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## Relationships in Lacustrine Ecosystems: Carbon, Color, and Precipitation in North Temperate Lakes

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Relationships in lacustrine ecosystems:  
Carbon, color, and precipitation in north temperate lakes

A thesis presented to the Environmental Studies Department

Macalester College

Spring 2024

In partial fulfillment of the requirements for the senior honors program

Submitted on April 27th, 2024

By: Emma Squires

Faculty Advisor: Christine O'Connell, Environmental Studies

## **Abstract**

Lakes are an important part of the global carbon cycle. Carbon from terrestrial sources washes into lakes where it can be processed and then emitted to the atmosphere, buried in sediments, or make its way downstream to an ocean. During rain events, precipitation can flush dissolved organic carbon (DOC)-enriched water from the upper soil layers into lakes. As climate change causes increased precipitation totals and precipitation events in the upper Midwest, this may cause increased DOC in lakes. Increased DOC in lakes leads to increased microbial respiration, contributing to increased greenhouse gas release from lakes. Thus, it is important to understand the effects of DOC on lake ecosystems. Here, I use long-term data and newly collected data from a set of lakes in Michigan and Wisconsin to analyze how precipitation affects DOC in lakes to better understand how changing precipitation patterns could affect the carbon cycle in lakes. I found that increased total annual precipitation leads to increased dissolved organic carbon within lakes. The lag period between when a precipitation event occurs and when the DOC-enriched water enters the lakes was less than 2 weeks in this study. Wet years generally have higher DOC than dry years. Furthermore, DOC and lake water color have a positive relationship at all depths within lakes, but there are some lakes where this relationship is weaker and the effect of DOC on water color decreases with depth. This relationship does not change with high or low precipitation years. My results suggest that climate-driven changes in local precipitation regimes could lead to shifts in lake

DOC-loading with potential implications for lake respiration, lake community ecology, and landscape-level carbon storage.

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## **Introduction**

Inland waters such as lakes are an important source of carbon to the global carbon cycle (Köhler et al. 2013). Carbon enters lakes from terrestrial sources and is processed before entering other reservoirs of carbon: sediments, the atmosphere, and the ocean (Pace et al. 2007). According to a recent study, lakes emit 4.4 GtC/year to the atmosphere, which is an increase of ~1 GtC/year from pre-industrial times (Pilla 2022). Compared to a land sink of 3.4 +/- 0.9 GtC and an atmospheric sink of 5.1 +/- 0.02 GtC (Friedlingstein et al. 2020), this is a significant portion of the global carbon cycle. The carbon released in lakes comes from respiration as bacteria feed on dissolved organic carbon (DOC) in the deepest waters, or hypolimnion, of a lake, as well as from terrestrial sources that are washed into a lake (Tranvik et al. 2009). Because the pool of DOC in aquatic systems is so large, small changes in DOC in a region of lakes can have significant impacts on carbon cycling (Pace & Cole 2002).

Due to climate change, precipitation events and annual totals are increasing in the Midwest (Angel et al. 2018). Because precipitation facilitates DOC transportation via groundwater and terrestrial sources to lakes (Pace & Cole 2002), this may affect DOC concentrations in lakes. In addition to climate impacts, DOC can impact lake community ecology by changing the visible color of lake water and thus how deeply into the lake light can penetrate (Wissel et al. 2003). A study of an alpine lake found that an extreme rain event washed enough



DOC into the lake to turn it from autotrophic to heterotrophic (Sadro & Melack 2012). Another study found that a tropical storm increased the DOC load in the inflow stream of a subtropical lake by  $189 \text{ kg km}^{-2} \text{ day}^{-1}$  (Jennings et al. 2012). However, these studies are not applicable to most lakes in the Upper Midwest due to differences in climate. A study on Lake Superior near Duluth, MN, found that storm water plumes associated with two storms washed significant portions of Lake Superior's annual DOC inputs into the lake (Cooney et al. 2018). However, Lake Superior's large size and the comparatively small area covered by the plumes makes it difficult to compare to other lakes in the Midwest. More research has also been done on the effects of storms on DOC in rivers (Dhillon & Inamdar 2014; Inamdar & Mitchell 2006; Vaughan et al. 2017). This research can be used as a comparison, but due to differences in water retention time between lakes and rivers, landscape characteristics are better able to predict DOC in rivers than in lakes (Gergel et al. 1999). Thus, precipitation impacts on DOC in lakes cannot be assumed from research done on rivers. Additionally, there is research on effects of longer periods of wet or dry weather on lake DOC, such as the effect of a particularly wet year (Strock et al. 2016), but much less work has been done relating discrete precipitation events to DOC loading in lakes in the Upper Midwest. Because the Upper Midwest contains the highest density of lakes in the United States apart from Florida (Cook & Jager 1991), it is important to understand how lakes in this region will respond to projected increases in extreme precipitation events.

In this thesis, I use historical data and newly collected field data from a series of lakes in the Upper Midwest to determine how precipitation affects DOC in lakes and the implications of that on lake ecosystems and lake carbon cycling with a changing climate. Specifically, I examine how DOC varies with water color at different depths. I also examine the lag time between precipitation events and the corresponding influx of DOC, in addition to general effects of precipitation on DOC. Finally, I examine how precipitation extremes affect the relationship between DOC and water color.

#### *Lake ecosystems and limnological principles*

Movement of water within lakes determines how quickly gas exchanges with the atmosphere. Many lakes in the Upper Midwest are stratified and mix 1-2 times per year, usually during the spring and fall. During the stratified period, little water is transferred between layers. Thus, little oxygen reaches the deepest layer of the lake, or hypolimnion, from the surface of the lake while many dissolved nutrients and gases such as CO<sub>2</sub> and CH<sub>4</sub> produced in the hypolimnion are trapped there until the lake mixes (Houser et al. 2003). These gases may also be released during the stratified period through ebullition, where gas bubbles up from the sediment to the surface (Dodds & Whiles 2020). How quickly carbon dioxide and methane can exchange with the atmosphere depends on turbulence, or chaotic movement of water, in the surface waters (Prairie & Cole 2022), so turbulence determines how much of a lake can exchange carbon dioxide and

methane with the atmosphere. Turbulence in the upper layer, or epilimnion, is caused by wind mixing and convection within the lake (Zwart et al. 2015). As wind mixing is dominant in larger lakes, the mixed layer stays deeper even in darker colored lakes (Zwart 2015). Convection is the main source of turbulence in the epilimnion of smaller lakes (Zwart et al. 2015). Thermocline and mixed layer depth determine where in a lake is suitable habitat for phytoplankton, zoobenthos, and fish (Zwart et al. 2015). Combined, these mechanisms for the movement of water within lakes determine how much and how quickly gas exchange occurs.

Lakes are often classified by trophic status. Historically, this has been dependent on nutrient concentrations on a gradient from oligotrophic (low nutrients, clear water) to eutrophic (high nutrients, green water) (Webster et al. 2008). More recently, colored dissolved organic carbon (CDOC) has been added as an indicator in determining trophic levels because CDOC is an important food source to lake food webs and, in addition to total phosphorus, controls the degree of autotrophy in lakes (Webster et al. 2008). This has resulted in the addition of dystrophic (low nutrients, brown water) and mixotrophic (high nutrients, murky water) as possible trophic status levels (Webster et al. 2008).

#### *Dissolved organic carbon*

DOC originates either from terrestrial sources that then wash into lakes via surface water flow, groundwater flow (Pace & Cole 2002), or fixed via

photosynthesis within lakes (Wilkinson et al. 2013). Carbon input from aquatic primary productivity is generally low (Pilla et al. 2022). Terrestrial inputs are estimated to be about 5.76 PgC/year, of which 73% is emitted, 10% is buried, and 17% is exported to oceans (Pilla et al. 2022). Interstitial water in upper soil layers is enriched with DOC and can be washed into nearby waters after precipitation events (Strock et al. 2016; Inamdar & Mitchell 2006). Dissolved Organic Matter (DOM) is organic matter which has become dissolved in water. DOC is a subset of DOM that specifically refers to the carbon in the dissolved organic matter, while DOM refers to the entire amount of dissolved organic matter. Large amounts of DOM in lakes originate in riparian wetland areas as wetlands produce large amounts of organic matter (Bertolet et al. 2018; Gergel 1999). The DOC concentrations in a lake are determined by inputs from both the terrestrial ecosystem and in-lake processes, in-lake degradation, and loss of water from the lake or loss of carbon through sedimentation (Pace & Cole 2002, Webster et al. 2008). In regions where eutrophication is minimal, DOC has a large impact on the clarity of the water (Pace & Cole 2002).

Within lakes, carbon can be found in different forms. One important division for freshwater carbon is into organic and inorganic carbon. Dissolved inorganic carbon (DIC) determines the pH of water based on the proportion of each form of DIC (Dodds & Whiles 2020; Prairie & Cole 2022). Organic carbon is composed of carbon compounds bonded with hydrogen, often oxygen, and

occasionally other elements (Dodds & Whiles 2020). Colored Dissolved Organic Carbon (CDOC) is a subset of DOC that is colored at 440 nm and thus can limit light penetration.

