Lake TEA: Changing Dynamics of Terrestrially-Derived Dissolved Organic Carbon Across the Land-Water Interface in Northern Wisconsin

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ABSTRACT

Increases in terrestrially-derived dissolved organic carbon (DOC) in lakes have altered the physiochemical structure of the water column, and have raised questions regarding the role of these ecosystems in the global carbon cycle. Understanding the sources and controls of the incoming DOC is essential for predicting water chemistry and ecosystem change in the lake-rich region of northern Wisconsin. I sought to determine how changes in soil temperature and moisture may affect both the concentration and molecular form of DOC leaching from soils into lakes in northern Wisconsin. Saturated soil cores were collected from a seepage lake in the Chequamegon-Nicolet National Forest, Wisconsin, USA and manipulated in the laboratory with simulated climate treatments for 28 days (n=5). Experimental treatments were chosen to understand potential warming and drying conditions predicted under climate change. Soil core leachate was then extracted and analyzed for DOC concentration and specific UV absorbance, a function positively correlated with aromaticity. Increased temperatures led to lower leachate DOC concentrations ($F_{24,1} = 37.280$, $P < 0.05$), while both increased temperatures and drier conditions caused a preferential breakdown of aromatic compounds ($F_{24,2} = 4.693$, $P < 0.05$). These trends can potentially be attributed to an increase in microbial decomposition of soil organic matter and mineralization to CO_2. In a lake, the smaller molecules are less colored and are typically more bioavailable to microorganisms. Therefore, my results provide some evidence that warmer and drier climate conditions may offset recent lake browning trends in northern Wisconsin.

KEYWORDS

climate change, carbon cycling, freshwater biogeochemistry, ecosystem change, lake browning

INTRODUCTION

In the last two decades, streams and lakes in the north temperate and boreal regions of the world have experienced increased inputs of terrestrially-derived dissolved organic carbon (DOC) from nearby peat soils (Solomon et al. 2015). These carbon inputs have altered the physical, chemical, and biological structure of lakes by providing an energy source for the microbial food web, while also limiting light availability and strengthening the thermal stratification of the water column (Thrane et al. 2014). High concentrations of DOC, on the range of 5-10 mg/L, can decrease whole-lake primary productivity, disrupt nutrient turnover rates, and slow the in-lake processing of heavy metal contaminants (Jones and Lennon 2015; O'driscoll et al. 2004). Furthermore, increases in DOC are often accompanied by increased inputs of nutrients, phosphorus and nitrogen, into the water basin (Solomon et al. 2015). Increased additions of limiting nutrients affect primary productivity and community composition in lakes, and are important indicators of water quality and ecosystem health (Jeppesen et al. 1994). Thus, understanding the sources and controls of the incoming DOC is essential for predicting water chemistry and ecosystem change in the lake-rich region of northern Wisconsin.

Suspected drivers of the increased export of carbon from soils include changes in climate and atmospheric deposition (Freeman et al. 2004). In particular, the reductions in sulfate emissions and the recovery of soils from acid deposition are most strongly correlated with the documented increase (Evans et al. 2012; Seifert-Monson et al. 2014). Since the Clear Air Act Amendments of 1990, increases in soil pH and decreases in the exchangeable Al pool have increased the solubility of organic matter in O soil horizons and promoted the export of DOC (Lawrence et al. 2015). Decreases of soil organic matter influence the potential C sequestration of the soil, as well as nutrient availability and water holding capacity (Li et al. 2004). By documenting the increased export of DOC from soils and the impact of DOC on lakes, these land-water linkages have become an important aspect of ecosystem change.

