Biological and Photochemical Degradation of Dissolved Organic Carbon in Peatland Ecosystems

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Abstract

Approximately one half of terrestrial carbon runoff is processed by inland waters and released into the atmosphere as carbon dioxide (CO_2) prior to reaching the oceans, and bacterial consumption of dissolved organic carbon (DOC) comprises a dominant proportion of this carbon loss. Though peatlands export more DOC per area than most other ecosystems, the sources and biodegradability of peatland DOC and their effects on downstream DOC loads and fluxes are poorly understood. Moreover, photochemical degradation plays an important role in the loss of carbon from aquatic ecosystems, especially in peatlands with high DOC concentrations rich in photochemically reactive humic and phenolic compounds, but its contribution to global CO_2 evasion from inland waters has not been quantified. This dissertation focuses on predictors of biodegradable DOC (BDOC) in aquatic ecosystems, the sources and biodegradability of DOC in peatland watersheds, and the contribution of photochemical degradation of DOC to global CO_2 evasion from peatlands and fluvial ecosystems. Key findings from these studies were that SUVA, a measurement broadly used in ecology and environmental engineering and fairly simple to obtain, is an excellent predictor of the amount of long-term BDOC concentrations in Minnesota lake ecosystems. The peatland bog may be the most important source of BDOC exported from peatlands annually, rather than the upland. And, photochemical enhancement of bacterial respiration in peatland and fluvial ecosystems contributes approximately 0.11–0.22 Pg C yr^{-1} to the total global CO_2 evasion from inland waters (~1.4 Pg C yr^{-1}), or 9–18% of all inland water CO_2 evasion. The results from this dissertation will lend insight into how future changes in hydrology and surface water DOC concentrations will alter the sources, biodegradability, and photochemical enhancement of DOC in aquatic ecosystems in the northern hemisphere, especially peatlands.

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Prologue

Dissolved organic carbon (DOC), a pool of structurally complex molecules with unknown exact chemical structure (McKnight *et al.* 2003), is the largest pool of organic carbon in freshwater ecosystems (Wetzel 2001). DOC is produced during cell lysis, grazing of algae and bacteria by zooplankton (Bertilsson and Jones 2003), aerobic and anaerobic metabolism as intermediate and end products (Schink 1988; Mattson and Likens 1993), and leaching of terrestrial plant detritus into overland flow (Aitkenhead-Peterson *et al.* 2003). DOC is lost from freshwater ecosystems through burial in sediments (Hwang *et al.* 2006, von Wachenfeldt *et al.* 2008), conversion to carbon dioxide during organismal respiration and photochemical oxidation (Hessen 1992; Gráneli 1996), and export to downstream waters.

Despite its small size and unknown structure, DOC plays an important and diverse role in aquatic ecosystems. DOC absorbs sunlight which alters the heat budget of lakes and protects organisms from harmful UV radiation. In addition, DOC participates in many biogeochemical reactions through its electron shuttling capabilities (Jiang and Kappler 2008) and controls metal speciation in aquatic ecosystems, especially iron (Miles and Brezonik 1981; Cotner and Heath 1990). But most importantly, DOC fuels food web metabolism in many temperate lakes, resulting in net heterotrophy of these systems (Cole *et al.* 1994), and is an important food and energy source for heterotrophic bacteria (Azam *et al.* 1983; Findlay *et al.* 1991).

The pool of DOC that can be consumed by bacteria (biodegradable DOC, BDOC) consists of organic matter that exists along a continuum of reactivity, including labile DOC that is degraded rapidly, semi-labile DOC that is degraded more slowly, and recalcitrant DOC that is degraded over very long time scales (Carlson 2002). Across this reactivity continuum, only a small proportion of the total DOC pool is reactive (biodegradable) and cycles on time scales of minutes to days, while the majority is resistant to organismal degradation (recalcitrant) and cycles on time scales of months to thousands of years (Søndergaard and Middelboe 1995; Hansell and Carlson 1998). DOC produced from aquatic photosynthesis and decomposition (autotrophic) tends to be comprised of low molecular weight monomers that are easily degraded by

microorganisms, while DOC produced from the leaching and decomposition of terrestrial detritus tends to be comprised of higher molecular weight, humic macromolecules that are more recalcitrant to microbial degradation (Amon and Benner 1994).

The role of biodegradable DOC has been studied extensively in marine, estuarine, fluvial, and lacustrine ecosystems (Søndergaard and Middelboe 1995; del Giorgio and Davis 2003; Stets and Cotner 2008). Previous studies have shown that BDOC is correlated with DOC concentration across a wide range of systems (Sondergaard and Middelboe 1995) and the percent of wetlands in the watershed (Stets and Cotner 2008; Morel *et al.* 2009; Pacific *et al.* 2010). However, it is still unknown how changes in the sources, production rates, and residence times of BDOC in freshwater ecosystems affect the cycling and export of DOC to downstream waters.

Another important characteristic of DOC in aquatic ecosystems is its ability to absorb sunlight and undergo photochemical reactions. Photo-exposure of DOC can result in direct oxidation to CO_2; the formation of low molecular weight, biologically labile photoproducts (Miller and Moran 1997); or alteration of its chemical structure into more recalcitrant forms (Tranvik and Bertilsson 2001). Direct photochemical losses account for up to 10% of total DOC lost as CO_2 in many freshwater ecosystems (Graneli *et al.* 1996) while photochemical enhancement of organismal respiration may increase total DOC loss by at least 1- or 2-fold (Mopper and Kieber 2005). The large losses of DOC from inland waters may be due in part to the photochemical alteration of the recalcitrant pool of DOC into forms that are more easily degradable by bacteria.

And the role of DOC in aquatic ecosystems goes beyond local biogeochemical cycles and aquatic food web functioning. Recent work has shown that freshwater ecosystems play an active role in the global carbon cycle with more than half of terrestrial carbon runoff into freshwater ecosystems buried in sediments or released into the atmosphere as carbon dioxide before reaching the ocean (Cole *et al.* 2007; Tranvik *et al.* 2009). Bacterial consumption of DOC comprises a dominant proportion of this carbon loss, and our understanding of the contribution of photochemical processes to inland carbon losses is increasing (Battin *et al.* 2008).

The focus of this dissertation is to examine the biological and photochemical degradation of DOC in peatland ecosystems and its effect on downstream carbon cycling. The first chapter explores the use of fluorescence and parallel factor modeling of excitation-emission matrices to predict the amount of BDOC in aquatic ecosystems. The second chapter investigates the sources and biodegradability of DOC in peatland ecosystems by comparing two peatland watersheds with different upland forest types. And the third chapter examines the role that photochemical processes play in the carbon dioxide evasion from peatland and other aquatic ecosystems and quantifies the contribution of photochemical degradation to global carbon dioxide evasion from inland waters.

Chapter 1 - Fluorescence and Absorbance Trends during Long-term Dissolved Organic Carbon Decomposition in Lakes

Approximately one half of terrestrial carbon runoff is processed by inland waters and released into the atmosphere as carbon dioxide prior to reaching the oceans, and bacterial DOC consumption comprises a dominant proportion of this carbon loss. However, direct measurements of bacterial degradation of DOC over time scales of months to years is extremely time consuming and therefore rarely used in inland water carbon budgets. The objective of this study was to investigate whether DOM fluorescence and PARAFAC modeling may be used to predict the amount of BDOC in aquatic ecosystems. We monitored absorbance and excitation-emission matrix spectra during 1-year microbial degradation of DOC collected from 23 Minnesota lakes using batch incubations. Absorbance and fluorescence parameters were correlated with the percent of the initial DOC pool remaining over time and with best-fit exponential decay constants. The key finding from this study was that initial SUVA (specific UV absorbance at 254nm normalized to DOC concentration) was a good predictor of long-term biodegradable DOC concentration ($r^2 = 0.61$). In a subset of the lakes that included the humic lakes and one extremely productive lake (> 25 μg Chl-*a* L^{-1}), SUVA predicted nearly all of the variability in BDOC ($r^2 = 0.99$). These results suggested that SUVA, a measurement broadly used in ecology and environmental engineering and fairly simple to obtain, is an excellent predictor of the amount of long-term BDOC concentrations in these lake ecosystems. In addition, contrasting results between this study and other published studies illustrated how the best predictors of BDOC depend on the time scale of DOC degradation, most likely due to the preferential degradation of labile DOM pools before more recalcitrant DOM pools by microorganisms. Finally, our study revealed strong redundancies between absorbance and fluorescence parameters suggesting that performing both analyses for DOM degradation studies does not provide additional information.

Introduction

Dissolved organic carbon (DOC) is the dominant pool of organic carbon in freshwater lakes and wetlands (Wetzel 2001). DOC is consumed primarily by heterotrophic bacteria (Luo *et al.* 2010), but only a fraction of the total DOC can be degraded over time scales of months to years (Søndergaard and Middelboe 1995; Hansell and Carlson 1998). Inland waters play an important and active role in the global carbon cycle with half of terrestrial carbon runoff released into the atmosphere as carbon dioxide prior to reaching the ocean (Cole *et al.* 2007; Tranvik *et al.* 2009). Therefore, the drivers and controls on bacterial degradation of DOC can have strong effects on the global carbon cycle.

The biodegradable pool of DOC (BDOC) consists of organic matter that exists along a continuum of reactivity, including labile DOC that is degraded rapidly, semi-labile DOC that is degraded more slowly, and recalcitrant DOC that is degraded over very long time scales (Carlson 2002). BDOC is commonly measured as the loss of DOC over time during dark, bottle incubations of size-fractionated water containing just the bacterial community and the DOM pool (Raymond and Bauer 2000; Stets and Cotner 2008). For lakes, the size of the semi-labile pool of DOC is often of interest because it has a similar time scale as the average residence time of lakes (months to years). However, measuring the semi-labile pool of DOC using batch incubations is time consuming and therefore difficult to obtain for most lake studies.

To avoid long batch incubations, several earlier studies have looked for chemical and physical proxies of BDOC that can be measured readily. Some relationships that have been observed are a positive correlation between BDOC and the total concentration of DOC (Sondergaard and Middelboe 1995; Stets and Cotner 2008), a negative correlation between BDOC and SUVA (Kalbitz *et al.* 2003; Fellman *et al.* 2009), and a positive correlation between BDOC and amino-acid like fluoresecent compounds (Fellman *et al.* 2009; Guillemette and Del Giorgio 2011). However, only the relationship between BDOC and DOC was based on observations from a large number of lakes so it remains unclear if the relationship between BDOC and SUVA or between BDOC and fluorescence are applicable to a wide range of lakes.

In this study, we monitored absorbance and excitation-emission matrix fluorescence spectra during 1-year microbial degradation of DOC using bottle incubations for 23 lakes in Minnesota with a wide range of DOC concentration, productivity, and color. The objective of this study was to identify a broad predictor of BDOC using DOM fluorescence and PARAFAC modeling. In addition, we investigated the relationships between absorbance and fluorescence parameters and identified appropriate applications for DOM fluorescence and PARAFAC modeling related to DOM degradation.

Methods

Sample collection

Water samples were collected from the surface layer of 23 lakes from three regions in Minnesota in 2006 and 2007. Eight lakes were located in the Twin Cities Metropolitan Area in east-central Minnesota dominated by urbanization and agriculture, eleven lakes were located in and around Itasca State Park in north-central Minnesota characterized by pine, aspen-birch, and mixed hardwood forests, and four lakes were located in the Boundary Waters Canoe Area Wilderness in north-east Minnesota characterized by pristine lakes surrounded by boreal and mixed conifer-hardwood forests. These lakes were chosen to represent a wide range of DOC concentration, phytoplankton productivity, and DOM color (Table 1-1). Lake surface areas ranged from < 0.02 to > 17 km^2 with maximum depths of < 5 to 28 m. Samples collected from Lake Minnetonka were from Carson's Bay, one of many numerous bays that make up this 57 km^2 lake. Dissolved organic carbon (DOC) concentrations ranged from 3.6 mg C L^{-1} in Long Lake (Itasca) to 11.7 mg C L^{-1} in West Twin Lake (Itasca) with an average DOC concentration of 6.9 mg C L^{-1} across all lakes. Chlorophyll *a* (Chl-*a*) concentrations ranged from 1.3 μg L^{-1} in Lake Ozawindib (Itasca) to 27.3 μg L^{-1} in Medicine Lake (Twin Cities) with an average Chl-*a* concentration of 6.1 μg L^{-1} across all lakes. In addition, UV-specific absorbance at 254 nm (SUVA) ranged from 2.21 L mg^{-1} m^{-1} in Long Lake (Itasca) to 8.25

L mg^{-1} m^{-1} in Devil Lake (Boundary Waters) with an average SUVA of 4.66 L mg^{-1} m^{-1} across all lakes.

For this study, the lakes were separated into two groups based on similar absorbance and fluorescence behavior: the four Boundary Water lakes (Brule, Devil, Homer, and Poplar) and one extremely productive lake (Medicine) were categorized as "colored lakes" and the other 18 lakes were categorized as "clear lakes".

Chemical analyses

Water samples were filtered through pre-combusted Whatman GF/F filters (0.7 µm nominal pore size) using low vacuum pressure for biodegradation and chemical analyses. DOC and total dissolved nitrogen (TDN) samples were acidified to a pH of 2 and stored in pre-combusted vials at 4°C in the dark. Total dissolved phosphorus (TDP) samples were stored in acid-washed, dark polyethylene bottles at 4°C for up to one month before analysis. Approximately 100 mL of lake water was filtered through pre-combusted 25 mm Whatman GF/F filters to capture phytoplankton for chlorophyll-*a* analyses and stored frozen until analysis.

DOC concentrations were measured as non-purgeable organic carbon on a Shimadzu TOC-V Auto-analyzer using potassium hydrogen phthalate as a reference standard. TDN concentrations were measured as chemiluminescence of nitrogen dioxide on a Shimadzu TNM-1 using potassium nitrate as a reference standard. TDP concentrations were measured as absorbance at 880 nm following a potassium persulfate digestion using the molybdenum blue colormetric assay with KH_2PO_4 as a reference standard (Murphy and Riley 1962). Chlorophyll-*a* concentrations were measured as fluorescence of chlorophyll pigments on a Turner Designs 10-AU using chlorophyll-*a* from spinach leaves as a reference standard. Prior to the fluorometric analysis, particles were extracted from the filters by incubating in 10 mL 90% acetone (v/v) at 4 °C for approximately 24 hours in the dark.

Long-term DOC degradation assays

Biodegradable DOC was determined by filling 1 L muffled, dark glass Pyrex bottles with 750 mL of 0.7 µm filtrate. Bottles were incubated in the dark at room

temperature (22°C) for 1 year with 20 mL subsamples removed at time points of approximately 0, 1, 3, 7, 21, 56, 154, and 365 days to measure changes in DOC concentration over time. At each time point, the bottle was inverted gently to re-aerate the water and prevent oxygen limitation of DOC degradation. DOC concentration, absorbance, and fluorescence were measured at every time point during the incubation.

Optical analyses

Water samples were filtered through muffled Whatman GF/F filters (0.7 μm nominal pore size) using low vacuum for chemical analyses and filtered again through 0.2 μm nitrocellulose membrane filters for optical analyses. Optical samples were stored in muffled amber vials at 4°C in the dark.

Absorbance scans were measured on a Cary 50 spectrophotometer using a 1 cm quartz cuvette over the wavelengths of 200 nm to 600 nm every 1 nm. Fluorescence was measured on a Horiba Jobin Yvon Fluoromax-3 in a 1 cm quartz cuvette. The emission intensity for each excitation wavelength was first adjusted to subtract the Nanopure water blank and eliminate Raman and Rayleigh scattering (Zepp *et al.* 2004), then divided by the Raman area of the Nanopure water blank to normalize fluorescence intensity to daily variability in the xenon lamp output using a Matlab program developed by Dr. Rose Cory (Cory and McKnight 2005). Fluorescence indices were calculated as the ratio of fluorescence intensity (in Raman units) at emission wavelengths of 470 nm and 520 nm for an excitation wavelength of 365 nm according to McKnight *et al.* (2001).

Statistical analyses

PARAFAC modeling of fluorescence EEMs was conducted with MATLAB using the DOMFluor toolbox version 7.5 freely downloadable from the Chemometrics site at the University of Copenhagen (www.models.life.ku.dk; Stedmon and Bro 2008). Only DOM samples with an absorbance less than 0.3 at 254 nm were used in the PARAFAC model (Miller *et al.* 2010). Additionally, we had to exclude 18 out of 283 DOM time point samples (representing 13 different lakes) where the EEM spectrum was dominated by a minor component (the phenol-like component) that was disproportionately weighting the model toward this component. We validated the model using a split plot

analysis, which consisted of randomly dividing our data array into two separate halves of 82 and 83 EEMs each (for a total dataset of 165 EEMs) and applying the PARAFAC model to each half separately and repeated the analysis stepwise from 3 to 7 components. We selected four components as the best model since we found good agreement in the spectral loadings for each dataset, the sum of squared residuals in the excitation and emission directions was lowest, and all significant peaks observed visually from corrected EEM plots were present.

Linear regressions were calculated in R version 2.12.1 (R Foundation for Statistical Computing, Vienna, Austria) to determine how strongly and significantly the optical and biodegradability parameters co-varied for all water samples. *P* values less than 0.05 were considered statistically significant.

Results

Long-term DOC degradation

BDOC concentrations over the 23 lakes ranged from 0.3 mg C L^{-1} (6% of the initial DOC pool) in a humic lake (Brule) to 2.5 mg C L^{-1} (45% of the initial DOC pool) in a very productive lake (Mitchell). BDOC was weakly but significantly correlated to initial DOC (Figure 1-3B) in the clear lakes ($r^2 = 0.24$, $p < 0.05$), which drove a weak, significant correlation in all lakes ($r^2 = 0.22$, $p < 0.05$).

Many of the lakes (> 60%) did not exhibit exponential loss of DOC until several weeks into the incubation period (Figure 1-1). During the first several weeks, DOC concentrations fluctuated and sometimes increased up to 7% of the initial DOC concentration. Due to the increase in DOC concentration with time, the time period over which the degradation constant *k* was calculated did not begin until 3 to 21 days into the incubation period, depending on the lake. DOC degradation constants ranged from 0.006 to 0.056 d^{-1} (mean and standard deviation = 0.019 ± 0.012 d^{-1}). *k* was positively correlated only to the initial proportion of the phenol-like component for colored lakes but was not correlated to SUVA (Figure 1-3G) or any other fluorescence components for clear or colored lakes. This is in contrast to a recent study by Koehler *et al.* (2012) that

showed significant positive correlations between k and fluorescence components related to algal-produced DOM and significant negative correlations between k and SUVA. BDOC or k was not significantly correlated to any of the other chemical parameters measured in these lakes (Table 1-1).

Absorbance trends

SUVA tended to increase during the incubation period for most lakes or increase temporarily during the early period of incubation (Figure 1-2). Increased SUVA with time may result from the preferential degradation of less aromatic compounds by the microbial community. For all lakes, initial DOC was strongly and significantly correlated to a_{254} ($r^2 = 0.61$, $p < 0.001$; Figure 1-3A) but initial DOC and SUVA were not strongly correlated. For the subset of clear lakes (see Methods), initial SUVA was strongly and significantly correlated to BDOC ($r^2 = 0.62$, $p < 0.001$) with a_{254} and initial DOC predicting 54% and 24% ($p < 0.01$ and $p < 0.05$, respectively) of the total variability in BDOC (Figure 1-3F). For colored lakes, SUVA was nearly perfectly correlated to BDOC ($r^2 = 0.99$, $p < 0.001$), with a_{254} and initial DOC predicting 69% and 16% of the variability in BDOC (Figure 1-3F). However, SUVA was not correlated to BDOC for all lakes combined ($r^2 = 0.02$). In addition, k was not correlated to DOC, BDOC, a_{254}, or SUVA for any group of lakes.

Fluorescence trends

We identified 4 fluorescence components using PARAFAC modeling of EEM spectra during the long-term DOC incubations (Figure 1-4). Two humic-acid like components dominated the EEM spectra for all samples at the beginning of the incubation (59–86%). The amino-acid component comprised the next largest proportion (11–37%) and the phenol-like component comprised the smallest proportion (0–4%) of the EEM spectra for all lakes. During the incubation, the trend of total fluorescence and the relative proportion of all four components were variable across all lakes with no particular pattern corresponding to the initial chemical characteristics of the lakes. Nine lakes (BWB, BWD, ITD, ITJ, ITL, ITT, ITW, TCJ, and TCO) exhibited an overall increase in total fluorescence during the incubation with a slight increase in the phenol-

like component over time coupled with either an increase or decrease in the humic-like components. Seven lakes (BWH, BWP, ITE, ITI, TCE, TCN, and TCT) exhibited a minimum or maximum of total fluorescence mid-incubation with the phenol-like component increasing during the second half of the incubation and the humic-like and amino acid-like components decreasing to nearly 0. Six lakes (ITA, ITB, ITM, ITO, TCM, and TCS) exhibited a temporary large increase in total fluorescence due to a temporary increase in the phenol-like component with a decrease in the humic-like and amino acid-like components to nearly 0, but all components returned to similar fluorescence before the temporary increase. One lake (TCC) exhibited a large increase in total fluorescence within the first few weeks of the incubation due to a large increase in the phenol-like component.

