Dissolved Organic Carbon: A Link to Vital Processes in Streams and Lakes

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ABSTRACT

Dissolved organic carbon (DOC) is a key component of the carbon cycle in aquatic systems and understanding the dynamics of DOC is essential for understanding aquatic ecosystem metabolism and functioning. However, higher levels of recent atmospheric deposition of DOC is causing increased staining, or browning, to occur in freshwater systems. This impacts the gross primary production (GPP), as browning interferes with light dependent biological processes. Chromophoric or colored dissolved organic material (CDOM) can be used to explain the optical properties of organic carbon. It is known for having a strong relationship with total DOC in many systems and has been used as a proxy for DOC in other studies. The objectives of this study were to determine the range in DOC and CDOM quantity in streams and lakes, and to assess any differences in trends between the two system types. Sampling a variety of stained and unstained systems, we predicted a wide range in DOC and CDOM with a positive relationship between the two parameters. We expected that this relationship would be stronger in lakes because less-open systems allow for longer retention of nutrients and greater decomposition of less-colored DOC with low molecular weight. Surface water grab samples were taken from 54 streams and lakes across the Northern Highlands region of Wisconsin and the upper peninsula of Michigan. In addition to DOC and CDOM, spectrophotometric properties of water samples were analyzed for color at 456_{nm}, specific ultraviolet absorption at 254_{nm} (SUVA), and spectral slope at $275\text{-}295_{nm}$ ($S_{275\text{-}295}$). Overall, DOC ranged from 3.01-25.01 mg/L and CDOM ranged from 4.25-32.29 mg/L. In both streams and lakes, the relationship between DOC and CDOM was highly linear, and spectrophotometric properties exhibit a strong relationship with DOC and CDOM. As expected, these relationships were tighter for lake samples than stream samples. Additionally, various samples possessed high values for color relative to DOC and CDOM quantity, which can be caused by the presence of other dissolved materials (e.g., iron) present in the system.

INTRODUCTION

Aquatic ecosystems have been subject to environmental changes for many eras, but there has been a disproportionately large impact on carbon cycling during the Anthropocene. Specifically, there has been a global increase is dissolved organic carbon (DOC) (Griffin et al. 2018, Monteith et al. 2007). Studying trends relating to DOC and other water quality parameters is key in understanding ecosystem responses the changes in land use, hydrology, and climate (Kelly at al. 2018). The most predominant natural source of DOC comes from terrestrial inputs from deciduous trees when leaves fall seasonally. However, there also has been an increase in anthropogenic inputs from wastewater effluent, agricultural or urban run-off, and atmospheric CO_2 deposition (Lottig et al. 2013, Griffin et al. 2018, Kelly et al. 2018, Monteith et al. 2007).

DOC is important because of its unique optical properties. Systems with high DOC are often stained a brown or yellow color caused by tannins leaching from terrestrial vegetation inputs, like leaves. This leads to a problematic phenomenon, “browning.” DOC absorbs light, increasing the light extinction factor in aquatic systems (Griffin et al. 2018, Brezonik et al. 2019). Not only does this decrease the water temperature, but this also restricts the light availability for aquatic primary producers (Houser 2006). Decreasing the amount of primary production can interfere with the food web community structure within a system by limiting food resources. The bottom-up impacts of browning can be seen through a decrease in fish catch per unit effort with increasing DOC concentrations in aquatic systems (Kelly et al. 2018, van Dorst 2020).

Chromophoric organic material has been highly correlated with DOC in many aquatic systems, like streams and small lakes (Griffin et al. 2018). CDOM is comprised of aromatically structured molecules that contribute to optical properties similar to DOC, specifically its visible color and ability to absorb light in systems. Additionally, CDOM is known to mobilize metals, like iron (Griffin et al 2018, Brezonik et al. 2019). Because of the similarities between these two water quality parameters, CDOM can often be used as a proxy for DOC in many streams and small lake ecosystems. However, this relationship of predictability between DOC and CDOM is not as strong in systems with low concentrations of DOC (Griffin et al. 2018).

