

Influence of soil temperature and moisture on the dissolved carbon, nitrogen, and phosphorus in organic matter entering lake ecosystems

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Abstract Concentrations of terrestrially derived dissolved organic matter (DOM) have been increasing in many north temperate and boreal lakes for over two decades. The concentration of DOM in lakes is influenced by a number of environmental factors, but there is still considerable debate about how the availability of terrestrial DOM, and associated dissolved nitrogen and phosphorus, may be affected by drivers of climatic change. Using experimental and observational methods, we considered how changes in

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B. L. Bertolet University of California-Berkeley, Berkeley, CA, USA soil temperature and moisture affected the composition of carbon, nitrogen, and phosphorus entering freshwater lakes. In our experiment, organic soil cores were collected from the wetland shoreline of a darklystained seepage lake in northern Wisconsin, USA and manipulated in laboratory with temperature and moisture treatments. During the 28-day study, soil leachate was sampled and analyzed for optical properties of DOM via UV/Vis absorbance, as well as concentrations of dissolved organic carbon (DOC), total dissolved nitrogen, and total dissolved phosphorus (TDP). DOM optical properties were particularly sensitive to moisture, with drier scenarios resulting in DOM of lower molecular weight and aromaticity. Warmer temperatures led to lower DOC and TDP concentrations. To consider long-term relationships between climate and lake chemical properties, we analyzed long-term water chemistry data from two additional Wisconsin lakes from the long term ecological research (LTER) project in a cross correlation analysis with Palmer drought severity index data. Analysis of the LTER data supported our experimental results that soil moisture has a significant

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effect on the quality of DOM entering lakes and that climate may significantly affect lake chemical properties. Although unexpected in terms of DOM loading for climate change scenarios, these results are consistent with patterns of decomposition in organic soils and may be attributed to an increase in soil DOM processing.

Keywords Allochthonous carbon · Climate change · Land–water linkages · Nutrients · Riparian

Introduction

In many north temperate and boreal lakes, allochthonous dissolved organic matter (DOM) is recognized as a major driver of lake functioning (Birge and Juday 1926; Shapiro 1957; Wetzel 2003). These carbon inputs alter multiple lake ecosystem processes by reducing light availability, strengthening thermal stratification, and supporting production of aquatic consumers (Marcarelli et al. 2011; Thrane et al. 2014; Solomon et al. 2015; Tanentzap et al. 2017). Further, terrestrially derived inputs of DOM often drive lake carbon processing and mineralization. It is estimated that inland waters receive 2.9 Pg C year⁻¹ in the form of DOM (Tranvik et al. 2009) and release 34-44% of this incoming pool to the atmosphere as CO₂ (Battin et al. 2009; Buffam et al. 2011). However, these estimates are uncertain for many reasons, including variation in the export of DOM into freshwaters due to differences in climate (Marschner and Bredow 2002; Kellerman et al. 2014) and hydrology (Scott et al. 1998; Laine et al. 2014). Given the prevalence of high DOM lakes in the north temperate region (Hanson et al. 2007), understanding drivers of DOM loading is necessary for predicting ecosystem change and representing these processes in Earth systems models.

The quality and quantity of DOM entering lake ecosystems is modulated by the strength of hydrologic connection between the lake and its surrounding riparian soils (Gergel et al. 1999; Creed et al. 2008).

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For many lakes, large fractions of allochthonous DOM are derived from OM-rich riparian wetland soils, then transported down-gradient either through groundwater that intersects these wetlands, or through inundation and saturation of the riparian zone by lake water during high water periods (Dillon and Molot 1997; Schiff et al. 1998). Estimates vary, but the proportion of shoreline wetland soils is recognized as a strong predictor of the allochthonous DOM load to individual lakes, and lakes surrounded by organic soils are characteristically brown in north temperate and boreal landscapes (Gergel et al. 1999; Xenopoulos et al. 2003; Creed et al. 2008; Laudon et al. 2011). Hence, this interface zone plays a critical role in both the quality and quantity of allochthonous materials delivered to lakes, with DOM quality being especially important when considering the effects of DOM on receiving freshwaters.

The pool of DOM in lakes is amorphous and composed of a complex mix of molecules (Kellerman et al. 2014) and several metrics based on optical properties have been developed to characterize DOM structure (Green and Blough 1994; Blough and Del Vecchio 2002). For example, the DOC-specific UV absorbance at wavelength 254 nm (SUVA₂₅₄) has been shown to be positively correlated with DOM aromaticity (Weishaar et al. 2003), and the spectral slope ratio (S_R) between wavelengths 275–295 and 350-400 nm has been shown to be inversely related to apparent molecular weight (Helms et al. 2008). Together, these optical properties can be used as a proxy for the molecular composition of DOM and provide a useful means of evaluating changes in DOM quality that may be associated with changing DOM concentrations in lakes.

