Increasing Dissolved Organic Carbon Concentrations in Northern Boreal Lakes: Implications for Lake Water Transparency and Thermal Structure

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Increasing dissolved organic carbon concentrations in northern boreal lakes: Implications for lake water transparency and thermal structure

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Abstract We evaluated trends in dissolved organic carbon (DOC) and associated changes in water transparency and epilimnion thickness to better understand the implications of regional increases in DOC concentration in lakes. Long-term monitoring of a suite of physical, chemical, and biological data from six to 12 lakes in Acadia National Park in Maine was paired with high-frequency sensor monitoring of one lake as a model system. Water transparency declined across study sites since 1995 as DOC increased and chlorophyll remained stable, suggesting that this was not a signal of increased eutrophication. As clarity declined, some lakes experienced reduced epilimnion thickness. The degree to which transparency changed across the lakes was dependent on DOC concentration, with a larger decline in transparency occurring in clear water lakes (−0.3 m yr⁻¹) than brown water lakes (−0.1 m yr⁻¹). DOC concentration was an important explanatory variable for reduced epilimnion thickness in short-term sensor measurements. A regional decline in water transparency across all lakes and reduction in epilimnion thickness in a limited number of systems appeared to be acting as a sentinel for changes in atmospheric deposition and regional weather that modified the delivery of DOC from the watershed.

1. Introduction

Dissolved organic carbon (DOC) concentrations have increased in lakes across many parts of the Northern Hemisphere, with an approximate doubling of DOC observed in some regions in recent decades [Roulet and Moore, 2006; Monteith et al., 2007, Zhang et al., 2010]. DOC in lakes is largely terrestrial in origin [Ball et al., 2010], and as a result it can serve as a link between terrestrial and aquatic ecosystems that is responsive to large-scale environmental change. Adrian et al. [2009] identified DOC as a sentinel for climate-related mechanisms that are mediated by interactions with the terrestrial watershed. This could be particularly important for oligotrophic lakes, where water transparency is primarily controlled by the concentration of DOC [Morris et al., 1995; Williamson et al., 1996; Gunn et al., 2001].

Water transparency is one of the most ecologically important features of aquatic ecosystems. Changes in water transparency can alter the amount of solar radiation absorbed in surface waters and affect lake thermal stratification [Fee et al., 1996; Keller et al., 2006]. In turn, changes in water transparency and thermal stratification can alter water chemistry and lead to changes in the productivity and diversity of lake ecosystems [Berger et al., 2006]. These characteristics make water transparency an important environmental variable for detecting and monitoring aquatic ecosystem response to natural and anthropogenic environmental change. Several studies highlight water transparency as a sentinel response variable that can be used to detect current effects of environmental change, forecast future effects, and adapt to future changes in environmental impacts at varying spatial scales [Williamson et al., 1999; Gunn et al., 2001; Adrian et al., 2009]. Water transparency is also one of the most highly valued features of lake ecosystems [Michaël et al., 1996].

Recent studies that used Landsat imagery to estimate water transparency identified regional patterns in water transparency change across lakes in Wisconsin [Chipman et al., 2004], Minnesota [Olmanson et al., 2008], and most recently in Maine [McCullough et al., 2013]. McCullough et al. [2013] detected a broad decline in water transparency from the mid-1990s to the present; however, recent work by Canfield et al. [2016] suggests that water clarity in Maine lakes has remained stable in recent decades and over the past century. Declining water transparency has mainly been linked with eutrophication in response to additional...
nutrient input and increased productivity. While the links between phosphorus enrichment and lake water transparency were clearly demonstrated through comparative studies and whole-lake experiments [Schindler, 1974], changes in the concentration of colored dissolved organic matter (measured as DOC) can also be an important factor for determining lake water transparency. Both water color and chlorophyll concentration were inversely correlated with Secchi disk depths in lakes across the state of Maine [Canfield et al., 2016]. An influx of DOC can influence transparency directly via altered light absorption [Jones, 1992] or indirectly as a carbon source for microbial plankton communities at the base of the food web [Pace et al., 2004]. The importance of including DOC in our understanding of how lakes are characterized across the landscape and how they can be influenced by environmental change is summarized by Williamson et al. [1999].

