AGU PUBLICATIONS

JGR

Journal of Geophysical Research: Biogeosciences

RESEARCH ARTICLE

10.1002/2013JG002527

Key Points:

- Peatland DOC concentrations increased in raised and lowered water table sites
- Quality and production of DOC were different across water table sites

Correspondence to:
J. A. Hribljan,
jahriblj@mtu.edu

Citation:
Hribljan, J. A., E. S. Kane, T. G. Pypker, and R. A. Chimner (2014), The effect of long-term water table manipulations on dissolved organic carbon dynamics in a poor fen peatland, *J. Geophys. Res. Biogeosci.*, *119*, 577–595, doi:10.1002/2013JG002527.

Received 2 OCT 2013
Accepted 14 MAR 2014
Accepted article online 28 March 2014
Published online 22 APR 2014

The effect of long-term water table manipulations on dissolved organic carbon dynamics in a poor fen peatland

John A. Hribljan[1,2], Evan S. Kane[1,2], Thomas G. Pypker[1,3], and Rodney A. Chimner[1]

[1]School of Forest Resources and Environmental Science, Michigan Technological University, Houghton, Michigan, USA, [2]Northern Research Station, U.S. Forest Service, Houghton, Michigan, USA, [3]Department of Natural Resource Sciences, Thompson Rivers University, Kamloops, British Columbia, Canada

Abstract Dissolved organic carbon (DOC) production, consumption, and quality displayed differences after long-term (~55 years) hydrological alterations in a poor fen peatland in northern Michigan. The construction of an earthen levee resulted in areas of a raised and lowered water table (WT) relative to an unaltered intermediate WT site. The lowered WT site had greater peat aeration and larger seasonal vertical WT fluctuations that likely elevated peat decomposition and subsidence with subsequent increases in bulk density, vertical hydraulic gradient, decreased hydraulic conductivity (K_{sat}), and a greater pore water residence time relative to the unaltered site. The raised WT site displayed a decreased K_{sat} combined with seasonal upwelling events that contributed to a longer residence time in comparison to the unaltered site. These differences are potentially contributing to elevated DOC concentrations at the lowered and raised WT site relative to the unaltered site. Additionally, spectrophotometric indices and chemical constituent assays indicated that the lowered site DOC was more aromatic and contained elevated concentrations of phenolics compared to the intermediate site. The raised site DOC was less aromatic, less humified, and also had a greater phenolic content than the intermediate site. Furthermore, an incubation experiment showed that DOC in the raised site contained the greatest labile carbon source. Based on our results, long-term WT alterations will likely impose significant effects on DOC dynamics in these peatlands; however, WT position alone was not a good predictor of DOC concentrations, though impoundment appears to produce a more labile DOC whereas drainage increases DOC aromaticity.

1. Introduction

Climate change is predicted to influence dissolved organic carbon (DOC) cycling in northern peatlands [*Pastor et al.*, 2003; *Freeman et al.*, 2004], and elevated DOC export has been observed from many high-latitude peatlands [*Freeman et al.*, 2001; *Worrall et al.*, 2003; *Evans et al.*, 2005; *Frey and Smith*, 2005; *Billett et al.*, 2010; *Yallop et al.*, 2010]. Peatland DOC export [5–40 g m^{-2} yr^{-1}; *Moore et al.*, 1998] represents an important component of the annual peatland carbon (C) balance [*Fraser et al.*, 2001; *Billett et al.*, 2004; *Nilsson et al.*, 2008] and is a significant factor determining if a peatland has a net positive or negative C accumulation rate [*Gorham*, 1991]. Because northern peatlands store up to 25% of the global soil C stocks [*Roulet et al.*, 2007] and are expected to experience changes in hydrology during the next century [*Schiff et al.*, 1998; *Roulet*, 2000; *Pastor et al.*, 2003; *Clark et al.*, 2009], it is important to understand the long-term effects of climate change on peatland hydrology and DOC dynamics.

Dissolved organic carbon is composed of a diverse mixture of recalcitrant humic substances and labile compounds including carbohydrates, peptides, amino acids, carboxylic acids, and alcohols [*Sachse et al.*, 2005] that are important substrates for microbial mineralization [*Chanton et al.*, 1995; *Fellman et al.*, 2008]. The production and consumption of DOC is dependent upon temperature [*Koehler et al.*, 2009; *Preston et al.*, 2011], moisture [*Kane et al.*, 2010], peat substrate quality [*Laiho et al.*, 2003; *Wickland et al.*, 2007], and redox status [*Freeman et al.*, 1993; *Moore and Dalva*, 2001], which are all tightly coupled to water table (WT) position. Furthermore, the hydrological processes of evaporative concentration, dilution by precipitation, ground water upwelling, and pore water mobility are additional factors effecting DOC dynamics in peatlands [*Siegel et al.*, 1995; *Waddington and Roulet*, 1997; *Whitfield et al.*, 2010]. In particular, peat hydraulic conductivity (K_{sat}) and pore structure are susceptible to changes in WT position [*Chow et al.*, 1992; *Whittington and Price*, 2006]. Peatlands experiencing WT drawdown have enhanced oxidation that accelerates decomposition resulting in primary peat compaction [*Price*, 2003]. Peat compaction reduces pore volume and K_{sat}, which can increase pore water residence time [*Beer et al.*, 2008]. Additionally, biogenetic gas bubbles can impede pore water transport by blocking advective water movement in deep anaerobic and surface peat experiencing an elevated WT [*Kellner et al*., 2005]. Thus, translocation of DOC through the peat matrix can be obstructed because of slow diffusion rates [*Cornel et al.*, 1986] and/or reduced advective movement of water from hydrologically influenced pore deformations and entrapped bubbles [*Price*, 2003].

Since peatland pore water residence time can effect microbial decomposition [*Wickland et al.*, 2007] and mobility of DOC, small changes in DOC residence time could have significant implications for peatland C cycling [*Olefeldt and Roulet*, 2012]. When conditions favor pore water export, mobilization of DOC from a peatland can provide a substantial and labile source of C to streams and lakes with the potential to be readily mineralized into CO_2 [*Kling et al.*, 1991; *Harrison et al.*, 2008]. Consequently, hydrological alterations in peatlands can have dramatic impacts on DOC cycling not only within the peatland but also on the watershed scale.

Despite the importance of DOC dynamics in peatland C budgets, research is inconclusive concerning the influence of WT alterations on DOC cycling in northern peatlands. Increases in DOC production and export have been reported from long-term drainage experiments [*Turunen*, 2008; *Höll et al.*, 2009; *Blodau and Siems*, 2012]. However, these studies represent peatlands drained for forestry and/or peat extraction with a dramatic WT drawdown ($>$ 30 cm) that is not comparable to the more subtle WT changes predicted for some northern peatlands under future climate change scenarios [*Roulet et al.*, 1992; cf. *Sebestyen et al.*, 2011]. Furthermore, predicted climate-induced changes in precipitation and temperature could produce either WT drawdown or inundation in high-latitude peatlands [*Moore*, 2002; *Tarnocai*, 2006, 2009]. Thus, it is unknown how small, multidirectional, long-term changes in the WT of a northern peatland will affect biogeochemical processes and contribute to changes in DOC production/consumption and export. It should also be noted that changes in DOC concentrations within a peatland are not always directly correlated to DOC export from the peatland [*Tranvik and Jansson*, 2002; *Roulet and Moore*, 2006]. Hydraulic connectivity of a peatland with the greater catchment is influenced by changes in WT position, catchment hydrology, season, and peat structure, which further reinforces the complexity of disentangling the processes that control DOC cycling in northern peatlands.

Short-term in situ WT manipulation studies have provided another type of representation of climate-induced hydrological changes on DOC dynamics in northern peatlands [*Blodau et al.*, 2004; *Strack et al.*, 2008; *Kane et al.*, 2010]. However, it is uncertain if peatlands will display similar trajectories in DOC dynamics between short-term and long-term WT alterations [*Evans et al.*, 2006; *Worrall et al.*, 2007]. Mesocosm investigations utilizing peat cores have demonstrated that WT manipulations can produce opposing trends in DOC production [*Freeman et al.*, 1993; *Clark et al.*, 2009; *Preston et al.*, 2011], and WT position is not always a primary predictor for peatland DOC production/consumption [*Pastor et al.*, 2003; *Blodau and Moore*, 2003]. Seasonal and multiyear drought events provide an approach to examine lowered WT effects on DOC cycling in peatlands that could closely resemble future climate-induced changes in hydrology; however, these results are also contradictory. *Freeman et al.* [2004] artificially created seasonal drought conditions in a peatland that did not produce an increase in DOC production during or following the WT manipulations. In contrast, *Worrall et al.* [2006] predicted increases in DOC export from peatlands coinciding with historic time periods of hydrological drought that temporarily lowered the WT position in the peatlands. However, a relationship was not developed between the predicted increase in DOC export and DOC production within the peatland.

To advance our understanding of climate-induced effects on northern peatland DOC dynamics, it is necessary to not only investigate parameters that influence DOC production/consumption and transport dynamics but also examine these parameters over multi-decadal changes in hydrology that parallel the expected long-term time frame of climate change. Hydrological manipulations in the Seney National Wildlife Refuge (SNWR) from the 1930s through the 1950s to improve wildlife habitat created a unique opportunity to explore the effects of long-term WT drawdown and inundation on peatland DOC dynamics. We established study sites to represent a gradient of WT positions (lowered and raised sites in contrast to an unaltered intermediate site). These sites represented approximately 55 years of subtle WT alterations ($\pm \sim 10$ cm) in a northern poor fen peatland.

The objective of our study was to examine how long-term WT alterations in a northern poor fen peatland influence DOC production/consumption, transport, and quality. We hypothesized that peatland pore water DOC concentration would (1) increase after long-term WT drawdown because of accelerated aerobic

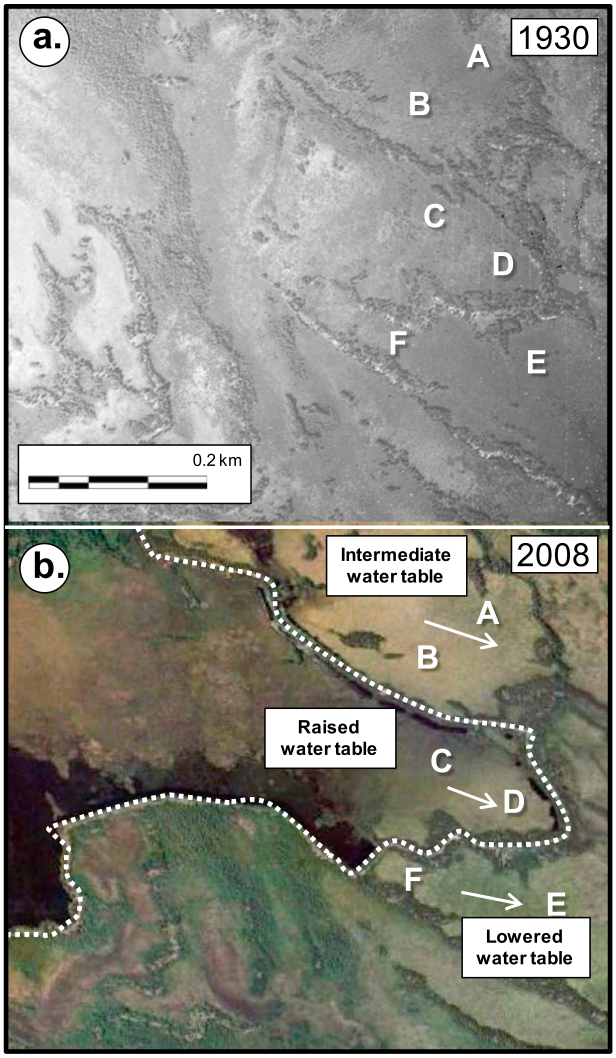

Figure 1. (a) Aerial photograph from 1930 before an earthen levee was constructed in circa 1955. (b) Aerial photograph from 2008 illustrating location of the six research plots positioned across the three WT sites relative to the levee (dotted line). Surface sheet flow impounding behind the levee has elevated the WT at plots C and D and lowered the WT at plots E and F. Arrows indicate approximate water flow paths within each WT site based on horizontal hydraulic gradients between plots. Image in Figure 1b: Google Earth 2012. Seney, Michigan, 46°11′15.22″N 86°00′54.93″W, elevation 208 m, Accessed 8 October 2012.

microbial activity and accumulation of water-soluble products of decomposition from an increased residence time; (2) decrease from a long-term raised WT because of suppressed decomposition and increased flushing of pore water from the peat due to a decreased water residence time. Lastly, we hypothesized that (3) peatland DOC quality (lability, aromaticity, and molecular size) is dependent on WT position and residence time of pore water. In particular, a long-term lowered WT position would result in the increase of DOC components that have a reduced lability because of increased aerobic decomposition resulting in an accumulation of refractory compounds. In contrast, a long-term raised WT would accumulate labile DOC components because of suppressed decomposition from anaerobic conditions.