BDOC was strongly and significantly positively correlated to total fluorescence (Figure 1-3D) for clear lakes ($r^2 = 0.56$, $n = 18$, $p < 0.001$) which drove a weak but significant correlation for all lakes ($R^2 = 0.24$, $P = 0.01$). BDOC was positively correlated to the percent fraction of humic acid-like components weakly and significantly in clear lakes ($r^2 = 0.23$, $p < 0.05$), strongly and significantly in colored lakes ($r^2 = 0.79$, $p < 0.05$), and not correlated for all lakes combined (Figure 1-3C). BDOC was negatively correlated to the fraction of the amino acid-like component weakly but significantly for clear lakes ($r^2 = 0.28$, $p < 0.05$), strongly but not significantly for colored lakes ($r^2 = 0.57$, $p = 0.086$), and not correlated for all lakes combined (not shown). k was strongly and significantly negatively correlated to the fraction of the phenol-like component in colored lakes ($r^2 = 0.78$, $p < 0.05$), which drove a weak but significant correlation for all lakes ($r^2 = 0.20$, $p < 0.05$; not shown). The fraction of humic acid-like components, the fraction of the amino acid-like component, the total fluorescence, and the fluorescence index were all significantly correlated to a_{254} ($r^2 = 0.58–0.87$ and $p < 0.0001$) for clear lakes and strongly but not significantly correlated for colored lakes, which drove significant correlations for all lakes combined (Figure 1-3E). Similar relationships were observed for initial DOC and SUVA.

Discussion

The results from this study revealed a strong positive correlation between long-term BDOC concentration in lakes and initial SUVA (Figure 1-3F) and strong correlations between absorbance at 254 nm and several PARAFAC EEM components (Figure 1-3E). Based on the results from this study, we will argue that SUVA, a common DOM measurement, can be used to predict long-term BDOC concentrations in these lakes. In addition, we discuss how predictors of BDOC largely depend on the time scale of degradation due to the preferential degradation of DOC by the microbial community over time. Finally, the observed redundancies between absorbance and fluorescence properties of DOM in this study and others suggest that performing both analyses for DOM degradation studies does not provide additional information.

DOC degradation

The BDOC concentrations from this study (6–45% of the initial DOC pool over one year) were similar to other published measurements for lakes despite large differences in time scales: Sondergaard and Middelboe (1995) reported an average of 14% loss of DOC over time scales of days to weeks, Guillemette and Del Giorgio (2011) measured an average of 12% loss of DOC over 28 days, Stets and Cotner (2008) measured a range of 15–63% loss of DOC over 15 months, and Koehler *et al.* (2012) measured an average of 32–40% loss of DOC over 3.7 years. The semi-labile BDOC decay constants (k) measured from this study ranged from 0.006 d^{-1} to 0.056 d^{-1}, equivalent to a turnover time of the semi-labile BDOC pool of 18 to 156 days. These decay constants were similar to the decay constants measured for freshwater plant, macroalgae, and seagrass detritus (Enriquez *et al.* 1993), but greater than (and with shorter turnover times than) marine DOC (Yamanaka and Tajika 1997) and terrestrial plant detritus (Enriquez *et al.* 1993).

We observed significant initial increases in DOC in most bottle incubations which prevented us from estimating k during the beginning of the incubation period. Initial increases in DOC at the beginning of the incubation period are common in long-term batch assays (Del Giorgio, *pers. comm.*) but rarely reported in the literature. There are

several possible sources of this additional DOC. One possible source is release of DOC from bacterial cells. However, we did not filter water samples extracted at each time point so it is unlikely that bacterial cells were the additional source of DOC in these incubations. Another possible source is from additional carbon fixation by nitrification or other chemosynthetic pathways during the initial stages of the degradation period. And finally, it may be possible that a small fraction of the initial pool of DOC could not be fully combusted by the Shimadzu TOC analyzer until after bacterial enzymes had time during the incubation period to breakdown the most complex DOC molecules. To avoid these initial increases in DOC during the early stages of DOC degradation, initial *k* should be measured using DOC degradation assays that measure loss of oxygen or production of carbon dioxide over short time scales as proxies for DOC consumption. For example, Guillemette and Del Giorgio (2011) combined bacterial production assays to measure short-term losses of DOC and batch incubations to measure long-term losses of DOC to develop a complete picture of DOC loss over the full time period.

In addition, the loss of DOC in this study did not follow a simple single exponential decay model for many lakes, similar to another recent study (Stets and Cotner 2008). Double exponential decay (Kalbitz *et al.* 2003) or continuous decay models (Koehler *et al.* 2012) have been used to more accurately model the complex loss of DOC resulting from continuous changes in DOM quality and the microbial community composition over time. However, we did not have enough time points later in the incubation to develop a more complex DOC decay model.

Initial increases in DOC concentration during the incubations obscured the degradation behavior of the most labile pool of DOC. As a result, the degradation constants calculated in this study represent an average long-term decay rate of the semi-labile pool of DOC. However, initial absorbance and fluorescence measurements characterized the initial pool of DOC which includes the most labile pool of DOC. This temporal disconnection between initial optical characteristics of DOC and the later degradation characteristics of the more semi-labile pool of DOC may explain why *k* in this study was not related to initial absorbance or fluorescence parameters in contrast to other studies (Guillemette and Del Georgio 2011; Koehler *et al.* 2012).

Predictors of BDOC

Long-term BDOC concentrations measured in this study were correlated with both initial DOC concentration and a_{254}. Initial DOC concentration has already been shown to be related to long-term BDOC concentration across a wide range of systems (Sondergaard and Middelboe 1995; Stets and Cotner 2008). By using SUVA, which normalizes the absorbance of DOM at 254 nm - a measure of DOM quality - to the initial DOC concentration, the correlation coefficient for predicting BDOC increased by 8% in clear lakes and 30% in humic lakes. However, the strong positive correlation between BDOC and SUVA observed in this study was in contrast with the negative correlation between BDOC and SUVA observed in terrestrial soils (Kalbitz *et al.* 2003; McDowell *et al.* 2006; Fellman *et al.* 2009). In addition, we observed a positive correlation between BDOC and the relative proportion of humic-like components and a negative correlation between absorbance at 254 nm (a proxy for BDOC) and the relative proportion of amino acid (protein)-like components. This was also in contrast to other studies that have shown that the percent BDOC was positively correlated with the relative proportion of protein-like components (Fellman *et al.* 2008; Guillemette and Del Giorgio 2011).

One potential explanation for the contrasting trends in our study relative to those mentioned above could arise from the different time scales of incubations over which the BDOC concentrations were measured. In this study, BDOC was measured as the loss of DOC over one year, while these other studies measured BDOC as the loss of DOC over 30 to 90 days. The time scale over which the loss of DOC is measured is a critical component of how the size and characteristics of the biodegradable pool of DOC are defined due to the preferential consumption of DOM compounds by microorganisms, whereby microorganisms consume the most labile pool of DOC first (Middelburg 1989). In this way, the amount of DOC consumed by microorganisms over shorter time periods (days to weeks) is controlled by the pool of very labile DOC which can be consumed rapidly, such as amino acids and carbohydrates (Amon *et al.* 2001), and there might be an inherent spuriousness to the degradation of these highly labile compounds. In contrast, the amount of DOC consumed by microorganisms over longer time periods (months to years) is controlled by the total amount of DOC available for degradation since both low

and high molecular weight DOC has been shown to be readily utilized by microorganisms (Amon and Benner 1996; Volk *et al.* 1997). This is similar to human digestion whereby stores of carbohydrates are digested quickly and depleted first while stores of fat are digested more slowly and depleted over longer periods of time.

Synthesizing our results with the results from other studies in terrestrially influenced aquatic ecosystems, we hypothesize that algal-derived DOC (characterized by lower SUVA and a greater proportion of amino-acid like fluorescent components) will best predict BDOC measured over time scales of days to one month because this is the time period during which most of the labile pool of DOC is consumed. In contrast, we hypothesize that terrestrially derived DOC (characterized by higher SUVA and a greater proportion of humic-like fluorescent components) will best predict BDOC measured over time scales of months to years because this is the time period during which most of the semi-labile pool of DOC is consumed and terrestrial ecosystems tend to export more DOC (Urban *et al.* 1989).

Absorbance or fluorescence?

We observed a strong redundancy between the absorbance and the fluorescence of DOM in our study. This redundancy is due to the dependence of DOM fluorescence on the absorbance of light energy by DOM molecules. All the lakes in this study were dominated by humic-like components and humic-like components fluoresce more strongly than non-humic-like components (Senesi *et al.* 1991). This resulted in the strong positive correlation between the relative proportion of humic-like components and the absorbance of DOC, and the strong negative correlation between the relative proportion of amino acid-like components and the absorbance of DOC. These trends are likely true for many other relatively small lakes because these lakes are net heterotrophic (Pace *et al.* 1994) and inland waters process the majority of terrestrially-derived DOC before it reaches the ocean (Tranvik *et al.* 2009). Redundancies between absorbance and fluorescence have also been noted in other studies across much larger ranges in ecosystem properties. For example, fluorescence index and SUVA were significantly and negatively correlated for DOM collected across a wide-range of long-term ecological

research (LTER) sites, including alpine, desert, tundra, forest, boreal, estuarine, coastal, and urban environments (Jaffe *et al.* 2008). In addition, Del Vecchio and Blough (2004) observed a nearly linear relationship between absorbance at 355 nm and fluorescence at 355 nm in ocean surface water samples.

Given the redundancies between the absorbance and fluorescence of DOM, we propose that there are limitations to the amount of additional information regarding DOM quality that can be gained from PARAFAC-EEM modeling beyond the information gained from absorbance. These limitations largely arise from the need to attribute PARAFAC components with ecologically important chemical compounds. For lake studies, DOM compounds are largely separated into algal/terrestrial or humic/non-humic categories. However, this information can also be obtained using absorbance at specific wavelengths, the ratio of absorbance at different wavelengths, and other basic chemical or physical characteristics of lakes such as chlorophyll-a concentration, DOC concentration, or the watershed to lake surface area ratio. In these cases, absorbance is a more efficient and cost effective tool than fluorescence for characterizing the quality and sources of lake DOM. Cases where fluorescence and PARAFAC modeling may be a more appropriate tool include characterizing certain chemical properties of DOM such as redox (Cory and McKnight 2005), determining rates of specific biogeochemical processes (Miller *et al.* 2006; Mladenov *et al.* 2010), and determining the effects of land use and land management practices on stream biogeochemistry (Wilson and Xenopoulos 2009; Williams *et al.* 2010).

Summary

In conclusion, SUVA predicted most of the variability in long-term BDOC concentration for lakes within a wide range of DOC concentration, phytoplankton productivity, and DOM color. This result suggests that SUVA, a measurement broadly used in ecology and environmental engineering and fairly simple to obtain, is an excellent predictor of the amount of long-term BDOC concentrations in these lake ecosystems. Future studies should investigate whether this relationship is applicable in other lake and freshwater ecosystems with different climatic patterns, terrestrial vegetation, terrestrial

soils, and lake residence times. In addition, we show that the best predictors of BDOC depend on the time scale of DOC degradation, most likely due to the preferential degradation of labile DOM pools before more recalcitrant DOM pools by microorganisms. Finally, our study revealed strong redundancies between absorbance and fluorescence parameters suggesting that performing both analyses for DOM degradation studies does not provide additional information.

Table 1-1. Chemical and absorbance properties of dissolved organic matter collected from 23 Minnesota lakes.

Dissolved organic carbon (DOC, mg C L^{-1}); total dissolved phosphorus (TDP, µM **P**); chlorophyll-*a* (Chl-*a,* µg Chl-*a* L^{-1}); total dissolved nitrogen (TDN, mg C L^{-1}); napieirian absorbance coefficient at 254 nm (a_{254}, m^{-1}); and DOC specific-ultraviolet absorbance at 254 nm (SUVA, L mg^{-1} m^{-1}).

	Lake	DOC *(mg C L^{-1})*	TDP *(µM P)*	Chl-*a* *(µg Chl-a L^{-1})*	TDN *(mg C L^{-1})*	a_{254} *(m^{-1})*	SUVA *(L mg^{-1} m^{-1})*
COLORED	TCE Medicine	5.9	10.7	27.3	0.54	33.1	5.59
	BWB Brule	4.8	3.4	1.4	0.19	23.0	4.83
	BWD Devil	6.8	4.0	2.0	0.27	55.9	8.25
	BWH Homer	8.1	3.6	4.5	0.28	56.3	6.95
	BWP Poplar	7.8	5.8	3.8	0.27	51.5	6.57
CLEAR	ITA Arco	7.3	9.7	7.6	0.54	23.5	3.22
	ITB Boot	5.3	1.7	3.8	0.27	15.1	2.85
	ITD Deming	8.5	5.6	5.3	0.52	37.2	4.35
	ITE Elk	7.3	4.7	7.4	0.38	29.9	4.11
	ITI Itasca	5.3	6.9	7.9	0.33	22.3	4.19
	ITJ Josephine	5.8	5.7	2.6	0.40	19.2	3.28
	ITL Long	3.6	2.5	2.4	0.29	8.1	2.21
	ITM Mary	8.1	5.3	3.6	0.35	37.7	4.64
	ITO Ozawindib	7.8	4.7	1.3	0.41	37.7	4.85
	ITT Twin East	9.8	4.3	12.5	0.51	52.6	5.38
	ITW Twin West	11.7	6.7	4.9	0.47	74.1	6.31
	TCC Christmas	5.5	8.2	1.5	0.50	19.5	3.56
	TCJ Johanna	5.5	12.7	8.1	0.62	28.2	5.13
	TCM Mitchell	5.5	10.5	4.5	0.77	36.6	6.62
	TCN Minnetonka	7.7	5.9	6.2	0.60	25.7	3.34
	TCO Owasso	6.9	16.5	8.2	0.81	32.0	4.63
	TCS Josephine	7.2	12.2	7.3	0.57	25.8	3.56
	TCT Turtle	6.8	5.5	6.0	0.68	18.0	2.66

Table 1-2. Degradation and fluorescence properties of dissolved organic matter collected from 23 Minnesota lakes.

Biodegradable dissolved organic carbon (BDOC, mg L^{-1}); DOC degradation constant (*k*, day^{-1}); BDOC turnover time (T, days); Fluorescence index (FI); fraction of humic acid-like components 1 and 2 (HA-like); fraction of amino acid-like component 3 (AA-like); fraction of phenol-like component 4 (Ph-like); and the total fluorescence in raman units (Fluor, R.U.).

	Lake	BDOC *(mg L^{-1})*	BDOC *(%DOC)*	*k* *(day^{-1})*	T *(days)*	FI	HA-like	AA-like	Ph-like	Fluor *(R.U.)*
COLORED	TCE Medicine	0.4	7%	0.056	18	1.42	0.77	0.23	0.00	1.98
	BWB Brule	0.3	6%	0.008	132	1.33	0.79	0.18	0.03	0.81
	BWD Devil	1.0	15%	0.012	81	1.27	0.86	0.11	0.04	1.94
	BWH Homer	0.7	8%	0.024	42	1.27	0.83	0.13	0.03	2.08
	BWP Poplar	0.6	8%	0.008	118	1.29	0.83	0.14	0.03	1.92
CLEAR	ITA Arco	1.7	23%	0.026	39	1.46	0.73	0.24	0.03	0.90
	ITB Boot	0.6	10%	0.031	32	1.44	0.75	0.25	0.00	0.65
	ITD Deming	1.4	17%	0.023	44	1.39	0.79	0.19	0.02	1.48
	ITE Elk	1.1	14%	0.040	25	1.43	0.79	0.21	0.00	1.38
	ITI Itasca	1.0	18%	0.031	33	1.46	0.80	0.18	0.02	1.09
	ITJ Josephine	1.2	21%	0.015	69	1.36	0.73	0.24	0.03	0.69
	ITL Long	0.6	16%	0.007	139	1.45	0.63	0.37	0.00	0.29
	ITM Mary	1.3	15%	0.017	60	1.41	0.81	0.19	0.00	1.57
	ITO Ozawindib	0.9	11%	0.020	51	1.40	0.82	0.18	0.01	1.81
	ITT Twin East	1.8	18%	0.019	54	1.39	0.83	0.15	0.02	2.34
	ITW Twin West	2.5	22%	0.012	80	1.34	0.85	0.13	0.02	3.16
	TCC Christmas	0.6	12%	0.010	102	1.36	0.59	0.37	0.04	0.75
	TCJ Johanna	1.3	23%	0.010	104	1.43	0.71	0.29	0.00	1.74
	TCM Mitchell	2.5	45%	0.015	66	1.45	0.75	0.23	0.01	1.92
	TCN Minnetonka	0.6	8%	0.006	156	1.45	0.72	0.25	0.03	1.03
	TCO Owasso	1.3	18%	0.011	90	1.44	0.75	0.24	0.01	1.52
	TCS Josephine	1.0	14%	0.011	90	1.45	0.72	0.26	0.02	1.25
	TCT Turtle	1.0	14%	0.016	64	1.48	0.69	0.30	0.01	0.63

Table 1-3. Linear regression coefficients (r^2) between sample fluorescence parameters. Fraction of humic-like components 1 and 2 (HA-like), fraction of amino acid-like component (AA-like), fraction of phenol-like component (Ph-like), total fluorescence intensity in raman units (Fluor., R.U.), and fluorescence index (FI), and other DOM parameters: biodegradable DOC (BDOC, mg C L^{-1}), DOC degradation constant (k, $days^{-1}$), initial DOC (DOC, mg C L^{-1}), Naiperian absorbance coefficient at 254 nm (a_{254}, m^{-1}), and UV-specific Naiperian absorbance at 254 nm (SUVA, L mg^{-1} m^{-1}). * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$. Strong correlations ($r^2 \geq 0.45$) shown in bold.

Dependent Variable	r^2	All (N=23)	Clear (N=18)	Color (N=5)	r^2	All (N=23)	Clear (N=18)	Color (N=5)
BDOC	**HA-like**	0.01	0.23 *	**0.79** *				
	AA-like	0.01	0.28 *	**0.57**	DOC	0.22 *	0.24 *	0.16
	Ph-like	0.00	0.00	0.15	**a_{254}**	0.16 *	**0.54** ***	**0.69**
	Fluor	0.24 *	**0.56** ***	0.14	**SUVA**	0.02	**0.62** ***	**0.99** ***
	FI	0.00	0.01	0.31				
k	HA-like	0.00	0.08	0.18				
	AA-like	0.00	0.04	0.37	DOC	0.00	0.00	0.00
	Ph-like	0.20 *	0.06	**0.78** *	a_{254}	0.00	0.00	0.00
	Fluor	0.00	0.00	0.00	SUVA	0.00	0.00	0.00
	FI	0.02	0.00	**0.51**				
DOC	**HA-like**	0.32 ***	**0.45** **	0.22				
	AA-like	0.34 ***	**0.53** ***	0.19				
	Ph-like	0.00	0.00	0.00	**a_{254}**	**0.61** ***	**0.76** ***	**0.79** *
	Fluor	**0.51** ***	**0.57** ***	**0.50**	SUVA	0.09	0.21 *	0.26
	FI	0.04	0.17 *	0.15				
a_{254}	**HA-like**	**0.58** ***	**0.51**	**0.65**				
	AA-like	**0.63** ***	**0.56**	**0.52**				
	Ph-like	0.02	0.00	0.00	**SUVA**	**0.69** ***	**0.66** ***	**0.77** *
	Fluor	**0.87** ***	**0.93**	**0.48**				
	FI	0.38 ***	0.26	0.36				
SUVA	**HA-like**	**0.48** ***	0.34	**0.76** *				
	AA-like	**0.53** ***	0.36	**0.52**				
	Ph-like	0.02	0.00	0.07				
	Fluor	**0.64** ***	**0.82**	0.27				
	FI	**0.45** ***	0.08	0.26				

Figure 1-1. DOC loss over the incubation period for 23 Minnesota lakes.

Dissolved organic carbon (DOC; mg C L^{-1}) loss over incubation length (days) for 23 Minnesota lakes. The best-fit exponential decay curves are represented by lines.