In surveys of clear lakes in Killarney Park, Ontario, Canada, large thermal [Snucins and Gunn, 2000] and optical changes [Gunn et al., 2001] occurred in response to small differences in DOC. These effects were identified by surveying a large number of lakes for a period of 1 to 3 years. It is less clear how changes in DOC in the same system over different time scales will alter lake water transparency and thermal structure; however, a recent analysis of two lakes over a 27 year period suggests that increased DOC concentration can increase surface water temperature by 2 to 3°C and reduce water transparency to ultraviolet radiation [Williamson et al., 2015]. Changes in water temperature by depth differed between the two lakes studied by Williamson et al. [2015]. Additional studies are needed to clarify the long-term effects of increasing DOC on water transparency to photosynthetically active radiation (PAR) and the subsequent effects on lake mixing and to assess how these effects may vary across lakes in a particular region. Modeling of the effects of DOC on the physical properties of small temperate lakes supports that the attenuation of PAR is regulated by DOC concentrations [Read and Rose, 2013].

We used a combination of long-term (14 years) monitoring data and short-term (3 weeks) but high-frequency (every 15 min) sensor measurements to investigate the linkages among DOC concentration, water transparency, and epilimnion depth. We selected a suite of lakes in northern New England, USA, for this study because previous research indicated that some lakes in this region experienced increasing DOC concentrations in recent decades [SanClements et al., 2012]. The goals of this study were to (1) assess how DOC has changed in these lakes in recent decades, (2) relate these factors to changes in water transparency and lake thermal stratification and assess whether long-term changes in water transparency were synchronous across lakes, (3) quantify the relationship between average DOC concentrations and the rate of change in water clarity across lakes, and (4) evaluate the controls on mixing depth at a high temporal resolution during 1 month of peak stratification.

2. Methods

2.1. Study Site

Acadia National Park (Maine, USA) comprises approximately 35,000 acres, of which freshwater lakes cover 2,600 acres (Figure 1). Granite underlies most of Acadia [Gilman et al., 1988], which is overlain with shallow, well-drained soils derived from granite and schist tills at high elevations and glaciomarine silts and clays of the Presumpscot formation at lower elevations [Gilman et al., 1988]. Much of Acadia is covered by spruce-fir forests representative of the northern boreal forest; however, stands of oak, maple, and beech typical of the eastern deciduous forest are also present and can dominate landscapes burned in a 1947 fire.

Acadia National Park staff have monitored a set of lakes in the park since 1980 for a suite of parameters (Table 1); the timeframe over which each variable has been measured has varied. The lakes range in size from 13 to 380 ha, have circumneutral pH, and range from oligotrophic (e.g., Jordan Pond) to mesotrophic (e.g., Seal Cove Pond) with low nutrient concentrations and algal biomass. Mean DOC concentrations in the lakes of Acadia range from less than 2 mg L$^{-1}$ for Jordan Pond to almost 7 mg L$^{-1}$ for Hodgdon Pond.

Based on linear regression analysis of data from Acadia National Park’s weather station, average annual temperatures in Acadia National Park increased at a rate of 0.076°C yr$^{-1}$ since 1983. Based on linear regression analysis of annual wet deposition concentrations of SO$_4^{2-}$ from the National Atmospheric Deposition
Program site ME98 (McFarland Hill in Acadia National Park), \(\text{SO}_4^{2-}\) in precipitation has been declining from 1985 to 2012 at a rate of \(-0.8\ \mu\text{eq L}^{-1}\ \text{yr}^{-1}\ (p < 0.001, R^2 = 0.80)\).

### 2.2. Long-Term Monitoring Data

Six core study lakes (Bubble, Eagle, Echo, Jordan, Long, and Seal Cove) were sampled consistently over recent decades for all of the parameters of interest to this study. Lakes were generally sampled monthly from May to October, though some lakes (Eagle and Long) were sampled less frequently. Six additional lakes (Upper Hadlock, The Bowl, Witch Hole, Hodgdon, Lower Hadlock, and Upper Breakneck) were used to assess the relationship between the rate of change in Secchi disk transparency and the mean concentration of DOC.