Specific UV absorbance (SUVA) is another variable that is helpful in predicting the amount of carbon in a system. SUVA is known to be influenced by a variety of water quality parameters, including iron (Weishaar et al. 2003). SUVA is measured at the absorbance 254 nm and normalized for DOC. It is highly correlated with the amount of aromatic carbon in a system (Weishaar et al. 2003). This is helpful in predicting the amount of DOC or CDOM since these water quality parameters are comprised of organic carbon molecules. While this analysis is helpful in predicting DOC and CDOM it does not explain any reactivity properties of the molecules comprising DOC and CDOM (Weishaar et al. 2003).

DOC and CDOM concentrations vary across lakes and streams. Streams are flowing systems, so the residence time of nutrients like DOC and CDOM in streams is ephemeral compared to lakes. Streams receive new terrestrial inputs of DOC yearly, with little or no retention of aged nutrients. Lakes are generally thought of as closed systems, so the residence time of nutrients is longer (Lottig et al. 2013). Lakes receive new inputs of DOC, but also retain old DOC inputs over time. The DOC is recycled within the system for a longer period (Lottig et al. 2013). Because of the differences between systems, it is expected that lakes will have generally tighter relationships between DOC and other parameters than those in streams.

By examining the optical properties of DOC and its relationship with other water quality parameters, the impact of environmental change on ecosystems can be better understood. The goals of this study are to (1) determine the range in DOC concentration in lakes and streams in the Northern Lakes and Forests (NLF) and the North Central Hardwood Forests (NCHF) regions, which comprise the Northern Highlands region of Wisconsin and the Upper Peninsula region of Michigan and (2) determine if there are differences in relationships between the two system types.

METHODS

Water sample collection and processing

The Northern Highlands region of Wisconsin and the Upper Peninsula region of Michigan show a disproportionally high concentration of carbon cycling activity (Lottig et al. 2013). Previously reported high correlations between DOC and CDOM (Griffin et al. 2018) make this a unique study region. A total of 27 streams and 27 lakes were sampled in May 2019 (Figure 1), with notable sites located at the University of Wisconsin Trout Lake Station and the University of Notre Dame Environmental Research Center. High density polyethylene (HDPE) bottles were acid washed, triple rinsed with deionized water, and rinsed with site water prior to sample being taken. Sample bottles were filled and capped below the surface of the water to avoid atmospheric CO_2 contamination. Samples were stored in a cooler until processing. Temperature, conductivity, dissolved oxygen, dissolved oxygen percent saturation, photosynthetic active radiation, and pH were taken on a Hydrolab probe at the site and recorded. GPS coordinates were recorded for each site access point.

Samples were processed within 24 hours of collection at the University of Wisconsin Trout Lake Research Station. Turbidity was measured prior to filtration. Remainder of sample was filtered through Whatman GF/B filters. A portion of the sample was used for titrimetric CO_2 analysis (APHA: 4500 CO_2 - C), and the remainder was stored in a refrigerator for analyses to be conducted at UWL.