Concentrations of DOM in lakes have been increasing in both the north temperate and boreal regions over the last three decades (Roulet and Moore 2006; Monteith et al. 2007) and may also be driving increases in N and P to these lakes (Corman et al. 2018) as these elemental cycles are often coupled (Solomon et al. 2015). While DOC concentrations and nutrient concentrations are not always related, this relationship has been shown in boreal and arctic lakes receiving large amounts of allochthonous inputs (Seekell et al. 2015). Additionally, because N and P are often limiting to primary production in aquatic ecosystems (Elser et al. 2007), changes in the accumulation of DOM and other dissolved nutrients in soil

leachate may have a stimulatory effect on gross primary production or respiration in receiving ecosystems as has been found in a recent experimental manipulation of DOM loads to a lake (Zwart et al. 2016).

Suspected drivers of the increase concentration of DOM in lakes are still debated but include changes in climate and atmospheric deposition (Freeman et al. 2004; Evans et al. 2006). In particular, reductions in sulfate emissions and recovery of soils from acid deposition are strongly correlated with the documented increase in many cases (Evans et al. 2012; Seifert-Monson et al. 2014; Lawrence et al. 2015). The processing and fate of DOM is expected to be further altered by climate change (Evans et al. 2006) and recent studies have highlighted the importance of considering the effects of climate on DOM quality and quantity separately, as moisture and temperature can have separate effects (Jane et al. 2017). Because the composition of DOM in soil leachate has been shown to be influenced by a number of different environmental factors, an understanding of how the availability of terrestrial DOM, and associated dissolved nitrogen and phosphorus, may be affected by drivers of climatic change is still needed.

In the present study, we ask how differences in soil temperature and moisture affect the composition of soil leachate in the north temperate region in northern Wisconsin. We focus our study on understanding the consequences of increased temperature and shifts in soil moisture regime, reflecting potential climate scenarios predicted for northern Wisconsin by midcentury (WICCI 2011). First, we use soil mesocosms to determine how increases in temperature and decreases in moisture conditions influenced the concentration of carbon, nitrogen, and phosphorus accumulating in soil leachate. We predict that higher temperatures and drier conditions would produce DOM with optical properties consistent with lower aromaticity and molecular weight due to an increase in soil microbial activity and DOM processing (Marschner and Bredow 2002). We also hypothesize that these scenarios would produce higher concentrations of dissolved organic carbon (DOC), total dissolved nitrogen (TDN), and total dissolved phosphorus (TDP) (Dillon and Molot 2005; Preston et al. 2011). Second, we consider whether lake chemical properties, DOM quantity and quality and N and P concentrations, are related to drought conditions. We predict that periods of drought would be followed by a decrease in DOM aromaticity and apparent molecular weight of, as well as increases in concentrations of DOC, TDN, and TDP in lake water.

Methods

Experiment description

Site description

Dissolved organic carbon in lakes in northern Wisconsin is mostly terrestrially derived (Wilkinson et al. 2013) and longitudinal data from the long term ecological research (LTER) project makes it possible to couple our experimental work with ongoing data collection. For the mesocosms, we collected organic soil from the surrounding wetland of Jupa Lake (hereafter, "JU"; 45.94070520N, - 90.09939670W), a darkly stained seepage lake that is part of a larger study considering the consequences of browning to lake ecological properties in the Chequamegon-Nicolet National Forest (e.g., Corman et al. 2018). JU is surrounded by wetlands and has a mean pH of 4.6, mean DOC concentration of 35.3 mg L^{-1} , and mean water color of 448 Pt/Co, based on periodically sampled long-term data beginning in 1984 (Corman et al. 2018). Vegetation in the surrounding wetland consists of tamarack (*Larix laricina*) and black spruce (Picea mariana) trees, with a thick understory of moss (Sphagnum spp.) and ericaceous shrubs, such as cranberry (Vaccinium spp.) and leatherleaf (Chamaedaphne calculate). JU is representative of the abundant, small, slightly acidic, and darkly stained bog lakes that make up a large fraction of lakes in the Northern Highland Lake District in northern Wisconsin (Hanson et al. 2007). The peatland that surrounds JU is fully saturated during summer, with soil moisture replenished by frequent precipitation and shallow subsurface runoff from the upland that is ultimately routed into the lake. Mean peat depth in the region is 2.1 ± 0.2 m, with depths up to 15 m in some locations (Buffam et al. 2010). As long-term records of lake DOM optical properties are not available for JU, we used the long-term records from two other seepage lakes in the region, Trout Bog ("TB", 46.02471N, - 89.41181W) and Crystal Bog ("CB", 46.00449N,