The carbon cycle is connected across terrestrial and aquatic landscapes. Terrestrially-derived DOC originates from plant materials, is transformed by microbial respiration and mineral interactions in the soil, and is then transported into lakes through the soil by ground and surface waters (Michalzik et al. 2003). The carbon contained in the water basin is typically ignored in regional and global carbon budgets (Kindler et 2011). Although inland aquatic

ecosystems account for only 1% of the global surface, they can play a disproportionately important role in the biogeochemical cycling of carbon (Buffam et al. 2011). Lakes and streams are estimated to receive about 1.9 Pg C per year in the form of dissolved organic matter, over double what is exported to the ocean (Cole et al. 2007), and may account for 9.5%-16.5% of the carbon that is released to the atmosphere from boreal and north temperate landscapes (Benoy et al. 2007). However, these numbers are often uncertain as the scaling process over simplifies parametric controls of DOC export, such as climate, hydrology, and vegetation (cite). Additionally, much of the prior research on DOC in aquatic ecosystems does not consider the quality of DOC as a measure for understanding its role in the carbon cycle.

Terrestrially-derived DOC is amorphous and comes in a variety of molecular forms (Kellerman et al. 2014), however the biological implications of this structural diversity is still unclear. The level of recalcitrance is thought to determine its residence time both in the soil and in the water basin, as well as its potential for light attenuation (McDonald et al. 2004). Molecules of high molecular weight and a higher degree of aromaticity absorb more photosynthetically active radiation and significantly structure the water column by limiting light availability (Thrane et al. 2014). The aromaticity refers to stable planar rings of six carbon molecules, which are energetically difficult to break. DOC aromaticity is positively correlated with specific UV absorbance (sUVa), with higher values corresponding to greater aromatic character (Hautala et al. 2000). Traditionally, DOC recalcitrance has been predicted based on molecular structure alone, but recent evidence suggests that environmental conditions may largely control bioavailability (Marin-Spiotta et al. 2014).

The transport of DOC across the terrestrial-aquatic landscape is expected to be further altered with climate change, as the decomposition of soil organic matter is largely dependent on soil temperature and moisture (Moldan et al 2012). Using experimental soil mesocosms, I sought to determine how changes in soil temperature and moisture may affect both the concentration and molecular form of dissolved organic carbon (DOC) leaching from soils into lakes in northern Wisconsin. I hypothesized that different climate regimes would produce significantly different soil leachate compositions, with increased temperature and decreased moisture producing a higher DOC concentration and molecules with a lesser degree of aromaticity in the soil leachate. Increased temperatures and decreased moisture would stimulate microbial activity and result in the increased production of DOC (Preston et al. 2011).

METHODS

Site Description and Sample Collection

Soil was collected from the forested watershed of Jupa Lake (45.94070520 W, -90.09939670 N), a bog lake in the Chequamegon-Nicolet National Forest of Wisconsin, USA with an area of 0.036 kilometers² and a maximum depth of 5.3 meters. Jupa Lake is a seepage lake that has been monitored since 2013 by the US Forest Service to assess environmental change in the Chequamegon-Nicolet National Forest (Table 1). The primary vegetation 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*). Soils are fully saturated with ground water filling all soil pore space. Cores of peatland soil were collected randomly from the southeast side of the watershed. Soil cores were collected from the top 10 centimeters of the soil using metal soils corers with a 2-inch diameter. Sampling was performed as to not disrupt soil structure or aggregation, however there may have been a slight degree of compaction. The soil cores were transported on ice to the laboratory where they were stored in a 4°C refrigerator for no more than two days prior to the start of the experiment. Additional soil was collected in the same sampling regime to assess soil characteristics in the laboratory (Table 2).

Table 1. Basic geographic and physiochemical parameters of Jupa Lake. Physiochemical data, reported as mean (standard error), are based on surface pelagic water sampled collected ≥3 times per year during the ice-free season in 2013 and 2014.

Lake Characteristic	Jupa Lake
Area (km^2)	0.036
Max depth (m)	5.3
pH	4.57 (0.56)
Water Color	448.9 (34.7)
DOC ($mg\ L^{-1}$)	38.1 (3.2)
Conductivity ($\mu S\ cm^{-1}$)	22.3 (6.5)
TN ($\mu g\ L^{-1}$)	386 (148)
PO_4^{-3} ($\mu g\ L^{-1}$)	3.08 (1.3)
SO_4^{-2} ($mg\ L^{-1}$)	1.3 (0.4)
Ca^{+2} ($mg\ L^{-1}$)	2.2 (0.67)
Fe ($mg\ L^{-1}$)	1.117 (0.18)

Table 2. Basic physiochemical parameters of soil collected from the surrounding forested watershed of Jupa Lake. Physiochemical data, reported as mean (standard error), are based on samples collected on July 2nd, 2015.