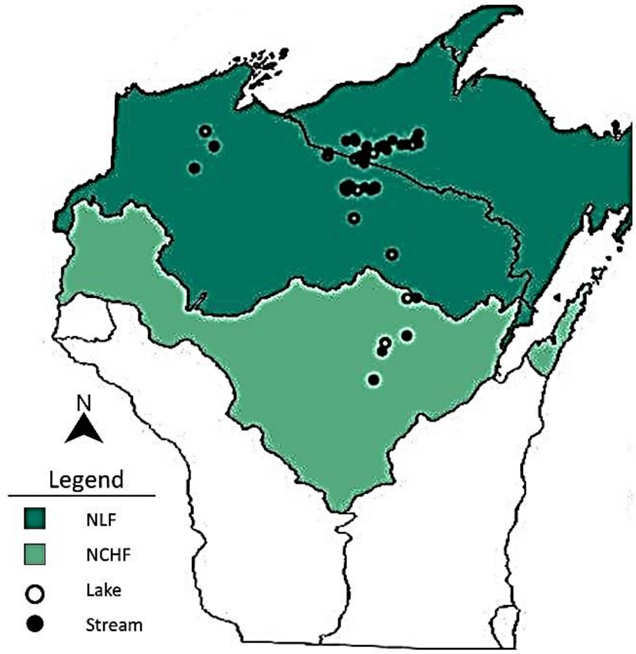

Figure 1. Sampling site locations in Wisconsin and the Upper Peninsula of Michigan. A total of 27 streams and 27 lakes were sampled during the summer of 2019. The Northern Lakes and Forests (NLF) region is represented by the darker shade, and the North Central Hardwood Forests (NCHF) region is represented by the lighter shade. Streams are represented by filled circles, and lakes are represented by open circles.

Sample analysis

DOC concentration was determined using a Shimadzu TOC Analyzer (APHA 5310 B). CDOM concentration was determined using a Turner Trilogy fluorometer with a CDOM filter cartridge (10200 H). Absorbances for color, $SUVA_{254}$, spectral slope ($S_{275-295}$, $S_{350-370}$), spectral ratio (S_r) were determined using a Thermoscientific Spectrophotometer Evolution 201.

Absorbances (A_λ) used for spectral slope and spectral ratio were converted to a Napierian absorption coefficient (Equation 1), correcting for path length (l) of 5 cm. Spectral slope was recorded for absorbance values in the ranges of 275-295 nm. Slope was calculated (Equation 2), with the first wavelength in the range as the reference.

$$Equation\ 1: \alpha_\lambda = 2.303\mathrm{A}_\lambda/\ell$$

$$Equation\ 2: \alpha_\lambda = \alpha(\lambda_{ref})e^{-S(\lambda-\lambda_{ref})}$$

Color was recorded for absorbance values at 456 nm, then concentration was calculated from a Platinum-Cobalt standard curve linear regression (APHA 2120 C). $SUVA_{254}$ was recorded for absorbance values at 254 nm, then concentration was calculated by normalizing for DOC concentration (Equation 3) (APHA 5910 B).

$$Equation\ 3: SUVA_{254} = \left(\frac{A_{254\,nm}}{[DOC]}\right)\ x\ 100$$

Data analysis

Water quality parameters were compared against each other to find any significant relationships. Lakes and streams were analyzed separately to determine if relationships varied between system types. Sigma Plot v. 14.0 was used for regression analysis for each variable. Significance was assumed at $\alpha = 0.05$.

RESULTS

Comparing DOC and CDOM, there are positive linear relationships between parameters for both streams and lakes (Fig. 2). However, lakes show a tighter relationship between DOC and CDOM than streams. This is as expected since lakes are generally considered closed systems, the DOC in the system has a longer residence time and combination of “old” and “new” DOC.

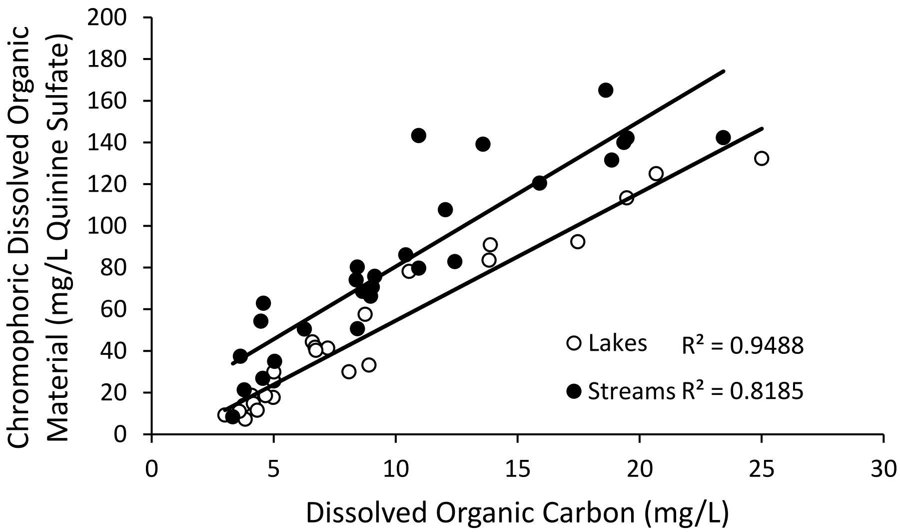

Figure 2. Positive linear relationship between DOC and CDOM. Regression analysis showed R^2 values for lakes and streams of 0.9488 and 0.8185, respectively.