2. Methods

2.1. Study Sites and Experimental Design

Our research site is within the SNWR in the central portion of the Upper Peninsula of Michigan (Schoolcraft County), USA. The greater landscape comprising SNWR is composed of a large sand plain [*Heinselman*, 1965] consisting of well-sorted sands, 0–60 m thick, deposited during the retreat of the Lake Michigan lobe of the Laurentide ice sheet [*Krist and Lusch*, 2004]. The sand plain has a gradual southeast slope of 1.89 m/km [*USFWS*, 2009]. The climate of the refuge is greatly influenced by Lake Michigan to the south and Lake Superior to the north. The average annual precipitation is 81 cm with an average annual snowfall of 312 cm [*USFWS*, 2009] and an annual average temperature of 5.1°C [*Wilcox et al.*, 2006].

A field experiment incorporating six plots was established east of the Marsh Creek flooding (46°11′18″W, 86°01′03″N) on a poor fen [*Vitt*, 2006] peatland complex (Figure 1). Hydrology across the refuge was altered from the 1930s through the 1950s when the U.S. Fish and Wildlife Service constructed a series of earthen levees by connecting together existing aeolian sand ridges [*Arbogast et al.*, 2002] to create open water impoundments for migratory waterfowl habitat [*Kowalski and Wilcox*, 2003]. The disturbance to surface sheet flow from the levees produced extensive inundation and drying of peatlands within the refuge. Six study plots were split equally across three different WT levels all within the same peatland complex: an unaltered intermediate site (plots A and B), a raised site (plots C and D), and a lowered site (plots E and F) (Figure 1b). The levee has restricted surface flow to plots E and F resulting in a drawdown of the WT and subsequently caused plots C and D to become inundated on the up-gradient side of the levee. Plots A and B were comparatively unaffected by the levee construction. Our WT sites still retain the natural WT variation in response to seasonal precipitation and evapotranspiration events that are common in northern peatlands. The lowered, raised, and intermediate sites are covered by a continuous moss mat of predominately *Sphagnum angustifolium*, *S. capillifolium*, and *S. magellanicum* and contain similar vegetation structure that is representative of a poor fen peatland in the Upper Great Lakes region [*Crum and Planisek*, 1988; *Johnston et al.*, 2007]. Dominant tracheophyte species included the shrubs *Chamaedaphne calyculata*, *Kalmia polifolia*, *Ledum groenlandicum*, and *Vaccinium oxycoccos*; graminoids *Carex oligosperma* and *Eriophorum vaginatum*; and trees *Larix laricina* and *Picea mariana* [*Hribljan*, 2012]. Elevated boardwalks were constructed at each plot to prevent peat disturbance around pore water sampling wells and piezometers.

Peat depth was measured at each plot ($n = 8$) with a tile probe. A sandy substratum (confirmed by augering) underlying the peat created a sharp transition that was easily detected with the tile probe. To measure peat physical properties, three 10 cm diameter × 50 cm deep soil cores were extracted at each plot (total of six cores for each WT site) from lawn microforms equally spaced along a 20 m transect adjacent to the plot well. Polyvinyl chloride (PVC) pipes were carefully inserted into the peat by cutting around the perimeter of the pipe with a sharp serrated knife as the pipe was lowered into the peat to prevent compaction of the core. After extracting the peat core, the bottom and top of the PVC pipe were immediately fitted with flexible rubber caps with steel clamps to prevent water loss. Cores were transported upright to Michigan Technological University Wetland Laboratory, frozen and sectioned into 10 cm horizons with a bandsaw. Bulk density was determined for each core horizon.

2.2. Hydrological Monitoring

Depth to WT at each plot was monitored (April–October, 2010 and 2011) with nonvented pressure transducers (Levellogger Junior Model 3001; Solinst, Georgetown, Ontario, Canada) set at an hourly recording interval in slotted 10 cm diameter PVC wells inserted to the mineral soil. A barologger (Baralogger Gold Model 3001; Solinst, Georgetown, Ontario, Canada) installed at the top of the well casing at plot B provided barometric compensation for all pressure transducers. Monthly manual WT depth measurements were conducted for each well as a check for pressure transducer logging accuracy. Water table elevations are in relation to the mean microtopography of each plot. Mean microtopography was measured with a transit level at 0.5 m increments along a 50 m transect centered at the monitoring well of each plot and referenced to the lowest point along the transect. Well elevations were surveyed relative to each other and referenced to a common datum. Vertical hydraulic gradients (VHG) and peat K_{sat} were measured in nests of three piezometers installed in a lawn microform at each plot (A–F). Piezometers were constructed of 2.5 cm diameter PVC pipe with a 10 cm slotted intake wrapped with nylon mesh centered at a depth of 25, 50, and 75 cm below the peat lawn surface. The piezometers were carefully inserted into an augured hole with a slightly smaller diameter than the piezometer pipe to ensure a tight seal between the surface of the pipe and peat. Stage heights were measured monthly from June through October 2010 and May through October 2011 immediately before pore water collection. Peat K_{sat} measurements were conducted in late summer 2011 utilizing bail tests recorded with pressure transducers (Levellogger Junior Model 3001; Solinst, Georgetown, Ontario, Canada) set at a recording interval of 0.5 s for 25 cm piezometers because of the rapid recharge and 60 s for 50 cm piezometers to accommodate the low K_{sat} of peat at this depth. Peat K_{sat} was calculated following *Hvorslev* [1951]. Pore water velocity and VHG was estimated following *Fetter* [1994]:

$$V = (K_{sat}/n)\ (dh/dl)$$

where V is pore water velocity, K_{sat} is the saturated pore water hydraulic conductivity (cm s^{-1}), n is the peat porosity, dh is the difference in head between piezometers (cm), and dl is the distance between piezometer intake (cm). The K_{sat} measurements from the piezometers represent a multidimensional conductivity within the peatland and therefore provide only an estimate of vertical velocity. Pore water VHG was calculated by

$$VHG = dh/dl.$$

2.3. Pore Water Sampling

Pore water was collected monthly from May to November 2010 and May to September 2011 from each piezometer nest (25, 50, and 75 cm depths) installed at each plot (A–F). Immediately preceding water sampling, 25 cm piezometers were pumped dry and allowed to recharge. Because of the extremely long recharge in the 50 and 75 cm piezometers, flushing was only possible 2 weeks before collection. Pore water pH, conductivity, and temperature were measured from the 25 cm piezometers immediately after water collection. Approximately 120 mL of sample was collected into sample-rinsed high-density polyethylene Nalgene bottles. Water samples were transported on ice in a cooler to Michigan Technological University Wetland Laboratory and placed in a refrigerator at 4°C. Pore water was filtered within 24 h through 0·45 μm nylon membrane filters. Water samples were then split into three aliquots: (1) 50 mL was acidified to pH2 with HCl and refrigerated at 4°C prior to DOC and total dissolved nitrogen (TDN) analysis, (2) 50 mL was frozen at −20°C prior to anion, element, organic acid, and phenolic analysis, (3) 20 mL was refrigerated at 4°C for spectrophotometer analyses. Additional pore water samples ($n = 4$) were collected (November 2010; May and August 2011) from 25 cm below the lawn microforms equally spaced within a 400 m^2 plot around the piezometer nest at each plot with a stainless steel sipper to confirm that piezometers were capturing variation at the site level.

2.4. Pore Water Chemistry and DOC Quality Analysis

Dissolved organic carbon and total dissolved nitrogen (TDN) were measured on a Shimadzu TOC-V Combustion Analyzer with a TNM-1 Total Nitrogen module (Shimadzu Scientific Instruments, Columbia, MD, USA) with a detection limit of 0.05 mg L^{-1} and 0.5 μg L^{-1} respectively. Bromide (Br^-), chloride (Cl^-), fluoride (F^-), nitrate (NO_3^-), nitrite (NO_2^-), phosphate (PO_4^{-3}), sulfate (SO_4^{-2}), acetate, propionate, formate, and oxalate were determined with an ICS-2000 ion chromatograph (Dionex Corporation, Bannockburn, IL, USA) from all three piezometer depths in 2010. Detection limits for ion chromatography were 0.02 mg L^{-1}. The elements calcium (Ca), magnesium (Mg), sodium (Na), iron (Fe), potassium (K), copper (Cu), aluminum (Al), and Zinc (Zn) were determined with a PerkinElmer Optima 7000 DV inductively coupled plasma optical emission spectrometer (ICP-OES) (PerkinElmer Corporation, Waltham, Ma, USA) from the 25 cm deep piezometers for the 2010 pore water samples.

Pore water absorbance (ABS) was measured at $\lambda = 254$, 365, 465, and 665 nm to characterize composition of DOC with a SpectraMax M2 multimode microplate reader (Molecular Devices Corporation, Sunnyvale, CA, USA) using a 1 cm quartz cuvette and reverse osmosis (RO) water for the blank. The ratio of absorption spectra at $\lambda = 254$ nm to $\lambda = 365$ nm (E2:E3) was used as an index for the molecular size of the dissolved organic matter (DOM) molecules [*Lou and Xie*, 2006]. Specific ultraviolet absorbance ($SUVA_{254}$) was calculated from absorption at $\lambda = 254$ nm divided by sample DOC concentration ($SUVA_{254}$ is reported in units of L mg C^{-1} m^{-1}). The value of $SUVA_{254}$ increases linearly with measured DOC aromaticity; therefore, it is an indicator of pore water aromaticity [*Weishaar et al.*, 2003]. The ratio of absorption spectra at $\lambda = 465$ nm to $\lambda = 665$ nm (E4:E6) was used as an indicator of DOC humification, with a larger ratio generally considered relatively more aromatic [*Worrall et al.*, 2002].

Ammonium (NH_4^+) and total phenolics were determined by reagent packets from Hach (Hach Co., Loveland, CO, USA) scaled down to a microplate technique. Total phenolics were quantified by adding 250 μL of sample to each microplate well and then adding 10 μL of TanniVer reagent (catalog no. 256032) to each well. Next, sodium pyrophosphate (NaP_2O_7) dissolved in RO water (0.2 g per 2 mL) was added to each well to eliminate possible ferrous iron interference followed by 50 μL of sodium carbonate solution (catalog no. 67549). The plate was shaken, incubated covered for 25 min, and ABS measured at $\lambda = 700$ nm. A total phenolic standard curve was produced from tannic acid diluted to 1.5, 3, 6, and 9 ppm. The Hach tannin and lignin method determines all hydroxylated aromatic compounds, so it is a test for total phenolics present in the assayed pore water. Ammonium was determined by methods outlined in *Sinsabaugh et al.* [2000] with a standard curve produced from ammonium acetate diluted to 0.01, 0.05, 1, 2, and 5 ppm.

An incubation experiment to test DOC potential mineralization was conducted in August 2011 with pore water from plots B, C, and E to represent the three different WT sites (intermediate, raised, and lowered respectively). Bulk pore water was collected at 25 cm below the peat surface with a stainless steel sipper from four locations equally spaced along a 20 m transect at each plot that included the 25 cm piezometer as one of the collection points. Water was placed on ice, transported back to Michigan

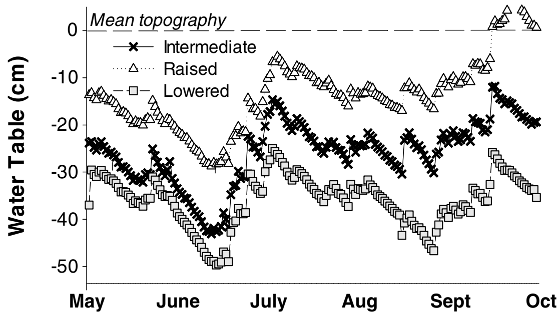

Figure 2. Seasonal 2 year mean (2010 and 2011) WT position below the peatland mean microtopography across the three WT sites (intermediate, raised, and lowered).

Technological University Wetland Laboratory, and processed for initial DOC, TDN, ABS indexes, and total phenolics within 24 h. Additional filtered water samples were placed in acid-washed bottles to provide four replicates for four harvest dates (3, 7, 14, and 28 days). A total of 20 samples (four for each sample date including time zero) were prepared for each site. Samples were inoculated with 1 mL of common innoculum prepared by mixing equal proportions of bulk pore water from each site then sequentially diluting to 10^{-3} [*Wickland et al.*, 2007]. Samples were incubated in the dark at a constant temperature of 20°C. Samples were filtered upon harvesting and analyzed for DOC, TDN, ABS indexes, and phenolic compounds as described above.