Soil Characteristics	Jupa Lake Watershed
pH	4.66 (0.046)
Water Holding Capacity	67.1 (3.3)
Texture	Sandy Loam

Experimental Manipulation

To understand the effects of different climate regimes on watershed leachate potential, I performed a laboratory experiment using the sampled soil cores. Soil cores were placed in controlled incubators where temperature and moisture were manipulated. The mesocosm construction was designed to maintain field conditions as much as possible. The bottom of the cores were capped to prevent any aeration and the top of the cores were left open. The soil cores were randomly assigned to six different experimental treatments to prevent any background

variation. A separate set of five soil cores were used to characterize field conditions and act as a control. These were stored in a refrigerator at 4°C until soil leaching was performed two days after initial collection. The experimental treatments were performed in full factorial with two temperature treatments and three moisture treatments (n=5) to understand the effects of increased temperatures and decreased moisture scenarios that are predicted for the north temperate region.

The annual soil temperature of the site is extremely variable, reflecting the seasonality of the annual air temperature (cite). So experimental temperatures were chosen based on the mean soil temperature for the summer months, June through August. Previous work suggested that mean soil temperature is not significantly variable between other broad leaf forested sites in the north temperate region, so estimates from other studies in northern Wisconsin could be used (Martin and Bolstad 2005). We estimated the mean soil temperature for the summer months to be about 22°C. Experimental temperatures of 25°C and 29°C were then chosen to understand the effects of increased soil temperature.

The site has a aquic soil moisture regime, with the soil pore space saturated with water long enough to cause oxygen depletion. Soil moisture is replenished by weekly precipitation so that soil is fully saturated even during the summer months. To understand potential drying conditions under drought, soil cores were allowed to dry without addition of water inputs. The three experimental treatments are as followed. “Dry” cores received no water inputs for the duration of the experiment. “Intermediate” cores received no water inputs until Day 20 of the experiment. “Wet” cores received water inputs everyday and were kept at full saturation for the entirety of the experiment. Water inputs were executed by weighing each core everyday and returning each core to its initial fresh weight with additions of deionized water.

The experiment ran for 28 days before collection of leachate, which was deemed long enough to experience a response of microbial activity to changing environmental conditions. After 28 days, the soil was homogenized by manual mixing and large rocks and debris were removed.

Soil Leachate Extraction

To collect the soil leachate from each soil core, about 8 grams of the homogenized soil core was placed in 200 mL of deionized water and then agitated on a horizontal shaker for two

hours. After two hours, all of the soluble material had entered into solution. The pH of the soil solution was recorded using a calibrated pH probe. The mixture was then filtered under vacuum suction through series to a final filtration at 0.45 um (Whatman GF/F filter). The filtered leachate was collected in acid-washed, amber-colored glass bottles for analysis of response variables. Samples were kept in a refrigerator at 4°C until analysis.

Soil Leachate Analysis

Analysis for DOC concentration was performed by oxidation of the organic carbon in the sample to CO_2 by UV digestion using the standard UV-persulfate method (APHA, 1998). Absorbance of the filtered samples was read at 254nm and normalized by the DOC concentration to obtain specific UV absorbance (sUVa) values. To answer my research question, I performed a two-way analysis of variance (ANOVA) test in R Studio (R Development Core Team 2014) for each response variable. This determined significant differences in the mean DOC concentration and mean sUVa value between the different experimental treatments and control, and reported all significant statistics. This test determined significance of each variable, temperature and moisture, separately as well as the interaction of the two variables together. The sample populations were approximately normally distributed and the samples were independent. This provided evidence on whether or not the climate treatments affected the mean of each response variable within the experimental groups.