DOC and color also showed very strong positive linear relationships for both lakes and streams, with little differences between the two systems (Fig. 3). Both system types were samples in the same region with similar vegetation serving as the primary terrestrial input for DOC, which likely contributed to similar color signatures.

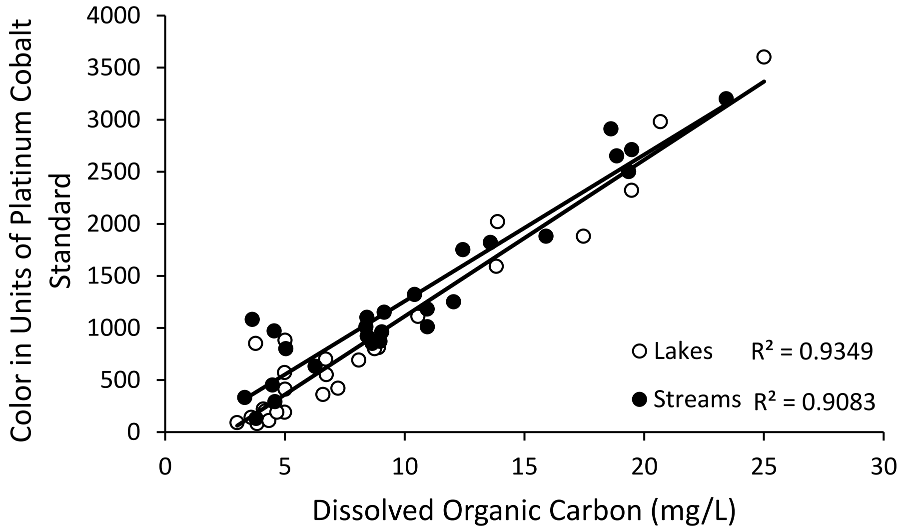

Figure 3. Positive linear relationship between DOC and color. Regression analysis showed R^2 values for lakes and streams of 0.9349 and 0.9083, respectively.

DOC and CO_2 have weak positive linear relationships with both systems; however, lakes had a relatively tighter relationship between the two parameters (Fig. 4). It is possible that this is linked to longer residence times in lakes or simply representing the overall human error possible when utilizing titration as a CO_2 analysis method.

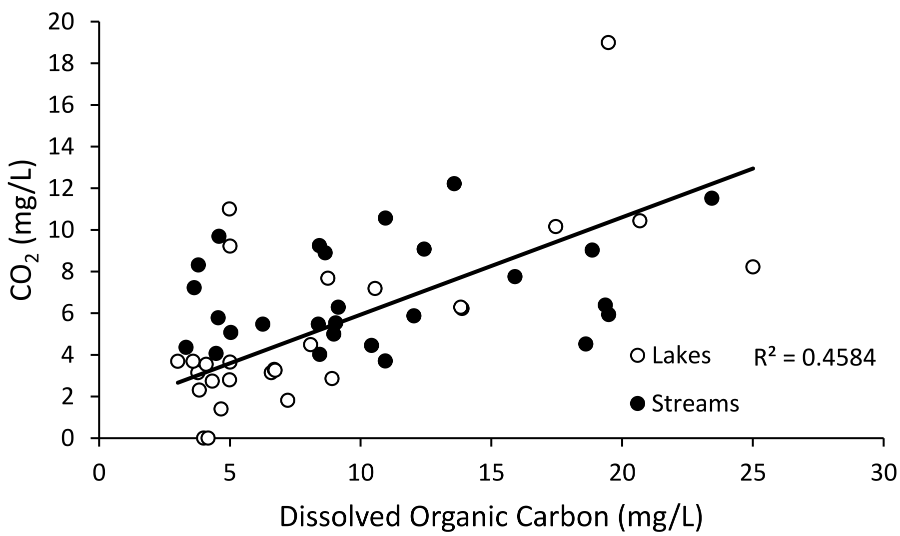

Figure 4. Positive linear relationship between DOC and CO_2. Regression analysis showed a significant relationship for lakes with an R^2 value of 0.4709. Streams did not show a significant relationship.