**Table 1.** Limnological Variables (1995–2008 Averages) for Study Lakes

<table>
<thead>
<tr>
<th>Lake</th>
<th>Area (ha)</th>
<th>Mean/Maximum Depth (m)</th>
<th>pH</th>
<th>Chl a (µg L(^{-1}))</th>
<th>TP (µg L(^{-1}))</th>
<th>DOC (mg L(^{-1}))</th>
<th>Secchi (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jordan</td>
<td>75</td>
<td>26/46</td>
<td>6.6</td>
<td>1.0</td>
<td>3.6</td>
<td>1.9</td>
<td>13</td>
</tr>
<tr>
<td>Seal Cove</td>
<td>103</td>
<td>5/13</td>
<td>6.5</td>
<td>2.8</td>
<td>7.0</td>
<td>4.7</td>
<td>7</td>
</tr>
<tr>
<td>Bubble</td>
<td>13</td>
<td>6/12</td>
<td>6.5</td>
<td>1.4</td>
<td>3.7</td>
<td>2.3</td>
<td>10</td>
</tr>
<tr>
<td>Eagle</td>
<td>189</td>
<td>13/34</td>
<td>6.6</td>
<td>3.2</td>
<td>4.0</td>
<td>2.1</td>
<td>11</td>
</tr>
<tr>
<td>Echo</td>
<td>96</td>
<td>9/20</td>
<td>6.7</td>
<td>2.3</td>
<td>4.0</td>
<td>3.0</td>
<td>9</td>
</tr>
<tr>
<td>Long</td>
<td>380</td>
<td>11/34</td>
<td>6.5</td>
<td>2.8</td>
<td>4.0</td>
<td>3.1</td>
<td>9</td>
</tr>
<tr>
<td>Upper Hadlock</td>
<td>15</td>
<td>4/11</td>
<td>6.3</td>
<td>2.6</td>
<td>6.1</td>
<td>3.7</td>
<td>7</td>
</tr>
<tr>
<td>The Bowl</td>
<td>4</td>
<td>4/9</td>
<td>6.0</td>
<td>2.8</td>
<td>7.3</td>
<td>2.8</td>
<td>6</td>
</tr>
<tr>
<td>Witch Hole</td>
<td>10</td>
<td>4/9</td>
<td>6.2</td>
<td>4.1</td>
<td>10.5</td>
<td>5.3</td>
<td>4</td>
</tr>
<tr>
<td>Hodgdon</td>
<td>18</td>
<td>3/7</td>
<td>6.4</td>
<td>2.0</td>
<td>11.4</td>
<td>6.6</td>
<td>5</td>
</tr>
<tr>
<td>Lower Hadlock</td>
<td>15</td>
<td>5/12</td>
<td>6.4</td>
<td>1.1</td>
<td>5.5</td>
<td>3.5</td>
<td>7</td>
</tr>
<tr>
<td>Upper Breakneck</td>
<td>4</td>
<td>2/4</td>
<td>6.5</td>
<td>2.2</td>
<td>10.0</td>
<td>5.6</td>
<td>4</td>
</tr>
</tbody>
</table>

*Data are from the U.S. National Park Service monitoring program. The six core study lakes are listed first; the six additional lakes used only for the analysis of rate of change in Secchi disk transparency are shaded in grey.*

*Figure 1. Map of the study area in Acadia National Park (Maine, USA), with the six core study lakes indicated by red outline and the six additional lakes indicated in dark blue outline.*
This analysis of 12 lakes included all lakes in Acadia National Park with DOC and Secchi disk transparency data from 1995 to 2008. These additional six lakes were not included in the full analysis because they were sampled at a lower temporal resolution than the six core study lakes.

For the six core study lakes, measurements included thermal profiles (1 m increments), Secchi disk transparency, DOC, and chlorophyll a. Changes in chlorophyll a are also assessed in this study because this is another parameter (in addition to DOC) that can influence water clarity. DOC measurements began in 1995; both DOC and chlorophyll data are used from 1995 to 2008. Water transparency (measured as Secchi disk transparency) records extend to 1981; we use the full record (1981–2008) to provide context for longer-term changes. July vertical temperature profiles, a month during which thermal stratification is always clearly established, were used in this analysis. If July thermal profiles were not collected in a particular year, no data are used from that year. These data span from July 1993 to July 2008.

Epilimnion thickness was defined as the first depth at which there was ≥1°C change per meter in the temperature profile. This definition is meant to describe the surface, mixed habitat (as defined by Mazumder and Taylor [1994] in a similar study). Brunt-Vaisala buoyancy frequency was calculated using the package “rLakeAnalyzer” [Read et al., 2011] and represents the steepness of the thermocline and resistance to vertical mixing. DOC and chlorophyll a samples were collected from an integrated epilimnion sample (4–10 m depth) at the deepest point in the lake if it was thermally stratified or from a half-meter grab sample if unstratified. Almost all of these samples were collected during stratified conditions with the exception of a limited number of early spring or late fall samples (less than ~5% of samples in any given year). Sample replicates (one field duplication for every 10 samples) were used to assess variability. Field and laboratory methods are summarized in detail by Gawley et al. [2015]. Samples were analyzed by the Sawyer Environmental Chemistry Research Laboratory at the University of Maine using Environmental Protection Agency methods and quality control/quality assurance. DOC concentration was measured by persulfate oxidation and infrared detection (U.S. EPA 415.1); chlorophyll a was analyzed with an in vitro acetone extraction APHA et al. [2000].