RESULTS

DOC Concentration

The mean leachate DOC concentration was significantly different across the temperature treatment groups ($F_{24,1} = 37.280$, $P < 0.05$), while the precipitation treatments did not significantly affect DOC concentration (Fig. 1). The high temperature treatment resulted in lower mean DOC concentration produced across all precipitation treatments, compared to that resulting from the low temperature treatment (Table 3). There is also a higher degree of variance under

warmer temperatures that is not observed under lower temperatures. There was no significant interaction of temperature and precipitation.

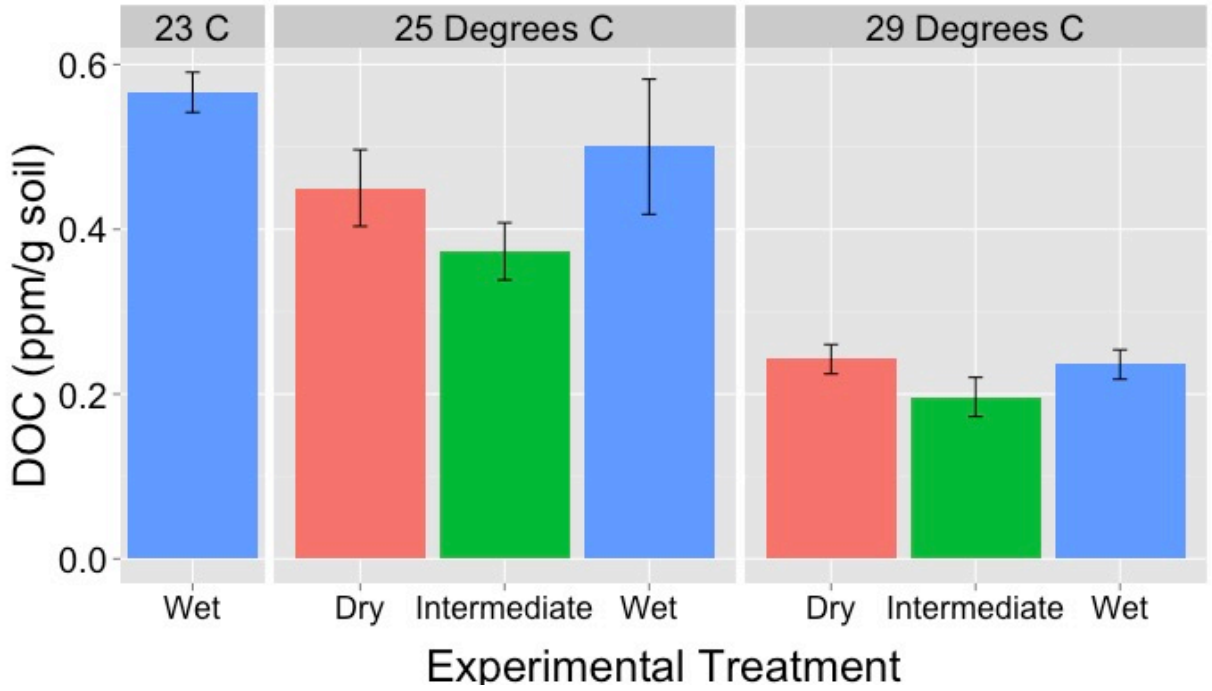

Figure 1. Dissolved organic carbon (DOC) concentration of experimental soil core leachate. Soil leachate filtered through series to a final filtration of 0.45 um. DOC concentration reported as mean with standard error.

DOC Aromaticity

The mean specific UV absorbance (sUVa) of the samples was significantly different across both temperature ($F_{24,1} = 6.356$, $P < 0.05$) and precipitation treatments ($F_{24,2} = 4.693$, $P < 0.05$). The increased temperature treatments resulted in lower mean sUVa values, indicative of a lesser degree of aromaticity (Table 4). Drier conditions also resulted in lower mean sUVa values, with the degree of variance being much larger under wetter conditions. There was no significant interaction of temperature and precipitation.

