2014). Principal component analysis (PCA) was used to describe broad trends in treatment chemistry and organic matter quality, incorporating a suite of chemical, absorbance, and fluorescence descriptors as previously described (Bro & Smilde, 2014; Kothawala et al., 2012). To account for repeated measures not being independent of one another, data were averaged by growing season (early vs. late season, by year) and by experimental treatment (high WT, low WT, crossed with ericoid, sedge, or unmanipulated vegetation); as such, $n = 36$ for PCA and related statistics. Parallel factor analysis and PCA were performed using PLS Toolbox (Eigenvector Research, Inc., Wenatchee, WA, USA) in Matlab R2014a.

2.5. Indicator Analysis

FTI-CR MS results were analyzed using indicator analysis in PC-Ord 5.0. The analysis identifies chemical formulas that indicate a specific group and assigns an indicator value and p value to each formula in an analysis. For each formula, we determined whether or not it was nitrogen containing. We summed the total
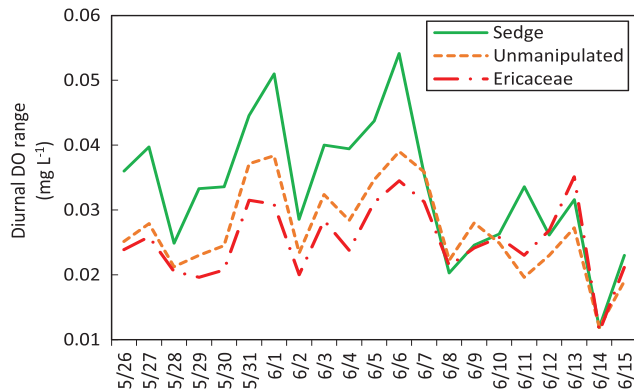
Figure 1. Mean diurnal ranges in dissolved oxygen measured in each meso-cosm bin by plant functional group treatment ($n = 8$) for the 2 weeks preceding the initiation of the water table treatments in 2012. Dissolved oxygen measurements occurred approximately 20 cm beneath the peat surface (10 cm beneath the water table) in each bin. Depicted are the differences between daily minimum and maximum, representing daytime/nighttime variation in the peak to peak amplitude of diurnal variation.

number of significant ($\alpha = 0.05$) indicators, and the number of significant indicators that were nitrogen containing, for each group. We then compared the observed pattern of nitrogenous versus total indicators with that expected by chance using a chi square test in Excel 2013 (Microsoft Inc, Redmond, WA, USA). We could not analyze the full set of depth × WT × PFG combinations because of missing data at 20-cm depth in the low-WT treatment (too dry for sampling at that depth). Therefore, we conducted tests for indicators within subsets of the data. We also plotted total indicators on van Krevelen diagrams and examined their overall patterns in response to treatments.

3. Results

3.1. WT and Vegetation Effects on Redox Environment

In the weeks prior to the initiation of WT treatments in 2012, there were higher-dissolved oxygen concentrations driving higher diel fluctuations in dissolved oxygen in the sedge vegetation treatments at 10-cm depth (Figure 1). With the onset of WT treatments, the degree of WT separation varied by year, with the average low-WT treatments reaching peak depths of 27.0 cm (12.3 cm lower than high WT), 46.3 cm (23.6 cm lower than high WT) and 47.7 (30.4 cm lower than high WT) for 2012, 2013, and 2014, respectively. WT position beneath the peat surface ($F = 349$, $p < 0.001$) and PFG ($F = 26$, $p < 0.001$) had strong main effects on pore water Eh7 across all samples and dates (denominator degrees of freedom = 486), but there was great variation among treatment years. Treatment year had a significant main effect on pore water Eh7 across all samples ($F = 313$, $p < 0.001$). Not surprisingly, depth also had a significant main effect on pore water Eh7 across all samples ($F = 9.8$, $p < 0.001$). After accounting for variation among annual campaigns and sampling depths, the biggest effects on pore water Eh7 were vegetation biomass, PFG treatment, and the interaction between PFG treatment and the position of the WT beneath the peat surface (Table 1). This PFG × WT interaction was caused by significant differences in Eh7 with depth from the peat surface as a function of WT treatment and PFG in the top 40 cm of peat (Figure 2), with the sedge PFG treatment having higher Eh and driving a PFG × WT interaction in the complete data set (Table 1).

3.2. WT and Vegetation Effects on DOM Composition

There was a strong association between Eh7 and different metrics of DOM character in PCA (Figure 3). PCA axis 1 was primarily defined by positive loading of Eh7 (loading of 0.25), ferric iron, molecular size or conjugation (E4:E6), and WT position and negative loading by ferrous iron, potential electron acceptor capacity (E2:E3), aromaticity (SUVA254), acetate, propionate, and formate concentrations (supporting information, Table S1; Figure 3). PCA axis 2 was primarily defined by the percent of DOM that was phenolic (loading of 0.37) versus oxalate concentrations (loading of −0.35). Axis 1 metrics reflected the position of the WT relative to peat surface (axis 1 loading of 0.23). WT position (depth below surface) changed significantly by treatment year and the progression of the growing season, with late season DOM being associated with oxidation and a deeper WT, as represented by positive loadings on axis 1 (Figure 3). Chloride is a largely conservative ion, and the chloride vector was orthogonal to WT position and total phenolics and only very weakly associated with DOC, suggesting evaporative concentration alone was not a strong mechanism for increased concentrations of DOM with lowered WT treatments. Eh7, which responded strongly to WT depth, was strongly positively correlated with molecular size and oxygen-containing bonds (E4:E6) and negatively correlated with E2:E3, tyrosine-like compounds (C5), and aromaticity (SUVA254; Figure 4).