DOC is also affected by variables internal to a lake such as colloidal iron concentrations (Köhler et al. 2013). Lakes with a long water residence time generally have lower concentrations of DOC while small lakes that water moves quickly through tend to have higher concentrations of DOC due to relatively large influxes of DOC-enriched water from outside of the lake (Pace & Cole 2002, Webster et al. 2008). Larger lakes generally have lower DOC, with lake area accounting for 10% of the variability in DOC in one study of lakes in the Upper Peninsula of Michigan (Xenopoulos et al. 2003). In-lake processes that affect carbon include sedimentation, which removes carbon from the water column, and photolysis which can degrade carbon in surface waters (Webster et al. 2008).

DOC is affected by external variables such as precipitation and ice-out timing (Pace & Cole 2002). Steep slopes in the watershed results in less DOC transportation to lakes because precipitation reaches lakes faster, so less organic matter dissolves as water percolates through the soil (Rasmussen et al. 1989). DOC can increase due to increases in production in the terrestrial ecosystems surrounding the aquatic system (Strock et al. 2016). Higher wetland cover in the watershed results in higher DOC (Rasmussen et al. 1989). Production in terrestrial

systems increases with increasing air temperature and increased atmospheric CO<sub>2</sub> (Strock et al. 2016), so may increase due to climate change. Anthropogenic changes in land cover have altered hydrology and changed the quality and quantity of carbon entering inland waters (Pilla et al. 2022). Deforestation has been found to cause elevated DOC concentrations in streams for 2-3 years after clear cutting though DOC concentrations returned to pre-cutting concentrations after ~5 years (Robinson et al. 2022). Urban streams have 7.8x more DIC and agricultural streams have 4x more DIC than do streams in undisturbed areas due to disturbances such as tilling, increased CO<sub>2</sub> production from management of urban green spaces such as lawns, and lime application (Barnes & Raymond 2009). Increases in acid rain lead to decreases in DOC (Monteith et al. 2007; Riise et al. 2018). Brownification, or the trend of darker water color from increased concentrations of DOC, has been recorded in lakes in northern Europe and northeastern North America as a result of recovery from acid rain (Meyer-Jacob et al. 2019).

Changes in DOC in lake ecosystems affect light penetration, lake stratification, and nutrients. Because high DOC concentrations limit how far light can travel into a lake, it can limit primary productivity which leads to a reduction in fish and invertebrate productivity (Zwart et al. 2015). Lakes with high concentrations of CDOD often have distinct algal communities and the selective absorption of UV light protects algae from sunlight in the surface waters of a lake

(Webster et al. 2008). Light penetration affects where deep chlorophyll maximums can form as phytoplankton need light to grow but also need the greater nutrients available deeper in lakes (Leach et al. 2017). Because DOC absorbs infrared light, the epilimnion in high DOC lakes is shallower and warmer while the hypolimnion is colder, which decreases the whole-lake temperature (Wissel et al. 2003; Zwart et al. 2015). For example, one study of a north-temperate bog found that a 50% decrease in DOC concentration caused the metalimnion to deepen by 44% and increased the average temperature of the whole lake (Zwart et al. 2015). This can have implications for carbon cycling by decreasing CO<sub>2</sub> concentrations in the epilimnion. For example, in a boreal lake, it was found that surface waters have lower CO<sub>2</sub> when the epilimnion is shallow and cold which may be due to reduced respiration, DOC, and dissolved nutrients (Åberg et al. 2010). Oxygen concentrations are lower in high DOC lakes partially because of increased bacterial production (Wissel et al. 2003). DOC has an impact on the availability of dissolved nutrients (Pace & Cole 2002). An increase of DOM in nutrient-rich waters can lead to conversion of inorganic nutrients to organic forms as bacteria feed on DOM and convert nutrients from inorganic to organic forms as they do so (Findlay & Sinsabaugh 1999).

Metabolism in lakes represents the balance between gross primary production and community respiration, where a lake is heterotrophic when respiration exceeds production and autotrophic when production exceeds

respiration (Sadro & Melack 2012). A heterotrophic lake has more external inputs of organic matter such as DOC to supply the food needs for the lake while in an autotrophic lake more of the food is produced internally (Houser et al. 2003). Autotrophic lakes can pull CO<sub>2</sub> from the atmosphere when photosynthetic demand exceeds the amount of aqueous CO<sub>2</sub> (Drake et al. 2017) and thus are carbon sinks while heterotrophic lakes are carbon sources. Metabolic rates are expected to increase due to global warming (Marotta et al. 2014), possibly increasing the amount of CO<sub>2</sub> and CH<sub>4</sub> produced.

Climate change has a number of effects on lakes in the north temperate region including warmer water temperatures, longer ice-free seasons, stratification earlier in the summer, and stratification for longer periods of time (Kalff 2002). Climate change can cause increased inputs of allochthonous DOC due to increased productivity in the catchment area, which is particularly pronounced in boreal areas (Adrian et al. 2009).

#### *Carbon processes by depth*

At depths where light is available for photosynthesis, primary producers fix carbon through photosynthesis (Prairie & Cole 2022). It then becomes food for heterotrophic organisms and eventually, as part of those organisms, settles to the bottom of the lake (Prairie & Cole 2022). Near the surface, DOC can be photo-oxidized to DIC at similar rates to planktonic respiration though



photo-oxidation decreases rapidly with depth because of light attenuation (Granéli et al. 1996).

Inputs of DOC to lakes determine how much greenhouse gas is released to the atmosphere, and much of the processing of this carbon happens in the hypolimnion. Carbon in the hypolimnion is largely of terrestrial origin, as well as some carbon in the remains of aquatic plants and animals (Prairie & Cole 2022). During the stratified period, the hypolimnion of a lake can become anoxic when bacteria use all the oxygen for respiration (Kalff 2002). This occurs when the hypolimnion receives enough organic matter that bacterial respiration increases enough to use up all of the oxygen, though some high latitude clearwater oligotrophic lakes can have higher concentrations of dissolved oxygen in the hypolimnion due to limited respiration and cold temperatures (Kalff 2002). When DOC is consumed, DIC and methane are released at a similar magnitude to the consumed DOC (Houser et al. 2003), so inputs of DOC to lakes determine how much greenhouse gas is released. Because gas is more soluble in cold water, global warming will lower gas solubility and increase respiration, leading to increased hypolimnion anoxia (Kalff 2002). At mid-latitudes such as my study area, temperature change is moderate compared to much higher Arctic rates of temperature change and lower rates in equatorial areas (Arias et al. 2021), so gas solubility should decrease at a moderate rate in the Midwest. One study of tropical lakes in the Amazon and boreal lakes in Sweden predicted that due to global

warming, sediment CO<sub>2</sub> and CH<sub>4</sub> production will increase 9-61% above present levels and 2.4-4.5 times higher in tropical regions than boreal regions (Marotta et al. 2014).

Respiration in lakes which have anoxic hypolimnions during most of the stratified period happens through anaerobic pathways (Houser et al. 2003). Organic carbon oxidations are distributed across a redox gradient in anoxic habits in accordance with the highest energy yield (Dodds & Whiles 2020). Aerobic respiration is preferred, but in the absence of oxygen, NO<sub>3</sub><sup>-</sup> is used first before Mn<sup>4+</sup>, Fe<sup>3+</sup>, and finally SO<sub>4</sub><sup>3+</sup> (Dodds & Whiles 2020). After oxidation, in anaerobic environments, fermentation happens in the form of methanogenesis (Kalff 2002). Methanogenesis reduces CO<sub>2</sub> to methane, causing elevated concentrations of methane in the hypolimnion (Kalff 2002).

In lakes where light reaches the hypolimnion and photosynthesis can occur, oxidation lasts longer before running out of electron acceptors because photosynthesis provides more electron acceptors (Rich 1980). Therefore, methanogenesis occurs less and thus less methane is produced (Rich 1980). Though rare, photosynthesis in the hypolimnion produces oxygen and consumes DIC (Houser et al. 2003).

Carbon can also be lost from the hypolimnion through permanent burial on the bottom of lakes (Prairie & Cole 2022). Organic carbon stored in the sediments can be released to the bottom waters during anoxic conditions as DOC and when water is reoxygenated, contributes to water column respiration and ebullition (Peter et al. 2016). Depending on the balance between mineralization of DOC to CO<sub>2</sub> and burial of organic carbon, an increase of CDOC can either increase or decrease the sequestration of greenhouse gases in lakes (Williamson et al. 2016). Increased burial can happen from colder temperatures and anoxia associated with water more darkly colored by DOC, and can reduce decomposition rates in the hypolimnion (Williamson et al. 2016). However, it can also increase the production of methane due to the anoxia as methane is produced via methanogenesis in anoxic conditions rather than CO<sub>2</sub> (Williamson et al. 2016; Dodds & Whiles 2020).

#### *Water color*

DOC and color are thought to be strongly correlated (Pace & Cole 2002). As water color is associated with the humic portion of DOC, it has been used as a stand-in for CDOC (Webster et al. 2008). The humic portion is a product of degraded lignin and cellulose from the terrestrial environment (Gergel et al. 1999). Water color is typically measured as the absorbance of light at 440 nm which is a measure of terrestrially derived colored dissolved organic material (CDOM) (Cuthbert & del Giorgio 1992; Brezonik et al. 2019). As this

measurement is focused on terrestrial DOC, there can also be DOC which does not absorb light at 440 nm. Thus, there can also be DOC which is non-colored in lakes (Xiao & Riise 2021). Furthermore, color of DOC can be reduced by DOC degradation by in-lake processing such as photobleaching and flocculation which more strongly affects the colored portion of DOC (Xiao & Riise 2021).