2.5. Statistical Analysis

We treated the three different WT sites created by hydrologic alterations as a natural experiment. A two-way, repeated measures analysis of variance was conducted using PROC MIXED to test for differences in pore water DOC and TDN concentrations across the WT sites (SAS Institute Inc., Cary, NC, USA, version 8). Each site was an experimental unit, so replicate measurements were averaged by site for each year of analysis. Individual plots within each WT site were used as replicates, WT sites were treated as whole plots, and depth was treated as subplots. Water table sites and depth interactions were treated as fixed effects, plots were treated as random effects, and sample years were treated as repeated measures. We used complex symmetry covariance structure for repeated measures analysis as determined by looking at the fit statistics and the Kenward and Roger's correction for degrees of freedom [*Littell et al.*, 2006]. Pore water constituents and spectrophotometer indices were analyzed with a general linear model [Minitab Inc. State College, PA, USA, version 16] with WT and depth as fixed effects, site as a random factor, and date as repeated measure. The relationship between DOC and Cl^-, TDN and DOC, and DOC and K_{sat} were explored with analysis of covariance (ANCOVA). Because of the non-normal distribution of the data, a Kruskal-Wallis test was used to compare seasonal mean DOC:Cl^- ratios across the WT sites. A multivariate principle component analysis (PCA) was applied to the entire 2011 pore water chemistry and K_{sat} data set from the 25 cm piezometers to determine the best predictor variables for WT sites. A PCA was additionally utilized to

Table 1. Bulk Density (D_b; g cm^{-3}), Hydraulic Conductivity (K_{sat}; cm s^{-1}), and Vertical Hydraulic Gradient (VHG) Across the Three WT Sites (Intermediate, Raised, and Lowered)[a]

	Water Table Site		
	Intermediate	Raised	Lowered
Peat horizon (cm)		D_b (g cm^{-3})	
0–10	0.01 (0.002)[a]	0.02 (0.003)[a]	0.02 (0.003)[a]
10–20	0.04 (0.003)[a]	0.05 (0.005)[a,b]	0.06 (0.003)[b]
20–30	0.04 (0.003)[a]	0.05 (0.003)[a,b]	0.06 (0.004)[b]
30–40	0.05 (0.003)[a]	0.07 (0.004)[b]	0.09 (0.008)
40–50	0.07 (0.007)[a]	0.10 (0.011)[b]	0.12 (0.008)[b]
Piezometer depth (cm)		K_{sat} (cm s^{-1})	
25	1.68 (0.03)[a]	0.52 (0.05)[b]	0.77 (0.14)[b]
50	0.51 (0.06)[a]	0.03 (0.02)[b]	3.6×10^{-4} (1.2×10^{-4})[b]
		VHG[b]	
25–50	−0.11 (0.04)[a]	−0.01 (0.03)[b]	−0.13 (0.02)[a]
50–75	0.34 (0.11)[a]	0.26 (0.14)[a]	0.74 (0.18)[b]

[a]Values are means with ± 1 standard error in parentheses. Different letters represent significant differences across WT sites for each depth (Tukey's $p < 0.05$).
[b]Negative values represent upwelling and positive values downwelling.

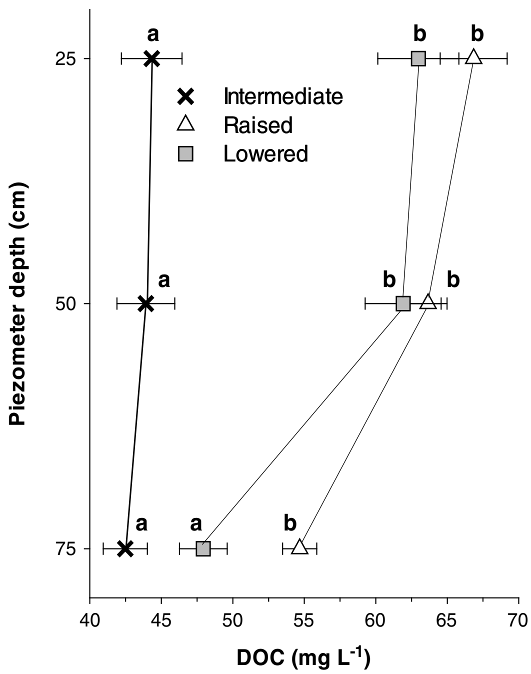

Figure 3. Two year (2010 and 2011) DOC concentrations (seasonal mean ± 1 SE) across the three WT sites (intermediate, raised, and lowered) by depth of piezometer (25, 50, and 75 cm). Different letters above bars represent significant differences across WT sites for each piezometer depth (Tukey's $p < 0.05$).

examine pore water element and organic acid relationships to WT sites using PC-ORD 6 (MjM Software, Gleneden Beach, OR, USA). Between WT sites, comparisons for the PCA-derived groups were explored with multiresponse permutation procedures (MRPP) using PC-ORD. One-way analysis of variance was used to analyze the mineralization experiment, and the most significant predictors (utilizing WT site, beginning DOC concentration, $SUVA_{254}$, E2:E3, E4:E6, phenolics, and TDN) of DOC mineralization were explored with a best subset regression analysis. The fit of the model was evaluated with Mallows' *Cp*, which should be smaller or equal to the number of degrees of freedom in the regression model [Minitab Inc. version 16]. Descriptive statistics were determined with SigmaPlot [Systat Software, Inc., San Jose, CA, USA, version 12.3] and comparisons between all WT sites were conducted using Tukey's post hoc test with differences at $p < 0.05$ considered significant.

3. Results

3.1. Water Table and Peat Physical Characteristics

The expected WT levels in the lowered and raised sites created by the levee relative to the unaltered site were confirmed for 2010 and 2011. The lowered WT site south of the impoundment experienced the greatest drawdown with the 2 year seasonal mean (April–October) WT of 36.6 ± 5.7 cm (mean ±1 SD below mean microtopography). The raised site had the highest WT (14.4 ± 6.9 cm), while the unaltered intermediate site (26.2 ± 7.1 cm) was staged between the raised and lowered WT sites (Figure 2). Direction of water flow across the peatland complex encompassing our sites estimated from hydraulic well head elevations matches the general northwest to southeast surface sheet flow across the greater SNWR landscape (Figure 1b).

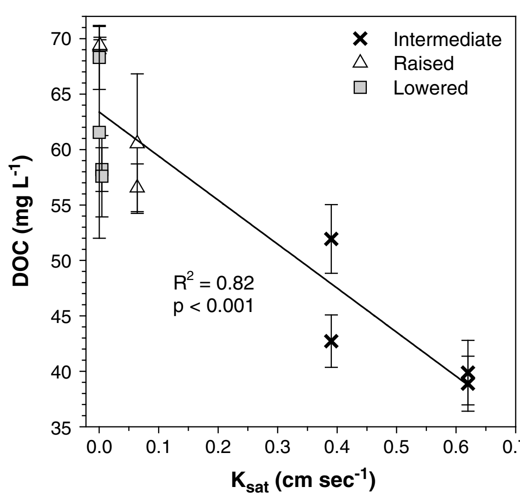

Figure 4. Relationship between peat hydraulic conductivity (K_{sat}) and 2 year seasonal mean pore water DOC concentrations (mean ± 1 SE) at 50 cm below the peat surface across the three WT sites (intermediate, raised, and lowered). There was an effect of K_{sat} on DOC across the WT sites (ANCOVA; $F = 35.57$, $p < 0.001$) and WT site by DOC interaction was significant (ANCOVA; $F = 7.58$, $p < 0.001$).

The two year mean VHG between the 50 and 75 cm deep piezometers displayed a general trend of downwelling indicating a recharge of peatland pore water into the groundwater across the peatland that was greatest in the lowered site ($p < 0.001$) (Table 1). The raised WT site VHG between the 50 and 75 cm piezometers exhibited seven upwelling episodes (ground water discharge into the peatland) in 2010 and 2011, whereas the only other reversal to downwelling was in plot B (May 2011; VHG of 0.04) (data not shown). In contrast, the 2 year mean VHG between the 25 and 50 cm piezometers showed a slight upwelling across the peatland (Table 1). The raised WT site had the smallest upward mean VHG ($p < 0.001$). The VHG between the 25 and 50 cm piezometers did reverse to downwelling in

Table 2. Seasonal Mean Pore Water Element Concentrations for 2010 Across the Three WT Sites (Intermediate, Raised, and Lowered) Sampled From the 25 cm Deep Piezometers[a]

WT Site	Ca ($mg\ L^{-1}$)	Fe ($mg\ L^{-1}$)	Mg ($mg\ L^{-1}$)	Na ($mg\ L^{-1}$)	K ($mg\ L^{-1}$)	Cu[b] ($mg\ L^{-1}$)	Al ($mg\ L^{-1}$)	Zn ($mg\ L^{-1}$)
Intermediate	0.58 (0.07)[a]	0.62 (0.09)[a]	0.21 (0.03)[a]	0.19 (0.02)[a]	0.08 (0.02)[a]	0.06	0.16 (0.03)[a]	0.03 (0.01)[a]
Raised	1.85 (0.09)[b]	1.54 (0.16)[b]	0.50 (0.02)[b]	0.54 (0.07)[b]	0.13 (0.02)[b]	0.02	0.29 (0.04)[b]	0.03 (0.004)[a]
Lowered	0.86 (0.05)[a]	0.93 (0.08)[a]	0.24 (0.02)[a]	0.25 (0.05)[a]	0.06 (0.01)[a]	0.06	0.36 (0.03)[c]	0.04 (0.01)[a]

[a]Values are seasonal means (2010) with ± 1 standard error in parentheses. Total sample $n = 6$. Different letters represent significant differences across WT sites (Tukey's $p < 0.05$).
[b]Copper (Cu) was detected in only one sample date.

the intermediate site in 2011 for September (plots A and B) and October (plot B), and the raised WT site displayed several upwelling episodes in 2010 and 2011(data not shown).

Hydraulic conductivity was lower in the raised and lowered sites in the 25 cm (69% and 54% respectively) and 50 cm (2 and 3 orders of magnitude respectively) deep piezometers compared to the intermediate site (Table 1). Bulk density (D_b) displayed a significant nonlinear inverse relationship to hydraulic conductivity ($R^2 = 0.67$, $p = 0.001$). Bulk density was higher in the lower WT site (10–50 cm) and raised site (30–50 cm) peat horizons than the intermediate site (Table 1).

3.1.1. Water Table Effects on DOC Concentrations

Dissolved organic carbon concentrations showed differences across the three WT sites and three piezometers depths ($F_{2,3} = 10.20$, $p = 0.04$ and $F_{2,24} = 12.50$, $p < 0.001$ respectively). The raised and lowered WT sites' 2 year mean DOC concentrations were significantly greater than the intermediate site in the 25 cm piezometers (33.5% and 29.6% respectively) and 50 cm piezometers (31.1% and 29.0% respectively) (Figure 3). Only the raised WT site was different from the intermediate site at the 75 cm depth (22.3%). Within the raised and lowered sites there was a consistent trend for DOC concentrations to decrease with depth. The raised and lowered WT site DOC concentrations decreased 18.2% and 25.0% respectively between the 25 cm and 75 cm piezometers, whereas the intermediate site declined only 4.3% (Figure 3). The additional pore water samples collected (November 2010; May and August 2011) across each plot displayed the same significant differences in DOC concentrations ($F_{2,3} = 18.25$, $p < 0.001$) as the seasonal mean concentrations measured in the piezometers, confirming that we were capturing pore water characteristic from the plot level and not just the microenvironment at each piezometer nest. In the 50 cm piezometers, seasonal mean DOC concentrations (2010 and 2011) for the six plots (A–F) were inversely correlated to K_{sat} ($R^2 = 0.91$, $p = 0.001$) (Figure 4), and there was a significant WT site by DOC interaction confirming that the raised and lowered WT sites were different than the intermediate site ($F_{2,10} = 7.58$, $p < 0.001$).

3.2. Pore Water Electrochemistry and Chemical Constituents

The raised WT site pore water pH (2 year seasonal mean; 3.84 ± 0.20 (±1 SD)) was greater than the intermediate site and lowered site pH (3.61 ± 0.27, and 3.56 ± 0.23 respectively; $F_{2,98} = 10.28$, $p < 0.002$).

Table 3. Pore Water Anion, Organic Acid, and Phenolic Concentrations Across the Three WT Sites (Intermediate, Raised, and Lowered) by Depth of Piezometer (25, 50, and 75 cm)[a]

WT Site	Depth (cm)	F^- ($mg\ L^{-1}$)	Cl^- ($mg\ L^{-1}$)	PO_4^{3-} ($mg\ L^{-1}$)	SO_4^{2-} ($mg\ L^{-1}$)	Acetate ($mg\ L^{-1}$)	Propionate ($mg\ L^{-1}$)	Formate ($mg\ L^{-1}$)	Oxalate ($mg\ L^{-1}$)	Phenolic ($mg\ L^{-1}$)
Intermediate	25	0.02 (0.01)	0.50 (0.16)	0.19 (0.05)	0.01 (0.01)	0.24 (0.15)	0.05 (0.02)	0.05 (0.01)	0.59 (0.35)	9.23 (0.27)
	50	0.04 (0.003)	0.70 (0.13)	0.11 (0.03)	0.03 (0.02)	0.28 (0.14)	0.03 (0.01)	0.05 (0.01)	0.11 (0.01)	9.65 (0.36)
	75	0.02 (0.01)	0.43 (0.04)	0.21 (0.04)	0.12 (0.05)	2.98 (0.92)	0.89 (0.21)	0.23 (0.04)	0.08 (0.01)	8.93 (0.79)
Raised	25	0.05 (0.01)	0.84 (0.12)	0.21 (0.03)	0.01 (0.01)	0.39 (0.24)	0.12 (0.07)	0.07 (0.01)	0.17 (0.05)	15.58 (1.30)
	50	0.06 (0.02)	0.95 (0.26)	0.14 (0.03)	0.12 (0.02)	0.62 (0.37)	0.15 (0.10)	0.07 (0.01)	0.11 (0.01)	14.62 (0.98)
	75	0.05 (0.02)	0.74 (0.16)	0.20 (0.02)	0.12 (0.02)	0.31 (0.27)	0.04 (0.04)	0.04 (0.01)	0.08 (0.01)	10.63 (0.32)
Lowered	25	0.04 (0.01)	0.61 (0.17)	0.16 (0.03)	0.01 (0.01)	0.43 (0.19)	0.08 (0.04)	0.08 (0.01)	0.18 (0.03)	12.57 (0.75)
	50	0.04 (0.01)	0.68 (0.17)	0.14 (0.04)	0.22 (0.03)	1.40 (0.65)	0.38 (0.20)	0.09 (0.02)	0.12 (0.01)	11.84 (0.76)
	75	0.02 (0.01)	0.34 (0.03)	0.21 (0.03)	0.13 (0.02)	1.17 (0.47)	0.33 (0.12)	0.10 (0.02)	0.10 (0.01)	8.03 (0.64)

[a]Values are seasonal means (2010) with ± 1 standard error in parentheses.

