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Limitations on using CDOM as a proxy for DOC in temperate lakes

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A B S T R A C T

Colored dissolved organic matter (CDOM) has been widely studied as part of efforts to improve understanding of the aquatic carbon cycle, by laboratory, *in situ*, and remote sensing methods. We studied ecoregion-scale differences in CDOM and dissolved organic carbon (DOC) to understand variability in organic matter composition and the use of CDOM as a proxy for DOC. Data from 299 lakes across the U.S. Upper Midwest showed that CDOM, measured as absorptivity at 440 nm (a_{440}), correlated strongly with DOC ($R^2 = 0.81$, $n = 412$). Colored lakes in the Northern Lakes and Forests (NLF) ecoregion drove this relationship. Lakes in the North Central Hardwood Forests (NCHF) had low color (most had $a_{440} < 3\ m^{-1}$) and weaker CDOM-DOC relationships ($R^2 = 0.47$). Spectral slopes and specific ultraviolet absorbance (SUVA), indicated relatively low aromaticity and non-terrestrial DOM sources in low color lakes. Multiple regression analyses that included total dissolved nitrogen (TDN) and CDOM, but not chlorophyll a, improved DOC estimates in low color lakes, suggesting a dominant contribution of non-planktonic sources of low color DOM in these lakes. Our results show that CDOM is a reliable, regional proxy for DOC in lakes where forests and wetlands dominate the landscape and the DOM is primarily terrestrial in origin. Mapping of lake DOC at broad spatial scales by satellite-derived CDOM has lower accuracy in low color lakes.

1. Introduction

Optical properties of dissolved organic matter (DOM) are widely used to estimate the composition and quantity of dissolved organic carbon (DOC) in aquatic systems (Helms et al., 2008; Massicotte et al., 2017). In particular, chromophoric (or colored) dissolved organic matter (CDOM), measured as light absorption at a specific wavelength (e.g., 350, 375, 420, or 440 nm), often correlates strongly with bulk DOC in a variety of freshwater and estuarine systems (Osburn and Stedmon, 2011; Spencer et al., 2012). Thus, CDOM has been used as an inexpensive and convenient proxy for DOC in applications such as satellite remote sensing across broad spatial scales (Del Castillo and Miller, 2008; Griffin et al., 2018; Kutser et al., 2015; Olmanson et al., 2016) and *in situ* sensors in streams (Pellerin et al., 2012; Sobczak and Raymond, 2015).

DOM originates from a variety of sources, including natural autochthonous and allochthonous sources, as well as anthropogenic sources such as wastewater effluent and agricultural and urban runoff. CDOM largely derives from leachate of decayed terrestrial and aquatic vegetation; in waters with relatively low CDOM levels autochthonous production of organic matter by phytoplankton and aquatic macrophytes is an important CDOM source. DOM consists of many diverse molecules (Sipler et al., 2017), and aromatic compounds are important components of CDOM (Hur et al., 2009; Yang et al., 2015), which is strongly related to the fraction of hydrophobic organic acids. By absorbing light in ultraviolet and visible wavelengths, CDOM plays a major role in lake functioning by reducing the depth at which photosynthesis can occur (Karlsson et al., 2015; Koizumi et al., 2018; Thrane et al., 2014), regulating temperature (Caplanne and Laurion, 2008; Houser, 2006), and shielding organisms from harmful UV irradiation (Leavitt et al., 2003; Sommaruga, 2001). Additionally, CDOM and associated humic substances can negatively affect water treatment processes and treated water quality, including increasing coagulant demand, fouling filtration membranes, and reacting with chlorine to form potentially toxic disinfection byproducts (Edzwald

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and Tobiason, 1999; Lee et al., 2004; Liang and Singer, 2003; Stevens et al., 1976). CDOM has further been associated with mobilization of metals (McKnight and Bencala, 1990) and hydrophobic organic compounds. Modification of landscapes, such as draining of wetlands for agriculture and urban land uses, has strong effects on the chemical composition of DOM and CDOM in rivers and lakes (Schindler, 2009; Wilson and Xenopoulos, 2009). In light of rapidly changing climate and land use in many temperate watersheds, an improved grasp of CDOM and DOC dynamics in lakes is essential to understanding whole-ecosystem functioning.

Over the past ~15 years, many studies have demonstrated that satellite remote sensing can be used to conduct synoptic “sampling” of CDOM across broad spatial scales, in both freshwater (e.g., Zhu et al., 2014; Olmanson et al., 2016b; Chen et al., 2017; Spyrakos et al., 2017) and marine ecosystems (e.g., Del Castillo and Miller, 2008; Xie et al., 2012; Fichot et al., 2016). Regression-based models relating laboratory-measured CDOM to satellite reflectance can result in large datasets that track CDOM through time and space (Kutser, 2012). These empirical models rely upon relationships between reflectance in the visible or near infrared spectrum to absorption at UV or blue wavelengths, which are influenced by both the quantity and composition of DOM. As ongoing work in our lab shows, remote sensing CDOM models generally must be calibrated on regional to local scales, as differences in atmospheric corrections and water quality parameters (such as suspended solids mineralogy, particle size, and algal communities) make it difficult to transfer models between regions (Brezonik et al., 2015; Griffin et al., 2018). Although CDOM itself is an inherently important variable due to its effects on light and photochemistry (Karlsson et al., 2009), CDOM is widely used to estimate DOC for study of freshwater carbon cycling (Chen et al., 2017; Spencer et al., 2012; Tehrani et al., 2013). In many riverine systems, estimation of DOC from CDOM works well (Stedmon et al., 2011; Yamashita et al., 2011), although important exceptions occur especially in large, impounded rivers (e.g., the St. Lawrence, Columbia, and Colorado Rivers; Spencer et al., 2012). Lakes and lake-influenced rivers may have weaker CDOM-DOC relationships owing to production of low-color, autochthonous DOM from phytoplankton and macrophytes. As well, inputs of low-color DOM from wastewater effluent or agricultural run-off to surface waters may shift the CDOM-DOC relationship from that found in forested watersheds.