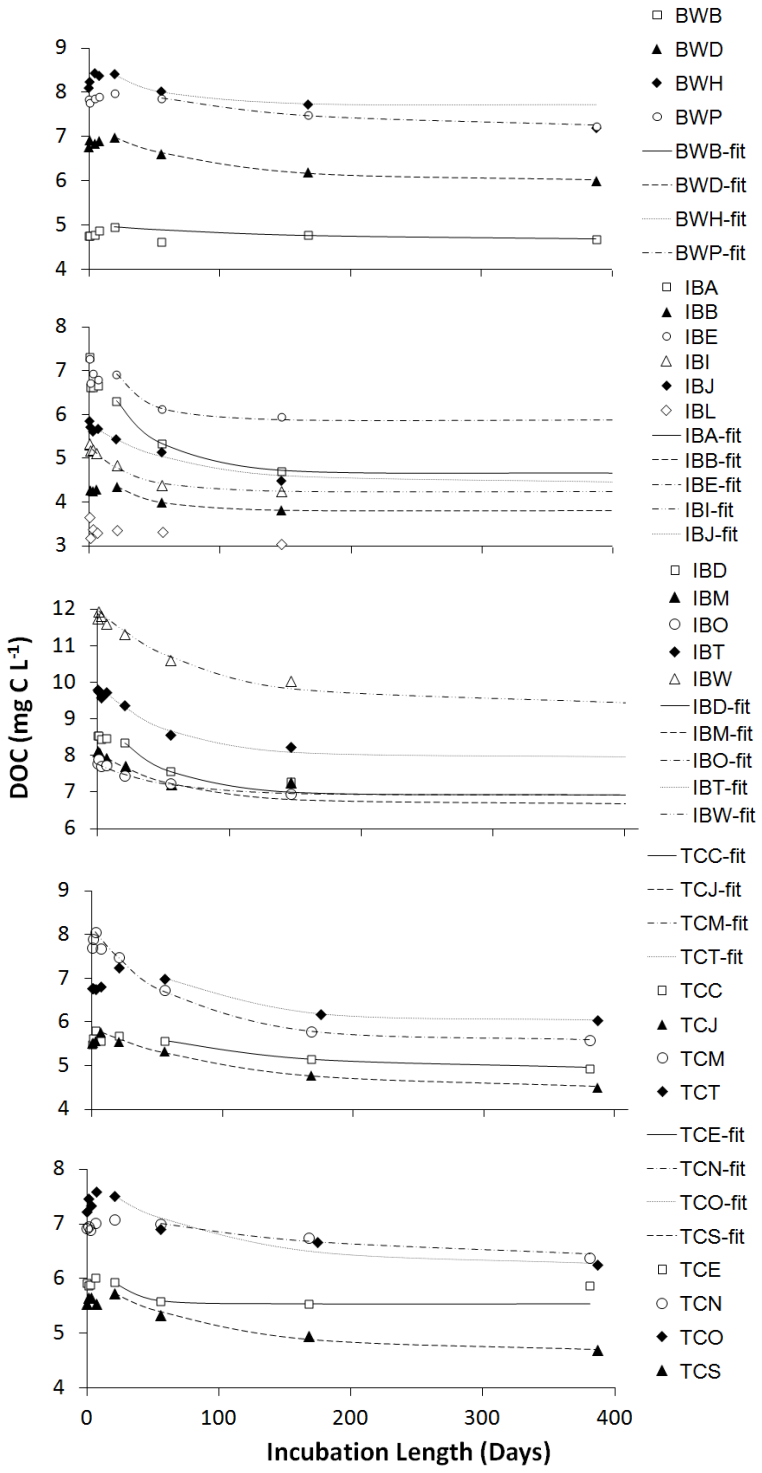


Figure 1-2. Change in SUVA over the incubation period for 23 Minnesota lakes.

Change in UV-specific absorbance at 254 nm (SUVA; L mg^{-1} m^{-1}) over incubation length (days) for 23 Minnesota lakes.

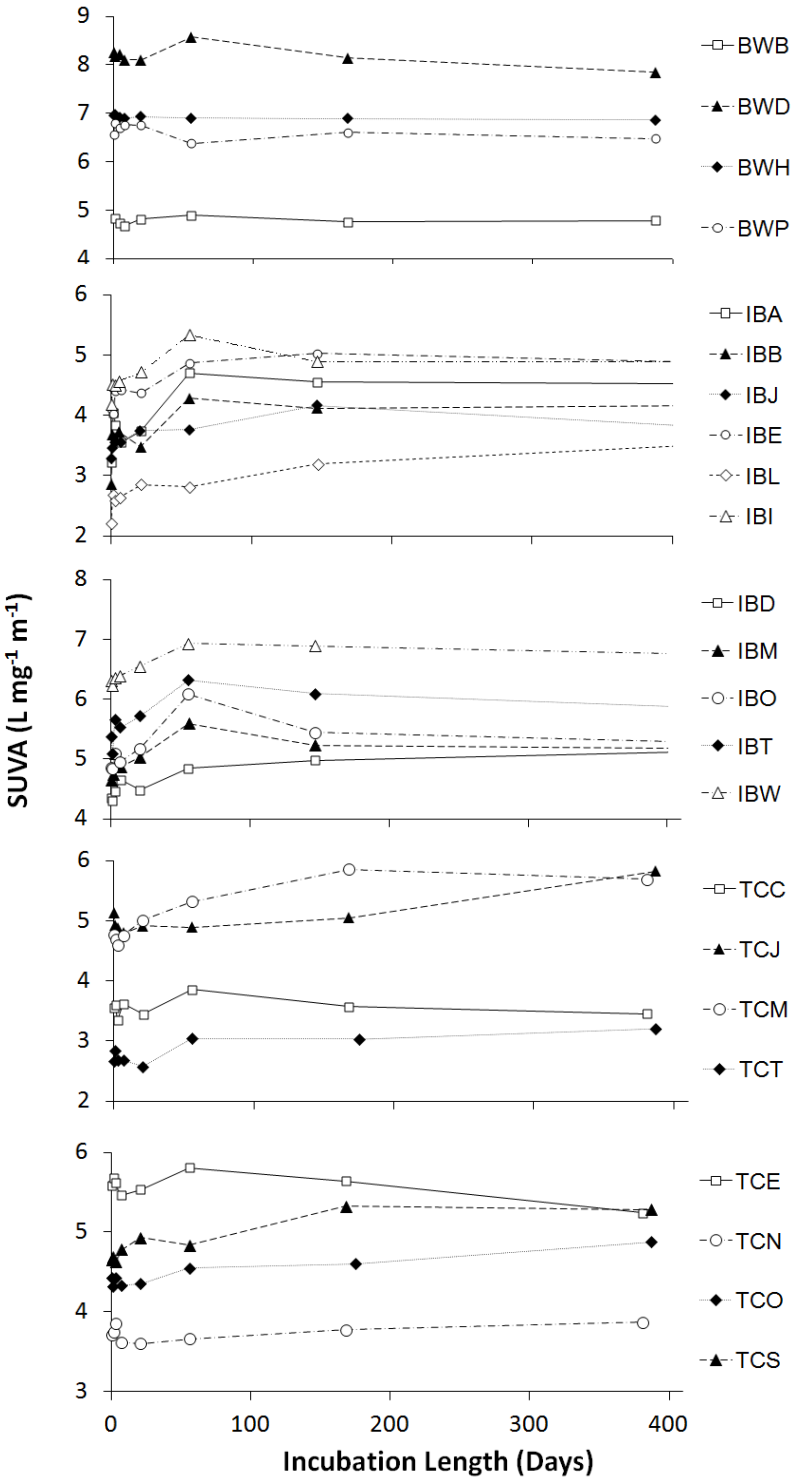


Figure 1-3. Relationships between BDOC and various absorbance and fluorescence parameters for 23 Minnesota lakes.

Scatterplots and linear regressions between **A.** dissolved organic carbon (DOC, mg C L^{-1}) and absorbance at 254 nm (a_{254}, m^{-1}); clear lakes: r^2 = 0.76, $p < 0.001$; colored lakes: $r^2 = 0.79$, $p < 0.05$; **B.** biodegradable DOC (BDOC, mg C L^{-1}) and DOC (mg C L^{-1}); clear lakes: $r^2 = 0.24$, $p < 0.05$; colored lakes: $r^2 = 0.16$, $p = 0.28$; **C.** BDOC and the fraction of humic acid-like components (HA-like, % relative contribution); colored lakes: r^2 = 0.79, $p < 0.05$; **D.** BDOC and total fluorescence (raman units, R. U.); clear lakes: $r^2 = 0.56$, $p < 0.001$; **E.** a_{254} (m^{-1}) and the fraction of humic acid-like components (HA-like, % relative contribution; $r^2 = 0.58$, $p < 0.0001$), the total fluorescence (raman units, R. U.; $r^2 = 0.87$, $p < 0.0001$), and the fraction of amino acid-like component (AA-like, % relative contribution; $r^2 = 0.63$, $p < 0.0001$); **F.** BDOC (mg C L^{-1}) and UV specific absorbance at 254 nm ($SUVA_{254}$, L mg^{-1} m^{-1}); clear lakes: $r^2 = 0.62$, $p < 0.0001$; colored lakes: $r^2 = 0.99$, $p < 0.001$; and **G.** BDOC decay constant (k, day^{-1}) and $SUVA_{254}$).

Figure 1-3 (continued).

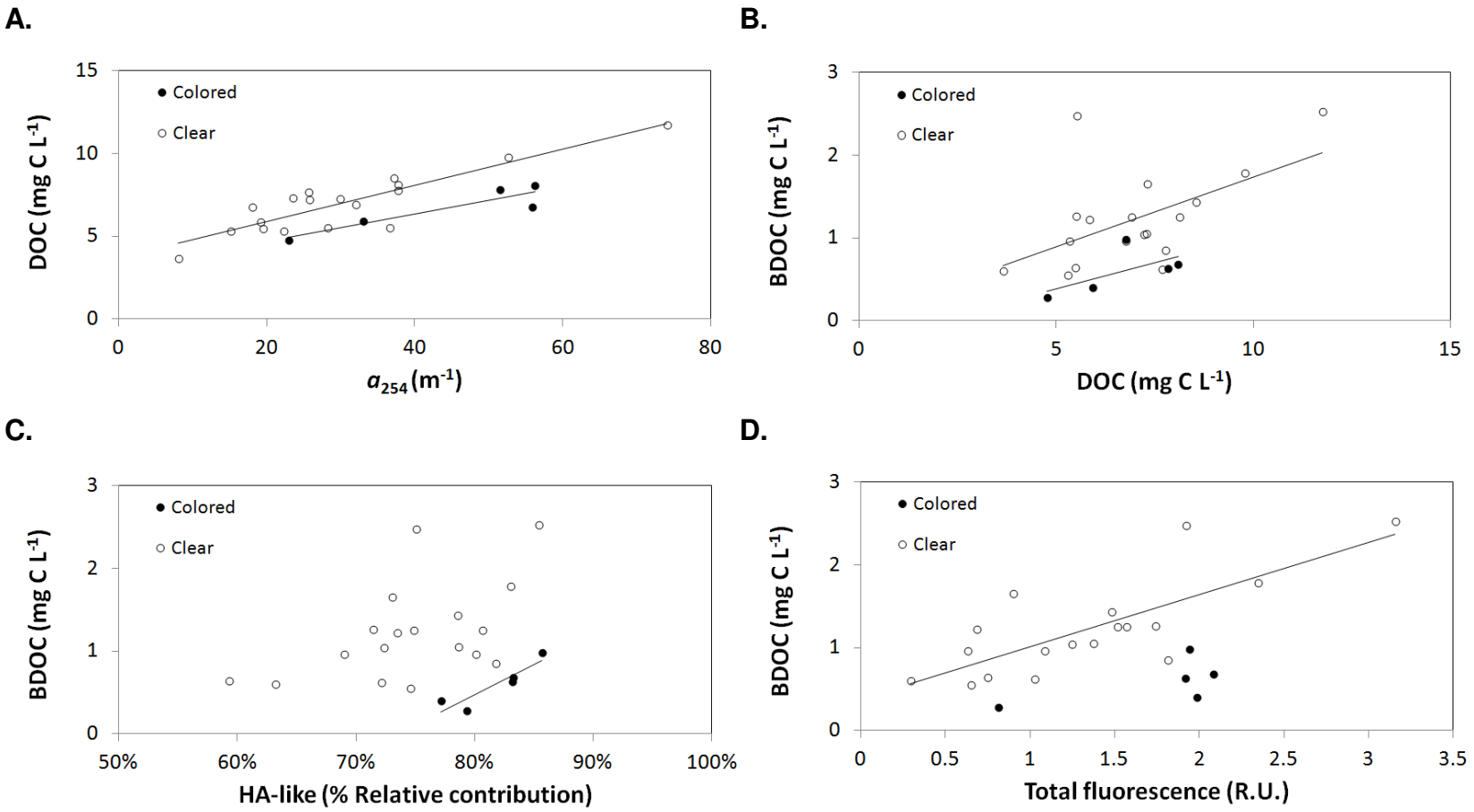
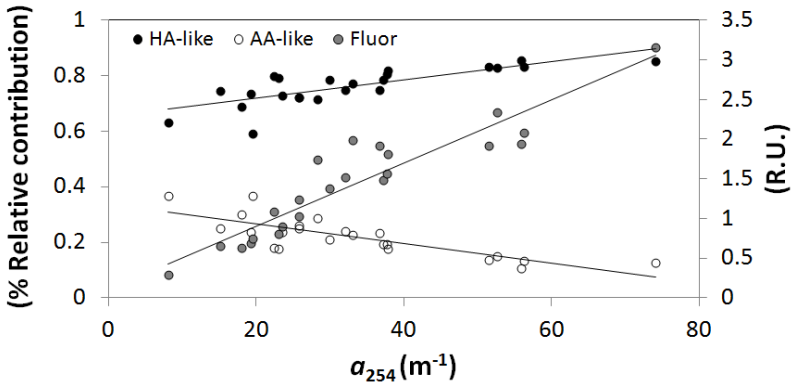
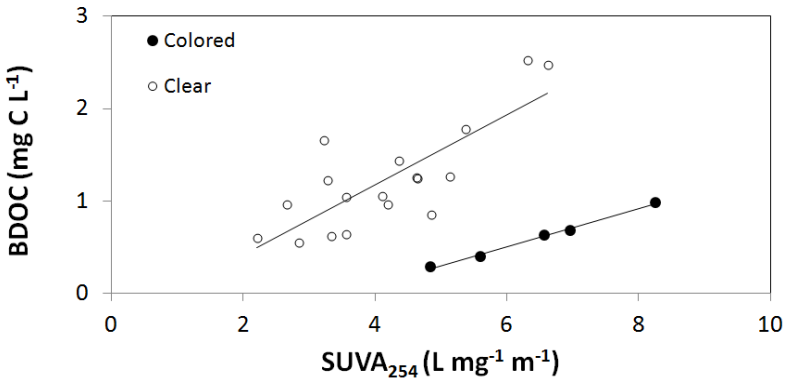


Figure 1-3 (continued).

E.



F.



G.

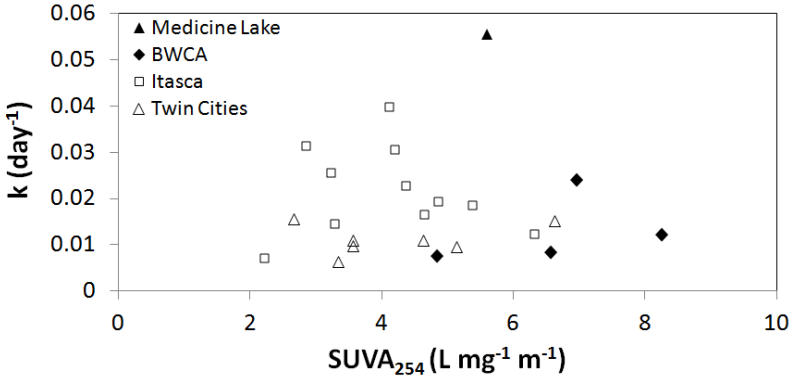
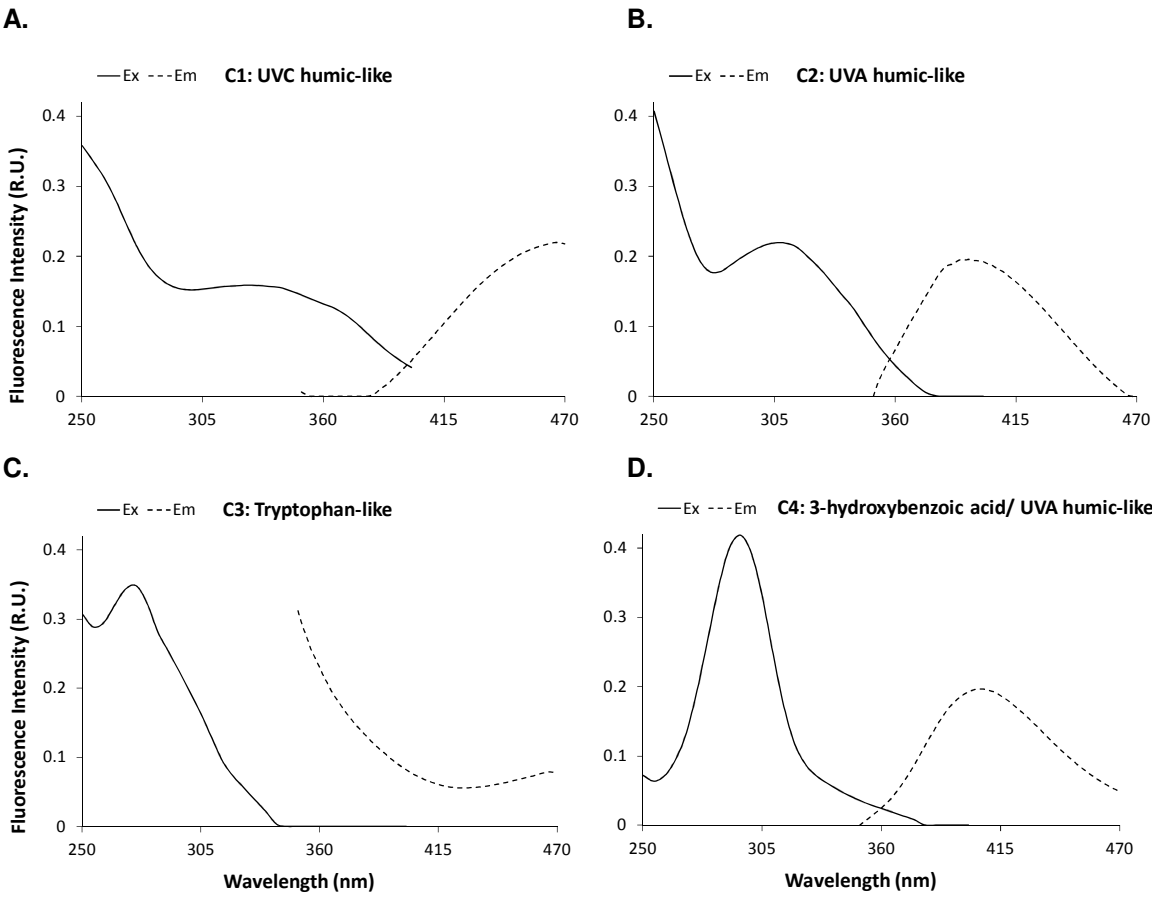


Figure 1-4. PARAFAC model component curves.

A. Component 1 - UVC humic-like; **B**. Component 2 - UVA humic-like; **C**. Component 3 - Tryptophan-like; and **D**. Component 3 - Hydroxybenzoic-acid/ UVA humic-like.



Chapter 2 - Sources of Biodegradable Dissolved Organic Carbon in Two Peatland Watersheds with Different Upland Forest Type, Minnesota, USA

Peatlands export more dissolved organic carbon (DOC) per area than forested ecosystems, but the sources and biodegradability of peatland DOC and their effects on downstream DOC loads and fluxes are poorly understood. In this study, we measured biodegradable dissolved organic carbon (BDOC) from multiple sources (upland surface runoff, upland subsurface flow, upland-peatland interface [lagg], and stream outlet) in two peatland watersheds with different upland forest type during spring snowmelt in the Marcell Experimental Forest, Minnesota, using short-term (48-hour bacterial respiration, BR) and long-term (one-year bottle incubations, BDOC) assays. The BDOC concentrations and BR were greater in upland surface runoff than in subsurface flow, the lagg, or the outlet of both watersheds, indicating that DOC in the upland surface runoff was most biodegradable. However, upland derived runoff from the coniferous and deciduous upland watersheds was 17% and 37% of total annual watershed flow, respectively, and most of the upland derived runoff was in the form of subsurface flow which had much less biodegradable DOC than surface runoff. Therefore, we propose that the peat bog may be the most important source of biodegradable DOC rather than the upland in these peatland watersheds annually. We also observed BDOC concentrations and BR that were greater in the outlet of the coniferous upland watershed than in the outlet of the deciduous upland watershed which could be due to greater nitrogen availability relative to carbon in the coniferous than in the deciduous upland watershed (C: N < 100 versus 130-150; respectively). The results from this study suggest that hydrology plays an important role in the export of BDOC from these systems – from influencing the export and degradation of DOC from upland soils to determining the proportion of upland versus bog-derived DOC in the outlet stream, and therefore changes in hydrology due to climate change are expected to significantly affect the amount and lability of DOC exported from these systems.