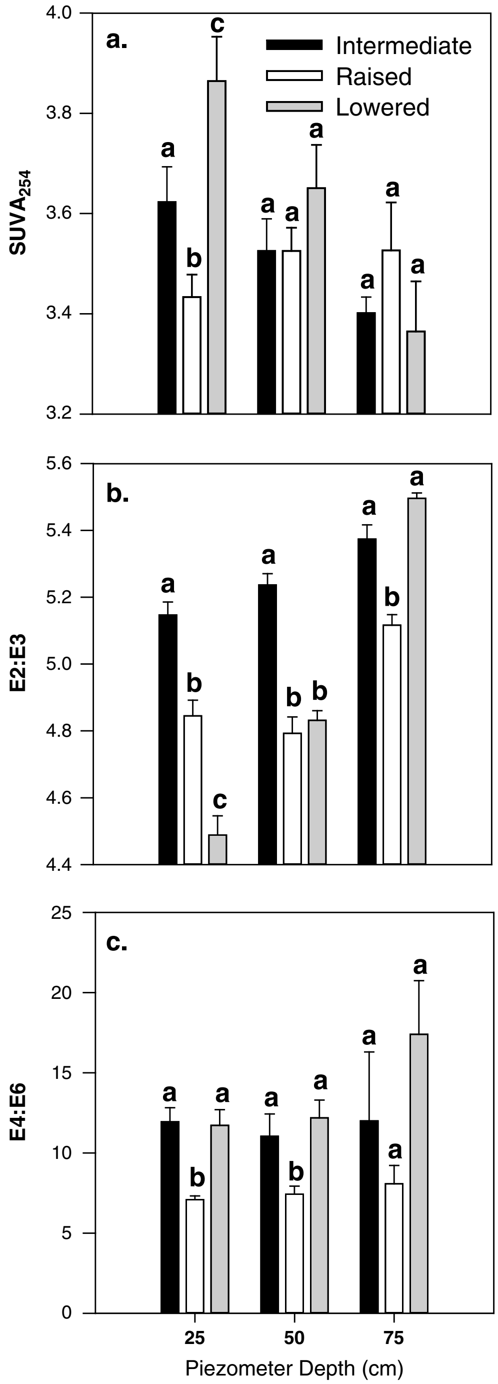

Figure 5. Pore water DOC spectral indices (seasonal mean + 1 SE) across the three WT sites (intermediate, raised, and lowered) and three piezometer depths (25, 50, and 75 cm) from the 2011 sampling season for (a) $SUVA_{254}$ (aromaticity), (b) E2:E3 (molecular size), and (c) E4:E6 (humification). Different letters above bars represent significant differences across WT sites for each piezometer depth (Tukey's $p < 0.05$).

The lowered WT site electrical conductivity (2 year seasonal mean; $71.6 \pm 8.5\ \mu S\ cm^{-1}$) was greater than the intermediate site ($60.2 \pm 7.8\ \mu S\ cm^{-1}$) and raised WT site ($56.9 \pm 5.8\ \mu S\ cm^{-1}$) ($F_{2,98} = 19.25$, $p < 0.001$). Pore water temperature (25 cm depth, 2 year seasonal means) was similar across the intermediate, raised, and lowered WT sites (14.2 ± 4.2°C, 15.5 ± 4.8, 14.0 ± 4.5 respectively; $F_{2,98} = 0.47$, $p = 0.63$).

The elements Ca, K, Mg, and Na (25 cm piezometers) were elevated in the raised WT site (Table 2). PCA ordination resulted in a strong positive relationship between measured elements and the raised WT site (not shown). Aluminum concentrations were different across WT sites with the lowered site exhibiting the highest concentrations ($0.36 \pm 0.03\ mg\ L^{-1}$) followed by the raised site and intermediate site ($0.29 \pm 0.04\ mg\ L^{-1}$, 0.16 ± 0.03 respectively). Concentrations of the anion SO_4^{-2} were greater in the raised and lowered WT site compared to the intermediate site in the 50 cm piezometers. To assess the possible influence of evaporation/evapotranspiration on changes in DOC concentration, we utilized Cl^- as a conservative tracer. Across the three different WTs, seasonal mean DOC:Cl^- ratios were not significantly different (Kruskal-Wallis; $H = 2.56$, $p = 0.28$) and the relationship of DOC versus Cl^- displayed similar trends in slope ($F_{2,45} = 0.54$, $p = 0.59$).

3.3. DOC Composition and Quality

Concentrations of organic acids were not significantly different across the three WT sites for each piezometer depth due to a large seasonal variation in species concentrations (Table 3). The highest concentrations of organic acids were recorded in the 75 cm piezometers in the early season samples (Data not shown for individual sample days). Furthermore, early season (May) samples combining all sites were elevated in acetate and propionate compared to late season samples (September–November) (MRPP; $T = -20.98$, $A = 0.28$, $p < 0.001$). Pore water phenolic concentrations decreased with depth in the raised and lowered WT sites ($F_{2,98} = 15.87$, $p < 0.001$). The raised and lowered WT sites displayed elevated phenolic concentrations compared to the intermediate site ($F_{2,98} = 29.21$, $p < 0.001$) (Table 3). Pore water TDN concentrations displayed a positive relationship with DOC for both sample years and all three piezometer depths across the WT sites ($R^2 = 0.61$, $p < 0.001$). However, we did not detect any influence of DOC on TDN concentrations as a function of WT (ANCOVA; $F_{2,202} = 0.38$, $p = 0.68$). Ammonium was present in very low concentrations in

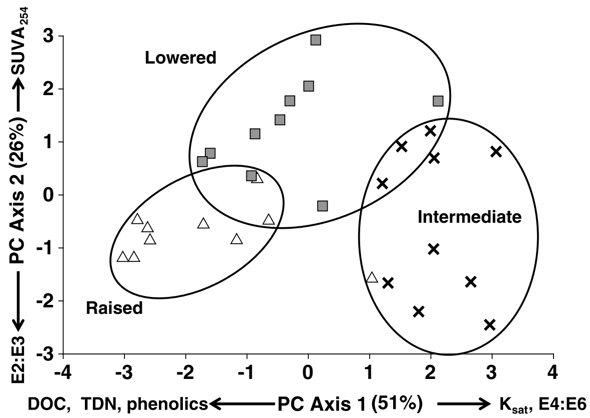

Figure 6. Principle component analysis (PCA) ordination of pore water movement and DOC quantity/quality from the 25 cm deep piezometers. Each point represents an individual water sample collected throughout the 2011 field season. The first and second axes explains 51% and 26% respectively of the variation in the ordination. The three WT sites were significantly different based on a multiresponse permutation procedure (MRPP). Ovals drawn around the individual WT sites are for illustrative purposes.

the raised (0.07 ± 0.02 mg L^{-1}), lowered (0.08 ± 0.01 mg L^{-1}), and the intermediate WT sites (0.05 ± 0.01 mg L^{-1}). Pore water concentrations of NO_3^- and NO_2^- were below detection limits.

The $SUVA_{254}$ ratio displayed differences with piezometer depth ($F_{2,41} = 4.92$, $p = 0.015$) and across the three WT sites ($F_{2,41} = 4.13$, $p = 0.027$) (Figure 5a). Ferric iron (Fe^{+3}) interference has been shown to increase $SUVA_{254}$ absorbance measurements [*Weishaar et al.*, 2003]. We did not quantify individual Fe species (Fe^{+2} and Fe^{+3}); however, total Fe was elevated in the raised site 25 cm piezometers (Table 2) which has the potential to influence the $SUVA_{254}$ measurements. Even with corrections utilizing the total Fe data, the $SUVA_{254}$ ratio results did not significantly change. Total Fe was not measured in the 50 cm and 75 cm piezometers.

The E2:E3 ratios were greatest for the intermediate WT site ($F_{2,41} = 115.19$, $p < 0.001$) and 75 cm depth ($F_{2,41} = 172.93$, $p < 0.001$). An interaction was present between WT and depth ($F_{4,41} = 58.31$, $p < 0.001$) that was predominantly the result of the large increase in the E2:E3 ratio (18%) from the 75 cm to the 25 cm piezometer (Figure 5b). The E4:E6 ratio displayed differences across WT sites ($F_{2,41} = 10.76$, $p < 0.001$) but not for depth with each site ($F_{2,41} = 1.38$, $p < 0.268$). Interaction between WT and depth was not present ($F_{4,41} = 0.95$, $p < 0.452$) (Figure 5c). The multivariate PCA analysis combining DOC, TDN phenolics, spectrophotometer indices ($SUVA_{254}$, E2:E3, and E4:E6), and K_{sat} showed a distinct separation in ordination space of the three WT sites (Figure 6) that was significant based on the MRPP analysis (Tables 4 and 5).

3.4. DOC Potential Bioavailability

Initial DOC concentrations in the pore water collected for the incubation experiment from the intermediate site (36.65 ± 2.03) and raised and lowered WT sites (76.78 ± 2.91 and 56.29 ± 1.63 respectively) displayed a similar significant difference ($F_{2,14} = 778.06$, $p < 0.001$) as the 2 year DOC means. The raised WT site mineralized more DOC (7.98 ± 0.85 mg) than the intermediate site (4.74 ± 0.28), and both were not significantly different from the lowered site (5.57 ± 0.79) over the 28 day incubation experiment (Figure 7a). Across the WT sites, there was not a significant difference in the percentage of pore water DOC mineralized. Spectrophotometer indices ($SUVA_{254}$, E2:E3, and E4:E6) and phenolic concentrations displayed the same trends as seasonal mean values. The best subset regression analysis ($R^2 = 0.72$) identified that the variables WT site ($p = 0.001$) and $SUVA_{254}$ ($p = 0.001$) were the best predictors of DOC mineralization.

Table 4. Principal Component Analysis Pearson (r^2) and Kendall Ranked (tau) Correlations of DOC and TDN Concentrations, Hydaulic Conductivity (K_{sat}), and Spectral Indices (E2:E3, E4:E6, and $SUVA_{254}$)

	Axis 1		Axis 2	
Parameter	r^2	tau	r^2	tau
DOC	0.91	−0.81	0.00	0.00
E2:E3	0.27	0.25	0.66	−0.60
E4:E6	0.55	0.62	0.14	0.27
Phenolics	0.47	−0.48	0.06	−0.14
$SUVA_{254}$	0.00	0.06	0.88	0.74
TDN	0.90	−0.84	0.02	−0.11
K_{sat}	0.47	0.37	0.05	−0.05

Table 5. Results of a Multiresponse Permutation Procedure (MRPP) Testing for Differences Across the WT Sites (Intermediate, Raised, and Lowered)

WT Site	MRPP[a] *T*	*A*	*P*
Intermediate versus raised	−9.810	0.422	<0.001
Intermediate versus lowered	−6.765	0.202	<0.001
Raised versus lowered	−2.681	0.086	0.025

[a]The *p* value tests for group differences, the more negative the *T* value the stronger the separation between groups, and the greater the *A* value the greater the similarity of sample units within groups.

4. Discussion

4.1. Long-Term Water Table Position Influences DOC Concentrations

We measured greater pore water DOC concentrations for 2 consecutive years in the lowered and raised WT sites compared to the unaltered intermediate site (Figure 2). The lowered WT site had the greatest WT drawdown and additionally displayed a large seasonal WT fluctuation (20% greater seasonal WT STD than the intermediate site in 2011). The variable and deeper WT of the lowered WT site is potentially creating oxygen enrichment in the peat column and stimulating microbial decomposition of peat that can enhance DOC production [*Fenner and Freeman*, 2011]. Furthermore, rewetting of peat with the rise of the WT can abiotically flush newly produced DOC from oxic peat into the ascending pore waters [*Chow et al.*, 2006; *Clark et al.*, 2009]. Abiotic flushing is especially effective in the upper peat surface that is rich with recently senescent plant litter undergoing aerobic microbial processing [*Fenner et al.*, 2011]. Additionally, the production of DOC can continue under reestablished anaerobic conditions due to a legacy effect of oxygen-activated phenolic oxidases reducing phenolic inhibition on microbial and enzymatic processes responsible for peat degradation [*Fenner and Freeman*, 2011]. Lastly, a lowered WT can increase the availability of recharged electron acceptors for microbial activity [*Knorr and Blodau*, 2009]. Interestingly, there is a greater accumulation of SO_4^{2-} in the lowered WT site than the intermediate site that could indicate the availability of more energetically favorable electron acceptors for microbial processing of peat. However, SO_4^{2-} has been shown to be positively [*Fenner et al.*, 2011] and negatively [*Clark et al.*, 2012] correlated with peatland DOC concentrations.