SUVA and DOC results showed that there was a positive logarithmic relationship between both parameters for both system types (Fig. 5). There was a tighter relationship between parameters for lakes, which could be linked back to the longer residence time of DOC.

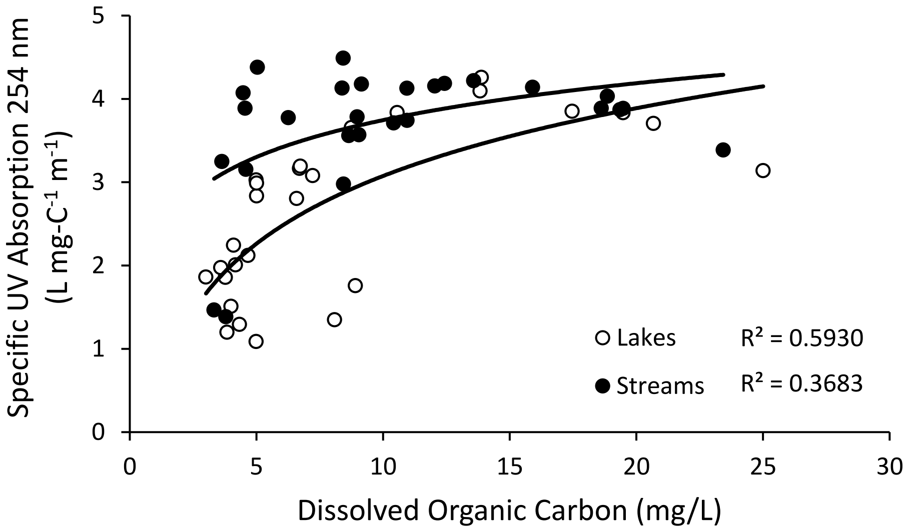

Figure 5. Positive logarithmic relationship between DOC and SUVA. Regression analysis showed R^2 values for lakes and streams of 0.5930 and 0.3683, respectively.

Comparing CDOM and color in lakes and streams, both site types have positive exponential relationships (Fig. 6). Trends in color between site types follow similarities seen in Figure 3, which adds support towards linking color signature to vegetation specific to the Northern Highlands region.

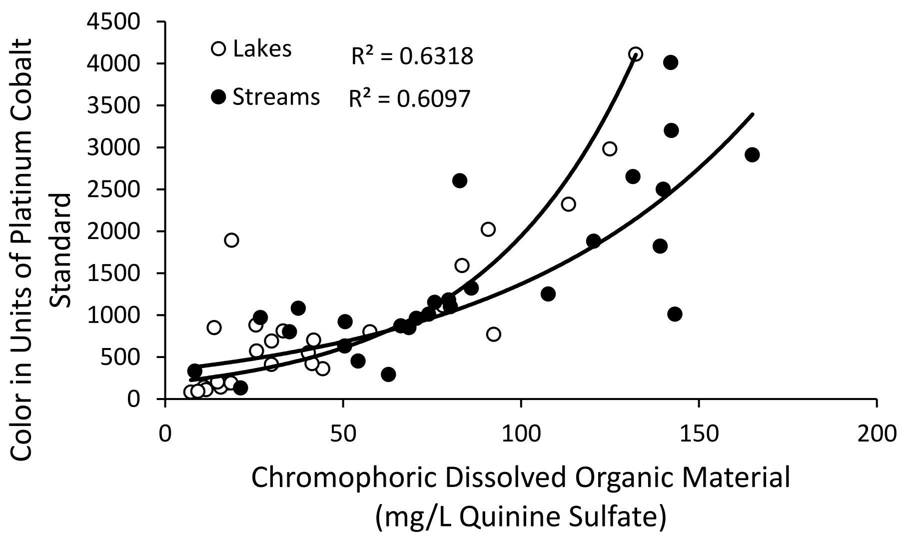

Figure 6. Positive exponential relationship between CDOM and color. Regression analysis showed R^2 values for lakes and streams of 0.6318 and 0.6097, respectively.