Here, we examine ecoregional variability in CDOM properties using a multi-year, multi-season dataset of lake samples across two north temperate ecoregions in the U.S. Upper Midwest: the North Central Hardwood Forests (NCHF) and Northern Lakes and Forests (NLF). We aimed to determine general conditions in which CDOM may be used as a reliable proxy for DOC on broad, regional scales. Our results indicate that CDOM and DOC are strongly related in highly colored lakes and the NLF generally, but DOC in low color lakes cannot be predicted reliably from CDOM alone.

2. Materials and methods

2.1. Water sample collection and processing

We collected 412 samples from 2014 to 2016 from 299 lake sites in the NLF and NCHF, which span the Upper Midwest states of Minnesota, Wisconsin, and Michigan (USA; Fig. 1). The NLF is heavily forested (49%), with many wetlands (27%) and areas of open water (5%) as calculated from the 2011 National Land Cover Data set (Homer et al., 2015). Developed land accounts for 4% of the NLF, and agriculture covers another 7% of the land surface. In contrast, 48% of the NCHF is used for agricultural purposes and 9% is urban, while wetlands only account for 10% of land cover and forests account for 26%. Many lakes were sampled repeatedly, 2–6 times, over the course of three years. Water was collected from ~0.25 m below the lake surface using acid-washed and triple-rinsed polycarbonate or high-density polyethylene (HDPE) bottles. The bulk of the lake water samples (301 out of 412) were collected by University of Minnesota personnel with the remainder collected by partner organizations. Samples for chlorophyll and dissolved constituents were filtered within 24 h of collection. The dissolved fraction was obtained by filtering the water through 0.45 μm Geotech High Capacity capsule filters. Samples for DOC and total dissolved nitrogen (TDN) were acidified using 2 M HCl and stored in pre-ashed 20 mL glass bottles at 4 °C. Filtered water for measurement of CDOM absorbance spectra was stored in pre-ashed 40 mL amber glass bottles, with no headspace. Samples for dissolved inorganic carbon (DIC) were filtered and stored in pre-ashed 20 mL glass bottles with no headspace. Chlorophyll-*a* was isolated from the water by vacuum filtering onto 0.22 μm cellulose nitrate filters and stored frozen until analysis. For the sampling done by partner organizations, water samples were filtered in the field with syringe-mounted Whatman GF/F filters, and DOC and TDN samples were placed in HDPE bottles and then frozen for storage. Other dissolved constituents were stored in the same manner as the UMN samples as described above. Samples collected by partner organizations were shipped overnight to the University of Minnesota for subsequent analyses. Chlorophyll-*a* was not collected by the partner organizations.

2.2. Sample analysis

DOC and TDN were measured on a Shimadzu TOC L CSN analyzer, after acidification and sparging. DIC was calculated as the difference in carbon between DOC and non-acidified water samples analyzed on the Shimadzu. UV–visible light absorbance of filtered water samples ($\lambda = 200–800$ nm) was measured using a Shimadzu 1601UV-PC dual beam spectrophotometer through 1 or 5 cm quartz cuvettes, against a nanopure water blank. Absorbance values were converted to absorptivity (absorption coefficients) using:

$$a(\lambda) = 2.303A(\lambda)\,/l \tag{1}$$

where: a is the absorption coefficient at a given wavelength (λ), A is absorbance at wavelength λ, and l is the cell path length (m). Absorbance scans were blank-corrected before conversion. Specific UV absorbance (SUVA) was calculated by dividing UV absorbance (A) at 254 nm by DOC concentration (in mg/L), after correcting for the cell path length. Spectral slope parameters (S) were calculated using a nonlinear fit of an exponential function to absorption in the ranges 275–295 nm, 350–400 nm, and 400–460 nm, as in the following equation:

$$a(\lambda) = a(\lambda_{ref})e^{-s(\lambda-\lambda ref)} \tag{2}$$

where a is the absorption coefficient at a given wavelength (λ), λ_{ref} is a reference wavelength, and S is the slope fitting parameter. S_r was calculated as the ratio of $S_{275\text{-}295}$ to $S_{350\text{-}400}$. Chlorophyll-*a* (chl-*a*) was measured using standard fluorometric methods after 90% acetone extraction. A subset of samples was analyzed for nitrate/nitrite (NO_3^-/NO_2^-) and ammonium using a Lachat Quickchem FIA (Hach Company) with a detection limit of 10 μg/L (n = 36).

2.3. Data analysis

Data analyses were performed in R using base code and packages ‘caret’, ‘segmented’, and ‘Metrics’. DOC and a_{440} failed Shapiro-Wilks normality tests, and were thus natural log-transformed for regression analyses. Figures were made in R using ‘ggplot2’ and ‘gridExtra’, except for Fig. 1 which was created in ArcGIS v10.5.1.