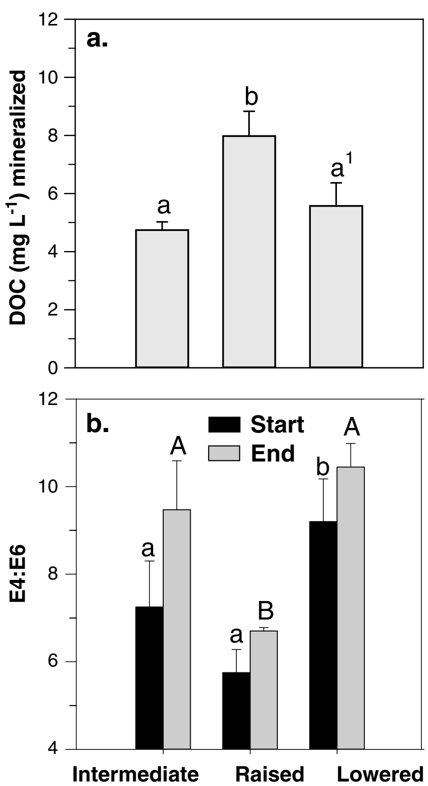

Figure 7. Incubation experiment conducted for 28 days with pore water collected at 25 cm below peat lawns across the three WT sites (intermediate, raised, and lowered). (a). Total DOC mineralized during the entire 28 day incubation. (b). E4:E6 spectral indices (index of humification) at the start (time 0) and end (time 28) of the incubation. Different letters above bars (mean + 1 SE) represent significant differences across the three WT sites (Tukey's $p < 0.05$, $^{1}p < 0.10$).

Measured differences in DOC concentrations between our long-term WT drawdown site and the unaltered intermediate site are comparable to changes in DOC concentrations reported in short-term in situ experimental WT drawdown manipulations. *Kane et al.* [2010] reported a 21.8% increase in DOC when the WT was lowered ~3 cm in an Alaskan fen over the course of 4 years. The enhanced DOC production was attributed to elevated peat temperatures and a greater seasonal thaw depth. After 11 years of WT drawdown (~4.5 cm), *Strack et al.* [2008] also documented an increase in DOC concentrations in a poor fen compared to an unaltered control site that was correlated to shifts in plant biomass and a greater seasonal fluctuation in WT position. Despite the aforementioned short-term WT manipulation studies reporting similar changes in pore water DOC concentrations to our study, they can only extrapolate to long-term ecological trajectories.

Thus, our study provides a valuable prediction that peatlands under long-term WT drawdown will experience sustained elevated DOC concentrations.

In contrast to the lowered WT site, the inundated raised site has likely caused anoxic conditions. The wettest site in the raised WT treatment (plot C) had standing water above the lawn microforms for 97% (2010) and 81% (2011) of the time period recorded for the seasonal WT levels. Regardless of the anaerobic conditions, the raised WT site DOC concentrations were significantly greater at all three piezometer depths compared to the intermediate unaltered WT site (Figure 2). The increased DOC concentrations measured in the raised site were unexpected and opposite the 12% reduction in DOC concentrations *Kane et al.* [2010] measured with a ~ 7 cm higher WT in raised WT plots relative to control plots. *Höll et al.* [2009] demonstrated that rewetting a peatland after long-term WT drawdown can increase DOC concentrations; however, to the best of our knowledge, our study is the first report of a peatland experiencing a sustained long-term raised WT position with elevated DOC concentrations.

Plant productivity is a predominate driver of DOC production from aboveground and belowground vegetation inputs into the peat matrix [*Kang et al.*, 2001]. However, we did not measure significant differences in total understory plant productivity (tracheophytes and bryophytes) across the gradient of WT sites [*Hribljan*, 2012]. Therefore, we suggest alternative mechanisms for increased DOC concentrations occurring with both long-term drainage (increased peat oxidation, peat density, and pore water residence time) and long-term inundation (nutrient recharge from ground water inputs and autochthonous DOC production). Our study demonstrates that multiple controls on DOC production/consumption are directly influenced by even subtle changes in the hydrological regime of a northern peatland. Furthermore, that both drying and wetting associated with future climate-influenced shifts in temperature and precipitation has the potential to significantly effect peatland DOC concentrations.

4.2. Peat Physical Controls on DOC Concentrations

Pore water residence time can influence DOC concentrations by increasing or decreasing vertical flushing of DOC-enriched water into the substratum [*Fraser et al.*, 2001]. *Reeve et al.* [2000] proposed that vertical flow can be enhanced when the WT drops to the base of the acrotelm (the upper peat horizon), reducing the influence of lateral pore water discharge from the peatland. Despite the lowered WT site displaying the largest VHG, pore water residence time was significantly longer than the intermediate site because of a lower K_{sat} and reduced peat porosity that resulted in a significantly smaller downward pore water velocity (7.95×10^{-4} cm s^{-1} and 0.27 cm s^{-1} respectively). In the raised WT site we also measured a low K_{sat} in the 50 cm piezometers; however, VHG was the lowest of all three sites. Reduced vertical advective flow, especially with an elevated WT position, has been demonstrated from anaerobic gas production creating bubbles blocking pores in the peat matrix [*Romanowicz et al.*, 1995; *Beckwith and Baird*, 2001; *Kellner et al.*, 2005], and increased methane (CH_4) emissions were measured in the raised sites [*Ballantyne et al.*, 2013]. Additionally, numerous upward flow reversals in the raised site were measured in the deep piezometers over the 2 year sampling period that can contribute to a reduced pore water residence time by countering downward flows [*Reeve et al.*, 2000]. The flow reversals were substantiated by elevated pore water Ca and Mg concentrations measured in the raised site (Table 2) that are known to commonly enter the peatland from upwelling ground water rich in minerals [*Siegel et al.*, 1995]. Thus, the combination of a low VHG, K_{sat}, and porosity with numerous upwelling events are all contributing to a pore water velocity of 0.02 cm s^{-1} that has created a high residence time in the raised site. The greater residence time in our raised and lowered WT sites is suggested as a significant variable explaining DOC production/consumption dynamics. Water residence time can significantly alter DOC concentrations by controlling flushing and retention of pore water [*Wickland et al.*, 2007] and DOC quality is strongly controlled by changes in microbial contact time with DOC substrates [*Beer et al.*, 2008].

The greater D_b in the lowered and raised sites is a contributing factor in the elevated residence times from decreased hydraulic conductivity [*Surridge et al.*, 2005]. The increase in D_b was expected and has been observed with a drawdown of the WT [*Minkkinen and Laine*, 1998]; however, the increased D_b measured in the raised WT site is in contrast to reported decreases in D_b associated with inundation. We propose that the increased D_b in the raised site is not an artifact of prelevee conditions and could be caused by decreased root production [*Finér and Laine*, 1998; *Kozlowski*, 1997] from the anoxic conditions in the peat column and/or from peat compression caused by the hydrostatic pressure of the seasonally high standing water table above the peat surface collapsing and reducing pore volume [*Lewis et al.*, 2011].

Lastly, we explored if evaporation/evapotranspiration was concentrating pore water constituents and therefore increasing DOC concentrations across our sites [*Whitfield et al.*, 2010], especially when combined with a greater pore water residence time limiting DOC export from the peatland [*Waiser*, 2006]. The use of Cl^{-} as a conservative tracer [*Waiser*, 2006; *Anderson and Stedmon*, 2007] displayed no significant increase relative to DOC concentrations in the near surface pore waters indicating that evaporation/transpiration was not significantly concentrating the DOC pool across the treatments. In addition, WT treatment was not a significant predictor of DOC:Cl^{-} across the three different WTs, substantiating the small influence of evaporative processes on solute concentrations across the peatland. Thus, the increase in DOC production in the raised and lowered WT treatments can be attributed to differences in physical and biological mechanisms presented in this study.

Lateral export of DOC from our sites was not quantified; however, we measured seasonal (May–October, 2011) DOC concentrations (18.6 ± 3.0 mg L^{-1}) and water discharge from a small stream located on the southern edge of our peatland catchment discharging into the Manistique River that flows into Lake Michigan. Seasonal export of DOC from this stream was 3.7 Gg tons of C representing 0.1% of the total seasonal DOC load of the Manistique River (USGS gauging station no. 04055000). The highly aromatic nature of the stream water ($SUVA_{254}$ seasonal mean, 4.14 ± 0.28) when compared to our sites (Figure 5) is indicating that source water is likely from sheet flow flushing across the upper more hydrologically conductive surface of the peatland landscape. It is also relevant to note that our shallow piezometers (25 cm) displayed the greatest differences in DOC concentration and quality across the WT sites. Therefore, increased concentrations of chemically altered DOC are positioned in a region of the peatland that could potentially experience the greatest pore water transport. Scaling-up small stream measurements to the entire drainage basin surrounding our peatland complex has significant implications for potential DOC transfer to the greater watershed catchment [*Ågren et al.*, 2007]. However, a thorough examination of hydrologic connectivity of the peatland complex with early order tributaries and solute export were outside the scope of this study. Future research investigating vertical and horizontal flow paths of peatlands to their greater catchment is needed to better understand the relationship between WT position, DOC dynamics, and C cycling in northern peatland systems.

4.3. Changes in DOC Chemical Characteristics

Pore water DOC quality indices between the impacted WT sites and the intermediate site displayed significant differences in aromaticity, composition of humic compounds, and molecular size of DOM. The lower $SUVA_{254}$ value measured in the upper peat profile of the raised site is indicative of DOC influenced primarily by an autochthonous (microbial and/or algal) source in contrast to an allochthonous (terrestrial) carbon pool [*Barber et al.*, 2001; *Mash et al.*, 2004] (Figure 5a). The elevated WT in the raised site is creating an increased surface water photic zone that potentially could support algae growth. The wettest plot in the raised WT site (plot C) had standing water above the lawn microforms for 97% (2010) and 81% (2011) of the time period recorded for the seasonal WT levels (April–October). We propose that algae activity could be a strong factor driving the elevated DOC concentrations and changes in pore water chemistry in the raised WT site. Algae have been shown to excrete approximately 19% of photosynthetically fixed carbon into the water column and influence pore water aromaticity [*Wyatt et al.*, 2012]. It is important to note that despite the overall seasonally elevated WT in the raised site we did record a drop of the WT position below the surface of the peatland for a period of the year, which has the potential to transport chemically altered surface water downward into the upper peat horizons and produce the differences measured in pore water spectrophotometric indices.

The greater mineralization of DOC measured from the raised WT site pore water incubation (Figure 7a) is potentially related to algal-derived inputs into the water column. Algae-derived DOC is readily assimilated by heterotrophic bacteria [*Wiebe and Smith*, 1977; *Brock and Clyne*, 1984; *Wyatt et al.*, 2012] and in select environments can comprise approximately half of the bacterial carbon requirement [*Malinsky-Rushansky and Legrand*, 1996]. Furthermore, algal-produced DOC is generally more labile than plant-derived DOC [*Klug*, 2005], which is supported by the low $SUVA_{254}$ values we measured throughout the growing season in the shallow piezometers at the raised WT site. Additionally, *Kalbitz et al.* [2003] demonstrated that $SUVA_{254}$ is a strong predictor of DOC mineralization. Surprisingly, published research on the effects of altered hydrology on algal community DOC contributions in northern peatlands is limited.

An additional variable that could influence the lability of the raised WT site pore water is photoproduction of highly labile organic compounds. As we previously noted, the raised site has a seasonally elevated WT above the lawn microforms creating a larger photic zone than the lowered and intermediate WT sites and contains a significantly higher fraction of humic acids in the pore water (Figure 5c). *Bano et al.* [1998] reported a 300% increase in bacterial degradation of humic acids exposed to sunlight. Furthermore, a lower $SUVA_{254}$ value in the raised WT site could also be indicative of suppressed microbial activity from anoxic conditions reducing production of water soluble aromatic carbon compounds from decomposition of aromatic surface litter [*Freeman et al.*, 1996].

In contrast to the raised WT site, the high $SUVA_{254}$ at the lowered WT site is likely caused by increased decomposition in the upper peat profile and accumulation of water soluble aromatic products from decomposition [*Wickland et al.*, 2007]. The greater aromaticity in the lowered WT site compared to the raised WT site is substantiated by the significantly higher E4:E6 ratio (Figure 5c and 7b).

When examining $SUVA_{254}$ in relation to piezometer depth, the intermediate and lowered WT sites are responding very differently than the raised site with a noticeable reduction from shallow (25 cm piezometers) to deep pore water (75 cm piezometers) (decreasing 9% and 14% respectively). *Kane et al.* [2010] reported increasing $SUVA_{254}$ with depth across a short-term WT manipulation that was explained as an accumulation of recalcitrant DOC in deeper peat profiles. Our results contradict these findings; however, decreasing $SUVA_{254}$ has been reported in forest and grassland systems and is attributed to selective adsorption of dissolved hydrophobic aromatic compounds onto the soil matrix [*Sanderman et al.*, 2008; *Fröberg et al.*, 2011]. In addition, deeper pore water (50–75 cm piezometers) across our peatland was shown to be hydrologically separated from the surface water (25 cm piezometers). The upper water column displayed mean negative VHG's flow reversals, possibly from high evapotranspiration rates [*Fraser et al.*, 2001] of *Sphagnum* mosses and rooted vascular vegetation. This could cause deeper pore water to be influenced primarily by humified peat than solely from downward migrating pore water from the upper peat horizon that has been in contact with surface vegetation litter that is rich in highly aromatic organic C compounds [*Freeman et al.*, 1996]. Research is limited on the effects of peatland pore water movement on DOC production/consumption dynamics and warrants further attention.