Introduction

Peatlands in the northern hemisphere play a large role in the global carbon (C) cycle relative to their size. Peatlands are concentrated in northern Russia, the Baltic states, Fenno-scandia, Canada, and the northern United States where they make up just 9.7% of the total land surface (Gorham 1995) but store between 270 and 455 Pg of C per year as peat (Gorham 1991; Turunen *et al.* 2002), approximately half of the carbon dioxide pool in the atmosphere (Solomon *et al.* 2007). The ability of peatlands to sequester atmospheric carbon at high rates results from the prevalence of waterlogged, anaerobic conditions which prevent phenol oxidase activity (Freeman *et al.* 2004), and dominance of a single genus *Sphagnum* (Turetsky 2003) that has low C mineralization rates (Hájek *et al.* 2009) and high phenolic content that strongly inhibits other enzyme activity (Freeman *et al.* 2004). However, peatlands also export up to one sixth of total C sequestrated in the peat as dissolved organic carbon (DOC; Moore *et al.* 2002), nearly one order of magnitude more DOC per unit area than forested upland ecosystems (5 to 40 g C m^{-2} yr^{-1}; Thurman 1985; Urban *et al.* 1989). Due to the large amount of DOC stored and exported from peatlands, it is important to determine the sources and biodegradability of peatland DOC to better understand how peatlands alter C sequestration, loads and fluxes downstream.

Uplands are generally considered more important sources of biodegradable DOC (BDOC) to streams than peatlands due to the refractory nature of peatland DOC. In forested stream catchments, BDOC concentrations in upper soil horizons were up to two times greater than in streams (Qualls and Haines 1992) and shifting DOC export from mineral to organic upland soils resulted in increased DOC concentrations and biodegradability in receiving streams (Dittman *et al.* 2010). Similar patterns have been observed in boreal stream catchments. Bacterial production rates in nine boreal streams were positively correlated to the percent of forest cover in the stream catchment (Aagren *et al.* 2008), and increased methyl mercury production at the upland-peatland interface was attributed to upland inputs of biodegradable DOC (Mitchell and Branfireun 2005; Mitchell *et al.* 2008b). And because most inputs of upland DOC to boreal peatlands occur during spring snowmelt (Kolka *et al.* 2001), greater biodegradability of peatland DOC

has been observed in the spring than in the summer or fall (Weigner and Seitzinger 2004; Aagren *et al.* 2008).

Upland sources of BDOC may also enhance degradation of peatland DOC through the priming effect: the stimulation of microbial degradation of refractory DOC in the presence of labile DOC (Guenet *et al.* 2010). The priming effect has long been recognized in soils (Blagodatskaya and Kuzyakov 2008), and has recently been observed in a wide range of aquatic ecosystems (Guenet *et al.* 2010). In most studies on the priming effect in aquatic ecosystems, refractory DOC mineralization increased 10% to 500% in the presence of labile DOC (de Haan 1977; Shimp and Pfaender 1985; Carlson *et al.* 2002; Farjalla *et al.* 2009; van Nugteren *et al.* 2009). The strength of the priming effect may differ based on the source of labile DOC, namely different upland forest litter types in peatlands. Across a wide range of forest ecosystems, decreased decomposition rates of litter have been observed with increasing initial carbon to nitrogen (C: N) ratios of the litter (Mellilo *et al.* 1982). This suggests that deciduous litter, with lower C: N than coniferous litter C: N (Currie *et al.* 1996; Magill and Aber 2000), should have greater decomposition rates and produce a more biodegradable leachate than coniferous litter. Moreover, global climate change has been predicted to shift upland forest types in the southern range of North American boreal ecosystems from predominantly coniferous to deciduous (Frelich and Reich 2009). The magnitude of atmospheric losses of C due to the priming effect in peatlands that is not accounted for in current global C budgets, and how changing upland forest type will affect the strength of this priming is currently unknown.

In this study, we measured the biodegradability of DOC in two peatland watersheds with different upland forest types (coniferous and deciduous) during a spring snowmelt event in the Marcell Experimental Forest, Minnesota. Our objective was to measure the biodegradability of DOC from multiple sources within the watershed (upland surface runoff, upland subsurface flow, upland-peatland interface, and peat bog) and of DOC exported from the watershed. In addition, we compared how DOC biodegradability differs with upland forest type and determined whether inputs of highly biodegradable upland DOC stimulated microbial degradation of less biodegradable peat bog DOC. We hypothesized that peatland watersheds would receive greater inputs of biodegradable

DOC from deciduous uplands than coniferous uplands, and that the biodegradability of upland DOC would determine the biodegradability of DOC exported from the watershed.

Methods

Study Area

The study was conducted in a coniferous upland and a deciduous upland peatland watershed located in the Marcell Experimental Forest, 40 miles north of Grand Rapids, Minnesota (Figure 2-1). The physical characteristics and vegetation of both watersheds have been described in great detail in previous publications (see Verry and Timmons 1982; Kolka *et al.* 2001; Mitchell *et al.* 2008a; Mitchell *et al.* 2009; Sebestyen *et al.* 2011). Briefly, the coniferous upland watershed consists of a 6.9-hectare coniferous upland dominated by white spruce and red pine, and a 2.0-hectare bog dominated by mature black spruce and tamarack. The deciduous upland watershed consists of a 6.5-hectare deciduous upland dominated by mature trembling aspen and paper birch, and a 3.2-hectare bog dominated by mature black spruce (Mitchell *et al.* 2008a; Mitchell *et al.* 2009). The soils in both watersheds consist of a sandy outwash, and this outwash is covered by a sandy clay loam in the deciduous upland watershed (Sebeysten *et al.* 2011).

Sample Collection

Event-based water samples were collected from pairs of runoff collectors installed on the north and south facing upland slopes of each watershed (Timmons *et al.* 1977). Overland surface runoff was collected using galvanized metal flattened funnels that route water in to a PVC pipe, which then flowed to a nearby polyethylene tank enclosed in a heated wooden structure. Upland subsurface flow was collected using a perforated stainless steel pipe buried horizontally at the interface of the A and B soil horizons (Timmons *et al.* 1977), connected to a separate polyethylene tank. The outlet flow from each watershed was monitored continuously by a V-notch weir in a heated wooden enclosure to prevent freezing. Precipitation and bog water elevation were reported daily in both watersheds by the United States Department of Agriculture (USDA) Northern Research Station in Grand Rapids, Minnesota.

Discrete water samples were collected for DOC biodegradability assays from the upland runoff collectors, the upland-bog interface (hereafter lagg; deciduous upland watershed only), and the outlet of both watersheds on March 24 and April 19 in 2009. Additional water samples were collected for chemical analyses bi-weekly and more frequently in response to precipitation events in the deciduous upland watershed only. All water samples were stored in dark, polyethylene bottles at 4°C and transported to the University of Minnesota in St. Paul for analysis. Samples were processed for chemical analyses and biodegradability assays within 24-48 hours of collection.

Chemical Analyses

Water samples were filtered through muffled Whatman GF/F filters (0.7 μm nominal pore size) using low vacuum pressure for chemical analyses. DOC samples were acidified to a pH of 2 and stored in muffled vials at 4°C in the dark. Soluble reactive phosphorus (SRP) samples were stored in acid-washed, dark polyethylene bottles at 4°C for up to one month before analysis.

Dissolved organic carbon (DOC) concentrations were measured as non-purgeable organic carbon on a Shimadzu TOC-V Auto-analyzer with potassium hydrogen phthalate as a reference standard. SRP was measured as absorbance at 880 nm using the molybdenum blue color metric assay with KH_2PO_4 as a reference standard (Murphy and Riley 1962). Total organic carbon (TOC) and total nitrogen (TN) were measured on unfiltered water samples by Standard Method 5310B on a Shimadzu TOC-V CPH and by in-line automated oxidation to nitrate on a Lachat QuikChem8000, respectively, at the USDA Forest Service Northern Research Station in Grand Rapids, Minnesota.

Bacterial Respiration

Bacterial respiration rates were determined from loss of dissolved oxygen during dark incubations of whole water in sets of nine−6 mL septum vials without headspace at 4°C. Mercuric chloride (1% by volume) was added to triplicate vials at 0, 1, and 2 weeks to stop bacterial activity. Dissolved oxygen concentrations were measured on a membrane-inlet mass spectrometer using ultrapure water (< 18.2 MW-cm) in gaseous

equilibrium with an air-saturated headspace at 4°C as a reference standard (Kana *et al.* 1994).

Long-term Biodegradable DOC

Biodegradable DOC was determined by filling 1 L muffled, dark glass Pyrex bottles with 750 mL of 0.7 µm filtrate. Bottles were incubated in the dark at room temperature (22°C) for 1 year with 20 mL subsamples removed at time points of 0, 3, 7, 21, 58, 154, and 370 days to measure changes in DOC concentration over time. At each time point, the bottle was inverted gently to re-aerate the water and prevent oxygen limitation of DOC degradation.

DOC Mixing Experiment

In 2011, water samples were collected from surface runoff and subsurface flow in the upland runoff collectors and from standing water in the lagg and peat bog of the deciduous upland watershed on April 12, 18, 25, and 28 during snowmelt. DOC was collected from water samples filtered through Millipore membranes (0.2 µm nominal pore size) to remove > 95% of bacterial cells (Biddanda *et al.* 2001). Additional lagg and bog water samples were filtered through Whatman GF/B filters (1.6 µm nominal pore size) and aerated at room temperature for an environmental bacterial community inoculate. A 2×2 factorial design experiment was conducted to examine bacterial respiration rates in upland (surface or subsurface) and peatland (lagg or bog) DOC mixed in 1:1 ratios and on upland and peatland DOC alone for a total of 8 treatments per sample date: surface + lagg, surface + bog, subsurface + lagg, subsurface + bog, surface, subsurface, lagg, and bog. Bacterial respiration was measured as described above, but amended with phosphorus (~40 µM as P) and nitrogen (~630 µM as N) based on an estimated average DOC concentration of ~4,200 µM C for most samples, for an approximate final C: N: P of 106:16:1 to minimize nutrient limitation of bacterial respiration (Redfield 1958). Stimulation of bacterial respiration was considered to have occurred when the observed rates of bacterial respiration on a mixed sample were statistically ($P < 0.05$) greater than the calculated mixed bacterial respiration rate due to conservative mixing of bacterial respiration rates on individual DOC sources.

Statistical Analyses

Multiple analyses of variances (MANOVA) were conducted in R version 2.12.1 (R Foundation for Statistical Computing, Vienna, Austria) to determine how much of the variability in chemical and biodegradability characteristics of the peatland DOM could be explained by the upland forest type (coniferous or deciduous), the date of sample collection (24 March or 19 April), the location within the watershed (surface runoff, subsurface flow, lagg, or outlet stream), or the interactions between watershed, date, and location. Linear regressions were also calculated in R to determine how strongly and significantly the chemical and biodegradability parameters co-varied for all water samples. *P* values less than 0.05 were considered statistically significant.

Results

Hydrology

The hydrology of the 2009 snowmelt in the peatland watersheds was characterized by a large rainfall event in March prior to snowmelt and a large snowmelt event in April without any rainfall (Figure 2-2). “Pre-snowmelt” was defined as the period from March 15 to April 6 corresponding to runoff that resulted from a large rainfall event while the snow pack was still well established. “Peak snowmelt” was defined as the period from April 7 to April 23 corresponding to the seasonal maximum runoff volume that resulted from rapidly increasing temperatures and melting snow without any precipitation events. “Post-snowmelt” was defined as the period of elevated runoff volume from April 24 to June 25. The bog water elevation in both watersheds increased sharply at the start of the spring snowmelt and declined over time, rising after major rainfall events during the post-snowmelt period.

Upland surface runoff was flowing into the north and south upland runoff collectors in both watersheds on March 24 and into the south runoff collector in the coniferous upland watershed on April 19. Subsurface runoff was flowing on March 24 and April 19 into the north and south upland runoff collectors in the deciduous upland

watershed and into the south upland runoff collector for the coniferous upland watershed. Lagg water samples were collected from the deciduous upland watershed on both dates.

Stream TOC and TN

TOC concentrations in the outlet stream of the deciduous and coniferous upland watersheds were highest in runoff at the start of the pre-snowmelt period. TOC then dropped to its lowest concentration several days later, increased during the rest of pre-snowmelt, decreased during peak snowmelt, and then increased gradually during post-snowmelt (Figure 2-3A). TOC to TN ratios (TOC: TN) in both watershed stream outlets increased during pre-snowmelt but declined and then remained stable during peak snowmelt and post-snowmelt (Figure 2-3B). During peak snowmelt, mean TOC: TN (± standard deviation; molar) in the stream outlet of the deciduous upland and coniferous upland watersheds were 133 (± 10) and 89 (± 12), respectively. Slightly greater daily flow-weighted TOC was exported from the deciduous upland watershed than the coniferous upland watershed summed over the 2009 snowmelt period (587 and 416 kg C, respectively; Figure 2-3C).

Peatland C, N, and P

The following results are from an analysis of DOC, TN, and SRP concentrations in upland runoff, peatland, and outlet stream water collected on March 24 and April 19 during snowmelt (Table 2-1; Figure 2-4A). The range of DOC concentration was lowest in subsurface flow (730–1,800 μM), higher in surface runoff and lagg water (970–2,900 μM and 1,600–2,500 μM, respectively), and highest in the outlet stream (2,500–4,100 μM). In a comparison of DOC measurements from the University of Minnesota and TOC measurements from the Northern Research Station, DOC concentrations were ± 300 μM (~10%) of TOC concentrations for each sample date.

The range of SRP concentrations was lowest in subsurface flow (0.1–0.2 μM), low and variable in lagg water and the outlet stream (0.1–1.3 μM and 0.1–0.8 μM, respectively), and highest in surface runoff (3.4–6.6 μM). The range of TN concentrations was lowest in subsurface flow (11–23 μM), higher in the outlet stream (26–54 μM), and highest and most variable in surface runoff and lagg water (14–147 μM

and 13–73 μM, respectively). TOC: TN were lowest in surface runoff and subsurface flow (23–92 and 60–94, respectively), higher in the outlet stream (62–126), and most variable in lagg water (44–137).

Based on MANOVA results, DOC and SRP were most strongly predicted by the location within the peatland watershed (surface runoff, subsurface flow, lagg, or outlet; $p < 0.01$ and $p < 0.001$, respectively). We observed variable DOC and SRP concentrations based on location (generally high in surface runoff, lower in subsurface flow, and highest at the outlet), indicating distinct sources and losses of DOC and SRP along hydrologic flow paths through the peatland watershed. SRP concentrations tend to decrease with increasing soil pore water depth as SRP produced from decomposing leaf litter and soil weathering is lost via plant uptake or becomes bound to soil minerals. In contrast, SRP concentrations tend to increase in the lagg due to the release of SRP bound to soil minerals under the anoxic, waterlogged conditions. Lagg water with high SRP concentrations is then transported to the outlet resulting in the high SRP concentrations observed at the outlet. TN was most strongly predicted by the date of sample collection (March or April; $p < 0.05$), which corresponded to increasing TOC: TN ratios observed in the outlet stream with time. This was likely due to decreased nitrogen inputs from the uplands following snowmelt and denitrification in the bog. In addition, TOC, SRP, and TN concentrations increased with time in the lagg and outlet stream, which corresponded to decreasing flow at the outlet and decreasing water table levels in both watersheds. This suggests that nutrients became concentrated over time following snowmelt in both watersheds.

Bacterial Respiration

Bacterial respiration rates over 48 hours were measured as a proxy for short-term DOC biodegradability on March 24 and April 19 from various locations within both watersheds (Table 2-1; Figure 2-4B). For both watersheds, the range of bacterial respiration was lowest in subsurface flow (0.6–1.5 μM d^{-1}), higher and variable in lagg water and the outlet stream (2.4–7.2 μM d^{-1} and 0.6–5.4 μM d^{-1}, respectively), and highest but most variable in surface runoff (3.9–17.4 μM d^{-1}). Comparing between

watersheds, respiration rates were at least two times greater in the outlet stream of the coniferous upland watershed than the deciduous upland watershed. In addition, bacterial respiration rates were greater in the surface runoff of the coniferous upland watershed than in the surface runoff of the deciduous upland watershed during pre-snowmelt, but were low and variable in subsurface runoff in both watersheds during peak snowmelt (0.6 – 1.5 μM
d^{-1}).

Estimates of carbon dioxide production due to bacterial respiration from this study (assuming a respiratory quotient of oxygen to carbon of 0.8; Biddanda *et al.* 2001) were of similar magnitude to previous published measurements of mean bacterial respiration in boreal forested catchment streams (66–191 μg C L^{-1} d^{-1} or 5.5–16 μM C d^{-1}; Berggren *et al.* 2007; Berggren *et al.* 2009). Based on MANOVA results, bacterial respiration rates were strongly predicted by the type of watershed, the location within the watershed, and the interaction between the location within the watershed and the date of sample collection ($p < 0.01$). Linear regressions between chemical parameters and BR (Figure 2-5) revealed statistically significant positive correlations between BR and SRP ($r^2 = 0.41$, $p < 0.01$) and BR and TN ($r^2 = 0.77$, $p < 0.0001$).

Long-term Biodegradable DOC

Long-term biodegradable DOC (BDOC) concentrations were measured on March 24 and April 19 from various locations within both watersheds (Table 2-1; Figure 2-4C; Figure 2-4D). For this study, we defined the pool of BDOC as the amount of DOC consumed during 1-year bottle incubations. The range of BDOC concentrations were lowest in subsurface flow (69–125 μM), higher in lagg water (234–378 μM), and highest in surface runoff and the outlet stream (219–566 μM and 263–594 μM, respectively). As a percent of the total DOC concentration, BDOC in the outlet stream was consistently lower than in surface runoff (9–23% versus 17–26%, respectively). Comparing between watersheds, BDOC concentrations and BDOC as a fraction of total DOC were greater in the coniferous upland runoff than in the deciduous upland runoff. In March, BDOC in the outlet of the coniferous upland watershed (594 μM, 23% of total DOC) was greater than

BDOC in the deciduous upland watershed (372 μM, 9% of total DOC). In April, the difference in BDOC exported from the two watersheds was less significant, with BDOC slightly greater in the outlet of the deciduous upland watershed.

The range of BDOC as a percent of the total DOC concentration for all samples (9–26%) was similar to BDOC values reported for many lakes and rivers (Sondergaard and Middelboe 1995) and for peat and forest floor soil extracts (4-9%; Kalbitz *et al.* 2003). Based on MANOVA results, BDOC concentrations were strongly predicted by the type of watershed and the location within the watershed ($p < 0.01$). As a percent of the total DOC, BDOC was strongly predicted by the type of watershed, the location within the watershed, the date of sample collection, and the interaction between them ($p < 0.01$). Linear regressions between chemical parameters and BDOC (Figure 2-6) revealed a statistically significant positive correlation between BDOC in μM and DOC ($r^2 = 0.44$, $p < 0.01$) and BDOC as a percent of total DOC and SRP ($r^2 = 0.47$, $p < 0.01$).

DOC Mixing Experiment

There was no statistically significant stimulation of BR on upland and peatland DOC mixed relative to BR calculated from additive mixing of upland and peatland DOC (Figure 2-7). Mixing bog DOC with subsurface and surface DOC resulted in a slight non-significant inhibition of BR normalized to DOC concentration ($-0.06\% \pm 0.07\%$ and $-0.07\% \pm 0.15\%$, respectively) averaged over the four sample dates (April 12, 18, 25, 28). Mixing lagg DOC with subsurface and surface DOC resulted in a slight non-significant stimulation of BR normalized to DOC concentration ($+0.01\% \pm 0.05\%$ and $+0.06\% \pm 0.02\%$) averaged over the four sample dates (April 12, 18, 25, 28).

Discussion

The results from this study revealed greater BDOC concentrations and BR in the outlet of the coniferous upland watershed than in the outlet of the deciduous upland watershed. In addition, we observed the strongest correlation between BR and TN in the lagg suggesting that bacterial growth was coupled to nitrogen in these peat systems and may help to explain differences in the degradability of DOC exported from the two

watersheds. Based on the results from this study, we will argue that the DOC produced in the peatland bog was more important to downstream OC export than DOC produced in the upland due to the more significant annual hydrologic contribution from the peatland bog to downstream waters relative to the upland, and the similar biodegradability of upland- and bog-derived DOC.

Biodegradability of upland DOC

We observed greater BDOC concentrations and higher BR in the coniferous upland runoff than in the deciduous upland runoff throughout snowmelt. This result was contrary to the hypothesis that deciduous upland DOC would be more biodegradable than coniferous upland DOC based on previous studies (Aagren *et al.* 2008; Mitchell and Branfireun 2005; Mitchell *et al.* 2008b). Similar to the present work, a previous study on forest litter from central Sweden observed higher rates of DOC mineralization of spruce and pine litter leachates compared to maple and ash litter leachates (Don and Kalbitz 2005). Many factors affect the decomposition of litter and therefore the biodegradability of litter leachate, including temperature (Trofymow *et al.* 2002), litter nitrogen concentration (Mellilo *et al.* 1982), and litter water content (Chadwick *et al.* 1998; Gallardo and Merino 1993). In this study system, the coniferous upland soils were sandier and likely had faster export rates of organic matter from the root zone than the deciduous upland soils. As a result, the organic matter being exported from the coniferous upland soils was likely less degraded than from the deciduous upland soils. Since the scope of this research did not include controlling for all environmental conditions affecting the decomposition of litter, we can only speculate why DOC from the coniferous upland was more biodegradable than from the deciduous upland. However, the difference in biodegradability of DOC from uplands with different forest types observed at the watershed scale suggests that soil characteristics may play a greater role in controlling the biodegradability of exported upland DOC than litter quality.