- 89.36376W), to investigate links between climate



conditions and lake chemical properties (similar to Jane et al. 2017). Like JU, TB and CB are small, darkly stained temperate bog lakes. TB has a mean pH of 5.0 and mean DOC concentration of 19.6 mg L^{-1} , while CB has a mean pH of 5.2 and mean DOC concentration of 10.1 mg L^{-1} (Jane et al. 2017).

Experimental design

To understand the effects of soil temperature and moisture on the composition of carbon, nitrogen, and phosphorus in soil leachate, 35 organic soil cores were collected from the southeast side of the watershed where soil was accessible and disturbance to vegetation could be minimized. Cores were collected from the top 10 cm using metal soil corers with inner diameters of 5.02 cm. We attempted to minimize disturbances to soil structure, though some minor compaction may have occurred. Organic soil cores were transported on ice to the laboratory where they were stored in a 4 °C refrigerator for 2 days prior to the start of the experiment. Five soil cores were randomly selected as reference cores (R) and were leached at the start of the experiment.

Initial leachate was extracted from a set of five soil cores by placing 8 grams of homogenized soil into 200 mL of deionized water and agitating the slurry on a horizontal shaker for 2 h. After two hours, the mixture was filtered under vacuum suction through a series of progressively smaller filters to a final filtration at 0.45 μm (Whatman GF/F filter). The filtered leachate was collected in acid-washed, amber glass bottles for analysis of UV/Vis absorbance and DOC concentration, and in 60 mL acid-washed, plastic bottles for TDP and TDN determination. Samples for DOM quality and quantity analyses were stored at 4 °C, while samples for nutrient analyses were preserved with 2% concentrated ultrapure HCl.

The other 30 soil cores were randomly assigned to one of six treatments. Experimental treatments were performed in full factorial with two temperature treatments and three moisture treatments (n = 5 replicates of each treatment). Experimental treatment temperatures consisted of 25 °C (hereafter referred to as "T1") and 29 °C ("T2"), both higher than the mean June–August temperatures of northern Wisconsin soils (~ 20 °C, Martin and Bolstad 2005), but within expected ranges under future climatic change scenarios. By mid-century, summertime average

temperatures in northern Wisconsin are predicted to increase by 3-5 °C (WICCI 2011). Concurrently, soil moisture content is also projected to decrease with higher evapotranspiration rates and decreased precipitation. Thus, experimental moisture treatments ranged from dry to field saturation and were chosen to simulate a range of potential drought scenarios. Cores were weighed daily to monitor moisture levels, and, dependent on the assigned moisture treatment, deionized water was added to the soil surface to replace water loss based on mass loss. Cores assigned to the "severe drought" moisture treatment ("M1") received no water inputs. Cores assigned to the "short drought" moisture treatment ("M2") were rewet daily starting on Day 20 of the experiment, and cores assigned to the "no drought" treatment ("M3") were rewet daily to replace mass lost from initial fresh weight. Using this method, M3 cores were kept at full saturation throughout the experiment.

Experimental cores were placed in temperaturecontrolled incubators and the bottom of each core was capped to prevent aeration, but included a drain to allow for gravity flow. The top of each core was uncapped, so water was lost via evaporation from the soil surface or from drainage out the bottom of the soil core. Gravity flow was only observed in cores assigned the lower temperature and highest moisture treatments (T1M3), and was not observed in cores from any other treatment combinations. Based on mass loss, this amount was never greater than 1.5 mL per day. The experiment ran for 28 days before collection of leachate, which we deemed adequate time for differences in moisture content among the treatments based on mass loss from initial fresh weight to occur. The weight of cores assigned to the lowest moisture treatment decreased by roughly 25% from the initial fresh weight by the end of the experiment. At the end of the experiment, leachate was extracted from the soils as previously described.

Determination of DOM quality

UV/Vis absorbance of each leachate sample was measured within one week of collection. Absorbance was measured from 200 to 800 nm on a Beckman DU 800 UV/Vis Spectrophotometer using a 1 cm quartz cuvette. Measurements were taken at 1 nm increments at 1200 nm/min speed, and blank-corrected using the



mean absorbance of DI water (n = 8). Blanks were measured before analysis and after every 5th sample.

