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Key Points:

- DOM quality characteristics are more synchronous than DOC concentration
- SUVA responds strongly to weather drivers, particularly the degree of moisture
- DOC trends are heterogeneous, in contrast to a predominance of increasing trends in many regions

Supporting Information:

- Supporting Information S1

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Long-term trends and synchrony in dissolved organic matter characteristics in Wisconsin, USA, lakes: Quality, not quantity, is highly sensitive to climate

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Abstract Dissolved organic matter (DOM) is a fundamental driver of many lake processes. In the past several decades, many lakes have exhibited a substantial increase in DOM quantity, measured as dissolved organic carbon (DOC) concentration. While increasing DOC is now widely recognized, fewer studies have sought to understand how characteristics of DOM (DOM *quality*) change over time. Quality can be measured in several ways, including the optical characteristics spectral slope ($S_{275–295}$), spectral ratio (S_R), absorbance at 254 nm (A_{254}), and DOC-specific absorbance (SUVA; A_{254}:DOC). However, long-term measurements of quality are not nearly as common as long-term measurements of DOC concentration. We used 24 years of DOC and absorbance data for seven lakes in the North Temperate Lakes Long-Term Ecological Research site in northern Wisconsin, USA, to examine temporal trends and synchrony in both DOC concentration and quality. We predicted lower S_R and $S_{275–295}$ and higher A_{254} and SUVA trends, consistent with increasing DOC and greater allochthony. DOC concentration exhibited both significant positive and negative trends among lakes. In contrast, DOC quality exhibited trends suggesting reduced allochthony or increased degradation, with significant long-term increases in S_R in three lakes. Patterns and synchrony of DOM quality parameters suggest that they are more responsive to climatic variations than DOC concentration. SUVA was particularly responsive to the degree of soil moisture. These results demonstrate that DOC quantity and quality can exhibit different complex long-term trends and responses to climatic drivers, with implications for carbon cycling and microbial communities in aquatic ecosystems.

1. Introduction

Dissolved organic matter (DOM) plays a central role regulating many aquatic ecosystem processes and characteristics. Often measured as dissolved organic carbon (DOC) concentration, it represents the largest reservoir of organic carbon in most lakes [*Prairie*, 2008] and is an important energy source fueling aquatic food webs [*Cole et al.*, 2011; *Karlsson et al.*, 2012]. The light-absorbing component of DOM, referred to as chromophoric or colored DOM (CDOM), gives many water bodies a brownish hue and strongly absorbs both ultraviolet and photosynthetically active radiation [*Morris et al.*, 1995]. By absorbing light, DOM also strongly influences the vertical distribution of heat within the water column in smaller lakes [*Fee et al.*, 1996; *Pérez-Fuentetaja et al.*, 1999; *Houser*, 2006]. Thus, lakes with high CDOM typically have a shallower mixed surface layer and a colder hypolimnion relative to lower CDOM lakes [*Persson and Jones*, 2008; *Read and Rose*, 2013]. Higher light attenuation in high CDOM systems also impacts primary productivity, reducing benthic algal production and shading phytoplankton [*Karlsson et al.*, 2009; *Jones et al.*, 2012]. In turn, CDOM impacts on primary production have consequences for the entire food web, with some studies showing reduced biomass of some fish species in high DOC lakes [*Finstad et al.*, 2014; *Benoît et al.*, 2016].

A number of studies have documented long-term and widespread increases in DOC in many lakes and other water bodies in recent decades [*Evans et al.*, 2005; *Roulet and Moore*, 2006; *Monteith et al.*, 2007; *Haaland et al.*, 2010]. Increases in DOC are particularly prevalent in the northeast U.S. and eastern Canada, as well as in western Europe [*Evans et al.*, 2005; *Roulet and Moore*, 2006; *Monteith et al.*, 2007]. Two of the primary drivers of increasing DOC include increases in precipitation [*Zhang et al.*, 2010; *Couture et al.*, 2012] and recovery from anthropogenic acid deposition [*Evans et al.*, 2006; *Monteith et al.*, 2007; *Haaland et al.*, 2010]. Increasing DOC concentrations facilitate a phenomenon commonly referred to as browning, which represents an increase in CDOM [*Roulet and Moore*, 2006; *Weyhenmeyer*, 2008; *Larsen et al.*, 2011; *Solomon et al.*, 2015]. However,