We also measured differences among the three WT sites in the degree of decomposition of the DOC fraction of the pore water. The intermediate site and lowered WT site displayed a greater E4:E6 ratio (index of humification) than the raised site that is most pronounced in the upper peat profile (25 and 50 cm piezometers). An elevated E4:E6 ratio is indicative of DOC with a high fulvic acid content [*Wallage et al.*, 2006; *Blodau and Siems*, 2012] produced from decomposition of plant litter in an aerobic environment [*McKnight et al.*, 2001]. The reduced E4:E6 ratio in the raised site is attributed to anaerobic conditions with depressed microbial activity on vegetation organic matter resulting in the accumulation of humic acids. Typical values for E4:E6 ratios for DOC containing predominantly fulvic acids are 8–9 (DOC with predominately humic acid is 5–6), values that are slightly lower than our ratios in the intermediate and lowered WT sites. However, *Chen et al.* [2010] stated that the E4:E6 ratio increases with additional oxygenated bonds, thus making our values very realistic because of the aerated peat surface at the intermediate site and lowered WT site. With sufficient oxygen, pore water compounds are formed containing high concentrations of carboxylic and ketonic bonds ($C = O$) [*Uyguner and Bekbolet*, 2005] in addition to aromatic bonds linked and substituted primarily by oxygen [*Chen et al.*, 2010]. These aforementioned bonds readily absorb light at $\lambda = 465$ nm (E4), thus elevating the E4:E6 ratio. The pore water E4:E6 ratios demonstrated that the three WT sites have different chemical properties potentially driven by the WT changes affecting redox and decomposition dynamics.

Another possible explanation for the lower E4:E6 index in the raised WT site is the reduction of the fulvic acid pool when algae are the main source of DOC production [*McKnight et al.*, 1994]. Algae can absorb fulvic acid in outer cell surfaces as a means to facilitate the uptake of carbon. This mechanism has been shown to sequester up to 31% of the DOC fulvic acid fraction during large blooms, especially in low pH environments with high DOC concentrations [*Knauer and Buffle*, 2001]. *Knauer and Buffle* [2001] reported fulvic acid adsorption by the algae *Chlamydomonas reihadrii*, *Scenedesmus* spp., and *Chlorella* spp., which are all found in northern peatlands

[*Quinn et al.*, 2002; *Klemenčič et al.*, 2010]. The significantly lower E4:E6 spectrophotometer ratio measured at the raised site in the upper 50 cm of the peatland is suggestive of a reduction of fulvic acid compounds in the DOC pool [*Wallage et al.*, 2006] (Figure 5c).

The WT changes are also influencing the size distribution of organic compounds in the pore water. The E2:E3 ratio, which is inversely related to the average molecular weight of DOC compounds [*Lou and Xie*, 2006], was significantly reduced in the lowered WT site compared to the raised site and the intermediate site. A reduced E2:E3 ratio is an indication of the pore water DOC fraction composed of a greater percentage of HMW (high molecular weight) molecules. Increased oxic conditions from WT drawdown can activate phenol oxidases [*McLatchey and Reddy*, 1998; *Freeman et al.*, 2004; *Fenner et al.*, 2011] and additionally recharge microbial electron acceptors creating a favorable environment for the enhanced breakdown of plant litter plentiful in HMW phenolic compounds, e.g., lignin and tannin [*Limpens et al.*, 2008]. This proposed process is substantiated by the elevated concentrations of phenolics in the pore water from the 25 cm deep piezometers in the lowered WT site. Quantification of phenolic oxidase enzymatic activities across our WT sites could help to further elucidate this process [*Kang et al.*, 2009]. We propose that WT drawdown stimulates phenol oxidase resulting in increased phenolic compounds [*Toberman et al.*, 2008], whereas phenolic accumulation in inundated peatlands is related to residence time and increased leaching of plant material.

The raised WT site also has a higher percentage of HMW compounds as indicated by the lower pore water E2:E3 ratio compared to the intermediate site. Interestingly, algae are known to release HMW compounds upon senescence [*Reddy and Delaune*, 2008] and leachates from algae have a lower E2:E3 value (~ 3) corresponding to a higher molecular size [*Cuassolo et al.*, 2011]. Additionally, complex HMW compounds leached from vegetation litter in a reduced environment can accumulate in pore water [*Reddy and Delaune*, 2008].

Lastly, we suggest that DOC compound size relative to reactivity needs to be interpreted with caution. Decomposition of DOC has been suggested to follow a size reactivity model based on four classes of molecules: labile, semilabile, recalcitrant, and refractory [*Sinsabaugh and Forman*, 2003]. The refractory class of this model is composed predominately of low molecular weight (LMW) compounds termed stable diagenetic products, which are no longer energetically favorable to microbial utilization and can accumulate in highly humified systems. Additionally, *Amon and Benner* [1996] suggested that age of DOM material is a better indicator of bioreactivity and liability than molecular weight. Applying the size reactivity model to our E2:E3 ratios explains the significant increase observed for all three WT sites in the 75 cm piezometers compared to the 25 cm piezometers, indicating an accumulation of refractory LMW compounds with depth in the pore water (Figure 5b).

5. Conclusions

Pore water DOC concentrations increased with impoundment and WT drawdown compared to an unaltered intermediate site following ~ 55 years of hydrological alterations in a poor fen peatland. We propose that the measured differences in DOC are primarily the result of altered WT positions within the peatland complex and not solely representing prelevee site level characteristics. Aerial photographs taken before and after levee construction illustrate that the levee caused extensive ponding on the up-gradient side with concurrent drying and tree established leeward of the levee.

Additionally, we believe that the original peatland complex that encompasses our sites was partitioned by the levee into three areas with similar poor fen vegetation communities. Although a full paleoecology investigation of our sites was outside the scope of this project, preliminary macrofossil analysis of peat cores from across the WT sites revealed similar historical vegetation successional processes (J. A. Hribljan and R. A. Chimner, unpublished paleoecological data, 2009). All three WT locations transitioned from a *Carex* dominated peatland to the current *Sphagnum*-dominated poor fen peatland at a similar depth horizon in the peat column (~ 70 cm below the lawn surface). Furthermore, of the total understory plant species currently present across the peatland complex, the intermediate WT site contained 89%, the raised 78%, and the lowered 78% of the 18 surveyed species. Moreover, the slight shifting of understory vegetation structure that was measured in the raised and lowered WT sites is in accord with documented plant successional trajectories in response to WT disturbance [*Hribljan*, 2012]. The greatest change in vegetation structure occurred at plot F, which experienced extensive tree encroachment after the levee induced WT drawdown. However, it is important to note that plot E was also impacted by the WT drawdown and did not experience significant tree establishment but is displaying similar elevated concentrations of DOC as plot F. Additionally, plots E and F as presented have significantly greater DOC concentrations than plot A that was treed before the levee was constructed. Therefore, taking into consideration the described site level characteristics across the greater peatland, the WT manipulations represent a comparable natural experiment demonstrating that a poor fen peatland impacted by changes in WT position will experience alterations to abiotic and biotic processes that have significant implications for peatland DOC dynamics.

The greater DOC concentrations in the lowered site are apparently driven by increased oxic conditions accelerating the decomposition and flushing of C compounds into the pore water. The aerobic conditions at the lowered site are coupled with a longer residence time reducing pore water flushing from the peatland and potentially contributing to DOC accumulation. Additionally, drawdown has increased DOC aromaticity and reduced substrate lability in the near-surface pore water, which is most likely resulting from the accumulation of refractory DOC compounds. The raised WT site displayed an unexpected greater pore water residence time, D_b, and DOC concentrations than the intermediate site. However, a possible explanation of the elevated DOC concentrations in the raised WT site is an increased photic zone, which is potentially supporting algae photosynthate production enhancing DOC release into the water column. Together, these factors have potentially created DOC that has a low aromaticity and high lability concurrent with long-term impoundment.

Based on our findings, long-term changes in peatland WT can have a significant effect on pore water DOC concentrations and chemical characteristics. Moreover, these data suggest that WT position alone is not a reliable predictor of DOC concentrations in northern peatlands. Pore water chemistry and transport is controlled by a complex relationship between physical and biological conditions within this poor fen peatland.

Acknowledgments
The authors thank Arielle Garrett, Elizabeth Boisvert, Chris Johnson, and Drew Ballantyne for help with site construction. We thank Arielle Garrett and Jim Bess for field assistance and Jennifer Eikenberry, Arielle Garrett, and Justina Silva for laboratory assistance and Merritt Turetsky for intellectual input on the study design. This research was supported by the U.S. Department of Energy's Office of Science (BER) through the Midwestern Regional Center of the National Institute for Climatic Change Research at Michigan Technological University. Additional support was provided by the Ecosystem Science Center at Michigan Technological University and the United States Forest Service Northern Research Station. Molly A. Cavaleri provided valuable comments on an earlier version of this manuscript. The project would not have been possible without the generous support of the Seney National Wildlife Refuge, in particular, R. Gregory Corace, III and Dave Olson, providing technical assistance and access to the research site.

References

Ågren, A., I. Buffam, M. Jansson, and H. Laudon (2007), Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export, *J. Geophys. Res.*, *112*, G03003, doi:10.1029/2006JG000381.

Amon, R. M. W., and R. Benner (1996), Bacterial utilization of different size classes of dissolved organic matter, *Limnol. Oceanogr.*, *41*(1), 41–51, doi:10.4319/lo.1996.41.1.0041.

Anderson, N., and C. A. Stedmon (2007), The effect of evapoconcentration on dissolved organic carbon concentration and quality in lakes of SW Greenland, *Freshwater Biol.*, *52*(2), 280–289, doi:10.1111/j.1365-2427.2006.01688.x.

Arbogast, A. F., A. G. Wintle, and S. C. Packman (2002), Widespread middle Holocene dune formation in the eastern Upper Peninsula of Michigan and the relationship to climate and outlet-controlled lake level, *Geology*, *30*(1), 55–58, doi:10.1130/0091-7613(2002)030<0055:WMHDFI>2.0.CO;2.

Ballantyne, D. M., J. A. Hribljan, T. G. Pypker, and R. A. Chimner (2013), Long-term water table manipulations alter peatland gaseous carbon fluxes in Northern Michigan, *Wetlands Ecol. Manage.*, *22*, 35–47, doi:10.1007/s11273-013-9320-8.

Bano, N., M. A. Moran, and R. E. Hodson (1998), Photochemical formation of labile organic matter from two components of dissolved organic carbon in a freshwater wetland, *Aquat. Microb. Ecol.*, *16*(1), 95–102, doi:10.3354/ame016095.

Barber, L. B., J. A. Leenheer, T. I. Noyes, and E. A. Stiles (2001), Nature and transformation of dissolved organic matter in treatment wetlands, *Environ. Sci. Technol.*, *35*(24), 4805–4816, doi:10.1021/es010518i.

Beckwith, C. W., and A. J. Baird (2001), Effect of biogenic gas bubbles on water flow through poorly decomposed blanket peat, *Water Resour. Res.*, *37*(3), 551–558, doi:10.1029/2000WR900303.

Beer, J., K. Lee, M. Whiticar, and C. Blodau (2008), Geochemical controls on anaerobic organic matter decomposition in a northern peatland, *Limnol. Oceanogr.*, *53*(4), 1393–1407, doi:10.4319/lo.2008.53.4.1393.

Billett, M., S. Palmer, D. Hope, C. Deacon, R. Storeton-West, K. Hargreaves, C. Flechard, and D. Fowler (2004), Linking land-atmosphere-stream carbon fluxes in a lowland peatland system, *Global Biogeochem. Cycles*, *18*, GB1024, doi:10.1029/2003GB002058.

Billett, M., D. Charman, J. Clark, C. Evans, M. Evans, N. Ostle, F. Worrall, A. Burden, K. Dinsmore, and T. Jones (2010), Carbon balance of UK peatlands: Current state of knowledge and future research challenges, *Clim. Res.*, *45*(1), 13–29, doi:10.3354/cr00903.

Blodau, C., and T. R. Moore (2003), Experimental response of peatland carbon dynamics to a water table fluctuation, *Aquat. Sci. Res. Across Boundaries*, *65*(1), 47–62, doi:10.1007/s000270300004.

Blodau, C., and M. Siems (2012), Drainage-induced forest growth alters belowground carbon biogeochemistry in the Mer Bleue bog, Canada, *Biogeochemistry*, *107*(1–3), 107–123, doi:10.1007/s10533-010-9535-1.

Blodau, C., N. Basiliko, and T. R. Moore (2004), Carbon turnover in peatland mesocosms exposed to different water table levels, *Biogeochemistry*, *67*(3), 331–351, doi:10.1023/B:BIOG.0000015788.30164.e2.

Brock, T. D., and J. Clyne (1984), Significance of algal excretory products for growth of epilimnetic bacteria, *Appl. Environ. Microb.*, *47*(4), 731–734.