2.3. High-Frequency Sensor Measurements

During 3 weeks of peak thermal stratification in 2015 (7 to 26 July), we deployed sensors measuring a suite of parameters every 15 min in one of the study lakes, Jordan Pond. Jordan Pond is the most transparent monitored lake in Maine and has the most complete long-term monitoring record for lakes in this region. Sensors were deployed on a NexSens CB400-S data buoy with a SDL500 data logger. Temperature was measured at every meter starting from 1 m with NexSens T-Node FR temperature sensors. A YSI EXO2 multiparameter water quality sonde suspended at 0.6 m depth measured colored dissolved organic matter (fDOM) and chlorophyll fluorescence. The fDOM sensor was calibrated immediately prior to deployment using a two-point calibration that included deionized water for 0 relative fluorescence unit (RFU) and a quinine sulfate dilute standard (300 μg/L; 300 QSU) for 100 RFU. The quinine sulfate dilute standard was made the day of calibration. The fDOM values were corrected for epilimnetic water temperature following methods described by Downing et al. [2012]. Water transparency was measured as attenuation of photosynthetically active radiation (PAR) between two LI-COR PAR sensors, one deployed at 0.6 m and the other at 3 m depth. PAR sensors were each attached to a 0.9 m mounting arm; the surface arm was on the opposite side of the buoy as the deeper arm. The paired measurements from these two sensors were used to calculate PAR vertical attenuation coefficients (K_{PAR}) as described by Kirk [1994]. A Vaisala WXT520 multiparameter weather station monitored on shore wind speed and direction at the same temporal resolution as the lake sensors; this system is mounted on a pole from the rooftop of a two-story building.

2.4. Statistical Methods

Mann-Kendall nonparametric trend tests were used to assess whether DOC, chlorophyll a, water transparency, epilimnion depth, and buoyancy frequency have changed in these lakes in recent decades. A trend was considered significant if P < 0.05. All statistical analyses and models were run using the “Kendall” package [McLeod and Kendall, 2011] and were completed in R (version 3.2.2). All data were graphed with locally weighted regression scatterplot smoothing (LOESS) trends.

To assess whether changes in water transparency were synchronous across lakes in this region, the temporal coherence of transparency changes over the full record (1981–2008) was assessed between all lake pairs.
Temporal coherence is the degree to which ecosystem features at different locations within a region behave similarly through time [Magnuson et al., 1990]. When changes in lake variables are highly synchronous over time across a region, this suggests that regional forcing is the primary mechanism regulating lake variability as opposed to local forcing (lake-specific characteristics such as watershed land use, morphometry, landscape position, or food web interactions) [Magnuson et al., 1990]. Spearman’s rank correlation coefficients comparing Secchi disk transparency data across the six core study lakes were considered significant if $p < 0.01$. This $p$ value is smaller than 0.05 due to a Bonferroni correction to avoid Type II errors. The significance level of 0.05 was divided by 5, because the data for each of the six lakes were used in five analyses.

The relationship between the rate of change in Secchi disk transparency and the mean concentration of DOC was explored using the set of 12 lakes described above. Sen’s slope was used to calculate a rate of
change in annual mean Secchi disk transparency values from 1995 to 2008 for each lake. The rate of change in Secchi disk transparency was plotted along a gradient of average DOC concentration from 1995 to 2008. Sen slopes and significance were calculated in R using the "zyp" package [Bronaugh and Werner, 2013]. All statistical analyses were conducted using R software (version 2.12.1 R Development Core Team [2011], Vienna, Austria).

To evaluate the controls on epilimnion depth at a high temporal resolution during 3 weeks of peak thermal stratification, forward stepwise regression was used on the sensor data from July 2015. In addition to metrics related to water transparency (fDOM, chlorophyll fluorescence, and PAR attenuation), additional factors with documented effects on lake mixing depths (epilimnetic temperature and wind) [von Einem and Granéli, 2010; Kraemer et al., 2015] were also included in this analysis. Measurements of mixing

Figure 3. Changes in Secchi disk transparency in each core study lake from 1981 to 2008. Data are graphed with LOESS smoothed trends. Mann-Kendall nonparametric trend tests were used for temporal trends of all variables with P and r values included for analyses from 1981 to 1995 (white portion of the plot) and from 1995 to 2008 (gray portion of the plot). Trends were considered significant if P < 0.05.
depth, fDOM, chlorophyll fluorescence, epilimnetic temperature, wind speed, and $K_{\text{PAR}}$ were used from the interval between 10:00 and 14:00 of each day. In the analyses, two different metrics were generated from average wind speeds: one using data from the same day as all other parameters and one from the previous day to explore potential lags in the influence of wind. $K_{\text{PAR}}$ values were ln transformed to meet the assumptions of normality and homogeneity of variance.