CDOM and CO_2 have weak positive linear relationships with both systems; however, lakes had a relatively tighter relationship between the two parameters (Fig. 7). Similar trends can be seen in Figure 4.

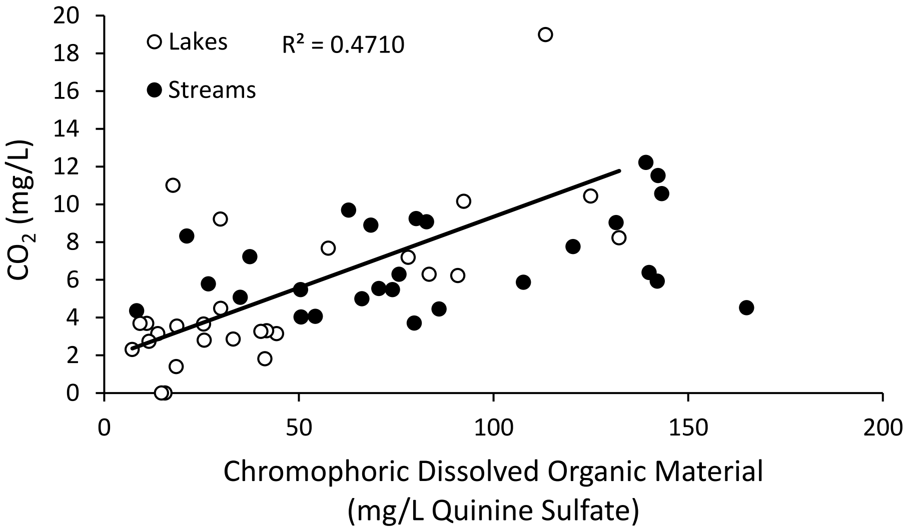

Figure 7. Positive linear relationship between CDOM and CO_2. Regression analysis showed a significant relationship for lakes with an R^2 value of 0.4710. Streams did not show a significant relationship.

SUVA and CDOM results showed that there was a positive logarithmic relationship between both parameters for both system types (Fig. 8). There was a tighter relationship between parameters for lakes, which could be linked back to the longer residence time of DOC as seen in previous results in Figure 5.

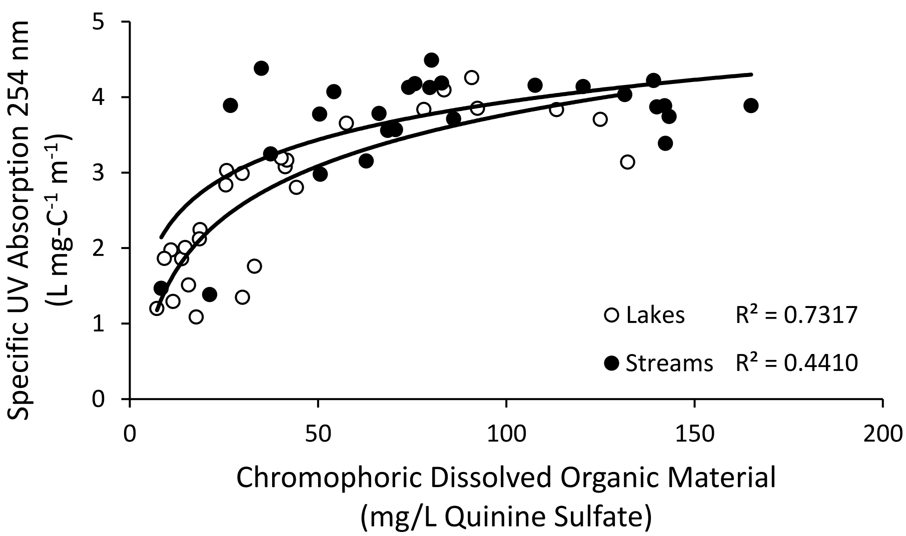

Figure 8. Positive logarithmic relationship between CDOM and SUVA. Regression analysis showed R^2 values for lakes and streams of 0.7317 and 0.4410, respectively.