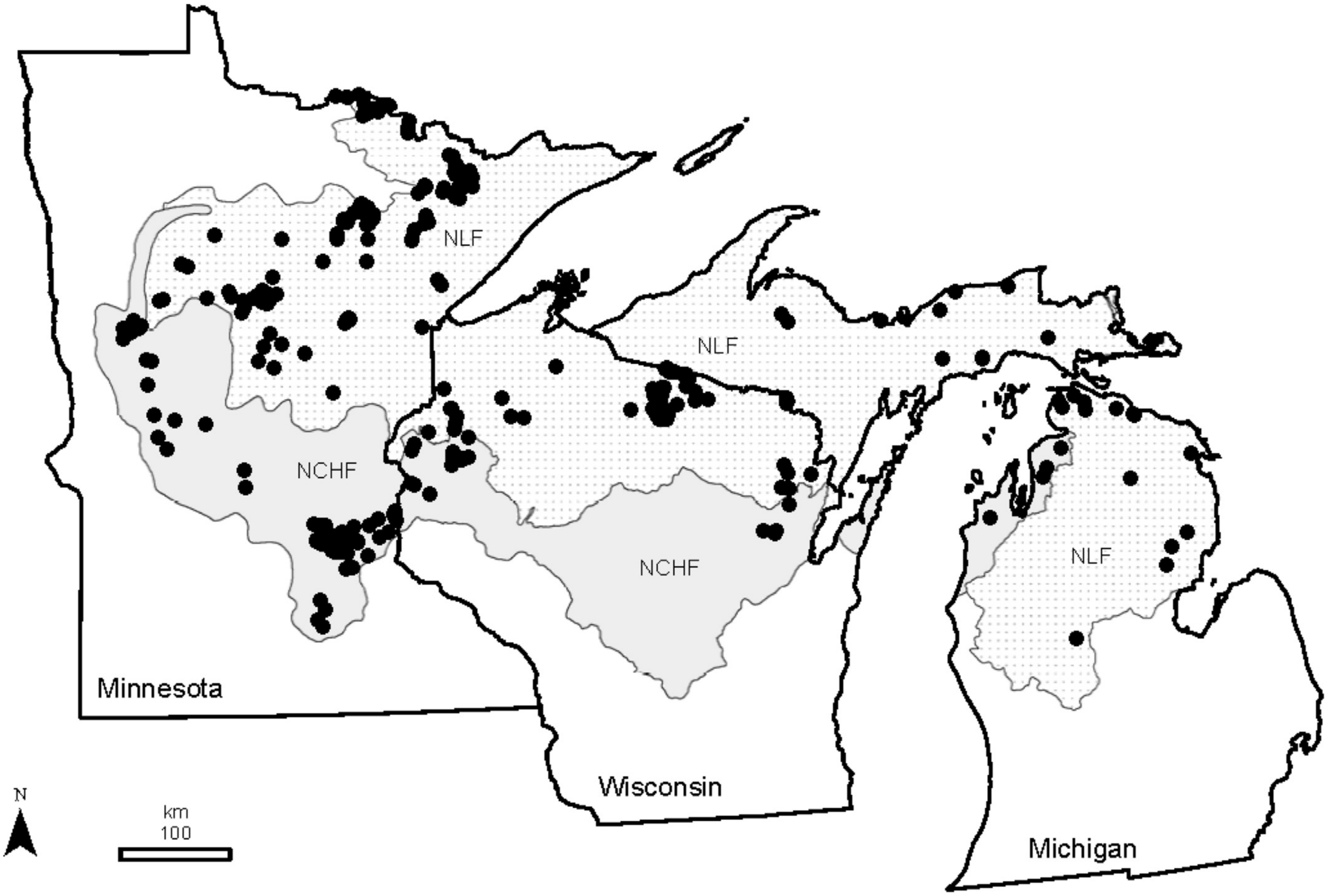

Fig. 1. Sampling sites across three Upper Midwest states from 2014 to 2016. The Northern Lakes and Forests (NLF) is represented by dotted fill, and NCHF by solid grey fill, with sampling locations indicated by filled circles.

3. Results

Lakes in the NLF generally had higher CDOM values and greater variability in CDOM quantity and compositional parameters than NCHF lakes (Table 1). For example, the mean (±standard deviation) a_{440} for NLF lakes was $6.05 \pm 7.03\ m^{-1}$ (n = 313) compared with $1.45 \pm 1.08\ m^{-1}$ (n = 107) for NCHF lakes. Similarly, SUVA, an indicator of aromaticity, was higher and more variable in the NLF lakes (3.09 ± 1.35 L mg $C^{-1}\ m^{-1}$) than in the NCHF lakes (2.09 ± 0.69 L mg $C^{-1}\ m^{-1}$). NCHF lakes generally contained higher chl-*a* concentrations (Table 1) and a greater range of TDN concentrations than NLF lakes. These results summarize all the individual measurements, including those for 58 lakes sampled multiple times across years and/or seasons.

Log-transformed CDOM (a_{440}) was strongly and linearly related to log-transformed DOC across the entire dataset ($R^2 = 0.81$; Table 2; Fig. 2):

$$\ln(\text{DOC}) = 1.946 + 0.388 * \ln a_{440} \tag{3}$$

High variability was observed in low color waters ($a_{440} < 3\ m^{-1}$). An a_{440} of $3\ m^{-1}$ was used to divide waters into "low" and "high" colored groups based on visual inspection of the DOC-a_{440} relationship; this threshold is approximately where waters become

Table 1
Summary statistics of variation in a_{440}(m^{-1}), DOC (mg/L), SUVA (mg/L m^{-1}), S_r by ecoregion.