3. Results

3.1. Long-Term Monitoring Data

DOC increased in three of the six core study lakes (Jordan Pond, Seal Cove Pond, and Echo Lake) from 1995 to 2008 (Figure 2). The other three lakes, Long Pond, Bubble Pond, and Eagle Pond, had a positive slope but did not ultimately have a significant trend. In Long Pond and Eagle Pond, this may be due to a gap in data collection between 1999 and 2006. Across all lakes, DOC increased at an average rate of 0.05 mg L\(^{-1}\) yr\(^{-1}\) from 1995 to 2008. DOC concentrations were between 0.3 and 1.4 mg L\(^{-1}\) higher in 2008 as compared to 1995 values.

There was an increase in transparency from the early 1980s to the mid-1990s in four of the six lakes ($P < 0.05$) followed by a decline in transparency across all lakes from the mid-1990s to 2008 (Figure 3). All but two of the lake pairs had trends in Secchi disk transparency that were significantly changing in the same direction over time (Table 2). From 1995 to 2008, a period with increasing trends in DOC, all lakes had a significant decline in Secchi disk transparency. The decrease in transparency from the mid-1990s to 2008 was occurring during a time with no significant change in chlorophyll $a$ concentrations in any of the six lakes (Figure 4). The measured decline in Secchi disk transparency values ranged from 0.7 m to over 3.0 m during this time. While DOC was increasing and water transparency was decreasing, epilimnion thickness was generally becoming shallower across the lakes (Figure 5); these trends were significant in two of the six lakes (Jordan Pond and Seal Cove Pond). There were no significant changes in buoyancy frequency (Figure 6).

3.2. Relating Changes in Transparency to a Gradient of DOC Concentration

Several additional lakes in Acadia National Park have both DOC and Secchi disk transparency data from 1995 to present, including Upper Hadlock, The Bowl, Witch Hole, Hodgdon, Lower Hadlock, and Upper Breakneck ponds. These data, along with the data from the six core study lakes discussed previously, were used to relate the rate of change in transparency over time to a gradient of average DOC concentration (Figure 7). The greatest declines in transparency ($-0.4$ m yr\(^{-1}\)) occurred in lakes with

Table 2. Results of Coherence Analyses (Reported as Pairwise Spearman’s Rank Correlation Analysis) of Secchi Disk Readings From 1981 to 2008 for the Six Core Study Lakes in Acadia National Park

<table>
<thead>
<tr>
<th>Lake Pair</th>
<th>Rho</th>
<th>p Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jordan:Bubble</td>
<td>0.49</td>
<td>&lt;0.001*</td>
</tr>
<tr>
<td>Jordan:Eagle</td>
<td>0.53</td>
<td>&lt;0.001*</td>
</tr>
<tr>
<td>Jordan:Echo</td>
<td>0.27</td>
<td>0.016</td>
</tr>
<tr>
<td>Jordan:Long</td>
<td>0.51</td>
<td>&lt;0.001*</td>
</tr>
<tr>
<td>Jordan:Seal Cove</td>
<td>0.44</td>
<td>&lt;0.001*</td>
</tr>
<tr>
<td>Bubble:Eagle</td>
<td>0.37</td>
<td>&lt;0.001*</td>
</tr>
<tr>
<td>Bubble:Echo</td>
<td>0.23</td>
<td>0.037</td>
</tr>
<tr>
<td>Bubble:Long</td>
<td>0.47</td>
<td>&lt;0.001*</td>
</tr>
<tr>
<td>Bubble:Seal Cove</td>
<td>0.32</td>
<td>0.003*</td>
</tr>
<tr>
<td>Eagle:Echo</td>
<td>0.30</td>
<td>0.004*</td>
</tr>
<tr>
<td>Eagle:Long</td>
<td>0.43</td>
<td>&lt;0.001*</td>
</tr>
<tr>
<td>Eagle:Seal Cove</td>
<td>0.32</td>
<td>0.003*</td>
</tr>
<tr>
<td>Echo:Long</td>
<td>0.29</td>
<td>0.005*</td>
</tr>
<tr>
<td>Echo:Seal Cove</td>
<td>0.37</td>
<td>&lt;0.001*</td>
</tr>
<tr>
<td>Long:Seal Cove</td>
<td>0.50</td>
<td>&lt;0.001*</td>
</tr>
</tbody>
</table>

*Significant $p$ values ($p < 0.01$) indicate that these lake pairs exhibit synchronous changes over this time.
DOC concentrations between 1 and 3 mg L$^{-1}$. As DOC concentration increased, the rate of change leveled off until approximately 5–7 mg L$^{-1}$ where transparency increased slightly over time in the lakes with the highest background DOC concentration.