Besides DOC, some factors that can impact water clarity in lakes include metals such as iron, copper, mercury, and aluminum; chlorophyll- $\alpha$ ; and non-algal suspended solids (Brezonik et al. 2019, Xiao & Riise 2021, Shao et al. 2017 ). Iron, which stains water, typically is transported to lakes from the catchment area, particularly in areas with high peatland coverage (Xiao & Riise 2021). DOC reacts with positively charged metal ions including iron, so that there is a greater increase in water color than either alone would have (Xiao & Riise 2021; Reitsema et al. 2018). Other metals including copper, cadmium, lead, and zinc, can also form complexes with organic matter and increase light absorption (Shao et al. 2017; Reitsema et al. 2018). These are released back into the water column when the DOC degrades (Reitsema et al. 2018). Algal growth can lead to reduced water clarity as measured by a Secchi disk, but as CDOM may suppress algal growth, algae is typically not an important part of water color in high CDOM lakes such as those found in the more northern parts of Wisconsin and Michigan and Northeastern Minnesota (Brezonik et al. 2019, Thrane et al. 2014). Lake color can vary seasonally in accordance with color source, where low nutrient and low

color oligotrophic lakes tend to have peak color during the spring phytoplankton bloom (Topp et al. 2021). Nutrient rich green lakes (algae dominated) tend to have two color peaks per year, in the spring and late summer/fall when the phytoplankton bloom; they may also gradually increase in color over the course of a summer (Topp et al. 2021). CDOM lakes experience the most intense color during spring and late summer or may also increase in color over the duration of the summer (Topp et al. 2021).

Water color affects animals living within lakes- for example, diel vertical migration by zooplankton is more limited in darker colored lakes and predation by planktivorous fish decreases (Wissel et al. 2003). High levels of water color can lead to decreased primary production and phytoplankton biomass due to the corresponding decrease in light availability (Carpenter et al. 2003). In darker lakes, zooplankton are more commonly found in the epilimnion while in clearer lakes, zooplankton are found more in the metalimnion and hypolimnion (Wissel et al. 2003). One study of yellow perch (*Perca flavescens*) found that yellow perch living in a clear water lake had sexual dichromatism with the males having a more colorful belly while perch living in darker lakes did not have sexual dichromatism (Kekäläinen et al. 2010). Coloring of water by DOC can limit the depths at which macrophytes can grow (Reitsema et al. 2018). An increase in water color may lead to a decline of more light-sensitive macrophytes (McElarney et al. 2010).

### *Precipitation and lake ecosystems*

In the United States, temporal variation of precipitation is likely to increase with increasing global temperatures, increasing the risk for wet periods and droughts (Strock et al. 2016). The Midwest has seen an increase in precipitation and an increase in the frequency of extreme precipitation events since 1901 which is projected to continue through the end of the 21st century (Angel et al. 2018). Examining how that could affect the relationship of DOC and color will help to be able to better predict future greenhouse gas fluxes. Since pre-industrial times, carbon input to inland waters has increased by  $\sim 1$  GtC/year (Pilla et al. 2022), suggesting that climate change has already caused important changes to freshwater carbon cycling.

Increased precipitation can lead to increased erosion in watersheds, leading to increased organic carbon inputs and concentrations in receiving waterbodies (Pilla et al. 2022). In wet years, DOC increases in lakes but the extent depends on the qualities of the surrounding landscape such as elevation (Strock et al. 2016), so increased precipitation from climate change could increase carbon inputs to lakes. A study found that CDOM loading is decreased during dry years (Rose et al. 2016). Increased coverage of wetlands in the watershed can also lead to higher DOC concentrations in surface waters during wet years (Strock et al. 2016) as increased flow through upper soil layers that washes interstitial water enriched with DOC into nearby waters (Strock et al. 2016). Wetlands have high

productivity and low decomposition rates, so they are rich in organic matter (Dodds & Whiles 2020). The effects of seasonal changes in precipitation on DOC levels may be less important than the frequency and intensity of precipitation events which bring new DOC to a lake (Pace & Cole 2002, Webster et al. 2008).

Significant research has been done on the impact of precipitation events on DOC loading in streams. In a study of four streams in western New York, peak DOC was delayed by a lag in displacement of DOC-rich soil waters (Inamdar & Mitchell 2006). Another study of three streams in Vermont found that the type of DOC washed into streams during storms was more aromatic and humic in type (Vaughan et al. 2017). In a stream in Maryland, DOC inputs after storms did not decline during frequent storms in a one-month period, indicating that DOC in the catchment rebounds within days of a storm event (Dhillon & Inamdar 2014). After a storm, DOC loads decreased gradually, typically without dropping to pre-storm values, indicating that effects of storms on DOC loads last well past a storm event (Dhillon & Inamdar 2014).

Storms have many impacts on nutrient concentrations and water clarity. Strong storms can deepen the thermocline of lakes and erode shorelines, uproot vegetation, resuspend sediments, and increase turbidity (Kasprzak et al. 2017). During dry years, surface water nutrients and sediment loading is decreased, thus increasing water clarity (Rose et al. 2016). However, in eutrophic lakes water

clarity can decrease during drought years as nutrients within the lakes become concentrated and promote algal blooms while during wet years, these nutrients are more likely to be flushed from the lakes (Lisi & Hein 2018). Another study indicated that while extreme precipitation may flush nutrients into lakes, larger annual precipitation can lead to an overall decrease in nutrient concentrations (Ho & Michalak 2019). There is some disagreement over the long-term effects of increased precipitation on nutrients and algal blooms- another study indicated that increased precipitation will lead to more nutrients and thus more harmful algal blooms (Reichwaldt & Ghadouani 2012). Large storms have been seen to reduce water clarity by 39-44% (Rose et al. 2012). In agricultural areas such as Southern Wisconsin, nutrient runoff can strongly affect water clarity (Rose et al. 2016). A study of Wisconsin lakes found that DOC-regulated lakes tend to have water clarity which is more strongly impacted by precipitation than algal-regulated lakes (Rose et al. 2016). Clear, deep lakes also tend to have water clarity more strongly impacted by precipitation (Rose et al. 2016).

### *My study*

This study focuses on relationships between precipitation, DOC, and water color at different depths to address research gaps on the impact of storms on DOC in lakes. As precipitation in the upper Midwest will increase under climate change, DOC loading to lakes will also increase. Greenhouse gas emissions from lakes are related to DOC processing within lakes, so it is important to better



understand these relationships. With this goal, I ask the questions: How do DOC and color relate at different depths? How does precipitation impact DOC and color trends? To answer these questions, I use historical data, linear regressions, and a time lag analysis.

## Methods

### *Study site*

The survey lakes used for the study of water color and dissolved organic carbon (DOC) at different depths are located at the University of Notre Dame Environmental Research Center (UNDERC) in the Northern Highland Lake District of Wisconsin and Michigan near Land o' Lakes, Wisconsin (Figure 1, Table 1). These lakes are on undeveloped land in the Northern Highland Lake District, which is defined by many glacial kettle lakes which are surrounded by forest or wetland (Wilkinson et al. 2013, Jones 2017). Several of the UNDERC lakes have had whole lake experiments conducted on them, including during the period that data for this study was collected. A curtain was added to Long Lake in 1991, increasing the nutrients in the east portion of the lake. That curtain was removed in 1996. A curtain was added in 2012, and a second curtain added in 2018. Both of those curtains were removed in September 2023 (D. Szydlowski, personal communication, October 26, 2023). Aquashade dye was added to Ward Lake in the summer of 2012 to a total concentration of 1.5ppm in order to decrease the photic zone to 2m from 4m in 2010 (Batt et al. 2015). In Peter Lake, nutrients were added 1993-1997, 2002, and 2013-2015. The nutrients added were phosphoric acid and ammonium nitrate (Pace et al., 2018).  $^{13}\text{C}$ -DIC was added to the metalimnion in 2012 (Wilkinson et al. 2013). In 2008-2010, Largemouth Bass were added to Peter Lake (Carpenter et al. 2011). Tuesday Lake received nutrient additions of phosphoric acid and ammonium nitrate in 2013-2015 (Wilkinson et

al. 2018). Some of the UNDERC lakes are primarily fed by groundwater flow such as springs or seepage while others have inlets (D. Szydlowski, personal communication, October 24, 2023).