	a_{440}	DOC	SUVA	$S_{275\text{-}295}$	S_r	Chl-*a*	TDN
NCHF							
mean (st dev)	1.45 (1.08)	8.07 (2.73)	2.09 (0.69)	23.23 (4.17)	1.251 (0.24)	16.50 (21.26)	0.61 (0.29)
median							
min	0.09	3.07	0.79	33.51	0.68	1.22	0.08
max	5.30	17.79	4.42	14.59	1.79	98.71	2.23
n	107	108	105	107	107	78	96
NLF							
mean (st dev)	6.05 (7.23)	12.18 (7.88)	3.09 (1.35)	19.40 (5.24)	1.08 (0.31)	4.74 (3.55)	0.49 (0.11)
median							
min	0	2.46	0.39	39.81	0.511	0.02	0.50
max	32.47	36.15	5.84	12.57	2.58	24.89	0.95
n	313	309	305	309	309	194	274

Table 2
Regression equations to predict log-transformed DOC from log-transformed a_{440} for lakes in three Upper Midwest states. Regressions using un-transformed, raw CDOM and DOC values are found in Table S1. All regressions were highly significant ($p < 0.0001$).

	n	Intercept	Slope	R^2	RMSE (mg/L)
ALL	412	1.95	0.39	0.81	2.52
<3 m^{-1}	257	1.95	0.29	0.44	1.82
>3 m^{-1}	154	1.56	0.57	0.9	2.00
NLF	307	1.91	0.40	0.85	2.54
NCHF	105	2.01	0.30	0.47	2.00
NCHF, < 3 m^{-1}	95	2.01	0.30	0.42	5.67
NLF, < 3 m^{-1}	162	1.86	0.27	0.45	5.22
NLF, > 3 m^{-1}	145	1.55	0.57	0.91	12.32

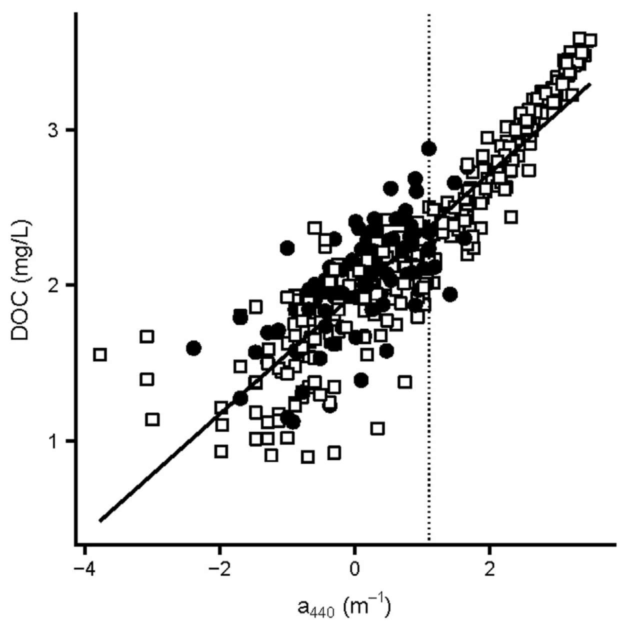

Fig. 2. DOC vs. CDOM for NCHF (filled circles) and NLF (open squares) ecoregions in MN, WI, and MI. Solid line indicates the regression line presented in equation (3). The dotted line is at $a_{440} = 3$ m^{-1}, indicating the separation between low and high colored lakes.

visibly brown or tea colored to the human eye. Although a piecewise regression analysis did not yield a significant "breakpoint" where the slope of the DOC-a_{440} relationship changed, the two groups (a_{440} < 3 and >3 m^{-1}) nonetheless showed strikingly different relationships between DOC and a_{440}. In addition, similar piecewise regression analyses of $S_{275\text{-}295}$ and SUVA vs. a_{440} showed significant inflection points at 2.67 and 3.44 m^{-1}, respectively. When only lakes with a_{440} exceeding 3 m^{-1} were considered, R^2 increased to 0.90 and the slope increased from 0.388 in Equation (3) to 0.569. In contrast, for a_{440} < 3 m^{-1}, DOC and a_{440} were only moderately correlated ($R^2 = 0.44$) with a lower slope (0.285) than either of the above regressions (Table 2; Fig. 2). NCHF lakes were predominantly low in color, with 95 samples having a_{440} < 3 m^{-1} and only 10 samples with a_{440} > 3 m^{-1} (maximum a_{440} of 5.3 m^{-1}). Further analysis of differences between ecoregions within low color samples showed differences in intercept and RMSE, but the slopes of DOC versus CDOM relationships were not significantly different between the two ecoregions (ANCOVA, $p = 0.4646$).

Additional optical characteristics, such as SUVA and spectral slopes, also showed differences in organic matter quality between low and high color lakes. Optical characteristics within the UV-B and UV-C regions correlated more closely with a_{440} than with DOC (Fig. 3). SUVA was correlated more strongly with natural log-transformed a_{440} ($R^2 = 0.89$) than with log-transformed DOC ($R^2 = 0.67$). $S_{275\text{-}295}$ similarly showed a more robust relationship with log-transformed a_{440} ($R^2 = 0.85$) than with log-transformed DOC ($R^2 = 0.57$; Fig. 3). In contrast, spectral slopes for UV-A and visible wavelengths ($S_{350\text{-}400}$ and $S_{400\text{-}460}$) had low R^2 values for both log-transformed a_{440} and DOC, ranging from 0.03 to 0.14. S_r, the ratio of $S_{275\text{-}295}$ and $S_{350\text{-}400}$, moderately correlated with a_{440} and DOC ($R^2 = 0.62$ and 0.43, respectively), as might be expected for a parameter that relies on both UV-B and UV-A wavelengths (Fig. S1). Low color samples ranged widely in spectral slope values, particularly for slopes at longer wavelengths (Fig. 2; S1). Above ~3 m^{-1}, however, most of these longer-wavelength optical characteristics were stable or showed small, positive increases.