### 3.3. High-Frequency Sensor Measurements

From 7 to 26 July 2015, epilimnion thickness in Jordan Pond deepened from 4 to 9 m, varying around 6 m until 18 July and then being more consistent at 7 m until the last day when it reached 9 m (Figure 8). Average epilimnion temperature only varied from 19 to 21.5°C, being higher and somewhat more variable during the first half of the period. In addition to temperature, pH was relatively stable during this time period (ranging from 6.80 to 6.98) suggesting little influence of either temperature or pH on changes observed in fDOM values during deployment. Turbidity measurements were not collected during this time, but Jordan Pond is typically a low-turbidity system. Fluorescence from fDOM declined over the sampling period, from 0.58 to 0.42 relative fluorescence units (RFU), reaching lower values around 17 July. Chlorophyll fluorescence declined from 7 to 12 July then remained fairly stable until the end of the sampling period when it increased. $K_d$ varied from 0.1 to 0.5 m$^{-1}$ but generally was between 0.2 and 0.3 m$^{-1}$ over this period. Wind speeds were generally variable though strong on the evening of 15 July.
Multivariate regression analysis indicated that fDOM explained the most variability in epilimnion thickness over this period ($R^2 = 0.682$, $p < 0.001$):

$$\text{Epilimnion thickness} = 18.89 \pm 26.0 \text{ (fDOM)}$$

### 4. Discussion

Like many lakes in boreal regions of the Northern Hemisphere [Roulet and Moore, 2006; Monteith et al., 2007; Zhang et al., 2010], DOC concentrations increased in three of the six core study lakes in Acadia National Park in recent decades. Water transparency declined from 1995 to 2008 across all lakes, while DOC concentrations increased and...
chlorophyll $a$ concentrations remained unchanged. This suggests that long-term declines in water clarity and an accompanying reduction in epilimnion thickness in two of the lakes appear to be largely the result of increased DOC. Similarly, fDOM explains the greatest amount of variability in high-frequency measures of epilimnion thickness in Jordan Pond. Our results underscore the importance of DOC as a regulator of lake physical structure and highlight key consequences of a long-term increase in DOC across lakes in a region.

Possible mechanisms for increasing DOC in these lakes include both recovery from atmospheric deposition and an associated increase in soil pH leading to reduced ionic strength and increased organic matter solubility and flux [Skjelkvale et al., 2005; Evans et al., 2006; Monteith et al., 2007], as well as enhanced organic matter production and/or release as a consequence of changes in climate [Freeman et al., 2004], including changes in precipitation [Pace and Cole, 2002; Weyhenmeyer et al., 2004; Zhang et al., 2010] and temperature [Weyhenmeyer and Karlsson, 2009; Clair et al., 2011]. As described above (section 2.1), sulfate deposition has been declining and air temperatures increasing in this area since the 1980s. In addition, the northeastern U.S. has experienced a 61% increase in the frequency of extreme precipitation events (defined as $>2.54$ cm in 24 h), making it the region of the U.S. with the most substantial increase in these events [Madsen and Figdor, 2007; Spiere et al., 2010]. A change in the delivery of precipitation can influence the transport of DOC to lakes, where increased flows through the upper soil horizon can flush DOC-enriched interstitial water to streams [McDowell and Likens, 1988; Boyer et al., 1997]. Increased concentrations of DOC were observed broadly across lakes in the northeastern U.S. during extreme wet years [Strock et al., 2016], suggesting that the mechanisms linking changes in precipitation to DOC may have effects on annual lake chemistry across a broad spatial scale. In estimates specific to rivers entering the Gulf of Maine, DOC export was sensitive to changes in hydrologic conditions over the past century with increases in export during winter months [Huntington et al., 2016]. In addition, the concentration of iron and the complexes formed between iron and DOC can influence water clarity [Weyhenmeyer et al., 2014]. Data on iron concentrations are limited in these study lakes, which precludes us from further exploring the role of iron in the browning observed in this region. Generally, the watersheds of Acadia National Park are underlain with chemically resistant granites which result in surface waters with low alkalinity that have marine aerosols (Na and Cl) as the dominant ions.