Table 1. Description of Metrics Used in Manuscript

Metric	Indicator of	Details
S_R	Average molecular weight (DOM quality)	S_R is the ratio of the spectral slope across 275–295 nm divided by the spectral slope across 350–400 nm. S_R increases with photobleaching and may decrease with microbial processing. Low S_R values are associated with terrestrially derived DOM [*Helms et al.*, 2008]
$S_{275-295}$	Average molecular weight (DOM quality)	$S_{275-295}$ is the spectral slope across the wave band 275–295 nm. It increases with photobleaching. Low values of $S_{275-295}$ are associated with terrestrially derived DOM [*Helms et al.*, 2008]
A_{254}	Correlates with DOC concentration (DOM quantity)	Correlates with DOC so is generally a measure of quantity, even though it is an absorbance metric [*Brandstetter et al.*, 1996]
SUVA	Aromaticity (DOM quality)	SUVA is the ratio of absorbance at 254 nm to the DOC concentration. SUVA is highly correlated with aromaticity ($r^2 > 0.97$) [*Weishaar et al.*, 2003]. Higher aromaticity is associated with allochthonous organic matter [*Cory and McKnight*, 2005]
DOC	Dissolved organic carbon concentration (DOM quantity)	A measure DOM quantity

despite the extensive knowledge of how DOC concentrations are changing and the widespread reports of browning, little is known about how other DOM qualities are changing concurrent with broad-scale environmental changes such as changes in climate and acid deposition.

While most studies assessing long-term trends in DOM have focused on DOC concentrations (a measure of DOM quantity), DOM quality can be variable and is an important factor influencing DOM roles in aquatic ecosystems [*Kothawala et al.*, 2014; *Kellerman et al.*, 2015; *Ruiz-Gonzalez et al.*, 2015]. DOM quality can be characterized in several different ways. Optical characteristics provide one of the most ecologically relevant means to both characterize DOM sources, as well as potential impacts on aquatic systems [*Amaral et al.*, 2016; *Hansen et al.*, 2016]. For example, DOC-specific absorbance (SUVA), which characterizes absorbance (typically at 254 nm) normalized to DOC concentration, is highly correlated with the degree of aromaticity of the DOM pool (Table 1) [*Weishaar et al.*, 2003]. In turn, highly aromatic DOM has relatively low biological availability to microbial communities [*McKnight et al.*, 2003; *Anesio et al.*, 2005; *Olefeldt et al.*, 2013]. Additionally, the spectral characteristics of dissolved absorbance provide information on the biochemistry of the DOM pool. For example, the spectral slope $S_{275-295}$ is a measure of the slope of sample absorbance over the wavelengths from 275 to 295 nm and is inversely related to average DOM molecular weight [*Fichot and Benner*, 2012]. Low molecular weight DOC represents an energy source that can be readily utilized by bacteria [*Berggren et al.*, 2010] and may stimulate net heterotrophy in lakes [*Solomon et al.*, 2013]. Similarly, S_R, the ratio of $S_{275-295}$ to $S_{350-400}$, is inversely related to average molecular weight [*Helms et al.*, 2008] and lower $S_{275-295}$ and S_R values are correlated with more allochthonous DOM pools [*Helms et al.*, 2008; *Rose et al.*, 2015]. In contrast to less bioavailable aromatic, high molecular weight organic matter [*Moran et al.*, 2000; *Anesio et al.*, 2005], highly labile lower molecular weight amino acids, polysaccharides, lipids, proteins, and carbohydrates are typically autochthonously derived from aquatic primary producers [*McDonald et al.*, 2004; *Helms et al.*, 2008]. Unlike these other absorbance metrics, raw absorbance at 254 nm (A_{254}), is highly correlated with DOC concentration; therefore, we refer to it as a measure of quantity rather than quality [*Brandstetter et al.*, 1996]. Cumulatively, these optical metrics can provide a great deal of information about the composition, source, and degree of degradation of aquatic DOM, as well as additional information complementing insights on the ecological effects of long-term trends in DOC concentrations and browning [*Williamson et al.*, 2014].

There are few long-term records and assessments of how DOM quality is changing. Using fluorescence as an indicator of DOM quality [*McKnight et al.*, 2001], one study conducted on nine Maine lakes experiencing decreasing SO_4^{2-} deposition found that as DOC increased in five of these lakes, the proportion of terrestrially derived DOM also increased [*SanClements et al.*, 2012]. Such responses to decreasing acidification are believed to be driven by increased solubility of DOM as pH increases, leading to increased terrestrial DOM loads in surface runoff. Similarly, *Williamson et al.* [2015] analyzed changes in DOC-specific absorbance (at 320 nm) in two lakes in northeastern Pennsylvania, USA, through 27 years. These lakes experienced both decreased acid deposition and increasing precipitation during the study period. Both DOC concentration and DOC-specific absorbance increased over this period, though significantly in only one lake, consistent with greater terrestrial, more aromatic DOM inputs to these lakes. While the results of these studies are compelling, we know of no observations of synchrony in DOM quality within a lake region or long-term