Chanton, J. P., J. E. Bauer, P. A. Glaser, D. I. Siegel, C. A. Kelley, S. C. Tyler, E. H. Romanowicz, and A. Lazrus (1995), Radiocarbon evidence for the substrates supporting methane formation within northern Minnesota peatlands, *Geochim. Cosmochim. Acta*, *59*(17), 3663–3668, doi:10.1016/0016-7037(95)00240-Z.

Chen, M. Y., Y. Z. Chang, F. J. Lu, and J. L. Chen (2010), Capillary electrophoretic determination of selected phenolic compounds in humic substances of well waters and fertilizers, *Anal. Sci.*, *26*(5), 561–567, doi:10.2116/analsci.26.561.

Chow, T., H. Rees, I. Ghanem, and R. Cormier (1992), Compactibility of cultivated *Sphagnum* peat material and its influence on hydrologic characteristics, *Soil Sci.*, *153*(4), 300–306, doi:10.1097/00010694-199204000-00006.

Chow, A. T., K. K. Tanji, S. Gao, and R. A. Dahlgren (2006), Temperature, water content and wet-dry cycle effects on DOC production and carbon mineralization in agricultural peat soils, *Soil Biol. Biochem.*, *38*(3), 477–488, doi:10.1016/j.soilbio.2005.06.005.

Clark, J. M., D. Ashley, M. Wagner, P. Chapman, S. Lane, C. Evans, and A. L. Heathwaite (2009), Increased temperature sensitivity of net DOC production from ombrotrophic peat due to water table draw-down, *Global Change Biol.*, *15*(4), 794–807, doi:10.1111/j.1365-2486.2008.01683.x.

Clark, J., S. Bottrell, C. Evans, D. Monteith, R. Bartlett, R. Rose, R. Newton, and P. Chapman (2010), The importance of the relationship between scale and process in understanding long-term DOC dynamics, *Sci. Total Environ.*, *408*(13), 2768–2775, doi:10.1016/j.scitotenv.2010.02.046.

Clark, J. M., A. Heinemeyer, P. Martin, and S. H. Bottrell (2012), Processes controlling DOC in pore water during simulated drought cycles in six different UK peats, *Biogeochemistry*, *109*(1–3), 253–270.

Cornel, P. K., R. S. Summers, and P. V. Roberts (1986), Diffusion of humic acid in dilute aqueous solution, *J. Colloid Interface Sci.*, *110*(1), 149–164, doi:10.1016/0021-9797(86)90364-4.

Crum, H. A., and S. Planisek (1988), *A Focus on Peatlands and Peat Mosses*, edited by M. Douglas, Univ. of Michigan Press, Ann Arbor, Michigan.

Cuassolo, F., M. B. Navarro, E. Balseiro, and B. Modenutti (2011), Leachates and elemental ratios of macrophytes and benthic algae of an Andean high altitude wetland, *J. Limnol.*, *70*(2), 168–176, doi:10.3274/JL11-70-2-02.

Evans, C., D. Monteith, and D. Cooper (2005), Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts, *Environ. Pollut.*, *137*(1), 55–71, doi:10.1016/j.envpol.2004.12.031.

Evans, C. D., P. J. Chapman, J. M. Clark, D. T. Monteith, and M. S. Cresser (2006), Alternative explanations for rising dissolved organic carbon export from organic soils, *Global Change Biol.*, *12*(11), 2044–2053, doi:10.1111/j.1365-2486.2006.01241.x.

Fellman, J. B., D. V. D'Amore, E. Hood, and R. D. Boone (2008), Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska, *Biogeochemistry*, *88*(2), 169–184, doi:10.1007/s10533-008-9203-x.

Fenner, N., and C. Freeman (2011), Drought-induced carbon loss in peatlands, *Nat. Geosci.*, *4*(12), 895–900, doi:10.1038/NGEO1323.

Fenner, N., R. Williams, H. Toberman, S. Hughes, B. Reynolds, and C. Freeman (2011), Decomposition 'hotspots' in a rewetted peatland: Implications for water quality and carbon cycling, *Hydrobiologia*, *674*(1), 51–66, doi:10.1007/s10750-011-0733-1.

Fetter, C. W. (1994), *Applied Hydrogeology*, Prentice Hall, Upper Saddle River, N. J.

Finér, L., and J. Laine (1998), Root dynamics at drained peatland sites of different fertility in southern Finland, *Plant Soil*, *201*(1), 27–36.

Fraser, C., N. Roulet, and T. Moore (2001), Hydrology and dissolved organic carbon biogeochemistry in an ombrotrophic bog, *Hydrol. Process.*, *15*(16), 3151–3166, doi:10.1002/hyp.322.

Freeman, C., M. Lock, and B. Reynolds (1993), Climatic change and the release of immobilized nutrients from Welsh riparian wetland soils, *Ecol. Eng.*, *2*(4), 367–373, doi:10.1016/0925-8574(93)90004-Y.

Freeman, C., G. Liska, N. Ostle, M. Lock, B. Reynolds, and J. Hudson (1996), Microbial activity and enzymic decomposition processes following peatland water table drawdown, *Plant Soil*, *180*(1), 121–127, doi:10.1007/BF00015418.

Freeman, C., C. Evans, D. Monteith, B. Reynolds, and N. Fenner (2001), Export of organic carbon from peat soils, *Nature*, *412*(6849), 785, doi:10.1038/35090628.

Freeman, C., N. Fenner, N. Ostle, H. Kang, D. Dowrick, B. Reynolds, M. Lock, D. Sleep, S. Hughes, and J. Hudson (2004), Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels, *Nature*, *430*(6996), 195–198, doi:10.1038/nature02707.

Frey, K. E., and L. C. Smith (2005), Amplified carbon release from vast West Siberian peatlands by 2100, *Geophys. Res. Lett*, *32*, L09401, doi:10.1029/2004GL022025.

Fröberg, M., K. Hansson, D. B. Kleja, and G. Alavi (2011), Dissolved organic carbon and nitrogen leaching from Scots pine, Norway spruce and silver birch stands in southern Sweden, *For. Ecol. Manage.*, *262*(9), 1742–1747, doi:10.1016/j.foreco.2011.07.033.

Gorham, E. (1991), Northern peatlands: Role in the carbon cycle and probable responses to climatic warming, *Ecol. Appl.*, *1*(2), 182–195, doi:10.2307/1941811.

Harrison, A. F., K. Taylor, A. Scott, J. Poskitt, D. Benham, J. Grace, J. Chaplow, and P. Rowland (2008), Potential effects of climate change on DOC release from three different soil types on the Northern Pennines UK: Examination using field manipulation experiments, *Global Change Biol.*, *14*(3), 687–702, doi:10.1111/j.1365-2486.2007.01504.x.

Heinselman, M. (1965), String bogs and other patterned organic terrain near Seney, Upper Michigan, *Ecology*, *46*(1/2), 185–188, doi:10.2307/1935270.

Holl, B. S., S. Fiedler, H. F. Jungkunst, K. Kalbitz, A. Freibauer, M. Drosler, and K. Stahr (2009), Characteristics of dissolved organic matter following 20 years of peatland restoration, *Sci.Total Environ.*, *408*(1), 78–83, doi:10.1016/j.scitotenv.2009.08.046.

Hribljan, J. A. (2012), The effect of long-term water table manipulations on vegetation, pore water, substrate quality, and carbon cycling in a Northern poor fen peatland, PhD dissertation, School of Forest Resources and Environmental Science, Houghton, Michigan, U.S.A.

Hvorslev, M. J. (1951), Time lag and soil permeability in ground-water observations, DTIC Document.

Johnston, C. A., B. L. Bedford, M. Bourdaghs, T. Brown, C. Frieswyk, M. Tulbure, and J. B. Zedler (2007), Plant species indicators of physical environment in Great Lakes coastal wetlands, *J. Great Lakes Res.*, *33*(sp3), 106–124, doi:10.3394/0380-1330(2007)33[106:PSIOPE]2.0.CO;2.

Kalbitz, K., J. Schmerwitz, D. Schwesig, and E. Matzner (2003), Biodegradation of soil-derived dissolved organic matter as related to its properties, *Geoderma*, *113*(3), 273–291, doi:10.1016/S0016-7061(02)00365-8.

Kane, E. S., M. R. Turetsky, J. W. Harden, A. D. McGuire, and J. M. Waddington (2010), Seasonal ice and hydrologic controls on dissolved organic carbon and nitrogen concentrations in a boreal-rich fen, *J. Geophys. Res.*, *115*, G04012, doi:10.1029/2010JG001366.

Kang, H., C. Freeman, and T. W. Ashendon (2001), Effects of elevated CO_2 on fen peat biogeochemistry, *Sci. Total Environ.*, *279*(1), 45–50.

Kang, H., S. H. Lee, S. M. Lee, and S. Jung (2009), Positive relationships between phenol oxidase activity and extractable phenolics in estuarine soils, *Chem. Ecol.*, *25*, 99–106, doi:10.1080/02757540902758743.

Kellner, E., J. Waddington, and J. Price (2005), Dynamics of biogenic gas bubbles in peat: Potential effects on water storage and peat deformation, *Water Resour. Res.*, *41*, W08417, doi:10.1029/2004WR003732.

Klemenčič, A. K., N. Smolar-Žvanut, D. Istenič, and T. Griessler-Bulc (2010), Algal community patterns in Slovenian bogs along environmental gradients, *Biologia*, *65*(3), 422–437, doi:10.2478/s11756-010-0033-7.

Kling, G. W., G. W. Kipphut, and M. C. Miller (1991), Arctic lakes and streams as gas conduits to the atmosphere: Implications for tundra carbon budgets, *Science*, *251*(4991), 298–301, doi:10.1126/science.251.4991.298.

Klug, J. L. (2005), Bacterial response to dissolved organic matter affects resource availability for algae, *Can. J. Fish. Aquat. Sci.*, *62*(2), 472–481, doi:10.1139/F04-229.

Knauer, K., and J. Buffle (2001), Adsorption of fulvic acid on algal surfaces and its effect on carbon uptake, *J. Phycol.*, *37*(1), 47–51, doi:10.1046/j.1529-8817.2001.037001047.x.

Knorr, K. H., and C. Blodau (2009), Impact of experimental drought and rewetting on redox transformations and methanogenesis in mesocosms of a northern fen soil, *Soil Biol. Biochem.*, *41*(6), 1187–1198, doi:10.1016/j.soilbio.2009.02.030.

Koehler, A. K., K. Murphy, G. Kiely, and M. Sottocornola (2009), Seasonal variation of DOC concentration and annual loss of DOC from an Atlantic blanket bog in South Western Ireland, *Biogeochemistry*, *95*(2–3), 231–242, doi:10.1007/s10533-009-9333-9.

Kowalski, K. P., and D. A. Wilcox (2003), Differences in sedge fen vegetation upstream and downstream from a managed impoundment, *Am. Midl. Nat.*, *150*(2), 199–220, doi:10.1674/0003-0031(2003)150[0199:DISFVU]2.0.CO;2.

Kozlowski, T. T. (1997), Responses of woody plants to flooding and salinity, *Tree Physiol. Monogr.*, *1*(1), 1–29.

Krist, F. J., and D. P. Lusch (2004), Glacial history of Michigan, U.S.A.: A regional perspective, *Dev. Quat. Sci.*, *2*(B), 111–117, doi:10.1016/S1571-0866(04)80191-X.

Laiho, R., H. Vasander, T. Penttilä, and J. Laine (2003), Dynamics of plant-mediated organic matter and nutrient cycling following water-level drawdown in boreal peatlands, *Global Biogeochem. Cycles*, *17*(2), 1053, doi:10.1029/2002GB002015.

Lewis, C., J. Albertson, X. Xu, and G. Kiely (2011), Spatial variability of hydraulic conductivity and bulk density along a blanket peatland hillslope, *Hydrol. Processes*, *26*(10), 1527–1537.

Limpens, J., F. Berendse, C. Blodau, J. G. Canadell, C. Freeman, J. Holden, N. Roulet, H. Rydin, and G. Schaepman-Strub (2008), Peatlands and the carbon cycle: From local processes to global implications–A synthesis, *Biogeosciences*, *5*(5), 1475–1491.

Littell, R. C., G. A. Milliken, W. W. Stroup, R. D. Wolfinger, and O. Schabenberger (2006), *SAS for Mixed Models*, SAS Institute Inc., Cary, N. C.

Lou, T., and H. Xie (2006), Photochemical alteration of the molecular weight of dissolved organic matter, *Chemosphere*, *65*(11), 2333–2342, doi:10.1016/j.chemosphere.2006.05.001.

Malinsky-Rushansky, N. Z., and C. Legrand (1996), Excretion of dissolved organic carbon by phytoplankton of different sizes and subsequent bacterial uptake, *Mar. Ecol. Prog. Ser.*, *132*(1–3), 249–255, doi:10.3354/meps132249.

Mash, H., P. K. Westerhoff, L. A. Baker, R. A. Nieman, and M. L. Nguyen (2004), Dissolved organic matter in Arizona reservoirs: Assessment of carbonaceous sources, *Org. Geochem.*, *35*(7), 831–843, doi:10.1016/j.orggeochem.2004.03.002.

McKnight, D. M., E. D. Andrews, S. A. Spulding, and G. R. Aiken (1994), Aquatic fulvic acids in algal-rich Antarctic ponds, *Limnol. Oceanogr.*, *39*(8), 1972–1979.