Color and CO_2 have weak positive linear relationships with both systems; however, lakes had a relatively tighter relationship between the two parameters (Fig. 9). Similar trends can be seen in Figure 4 and Figure 7.

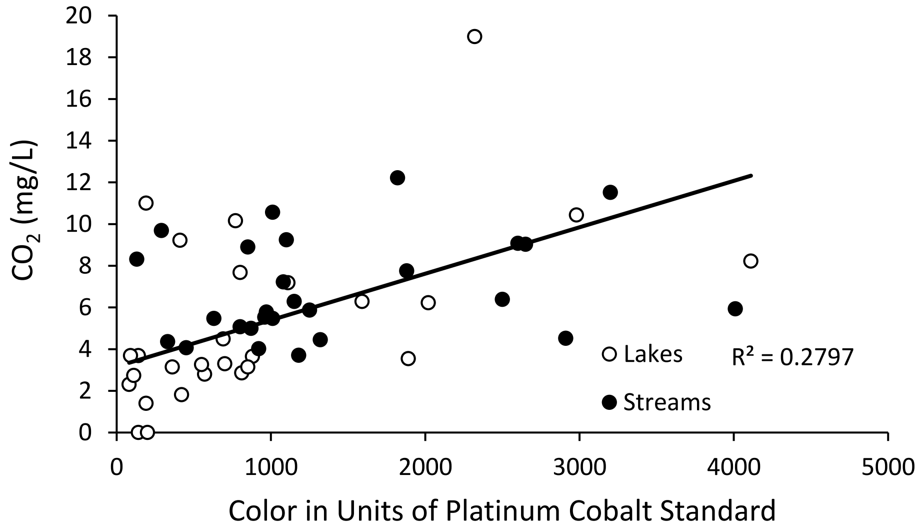

Figure 9. Positive linear relationship between color and CO_2. Regression analysis showed a significant relationship for lakes with an R^2 value of 0.2797. Streams did not show a significant relationship.

Color and SUVA results showed that there was a positive logarithmic relationship between both parameters for both system types (Fig. 10). There was a tighter relationship between parameters for lakes, which could be linked back to the longer residence time of DOC as seen in previous results in Figure 5 and Figure 8.

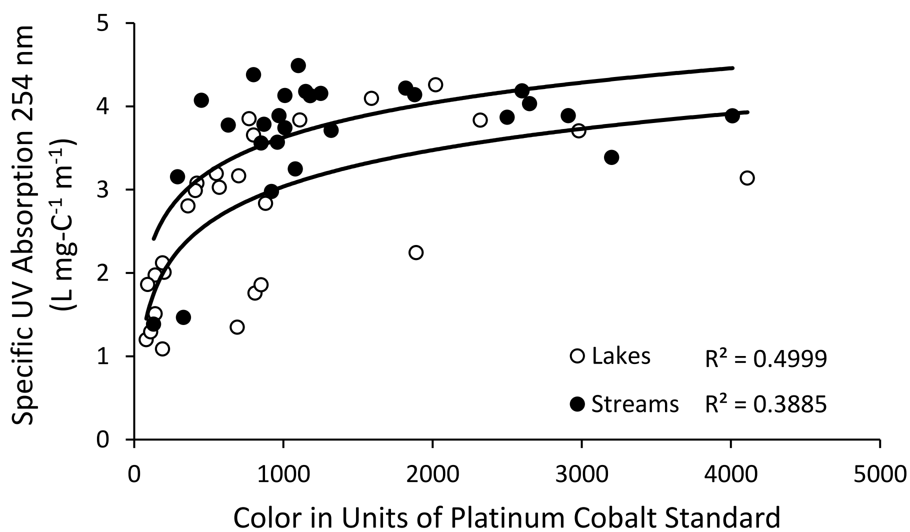

Figure 10. Positive logarithmic relationship between color and SUVA. Regression analysis showed R^2 values for lakes and streams of 0.4999 and 0.3885, respectively.