We also explored whether other limnological properties, such as DIC, chl-*a*, and TDN, provided useful information on DOM properties. DIC did not correlate with CDOM or DOC, and was not a significant parameter in multiple regressions to predict DOC with other variables. Chl-*a* was not strongly related to CDOM, DOC, or SUVA when all samples were considered together, but separating the NLF and NCHF samples produced clear differences in chl-*a* patterns with the three parameters (Fig. 4). For NLF sites, chl-*a* did not correlate with CDOM, DOC, and SUVA ($R^2 = 0.05$, 0.05, 0.12, respectively), and chl-*a* concentrations changed little across the ranges of these organic matter metrics. Chl-*a* varied widely across NCHF sites, but regressions between organic matter spectral characteristics and chl-*a* remained weak. For example, a_{440} had the weakest relationship with chl-*a* for NCHF samples ($R^2 = 0.07$, $p = 0.014$), while that for DOC was slightly higher ($R^2 = 0.13$, $p = 0.001$).

Because DOC can be a product of both allochthonous (usually colored) and autochthonous (low-colored) DOM sources, we considered whether a multiple regression using both chl-*a* and CDOM would improve DOC predictions compared to Equation (3) (Table 3). For 264 samples where chl-*a*, a_{440} and DOC were all available, chl-*a* was only a weakly significant parameter in multiple regression ($p = 0.0339$). Compared to equation (3), including chlorophyll-*a* with CDOM to predict DOC increased R^2 marginally, from 0.81 to 0.84. In low colored lakes, chl-*a* was significant ($p = 0.0001$), but the R^2 did not change with its inclusion in a multiple regression. Chl-*a* was not a significant predictor of DOC in highly colored lakes ($p = 0.522$).

Nitrate and ammonium concentrations were low in the subset analyzed, with many samples falling below the detection limit of 10 µg/L (72% and 69%, respectively). These results show that TDN was dominated by dissolved organic nitrogen, as expected during summer conditions in lake surface waters (Finlay et al., 2013). Overall concentrations of TDN were moderate to low (<1.5 mg/L). As with chl-*a*, the TDN-a_{440} relationship was different for NLF and NCHF sites. In the NLF, TDN increased with a_{440} (Fig. 4c) ($R^2 = 0.68$, slope = 0.0267, $p < 0.0001$). The a_{440}-TDN relationship explained less of the TDN variance in the NCHF and had a much higher slope (Fig. 4d) ($R^2 = 0.29$, slope = 0.151, $p < 0.0001$). When TDN and CDOM were used in a multiple regression analyses for DOC, R^2 improved to 0.92 for the whole data set, and TDN was a highly significant parameter ($p < 0.0001$; Table 3). When only sites with a_{440} < 3 m^{-1} were used, a large increase in R^2 (from 0.44 to 0.77) was found when TDN was included. Highly colored sites showed only slight improvement in accuracy with the inclusion of TDN, in part because of the already strong relationship between a_{440} and DOC.

Two-term and three-term models have also been used to predict DOC in freshwater and marine environments. A variety of parameters have been used including absorbance at 254, 270 and/or