DOC-specific absorbance at 254 nm ($SUVA_{254}$) was calculated using absorbance at 254 nm and normalized by the path length and DOC concentration (Weishaar et al. 2003). The spectral slope ratio (S_R) was calculated using Naperian absorption coefficients, which were transformed from absorbance values with the following equation:

$$a = 2.303A/l \tag{1}$$

where a is the absorption coefficient (m⁻¹), A is the absorbance, and l is the path length (m) (Green and Blough 1994). Spectral slopes of the intervals 275–295 and 350–400 nm were calculated using a log-transformed linear regression of the absorption coefficients and the $S_{\rm R}$ was calculated as the ratio of the 275–295 and 350–400 nm intervals (Helms et al. 2008).

Determination of water chemistry

The concentration of DOC was measured by high temperature combustion of organic carbon to CO₂ by ultraviolet digestion using the standard UV-persulfate method on a Shimadzu TOC-L (APHA 1998). Concentrations of TDN and TDP were measured using persulfate digestion, followed by the cadmium reduction method for NO₃-N, the phenolate method for NH₄-N, and the molybdate-ascorbic acid method for PO₄-P on a Lachat Quickchem (APHA 1998). Concentrations were above the detection limits of 0.5 ppm for DOC, 3 ppb for TDP, and 21 ppb for TDN. As soil moisture conditions at the end of the experiment purposely varied across treatments, final leachate concentrations are reported as mg C g⁻¹ dry soil and mg P or N g⁻¹ dry soil, in which dry weight was measured on a separate subset of pre-leached soil cores. Thus, leachate solutions can be compared on a scale independent of soil moisture condition.

LTER data description

Records of UV/Vis absorbance, DOC concentration, TDN concentration, and TDP concentration were retrieved from the North Temperate Lakes Long-Term Ecological Research network (Lead PI NTL et al. 2010). Though data were available for more lakes and depths, we only included surface water data from

the two stained, seepage lakes at the LTER site, Trout Bog (TB) and Crystal Bog (CB). The dataset spanned from 2001 to 2014 for TB (DOC data from TB spanned 1985–2014) and 1989–2014 for CB. $SUVA_{254}$ and S_R were calculated as described above from spectral scans and DOC concentrations. To determine how each variable responded to soil moisture conditions, we retrieved the Palmer drought severity index (PDSI) of WI sites from the NOAA Center for Weather and Climate Conditions to use as a proxy of weather condition. Higher PDSI scores correspond with higher drought severity.

Statistical analyses

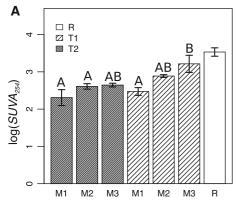
Experiment analyses

All statistical analyses were performed in R version 3.4.0 (R Core Team 2016). To understand changes in the quality of DOM leaching from the experimental and reference soil cores, $SUVA_{254}$ and S_R scores were first log-transformed to achieve normality. We first performed a t test to determine whether experimental cores significantly differenced from reference cores (at $\alpha = 0.95$). We then performed a two-way analysis of variance (ANOVA) test on the log-transformed $SUVA_{254}$ and S_R scores to determine significant differences (at $\alpha = 0.95$) across the six treatment groups. A Tukey's honest significant differences (Tukey HSD) test was then performed to differentiate differences among treatments (Tukey 1949). Similarly, to understand changes in the concentration of DOC, TDN, and TDP in the soil leachate across the treatments, we performed a two-way ANOVA and Tukey HSD test on the concentration of each logtransformed chemical specie, as described above. Finally, we performed linear correlations between logtransformed $SUVA_{254}$ and S_R scores and the concentrations of DOC, TDN, and TDP to identify relationships between quality and quantity of DOM and total dissolved nutrients in the treatment and reference leachates. Data are available at the LTER/EDI database as "CNNF Soil Experiment Data".