Lake	Data Years	Experiments	Surface Area (ha)	Catchment Area (ha)	Max Depth (m)	Mean Depth (m)	Visible Outlet	Trophic Status	Chl A (ug/L)
Bolger	2023	No	1.1†	-	3.5†	-	Yes†	-	5.84
Crampton	2003-2006, 2023	No	25.8*	54.3‡	15.3*	3.9*	No†	Oligotrophic¶	2.99
Cranberry	2023	No	1.4*	29.2‡	7.3*	4.3*	No†	-	6.43
East Long	1996-1999, 2004, 2006	Yes	2.3*	-	16.0*	5.4*	Yes§	-	20.96
Hummingbird	1999, 2001, 2023	No	0.8*	11.1‡	7.5*	3.7*	Yes†	-	32.50
Morris	2023	No	5.9*	120.0‡	6.8*	2.6*	Yes†	-	6.81
Paul	1996-1999, 2001 - 2016	No	1.7*	9.2‡	12*	3.7*	-	Mesotrophic¶	3.84
Peter	1996-1999, 2001 - 2016	Yes	2.7*	15.7‡	19*	5.7*	-	Mesotrophic¶	9.67
Tenderfoot	2023	No	165.2*	5839.8‡	9.3*	5.3*	Yes†	-	5.36
Tuesday	1999, 2002, 2012-2016	Yes	0.8*	2.7‡	18*	6.9*	No†	Dystrophic¶	7.32
Ward	2010, 2012, 2023	Yes	2.7*	57.6‡	8.3*	2.7*	Yes†	-	13.24
West Long	1996-1999, 2003-2004, 2006	Yes	5.5*	14.1‡	17*	3.6*	No§	-	8.44

**Table 1. Lake Characteristics** ¶Carpenter *et al.* 2016, \* Houser *et al.* 2003, † Pace & Cole 2002, ‡ Wilkinson *et al.* 2013, §Zwart *et al.* 2015. Average chlorophyll- $\alpha$  values are reported for the surface of each lake. For Bolger, Cranberry, Morris, and Tenderfoot, historical chlorophyll- $\alpha$  values were not available so the 2023 epilimnion value was used instead.

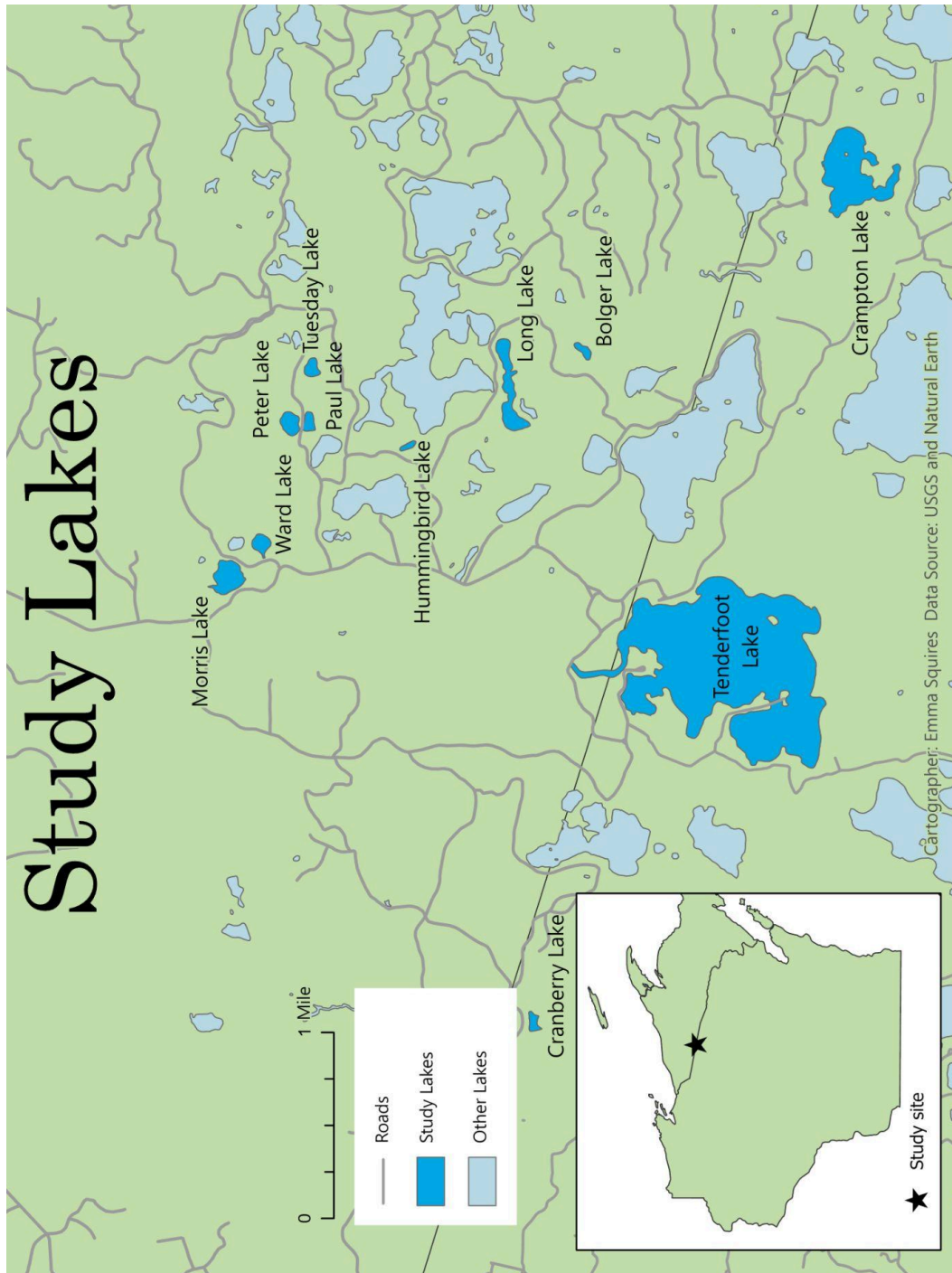


Figure 1. Map of the study lakes

### *Aquatic field data collection*

I collected field data in July 2023 from 10 lakes at UNDERC in order to measure DOC, chlorophyll- $\alpha$ , and water color. Water samples were taken from the epilimnion, metalimnion, and hypolimnion of each lake using a Van Dorn at the deepest point in the lake. The epilimnion was calculated to be the top layer of a lake where temperature change was no more than 1°C per meter; the epilimnion sample was taken from the middle of the epilimnion. The metalimnion was calculated to be the range of depths where temperature change was greater than 1°C, the metalimnion sample was taken 0.5 meters below the thermocline, where the temperature change was greatest. The hypolimnion was calculated to be the layer below the metalimnion where temperature change was no more than 1°C per meter; the hypolimnion sample was taken from the middle of the hypolimnion. In 2 lakes, Ward and Bolger, no hypolimnion was found. A sample was taken from the deepest point of those lakes but the data was not used as there was not true hypolimnion.

A temperature/dissolved oxygen profile was taken using a YSI optical probe. Water samples were kept in a cooler with ice until returning to the lab. Upon return, water for color analysis was filtered through a 25 mm Whatman GF/F push filter and refrigerated until analysis. Samples for DOC were filtered through 25 mm Whatman GF/F filters into glass vials and refrigerated until analysis. Color analysis was done by measuring light absorbance at 440 nm on a

spectrophotometer in a 10 cm cuvette. This value was then converted to a g440 scale using the equation:

$$g440 = 2.303 \times (\text{absorbance at } 440 \text{ nm} \div 0.1 \text{ m})$$

where 0.1m is the length of the cuvette. The g440 value is a measure of the humic content of the water (Cuthbert & del Giorgia 1992). DOC vials were sent to the Hasler Lab at the UW-Madison Center for Limnology for analysis. Samples for chlorophyll- $\alpha$  were filtered onto 47 mm Whatman GF/F and frozen for at least 24 hours, extracted in methanol for 24 hours, and analyzed using a fluorometer.

#### *Historical aquatic data*

Field data was combined with historical DOC, color and chlorophyll- $\alpha$  data from 1996-2016 for lakes at UNDERC; the historical data was pulled from the LTER data portal (Carpenter et al. 2022a; Carpenter et al. 2022b) in Fall 2023. Samples for this data were taken using a Van Dorn at the epilimnion, metalimnion, and hypolimnion. Water color was analyzed by measuring the absorbance at 440 nm on a spectrophotometer in a 10 cm cuvette. This value was then converted to a g440 scale using the equation:

$$g440 = 2.303 \times (\text{absorbance at } 440 \text{ nm} \div 0.1 \text{ m})$$

where 0.1m is the length of the cuvette. The g440 value is a measure of the humic content of the water (Cuthbert & del Giorgio 1992). Water was filtered into vials for DOC and sent to the Hasler Lab at the UW-Madison Center for Limnology for analysis. Frequency of data varies by lake but spans the months of May to September and covers the years 1996-2016 (Table 1).

#### *Local climatic data*

Climate data was pulled from the Purdue Midwest Regional Climate Center's website at <https://mrcc.purdue.edu/CLIMATE/welcome.jsp>, station number 475516 in Minocqua, Wisconsin. The climate data from this station dates from 1903 to present day, and offers precipitation, snowfall, snow depth, maximum temperature, and minimum temperature. This station is approximately 25 miles from the UNDERC lakes.

#### *Statistical analyses*

Statistical analyses were performed in R 4.3.2. Linear regression was used to analyze the relationship between DOC and color (g440). This was done with data separated by depth to examine how the relationship differed between depths (Figures 2-4, Table 2).