Figure 8. High-frequency sensor measurements from 7 to 26 July 2015 in Jordan Pond. Data are from 15 min intervals between 10:00 and 14:00 each day.
Synchronous changes in Secchi disk transparency suggest a common environmental forcing in the lakes of Acadia National Park. Coherence has been observed to varying degrees in physical (e.g., Baines et al. [2000] for surface water temperature), chemical (e.g., Pace and Cole [2002] for DOC), and biological variables (e.g., Rusak et al. [1999] for zooplankton). Metrics that are most directly influenced by large-scale drivers, such as surface water temperature and other physical lake variables, often have a greater degree of coherence than chemical and biological variables which can be strongly influenced by catchment- and lake-specific characteristics (Arnott et al., 2003; Vogt et al., 2011). In this study, water transparency was measured as Secchi disk transparency, which is influenced by physical, chemical, and biological conditions within a lake. The synchronous changes observed across lakes in a variable that can be influenced by a wide variety of lake- and catchment-specific variables were unexpected and suggest that one or more regional-scale environmental drivers were acting across this area.

The observed declines in water transparency across the study lakes since the mid-1990s are in agreement with the Landsat imagery analysis of water transparency change broadly across the state of Maine by McCullough et al. [2013], which documented a decline in lake water transparency broadly across the state from 1995 to 2010. McCullough et al. [2013] suggested that this decline was due to eutrophication; however, in our study, there was no increase in algal biomass as transparency declined. In addition to inorganic nutrient enrichment, increased delivery of DOC may alter algal growth through two primary mechanisms: increased delivery of organic nutrients to the base of the food web that may increase algal biomass or reduced light availability limiting algal growth (evidence for these mechanisms reviewed by Solomon et al. [2015]). There is little evidence that increased DOC altered algal biomass in this study. DOC concentrations increased in several lakes as water transparency declined, and the extent to which transparency declined in lakes was related to average DOC concentration.

Water transparency increased in four of the lakes from 1981 to 1995. There are limited chemical and biological data collected during this time. As a result, we have focused our discussion on reductions in water clarity observed since 1995. However, the synchronous changes across all lakes prior to 1995 suggest that the effects of regional drivers on water clarity extend throughout the last three decades. If DOC was also driving water clarity during this period, it would suggest that DOC concentrations may have been declining from 1981 to 1995 despite ongoing reductions in sulfur deposition in this region. A lag in recovery from acidic deposition has been observed throughout this region with more dramatic declines in sulfate concentrations in the 1990s [Stoddard et al., 1999] and the 2000s [Strock et al., 2014] as compared to the 1980s. This is also true for the lakes in Acadia National Park (data not shown). Only one of the six study lakes had a significant decline in sulfate concentration from 1982 to 1995; however, all lakes had a significant decline in sulfate from 1996 to 2008. The average rate of sulfate decline (estimated from simple linear regression) across all lakes from 1982 to 1995 was $-0.56 \mu$eq L$^{-1}$ yr$^{-1}$ of sulfate per year. The rate of decline from 1996 to 2008 was almost 3 times that amount ($-1.63 \mu$eq L$^{-1}$ yr$^{-1}$). In addition to changes in watershed acidification, differences in weather may have reduced DOC and increased water transparency in the 1980s (e.g., increased drought frequency [Parker et al., 2009]).