LTER data analyses

To determine how optical properties of DOM and concentrations of DOC, TDN, and TDP in each of the LTER lakes responded to severe drought years, we





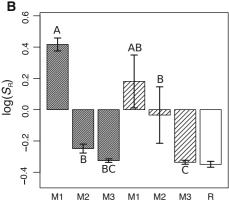


Fig. 1 Two-way analyses of variance of **a** the DOC-specific UV absorbance $(SUVA_{254})$ and **b** the spectral slope ratio (S_R) in soil core leachate to determine differences across temperature (T1: 25 °C; T2: 29 °C) and moisture (M1: dry; M2: intermediate; M3: wet) treatments in our experiment. Letters A–C are used to denote significant differences based on Tukey's Honest Significant Differences Test (p < 0.05), and data are reported in Table 1

first calculated the mean seasonal value for each variable in each lake separately. This was necessary to achieve an equal number of observations between water quality variables and PDSI. Seasons were defined by yearly quarters: winter, spring, summer, and fall. We then performed a cross correlation function (CCF) analysis in each lake, considering correlations between each water quality record and the change in PDSI between each season. We chose to consider the change in PDSI, as we sought to determine how the magnitude of a change in drought severity may affect water quality variables. Higher PDSI values correspond with higher drought severity, so a positive change in PDSI corresponds with increased drought severity in succeeding year. As

our experimental data suggested short-term changes to be significant, we considered only lags up to four time steps (i.e., one year). Data are available at the LTER/ EDI database as "CNNF DOM-Drought Correlation Data".

Results

Experimental influence of soil temperature and moisture on soil leachate composition

The composition and quality of DOM in soil leachate varied across the experimental treatments. Leachate $SUVA_{254}$ scores significantly differed between both temperature ($F_{24,1} = 8.68$, p < 0.01) and moisture ($F_{24,2} = 7.67$, p < 0.01) treatments, with warmer and drier treatments resulting in lower $SUVA_{254}$ values. In contrast leachate S_R scores only differed between moisture treatments ($F_{24,2} = 19.5$, p < 0.001). Drier moisture treatments led to significantly higher S_R values, indicating lower apparent molecular weight.

The concentration of DOC leaching from the soil was significantly influenced by temperature ($F_{24.1} = 37.28, p < 0.001$) but not moisture treatments (Table 1, Fig. 2a). Higher temperature treatments resulted in lower DOC concentrations in soil leachate (Fig. 2a). Furthermore, the DOC concentration in the highest temperature treatment (T2: 0.60 ± 1.43 mg C g⁻¹ soil) was always lower than the concentration of DOC leached from the reference cores (R: 2.56 ± 3.20 mg⁻¹ C g soil). The concentration of DOC in soils leachate was also negatively correlated with $SUVA_{254}$ scores (Table 2, Fig. 3a).

Temperature and moisture treatments had different effects on nitrogen and phosphorus concentrations. The concentration of TDN was unchanged by any treatment. The concentration of TDP was significantly influenced by temperature ($F_{24,1} = 8.03$, p < 0.001) and moisture ($F_{24,2} = 4.49$, p < 0.05) treatments (Table 1), with cores from the lower temperature (T1) and wettest condition (M3) significantly different from all other treatment conditions (Fig. 2b). Additionally, concentrations of TDP and TDN were positively correlated with each other, as well as with DOC concentration (Table 2, Fig. 4).



Fig. 2 Two-way analyses of variance of the logtransformed concentrations of a dissolved organic carbon (DOC), b total dissolved phosphorus (TDP), and c total dissolved nitrogen (TDN) to determine differences across temperature (T1: 25 °C; T2: 29 °C) and moisture (M1: dry; M2: intermediate; M3: wet) treatments in our experiment. Letters A-B are used to denote significant differences based on Tukey's honest significant differences test (p < 0.05), and data are reported in Table 1

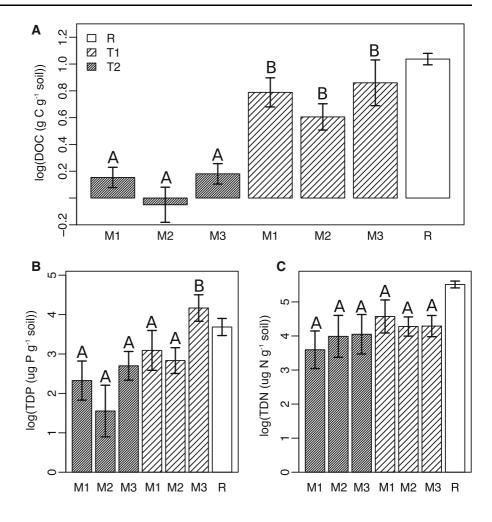


Table 1 Summary table for statistical results of two-way ANOVA test for each variable across the 6 treatments, where n = 5