DOC and $S_{275\text{-}295}$ results show a positive power function relationship (Fig. 11). Regression analysis shows significant trends in both lakes and streams; however, streams had a tighter relationship than lakes. This is different from other comparisons in this project. Spectral slope describes how the lake or stream reflects wavelength of light, influencing the color perceived by the human eye, like yellow or red. From these results it appears that there is more variation in spectral slope, or color appearance, in lakes than streams related to DOC.

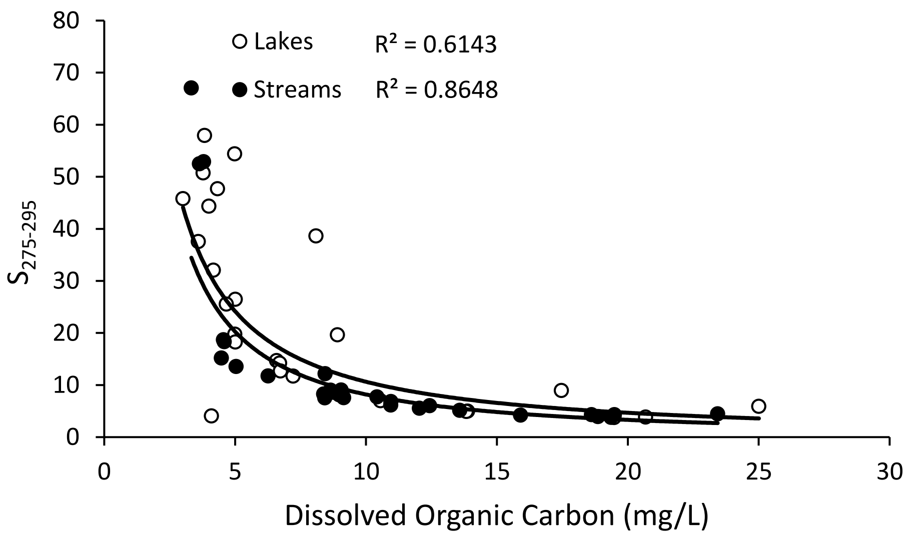

Figure 11. Positive power function relationship between DOC and $S_{275\text{-}295}$. Regression analysis showed a significant relationship for lakes and streams with R^2 values of 0.6143 and 0.8648, respectively.

CONCLUSIONS

The range in DOC concentration was determined for a sample of lakes and streams in the Northern Highlands region of Wisconsin and the Upper Peninsula region of Michigan. Sites showed variation in DOC and other water quality parameters like color, CDOM, CO_2, SUVA, and $S_{275\text{-}295}$. Lakes and streams were found to be differentiated by their unique patterns in water chemistry properties. CO_2 trends were only significant in lakes, which was an expected result due to the longer residence time of carbon in closed systems, like lakes. This can also be seen with the generally tighter relationships between DOC and CDOM in lakes than streams. Trends with color and SUVA showed little variation between system types, which could be due to color signatures of vegetation specific to the Northern Highlands region. DOC and CDOM also showed highly linear relationships with variation between systems. Since SUVA and CDOM are comparable measurements, the differences in relationships between these parameters were not expected.

Future directions include addressing other inorganic materials contributing to color in systems where color values were high relative to the DOC and CDOM quantity. One possible material involved in the optical properties of these sites is iron because of its red and orange appearance when oxidized (van Dorst et al 2020). While this study focused on the Wisconsin and the Upper Peninsula of Michigan, further time and resources should be invested into expanding sample area into the Northern Highlands region of Minnesota and increasing overall sample quantity. Overall, this study reinforced that it is important to measure multiple parameters to gain a holistic understanding of the optical properties of carbon in lakes and streams.

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