McKnight, D. M., E. W. Boyer, P. K. Westerhoff, P. T. Doran, T. Kulbe, and D. T. Andersen (2001), Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity, *Limnol. Oceanogr.*, *46*(1), 38–48, doi.10.4319/lo.2001.46.1.0038.

McLatchey, G. P., and K. Reddy (1998), Regulation of organic matter decomposition and nutrient release in a wetland soil, *J. Environ. Qual.*, *27*(5), 1268–1274, doi:10.2134/jeq1998.00472425002700050036x.

Minkkinen, K., and J. Laine (1998), Effect of forest drainage on the peat bulk density of pine mires in Finland, *Can. J. For. Res.*, *28*(2), 178–186.

Minkkinen, K., R. Korhonen, I. Savolainen, and J. Laine (2002), Carbon balance and radiative forcing of Finnish peatlands 1900–2100–The impact of forestry drainage, *Global Change Biol.*, *8*(8), 785–799, doi:10.1046/j.1365-2486.2002.00504.x.

Moore, P. D. (2002), The future of cool temperate bogs, *Environ. Conserv.*, *29*(1), 3–20, doi:10.1017/S0376892902000024.

Moore, T., and M. Dalva (2001), Some controls on the release of dissolved organic carbon by plant tissues and soils, *Soil Sci.*, *166*(1), 38–47, doi:10.1097/00010694-200101000-00007.

Moore, T., N. Roulet, and J. Waddington (1998), Uncertainty in predicting the effect of climatic change on the carbon cycling of Canadian peatlands, *Clim. Change*, *40*(2), 229–245, doi:10.1023/A:1005408719297.

Nilsson, M., J. Sagerfors, I. Buffam, H. Laudon, T. Eriksson, A. Grelle, L. Klemedtsson, P. Weslien, and A. Lindroth (2008), Contemporary carbon accumulation in a boreal oligotrophic minerogenic mire—A significant sink after accounting for all C-fluxes, *Global Change Biol.*, *14*(10), 2317–2332, doi:10.1111/j.1365-2486.2008.01654.x.

Olefeldt, D., and N. T. Roulet (2012), Effects of permafrost and hydrology on the composition and transport of dissolved organic carbon in a subarctic peatland complex, *J. Geophys. Res.*, *117*, G01005, doi:10.1029/2011JG001819.

Pastor, J., J. Solin, S. D. Bridgham, K. Updegraff, C. Harth, P. Weishampel, and B. Dewey (2003), Global warming and the export of dissolved organic carbon from boreal peatlands, *Oikos*, *100*(2), 380–386, doi:10.1034/j.1600-0706.2003.11774.x.

Preston, M. D., M. C. Eimers, and S. A. Watmough (2011), Effect of moisture and temperature variation on DOC release from a peatland: Conflicting results from laboratory, field and historical data analysis, *Sci. Total Environ.*, *409*(7), 1235–1242, doi:10.1016/j.scitotenv.2010.12.027.

Price, J. S. (2003), Role and character of seasonal peat soil deformation on the hydrology of undisturbed and cutover peatlands, *Water Resour. Res.*, *39*(9), 1241, doi:10.1029/2002WR001302.

Quinn, J. M., M. Eriksson, J. L. Moseley, and S. Merchant (2002), Oxygen deficiency responsive gene expression in *Chlamydomonas reinhardtii* through a copper-sensing signal transduction pathway, *Plant Physiol.*, *128*(2), 463–471, doi:10.1104/pp.010694.

Reddy, K. R., and R. D. DeLaune (2008), *Biogeochemistry of Wetlands: Science and Applications*, CRC Press, Taylor and Francis Group, Boca Raton, Fla.

Reeve, A., D. Siegel, and P. Glaser (2000), Simulating vertical flow in large peatlands, *J. Hydrol.*, *227*(1–4), 207–217, doi:10.1016/S0022-1694(99)00183-3.

Romanowicz, E. A., D. I. Siegel, J. P. Chanton, and P. H. Glaser (1995), Temporal variations in dissolved methane deep in the Lake Agassiz peatlands, Minnesota, *Global Biogeochem. Cycles*, *9*(2), 197–212, doi:10.1029/95GB00634.

Roulet, N., and T. R. Moore (2006), Environmental chemistry: Browning the waters, *Nature*, *444*(7117), 283–284, doi:10.1038/444283a.

Roulet, N., T. Moore, J. Bubier, and P. Lafleur (1992), Northern fens: Methane flux and climatic change, *Tellus B*, *44*(2), 100–105, doi:10.1034/j.1600-0889.1992.t01-1-00002.x.

Roulet, N. T. (2000), Peatlands, carbon storage, greenhouse gases, and the Kyoto Protocol: Prospects and significance for Canada, *Wetlands*, *20*(4), 605–615, doi:10.1672/0277-5212(2000)020[0605:PCSGGA]2.0.CO;2.

Roulet, N. T., P. M. Lafleur, P. J. H. Richard, T. R. Moore, E. R. Humphreys, and J. Bubier (2007), Contemporary carbon balance and late Holocene carbon accumulation in a northern peatland, *Global Change Biol.*, *13*(2), 397–411, doi:10.1111/j.1365-2486.2006.01292.x.

Sachse, A., R. Henrion, J. Gelbrecht, and C. Steinberg (2005), Classification of dissolved organic carbon (DOC) in river systems: Influence of catchment characteristics and autochthonous processes, *Org. Geochem.*, *36*(6), 923–935, doi:10.1016/j.orggeochem.2004.12.008.

Sanderman, J., J. A. Baldock, and R. Amundson (2008), Dissolved organic carbon chemistry and dynamics in contrasting forest and grassland soils, *Biogeochemistry*, *89*(2), 181–198, doi:10.1007/s10533-008-9211-x.

Schiff, S., R. Aravena, E. Mewhinney, R. Elgood, B. Warner, P. Dillon, and S. Trumbore (1998), Precambrian shield wetlands: Hydrologic control of the sources and export of dissolved organic matter, *Clim. Change*, *40*(2), 167–188, doi:10.1023/A:1005496331593.

Sebestyen, S., E. S. Verry, and K. N. Brooks (2011), Hydrological responses to changes in forest cover on uplands and peatlands, in *Peatland Biogeochemistry and Watershed Hydrology at the Marcell Experimental Forest*, edited by R. Kolka et al., pp. 401–432, CRC Press, N. Y., U.S.A.

Siegel, D., A. Reeve, P. Glaser, and E. Romanowicz (1995), Climate-driven flushing of pore water in peatlands, *Nature*, *374*(6522), 531–533, doi:10.1038/374531a0.

Sinsabaugh, S. E., and C. M. Forman (2003), Integrating dissolved organic matter metabolism and microbial diversity: An overview of conceptual models, in *Aquatic Ecosystems: Interactivity of Dissolved Organic Matter*, edited by S. E. Findlay and R. L. Sinsabaugh, pp. 426–454, Academic Press, Calif.

Sinsabaugh, R., H. Reynolds, and T. Long (2000), Rapid assay for amidohydrolase (urease) activity in environmental samples, *Soil Biol. Biochem.*, *32*(14), 2095–2097, doi:10.1016/S0038-0717(00)00102-4.

Strack, M., J. Waddington, R. Bourbonniere, E. Buckton, K. Shaw, P. Whittington, and J. Price (2008), Effect of water table drawdown on peatland dissolved organic carbon export and dynamics, *Hydrol. Processes*, *22*(17), 3373–3385, doi:10.1002/hyp.6931.

Surridge, B. W., A. J. Baird, and A. L. Heathwaite (2005), Evaluating the quality of hydraulic conductivity estimates from piezometer slug tests in peat, *Hydrol. Processes*, *19*(6), 1227–1244.

Tarnocai, C. (2006), The effect of climate change on carbon in Canadian peatlands, *Global Planet. Change*, *53*(4), 222–232, doi:10.1016/j.gloplacha.2006.03.012.

Tarnocai, C. (2009), The impact of climate change on Canadian peatlands, *Can. Water Resour. J.*, *34*(4), 453–466.

Toberman, H., C. Freeman, R. R. E. Artz, C. D. Evans, and N. Fenner (2008), Impeded drainage stimulates extracellular phenol oxidase activity in riparian peat cores, *Soil Use Manage.*, *24*(4), 357–365, doi:10.1111/j.1475-2743.2008.00174.x.

Tranvik, L. J., and M. Jansson (2002), Climate change (communication arising): Terrestrial export of organic carbon, *Nature*, *415*(6874), 861–862.

Turunen, J. (2008), Development of Finnish peatland area and carbon storage 1950–2000, *Boreal Environ. Res.*, *13*(4), 319–334.

U.S. Fish and Wildlife Service (USFWS) (2009), Seney national wildlife refuge comprehensive conservation plan, Regional Office, Fort Snelling, Minnesota.

Uyguner, C. S., and M. Bekbolet (2005), Evaluation of humic acid photocatalytic degradation by UV–vis and fluorescence spectroscopy, *Catal. Today*, *101*(3–4), 267–274, doi:10.1016/j.cattod.2005.03.011.

Vitt, D. H. (2006), Functional characteristics and indicators of boreal peatlands, in *Boreal Peatland Ecosystems*, edited by R. K. Wieder and D. H. Vitt, pp. 9–24, Springer-Verlag, Berlin Heidelberg, Germany.

Waddington, J., and N. Roulet (1997), Groundwater flow and dissolved carbon movement in a boreal peatland, *J. Hydrol.*, *191*(1–4), 122–138, doi:10.1016/S0022-1694(96)03075-2.

Waiser, M. J. (2006), Relationship between hydrological characteristics and dissolved organic carbon concentration and mass in northern prairie wetlands using a conservative tracer approach, *J. Geophys. Res.*, *111*, G02024, doi:10.1029/2005JG000088.

Wallage, Z. E., J. Holden, and A. T. McDonald (2006), Drain blocking: An effective treatment for reducing dissolved organic carbon loss and water discoloration in a drained peatland, *Sci. Total Environ.*, *367*(2–3), 811–821, doi:10.1016/j.scitotenv.2006.02.010.

Weishaar, J. L., G. R. Aiken, B. A. Bergamaschi, M. S. Fram, R. Fujii, and K. Mopper (2003), Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon, *Environ. Sci. Technol.*, *37*(20), 4702–4708, doi:10.1021/es030360x.

Whitfield, C. J., J. Aherne, J. J. Gibson, T. A. Seabert, and S. A. Watmough (2010), The controls on boreal peatland surface water chemistry in Northern Alberta, Canada, *Hydrol. Processes*, *24*(15), 2143–2155, doi:10.1002/hyp.7637.

Whittington, P. N., and J. S. Price (2006), The effects of water table draw-down (as a surrogate for climate change) on the hydrology of a fen peatland, Canada, *Hydrol. Process.*, *20*(17), 3589–3600, doi:10.1002/hyp.6376.

Wickland, K. P., J. C. Neff, and G. R. Aiken (2007), Dissolved organic carbon in Alaskan boreal forest: Sources, chemical characteristics, and biodegradability, *Ecosystems*, *10*(8), 1323–1340, doi:10.1007/s10021-007-9101-4.

Wiebe, W. J., and D. F. Smith (1977), Direct measurement of dissolved organic carbon release by phytoplankton and incorporation by microheterotrophs, *Mar. Biol.*, *42*(3), 213–223, doi:10.1007/BF00397745.

Wilcox, D. A., M. J. Sweat, M. L. Carlson, and K. P. Kowalski (2006), A water-budget approach to restoring a sedge fen affected by diking and ditching, *J. Hydrol.*, *320*(3–4), 501–517, doi:10.1016/j.jhydrol.2005.07.026.

Worrall, F., T. Burt, R. Jaeban, J. Warburton, and R. Shedden (2002), Release of dissolved organic carbon from upland peat, *Hydrol. Processes*, *16*(17), 3487–3504, doi:10.1002/hyp.1111.

Worrall, F., M. Reed, J. Warburton, and T. Burt (2003), Carbon budget for a British upland peat catchment, *Sci. Total Environ.*, *312*(1–3), 133–146, doi:10.1016/S0048-9697(03)00226-2.

Worrall, F., T. Burt, and J. Adamson (2006), Trends in drought frequency—The fate of DOC export from British peatlands, *Clim. Change*, *76*(3–4), 339–359, doi:10.1007/s10584-006-9069-7.

Worrall, F., A. Armstrong, and J. Holden (2007), Short-term impact of peat drain-blocking on water colour, dissolved organic carbon concentration, and water table depth, *J. Hydrol.*, *337*(3), 315–325.

Wyatt, K. H., M. R. Turetsky, A. R. Rober, D. Giroldo, E. S. Kane, and R. J. Stevenson (2012), Contributions of algae to GPP and DOC production in an Alaskan fen: Effects of historical water table manipulations on ecosystem responses to a natural flood, *Oecologia*, *169*(3), 821–832, doi:10.1007/s00442-011-2233-4.

Yallop, A. R., B. Clutterbuck, and J. Thacker (2010), Increases in humic dissolved organic carbon export from upland peat catchments: The role of temperature, declining sulphur deposition and changes in land management, *Clim. Res.*, *45*(1), 43–56, doi:10.3354/cr00884.