Variable	Temperature tre	atments	Moisture treatments		
	$F_{24,1}$	p value	$F_{24,2}$	p value	
SUVA ₂₅₄	8.68	< 0.01	7.65	< 0.01	
S_{R}	0.02	0.89	19.5	< 0.001	
DOC (mg C g ⁻¹ soil)	48.9	< 0.001	2.06	0.15	
TDP (µg P g ⁻¹ soil)	9.61	< 0.01	3.63	< 0.05	
TDN (μg N g ⁻¹ soil)	1.58	0.22	0.01	0.98	

Data were calculated in R and the mean and standard error are represented in Figs. 1 and 2. Significant results are bolded. There was never a significant interaction between the temperature and moisture treatments

Relationship between lake chemistry and drought severity

Trends between climate and long-term water chemistry data from Crystal Bog and Trout Bog were

partially consistent with our experimental data. In CB, the seasonal change in drought severity was significantly correlated with DOM optical properties (Table 2), as well as the concentration of DOC and TDN. Particularly, seasons of severe drought were



Table 2 Cross-correlation table for linear correlations between Palmer drought severity index (PDSI) data and water chemistry variables from Crystal Bog

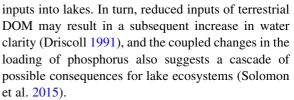
Lake	Lag	$SUVA_{254}$	$S_{\rm R}$	DOC	TDN	TDP
СВ	- 4	- 0.003	- 0.20	- 0.17	- 0.11	- 0.18
CB	- 3	0.039	- 0.19	-0.09	- 0.10	-0.08
CB	- 2	0.12	- 0.24	-0.05	- 0.19	- 0.13
CB	- 1	0.17	- 0.26	-0.07	- 0.11	- 0.02
CB	0	0.40	- 0.39	0.19	-0.02	-0.08
TB	- 4	-0.10	-0.17	0.13	0.08	- 0.15
TB	- 3	0.14	-0.06	0.06	0.11	-0.07
TB	- 2	-0.15	0.04	-0.02	-0.10	-0.05
TB	- 1	- 0.19	0.08	0.05	0.10	- 0.09
ТВ	0	0.19	- 0.05	0.006	0.03	- 0.01

Lags correspond to seasonal lags. Significant results are bolded

negatively correlated with S_R scores in CB lake (Figs. S1–S12). Conversely, TB responded differently and only $SUVA_{254}$ scores significantly correlated with the change in drought severity.

Discussion

Differences in regional temperature and precipitation have been shown to influence organic matter decomposition and the leaching of carbon, nitrogen, and phosphorus into freshwater ecosystems (Dillon and Molot 2005; Benoy et al. 2007). Our results provide insight into potential consequences of drivers of climatic change (i.e., warming and drying) for DOM and nutrient loading into north temperate seepage lakes. As we hypothesized, drier moisture conditions led to changes in DOM optical properties that are associated with lower aromaticity and lower molecular weight (Fig. 1). This finding was consistent with correlations between climatic conditions and lake DOC optical properties that were observed in longterm lake data (Table 2) and by others (Jane et al. 2017; Peczuła 2014). Higher temperatures were also associated with a significant decrease in both DOC and TDP concentrations in soil leachate (Fig. 2), and it logically follows that drying would also be associated with less runoff of water, DOC, and TDP to lakes. Together, these findings suggest that warmer, drier conditions may result in a net reduction of terrestrial



The mechanism behind the decrease in the quality and quantity of DOM in soil leachate is still uncertain, but we hypothesize that higher temperatures and lower moisture treatments may have led to an increase in microbial processing and decomposition of soil DOM. In a similar soil core experiment, Fang and Moncrieff (2001) found that higher temperatures exponentially increased soil respiration while high soil moisture contents inhibited decomposition. Soil temperature and moisture affects microbial activity and DOM processing across space as well, with the highest rates of processing occurring under high temperatures and intermediate moisture regimes (Davidson et al. 1998; Striegl et al. 2005; Moldan et al. 2012). In our experiment, higher temperatures led to significant decreases in DOC concentration and lower moisture decreased DOM aromaticity and apparent molecular weight. However, we analyzed soil leachate from the cores at the end of the experiment only, and did not evaluate the chemical properties of the water that was allowed to flow from the cores due to gravity during the 28-day period. Furthermore, gravity flow only occurred from 5 treatment cores—those that were assigned the lowest temperature and wettest moisture treatments (T1M3)—and despite drainage from these cores, T1M3 cores actually resulted in the highest mean DOC concentration in soil leachate. Thus, we suggest that our results are conservative since losses of DOC (and TDN and TDP) may have been underestimated under the lower temperature and high moisture condition.