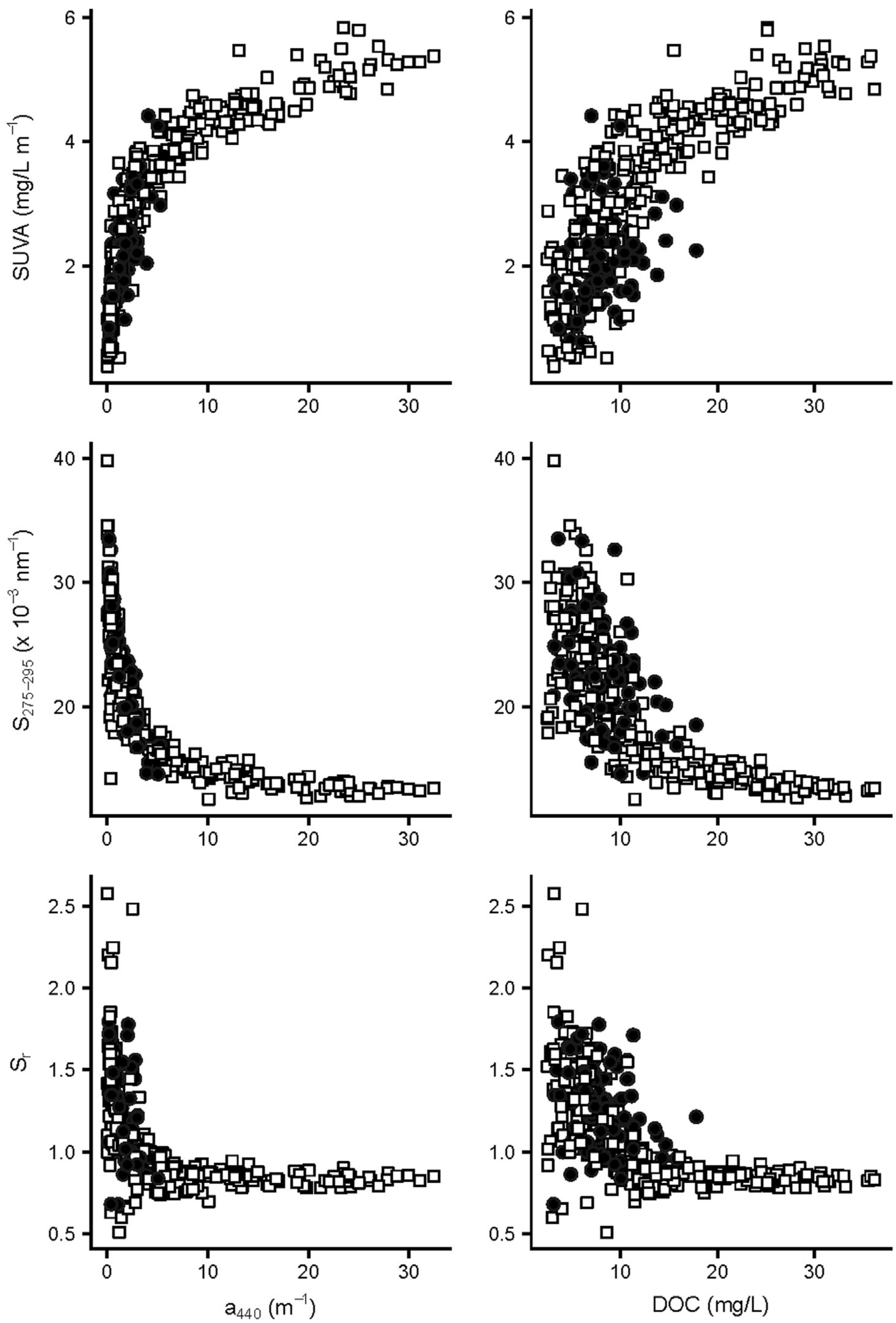

Fig. 3. Plots of SUVA, spectral slope for 275–295 nm, and the slope ratio, S_r vs. a_{440} (left column) and DOC (right column).

350 nm (Carter et al., 2012; Tipping et al., 2009), absorptivity at 275 and 295 nm (Fichot and Benner, 2011), and inclusion of spectral slopes (Asmala et al., 2012). We used a_{254} in addition to a_{440} because wavelengths in the UV-C spectrum resulted in the most robust models in previous studies. The two-term absorptivity models increased R^2 by 0.05–0.09 relative to a single term model for groups of low-color, high-color, and all lakes (Table 3). Nonetheless, two-term models using TDN and a_{440} were more effective at estimating DOC than using absorption at two different wavelengths, particularly for low-color lakes.

4. Discussion

The central goal of this study was to assess the regional variability in CDOM-DOC relationships across a wide range of lakes and examine factors that control such variability. Overall, CDOM and DOC were highly correlated, particularly in lakes with $a_{440} > 3\ m^{-1}$. In less colored lakes, particularly in the mixed land-cover conditions of the NCHF, the composition of DOM varied more widely leading to weaker relationships between CDOM and DOC. CDOM has become widely used as a proxy for DOC in freshwater systems (Brezonik et al., 2015; Spencer et al., 2012), but its validity has yet to

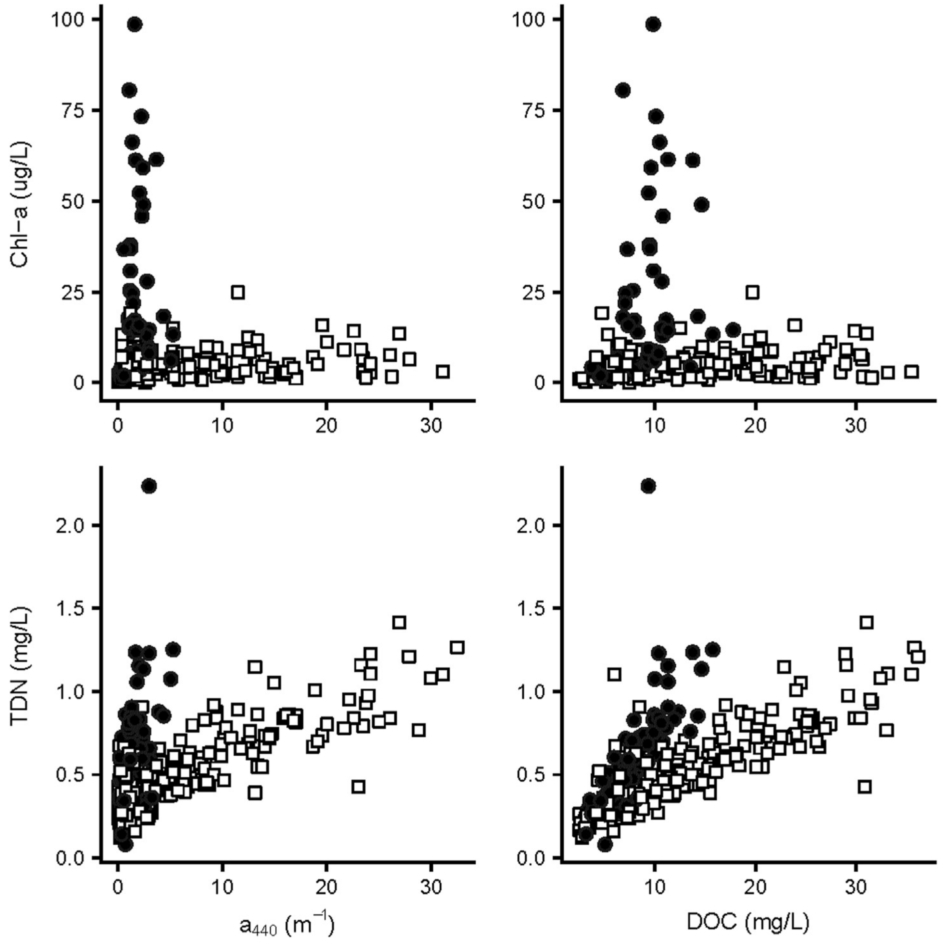

Fig. 4. (Upper) Plots of chl-*a* vs. a_{440} (left) and DOC (right), and (lower) plots of TDN vs. a_{440} (left) and DOC (right) for NCHF sites (filled circles) and NLF (open squares).