After accounting for variation among campaigns, treatment years and sampling depths, the biggest effects on phenolic concentrations across all the data were WT position and PFG treatment (Table 2a), which is consistent with the observed increases in DOC as well (Table 2b). More oxidizing conditions occurring within the lowered-WT treatments generally resulted in higher E4:E6 and total phenolic concentrations, and the character of the phenolic pool also changed with WT treatment. Samples in the high-WT treatment had E4:E6 < 6 (lower molecular weight), regardless of concentration, whereas there was an increase in E4:E6 with phenolic content in the low-WT treatment (Figure 5).

Table 1
General Linear Mixed Model Effects on Reduction-Oxidation Potential

Variable			(a) Reduction-oxidation potential	
Effect	Num df	Den df	*F* Value	Pr > *F*
Water table position	1	480	1.34	0.2484
Total vegetation mass	1	480	6.42	**0.0116**
WT pos. × vegetation mass	1	480	2.99	0.0846
PFG treatment	2	480	3.91	**0.0207**
WT position × PFG treatment	2	480	3.76	**0.024**
Vegetation mass × PFG treatment	2	480	1.47	0.2311
WT position × vegetation mass × PFG treatment	2	480	1.56	0.211

Note. Values in bold text are significant at $P < 0.05$. Abbreviations: PFG, plant functional groups; WT, water table.

While TDN concentrations tracked DOC and total phenolics as expected (similar loadings in Figure 3; Table S1), the ratio of TDN:phenolics changed with vegetation mass and WT treatment (Table 2c). The amount of TDN per unit phenolics increased in the lowered-WT sedge treatments at a rate more than double that of all the high-WT treatments (Figure 6). The slope of the increase in TDN with phenolics for the high-WT unmanipulated PFG treatments was the same as that of the high-WT sedge treatments (slope = 0.06). As such, there was an interaction between vegetation treatment and WT in explaining the ratio of TDN:phenolics, and a three-way interaction with changes in vegetation mass (Table 2c).

FT-ICR MS analyses of samples obtained in July of 2014 demonstrated changes in the N-containing compounds with depth and plant functional type that agreed with trends in the ratio of TDN:phenolics observed in the broader dataset. The number of different C-, H-, O-, and N-containing compounds was higher in the lowered-WT treatment at 40 cm ($p = 0.04$) and 70 cm ($p = 0.03$) than in the high-WT treatment (supporting information, Figure S1). CHON compounds were clustered in two regions: (i) condensed hydrocarbons region $0.1 < O/C < 0.4$, $0.2 < H/C < 0.6$ and (ii) lignin-like region: $0.5 < O/C < 0.9$ and $0.6 < H/C < 1.4$. A higher abundance of N-containing compounds associated with condensed aromatic DOM were observed at 40 and 70 cm in response to the lower-WT treatment ($p = 0.01$). At 40 cm, there was a greater accumulation of aromatic N-containing compounds in response to the lower-WT treatment in the sedge and unmanipulated vegetation treatments, which were almost absent in the ericoid vegetation treatment, that is, the only treatment without sedges (Figure 7). At 70 cm, the greatest accumulation of aromatic N-containing compounds in both low- and high-WT treatments occurred in the mixed rhizosphere of the unmanipulated PFG treatment.
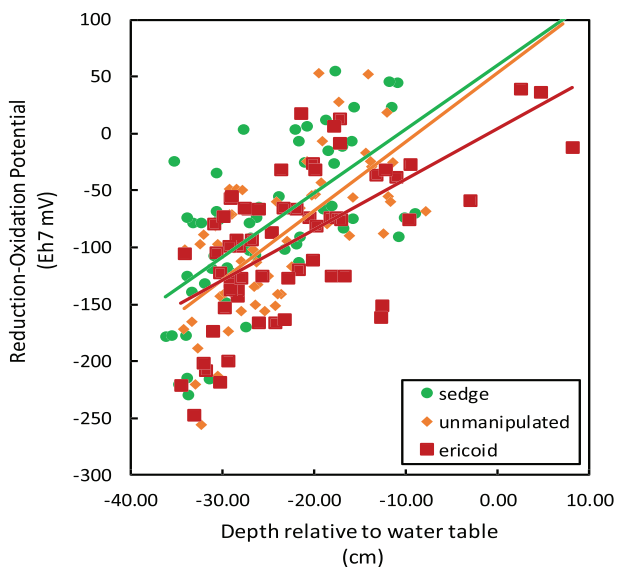
3.3. DOM Transformations and Unique Compounds

Within the subset of samples analyzed by FT-ICR MS, there was a strong association between WT treatment and different biomolecular classes (including all elements, CH, H, O, N, S, and P) in PCA (Figure 8). PCA axis 1 was primarily defined by positive loadings of condensed hydrocarbons and molecular mass (loadings of 0.88 and 0.68, respectively) and negative loadings of lignin-like compounds (loading of −0.66). PCA axis 2 was primarily defined by WT treatment, with positive loadings being associated with high WT, the unmanipulated treatment, carbohydrates, lipids, proteins, and amino sugars; and negative loadings associated with low WT, NOSC, tannins, and the sedge treatment (supporting information, Table S2). Parallel factor analysis-modeled fluorescence component vectors C1, C3, and C4 were all in the same sector as molecular mass and NOSC (axis 1 loadings ranging from 0.45–0.50), while C5 was aligned