Given these relationships between soil temperature, moisture, and respiration rates, the coupled decrease in the complexity and quantity of DOM leaching from soils may provide support for long-term trends in DOM quality and quantity in north temperate lakes. However, it is worth noting that our experiment manipulated soil temperature and moisture, while DOM leaching from organic soils is often influenced by a number of other environmental factors (Marín-Spiotta et al. 2014; Staarthof et al. 2014). For example, in near-neutral and alkaline soils, DOM solubility can be affected by redox conditions and sulfate deposition



(Lawrence et al. 2015). The transport of DOM is also often driven by lake geographic characteristics, such as landscape position and catchment area (Worrall et al. 2002).

In our experiment, we eliminated the effects of hydrology and landscape heterogeneity as cores were sampled from only one side of one watershed and placed in controlled incubators. Thus, we provide only mechanistic support of the relationship between soil temperature, moisture, and DOM leaching from organic soils. Furthermore, it is worth noting that changes in soil temperature with climate change are likely to occur over time, unlike the instantaneous increase in our experiment, and may also be associated with concurrent changes in terrestrial plant and microbial communities. Thus, the relationship between temperature and DOC concentration may be more nuanced. Based on the results of our study, DOC concentration may increase slowly over time with temperature and then eventually plateau. Conversely, DOC concentration may initially increase and then decrease once the pool of soil organic matter has been depleted. While landscape-scale prediction of DOM leaching is beyond the scope of our experimental design, our results do highlight the importance of both soil temperature and moisture as drivers of DOM in soil leachate.

Our experimental results are bolstered by long-term monitoring data, even while drivers of DOM changes in soil leachate have been shown to differ across spatial scales (Preston et al. 2011). Our cross-correlation analysis of water chemistry from two Wisconsin bog lakes and PDSI suggests that drought was a significant predictor of the concentration and quality of lake DOM in CB (Table 2). Interestingly, however, this response differed in TB. The chemical properties of CB were more related to the change in climate conditions, both current and antecedent, than the chemical properties of TB. This difference may be a reflection of the importance of other catchment variables for driving differences in lake DOM. At the whole-lake scale, shoreline vegetation composition, peatland drainage, and location of peatland can be important drivers of DOM composition in the lake (Preston et al. 2011), and differences in hydrology and landscape position between TB and CB may as explain why PDSI scores was a less important predictor in TB. TB is believed to be connected hydrologically to a neighboring drainage lake and thus, influences of peatland processes on lake DOC concentration measurements would be muted by hydrological inputs from connected waterbodies. In contrast, CB is more hydrologically-isolated and therefore DOC dynamics may be more exclusively linked to processes occurring in fringing peatlands. These results further highlight the need to incorporate knowledge about the boundary conditions (i.e., type and magnitude of groundwater exchange vs. near-surface runoff to seepage lakes) and other spatial heterogeneities in future investigations.

Previous research has also identified the importance of soil moisture in influencing the DOM quality in lakes. In another study of seven northern Wisconsin lakes based on LTER data, researchers found that drought years corresponded with a reduction in the molecular complexity of the pool of DOM entering lakes and that DOC concentrations were also variable across lakes, with a majority of lakes decreasing in DOC concentration over time (Jane et al. 2017). Similar to our results, their observed correlations of water quality variables and PDSI through time were not always consistent and were especially driven by drought years (Jane et al. 2017). Here, we extended this analysis to include antecedent conditions for each lake by using the change in PDSI. We show that the quality and quantity of DOM exhibited different responses to drought severity but these relationships may be dependent on lake characteristics. DOM loading in seepage lakes like CB and JU may be more strongly tied to localized changes in soil temperature and moisture in lake-fringing peatlands that are sources of water and solutes, while greater exchange with groundwater from an aquifer may be more influential in flow-through and drainage lakes.

Although nutrient concentrations in TB and CB were not strongly correlated with PDSI, our experimental results generated some understanding for how dissolved nutrients in soil leachate may change concomitantly with shifts in soil carbon quality and quantity. Previous research has suggested changes in lake nutrients concentrations may be associated with increased organic matter runoff to lakes (Dillon and Molot 2005; Zwart et al. 2016), and that carbon and nutrient cycles are coupled when DOM is processed in soils (Amador and Jones 1993). Our results suggest a more variable role for phosphorus than nitrogen in terms of soil leachate composition (Figs. 3b, 4a). Nitrogen, which often limits primary production in wetlands (Aerts et al. 1992; Saunders and Kalff 2001),