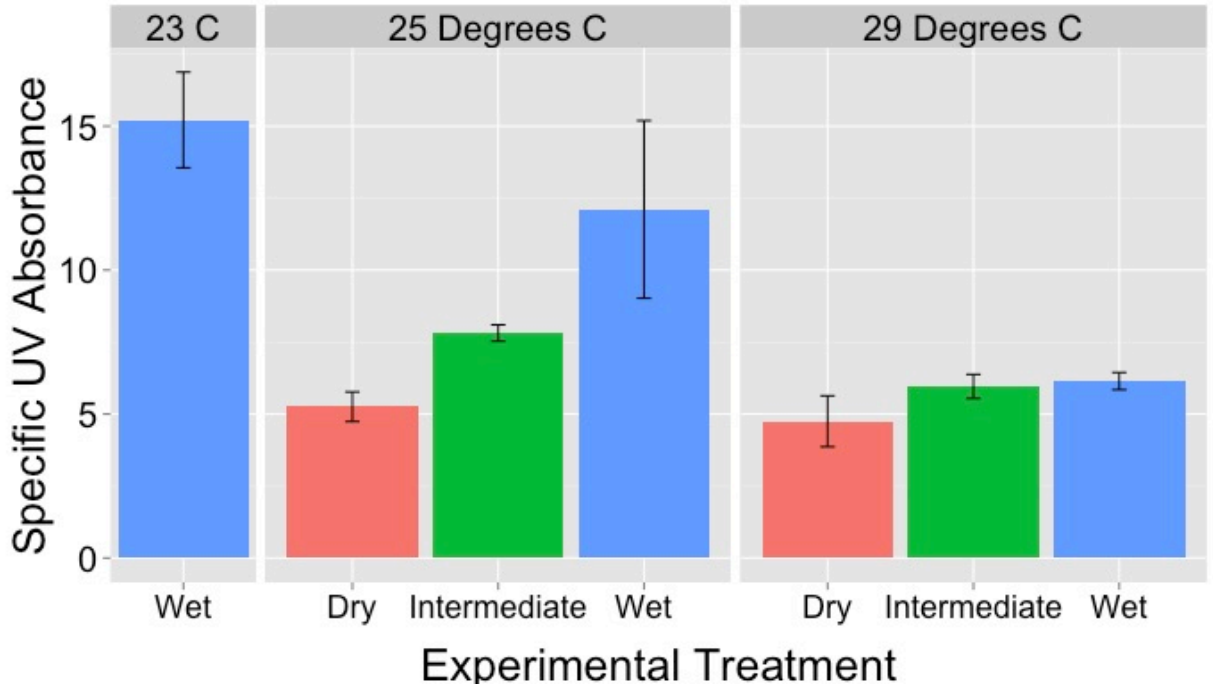

Figure 2. Specific UV absorbance of experimental core leachate. Absorbance read at 254 nm and normalized by DOC concentration. Specific UV absorbance reported as mean with standard error.

DISCUSSION

The decomposition of soil organic matter and the leaching of DOC into freshwater systems is dependent on a variety of site characteristics, not limited to soil temperature, moisture, pH, texture, and landscape position. Despite this, its predictability under climate change is very unclear. Contrary to my hypothesis, increased temperature did not increase leachate DOC concentration, but acted in the opposite direction. Increased temperatures led to a decrease in leachate DOC concentration. Simulated drought conditions had no effect on DOC concentration, but did affect molecular form. Aromaticity of DOC decreased under increased temperature and decreased moisture, as I hypothesized. My data provides some evidence that climate change may offset recent lake browning trends in the north temperate region and will be imperative for predicting ecosystem change across the landscape.