Figure 2. There was an interaction between plant functional group (PFG) and water table (WT) position governing reduction oxidation potential in peat, with sedge-containing PFGs having higher slopes and intercepts of Eh7 with depth. To illustrate the oxidative effects of sedge PFGs with varying WT in the upper 40 cm, depicted here are measurements just from 2012–2013 (2014 had much larger peak drawdown in WT), though this interactive effect was significant across the entire data set (Table 1). Coefficients describing the trend lines are ($p < 0.001$ for all), Sedge: $\beta_0 = 59.9 \pm 21.9$, $\beta_1 = 5.6 \pm 0.9$, $R^2 = 0.41$; Unmanipulated: $\beta_0 = 52.8 \pm 22.6$, $\beta_1 = 6.0 \pm 0.9$, $R^2 = 0.44$; Ericoid: $\beta_0 = 4.2 \pm 14.4$, $\beta_1 = 4.4 \pm 0.6$, $R^2 = 0.45$.
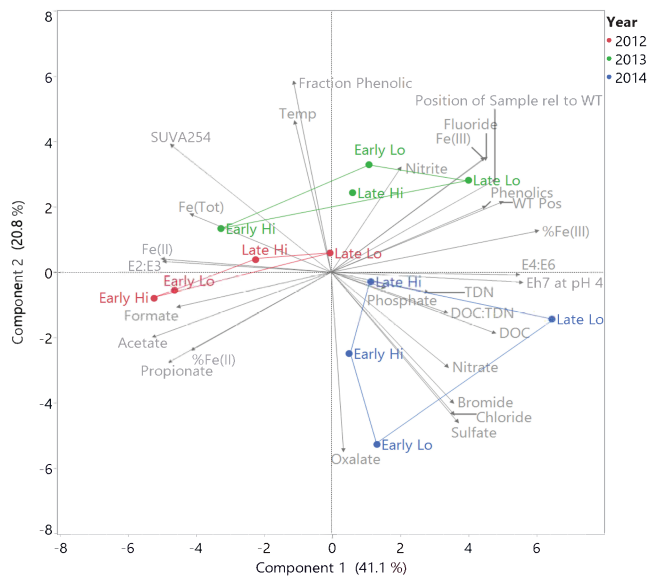
Figure 3. Graphical representation of principal component analysis of pore water chemical and absorption and fluorescence spectroscopic properties. Data are averaged by field campaign (early and late), water table treatment ("Hi" and "Lo"), and year. Scores on principal component analysis axes are provided in supporting information, Table S1.

with proteinaceous and amino sugar biomolecules (Table S2). Across all samples, NOSC increased with molecular mass ($R^2 = 0.20$, $p < 0.001$), but this trend was not significant at 40 cm in the sedge treatment owing to consistently high NOSC in DOM with relatively higher molecular masses in this treatment (Figure 9). In the sedge treatments, molecular mass was >475 Da (Figure 9b), corresponding with higher NOSC.

WT treatment effects on unique biomolecular components were reflected in samples obtained at different depths. The distribution of indicator biomolecules (probably unique) among PFGs in samples from 20-cm depths (high WT only) was similar to that of indicator biomolecules in low-WT treatment at 70 cm, with the greatest diversity in DOM character happening in the unmanipulated PFG treatment and much lower diversity in the other PFG treatments (Table 3a; "total" values). Isolating the 70-cm depth, the highest number of indicator compounds occurred in the unmanipulated PFG treatment with lowered WT (Table 3a), suggesting that the unique compounds of both sedge and ericaceous shrub rhizospheres can accumulate at depth beneath a lowered WT. This is also reflected by the increase in aromatic N-containing compounds at 70 cm in the unmanipulated mixed PFG treatment (Figure 7). In comparing across all treatments at the deeper depths (40 and 70 cm), the highest number of indicator compounds were found at 40 cm within the sedge treatment (Table 3b). Together, these findings suggest that sedge rhizospheres promoted the diagenesis of DOM and the water-soluble products of decomposition at 40 cm with a lower WT, while the combined effects of lower WT and diverse rhizospheres maximized the accumulation of indicator compounds at 70 cm.

Unique N-containing indicator species followed the trends in total indicator species, with three notable exceptions: 1) At 20 cm, the N-indicators were a lower percentage of the total indicators in the unmanipulated PFG treatment; this might suggest they were more effectively mined or precipitated at this depth when ericoid roots are more oxygenated; 2) There were few N indicators present in the high-WT treatments at 40–70 cm; and 3) In the combined 40- and 70-cm analysis, there were no N-indicators present at 70-cm depth in the low-WT sedge treatment. In considering 40- and 70-cm depths together, most of the unique indicators were present in the low-WT sedge treatment, in which 10% of all unique indicators contained N (Table 3b).