To investigate the relationship between precipitation patterns and lake DOC, a lag variable was created that linked precipitation with DOC a given

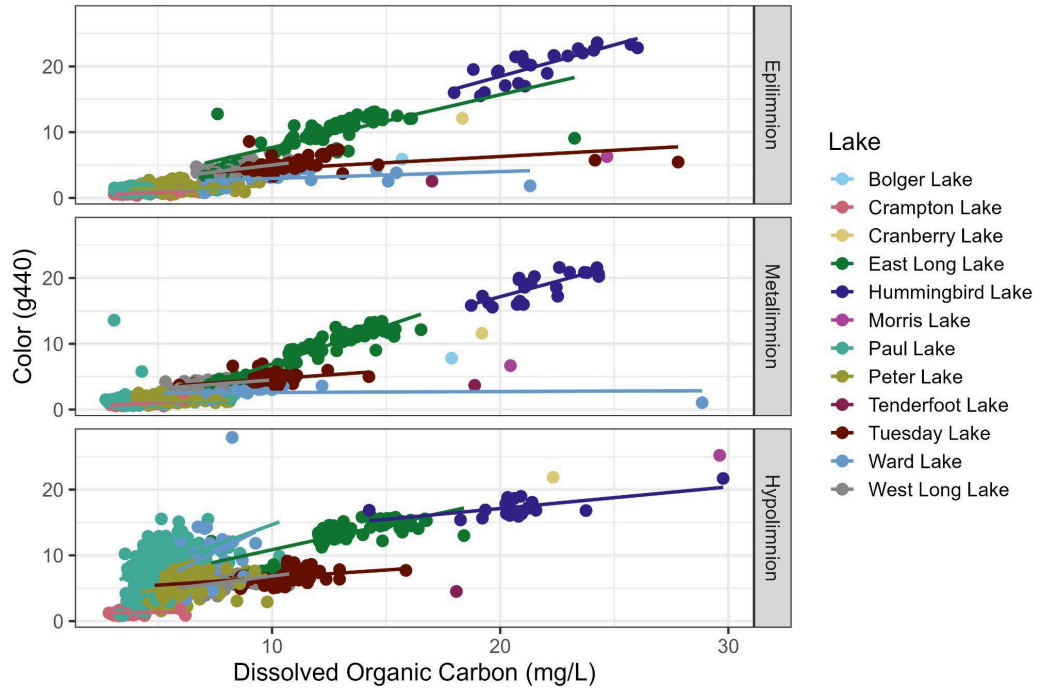


number of weeks later. This variable allowed us to examine how long it took for a DOC “signal” to wash into lakes after a precipitation event. These lag variables were only calculated for Paul and Peter lakes as those were the only lakes with consistent weekly data available for summer months. A time series analysis was not able to be completed because the data only covered summer months and time series models expect regular time intervals without gaps. Instead, a Generalized Estimating Equations Model (GEEM) was run to examine the relationship between precipitation and DOC using the lag variable (Tables 3 & 4). GEEMs allow for the possibility of correlation within the data while linear models assume that the data is independent (Salazar et al. 2016). GEEMs have been used in ecological case studies previously, including in a time series analysis of susceptibility of winter wheat, barley, and rapeseed to drought (Zarei et al. 2021) and to analyze timing of dolphin sightings (Bailey et al. 2012). In this case, correlation was possible because it was a longitudinal study and the effects of precipitation may depend on antecedent conditions. The GEE model was estimated using the geeM R package (v. 0.10.1) (McDaniel et al. 2013).

Data was separated into precipitation quartiles to examine the relationship between DOC and color (g440) on a graph. A linear regression was run to calculate effects of mean yearly DOC and yearly sum precipitation using an interaction term on the yearly mean color.

## Results

*DOC vs. color*



**Figure 2. Relation between summer DOC and color at different depths.** Points represent sampling events while lines indicate the slope of the linear regression line for each lake. Color indicates different lakes.

LAKENAME	DEPTH	SLOPE	P VALUE
Paul	Epilimnion	0.02	0.00
Peter	Epilimnion	0.07	0.00
West	Epilimnion	0.42	0.20
East	Epilimnion	0.80	0.73
Hummingbird	Epilimnion	0.96	0.84
Tuesday	Epilimnion	0.19	0.00
Crampton	Epilimnion	0.14	0.20
Ward	Epilimnion	0.10	0.01
Bolger	Epilimnion	NA	NA
Cranberry	Epilimnion	NA	NA
Morris	Epilimnion	NA	NA
Tenderfoot	Epilimnion	NA	NA
Paul	Metalimnion	-0.06	0.00
Peter	Metalimnion	0.00	0.00
West	Metalimnion	0.26	0.00
East	Metalimnion	1.16	0.00
Hummingbird	Metalimnion	0.94	0.68
Tuesday	Metalimnion	0.24	0.00
Crampton	Metalimnion	0.19	0.47
Ward	Metalimnion	0.01	0.00
Bolger	Metalimnion	NA	NA
Cranberry	Metalimnion	NA	NA
Morris	Metalimnion	NA	NA
Tenderfoot	Metalimnion	NA	NA

Paul	Hypolimnion	1.25	0.02
Peter	Hypolimnion	0.47	0.00
West	Hypolimnion	0.44	0.00
East	Hypolimnion	0.75	0.00
Hummingbird	Hypolimnion	0.33	0.00
Tuesday	Hypolimnion	0.23	0.00
Crampton	Hypolimnion	0.03	0.00
Ward	Hypolimnion	1.76	0.70
Cranberry	Hypolimnion	NA	NA
Morris	Hypolimnion	NA	NA
Tenderfoot	Hypolimnion	NA	NA

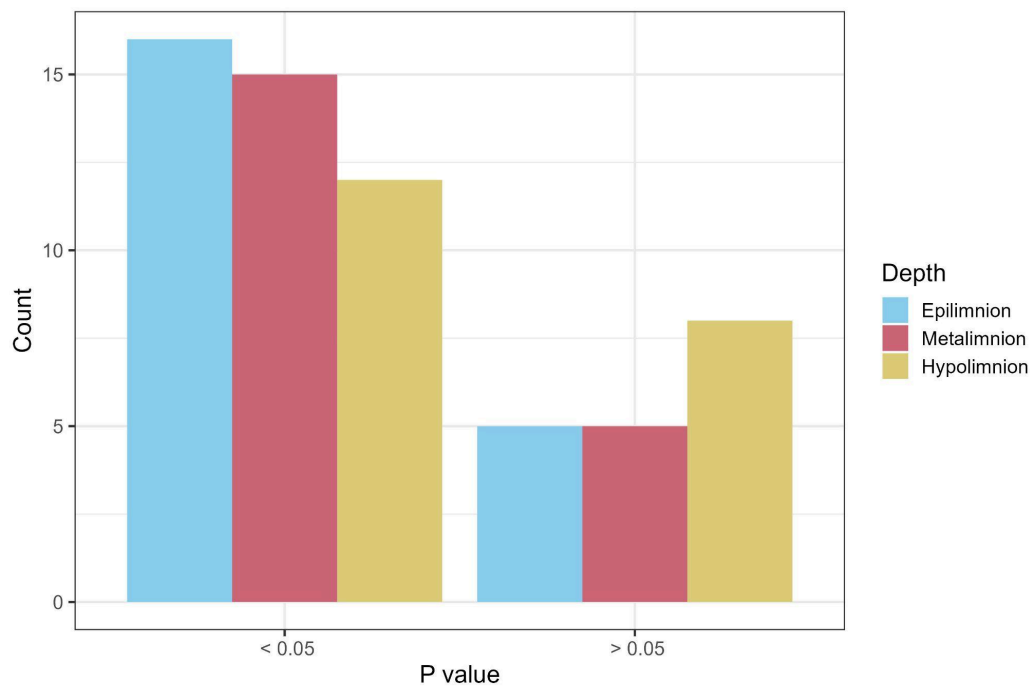
**Table 2. Relationship of summer DOC and color at different depths for each lake.** Slope indicates the slope of the linear regression for each lake and depth. A greater intensity of color indicates a more positive slope. A colored P Value indicates that the P Value is significant for that lake and depth. Lakes with NA values did not have enough data to run linear regressions.

I found a statistically significant positive relationship between summer DOC and color at each depth, with a weaker relationship in the hypolimnion than the epilimnion and metalimnion (Figure 2, Table 2, the p-value for each depth with all lakes combined is  $<2.2e^{-16}$ ). For the epilimnion, the r-squared for all lakes combined is 0.79, metalimnion is 0.82, and the hypolimnion is 0.37. Thus, the relationship between color and DOC is weaker in the hypolimnion and stronger in the epilimnion and metalimnion. The relationship in Ward Lake is notable as being only slightly positive in the epilimnion and had no relationship in the

metalimnion. This suggests that something other than DOC is affecting the color in that lake.

Lakes had a 6.45-fold variability in measured DOC across depths (Figure 1). Morris Lake had a mean DOC of 24.92 mg/L, while in contrast Crampton Lake had a mean DOC of only 3.86 mg/L. The range was similar when restricted to epilimnion depths. In the metalimnion, the range was lower at 5.72 fold. Hummingbird Lake had the highest mean DOC at 21.70 mg/L while Crampton Lake had the lowest at 3.80 mg/L. In the hypolimnion, the range was 7.99 fold with Morris Lake having the highest mean DOC at 29.62 mg/L and Crampton Lake had the lowest mean at 3.71 mg/L.