Sources of BDOC within peatland watersheds

We compared the biodegradability of DOC from multiple locations within each peatland watershed to identify important sources of BDOC. In both watersheds, we

observed greater BDOC concentrations and greater BR in upland surface runoff compared to subsurface flow, the lagg, or the outlet. Other work has shown that DOC from the forest floor is typically less degraded than DOC from the subsoil (Qualls and Haines 1992) because much of the biodegradable DOC is consumed by soil microorganisms in upper soil horizons before DOC is transported to lower soil horizons. In addition, we also observed greater BDOC concentrations and greater BR in the surface runoff of the coniferous upland than the deciduous upland, which corresponded to greater BDOC concentrations and greater BR in the outlet of the coniferous upland watershed than in the outlet of the deciduous upland watershed. The only exception was slightly lower BDOC concentrations in the outlet of the coniferous upland watershed in April when there was little to no surface runoff and subsurface flow in the runoff collectors. Based on these results, we investigated the relative importance of upland DOC on the biodegradability of peat bog DOC through the priming effect and on the biodegradability of DOC exported from the peatland watersheds.

Priming effects of upland DOC on peat bog DOC

In a test of the priming effect of upland DOC on peat bog DOC degradation, we did not observe any stimulation of bacterial respiration on lagg or bog DOC due to addition of surface or subsurface DOC. This was in contrast to a recent study by Farjalla *et al.* (2009) that measured significantly higher BR in mixed cultures of labile DOC leached from aquatic macrophytes and refractory DOC from a tropical humic lagoon, than on labile or refractory DOC alone. One possible reason for the lack of observed priming effect in these peat systems is that the source of labile DOC (upland terrestrial plants) was much less labile than DOC produced from aquatic macrophytes. This is because aquatic macrophytes have less supportive tissues and lower C: N ratios and therefore decompose more quickly than terrestrial plants (Webster and Benfield 1986). Due to less labile organic matter, the priming effect in these peat ecosystems may not have been as significant as in aquatic ecosystems. Another reason for the lack of observed priming effect in these peat systems is that the effects of priming were very rapid and occurred prior to sample collection. In another peatland system, the reduction

of iron and sulfate at the upland-peatland interface lasted on the scale of a few hours (Mitchell and Branfireun 2005). If the transport time of samples collected from the field (~24 hours) is longer than the half life of the most labile DOC pool responsible for the priming effect, a laboratory experiment may miss short-term priming effects that occur in the natural environment. Moreover, lagg DOC may already have been mixed with and stimulated by upland DOC in the field so any further addition of upland DOC would not result in a priming effect. We recommend that future tests to quantify the priming effect of upland DOC on peat bog DOC degradation should be conducted *in situ*.

Upland contributions to exported BDOC

The relative contribution of upland BDOC to total BDOC exported from peatland watersheds is dependent on the proportion of total annual flow originating from the uplands that transports upland BDOC to the outlet. Previous studies in these two watersheds determined that upland derived runoff from the coniferous and deciduous upland watersheds was 17% and 37% of total annual watershed flow (Mitchell *et al.* 2008a), and that most (> 85%) of the annual upland derived runoff was in the form of subsurface flow (Kolka *et al.* 2001). Combining the results from these two studies, surface runoff accounts for only 2 to 5% of total annual watershed flow. Similarly, in the present study only one surface runoff sample was collected during peak snowmelt and the flow into this runoff collector was very low. Because DOC in subsurface flow is less biodegradable than DOC in surface runoff, upland sources of BDOC in these peat systems may be less than expected because the majority of upland runoff is in the form of subsurface flow. As a result, we question the importance of biodegradable upland DOC inputs to the overall carbon budget of peatland watersheds because of the minor role upland surface runoff – the source of most biodegradable DOC – plays in the annual hydrology of these watersheds. In addition, the results from this study suggest that changes in hydrology due to climate change are expected to significantly affect the amount and lability of DOC exported from these systems.

Peatland production of BDOC

We propose that the peat bog is an additional and potentially more important source of biodegradable DOC than the upland in these peatland watersheds over annual time scales. While peatlands are a major carbon sink due to low rates of decomposition in the anaerobic catotelm, a significant amount of organic matter decomposition occurs in the upper, seasonally saturated acrotelm of peat (Beer *et al.* 2008) where DOC mineralization can be very rapid (Moore and Basiliko 2006). One recent study in a Welsh peatland attributed increased DOC concentrations during storm events to drainage of the less degraded DOC-rich acrotelm (Austnes *et al.* 2010), suggesting that the peat acrotelm is a BDOC source. In addition, lower water table depths in peatlands, i.e. deeper acrotelm layer, have been associated with higher DOC concentrations and sometimes enhanced biodegradability of exported DOC (Fraser *et al.* 2001; Bubier *et al.* 2003; Kane *et al.* 2010). Another study attributed higher mercury methylation in the lagg zone relative to the peat interior to high rates of C mineralization in the lagg which may have produced labile C substrates necessary for increased methylation (Mitchell *et al.* 2008a). Moreover, carbon-14 dating of DOC exported from boreal ecosystems has shown that pore-water DOC derived from peat is very young (~5 years) compared to the DOC stored in deep peats and soils for thousands of years (Schiff *et al.* 1998; Palmer *et al.* 2001). Biodegradable DOC in freshwater lakes has been found to be positively correlated to the percent of wetland surface area within the watershed (Stets and Cotner 2008), and other studies have related DOC concentration and biodegradability in catchment streams to the proportion of wetland to forest cover (Morel *et al.* 2009; Pacific *et al.* 2010). In the same way that decomposing wetland plants are a major source of biodegradable DOC to lakes and streams, the freshly decomposing bog acrotelm and lagg may also be major sources of biodegradable DOC exported from peatland watersheds.

Biodegradability of exported DOC

However, supporting the prevailing view that uplands are the dominant source of BDOC to peatlands, we observed greater BDOC concentrations and greater BR in the surface runoff of the two uplands relative to the lagg (Figure 2-4). In addition, we found

greater BDOC concentrations and greater BR in the outlet of the coniferous upland watershed relative to the deciduous upland watershed. Because we have identified the peat bog as an additional and potentially more important source of BDOC that is exported from peatlands annually, we looked for other differences between the two watersheds that might also explain why the coniferous upland watershed exported more BDOC than the deciduous upland watershed. We hypothesized that nutrient availability within the peat bog might be important to the lability of exported organic matter because of important differences among this parameter within the two watersheds.

First, the mean TOC: TN ratio in the outlet of the deciduous upland watershed was 150% greater than in the coniferous upland watershed (133 and 89, respectively) indicating that there was less nitrogen available relative to carbon in the deciduous watershed. One possible cause for the difference in TOC: TN ratios between the two watersheds could be greater losses of nitrogen, such as denitrification, in the deciduous watershed. However, we observed nitrate concentrations in the outlet stream of both watersheds of ~30 μM on March 24 which decreased to below detection limit (< 1.4 μM) by April 19, suggesting that denitrification rates may be similar in these two watersheds. Another possible cause for the difference in TOC: TN ratios between the two watersheds could be greater inputs of nitrogen in the coniferous watershed. This was supported by TN concentrations that increased in the outlet stream of the coniferous upland watershed between March 24 and April, while TN concentrations decreased in the outlet stream of the deciduous upland watershed.

Second, BR was strongly correlated with TN suggesting that bacterial growth was limited by nitrogen ($r^2 = 0.77$, $p < 0.001$; Figure 2-5B). BR was also correlated with SRP, but less strongly than the correlation between BR and TN in these peat systems (Figure 2-5A). A similar positive correlation between BR and TN was observed in streams draining coniferous forests and peatlands in Sweden ($r^2 = 0.80$, $p < 0.01$; Berggren *et al.* 2009).

Nitrogen is often more limiting to microbial growth than phosphorus in northern temperate and boreal terrestrial ecosystems because the recently glaciated soils provide an adequate source of phosphorus for microorganisms (Newman 1995). Because peatland ecosystems are in a late successional stage, their nutrient dynamics are more terrestrial-

like than aquatic-like. DOM with high C: N is decomposed more slowly than DOM with a low C: N because the microorganisms must supplement their nitrogen requirement with an external source (Taylor *et al.* 1989). In studies of initial lignin (carbon): nitrogen of leaf litter, the decomposition rates were slowest for high C: N, or low availability of nitrogen (Mellilo *et al.* 1982). Therefore, we hypothesize that the BDOC concentrations and BR were greater in the outlet of the coniferous upland watershed than the deciduous upland watershed because nitrogen was less limiting (lower C: N) in the coniferous upland watershed.

Summary

In conclusion, we observed that the source of the most biodegradable DOC was the upland surface runoff but we also determined that upland BDOC likely plays a minor role in the overall carbon budget of peatland watersheds due to the small contribution of upland surface runoff to total annual flow (2–5%). In addition, we proposed that the peat bog may be an additional and potentially more important source of biodegradable DOC than the upland in these peatland watersheds annually, and differences in the biodegradability of DOC exported from peatland watersheds may be explained by differences in nitrogen availability in the bog and lagg. Finally, due to the important role hydrology plays in the export of BDOC from these systems – from influencing the export and degradation of DOC from upland soils to determining the proportion of upland versus bog-derived DOC in the outlet stream, changes in hydrology due to climate change are expected to significantly affect the amount and lability of DOC exported from these systems.

Table 2-1. Chemical and biodegradability characteristics

Chemical and biodegradability characteristics of dissolved organic carbon collected from the deciduous upland and coniferous upland peatland watersheds in 2009. DOC, dissolved organic carbon; TN, total nitrogen; SRP, soluble reactive phosphorus; BDOC, biodegradable dissolved organic carbon; BR, bacterial respiration.

Date	Watershed	Location	DOC (µM C)	TN (µM N)	TOC:TN (Molar)	SRP (µM P)	BDOC (µM)	BDOC (%DOC)	BR (µM O_2 d^{-1})
24-Mar	Deciduous	Surface - N	968	14	67	5.6	219	23%	3.9
		Surface - S	1,156	67	52	6.6	284	25%	4.9
		Subsurface - N	810	11	84	0.2	100	12%	0.6
		Subsurface - S	1,784	23	94	0.2	–	–	1.5
		Lagg - N	1,623	13	137	1.3	234	14%	2.4
		Lagg - S	–	–	–	–	–	–	–
		Outlet	4,123	54	79	0.8	372	9%	2.9
24-Mar	Coniferous	Surface - N	1,962	46	48	3.4	513	26%	4.8
		Surface - S	2,153	25	92	3.4	566	26%	5.7
		Subsurface - N	–	–	–	–	–	–	–
		Subsurface - S	968	16	70	0.1	125	13%	1.0
		Outlet	2,543	36	64	0.4	594	23%	5.4
19-Apr	Deciduous	Surface - N	–	–	–	–	–	–	–
		Surface - S	–	–	–	–	–	–	–
		Subsurface - N	728	13	62	0.2	69	9%	0.3
		Subsurface - S	1,024	15	60	0.2	106	10%	0.7
		Lagg - N	2,461	73	44	1.8	378	15%	7.2
		Lagg - S	1,839	56	33	0.1	256	14%	3.2
		Outlet	3,096	26	126	0.2	375	12%	0.6
19-Apr	Coniferous	Surface - N	–	–	–	–	–	–	–
		Surface - S	2,895	147	23	5.9	484	17%	17.4
		Subsurface - N	–	–	–	–	–	–	–
		Subsurface - S	815	11	86	0.1	116	14%	1.4
		Outlet	2,683	49	62	0.1	263	10%	1.8

Figure 2-1. Site locations

Topographic map of the **A.** deciduous upland and **B.** coniferous upland watersheds located 40 miles north of Grand Rapids, Minnesota. The long dashed line denotes the watershed boundary, and the short dashed line represents the peatland boundary.

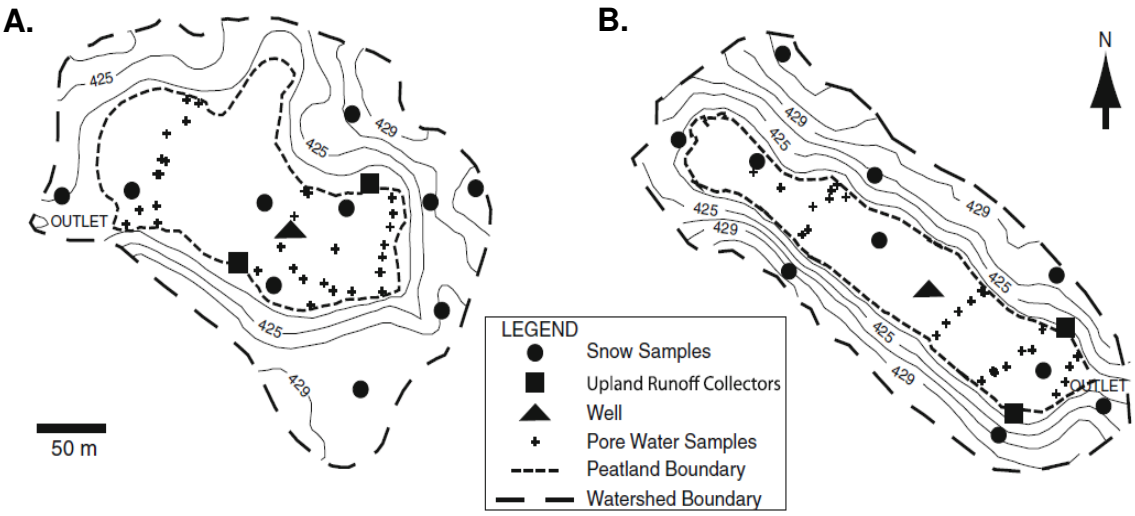


Figure 2-2. Hydrologic trends

Hydrologic trends for the deciduous upland and coniferous upland watersheds during the 2009 snowmelt. Precipitation (dashed black line). Deciduous upland watershed stream outlet discharge (gray solid line). Coniferous upland watershed stream outlet discharge (black solid line).

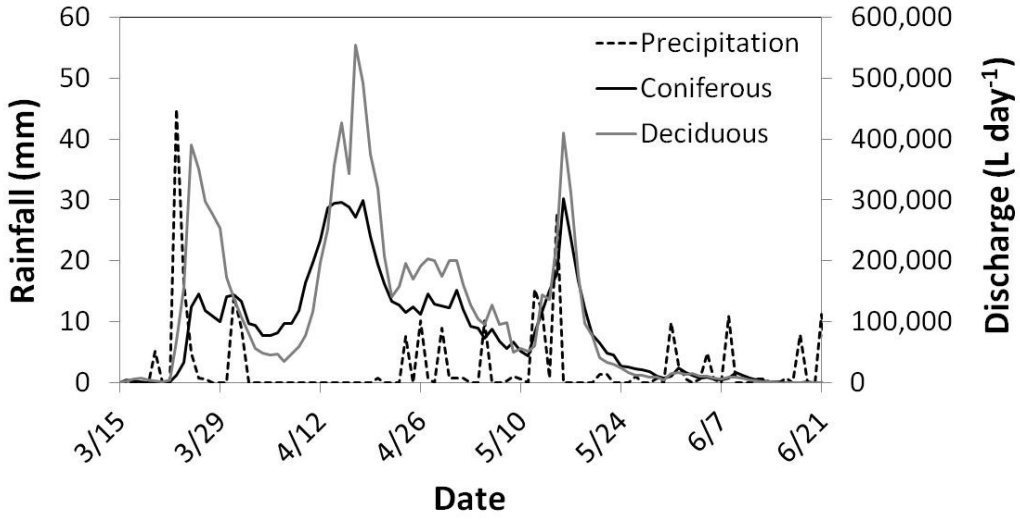


Figure 2-3. TOC and TOC: TN in the deciduous upland outlet stream

Comparison of nutrients in the outlet of the deciduous upland (open diamond) and coniferous upland (closed diamond) peatland watersheds: **A.** Total organic carbon (TOC; mM C), **B.** TOC to total nitrogen (TOC: TN, Molar), and **C.** Flow weighted TOC (kg day^{-1}).

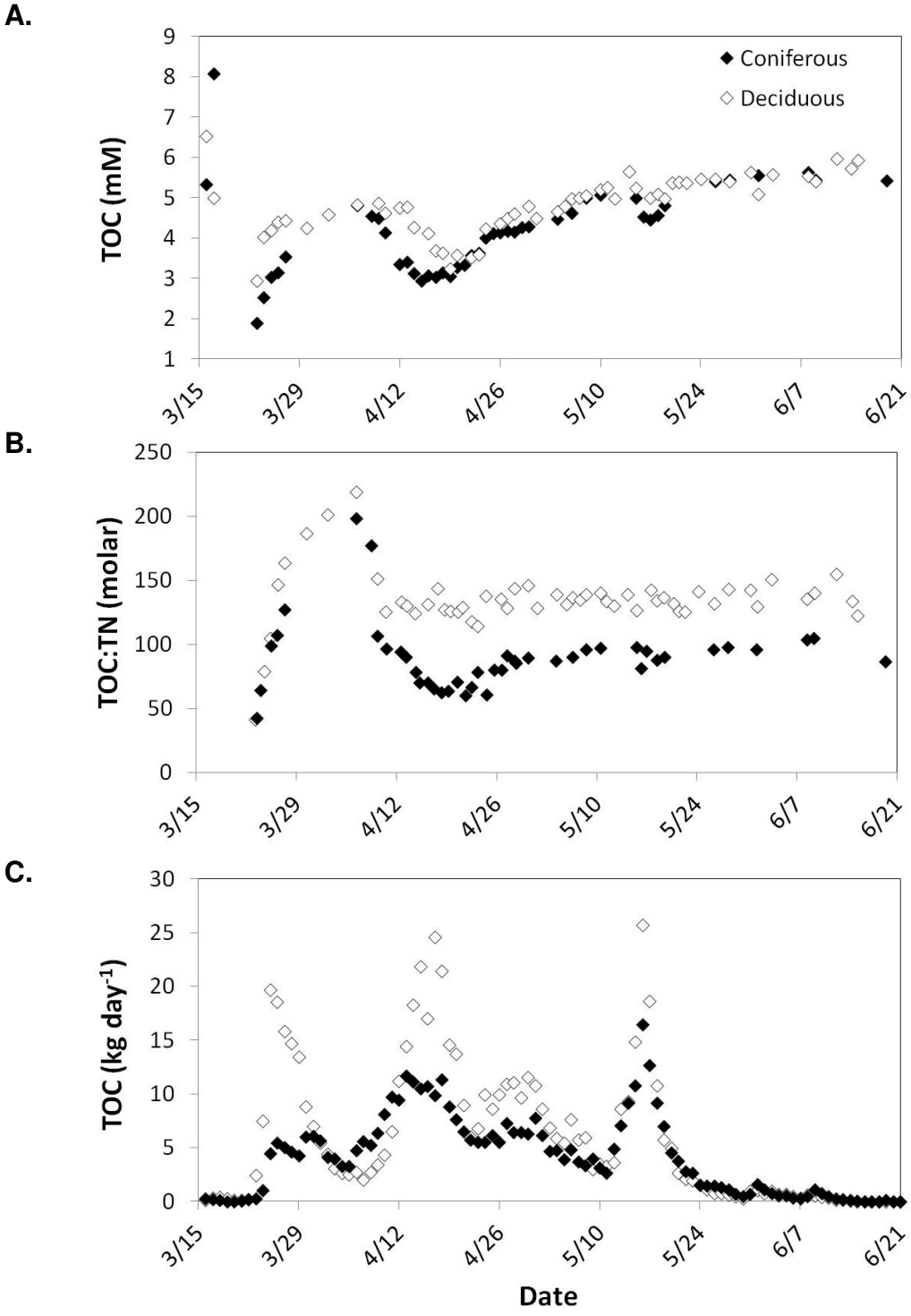


Figure 2-4. DOC, BR, and BDOC by source within the watersheds

Bar graphs of **A.** Dissolved organic carbon (DOC, µM C), **B.** bacterial respiration (BR, µM O_2 day^{-1}), **C.** biodegradable DOC (BDOC, µM C), and **D.** biodegradable DOC (BDOC, as % DOC) by location within each watershed (surface runoff, subsurface flow, lagg, and outlet).