Table 3
Predictions of DOC using a_{440} with chl-*a*, TDN, or a_{254}. Coefficient a_0 is the intercept and a_2 is chl-a, TDN, or a_{254}. All regressions were performed using natural log-transformed data.

	n	$\mathbf{a_0}$		$\mathbf{a_{440}}$		$\mathbf{a_2}$		$\mathbf{R^2}$	*p*
		coefficient	*p*	coefficient	*p*	coefficient	*p*		
+ chl-*a*	264	1.95	«0.0001	0.37	«0.0001	0.03	0.0339	0.84	«0.0001
+ chl-*a*, < 3 m^{-1}	151	1.88	«0.0001	0.24	«0.0001	0.07	0.0001	0.48	«0.0001
+ chl-*a*, > 3 m^{-1}	111	1.56	«0.0001	0.56	«0.0001	0.01	0.522	0.89	«0.0001
+ TDN	369	2.36	«0.0001	0.30	«0.0001	0.44	«0.0001	0.92	«0.0001
+ TDN, < 3 m^{-1}	243	2.34	«0.0001	0.22	«0.0001	0.46	«0.0001	0.77	«0.0001
+ TDN, > 3 m^{-1}	125	1.88	«0.0001	0.48	«0.0001	0.21	«0.0001	0.94	«0.0001
+ a_{254}	368	2.25	«0.0001	0.55	«0.0001	−0.44	«0.0001	0.87	«0.0001
+ a_{254}, <3 m^{-1}	242	2.15	«0.0001	0.44	«0.0001	−0.31	«0.0001	0.53	«0.0001
+ a_{254}, >3 m^{-1}	125	2.28	«0.0001	0.74	«0.0001	−0.76	«0.0001	0.95	«0.0001

be widely evaluated in lakes (Li et al., 2016; Massicotte et al., 2017; Wilkinson et al., 2013). Using a large database of lake measurements from three Upper Midwest states, we found clear differences in DOM composition associated with CDOM levels and two large ecoregions. Low-color lakes in both ecoregions show a greater diversity of spectral characteristics and relatively weak relationships between CDOM and DOC than highly-colored lakes (Table 2). Thus, mapping lake carbon pools using satellite remote sensing of CDOM is most reliable for lakes of $a_{440} > 3\ m^{-1}$.

Low color DOM in lakes can be sourced from both anthropogenic landscapes and autochthonous production. Widespread wetland drainage (Dahl, 1990), land use change, and hydrological management practices (e.g., tile drainage) leads to decreased inputs of highly colored DOM to aquatic systems from the landscape (Dalzell et al., 2011; Giling et al., 2014; Li et al., 2018). Allochthonous organic matter inputs from agricultural or urban landscapes may be substantial (Hosen et al., 2014; Xenopoulos et al., 2003), but overall the organic matter in such systems lacks abundant aromatic, light-absorbing compounds (Tsui and Finlay, 2011). Landscape modification has also led to increasing eutrophication of Midwestern lakes, with substantial autochthonous production of low color DOM from both phytoplankton and macrophytes (Meili, 1992; Sommaruga and Augustin, 2006; Zhang et al., 2009). Only 12 colored lakes had chl-*a* concentrations exceeding 10 μg/L, reflecting low standing stocks of algal biomass and productivity typical of oligotrophic and mesotrophic lakes. In contrast, 30% of low color lakes had chl-a levels exceeding 10 μg/L (Fig. 4), indicating potentially substantial production of low-color, autochthonous DOM through processes such as cell lysis, zooplankton grazing, and microbial exudates. In the lakes studied here, TDN is dominated by dissolved organic nitrogen (DON) and is strongly related to DOC concentrations (Fig. 4). In low color lakes, the DOC:TDN ratio averaged 17.3, in line with the C:N ratio of autochthonous DOM from both phytoplankton and macrophytes (Qu et al., 2013; Zhou et al., 2016). The higher average C:N ratio of 28.0 for colored lakes ($a_{440} > 3\ m^{-1}$) is indicative of greater terrestrial DOM inputs.

In addition to phytoplankton, abundant macrophytes in many lakes could have produced substantial amounts of low-color, autochthonous DOM (Ginger et al., 2017; Lapierre and Frenette, 2009; Mann and Wetzel, 1996). Chl-*a*, primarily an indicator of phytoplankton biomass, thus by itself cannot explain the variability in CDOM-DOC relationships introduced by macrophytic DOM. The low C:N ratio of DOM from both phytoplankton and macrophytes contributes to the power of TDN in multiple regression with CDOM to predict DOC (Table 3).

Previous studies accounted for the presence of low-color DOC in natural waters by using two-term models, often absorbance at 254 nm and 350 nm (Carter et al., 2012) although other wavelengths could be used (Fichot and Benner, 2011). As with spectral slope values or ratios (e.g., a_{250}:a_{365}, as in Peuravuori and Pihlaja, 1997), two-term models allow for variations in absorbance to reflect both the total amount and composition of organic matter. Compositional changes, even as DOC remains constant, would lead to shifts in absorbance at one wavelength, relative to another (Adams et al., 2018). Such two term models generally are most effective when using absorption in UV wavelengths, which limits their use in remote sensing contexts. Both field observations and experimental mesocosm results (Adams et al., 2018) have shown that these two-term models can be effective when phytoplankton are the major source of DOC. The limited significance of chl-*a* in our own models suggests, however, that additional sources of low-color DOM are important from either macrophytes or anthropogenic run-off. The optical characteristics of these sources have not yet been as thoroughly characterized as more humic end-members or phytoplankton-derived DOM. Further, forest type is an important factor in determining CDOM-DOC relationships that cannot be explained by chl-*a*. For instance, Li et al. (2018) found that DOC:CDOM ratios were consistent in evergreen leaf leachate, but could vary widely in leachate from deciduous plants. The transition from mixed broadleaf forest to evergreen forests between the NCHF and NLF could thus also drive the differences in CDOM-DOC relationships between the two ecoregions. Fe previously has also been implicated in increasing absorptivity in boreal waters (e.g., Weyhenmeyer et al., 2014), but such interference does explain CDOM-DOC variance in low color lakes of the Upper Midwest, where Fe is also typically low (Eilers et al., 1988; Poulin et al., 2014; *unpublished data*). Additionally, Asmala et al. (2012) demonstrated Fe was only important in two-term DOC predictive models if absorption at 520 nm or more was used as the second term.