Lakes with low overall concentrations of DOC had the greatest magnitude of reduced water transparency. This is in agreement with previous studies that detected large thermal [Snucins and Gunn, 2000] and optical changes [Gunn et al., 2001] in response to small differences in DOC in clear lakes located in Killarney Park, Ontario, Canada. Using the results from a survey of a large number of lakes for 1 to 3 years, these authors predicted that clear lakes would be more sensitive to changes in DOC as a result of changes in climate or acidification. More recent research, using a 20 year model simulation, also documented a greater sensitivity (more variability in lake temperature) in response to climate variability in lakes with low DOC concentrations [Read and Rose, 2013]. These findings were further supported in a comparison of a clear lake and brown lake over a 27 year period, where comparatively stronger changes in vertical thermal and optical habitat gradients were observed in response to increased DOC concentrations in the clear lake [Williamson et al., 2015]. Our findings, which documented whole-lake response to long-term environmental change in 12 lakes, suggests that the greater sensitivity of clear lakes to environmental change predicted in the studies by Snucins and Gunn [2000] and Gunn et al. [2001] and modeled by Read and Rose [2013] was occurring in response to documented long-term environmental change in the lakes of Acadia National Park.
While only significant in two lakes, epilimnion thickness generally became shallower in the six core study lakes from 1993 to 2008, while DOC increased and water clarity declined. From 1993 to 2008, epilimnion depths declined by an average of 1 m across all lakes. These changes in physical lake habitat, along with the results of high-frequency monitoring in 2015, underscore the importance of water transparency in controlling lake thermal structure in small lakes [Fee et al., 1996] and highlight the important changes to lake physical structure that DOC changes can elicit. It is important to note that the relationship between short-term variations in epilimnion thickness and fDOM observed in the high-frequency monitoring data is correlative and may be influenced by other covarying factors. For example, short-term variations in solar radiation may influence both fDOM (via photobleaching [Morris and Hargreaves, 1997]) and thermocline depth (via shortwave radiation [Fee et al., 1996]). However, surface radiation data collected at a weather station at Jordan Pond in Acadia National Park do not improve our statistical model explaining variability in epilimnion thickness (data not shown). In addition, epilimnion thickness strongly controls resource availability to phytoplankton and has effects independent of those of temperature and, in turn, can alter phytoplankton biomass and community structure with implications for higher trophic levels [Berger et al., 2006]. Future studies on the implications of changing DOC for lake physical structure should include additional biological metrics to enable assessment of changing ecosystem function.

Although absolute changes in DOC concentration were relatively small across this subset of lakes (concentrations were between 0.3 and 1.4 mg L$^{-1}$ higher in 2008 as compared to 1995), half of our study lakes crossed the critical 2 mg L$^{-1}$ threshold value identified by Snucins and Gunn [2000]. This suggests that these relatively small changes may have had a disproportionately large effect on thermal habitat. Overall, DOC concentrations increased by an average of 35%, while epilimnion depths declined by an average of 14% from 1995 to 2008. This is slightly lower than what was predicted by modeled 50% reductions in DOC (resulting in a 44% deepening of the thermocline) [Read and Rose, 2013] and similar to findings of a whole-lake manipulation where doubling of DOC resulted in a 30% mean decrease in thermocline depth [Christensen et al., 1996]. In addition to changes in DOC, any concurrent changes in wind speed from 1995 to 2008 may have influenced long-term trends in epilimnion thickness. However, average wind speed did not explain as much variability in epilimnion thickness as fDOM when analyzing high-frequency sensor data.

The proposed mechanisms associated with increasing concentrations of DOC vary in the scale at which they could influence water clarity and epilimnion thickness over time in lakes. For example, mechanisms that are related to DOC production (e.g., elevated carbon dioxide levels) [Freeman et al., 2004] most likely would not be influencing short-term changes in water clarity and epilimnion thickness, however, could have strong influences on long-term trends. In comparison, an analysis of episodic weather events using high-frequency sensor data identified episodic increases in DOC, reduced water clarity, and deeper mixing in lakes across the globe [Jennings et al., 2012]. Often, routine monitoring can miss these short-term effects. It is less clear if these episodic events are influencing decadal-scale trends in DOC and resulting in subsequent effects on water clarity and epilimnion thickness. Considerable strength comes from pairing both high-frequency monitoring techniques with decadal-scale monitoring of lakes. By pairing these methods in the lakes of Acadia National Park, we see that DOC is playing a role in both long-term declines in water clarity and reduced epilimnion thickness and in the short-term response of epilimnion thickness.

The results presented here suggest that regional increases in DOC concentration resulted in long-term declines in water transparency since 1995 and reduced epilimnion thickness in both short-term measurements and long-term monitoring. These long-term changes in water clarity and thermal habitat may have lasting effects on water chemistry and changes in the productivity and diversity of lakes in this region (as suggested by Berger et al. [2006]). The strong degree of coherence in Secchi disk transparency suggests that these changes are the result of a large-scale, regional driver, most likely reduction in sulfate deposition, increasing precipitation, and/or climate warming. The decline in clarity from 1995 to 2008 was not accompanied by an increase in algal biomass, which suggests that this was not a signal of increased eutrophication in this region. Instead, this response in water transparency appeared to be acting as a sentinel for changes in regional drivers of DOC concentrations such as changes in atmospheric deposition and climate. Future studies examining changes in water transparency would benefit from including both changes in organic matter and algal biomass as potential explanatory variables. Continued work pairing high-frequency sensors with long-term monitoring of lakes in this region will help to clarify how short-term increases in DOC concentration may be influencing long-term declines in water transparency and reduced epilimnion thickness.