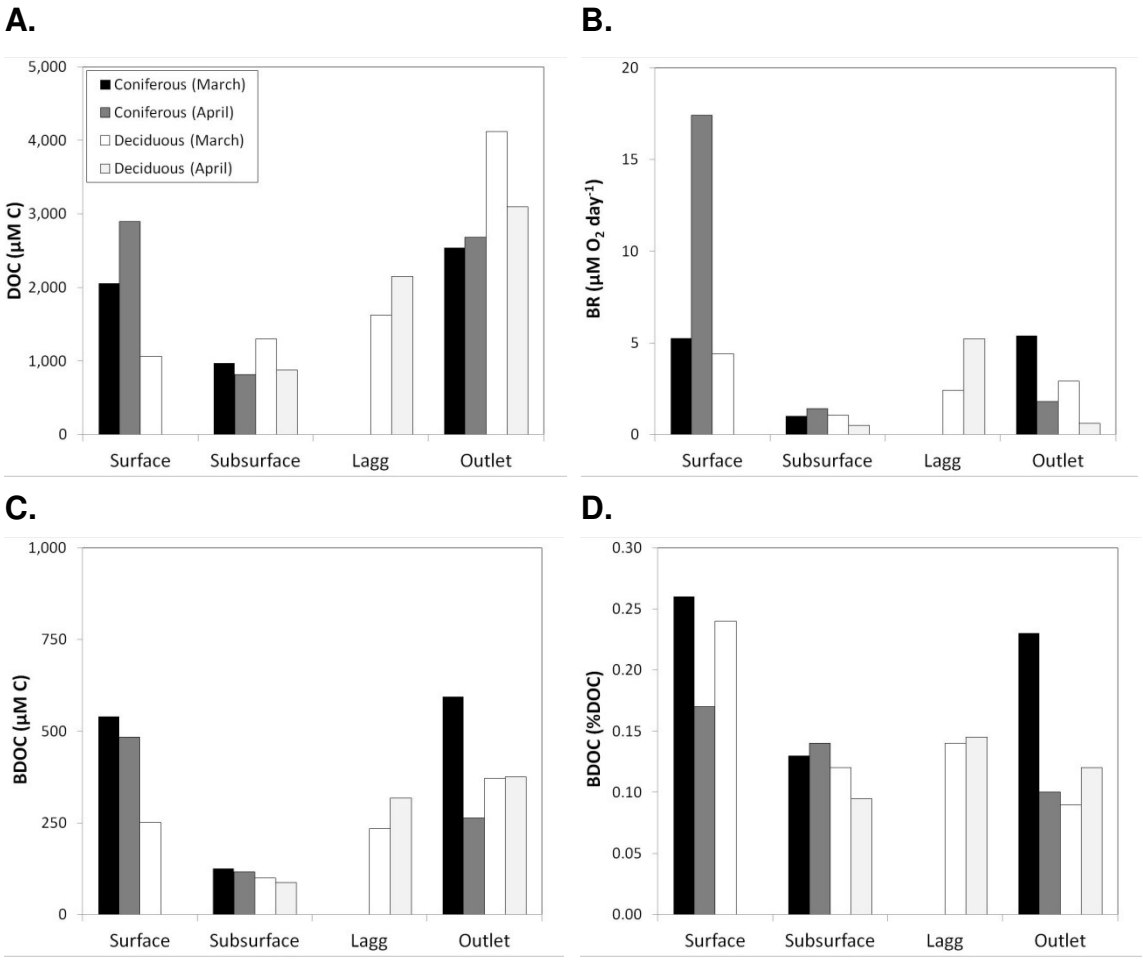


Figure 2-5. Chemical predictors of BR

Scatterplots with linear regressions of bacterial respiration, BR (μM O_2 d^{-1}) predicted by **A.** soluble reactive phosphorus, SRP (μM P; $r^2 = 0.41$, $p < 0.01$) and **B.** total nitrogen, TN (μM N; $r^2 = 0.77$, $p < 0.0001$) in two peatland watersheds.

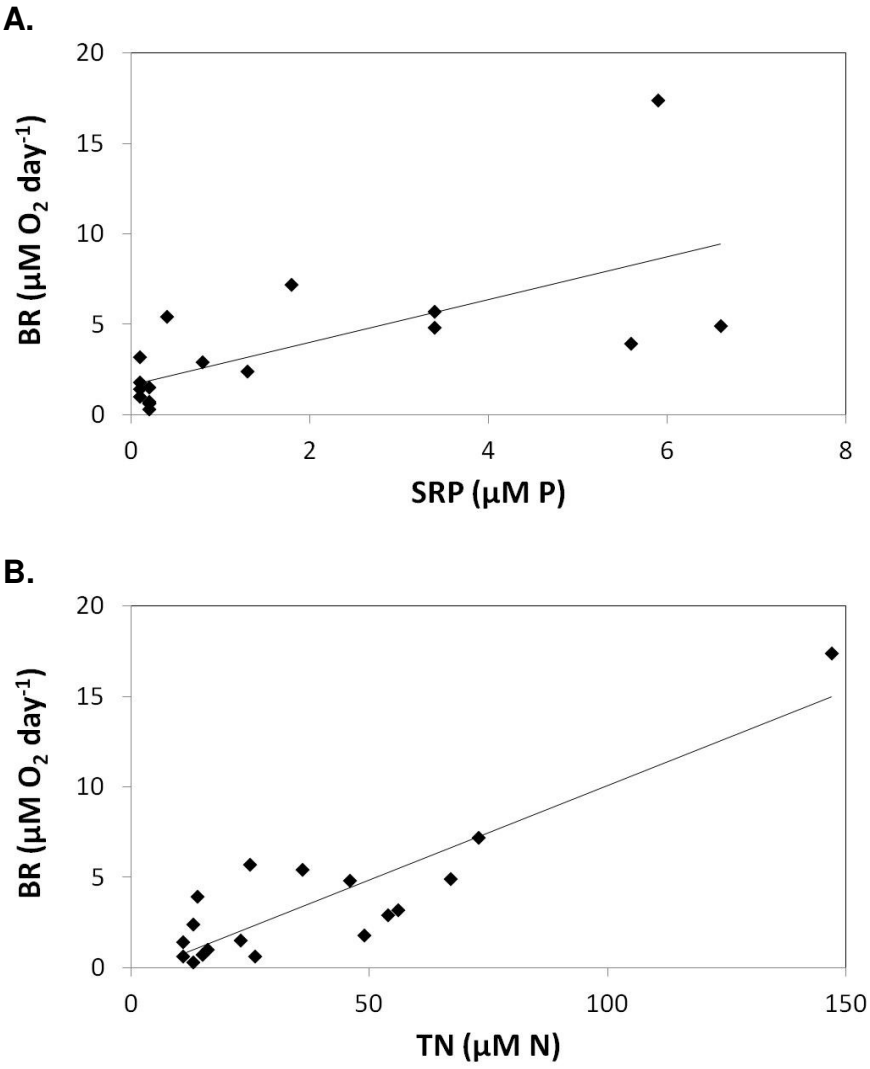


Figure 2-6. Chemical predictors of BDOC

Scatterplots with linear regressions of biodegradable dissolved organic carbon, BDOC (µM C) predicted by **A.** dissolved organic carbon, DOC (µM C; $r^2 = 0.44$, $p < 0.01$) and **B.** soluble reactive phosphorus, SRP (µM P; $r^2 = 0.44$, $p < 0.01$) in two peatland watersheds.

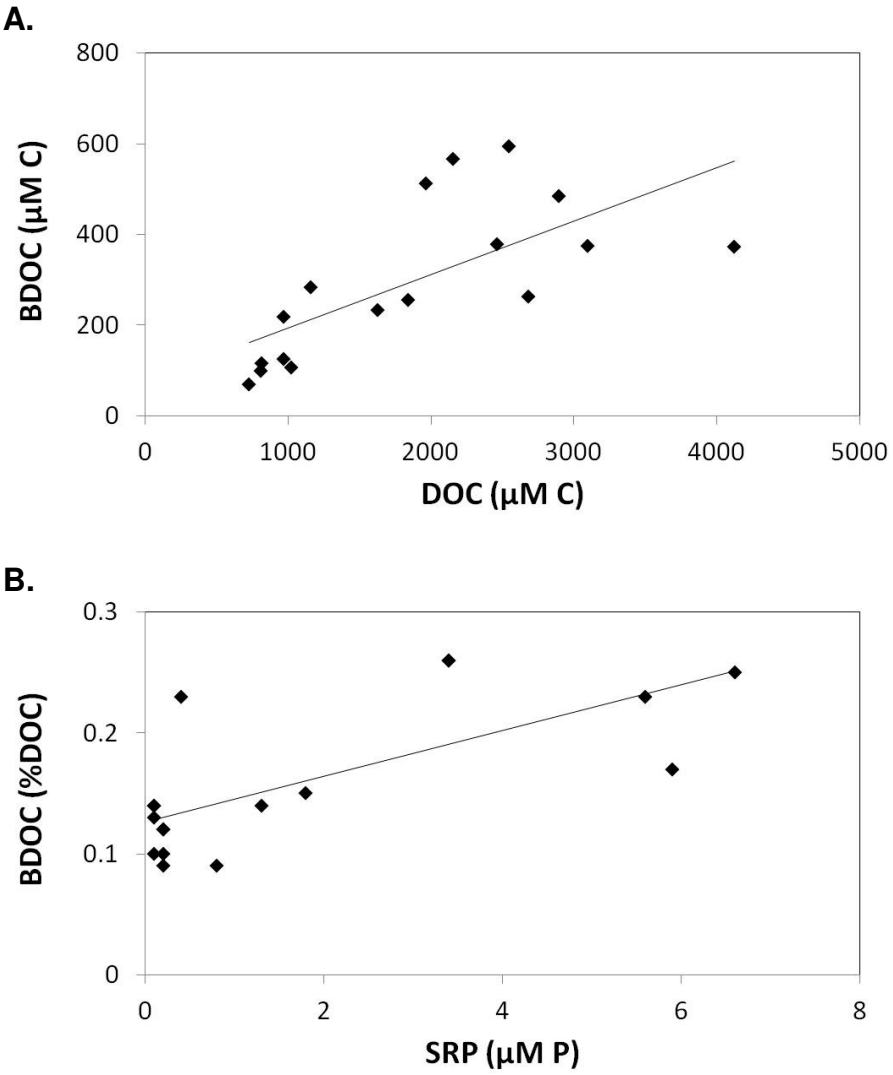
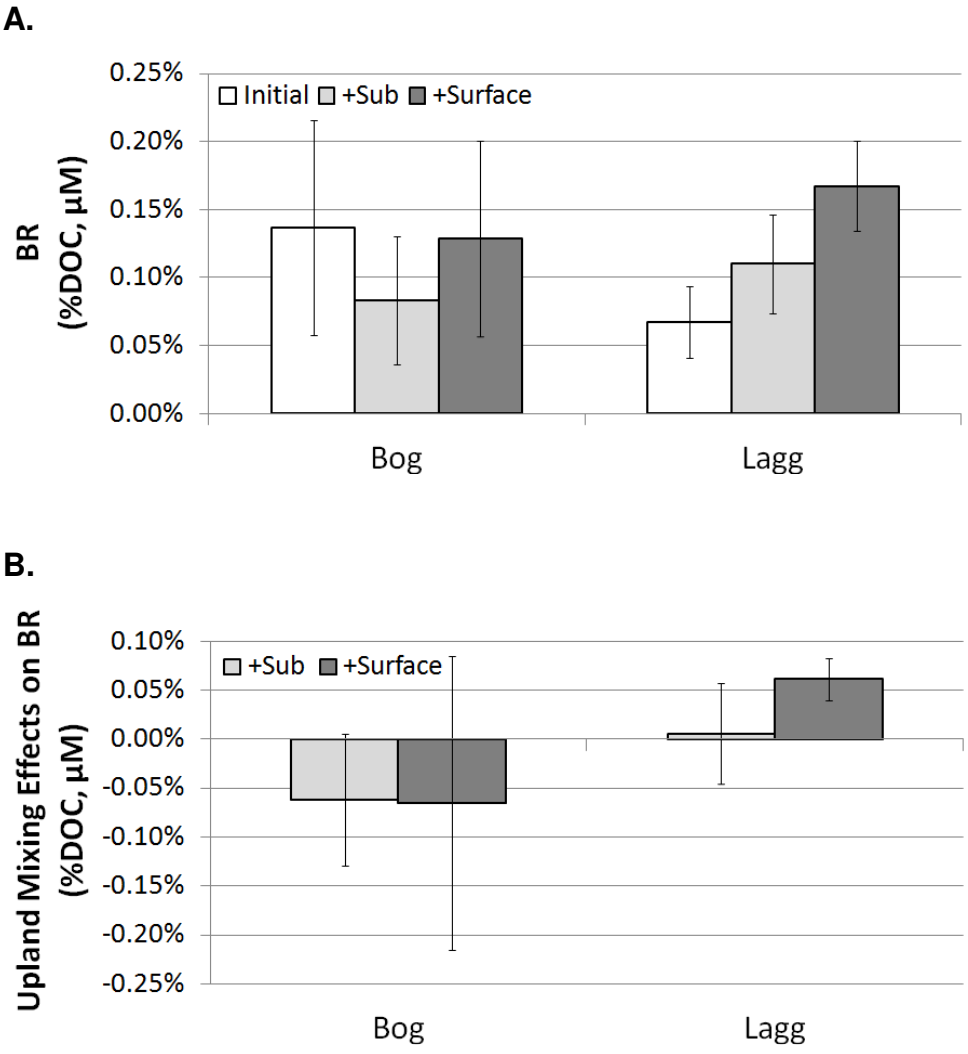


Figure 2-7. Upland mixing effects on bog and lagg BR

Bar graphs of **A.** bacterial respiration (BR; %DOC, μM) on peatland DOC alone (bog or lagg) and peatland and upland DOC mixed (peatland + subsurface or surface DOC) and **B.** the effects of mixing upland and peatland DOC represented as the difference in the measured mixed BR and the calculated BR assuming conservative mixing (i.e., no stimulation of BR due to mixing). No mixing effects were statistically significant due to large observed standard deviations.



Chapter 3 - The Importance of Photo-exposure to Carbon Dioxide Evasion from Peatland Streams

Photochemical processes play an important but previously un-quantified role in the global carbon dioxide evasion from aquatic ecosystems, especially in peatland ecosystems with high dissolved organic carbon (DOC) concentrations rich in photochemically reactive humic and phenolic compounds. We collected 74 independent samples from two Minnesota peatland watersheds from 2010-11 to estimate the extent of photochemical enhancement of bacterial respiration (BR) following 13-hour simulated sunlight exposure. We observed an upper bound to dark BR oxygen losses of ~10 μM O_2 d^{-1} across a wide range of DOC concentrations (600−7,500 μM C), but after photoexposure, BR increased to > 30 μM O_2 d^{-1} at high DOC concentrations. Photo-exposure increased dark BR by 2 to > 10-fold and increased linearly with DOC concentration. The photochemical enhancement of BR observed in these peatlands was greater than in most other freshwater ecosystems by up to 2-fold. Based on photochemical enhancement estimates from this and other studies, we estimated that approximately 0.11−0.22 Pg C yr^{-1} of the total global CO_2 evasion from inland waters (~1.4 Pg C yr^{-1}) could be attributed to the photochemical enhancement of BR in streams and rivers, or approximately 9−18% of all inland water CO_2 evasion. In addition, we hypothesize that the effects of photo-exposure on CO_2 evasion from inland waters will increase with increasing surface water DOC concentrations and hydrologic fluxes in the northern hemisphere, especially in peatland ecosystems.

Introduction

Our understanding of the role of inland waters in the global carbon cycle has changed drastically in recent years from a perspective of freshwaters as passive transporters to active processors of terrestrial carbon exports. Traditionally rivers were viewed as "gutters down which flow the ruin of continents" (Leopold *et al.* 1964). More recently, research has indicated that inland water carbon budgets are heavily subsidized by terrestrial carbon, resulting in a net release of carbon dioxide (CO_2) to the atmosphere (Pace *et al.*1994). Recent syntheses of inland water carbon budgets have estimated that the amount of carbon released into the atmosphere from inland waters is of the same order of magnitude as carbon emissions from fossil fuel combustion (~0.75–1.4 Pg C y^{-1}; Cole *et al.* 2007; Tranvik *et al.* 2009). Yet these estimates exclude the role of small streams and fluvial floodplains which could nearly double CO_2 evasion from inland waters (~1.65 Pg C yr^{-1}, Cole *et al.* 2007).

The magnitude of the total stream and river CO_2 evasion in the global carbon budget remains uncertain due to unaccounted evasion rates from regions of streams and rivers in published estimates. One early study used published pCO_2 values from 46 large rivers to extrapolate a global fluvial CO_2 evasion of ~0.3 Pg C yr^{-1} (Cole and Caraco 2001), excluding small streams and fluvial floodplains. A later study used 130 published whole-ecosystem measurements of gross primary production and respiration to estimate global CO_2 evasion rates of 0.12 Pg C yr^{-1} from streams and 0.17 Pg C yr^{-1} from rivers (Battin *et al.* 2008). However, the authors of this study also report that their fluvial CO_2 evasion rates were likely underestimated due to the exclusion of fringing floodplains and an underrepresentation of tropical systems. For example, CO_2 evasion from rivers and wetlands in the Amazon River basin alone were estimated to be ~0.5 Pg C yr^{-1} (Richey *et al.* 2002). In addition, uncertainties in fluvial CO_2 evasion rates may result from an unknown global areal extent of streams and rivers, seasonally changing fluvial channel and floodplain surface areas (Cole *et al.* 2007), and rapid anthropogenic and climate changes to fluvial ecosystems (Battin *et al.* 2009).

What is known about streams and rivers in the global carbon cycle is their role in the degradation of large amounts of labile and semi-labile carbon over short periods of

time. Most of the CO_2 evasion from the Amazon watershed was found to originate from organic matter that was respired during transit times of just 10–14 days (Richey *et al.* 2002). Similarly, between 30–70% of organic matter that enters the Hudson River was respired during transit times of ~30 days (Cole and Caraco 2001). These and other similar observations have raised the question: how can large amounts of terrestrial organic carbon enter surface waters and be decomposed during fluvial transit times of just a few weeks? One suggested answer was that photochemical processes play a key role in degrading organic carbon and enhancing rates of microbial degradation over short timescales (Battin *et al.* 2008).

Photochemical exposure times of just a few hours can degrade a significant amount of organic carbon through both direct oxidation to carbon dioxide and through alteration of organic carbon into forms more readily degradable by bacteria. Numerous studies have shown that carbon losses in lakes and rivers from photochemical degradation are comparable to carbon losses from microbial degradation (Jonsson *et al.* 2001; Granéli *et al.* 1996; De Haan 1993), and that photochemical losses of carbon can account for a significant fraction of the total carbon budget (5–20%; Amon and Benner 1996; Bertilsson and Tranvik 2000; Jonsson *et al.* 2001). Moreover, photochemical processes can modify DOC and increase rates of microbial degradation by up to 3-fold (Miller and Moran 1997; Tranvik and Bertilsson 2001; Biddanda and Cotner 2003; Obernosterer and Benner 2004; Amado *et al.* 2007) even for extensively degraded DOC (Moran *et al.* 2000). Therefore, aquatic photochemical reactions that abiotically alter the chemical structure of DOC and enhance its biological biodegradability may be an important but underestimated component of DOC losses in inland waters.

Peatlands in the northern hemisphere play a large role in the global carbon cycle relative to their size where they make up just 9.7% of the total land surface (Gorham 1995) but store between 270 and 455 Pg of C per year as peat (Gorham 1991; Turunen *et al.* 2002), approximately half of the carbon dioxide pool in the atmosphere (Solomon *et al.* 2007). Mean DOC fluxes in rivers draining peat-dominated areas are 5–10 g C m^{-2} yr^{-1}, higher than any other river system except swamps (Aitkenhead and McDowell 2000). DOC is the most important dissolved component in natural waters that absorbs

light (Zepp and Cline 1977; Wetzel 2001) and fuels photochemical reactions (Bertilsson and Tranvik 2000). While most photochemical enhancement measurements have been made in waters with DOC concentrations less than 25 mg C L^{-1}, DOC concentrations can exceed 100 mg C L^{-1} in peatlands (Gorham *et al.* 1985; Buffam *et al.* 2007; Jacobson *et al.* unpublished data). Moreover, peatland DOC contains a large fraction of partially degraded plant materials (humic compounds) that can be biologically unreactive but very photochemically reactive (Bertilsson *et al.* 1999; Anesio *et al.* 2005). And, DOC exported from peatlands is characterized by high phenol concentrations, high Fe concentrations, and low pH (Freeman *et al.* 2004; Urban *et al.* 2011), which all increase the susceptibility of DOC to photo-degradation (Canonica and Freiburghaus 2001; Gennings *et al.* 2001; Benner and Kaiser 2010). Therefore, photochemical losses of DOC may account for a much greater proportion of total DOC losses in peatland ecosystems than other freshwater ecosystems.

In this study, we collected 74 independent measurements of the photochemical enhancement of bacterial respiration in two peatland watersheds from 2010 and 2011. Our objective was to gather experimental evidence to understand the role photochemical processes play in CO_2 evasion from peatland waters and compare peatland photochemical CO_2 evasion with other inland waters. In addition, we present a preliminary estimate of the magnitude of global photochemical CO_2 evasion from peatlands and other inland waters, and highlight the growing importance of photochemical enhancement of microbial DOC degradation due to recent anthropogenic and climatic changes.

Methods

Sample collection

This study was conducted in two peatland watersheds located in the Marcell Experimental Forest, 40 miles north of Grand Rapids, Minnesota. The physical characteristics and vegetation of both watersheds have been described in great detail in previous publications (see Verry and Timmons 1982; Kolka *et al.* 2001; Mitchell *et al.* 2008b; Mitchell *et al.* 2009; Sebestyen *et al.* 2011). Briefly, the S6 watershed consists of

a 6.9-hectare coniferous upland dominated by white spruce and red pine, and a 2.0-hectare bog dominated by mature black spruce and tamarack. The S2 watershed consists of a 6.5-hectare deciduous upland dominated by mature trembling aspen and paper birch, and a 3.2-hectare bog dominated by mature black spruce (Mitchell *et al.* 2008b; Mitchell *et al.* 2009).