4. Discussion

4.1. Interaction Between DOM Properties and Redox Environment

The interactive effects of vegetation and WT position not only altered pore water redox environment, but also resulted in an intrinsically different character of DOM. The enzymic latch hypothesis (Freeman et al., 2001) proposes that oxidizing conditions, such as with the proliferation of sedges or a lower WT, would result in the breakdown of humic substances. We have shown here that oxidizing conditions can result in novel compound generation with larger molecular weights and higher NOSC—which is not necessarily inconsistent with "enzymic latch." A parsimonious explanation for this is enzymatically mediated polymerization of the partial breakdown products of decomposition, as has been demonstrated with relatively recalcitrant substrates containing lignin (Martin & Haider, 1971; *see review by* Zavarzina et al., 2011). Polymerization can be attributed to the activity of suites of oxidative enzymes, particularly laccases, which contribute to partial degradation of lignin in a manner similar to that of "brown rot" fungal decomposition (Baldrian, 2006; Chefetz et al., 1998; Lee et al., 2004; Suflita & Bollag, 1981). Oxidized lignin breakdown products enriched in phenolic and carboxylic groups (Kirk, 1975) are polymerized in this process, resulting in the synthesis of larger molecular weight DOM (Rypacek & Rypackova, 1975). In bog ecosystems, decomposition of recalcitrant compounds associated with the breakdown of *Sphagnum* could be analogous to prior models of aromatic lignin decomposition (Straková et al., 2010; cf. Wiedermann, Kane, Potvin, et al., 2017; Worrall et al., 2017). The strong negative relationships between SUVA254 (an indicator of aromatic C) and Eh7, as well as between SUVA254 and E4:E6 presented herein (Figure 4) are consistent with increased breakdown of
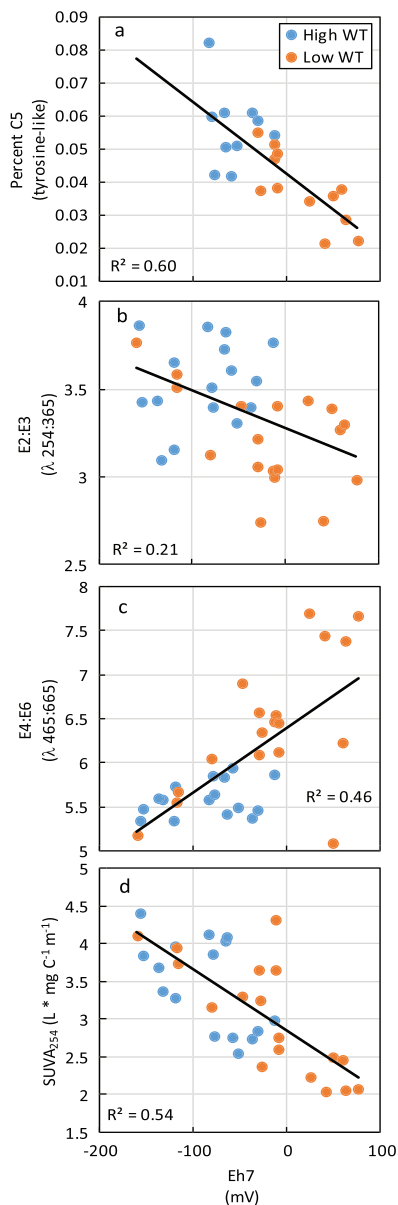
Figure 4. Dominant changes in pore water absorption and fluorescence spectroscopic properties with reduction-oxidation potential, as presented in Figure 3. Percentage of C5 from parallel factor analysis modeling (a) declined with Eh7 following $\beta_0 = 0.043 \pm 0.002$, $\beta_1 = -0.0002 \pm 0.00004$, $p < 0.001$; E2:E3 (b) declined with Eh7 following $\beta_0 = 3.278 \pm 0.059$, $\beta_1 = -0.0021 \pm 0.0007$, $p = 0.005$; E4:E6 (c) increased with Eh7 following $\beta_0 = 6.39 \pm 0.11$, $\beta_1 = 0.007 \pm 0.001$, $p < 0.001$; and SUVA254 (d) declined with Eh7 following $\beta_0 = 2.84 \pm 0.11$, $\beta_1 = -0.008 \pm 0.001$, $p < 0.001$. WT, water table.

aromatic biomolecules co-occurring with the synthesis of larger macromolecules at higher Eh. Prior research in the mesocosms demonstrated that pore water phenol oxidase (a class of oxidative enzymes involved in oxidation of phenolic compounds) activities increased with Eh and ericaceous shrub root abundance but did not relate to the pool size of total phenolics (Romanowicz et al., 2015). This earlier interpretation of a lack of enzymatic controls over total phenolic concentrations, and therefore mixed support for the enzymic latch mechanism, was likely obscured because the phenolic character was greatly affected by the WT and PFG treatments (Table 2a; Figure 5); the colorimetric methods for total phenolics likely cannot distinguish changes in quinone moieties. We suggest that the observed increase in pore water E4:E6 coincident with WT draw-down is an indicator of the polymerization of the partial breakdown products of complex substrates, such as *Sphagnum* tissue. More accurate representation of changes in the molecular weight of different pools of phenolics, in response to enzymatic activities or dominant PFGs present, would likely elucidate their controls on phenolic concentrations.

The presence of phenolics with different characteristics likely depends on how the intrinsic oxidation state varies in relation to redox oscillations within the peat (Tfaily et al., 2018) and changes in root functional traits (Dieleman et al., 2017). For example, when filtered pore water from the mesocosms was incubated in sealed jars over 7 weeks (and hence, isolated from rhizosphere or fluctuating WT effects), E4:E6 gradually declined as the DOC pool was mineralized, and the pore water became more humified and reduced (Veverica et al., 2016). This highlights the importance of biological and physical interactions mediating the redox activity of these peat pore waters.

