

Browning-related oxygen depletion in an oligotrophic lake

Lesley B. Knoll, Craig E. Williamson, Rachel M. Pilla, Taylor H. Leach, Jennifer A. Brentrup & Thomas J. Fisher

To cite this article: Lesley B. Knoll, Craig E. Williamson, Rachel M. Pilla, Taylor H. Leach, Jennifer A. Brentrup & Thomas J. Fisher (2018) Browning-related oxygen depletion in an oligotrophic lake, *Inland Waters*, 8:3, 255-263, DOI: [10.1080/20442041.2018.1452355](https://doi.org/10.1080/20442041.2018.1452355)

To link to this article: <https://doi.org/10.1080/20442041.2018.1452355>



View supplementary material [↗](#)



Published online: 01 Aug 2018.



Submit your article to this journal [↗](#)



Article views: 41



View Crossmark data [↗](#)

Browning-related oxygen depletion in an oligotrophic lake

Lesley B. Knoll,^a Craig E. Williamson,^b Rachel M. Pilla,^b Taylor H. Leach,^b Jennifer A. Brenttrup,^b and Thomas J. Fisher^c

^aItasca Biological Station and Laboratories, University of Minnesota Twin Cities, Lake Itasca, MN, USA; ^bDepartment of Biology, Miami University, Oxford, OH, USA; ^cDepartment of Statistics, Miami University, Oxford, OH, USA

ABSTRACT

In recent decades, terrestrial dissolved organic matter (DOM) has increased in many northeastern North American and European lakes and is contributing to long-term browning. We used a long-term dataset (1988–2014) to study the consequences of browning-related decreased water transparency on dissolved oxygen dynamics in 2 small temperate lakes in Pennsylvania, USA, that differ in their dissolved organic carbon concentrations. The oligotrophic (“clearer”) lake has low productivity and historically oxygenated deep waters. The mesotrophic–slightly dystrophic (“browner”) lake also has relatively low productivity but historically anoxic deep waters. We examined whether browning coincided with changes in summer dissolved oxygen dynamics, with a focus on deep-water oxygen depletion. In the clearer lake, we found that minimum oxygen concentrations decreased by $\sim 4.4 \text{ mg L}^{-1}$ over the 27-year period, and these changes were strongly associated with both decreased water transparency and increased water column stability. We also found a shallowing of the maximum dissolved oxygen depth by $\sim 4.5 \text{ m}$ and anoxic conditions established in more recent years. In the browner lake, the metrics we used did not detect any significant changes in dissolved oxygen, supporting the prediction that vertical temperature and oxygen patterns in clearer lakes may be more sensitive to increasing DOM than darker lakes. Anoxia is traditionally considered to be a consequence of anthropogenic nutrient loading and, more recently, a warming climate. We show that browning is another type of environmental change that may similarly result in anoxia in oligotrophic lakes.

ARTICLE HISTORY

Received 13 September 2017
Accepted 9 March 2018

KEYWORDS

anoxia; browning; dissolved organic carbon; dissolved oxygen; lakes

Introduction

Water color and concentrations of terrestrial dissolved organic matter (DOM) are increasing in lakes in parts of northeastern North America and northern Europe (Monteith et al. 2007). The terms browning and brownification have been used to describe this phenomenon (Roulet and Moore 2006, Kritzberg and Ekström 2012). Increases in DOM that lead to lake browning are likely the result of multiple drivers. Recovery from acidification was initially suspected to play the primary role (Evans et al. 2006, Monteith et al. 2007), and more recent work suggests that climate variables such as increased precipitation and temperature may also be important, even in regions where acid deposition has decreased (Zhang et al. 2010, Couture et al. 2012). Increased terrestrial vegetation cover from climate and land use change (Finstad et al. 2016) as well as increased iron concentrations (Kritzberg and Ekström 2012, Weyhenmeyer et al. 2014) can also contribute to browning.

DOM acts as an ecosystem regulator in lakes by attenuating light, altering nutrient availability, and influencing the balance between heterotrophy and autotrophy

(Williamson et al. 1999). Research has also highlighted the importance of lake DOM pools, transformations, and fluxes to regional and global carbon cycling (Cole et al. 2007, Tranvik et al. 2009). Thus, long-term browning has the potential to greatly alter aquatic systems, and increasing evidence shows profound effects on lake ecosystem structure and function (Solomon et al. 2015, Williamson et al. 2015). For example, a unimodal response to changes in DOM and related changes in light and nutrient availability has been observed for both phytoplankton production (Seekell et al. 2015) and fish production (Finstad et al. 2014) in arctic and boreal lakes. The shading effect of increased colored DOM can also lead to stronger thermal stratification and shallower mixing depths in small lakes via changes in vertical heat absorption and distribution (Fee et al. 1996, Snucins and Gunn 2000). Shallower mixing depths can in turn lead to increases in organic carbon burial in lake sediments (Fortino et al. 2014).

Naturally occurring brown-water lakes are often net heterotrophic and can experience low oxygen conditions at depth during the summer (Nürnberg and Shaw 1998,

Wetzel 2001). This relationship has also been documented in prior studies in high DOM lakes that show the effects of short-term increases in DOM on oxygen dynamics. In a 4-year whole-lake manipulation, a near doubling of dissolved organic carbon (DOC) concentrations (7.5–14.1 mg L⁻¹) resulted in a shift to shallower chlorophyll *a* distributions and a simultaneous shift to a shallower depth of maximum oxygen concentrations (Christensen et al. 1996). A second study illustrated a short-term response to browning in a shallow, highly humic lake (Brothers et al. 2014). In this shallow lake system dominated by benthic primary production, 2 years of heavy precipitation increased already-high DOC concentrations in the lake, which led to decreases in light availability, reduced benthic primary production, and increased anoxia.

Few studies have examined the link between long-term browning and deep-water oxygen depletion. A recent modeling study for an oligotrophic lake examined the combined and independent effects of warming water temperature and increasing DOM on dissolved oxygen (Couture et al. 2015). The authors found that the combined effect resulted in the largest impact on oxygen consumption, but the long-term increases in DOM played a larger role in controlling dissolved oxygen consumption than warming lake temperatures. Another study provided a brief summary of observed changes in oxygen, along with many other limnological changes, that accompanied lake browning in 2 temperate lakes, Lake Giles and Lake Lacawac (Williamson et al. 2015). This study described observed shifts in the depth of peak and minimum dissolved oxygen saturation in a subset of years in a long-term dataset, but only in summary form. We extend the findings in Lakes Giles and Lacawac by using an expanded long-term dataset to more fully document and statistically analyze the relationship between long-term browning and changes in oxygen over depth and time. We also relate dissolved oxygen trends with potential drivers to better understand the mechanisms behind oxygen changes.

Exploring the connection between long-term browning and anoxia, defined here as dissolved oxygen <1 mg L⁻¹ (Nürnberg 1995), is critical because oxygen conditions contribute to many core ecosystem functions. Oxygen is important for nutrient cycling, determining the contribution of lakes to global carbon cycling, habitat suitability for aquatic organisms, as well as water quality and general ecosystem health. Given the fundamental role of oxygen in aquatic systems, a long-standing tradition is aimed at studying the causes and consequences of oxygen depletion. For example, nutrient-driven eutrophication is widely known to cause anoxia in lakes (Smith 2003, Schindler 2006, Jenny et al. 2016) as well

as in coastal marine systems such as those in the Gulf of Mexico (Diaz and Rosenberg 2008) or the Chesapeake Bay (Kemp et al. 2005). Warming air temperatures can also lead to oxygen depletion in lakes because oxygen solubility is reduced in warmer waters, and warmer surface waters lead to increased strength and duration of stratification with reductions in vertical mixing (Janowski et al. 2006, Foley et al. 2012, North et al. 2014). Warming-induced oxygen declines are not just a concern for lakes. Recent evidence suggests that since 1960, the Earth's oceans have lost 2% of their oxygen content, and the volume of anoxic water has increased 4-fold (Schmidtke et al. 2017).

Here we examined the potential for an alternative pathway to oxygen depletion via long-term increases in terrestrial DOM in 2 undisturbed lakes in a region experiencing browning. We also explored mechanisms by which browning may influence dissolved oxygen trends. Specifically, we examined lake stability (Schmidt stability) and water transparency (1% photosynthetically active radiation [PAR] depth). We analyzed a long-term dataset (1988–2014) for 2 small lakes—an oligotrophic (“clearer”) lake and a mesotrophic–slightly dystrophic (“browner”) lake—located in protected watersheds. Both lakes have experienced significantly decreasing water transparency (i.e., 1% PAR depth) over the 27-year dataset and have shown trends of increasing DOC concentration, but because of the high interannual variability of DOC concentration in the browner lake, the trend is statistically significant only in the clearer lake (Williamson et al. 2015). The observed reductions in water clarity do not seem to be associated with an increase in phytoplankton biomass because summer chlorophyll concentrations have not changed significantly over the past 27 years in either lake (Williamson et al. 2015). Rather, DOC is the primary factor controlling light attenuation in these lakes (Morris et al. 1995, Williamson et al. 1996). The mechanism driving browning is likely related to both increases in precipitation and recovery from acidification because during the study period, total precipitation significantly increased and sulfate deposition decreased, with concomitant significant increases in pH and acid neutralizing capacity in both lakes (Williamson et al. 2015).

Methods

Study sites

Our dataset is from 2 small, natural glacial lakes located in northeastern Pennsylvania, USA. Lake Giles has a surface area of 0.48 km² and Lake Lacawac has a surface area of 0.21 km². Lake Giles is a deeper (maximum

depth = 24 m), oligotrophic, low-productivity lake (mean summer chlorophyll = $0.8 \mu\text{g L}^{-1}$; total phosphorus = $3.5 \mu\text{g L}^{-1}$; DOC = 1.3 mg L^{-1}), whereas Lake Lacawac is a shallower (maximum depth = 13 m), mesotrophic–slightly dystrophic lake (mean summer chlorophyll = $3.8 \mu\text{g L}^{-1}$; total phosphorus = $9.0 \mu\text{g L}^{-1}$; DOC = 5.1 mg L^{-1}). Both lakes have watersheds that are well protected, showing minimal disturbance or land use change over the study period (1988–2014). Although forests dominate the land cover of the watersheds of both lakes, the watershed is ~25% peat wetlands for Lacawac but only 1.9% for Giles (Moeller et al. 1995). Both lakes are seepage lakes, and DOC is the primary factor controlling light attenuation (Morris et al. 1995, Williamson et al. 1996). The peat wetlands in Lacawac are the main source of the higher and darker DOM in this lake versus DOM in Giles. We refer to Giles as the clearer lake and Lacawac as the browner lake.

Field and laboratory analyses

We assessed water transparency using the 1% PAR (400–700 nm) depth (the depth at which irradiance is 1% of subsurface values for PAR), which approximates the compensation depth below which respiration generally exceeds photosynthesis, resulting in net oxygen depletion. The 1% PAR depths were collected with a Biospherical Instruments Cosine (BIC) or Profiling Ultraviolet (PUV) radiometer (Biospherical Instruments, Inc., San Diego, CA) in July for both lakes (1993–2014). The BIC and PUV are medium bandwidth submersible radiometers with a depth resolution of 0.01 m. A deck cell simultaneously records the same PAR wavelengths as the submersible radiometer to account for short-term changes in cloud cover. This type of measurement is an accurate method for measuring water transparency and also meaningful in terms of oxygen dynamics in lakes (Horne and Goldman 1994).

Vertical dissolved oxygen and temperature profiles were taken at 1 m intervals at the deepest location in each lake using a calibrated YSI Model 57 or 58 oxygen-temperature meter (YSI Inc., Yellow Springs, OH). We present data on both dissolved oxygen seasonal trends from May to August as well as data from July only (samples ranging from 10 to 28 July) during the period of generally strong summer thermal stability. Seasonal dissolved oxygen data (as percent saturation) are presented to show long-term patterns but are only included when at least 2 months of data were available between May and August (1988–1997, 2007–2014 for Giles, and 1988–1997, 2005–2014 for Lacawac). July dissolved oxygen data for Lake Giles (1988–1996 and 2008–2014; $n = 16$) and Lake Lacawac (1988–1996 and 2007–

2014, excluding 1995; $n = 16$) were used for quantitative comparisons between time periods. Using the rLakeAnalyzer package (Read et al. 2011, Winslow et al. 2014) and temperature data from the same July profiles, we also assessed changes in midsummer lake stability by calculating Schmidt stability, S (Idso 1973), as:

$$S = \frac{g}{A_s} \int_0^{z_D} (z - z_v) \rho_z A_z dz, \quad (1)$$

where g is acceleration due to gravity (m s^{-2}), A_s is surface area of the lake (m^2), z is depth of the lake at any given interval (m), z_D is maximum depth of the lake (m), z_v is depth to the center volume of the lake (m), ρ_z is density of water at depth z (kg m^{-3}), and A_z is surface area of the lake at depth z (m^2). Stability increases with stronger thermal stratification.

We used 3 metrics to quantify changes in dissolved oxygen. The first, the minimum dissolved oxygen concentration in the water column, is our primary metric of interest and is a straightforward metric of oxygen depletion in deep-waters. This metric also shows the potential for sediment phosphorus release due to deep-water oxygen depletion and is related to the size of the zooplankton refuge from visual predation, which can have large impacts on zooplankton population dynamics (Wright and Shapiro 1990, Vanderploeg et al. 2009a). The second metric, the depth of the maximum dissolved oxygen concentration in the water column, provides information on the potential for changes in oxygen due to physical processes as well as the vertical distribution and productivity of photosynthetic/autotrophic and heterotrophic plankton (Wilkinson et al. 2015), and it is directly related to changes in water transparency. The third metric, oxygen saturation range, is the maximum dissolved oxygen percent saturation in the water column minus the minimum dissolved oxygen percent saturation in the water column, and it represents both the vertical heterogeneity of dissolved oxygen and the habitat gradient experienced by higher trophic levels (i.e., zooplankton and fish), which can have strong influences on trophic interactions (Vanderploeg et al. 2009b).

Statistical analyses

We selected July data for the metrics because we were interested in the midsummer dynamics when the lakes were strongly thermally stratified, and we wanted to restrict the analyses to the same time period each year when the most data were consistently available.

The analyzed data (dissolved oxygen metrics and Schmidt stability) were composed of time series

(specifically annual July measurements) over 2 distinct regimes or periods (1988–1996, $n = 9$; 2007–2014, $n = 8$). Given the large break between observations and possible serial correlation in the underlying time series, we analyzed the data using a linear model with autocorrelated errors. Specifically we considered a mean model with a covariate term specifying the regime and autoregressive moving average (ARMA) modeled errors. Mathematically this can be constructed as:

$$Y_t = \mu + \beta \cdot X_t + Z_t, \quad (2)$$

where μ is the mean of the time series in the first regime, β is the influence of the second regime (2007–2014) with X_t an indicator variable determining the regime:

$$X_t = \begin{cases} 0 & \text{if } 1988 \leq t \leq 1996 \\ 1 & \text{if } 2007 \leq t \leq 2014 \end{cases}, \quad (3)$$

and Z_t is a mean zero ARMA (p, q) process defined as:

$$Z_t = \sum_{i=1}^p \phi_i Z_{t-i} + \sum_{j=1}^q \theta_j \varepsilon_{t-j} + \varepsilon_t, \quad (4)$$

for underlying error series $\varepsilon_t \sim N(0, \sigma^2)$. Determining a difference in regimes is equivalent to testing the significance of β in equation (2). This approach is fundamentally similar to fitting a generalized least squares model or intervention analysis (Montgomery et al. 2008), wherein the effect of a covariate can be measured while also accounting for serially correlated errors. This process is analogous to a 2-sample t -test but for autocorrelated data, which is known to distort standard errors and p values. We fit our model using maximum likelihood with the *forecast* package (Hyndman 2016) and determined the significance of β based on the asymptotic sampling distribution of maximum likelihood estimators. If we found a significant change in minimum dissolved oxygen concentrations between the early and late time periods, we used Pearson's correlation coefficients to explore the relationships between this variable and 2 potential driver variables: 1% PAR depth and Schmidt stability. We used this exploratory approach to assess the magnitude of the correlations, but we did not perform hypothesis tests because of limitations based on correlations with time and sample sizes. We only performed this test with the minimum dissolved oxygen concentration metric and not the other oxygen metrics because we were most interested in whether browning led to oxygen depletion.

Earlier ice break-up can lead to an earlier onset of thermal stratification, potentially increasing growing season deep-water oxygen depletion. We lack long-term ice-off records, but ice break-up dates are influenced by air temperatures (Weyhenmeyer et al. 2004,

Jensen et al. 2007). We therefore examined winter air temperatures collected from the National Oceanic and Atmospheric Administration (NOAA) National Climatic Data Center. Data, primarily collected from Hawley, Pennsylvania (USC00363758; 14.8 km from Lacawac, 12.7 km from Giles), included maximum daily air temperature and minimum daily air temperature. To calculate mean daily air temperature, we simply averaged the daily maximum and daily minimum air temperature. For each winter month (defined here Dec–Mar), the 3 daily air temperature variables were each averaged from the beginning through end of each month across all 27 years of data. The overall wintertime seasonal average for each variable was the average daily air temperature from 1 December through 31 March of each year. We used Mann-Kendall nonparametric tests to assess the statistical significance of temporal trends in each of the 3 air temperature variables for the 4 individual winter months as well as the wintertime seasonal average, using an alpha level of $\alpha = 0.05$. All statistical analyses were completed in the programming language R (R Development Core Team 2015).

Results

The clearer lake showed strong changes in dissolved oxygen from the earlier (1988–1997) to the later (2007–2014) years. In the earlier years, dissolved oxygen percent saturation was rarely below 50% and was not low enough to suggest sustained deep-water depletion (Fig. 1a). Percent saturation often peaked deep in the water column corresponding with high water transparency, indicated by deeper compensation depths (1% PAR depth; Fig. 1a). In the later years, dissolved oxygen percent saturation was lower overall throughout the deeper portions of the water column and oxygen depletion was more common, prolonged, and extended into shallower waters (Fig. 1b). The shallower peak of dissolved oxygen supersaturation and the smaller breadth of the peak in the later years corresponded with shallower compensation depths (Fig. 1b). The volume of anoxic water varied over summer through early fall. In more recent years, this volume generally included the bottom 3 m of the clearer lake initially and then as the summer progressed included the bottom 6 m (6–14% of the total lake volume). Seasonal patterns of dissolved oxygen showed only subtle changes between the 2 study periods in the browner lake. Earlier profiles in this lake showed anoxia, a pattern that remained in later years (Fig. 1c–d). While the duration and vertical extent of oxygen depletion showed signs of increasing in later years compared with earlier years in the browner lake, these patterns were modest.

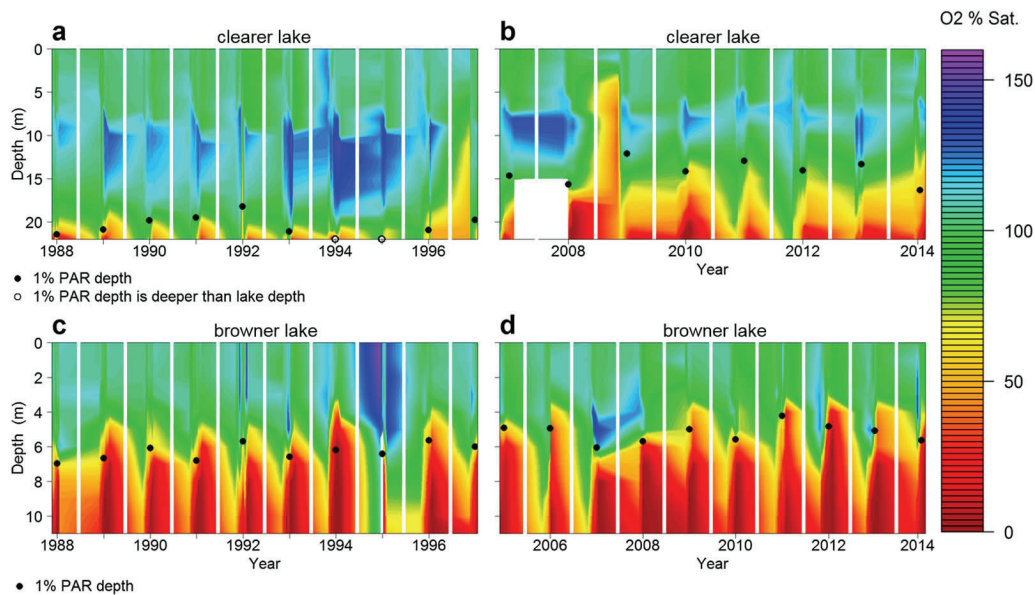


Figure 1. Seasonal summer dissolved oxygen as percent saturation ($O_2\%$ Sat) in (a) the clearer lake earlier years (1988–1997), (b) clearer lake later years (2007–2014), (c) browner lake earlier years (1988–1997), and (d) browner lake later years (2005–2014). Midsummer compensation depths (1% PAR depth) are shown with black circles, and white circles represent dates when the compensation depth exceeded the maximum depth of the lake. White vertical lines separate years.

Water column stability shifted over the 27-year record, with significantly higher water column stability in later years compared to earlier years in the clearer lake (Fig 2; $p < 0.0015$) but not the browner lake (Fig. 2; $p = 0.133$).

Quantitative analysis of midsummer July dissolved oxygen changes from the earlier (1988–1996, $n = 9$) to the later years (2007–2014, $n = 8$) showed the minimum dissolved oxygen concentration in the water column decreased in the clearer lake by $\sim 4.4 \text{ mg L}^{-1}$ but showed no change in the browner lake ($p < 0.00001$, $p = 0.19$, respectively). Minimum dissolved oxygen concentrations in the clearer lake were strongly associated with both 1% PAR depth (Fig 3a; $r = 0.76$) and Schmidt

stability (i.e., a measure of water column stability; Fig 3b; $r = -0.69$). We found a significantly shallower depth of

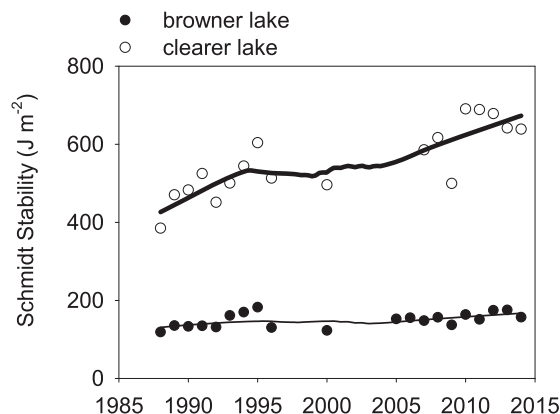


Figure 2. Long-term trends in Schmidt stability. Lines are LOW-ESS smoothed trends, and the bold line indicates a statistically significant trend ($p < 0.05$).

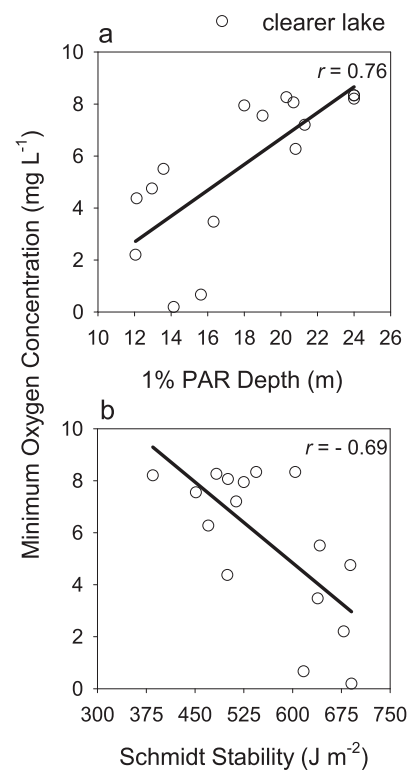


Figure 3. Relationships between (a) minimum dissolved oxygen concentrations and 1% PAR depth ($r = 0.76$, Pearson correlation coefficient), and (b) minimum dissolved oxygen concentrations and lake stability ($r = -0.69$, Pearson correlation coefficient) in the clearer lake. Lines represent linear regressions.

maximum dissolved oxygen concentrations in the clearer lake by ~ 4.5 m, but again not in the browner lake ($p < 0.003$, $p = 1.0$, respectively). In addition, the range in dissolved oxygen as percent saturation (water column maximum oxygen minus minimum oxygen) increased in the clearer lake but not in the browner lake ($p < 0.000001$, $p = 0.94$, respectively).

For minimum, mean, and maximum daily air temperature in the region, no significant trends were detected over this 27-year time span for the 4 individual months of December ($p = 0.80$, $p = 0.87$, $p = 0.74$, respectively; $n = 27$), January ($p = 0.43$, $p = 0.40$, $p = 0.34$, respectively; $n = 27$), February ($p = 0.90$, $p = 0.56$, $p = 0.48$, respectively; $n = 27$), or March ($p = 0.69$, $p = 0.71$, $p = 0.74$, respectively; $n = 27$), or for the wintertime seasonal average ($p = 0.48$, $p = 0.89$, $p = 0.69$, respectively; $n = 27$).

Discussion

Previous work has demonstrated oxygen depletion in response to increased anthropogenic nutrient loading and eutrophication (Jenny et al. 2016), extreme weather (Jankowski et al. 2006), and short-term browning in shallow lakes (Brothers et al. 2014). Our results indicate that long-term browning may also promote oxygen depletion and the onset of anoxia in oligotrophic lakes by decreasing water transparency and increasing lake stability. We observed pronounced changes in summer dissolved oxygen conditions, including the onset of oxygen depletion in previously oxygenated deep waters and a shallower depth of maximum dissolved oxygen in a clear lake. