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## **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 water tables. 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 water table, 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 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 mini-ecosystems. 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.

**1.0. 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 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 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 water table variation at the local scale, including large mid-summer declines in water table 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 [Weltzin *et al.* 2000; Churchill *et al.*, 2015; Dieleman *et al.*, 2015] and net primary production in peatlands [Strack and Waddington 2007; Chivers *et al.*, 2009; Chimner *et al.*, 2017; Radu and Duval, 2018]. 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 co-exist, 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 water table 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 and Burke, 1998; Cairney and 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 water table [Ohlson and Dahlberg 1991; Belyea and Malmer 2004]. As such, there are interactive effects between altered hydrology and plant functional groups which have been shown to influence decomposition dynamics in peat [Wiedermann *et al.*, 2017a]. 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 [Meronigal *et al.*,

2004]. However, several studies have demonstrated relatively high rates of decomposition in peat (as heterotrophic production of CO<sub>2</sub>) when the thermodynamic yield indicated by inorganic TEAs would suggest otherwise [Vile *et al.*, 2003; Dettling *et al.*, 2006; Keller and Bridgham, 2007; Deppe *et al.*, 2010; Kane *et al.*, 2013]. A growing body of literature draws attention to the importance of humic substances and organo-metallic complexes in governing anaerobic metabolism in organic soil [Heitmann *et al.*, 2007; Lipson *et al.*, 2010; Klüpfel *et al.*, 2014; Lau *et al.*, 2015]. 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 water table 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 [Keller and Bridgham 2007; Wüst *et al.* 2009; Boye *et al.*, 2017], quinone or quinone-like moieties in dissolved organic matter (DOM) are likely driving reduction-oxidation dynamics [Schwarzenbach *et al.*, 1990; Nurmi and Tratnyek, 2002]. 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; Wang et al., 2015; Pinsonneault et al., 2016; Wiedermann et al., 2017b*].

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 water table. 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 water table position in peat mesocosm experiments controlling for plant functional groups and water table position [*Romanowicz et al., 2015; Dieleman et al., 2016*]. In this same experimental framework, the highest phenolic concentrations were observed in treatments with lowered water table 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., *Schnitzer, 1985; Northup et al., 1995*]. 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 and 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 [Helburn and MacCarthy, 1994; Bauer *et al.* 2007]. 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 and 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 water table 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 water table (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 three 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 water table 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 vs. 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 bi-weekly for three 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.

## **2.0. 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 water table positions and vascular plant functional groups in peat mesocosms to simulate potential climate change impacts as previously described in detail [*Potvin et al., 2015; Haynes et al., 2017*]. Briefly, twenty-four 1 m<sup>3</sup> (1 m x 1 m x 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 2x3 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 non-mycorrhizal 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 water table 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 water table profiles were modelled after typical variability, average water table years (‘high WT’) and high variability, low water table 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 water table 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 was 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 micro-piezometer 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  $\mu\text{m}$ ) 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 reduction-oxidation potential [Magonigal and Rabenhorst, 2013]. Pore water was harvested by purging the lines through a 3-way stopcock prior to sampling with a syringe. Approximately bi-

weekly 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 pre-rinse for sample collection in high density polyethylene (HDPE) Nalgene bottles. Approximately 100 mL of sample was collected and then filtered through 0.45  $\mu\text{m}$  nylon membrane filters (within 3 hours; 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 dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) using a Shimadzu TOC-V Combustion Analyzer with a nitrogen module (Shimadzu Scientific Instruments, Columbia, MD, USA). Anions (nitrate, sulfate, chloride, 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 reduction-oxidation potential (Eh) was measured within five minutes 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 and De Boer 1987; Helms *et al.*, 2008; Zhang and 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 [Wallage *et al.*, 2006; Blodau and Siems, 2012]. 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  $\lambda=465$  nm (E4) [Uyguner and Bekbolet, 2005; Chen *et al.*, 2010; Hribljan *et al.*, 2014]. We measured DOC specific absorbance at  $\lambda = 254$  (SUVA<sub>254</sub>), 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 second 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 OM 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 ( $0 < O/C \leq 0.3$ ,  $1.5 \leq H/C \leq 2.5$ ), unsaturated hydrocarbons ( $0 \leq O/C \leq 0.125$ ,  $0.8 \leq H/C < 2.5$ ), proteins ( $0.3 < O/C \leq 0.55$ ,  $1.5 \leq H/C \leq 2.3$ ), amino sugars ( $0.55 < O/C \leq 0.7$ ,  $1.5 \leq H/C \leq 2.2$ ), lignin ( $0.125 < O/C \leq 0.65$ ,  $0.8 \leq H/C < 1.5$ ), tannins ( $0.65 < O/C \leq 1.1$ ,  $0.8 \leq H/C < 1.5$ ), and condensed hydrocarbons ( $0 \leq O/C \leq 0.95$ ,  $0.2 \leq H/C < 0.8$ ). 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 three-year dataset, we examined changes in pore water Eh, DOC, TDN, and phenolic content in response to environmental (water table 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 (PARAFAC) of all fluorescence EEMs as previously described [Veverica *et al.*, 2016; following Stedmon and 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 [Olefelt *et al.*, 2013; Kothawala *et al.*, 2014]. 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 and 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 [Kothawala et al., 2012; Bro and Smilde, 2014]. 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**

FTICR-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 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 vs. 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 x WT x 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.

### **3.0. 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. Water table 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 x WT interaction was caused by significant differences in Eh7 with depth from the peat surface as a function of water table

treatment and PFG in the top 40 cm of peat (Figure 2), with the sedge PFG treatment having higher Eh and driving a PFG x WT interaction in the complete dataset (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 water table position; and negative loading by ferrous iron, potential electron acceptor capacity (E2:E3), aromaticity (SUVA254), acetate, propionate, and formate concentrations (Supplemental Table 1; Figure 3). PCA axis 2 was primarily defined by the percent of DOM that was phenolic (loading of 0.37) vs. oxalate concentrations (loading of -0.35). Axis 1 metrics reflected the position of the water table relative to peat surface (axis 1 loading of 0.23). Water table 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 water table, as represented by positive loadings on axis 1 (Figure 3). Chloride is a largely conservative ion, and the chloride vector was orthogonal to water table 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).

While TDN concentrations tracked DOC and total phenolics as expected (similar loadings in Figure 3; Supplemental Table 1), the ratio of TDN:phenolics changed with vegetation mass and water table 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 3-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 (Supplemental 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, i.e., 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 (Supplemental Table 2). PARAFAC-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 with proteinaceous and amino sugar biomolecules (Supplemental Table 2). 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.

Water table 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 water table. 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 water table, 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 & 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 N-indicators were present in the low WT sedge treatment, in which 10% of all unique indicators contained N (Table 3b).

## **4.0. Discussion**

### **4.1. Interaction between DOM properties and redox environment**

The interactive effects of vegetation and water table 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 water table, 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 and 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 [Suflita and Bollag, 1981; Chefetz et al., 1998; Lee et al., 2004; Baldrian, 2006]. 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 and 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 et al., 2017a; Worrall et al., 2017]. The strong negative relationships between SUVA<sub>254</sub> (an indicator of aromatic C) and Eh<sub>7</sub>, as well as between SUVA<sub>254</sub> and E<sub>4</sub>:E<sub>6</sub> presented herein (Figure 4) are consistent with increased breakdown of 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 water table 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 seven 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 [Aeschebacher *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 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 water table. In turn, this could be an important mechanism for the regeneration of electron acceptors associated with solid phase peat as well [Keller and 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. Aeschebacher *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 (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.

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  $Eh_7 > 0$  mV occurring with lowered WT (Figure 4a) and were negatively associated with sedge PFG treatments (Figure 8; Supplemental Table S2). These low molecular weight N-compounds were likely rapidly immobilized [*Cory and 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 70cm. 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 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.

### **4.3. 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 water table. 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 very important pools of electron acceptors and donors in anaerobic decomposition.

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Table 1: General linear mixed model effects on reduction-oxidation potential.

Effect	(a) Reduction-Oxidation Potential			
	Num DF	Den DF	F Value	Pr > F
Water Table Position	1	480	1.34	0.2484
Total Vegetation Mass	1	480	6.42	<b>0.0116</b>
WT Pos. x Veg Mass	1	480	2.99	0.0846
PFG treatment	2	480	3.91	<b>0.0207</b>
WT Pos. x PFG Trtmt.	2	480	3.76	<b>0.024</b>
Veg Mass x PFG Trtmt.	2	480	1.47	0.2311
WT Pos. x Veg Mass x PFG Trtmt	2	480	1.56	0.211

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.

Effect	(a) Total Phenolics				(b) Dissolved Organic Carbon				(c) Ratio Total Dissolved N:Phenolics			
	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	<b>&lt;.0001</b>	1	625	23.05	<b>&lt;.0001</b>	1	641	0.4	0.5253
Total Vegetation Mass	1	641	0.01	0.9137	1	625	7.03	<b>0.0082</b>	1	641	11.96	<b>0.0006</b>
WT Pos. x Veg Mass	1	641	3.32	0.069	1	625	7.9	<b>0.0051</b>	1	641	2.5	0.1141
PFG treatment	2	641	3.27	<b>0.0385</b>	2	625	8.2	<b>0.0003</b>	2	641	1.31	0.2699
WT Pos. x PFG Trtmt.	2	641	0.77	0.4645	2	625	0.03	0.9689	2	641	5.32	<b>0.0051</b>
Veg Mass x PFG Trtmt.	2	641	0.3	0.7383	2	625	0.16	0.8496	2	641	3.44	<b>0.0325</b>
WT Pos. x Veg Mass x PFG Trtmt	2	641	0.71	0.4913	2	625	2.51	0.0819	2	641	4.75	<b>0.009</b>

Table 3: Unique indicator analysis of pore water analyzed by FT-ICR MS. The total numbers of unique biomolecular assignments by treatment (Low and High WT treatments; ericoid (E), sedge (S) and unmanipulated (U) PFG treatments) are in grey and the percentage of these indicators that are nitrogenous (%N) are depicted. Chi<sup>2</sup> tests for significant differences are separated by depth class (a) and include 20 and 40 cm depths together (b; WT x PFG). The WT was < 20 cm in the Low treatments, precluding sampling at that depth in that treatment.

**(a) Calculated separately by depth**

Depth (cm)	Low E		Low S		Low U		High E		High S		High U		Chi <sup>2</sup> test
	%N	total	%N	total	%N	total	%N	total	%N	total	%N	total	
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		Low S		Low U		High E		High S		High U		Chi <sup>2</sup> test
	%N	total	%N	total	%N	total	%N	total	%N	total	%N	total	
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	

**Figure Captions:**

Figure 1: Mean diurnal ranges in dissolved oxygen measured in each mesocosm bin by PFG treatment (n=8) for the two weeks preceding the initiation of the WT treatments in 2012. DO measurements occurred approximately 20 cm beneath the peat surface (10 cm beneath the WT) 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.

Figure 2: There was an interaction between PFG and 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 dataset (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), WT treatment (“Hi” and “Lo”), and year. Scores on PCA axes are provided in Supplemental Table S1.

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 PARAFAC modelling (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  $\beta_0 = 2.84 \pm 0.11$ ,  $\beta_1 = -0.008 \pm 0.001$ ,  $p < 0.001$ .

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 3-4.

Figure 6: The rate of increase in TDN with total phenolics in sedge PFG low WT treatment was more than double that of the high WT treatments for all PFGs (cf. Table 2c).

Figure 7: There was an increase in aromatic N-containing compounds (as determined by FT-ICR MS) in response to the lowered WT treatment across all depths ( $p = 0.01$ ; One-way ANOVA with post-hoc Tukey HSD Test).

Figure 8: Graphical representation of Principal Component Analysis of pore water FT-ICR MS data and fluorescence spectroscopic properties, parsed by PFG, high and low WT treatment, and sampling depth, highlights similarities among these two distinct analytical methods. Scores on PARAFAC Component 5 (tyrosine-like) reflected proteinaceous compounds and Component 4 was associated with NOSC and low WT. Scores on PCA axes are provided in Supplemental Table S2.

Figure 9: The increase in nominal oxidation state of carbon (NOSC) with molecular mass relationship was different across the three PFG treatments, and parsed by WT 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).





