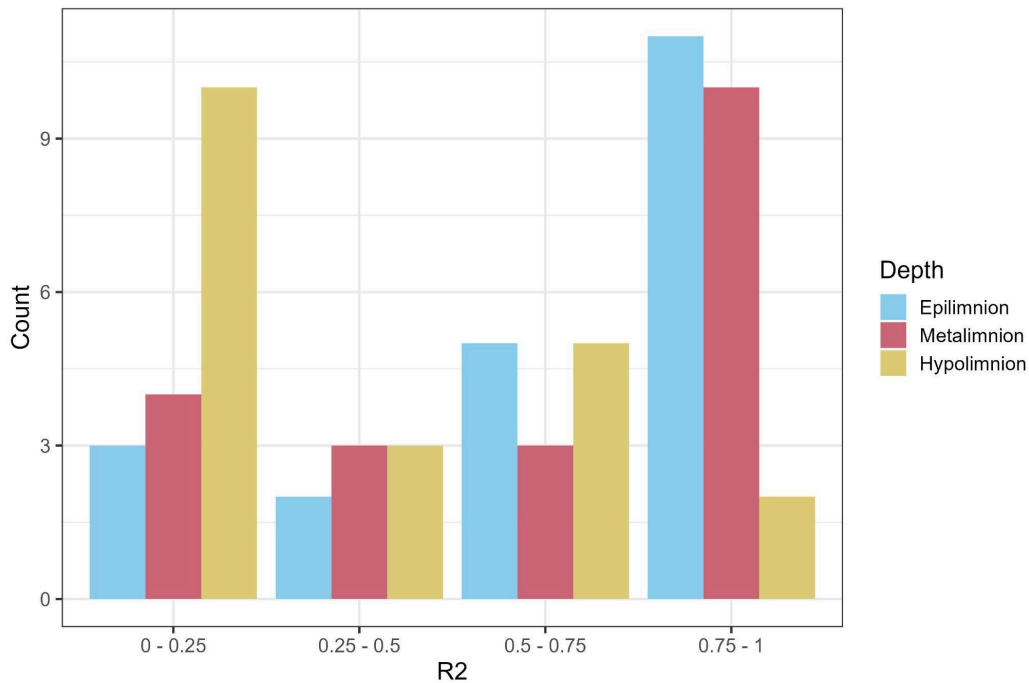
### *Significance of color vs DOC*



**Figure 3. Number of summers with a significant relationship between color and DOC.** A linear regression was run across lakes separated by year and depth. P values are sorted into significant ( $<0.05$ ) and not significant ( $>0.05$ ). Color indicates depth.

Color was significantly related to DOC in most summers at all depths.

There were more years with a p-value greater than 0.05 in the hypolimnion than the epilimnion and metalimnion. One of the years that is not significant that was not significant at any depth, 2023, has less data available than any other years, so it is possible that there was not enough data to produce significant results.



**Figure 4. R<sup>2</sup> values between color and DOC by year and depth.** A linear regression was run for all lakes separated by year and depth. R<sup>2</sup> values are binned into quantiles. Color indicates depth.

The r-squared values for the relationship between color and DOC are generally higher in the epilimnion and metalimnion than in the hypolimnion. In the majority of years, the r-squared in the epilimnion and metalimnion are greater than 0.5, so in those years and depths, DOC explains at least 50% of the water color. The hypolimnion r-squared values are lower and the majority of hypolimnion r-squared values are less than 0.25 so DOC does not explain much of the color that is present in the hypolimnion. There were no clear similarities in the lakes which had a higher hypolimnion r-squared value.

*Precipitation time lag*

LAG	ESTIMATE	ROBUST SE	WALD	P VALUE
Intercept	5.3170	0.1711	31.0800	0.00000
Week 1	0.2619	0.2774	0.9440	0.34520
Week 2	0.8896	0.4139	2.1490	0.03161
Week 3	-0.3017	0.3556	-0.8483	0.39630
Week 4	0.2709	0.3225	0.8398	0.40100

**Table 3. Paul Lake Epilimnion Precipitation Lag:** Results of a GEEM run for Paul Lake to determine a correlation between precipitation and DOC. Lag indicates the number of weeks between the precipitation and DOC measurements. The highlighted rows indicate which data is significant ( $P < 0.05$ ).

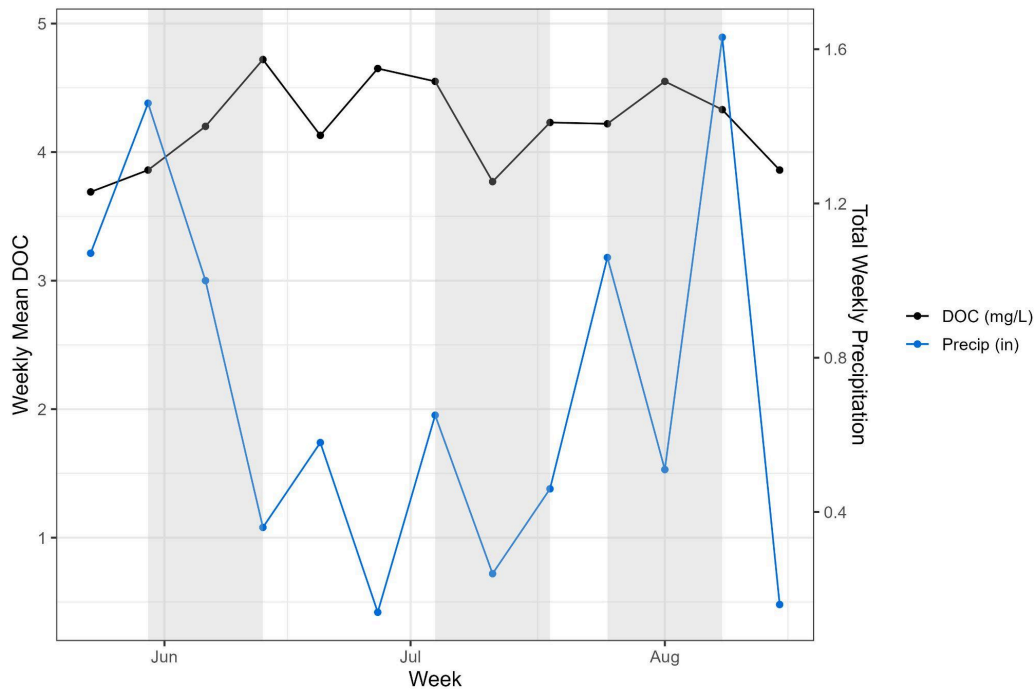
LAG	ESTIMATE	ROBUST SE	WALD	P VALUE
Intercept	5.3170	0.1711	31.0800	0.00000
Week 1	0.2619	0.2774	0.9440	0.34520
Week 2	0.8896	0.4139	2.1490	0.03161
Week 3	-0.3017	0.3556	-0.8483	0.39630
Week 4	0.2709	0.3225	0.8398	0.40100

**Table 4. Peter Lake Epilimnion Precipitation Lag:** Results of a GEEM run for Peter Lake to determine a correlation between precipitation and DOC. Lag indicates the number of weeks between the precipitation and DOC measurements. The highlighted rows indicate which data is significant ( $P < 0.05$ ).

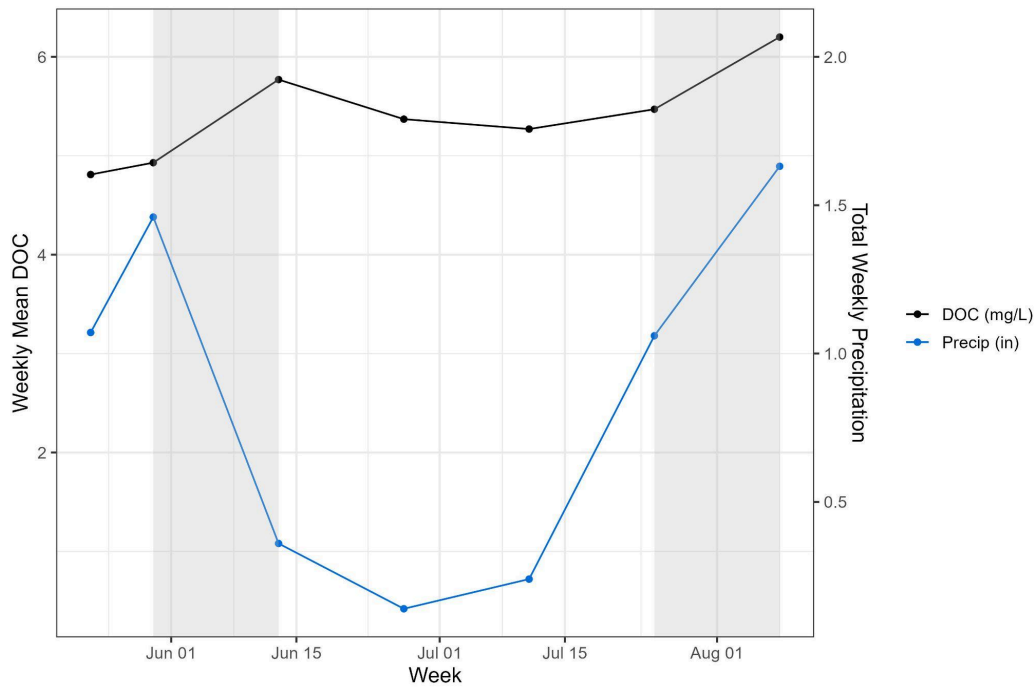


In both Peter and Paul Lakes, two weeks after a rain event show a corresponding increase in DOC with a slope of 0.8896 in both lakes while no other time lag is significant (Tables 3 & 4). The intercepts are also significant which indicates that precipitation does have a significant effect on DOC in these lakes. Only epilimnion data is shown as no other depths displayed significant results.