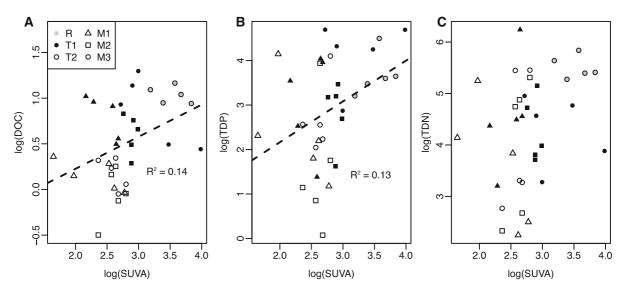


Fig. 3 Correlations between the log-transformed concentrations of **a** dissolved organic carbon (DOC), **b** total dissolved phosphorus (TDP), and **c** total dissolved nitrogen (TDN) concentration and the $SUVA_{254}$ scores in response to experimental climate treatments. Points are denoted as either reference

(R) or treatment group, which includes temperature (T1: 25 °C; T2: 29 °C) and moisture (M1: dry; M2: intermediate; M3: wet) treatments denoted in factorial. Dashed line signifies a significant correlation (p < 0.05)

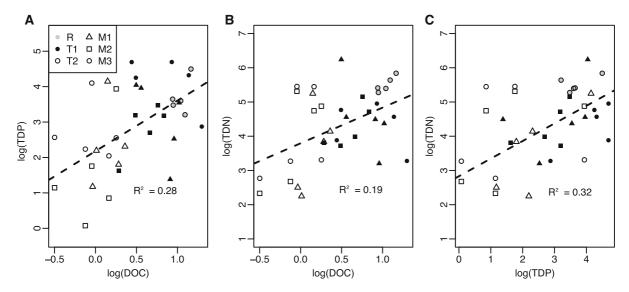


Fig. 4 Correlations between the log-transformed concentrations of a dissolved organic carbon (DOC), b total dissolved phosphorus (TDP), and c total dissolved nitrogen (TDN) concentration in response to experimental climate treatments. Points are denoted as either reference (R) or treatment group,

which includes temperature (T1: 25 °C; T2: 29 °C) and moisture (M1: dry; M2: intermediate; M3: wet) treatments denoted in factorial. Dashed line signifies a significant correlation (p < 0.05)

is quickly consumed and retained in microbial biomass (Wardle 1992). The TDN concentrations in soil leachate were also much lower in treatment cores than reference cores (Fig. 2), and the N:P ratio of the soil leachate from treatment cores (mean = $3.31 \pm$

2.59) was also lower than that of reference cores(-mean = 5.70 ± 1.23), suggesting an increase in microbial processing that could be driven by either a preferential uptake of nitrogen or an increase in denitrification. However, between experimental



treatments, TDN concentration was not significantly different.

While nitrogen may be scarce, many temperate wetlands often have low phosphorus retention efficiencies and export a large proportion of their phosphorus inputs (Richardson 1985). However, some peatlands have also been shown to be phosphorus limited (Hill et al. 2014), and these relationships have the potential to shift with the warming and drying of peatland soils. TDP concentration, which was lower in leachates exposed to warmer and drier scenarios and which was correlated with DOC concentration and DOM spectral properties, has the potential to become biologically immobilized as organic matter is consumed and mineralized under drier conditions (Dillon and Molot 2005). However, because leachate phosphorus concentrations can be affected by soil sorption properties, redox conditions, and microbial activity, further research is needed to decipher the extent of the physical, chemical, and biological controls on phosphorus immobilization and mineralization. Regardless of a mechanistic explanation, which we cannot offer, our results show increased DOM and TDP concentrations with lower soil moisture conditions.

Conclusion

Changes in soil temperature and moisture in the north temperate region may alter the quantity and quality of terrestrial inputs entering freshwater lakes. With a combination of experimental and observational data, we suggest that under drier scenarios, DOM will be less aromatic and have a lower molecular weight, with no change in DOC concentration. With warmer temperatures, however, the less aromatic and lower molecular weight DOC may be biodegradable or adsorb to mineral surfaces, resulting in a decrease in DOC concentration in soil leachate. Thus, warmer and drier (or more variable) precipitation regimes may decrease the flux of DOM from peatland soils and soil leachate may be composed of fewer high molecular weight, aromatic molecules and potentially lower concentrations of DOC and TDP. If these solutes are flushed into lakes, changes in organic matter metabolism in surrounding peatland soils may have direct consequences for the stability and function of the receiving freshwater ecosystems.

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