Prior work has indicated the oxidative transformation of phenolics coupled with relative increase in quinone-like, carbonyl-containing moieties as a mechanism for increasing electron accepting capacity, across a broad range of humic substances (Aeschbacher et al., 2012). The observed increase in E4:E6 with Eh7 observed in this study may suggest a higher electron acceptor capacity, particularly in the low-WT treatments (Figure 4). In support of this, there was a strong negative association between E4:E6 and E2:E3 across all samples, indicating an increase in electron acceptor capacity (Sharpless et al., 2014), and NOSC increased at depth in the sedge PFG treatments as hypothesized. Prior research has shown how aerenchymal oxygen delivery can effectively recharge the electron acceptor capacity of DOM (Agethen et al., 2018), and we suggest here that in addition to this mechanism, changes in the intrinsic composition of the DOM pool over time interact with oxygen delivery in affecting pore water redox dynamics (e.g., Table 1). For example, higher molecular weight fractions of aquatic DOM are often richer in oxygen than are lower molecular weight compounds over the course of progressive humification (Visser, 1983b). In this study, most of the larger molecular weight compounds with more carbonyl-containing derivatives (E4:E6 > 6) of phenolic precursors were formed in more oxidizing conditions (Eh7 > 0 mV) coincident with the low-WT treatments and higher NOSC (Figure 5; Figure 9d). Our findings indicate that optical properties of the DOM are linked more strongly to Eh7 than the accumulation of phenolics within the DOM pool (Figure 5). This interpretation is in line with recent work highlighting the importance of intermediate carbonyl-containing compounds (ketones and aldehydes) as electron acceptors in charge-transfer interactions with phenolic donors, which largely affect the optical properties of DOM (Del Vecchio et al., 2017; Schendorf et al., 2019). Taken together with FT-ICR MS analyses demonstrating a positive relationship

Table 2
General Linear Mixed Model Effects on (a) Total Phenolic Concentrations, (b) Dissolved Organic Carbon (DOC) Concentrations, and (c) The Ratio of Total Dissolved Nitrogen (TDN) to Total Phenolics.

Variable	(a) Total phenolics				(b) Dissolved organic carbon				(c) Ratio total dissolved N: Phenolics			
Effect	Num df	Den df	F Value	Pr > F	Num df	Den df	F value	Pr > F	Num df	Den df	F Value	Pr > F
Water table position	1	641	20.98	**<.0001**	1	625	23.05	**<.0001**	1	641	0.4	0.5253
Total vegetation mass	1	641	0.01	0.9137	1	625	7.03	**0.0082**	1	641	11.96	**0.0006**
WT position × vegetation mass	1	641	3.32	0.069	1	625	7.9	**0.0051**	1	641	2.5	0.1141
PFG treatment	2	641	3.27	**0.0385**	2	625	8.2	**0.0003**	2	641	1.31	0.2699
WT position × PFG Trtmt.	2	641	0.77	0.4645	2	625	0.03	0.9689	2	641	5.32	**0.0051**
Vegetation mass × PFG treatment	2	641	0.3	0.7383	2	625	0.16	0.8496	2	641	3.44	**0.0325**
WT position × vegetation mass × PFG treatment	2	641	0.71	0.4913	2	625	2.51	0.0819	2	641	4.75	**0.009**

Note. Values in bold text are significant at $P < 0.05$. Abbreviations: PFG, plant functional group; WT, water table.

between NOSC and molecular weight, these results strongly suggest that the DOM pool associated with increased redox conditions (as occurred in our WT and PFG treatments) is intrinsically different, resulting in a higher electron accepting capacity.

The accumulation of oxidized compounds occurring with WT draw-down and in association with sedge rhizospheres (Figure 9d) could be very important pools of electron acceptors—in being more redox active than antioxidant phenolics—beneath the WT. In turn, this could be an important mechanism for the regeneration of electron acceptors associated with solid-phase peat as well (Keller & Takagi, 2013), which deserves further study. The extent to which changes in intrinsic DOM properties interact with altered redox environment in governing decomposition processes in the saturated zone needs to be elucidated with controlled experiments of changes in the electrochemistry (*cf.* Aeschbacher et al., 2010) of "end members" contributing to peat pore water DOM (*cf.* Worrall et al., 2017) in different scenarios of altered hydrology and PFGs.

4.2. Novel Compounds With Altered Hydroclimate and Vegetation

There were interesting controls among Eh, WT, and PFG treatments on the presence of novel compounds at different depths within the peat profile. In considering the 40- and 70-cm sampling depths together, the highest relative numbers of novel compounds were measured in PFG treatments containing sedges at 40 cm (Table 3b). In considering just deeper depths (70 cm), there appears to be a "one-two punch" when there is both a mixed group of PFGs and a lowered WT in determining the accumulation of novel DOM species
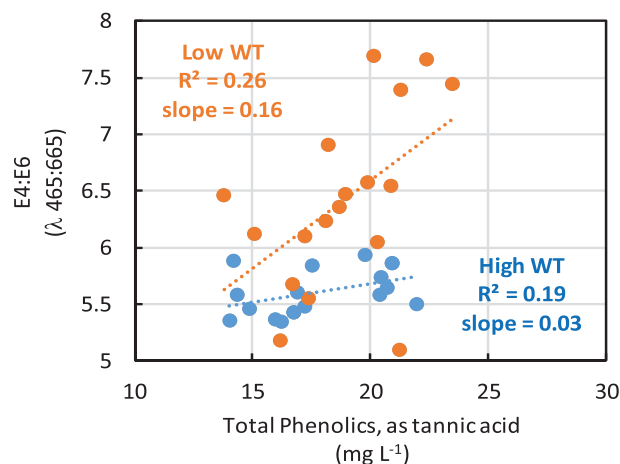