Changing DOC Concentrations in Lakes

It is well supported that increased temperature stimulates microbial activity, and most research predicts that DOC will increase with temperature (Preston et al. 2011, Tipping and Woof 1991). This is based on a traditional view that terrestrially derived DOC is very recalcitrant and a product of the incomplete mineralization of particulate organic carbon to CO_2 (Staarthof et al. 2014). Prior research from the boreal region found that increased temperatures increased the production and export of DOC, as decomposition is extremely limited in permafrost soils (Laine et al. 2014). However, my data suggests that DOC recalcitrant may be heavily influences by environmental conditions. Interpretation of my results suggest that increased temperatures stimulated heterotrophic microbial respiration and led to lower leachate DOC concentrations, as more organic carbon was fully mineralized and lost as CO_2. This result may have occurred because treatment temperatures were higher than those used in experiments in the boreal region (Scott et al. 1998). Given that interpretations from the boreal region are not directly congruent to the north temperate biome, my data suggests that warmer temperatures may offset recent browning trends in the northern Wisconsin by decreasing the amount of DOC leaching into lakes. However, the implications for ecosystem change cannot be viewed within only concentration metrics and predictions must also consider the molecular form of DOC.

Implications of Molecular Form for DOC Bioavailability

The persistence and reactivity of terrestrially derived DOM in soils and lakes is highly debated. Recent theory suggests that environmental conditions and solubility in soil solution, and not molecular form, are most important in influencing the bioavailability of DOC (Marin-Spiotta et al. 2014). The importance of environmental conditions was supported by my data, as aromaticity decreased with warmer temperatures and drier conditions, evidence for a preferential breakdown of aromatic compounds. Others have also witnessed a decline in the ratio of humic acids to total DOC over time (Staarthof et al. 2014), indicating that the availability of terrestrially derived DOC may be linked to environmental conditions. Coupled with the decreased concentration under warmer conditions, the decrease in aromaticity supports the idea that

warmer temperatures may lead to greater extent of soil organic carbon being fully mineralized before it is leached into the lakes or rivers.

Climate change in the north temperate region may then decrease the impact of DOC on freshwater lakes, because soil leachate will be composed of fewer high molecular weight, aromatic molecules. In the lake basin, DOC molecules of lower molecular weight and aromaticity absorb less photosynthetically active radiation and do not limit light availability as severely (Kohler et al. 2013). They are also typically more bioavailable to microorganisms in the water basin (Vinebrooke and Leavitt 1998). Despite the potential to reverse lake browning trends, these changes in organic matter metabolism in upland peat soils may have consequences for carbon cycling at the landscape level.

Limitations and Future Directions

Given the spatial complexity of these terrestrial-aquatic systems, the mesocosm experimentation oversimplified the importance of hydrology for the transport of DOC across the landscape. Multiple studies link precipitation, increased hydraulic flow, and low elevation position to an increase of DOC in lakes (Worrall et al. 2002). Flushing and episodic rain events may also result in different temporal patterns (Vinebrooke and Leavitt 1998), and my experimental design provided only an instantaneous measure that does not reflect temporal variation. Furthermore, although the mesocosm construction attempted to maintain the natural soil structure, there were some potential artifacts, including compression of soil pore space in the soil cores and slight aeration of the bottom layers of the soil core due to leakiness in the tubing. It is not confirmed that this affected any significant results, but a longitudinal field manipulation would provide stronger evidence and control for any artifacts.

Additionally, while the central research question focused on DOC production and leaching, this study would have greatly benefitted from data on CO_2 emissions and respiration. I infer that the decrease in DOC concentration produced under warmer conditions during experimentation was due to full mineralization to CO_2 (Staarthof et al. 2014). Data on CO_2 emissions would confirm this hypothesis.

Conclusions

Climate change in the north temperate region has the potential to greatly alter the role of lake and wetland ecosystems in the biogeochemical cycling of carbon. While trends in DOC metabolism are variable between geographic regions, my data does provide some evidence that warmer temperatures and drier scenarios could lead to a decreased export of DOC to lakes in the north temperate biome. Both warmer temperatures and drier scenarios may also decrease the ratio of high molecular weight and aromatic molecules contributing to the browning phenomenon in lakes. However, if attributing these trends to an increase in microbial decomposition of soil organic carbon, these conditions may also decrease the pool of soil organic carbon and lead to an increased export of carbon to the atmosphere in the form of CO_2. As climate change continues, it could be expected that carbon loss across the land-water interface may continue to accelerate this process.

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