Microbial transformation and removal of DOM also may influence CDOM-DOC relationships (Mann et al., 2012; Ostapenia et al., 2009). Compositional characteristics of DOM in the NCHF, such as low C:N ratios, high $S_{275\text{-}295}$, and low SUVA, suggest that this DOM is labile and can be quickly removed from the waterscape (Frey et al., 2016). Such preferential removal of low color DOM can shift CDOM-DOC relationships, as recalcitrant humic material tends to remain in the water column and undergoes further microbial degradation or photochemical processing only slowly, as described in many river systems (Creed et al., 2015; Stackpoole et al., 2017). Microbial degradation may have driven some of the large variability in DOM composition within low color lakes, where labile and semi-labile DOM may have been consumed at varying rates. Evidence from the Upper Mississippi River, however, indicates that terrestrially-derived DOC is preserved even as the DOC is transported downstream (Voss et al., 2017) in a drainage basin that overlaps with both the NCHF and NLF.

Photochemical processes often play important roles in transforming DOM from both terrestrial and microbial sources in lake-rich environments. In contrast to microbial processing, which leads to the loss of low-color DOM, photobleaching leads to preferential loss of CDOM relative to overall DOC concentrations in lake epilimnia (Berto et al., 2013; Osburn et al., 2009). The highly connected waterscape of the NLF may lead to long exposure of DOM to solar radiation. The importance of photodegradation to DOM loss on a watershed or ecoregional scales has yet to be quantified for the Upper Great Lakes region. $S_{275\text{-}295}$ has been previously used as an indicator of photobleaching (Helms et al., 2008). If photobleaching were a strong driver of DOM composition, we would expect marked variability in $S_{275\text{-}295}$ relative to DOC in colored lakes, and, indeed, $S_{275\text{-}295}$ had a weaker relationship with DOC than with CDOM in waters with $a_{440} > 3\ m^{-1}$, indicating that photochemical reactions might influence DOM composition. Despite this, S275-295 and Sr both remain unchanging where a_{440} exceeds $3\ m^{-1}$, contrary to what would be expected if photobleaching was a significant driver of changes in DOM composition in highly colored lakes. Additionally, consistency of the relationship between DOC and CDOM above $3\ m^{-1}$ across our dataset suggests that photobleaching had limited influence on colored lakes. Solar irradiation can also lead to the formation of humic-like substances from proteinaceous material in clear, shallow lakes where UV-B is not absorbed by other material (Berto et al., 2013; Bianco et al., 2014). Such processes may be important in oligotrophic groundwater-fed lakes like (Dean and Schwalb, 2002), but are unlikely to be major factors controlling CDOM in most lakes within our study region.

The composition of DOM (and thus a_{440}-DOC relationships) also has temporal components, such as the introduction of photo-labile, humic, microbial DOM to the epilimnion during spring turnover (Osburn et al., 2001). Indeed, our sampling included the unusual hydrological year of 2016, where record-breaking precipitation throughout Minnesota led to extensive flooding and mobilization of sediments and nutrients. Our intra-annual sampling of Minnesota lakes showed that a_{440}-DOC relationships remained mostly stable (Table S2), reflecting the idea that the drivers of CDOM levels act on longer timescales than the drivers of suspended solids or chlorophyll-*a* levels in lakes (Stadelmann et al., 2001). A few sites did show large changes in DOM composition over the course of the summer and fall. Staring Lake, in suburban Minneapolis, showed large deviations from the DOC expected based on Equation (3), with residuals as much as 6 mg/L. Staring Lake has undergone significant restoration efforts, including carp removal, which may have contributed to changing patterns of autochthonous production. In most lakes, however, storage effects and long residence times mute the hydrological and biogeochemical signals that might be expected in response to storm or snow-melt events (Strock et al., 2016).

5. Conclusions: can CDOM be used as a proxy for DOC in temperate lakes?

CDOM-DOC relationships in lakes are products of variability in watershed land use, hydrological connectivity, and autochthonous production. Our results show that autochthonous production and anthropogenic influences on landscapes lead to large variations in DOC relative to CDOM in low color, temperate lakes. DOC in low colored lakes showed only moderate correlations with a_{440} in both the NLF and NCHF ecoregions. Incorporating TDN data into predictive models for low color lakes improved estimates of DOC in both ecoregions, although chl-*a* was not predictive. Low-color DOC may thus be derived from macrophytes and phytoplankton within a lake or external, anthropogenic sources, such as wastewater and urban run-off. Real-time mapping of DOC from CDOM in low color lakes is thus limited without ancillary water quality data. In visibly colored lakes ($a_{440} > 3\ m^{-1}$), however, CDOM can be used as a reliable proxy for DOC throughout the U.S. Upper Midwest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.watres.2018.08.007.

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