Figure 5. There was a ~5 fold increase in the slope of E4:E6, an index of molecular size, with increasing phenolic concentrations in the low-WT treatment ($\beta_0 = 3.41 \pm 1.20$, $\beta_1 = 0.16 \pm 0.06$; $p = 0.03$) relative to the high-WT treatment ($\beta_0 = 5.00 \pm 0.31$, $\beta_1 = 0.03 \pm 0.02$; $p = 0.07$). Data are averaged as depicted in Figures 3 and 4. WT, water table.
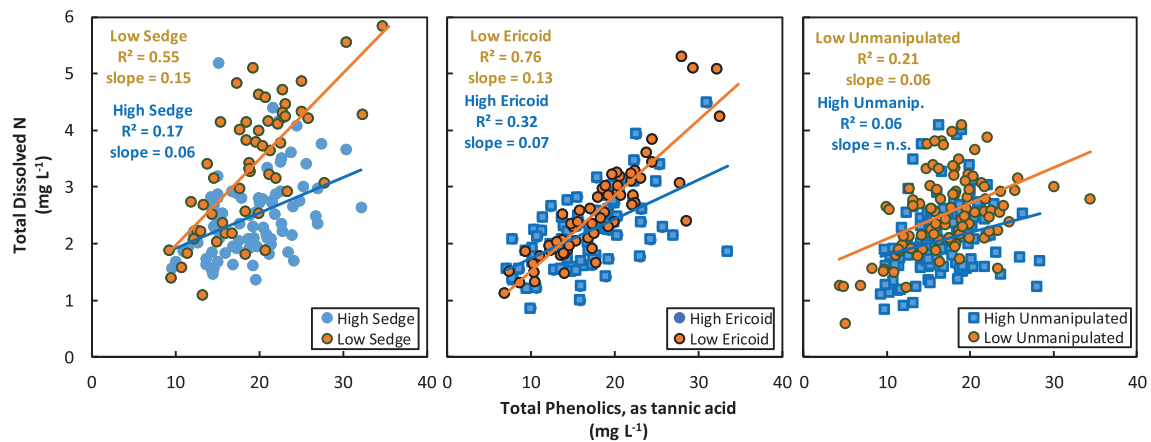
Figure 6. The rate of increase in total dissolved nitrogen with total phenolics in sedge plant functional group low-water table treatment was more than double that of the high-WT treatments for all plant functional groups (cf. Table 2c).

(Table 3a). Consistent with this, fungal communities associated with mixed rhizospheres (fungal co-cultures) appear to be advantageous for ligninolytic enzyme production compared to single fungal strains (Wiberth et al., 2019; *cf*. Robroek et al., 2016). It is likely that the combined unique enzymology of the ericoid PFGs as well as increased aerenchymal delivery of oxygen via sedge roots at ~40 cm resulted in increased decomposition products and humic substance precursors, which then accumulated at deeper depths upon polymerization. It could be that there are priority decomposition effects when the products of ericoid mycorrhizal fungal decomposition are secondarily acted upon by free-living saprotrophs associated with sedge rhizospheres deeper in the peat profile. These changes in the breakdown pathways of DOM therefore likely have consequences for the vertical stratification of different and novel compounds, but potential interactive effects of different decomposition strategies on DOM stabilization need further study.
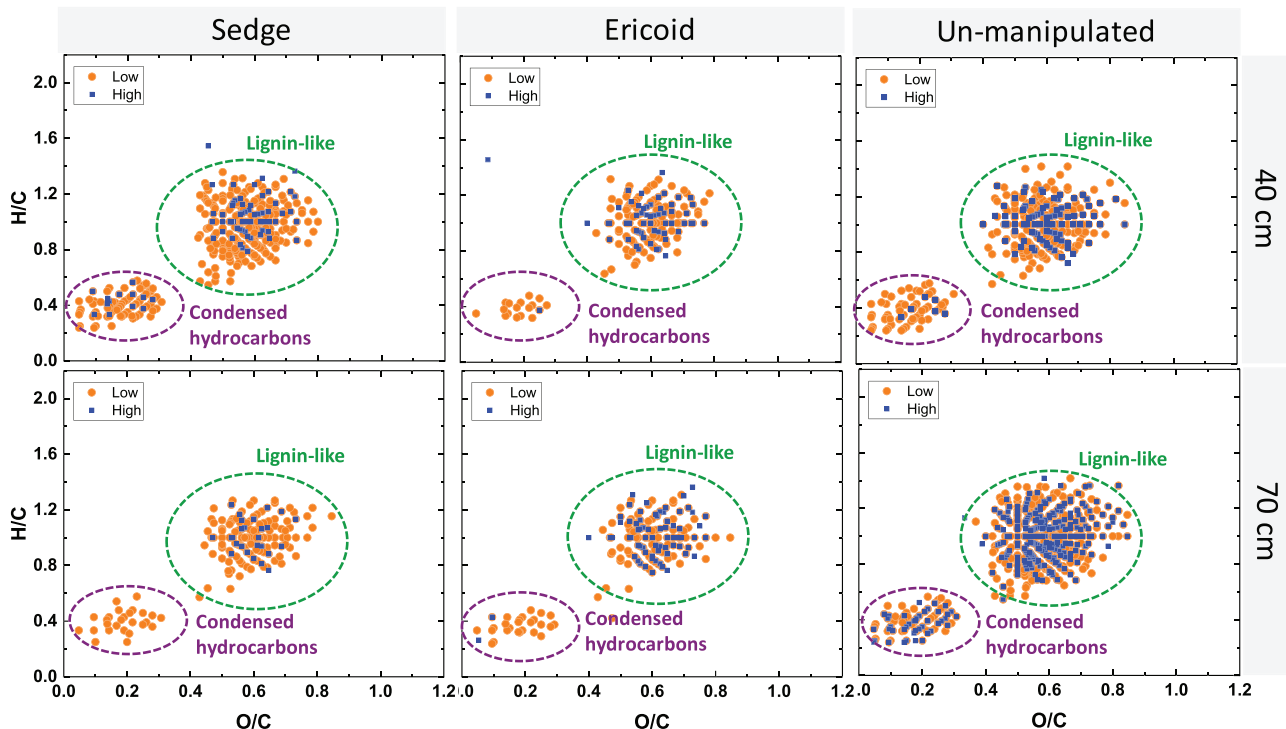