Water samples were collected over two snowmelt seasons from upland runoff collectors, the upland-bog interface (hereafter lagg), and the outlet. Samples were collected from both watersheds in 2010 on March 16, April 18, and June 15. Numerous lagg samples and one outlet sample were collected from both watersheds on all dates, but surface runoff and subsurface flow were only collected on March 16 due to a short snowmelt in 2010. Samples were collected from surface runoff (when flowing), subsurface flow, the lagg, and the outlet from the S2 watershed in 2011 on April 12, 18, 25, and 28. Water samples were stored in dark, polyethylene bottles and transported overnight on ice to the University of Minnesota in St. Paul for analysis. All sample filtration, photo-exposure, and bacterial respiration assays were begun within 24-48 hours of collection.

Dissolved organic carbon

Water samples were filtered through muffled Whatman GF/F filters (0.7 μm nominal pore size) using low vacuum pressure for DOC analysis. DOC samples were acidified to a pH of 2 and stored in pre-combusted vials at 4°C in the dark. DOC concentrations were measured as non-purgeable organic carbon on a Shimadzu TOC-V Auto-analyzer with potassium hydrogen phthalate as a reference standard.

Photo-exposure

Water samples were filtered through pre-rinsed Millipore membranes (0.2 μm nominal pore size) to remove > 95% of bacterial cells (Biddanda *et al.* 2001) prior to photo-exposure. In 2011, a 2×2 factorial design experiment was conducted for bacterial respiration rates on upland (surface or subsurface) and peatland (lagg or bog) DOC mixed in 1:1 ratios and on upland and peatland DOC alone for a total of 8 treatments per sample date: surface + lagg, surface + bog, subsurface + lagg, subsurface + bog, surface,

subsurface, lagg, and bog. For each water sample (50 field and 24 mixed), two quartz tubes were filled with 0.2 μm filtered water without headspace. One tube was wrapped in thick, black plastic as a dark control. Each pair of quartz tubes was placed under simulated sunlight (3 – 40W T12 fluorescent bulbs and 3 UVA-340 fluorescent tubes) for 13 hours at a constant temperature of 21 °C.

Respiration

Following photo-exposure, the remaining dark and photo-exposed water samples were amended with phosphorus (~40 μM as P) and nitrogen (~630 μM as N) based on an estimated average DOC concentration of ~4,200 μM C for most samples, for an approximate final C: N: P of 106:16:1 to control for nutrient limitation of bacterial respiration (Redfield 1958). Next, samples were inoculated with a natural bacterial community (bog or lagg water filtered through Whatman GF/B filters, nominal pore size of 1.6 μm). Bacterial respiration rates were determined from the loss of dissolved oxygen during dark incubations of sample water in sets of nine−6 mL septum vials without headspace at room temperature (~21°C). Mercuric chloride (1% by volume) was added to triplicate vials at 0, 24, and 48 hours to stop bacterial activity. Dissolved oxygen concentrations were measured on a membrane-inlet mass spectrometer using ultrapure water (< 18.2 MW-cm) in gaseous equilibrium with an air-saturated headspace at room temperature (~21°C) as a reference standard (Kana *et al.* 1994).

Statistical analyses

Multiple analyses of variances (MANOVA) were conducted in R version 2.12.1 (R Foundation for Statistical Computing, Vienna, Austria) to determine how much of the variability in DOC, dark BR, and photo-exposed BR could be explained by the watershed (S2 or S6), the date of sample collection (March 2010, April 2010, June 2010, or April 2011), the location within the watershed (surface runoff, subsurface flow, lagg, or outlet stream), or the interactions between watershed, date, and location. Linear regressions were calculated in R to determine how strongly and significantly DOC and BR (dark and photo-exposed) co-varied for all water samples. *P* values less than 0.05 were considered statistically significant.

Results

Spatial and temporal variability

We collected 74 independent measurements of DOC, dark BR, and BR following DOC photo-exposure (photo-exposed BR; Table 3-1, Figure 3-1, and Figure 3-2) from two upland-peatland watersheds in 2010 and 2011. Of all the measurements, 50 were from field samples collected over two snowmelt seasons, and an additional 24 were from laboratory mixtures of upland and peatland DOC in 2011. Based on ANOVA results, variations in mean DOC, dark BR, and photo-exposed BR were most significantly explained by the date of sample collection ($p < 0.0001$). Location within the watershed (surface runoff, subsurface flow, lagg, or outlet stream) also had a highly significant explanatory power for DOC ($p < 0.0001$) and exposed BR ($p < 0.01$), but not dark BR ($p = 0.41$). Mean DOC, dark BR, and photo-exposed BR were slightly greater in the S6 watershed than in the S2 watershed, but these differences tended to be less significant ($p < 0.05$, $p = 0.069$, and $p < 0.01$, respectively) than the differences due to the date of sample collection or the location within the watershed.

Mean DOC, dark BR, and photo-exposed BR increased with time during the snowmelt season, except for dark BR in April which was less than dark BR in March (Figure 3-1 and Figure 3-2). Solute concentrations and metabolic activity on a per volume basis tend to increase with time in these upland-peatland watersheds because evapo-transpiration is greater than precipitation following spring snowmelt resulting in the concentration of peatland waters (Urban *et al.* 2011), along with increased DOC production from bog vegetation during the growing season. Comparing between years, mean DOC, dark BR, and photo-exposed BR were less in April 2011 than in April 2010 due to dilution from a large winter snowpack and snowmelt in 2011. Comparing among watershed locations, mean DOC was lowest in upland runoff and highest in the outlet stream. Similar patterns were observed in dark BR and photo-exposed BR, except that dark BR and photo-exposed BR in bog waters were similar in magnitude to upland waters. These patterns followed that of increasing concentration of peatland waters from

source (upland and bog) to outlet due to evapo-transpiration and increased DOC production from bog vegetation within the upland-peatland watershed.

Bacterial respiration rates

Most previous studies have reported the effects of photo-exposure in terms of changes in bacterial production or bacterial growth efficiency. However, the objective of this study was to improve estimates of CO_2 evasion rates from fluvial ecosystems so the effects of photo-exposure were reported as the photochemical enhancement of bacterial respiration because most DOC consumed by bacteria is lost to respiration and does not contribute to bacterial growth (Del Giorgio and Cole 1998). In addition, other studies have reported CO_2 production rates from photo-oxidation which can be very high at water surfaces (De Haan 1993), but this study focused on the photochemical enhancement of BR which is more important averaged over the total water column (Granéli *et al.* 1996).

There was no relationship between dark bacterial respiration rates and DOC concentration (Figure 3-3A). For all DOC concentrations, there appeared to be an upper bound to dark BR oxygen losses of ~10 μM O_2 day^{-1} regardless of the watershed, the location within the watershed, or the date of sample collection (Figure 3-3A), except for five samples in the lagg and outlet stream collected in June 2010 that were characterized by DOC greater than 6,000 μM C and BR up to 20 μM O_2 day^{-1}. The June 2010 sample characteristics were more similar to exposed BR than dark BR, suggesting that these samples might have been photo-exposed in the field prior to collection later in the season. Following photo-exposure, bacterial respiration rates were positively and significantly correlated to DOC concentration ($r^2 = 0.57$, $p < 0.0001$; Figure 3-3A).

The difference between photo-exposed BR and dark BR – the photochemical enhancement of BR – was positively correlated with DOC across a wide range of DOC concentrations (Figure 3-3B). At very low DOC concentrations, photo-chemical enhancement can be negative due to competition between biological and photochemical processes for substrates (Amado *et al.* 2007; Cory *et al.* 2010). However, the overall trend we observed was increased photochemical enhancement that was proportional to

DOC concentrations. Based on results from a linear regression, 30% of the variability in photochemical enhancement was explained by DOC concentration ($r^2 = 0.30$, $p < 0.0001$).

Photo-chemical enhancement of bacterial respiration

To scale more easily across ecosystems, photochemical enhancement can also be presented as the percent increase in dark BR following photo-exposure (Table 3-1; Figure 3-4). Photochemical enhancement of BR in the two peatland watersheds was not strongly predicted by the watershed, the location within the watershed, or the date of sample collection ($p > 0.10$). Photo-exposed BR was greater than dark BR by 120% for 75% of the observations, by 240% for 50% of the observations, and by 350% for 25% of the observations. Photo-exposed BR was greater than dark BR by at least 400% for eleven samples and was representative of both years, both watersheds, and multiple locations within the watershed. Photo-exposed BR was less than dark BR for two samples: one subsurface flow in June 2010 and a mixed sample of bog and upland water in April 2011, both of which were previously identified as sources of labile DOC within the upland-peatland watershed (see Chapter 2).

Discussion

The results from this study revealed high rates of BR on photo-exposed DOC and highly positive photochemical enhancement of BR throughout peatland ecosystems (Figure 3-2). In addition, BR of photo-exposed DOC increased linearly with DOC concentration (Figure 3-3A), with photo-exposed BR greater than dark BR by at least 200% for most samples (Figure 3-4). Based on the results from this study and previous work, we demonstrate that (a) the positive effects of photo-exposure on microbial activity in peatlands are greater than in most other freshwater ecosystems; (b) the contribution of photo-chemically enhanced BR represents a significant fraction of global CO_2 evasion from streams and rivers; and (c) the effects of photo-exposure on CO_2 evasion from inland waters will increase with increasing surface water DOC concentrations and hydrologic fluxes in the northern hemisphere, especially for peatland ecosystems.

Photochemical enhancement in peatlands

The range of DOC and bacterial respiration in this study (Table 3-1) was similar to other reported measurements of DOC (Urban *et al.* 2011) and BR (69–191 μg C L^{-1} day^{-1}; Berggren *et al.* 2009) in peatland and boreal ecosystems. We observed little variation in dark BR across a wide-range of DOC concentrations and from multiple locations within two peatland watersheds (Figure 3-3A). This upper-bound to BR on peat-derived DOC without photo-exposure suggests that there is a large pool of recalcitrant DOC unavailable to microbial degradation (i.e., low BR at high DOC concentration). After photo-exposure, BR increased linearly with DOC concentration suggesting that photo-exposure increased the biological lability of DOC (higher BR at high DOC concentration). Other work has indicated that photo-exposure can enhance bacterial growth by increasing the availability of nutrients, such as phosphorus (Cotner and Heath 1990; Francko and Heath 1982) and nitrogen (Moran and Zepp 1997), but all DOC samples in this study were amended with N and P so observed enhancements in bacterial activity were most likely due to photochemical increases in the availability of carbon.

The photochemical enhancement of BR in both peatland watersheds (increases in dark BR of a median of 240% to maximum of 1,050%; Table 3-1) were greater than for previously published measurements on humic substances (18% ± 5%; Anesio *et al.* 2005), freshwater dissolved organic matter (150–260%; Biddanda and Cotner 2003), and boreal streams (170%; Bertilsson *et al.* 1999), but similar to measurements from a humic lagoon in Brazil (up to 500%; Amado *et al.* 2007). Higher photochemical enhancement of BR in peatland ecosystems than other freshwater ecosystems may be explained by high, recalcitrant DOC concentrations in peatland ecosystems (Aitkenhead *et al.* 1999). Peatland DOC is derived largely from bog vegetation that is rich in phenols and humic materials that are difficult for organisms to degrade (recalcitrant) but are capable of absorbing large quantities of solar energy and are photochemically reactive (Tranvik and Bertilsson 2001; Canonica and Freiburghaus 2001).

The effects of photochemical exposure on DOC degradation tend to be inversely related with initial DOC lability (Bertilsson *et al.* 1999). Photochemical processes alter

recalcitrant DOC molecules into forms that are more easily degradable by organisms resulting in a net increase in biological DOC degradation (Bertilsson *et al.* 1999; Benner and Kaiser 2010), while photochemical processes completely or partially oxidize labile DOC molecules and consequently compete with organisms for labile DOC substrates resulting in a net decrease in biological DOC degradation (Amado *et al.* 2007; Cory *et al.* 2010). Many studies have reported both positive and negative effects of photo-exposure on DOC degradation (Tranvik and Bertilsson 2001; Biddanda and Cotner 2003; Abboudi *et al.* 2008), but our study is the first to illustrate this as a linear relationship between DOC concentration and lability (Figure 3-3B).

We also found evidence for prior photo-exposure in the field increasing dark BR in some samples. Dark BR samples collected in June 2010 were more characteristic of other photo-exposed BR samples with high rates of BR at high DOC concentrations (Figure 3-3A). Because photochemical processes act over short time scales (hours), peatland DOC has ample time to be exposed to sunlight in the field during its approximately 2–4 day transit time to the outlet stream (Mitchell *et al.* 2009) and this may have contributed to these anomalously high dark BR rates. In other work, boreal ecosystems were found to have BR roughly proportional to the concentration of allochthonous DOC (Berggren 2009), also suggesting some prior exposure to sunlight. Prior photo-exposure likely confounds true estimates of DOC lost via direct photo-oxidation and photochemical enhancement of biological degradation. In this study, samples were collected during spring snowmelt to minimize the effects of prior photo-exposure. This may explain why our estimates of photochemical enhancement of DOC degradation are greater than previously reported estimates, and also suggests that previously reported estimates may be underestimated due to prior photo-exposure.

Contributions of photochemical enhancement to global stream CO_2 evasion

Based on the high levels of photochemical enhancement in peatlands reported in this study and elsewhere (see Appendix 1 from Mopper and Kieber 2005), we hypothesize that the contribution of photochemically enhanced BR represents a significant fraction of global CO_2 evasion from inland waters. We assigned a

photochemical enhancement range for different inland waters to determine the fraction of previously published estimates of CO_2 evasion attributable to photochemical enhancement (Table 3-2). For inland waters in peatland ecosystems, we assigned a range of photochemical enhancement of a 250–350% increase in dark BR based on the 50^{th} and 75^{th} percentile factors from this study. For other inland waters, we assigned a range of photochemical enhancement of a 50–300% increase in dark BR to represent the broad range of photochemical enhancement reported in the literature (Mopper and Kieber 2005).

We assumed that the net photochemical effects on microbial activity were positive in streams and rivers, but negligible (~0) in lakes, reservoirs and estuaries where positive and negative photochemical effects on microbial activity have been reported (Mopper and Kieber 2005). At the ecosystem level, these are reasonable assumptions because the effects of photo-exposure on microbial activity tend to decrease as water residence time increases. For example, DOC quantity and quality (i.e., color, molecular weight, and aromaticity) decreased along two downstream transects from headwaters to outlets in two U.S. river basins (Stephens and Minor 2010). We also assumed that the total inland water DOC pool would be exposed to sunlight and undergo photochemical reactions at some point during the lifetime of DOC as it travels from land to sea. This is a reasonable assumption because although photochemical activity is concentrated at water surfaces (Amon and Benner 1996; Granèli *et al.* 1996), bottom and surface waters mix on a daily to weekly basis in streams and rivers and on an annual to semi-annual basis in mid-latitude lakes and reservoirs, bringing un-exposed DOC to the surface. Moreover, the time scales on which photochemical reactions occur are very short (hours) compared to average inland water DOC half lives (4–7 years; Weyhenmeyer *et al.* 2012).

Based on the above assumptions, we estimated that approximately 0.11–0.22 Pg C yr^{-1} of the total global CO_2 evasion from inland waters (~1.4 Pg C yr^{-1}) can be attributed to photochemical enhancement of BR in streams and rivers, or approximately 9–18% of all inland water CO_2 evasion (Table 3-2). This estimate assumes that published inland water CO_2 evasion rates (Cole *et al.* 2007; Battin *et al.* 2008; Tranvik *et al.* 2009; Table 3-2) already include photochemical enhancement on respiration. If this is not the

case, photochemical enhancement of BR could *increase* current CO_2 evasion from inland waters by an additional 0.49–1.17 Pg C yr^{-1}, equivalent to a 40–95% increase in total inland water CO_2 evasion.

Finally, we hypothesize that the effects of photo-exposure on CO_2 evasion from inland waters are increasing in the northern hemisphere, especially from peatland ecosystems. First, long-term DOC concentration records reveal increasing surface water DOC concentrations in the United Kingdom (Worrall *et al.* 2003), Finland (Vuorenmaa *et al.* 2006), eastern Canada (Zhang *et al.* 2010), and Minnesota (Urban *et al.* 2011). In addition, the export of photochemically reactive phenols is expected to increase at a greater rate than total DOC in response to rising temperatures in boreal ecosystems due to increased decomposition of phenol-rich peat resulting from greater phenol oxidase activity at higher temperatures (Freeman *et al.* 2001). Higher DOC concentrations also result in a greater absorption of solar energy that fuels increased rates of photochemical activity (Bertilsson and Tranvik 2000). Results from a previous study indicated that photochemical singlet oxygen production increased proportionately to the square of the DOC concentration, suggesting that increases in DOC concentration could result in proportionately greater increases in photochemical activity (Cory *et al.* 2010). Moreover, the effects of increased DOC concentrations on photochemical activity will be pronounced in peatland and other ecosystems with high phenol concentrations, high Fe concentrations, or low pH (Freeman *et al.* 2004; Urban *et al.* 2011) which stimulate photochemical reactions (Canonica and Freiburghaus 2001; Gennings *et al.* 2001; Benner and Kaiser 2010). Therefore, we hypothesize that the photochemical enhancement of CO_2 evasion will increase with increasing DOC concentrations.

Second, human activities have increased river discharge in northern latitudes (Curry *et al.* 2003; Wu *et al.* 2005) resulting in a net decrease in fluvial residence times, especially in heavily managed ecosystems such as row crop systems (Schilling *et al.* 2008). Although biological DOC degradation in inland waters is positively correlated with residence time and decreased fluvial residence time should result in decreased biological DOC degradation (Algesten *et al.* 2004; Hanson *et al.* 2011; Weyhenmeyer *et al.* 2012), the photochemical enhancement of biological degradation works on shorter

time scales (days) potentially increasing the relative significance of photochemical processes on the degradation of DOM. Therefore, we also hypothesize that CO_2 evasion resulting from photochemical enhancement will become an increasingly important component of global fluvial CO_2 evasion as fluvial residence times decrease.

Summary

Our study revealed relatively low dark BR across a wide range of DOC concentrations but high photochemical enhancement of BR in peatland ecosystems. Using photochemical enhancement ranges from this and other studies, we estimated that approximately 9–18% of global CO_2 evasion from inland waters could be attributed to photochemical enhancement of BR in streams and rivers. In addition, the impact of photochemical enhancement is likely to increase with increasing surface water DOC concentrations and hydrologic fluxes in the northern hemisphere, particularly in peatland ecosystems but also in heavily managed ecosystems such as row crop systems. One of the important climate feedback implications of this work is that photochemical processes have the potential to move organic matter from recalcitrant to labile pools at rates much faster than changes in biological processes in response to global warming, potentially increasing both the extent and variability of DOC degradation. Future work is needed to better quantify the photochemical enhancement of CO_2 evasion across a wide range of DOC concentrations and in other inland waters to determine the extent that prior photo-exposure may contribute to CO_2 evasion from inland waters.

Table 3-1. Summary table of DOC and BR grouped by watershed, watershed location, and sample date

Mean (± standard deviation) dissolved organic carbon concentrations (DOC, μM C), dark bacterial respiration (BR_{dark}, μM O_2 day^{-1}) rates, and bacterial respiration rates on photo-exposed DOC (BR_{exp}, μM O_2 day^{-1}) grouped by watershed (S2 and S6), location within the watershed (upland, lagg, bog, and outlet), date of sample collection (March 2010, April 2010, June 2010, and April 2011), and sample type (field and mixed). The effects of photo-exposure on BR are shown as the difference between BR_{exp} and BR_{dark} ($BR_{exp-dark}$, μM O_2 day^{-1}) and as the photochemical enhancement (PE) of BR_{dark} shown as the percent change in BR_{dark} *(%Δ BR_{dark})* following photo-exposure.