*Precipitation influence on DOC in Paul and Peter Lakes in a median precipitation year*



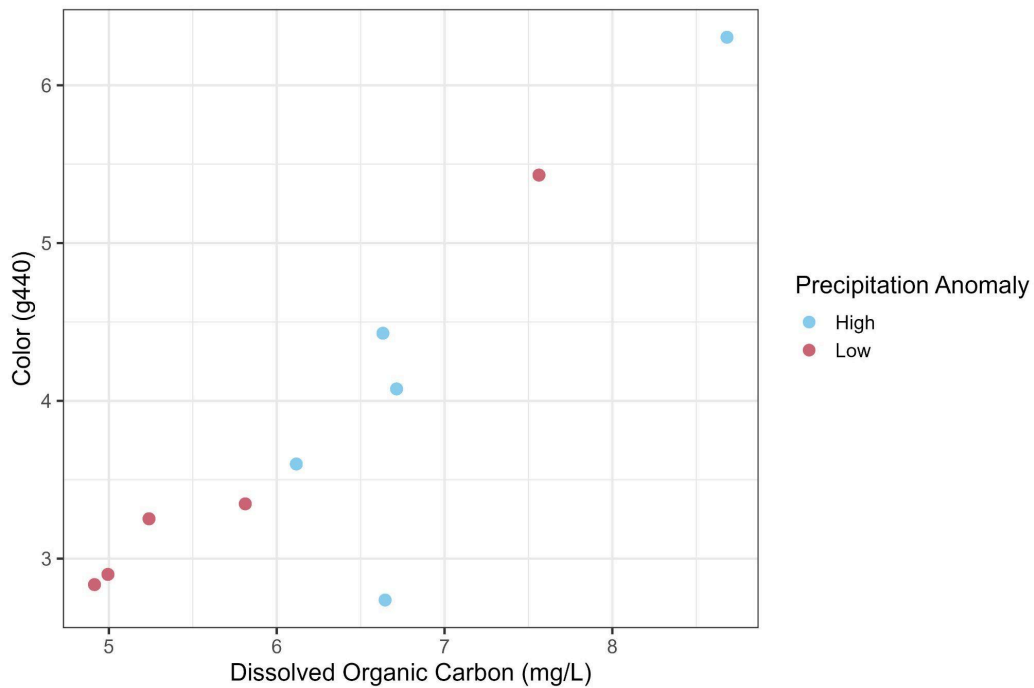
**Figure 5. Weekly mean DOC in Paul Lake compared to precipitation in a median precipitation year.** Line color indicates whether data is DOC or precipitation. Each point for DOC indicates 1 sampling event while each point for precipitation indicates a sum of precipitation for the week. Data is from the epilimnion only as the GEEM model only displayed significance in the epilimnion. The year used was 2004, the median precipitation year to demonstrate how DOC and precipitation are related in an average year. Grey shaded areas indicate 2 week periods post precipitation event (based on GEEM, see Tables 3 and 4) and the starting location is paired with a spike in precipitation to indicate the period in which DOC may be washed into the lake.



**Figure 6. Weekly mean DOC in Peter Lake compared to precipitation in a median precipitation year.** Line color indicates whether data is DOC or precipitation. Each point for DOC indicates 1 sampling event while each point for precipitation indicates a sum of precipitation for the week. Data is from the epilimnion only as the GEEM model only displayed significance in the epilimnion. The year used was 2004, the median precipitation year to demonstrate how DOC and precipitation are related in an average year. Grey shaded areas indicate 2 week periods post precipitation event (based on GEEM, see Tables 3 and 4) and the starting location is paired with a spike in precipitation to indicate the period in which DOC may be washed into the lake.

The influence of this two-week time lag can be seen in example “median” precipitation summers in Peter and Paul lakes (Figures 5 and 6). In both cases, the year used was 2004, which is the median year for precipitation out of all years sampled, so that the response of DOC can be analyzed in a normal year. In these graphs, it can often be seen that following a spike or dip in precipitation, the DOC concentrations show a corresponding spike or dip in 1-2 weeks to show up in the DOC concentrations.

### Precipitation influence on DOC and color



**Figure 7. Summer DOC and color in high and low precipitation years.** Points indicate the year average of DOC and color measurements from all lakes and depths during the highest and lowest precipitation quartiles during the study period. Color indicates whether a year is in the highest or lowest precipitation quartile.

variable	Estimate	Std Error	T value	P value
Intercept	-3.05	0.290	-10.406	<2E-16
DOC	1.13	0.040	28.286	<2E-16
Yearly sum precip	0.06	0.010	6.833	8.62E-12
DOC\$Precip	-0.01	0.001	-8.014	1.18E-15

**Table 5. Yearly summer color response to DOC and precipitation.** Results of a linear regression run to determine the effects of DOC and yearly sum precipitation using an interaction term. All coefficients had a significant p value ( $p < 0.05$ ).

Both high and low precipitation years follow the expected linear relationship for color and DOC (Figure 7). Thus, it appears that anomalous precipitation does not affect the relationship between water color and DOC. Generally wet years had higher DOC than did dry years. The only dry year with higher DOC than a wet year was 1996. That anomaly may be explained by nutrient additions in several of the lakes during that year (Carpenter et al. 2001). The r-squared for the model was 0.56. All coefficients used in the model were significant, so DOC does affect color when controlling for precipitation and precipitation affects color when controlling for DOC, though to a much smaller extent. When the effects of DOC and precipitation are combined, the effect on color is less than the sum of the individual effects.

## Discussion

This study found that DOC and lake water color were related at all depths within lakes, but there were some lakes where this relationship was weaker and the effect of DOC on water color decreased with depth. There was a 1-2-week lag period between when a precipitation event occurs and when the DOC-enriched water enters the lakes in this study. Wet years generally had higher DOC than dry years, indicating that increased annual precipitation associated with climate change in the Midwest could lead to increased DOC in lakes. When DOC was high and precipitation was also high, water color values were slightly lower than with high DOC alone.

### *DOC and color at different depths*

My research was consistent with previous research in that a correlation was found between water color and DOC (Pace & Cole 2002). At all depths, there was a significant correlation between color and DOC, suggesting that there was colored organic carbon at all depths. However, DOC explains much more of the color present in the epilimnion and metalimnion than the hypolimnion. Previous isotope analysis has determined that organic matter including DOC in the epilimnion and metalimnion of these lakes is largely of terrestrial origin while hypolimnetic organic matter was not studied (Wilkinson et al 2013).

Some lakes had weaker associations between color and DOC, such as Ward Lake, suggesting that either those lakes had an autochthonous source of DOC or a different source of color. Water clarity can be affected by chlorophyll- $\alpha$  content, non-algal suspended solids, or CDOM (such as CDOC) (Brezonik et al. 2019). As non-algal suspended solids typically are derived from soil erosion in the watershed and are not typically less important than chlorophyll- $\alpha$  and CDOC in determining water clarity in Upper Midwest Lakes (Brezonik et al. 2019), it is unlikely that non-algal suspended solids are responsible for the color of water in Ward Lake. Previous studies of Ward Lake have indicated that Ward Lake has high chlorophyll- $\alpha$  concentrations and is a productive lake (Batt et al. 2012) and thus algal production may influence the water color in Ward Lake. A few of the lakes did not have a significant relationship between color and DOC in the epilimnion and metalimnion, possibly due to not enough data available for those lakes to produce significant results. Tuesday also had a weaker relationship in the epilimnion but it appears that this may have been due to a few outlying points which have high DOC and relatively low color as the majority of points from that lake follow the more common 1:1 ratio of color to DOC. There are only two data points in the epilimnion which have substantially higher DOC than would be expected; of these, one point is from 2014 and may have been taken from a deeper layer and mislabeled (D. Szydlowski, personal communication, February 29, 2024).

The hypolimnion had a weaker relationship between color and DOC. Some of the lakes had much more color than would be expected from DOC alone. Other sources of color to lakes include dissolved metals such as iron (Xiao & Riise 2021, Shao et al. 2017) and algal growth (Brezonik et al. 2019). As light does not reach the hypolimnion in many of the studied lakes, it is unlikely that algal growth is the source of color seen in the hypolimnion. However, algae which grow in the epilimnion die and sink into the hypolimnion (Lee & Jones-Lee 1995) where they may add to color readings. Processing of carbon in the hypolimnion often happens in anoxic conditions, unlike the upper layers of the lakes. Therefore, possible additional sources of water color include dissolved metals from the sediments or partially degraded DOC. Some DOC in the hypolimnion may have been less colored as not all DOC absorbs light at 440 nm, particularly after it has been processed (Xiao & Riise 2021).

Some years had weaker relationships between DOC and color (Figures 3-4). One of these years was 2023, which had much less data available than any of the other years, so it is possible that there was not enough data to provide significant results. A factor that affects DOC and color is terrestrial production (Strock et al. 2016) which can vary by year and thus could result in some years with weaker relationships between DOC and color. Furthermore, several of the lakes studied were experimental lakes and experiments done could have caused weaker relationships. 2013 had a weak relationship between color and DOC in the

epilimnion while in 2014 the relationship was weak in the metalimnion. From 2013 to 2015, Peter Lake and Tuesday Lake received nutrient additions while Ward Lake received Aquashade dye in 2012, which could have changed the DOC-color relationship.

As water color is frequently used as a proxy for DOC (Webster et al. 2008), it is important to understand how the relationship between color and DOC changes with depth so that estimations of DOC content are accurate. This correlation is well known for upper layers, but low  $R^2$  values imply that hypolimnion DOC is less colored and therefore has a different chemical structure.

#### *Precipitation events*

In both Peter and Paul Lakes, it took two weeks after a rain event for a significant effect on DOC to be found. Precipitation is an important variable to consider due to the high percentage of terrestrial DOC in the lakes studied. In a previous study of epilimnetic particulate organic carbon, Paul Lake had 38% particulate organic carbon of terrestrial origin, Peter Lake had 47%, Tuesday Lake had 57%, and the clearer-water Crampton Lake had 12% (Carpenter et al. 2016). Due to the importance of hydrologic variables such as watershed characteristics in determining how much and how quickly precipitation reaches a lake, it is important to know how long that takes before determining the effects on DOC. The lag time likely varies from lake to lake as factors such as watershed size vary



greatly between lakes (Table 1). It may also be affected by wetland extent, elevation, land use/cover, and vegetation type in the catchment area (Strock et al. 2016; Vaughan et al. 2017; Inamdar & Mitchell 2006). Because Peter and Paul are very close to each other and have similar watershed sizes and other characteristics, it is not surprising that they would have the same lag period. Previous research on several of these lakes (Peter, East Long, and West Long lakes) has indicated that groundwater does not enter or exit the hypolimnion during the stratified period, so water would not enter the lakes this way (Houser et al. 2003). Thus, the precipitation lag time is more important to consider for the upper layers as it is unlikely to affect the hypolimnion.

The water level of Peter and Paul Lakes has been noted to rise in a few hours after a rain event as the watershed size of both lakes is quite small (D. Szydlowski, personal communication, February 29, 2024). However, the lag time was longer than the amount of time that it takes for the water level to rise. DOC-enriched interstitial water from upper soil layers can be washed into inland waters after a rain event (Strock et al. 2016; Inamdar & Mitchell 2006), so it is likely that the lag time is caused by the extra time needed for precipitation to sink into the ground and cause groundwater flow to carry DOC-enriched water to the lakes. The variation in time that it takes for DOC concentrations to reflect the precipitation may be due to the timing of data collection, as the DOC is taken weekly and precipitation is a sum for the week. If the majority of the rainfall

occurs at the beginning of the week and DOC data was collected later in the week, it may look like the DOC concentration changes faster than it actually does.

Precipitation increased DOC in lakes after each precipitation event. This is consistent with past research on lakes outside of the temperate zone (Sadro & Melack 2012; Jennings et al. 2012), and for Lake Superior (Cooney et al. 2018). It is also consistent with research done on streams in the temperate zone (Vaughan et al. 2017; Inamdar & Mitchell 2006; Dhillon & Inamdar 2014). Past research on streams has indicated the highest DOC was related to the largest and most intense storms (Inamdar & Mitchell 2006). Color likely also increases after each rain event as the terrestrial DOC that is washed in tends to be highly colored (Webster et al. 2008; Inamdar et al. 2011). In several studies of streams in New England, it was found that DOC increased after precipitation events and that this DOC was more humic compared to non-storm periods (Inamdar et al. 2011; Yoon & Raymond 2012) and as humic DOC tends to be highly colored, this suggests that color will also increase after storms.

Further research is needed that uses daily DOC, color, and precipitation measurements as it is possible that the weekly data used here was not precise enough to provide an accurate estimate of the lag time between a precipitation event and the corresponding wash of DOC into a lake. One study on DOC in streams after storms suggested that traditional grab sampling would not be

frequent enough for measuring storm effects because of the highly variable nature of storms thus making in situ optical sensors a better option (Vaughan et al. 2017). Many of the studies on storm effects on streams use a mix of automated grab sampling, automated sensors, and grab sampling by hand (Inamdar & Mitchell 2006; Dhillon & Inamdar 2014; Yoon & Raymond 2012). In lakes, sampling is often less frequent. Of the studies looking at DOC on lakes outside of the temperate region, one study sampled every week to 2 weeks to look at 13 separate weather events (Jennings et al. 2012) while the other took monthly samples and only looked at one weather event (Sadro & Melack 2012). Sampling on Lake Superior which included DOC measurements took samples weekly after one storm event and one week after another storm event with the sampling focused in the part of the lake affected by the storm (Cooney et al. 2018). Only one study of lakes used data that was more frequent than weekly and did not include DOC measurements while also only looking at a 5-day period (Abell & Hamilton 2015). It is possible that lakes do not react as quickly to storms as streams do because they have longer residence times. However, taking more frequent samples would help to understand how quickly storms impact lakes and what the lifetime of those effects is, though this is labor intensive and thus not always possible.

### *Precipitation years*

In high precipitation years, DOC concentrations were generally higher and thus color was also generally higher. Precipitation appears to increase color via increased transportation of terrestrial DOC to lakes. However, when the effects of DOC and precipitation are combined, the effect on color is less than the sum of the individual effects. This could possibly be a dilution effect which has been observed in streams during peak flow following a rain event (Dhillon & Inamdar 2014).

Many past studies have found evidence of brownification, or increased lake water color, in Europe and the Eastern United States caused by increased transportation of DOC from the terrestrial environment (for example Köhler et al. 2013, Williamson et al. 2016, Redden et al. 2021). Several theories exist for this phenomenon. One past study has indicated that during extreme wet years, there is increased transportation of DOC to lakes, particularly for lakes with wetlands in their watershed (Strock et al. 2016). Another explanation is the decrease of acid rain due to stricter regulations on air pollution- one study of time series data from 522 lakes and streams in North America and northern Europe found that an upward trend in DOC between 1990 and 2004 can be explained by a decrease in acid rain (Monteith et al. 2007). Acid rain decreases soil pH and increases the strength of ionic bonding within soils, making it harder for organic matter in soils to dissolve into groundwater (Monteith et al. 2007). Thus organic matter is more

easily washed out of soils that have recovered from acid rain. A study of 24 lakes near Oslo, Norway found that during the peak of anthropogenic sulfur in the 1970s, there was a minimum accumulation of organic matter in lakes (Riise et al. 2018), indicating acid rain decreasing transportation of DOC.

Although some studies in the Midwest have found inconclusive evidence of brownification (Brezonik et al. 2019; Jane et al. 2017), a study in western Ontario just north of Minnesota found evidence of brownification (Meyer-Jacob et al. 2019). This study indicated that acid deposition in western Ontario was more limited than on the East Coast of North America so DOC rebound from acidification was more limited, but DOC concentrations in that study were higher than pre-industrial DOC levels, indicating that climate change drivers including rising annual mean temperatures and increased annual precipitation are responsible for brownification in this region (Meyer-Jacob et al. 2019). Another study of water clarity of over 5000 lakes in Wisconsin lakes in wet and dry years found that CDOM loading was much higher in wet years than in dry years (Rose et al. 2016). The Midwest has seen an increase in precipitation and an increase in the frequency of extreme precipitation events which is predicted to continue increasing (Angel et al. 2018), and thus may facilitate increased transportation of DOC to lakes in the Midwest. Because increased DOC leads to an increase in microbial respiration in lakes, particularly with warmer temperatures, this will

lead to increased greenhouse gas release from lakes and further contribute to climate change.

## **Conclusion**

It is important to understand the relationship between DOC and color because that can help to understand the flow of carbon through lakes and the carbon processes that happen in them. DOC and lake water color are related at all depths within lakes, but there are some lakes where this relationship is weaker and the effect of DOC on water color decreases with depth. Future study of DOC within lakes should take into account how carbon processing at different depths affects characteristics of carbon and thus the impacts that carbon has on other processes within the lake such as metabolism.

Lakes are an important part of the carbon cycle and are closely tied to the environments surrounding them due to the many inputs they receive from the atmospheric and terrestrial environments, so it is important to understand the effects that precipitation events and long-term precipitation increases have on lakes. Increased precipitation led to increased dissolved organic carbon within lakes. There was a 2-week lag period between when a precipitation event occurred and when the DOC-enriched water entered the lakes in this study. Furthermore, wet years had generally higher levels of DOC than did dry years. As precipitation in the Midwest will increase over the next century due to climate change, this could lead to an increase in brownification in Midwestern Lakes. Increased DOC in lakes will result in increased respiration and thus increased greenhouse gas release.

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