Figure 7. There was an increase in aromatic N-containing compounds (as determined by Fourier-transform ion-cyclotron-resonance mass spectrometry) in response to the lowered water-table treatment across all depths ($p = 0.01$; One-way analysis of variance with post hoc Tukey honest significant difference test).
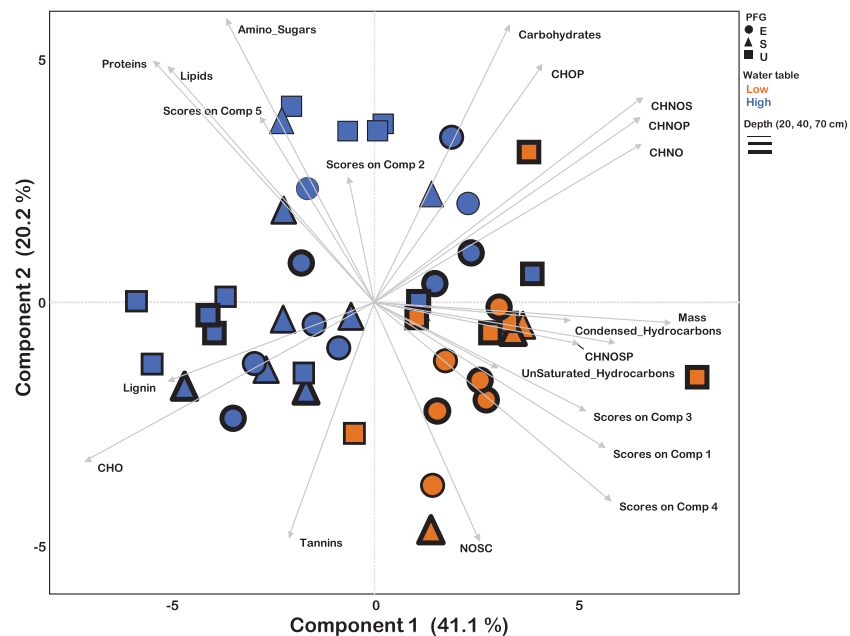
Figure 8. Graphical representation of principal component analysis of pore water Fourier-transform ion-cyclotron-resonance mass spectrometry data and fluorescence spectroscopic properties, parsed by plant functional group, high- and low-WT treatment, and sampling depth, highlights similarities among these two distinct analytical methods. Scores on parallel factor analysis Component 5 (tyrosine-like) reflected proteinaceous compounds and Component 4 was associated with nominal oxidation state of carbon and low water table. Scores on principal component analysis axes are provided in supporting information, Table S2.

Factors controlling TDN concentrations were generally correlated with phenolic concentrations in the peat, but there were big changes in N concentrations in response to our treatments. There were higher order interactions among PFG, plant biomass, and WT position in controlling phenolic concentrations and the amounts of TDN per unit phenolics (Table 2c), with higher concentrations occurring in the PFG treatments containing sedges, particularly with low WT (Figure 6). Contrary to patterns of TDN and phenolics, tyrosine-like nitrogenous compounds and amino sugars were virtually absent at $Eh7 > 0$ mV occurring with lowered WT (Figure 4a) and were negatively associated with sedge PFG treatments (Figure 8; Table S2). These low molecular weight N-compounds were likely rapidly immobilized (Cory & Kaplan, 2012) and/or acted as precursors in the polymerization of humic substances. Moreover, the breakdown products of amino sugar decomposition would be readily complexed with redox-active phenolics (Thoss et al., 2004) or could undergo condensation reactions and hence be rendered as particulate organic matter (not DOM). The polymerization of compounds to oxidized semiquinones and quinones upon reacting with relatively low molecular weight N-containing compounds, as mediated by oxidative enzymes, is consistent with these ideas (*see "polyphenol theory";* Stevenson, 1994). Taken together, these findings suggest that there is significant diagenesis of N-containing compounds with increased oxidation, resulting in altered phenolics with higher N content, molecular weight, and NOSC.