			DOC *(μM C)*	**BR_{dark}** *(μM O_2 d^{-1})*	*(%DOC μM)*	**BR_{exp}** *(μM O_2 d^{-1})*	(%DOC *μM*)	**BR_{exp}–BR_{dark}** *(μM O_2 d^{-1})*	**PE** *(%Δ BR_{dark})*
Field Samples	Location	Upland (13)	1,590 (570)	4.2 (2.5)	0.27 (0.16)%	9.8 (5.6)	0.64 (0.25)%	5.7 (5.4)	+200 (80)%
		Lagg (27)	4,270 (1,790)	5.7 (4.7)	0.14 (0.10)%	16.6 (6.8)	0.46 (0.20)%	11.0 (4.8)	+310 (100)%
		Bog (4)	2,530 (430)	3.2 (1.3)	0.14 (0.08)%	10.0 (4.3)	0.40 (0.13)%	6.8 (5.6)	+360 (370)%
		Outlet (6)	5,310 (1,650)	7.9 (7.0)	0.14 (0.09)%	20.0 (5.8)	0.41 (0.11)%	12.2 (4.8)	+310 (140)%
	Water-shed	S2 (38)	3,250 (1,900)	4.7 (3.9)	0.17 (0.13)%	13.3 (6.6)	0.49 (0.22)%	8.6 (5.1)	+300 (150)%
		S6 (12)	4,520 (1,900)	7.4 (5.5)	0.18 (0.11)%	19.3 (6.8)	0.51 (0.21)%	11.9 (6.1)	+240 (40)%
	Date	2010 March (16)	2,470 (940)	4.8 (1.5)	0.23 (0.13)%	14.7 (3.2)	0.68 (0.18)%	9.9 (3.8)	+260 (60)%
		2010 April (10)	5,190 (770)	3.9 (1.1)	0.08 (0.04)%	15.2 (4.3)	0.31 (0.10)%	11.3 (4.1)	+320 (40)%
		2010 June (10)	5,920 (1,660)	11.9 (6.1)	0.23 (0.17)%	23.3 (8.4)	0.42 (0.12)%	11.5 (8.4)	+160 (70)%
		2011 April (14)	1,950 (730)	2.3 (1.1)	0.14 (0.08)%	8.4 (3.9)	0.48 (0.22)%	6.0 (4.3)	+380 (220)%
Mixed Samples (24)			1,570 (380)	2.2 (1.0)	0.15 (0.09)%	7.3 (2.5)	0.50 (0.18)%	5.2 (2.7)	+360 (210)%

Table 3-2. The contribution of photochemical enhancement (PE) to global inland water CO_2 evasion estimates

We assigned a photochemical enhancement range for different inland waters to determine the fraction of previously published estimates of CO_2 evasion attributable to photochemical enhancement. For inland waters in peatland ecosystems, we assigned a range of photochemical enhancement of a 250-350% increase in dark BR based on the 50th and 75th percentile factors from this study. For other inland waters, we assigned a range of photochemical enhancement of a 50-300% increase in dark BR to represent the broad range of photochemical enhancement reported in the literature (Mopper and Kieber 2005). We assumed that the net photochemical effects on microbial activity were positive in streams and rivers, but negligible (~0) in lakes, reservoirs and estuaries where positive and negative photochemical effects on microbial activity have been reported (Mopper and Kieber 2005). We also assumed that the total inland water DOC pool would be exposed to sunlight and undergo photochemical reactions at some point during the lifetime of DOC as it travels from land to sea. The global CO_2 evasion from inland waters that can be attributed to photochemical enhancement of BR in streams and rivers was reported in Pg C yr^{-1} and as the percent of total global CO_2 evasion from inland waters. Data sources are listed below the table.

	Surface Area		CO_2 Evasion	Fraction of Total Area		PE Range		CO_2 Evasion due to PE	
	× 10^6 km^2	*% of Total*	*Pg C yr^{-1}*	*Peatland*	*Non-peatland*	*Peatland*	*Non-peatland*	*Pg C yr^{-1}*	*% of Total*
Streams	0.275[1]	0.18%	0.12[1]	9.7%	90.3%	250%–350%	50%–300%	0.044–0.090	37–75%
Rivers	0.295[1]	0.20%	0.17[1]	9.7%	90.3%	250%–350%	50%–300%	0.063–0.128	37–75%
Lakes	4.2[2]	2.82%	0.53[3]				~0		
Reservoirs	0.26[2]	0.17%	0.28[4]				~0		
Estuaries	0.94[2]	0.63%	0.13[1]				~0		
Land Total	148.94	100.00%	1.13[±]					0.11–0.22	9–18%

[1] Battin *et al.* 2008
[2] Downing *et al.* 2006
[3] Tranvik *et al.* 2009
[4] Cole *et al.* 2007
[±]Note that the total CO_2 evasion reported in this table is less than the total reported in Tranvik *et al.* 2009 (1.4 Pg C yr^{-1}). The authors were unable to separate the Tranvik *et al.* 2009 total by all inland water types. References used to derive the Tranvik *et al.* 2009 estimate were used instead.

Figure 3-1. Box and whisker plots of DOC and BR grouped by watershed, watershed location, and sample date

Box and whisker plots of **A.** peatland dissolved organic carbon (DOC, μM C) and **B.** bacterial respiration rates (BR, μM O_2 day^{-1}) grouped by the date of sample collection (March 2010, April 2010, April 2011, and June 2010), the location within the watershed (bog, lagg, outlet stream, and upland runoff), and the watershed (S2 and S6).

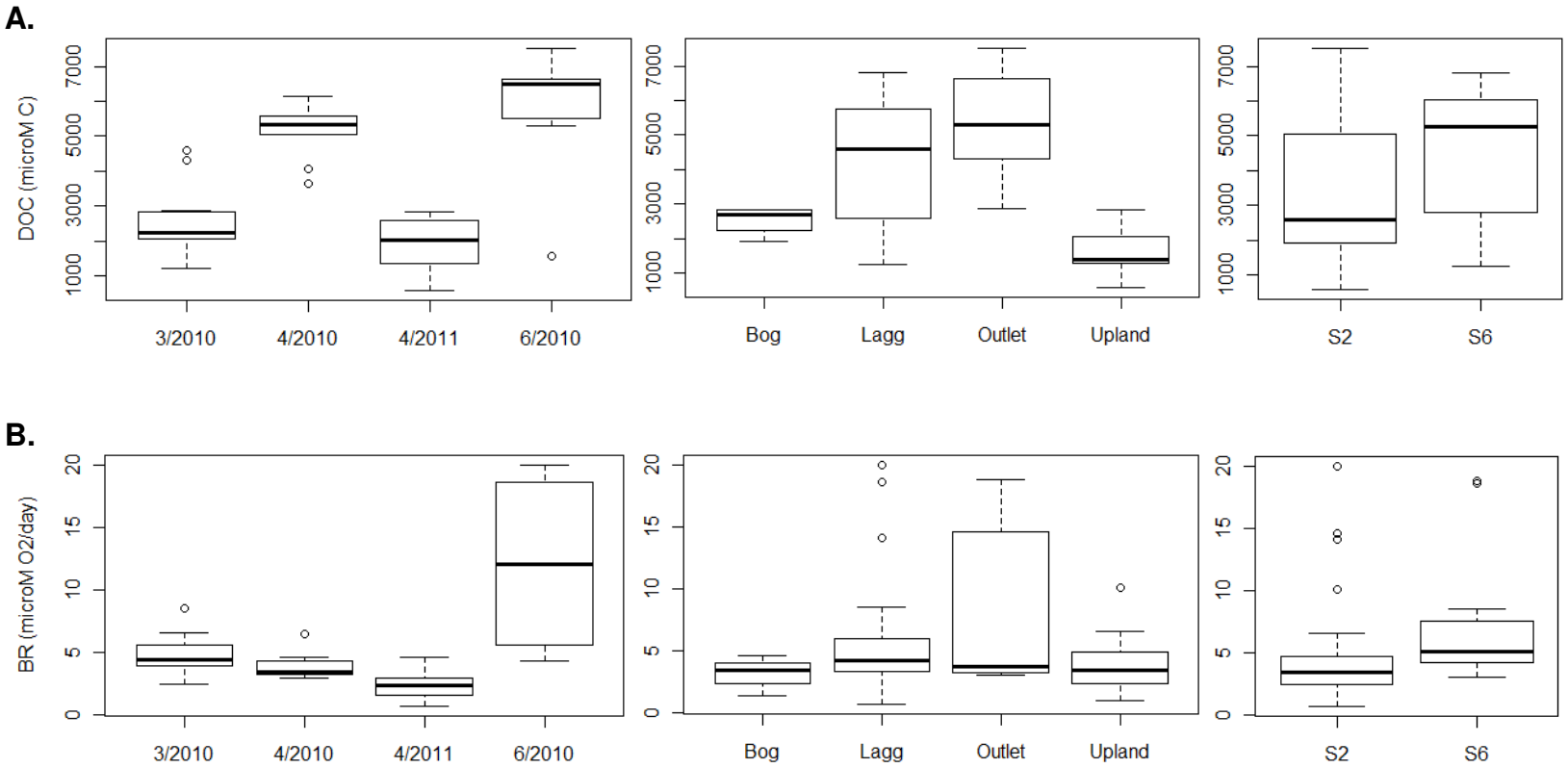


Figure 3-2. Box and whisker plots of photo-exposed BR grouped by watershed, watershed location, and sample date

Box and whisker plots of **A.** bacterial respiration (BR) rates on photo-exposed DOC (BRexp, μM O_2 day^{-1}) and **B.** the photochemical enhancement ratio of BR on exposed DOC to BR on dark DOC (BRexp/BRdark) grouped by the date of sample collection (March 2010, April 2010, April 2011, and June 2010), the location within the watershed (bog, lagg, outlet stream, and upland runoff), and the watershed (S2 and S6).

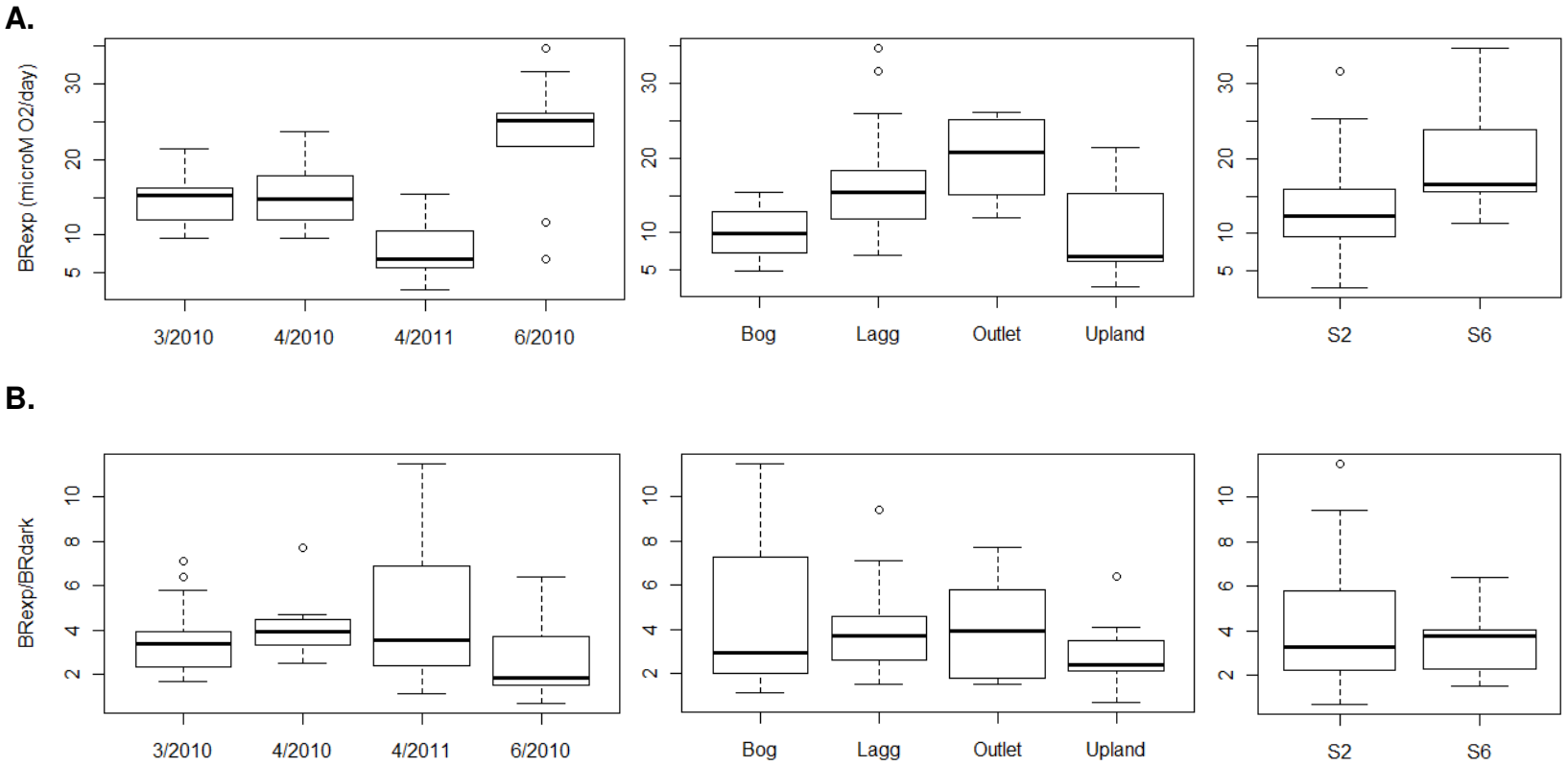


Figure 3-3. Scatterplots of dark and exposed BR versus dark DOC

A. The relationship between dark dissolved organic carbon concentration (DOC_{dark}, µM C) and bacterial respiration (BR, µM O_2 day^{-1}). Exposed BR (open circles, $r^2 = 0.57$, $p < 0.0001$); dark BR (closed circles), except dark BR from June 2010 which are denoted by "**x**". **B**. The relationship between dark DOC concentration (DOC_{dark}, µM) and the enhancement of BR on photo-exposed DOC relative to BR on dark DOC (as a percent of DOC, µM); $r^2 = 0.30$, $p < 0.0001$.

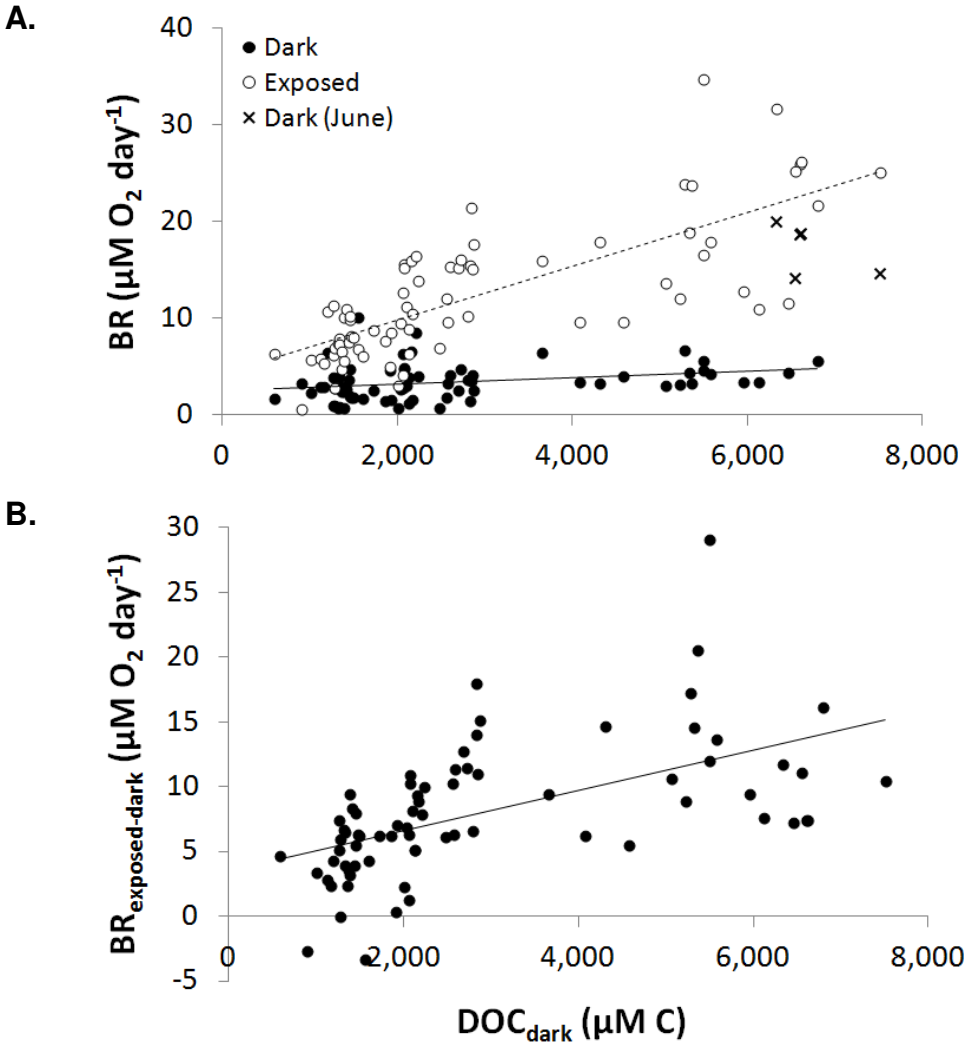
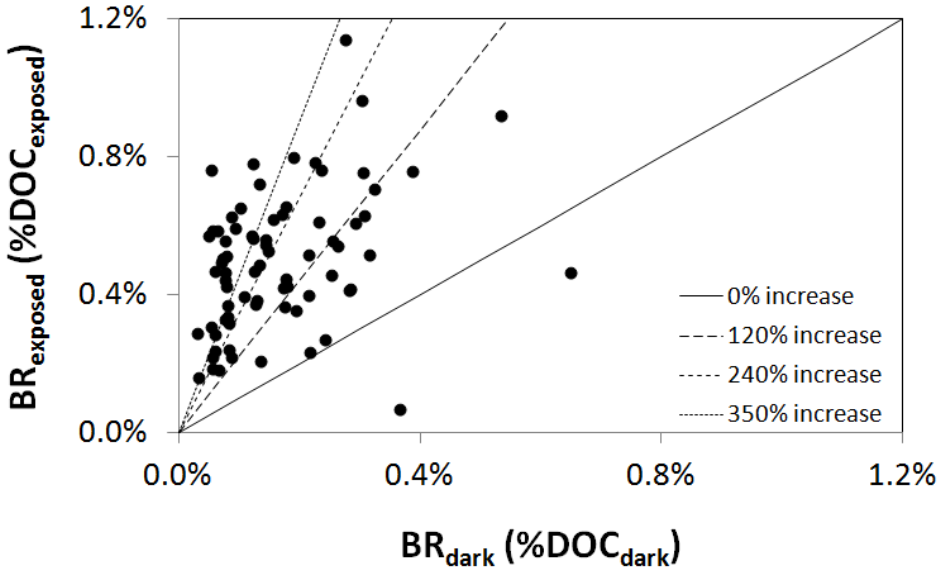


Figure 3-4. Scatterplots of exposed BR versus dark BR

The relationship between bacterial respiration (BR) on dark dissolved organic carbon (DOC; as a percent of dark DOC, µM) and BR on photo-exposed DOC (as a percent of photo-exposed DOC, µM) in two peatland watersheds. Lines are shown representing equal BR_{exp} and BR_{dark} (0% increase in dark BR, solid line), the 25th percentile of BR_{exp} relative to BR_{dark} (120% increase in dark BR, long dashed line), the 50th percentile of BR_{exp} relative to BR_{dark} (240% increase in dark BR, short dashed line), and the 75th percentile of BR_{exp} relative to BR_{dark} (350% increase in dark BR, dotted line).



Conclusions

In conclusion, we observed that the source of the most biodegradable DOC in peatlands was the upland surface runoff but we also determined that upland BDOC likely plays a minor role in the overall carbon budget of peatland watersheds due to the small contribution of upland surface runoff to total annual flow (2–5%). We proposed that the peat bog may be an additional and potentially more important source of biodegradable DOC than the upland in these peatland watersheds annually, and differences in the biodegradability of DOC exported from peatland watersheds may be explained by differences in nitrogen availability in the bog and lagg. And, due to the important role hydrology plays in the export of BDOC from these systems – from influencing the export and degradation of DOC from upland soils to determining the proportion of upland versus bog-derived DOC in the outlet stream – changes in hydrology due to climate change are expected to significantly affect the amount and lability of DOC exported from these systems.

Moreover, we found that SUVA, a measurement broadly used in ecology and environmental engineering and fairly simple to obtain, is an excellent predictor of the amount of long-term BDOC concentrations in lake ecosystems. Future studies should investigate whether this relationship is applicable in other lake and freshwater ecosystems with different climatic patterns, terrestrial vegetation, terrestrial soils, and lake residence times. In addition, we show that the best predictors of BDOC depend on the time scale of DOC degradation, most likely due to the preferential degradation of labile DOM pools before more recalcitrant DOM pools by microorganisms.

Finally, we observed relatively low dark BR across a wide range of DOC concentrations but high photochemical enhancement of BR in peatland ecosystems. Using photochemical enhancement ranges from this and other studies, we estimated that approximately 6–13% of global CO_2 evasion from inland waters could be attributed to photochemical enhancement of BR in streams and rivers. In addition, the impact of photochemical enhancement is likely to increase with increasing surface water DOC concentrations and hydrologic fluxes in the northern hemisphere, particularly in peatland

ecosystems but also in heavily managed ecosystems such as row crop systems. One of the important climate feedback implications of this work is that photochemical processes have the potential to move organic matter from recalcitrant to labile pools at rates much faster than changes in biological processes in response to global warming, potentially increasing both the extent and variability of DOC degradation. Future work is needed to better quantify the photochemical enhancement of CO_2 evasion across a wide range of DOC concentrations and in other inland waters to determine the extent that prior photo-exposure may contribute to CO_2 evasion from inland waters.

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