Generation of novel nitrogenous compounds with the lowered-WT treatment appeared to be manifest through dehydrogenation (e.g., phenol to quinone), as most of the indicators of low WT possessed this signature. This was particularly evident for the sedge-containing PFGs at 40 cm, and for the unmanipulated mixed community at 70 cm, where N-containing compounds in the lowered-WT treatments generally were more condensed and had lower H:C ratios (Figure 7). Interestingly, when considering comparisons across all depths and treatments, the highest percentage of indicator (probably novel) N-containing compounds occurred in the lowered-WT unmanipulated PFG treatment at 40 cm (Table 3b). While the total number of indicator compounds (not just those containing N) was highest in the lowered-WT sedge PFG treatment at 40 cm, N-containing indicators were absent in the sedge PFG treatment at 70 cm. These findings again suggest that decomposition pathways associated with mixed PFGs, with different functional traits at different depths, resulted in the accumulation of the highest diversity of N compounds deep in the peat profile. Decomposition pathways associated with the unique enzymology of the ericoid shrubs (10–40 cm) in combination with higher Eh associated with sedge rhizospheres (40–70 cm) and lowered WT resulted in a more
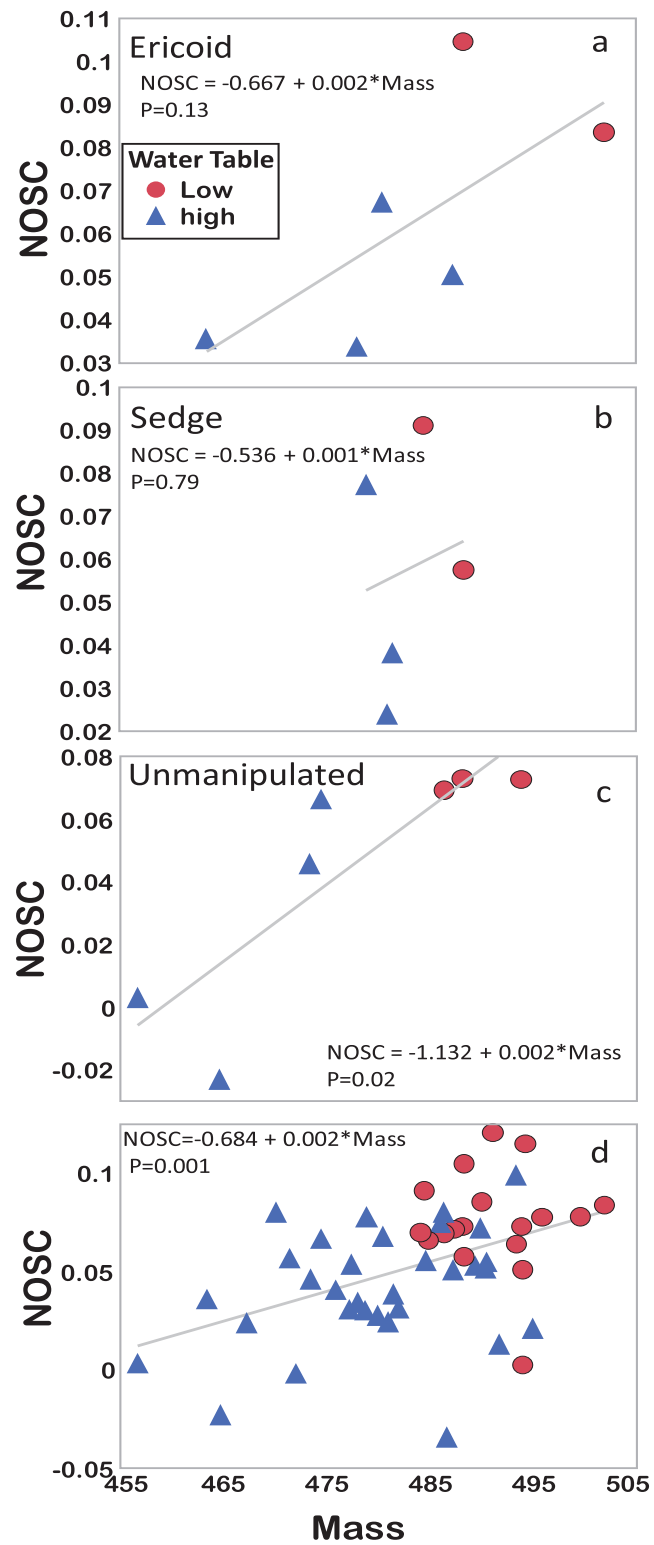
Figure 9. The increase in nominal oxidation state of carbon (NOSC) with molecular mass relationship was different across the three plant functional group treatments, and parsed by water table treatment. Depicted are changes at 40 cm for different vegetation treatments a (ericoid), b (sedge), c (unmanipulated), and across all depths and all treatments (d).

Table 3

Unique Indicator Analysis of Pore Water Analyzed by Fourier-Transform Ion-Cyclotron-Resonance Mass Spectrometry

(a) Calculated separately by depth

Depth (cm)	Low E %N	Low E total	Low S %N	Low S total	Low U %N	Low U total	High E %N	High E total	High S %N	High S total	High U %N	High U total	Chi^2 test
20		na		na		na	52	12	36	11	5	251	<0.001
40	39	36	21	132	41	51	3	37	0	28	12	26	<0.001
70	39	18	25	4	8	556	5	63	0	12	0	31	0.001

(b) Calculated in a single model for 40–70-cm depths

Depth (cm)	Low E %N	Low E total	Low S %N	Low S total	Low U %N	Low U total	High E %N	High E total	High S %N	High S total	High U %N	High U total	Chi^2 test
20		na		na		na		na		na		na	
40	18	61	10	180	42	33	0	28	0	16	16	19	0.001
70	14	7	0	2	29	28	0	14	0	1	0	18	

Note. The total numbers of unique biomolecular assignments by treatment (low- and high-WT treatments; ericoid [E], sedge [S], and unmanipulated [U] PFG treatments), and the percentage of these indicators that are nitrogenous (%N) are depicted. Chi^2 tests for significant differences are separated by depth class (a) and include 20- and 40-cm depths together (b; WT × PFG). The WT was <20 cm in the low treatments, precluding sampling at that depth in that treatment.

diverse suite of nitrogenous compounds or altered the composition (more condensed, lower H:C; or precipitated out of the DOM pool) such that they could not be taken up or mineralized by deep sedge roots.

5. Conclusions

There were direct and interactive effects of PFG and WT position mediating redox environment and DOM characteristics. In particular, sedges had an overall oxidizing effect on peat pore water, and there was an interactive effect between sedges and low-WT position resulting in even higher Eh, molecular weight, phenolic content, and TDN. We suggest that enzymatic processes associated with ericoid rhizospheres promoted the diagenesis of DOM, creating precursors for the synthesis of larger MW, oxidized humic substances when also exposed to sedge rhizospheres, and a fluctuating WT. These factors in turn likely controlled the stabilization of DOM deeper in the peat profile with a change in redox environment. The generation of these intrinsically different compounds with changes in PFG and a low WT (higher molecular weight and more oxidized, higher TDN content) could act as important pools of electron acceptors and donors in anaerobic decomposition.

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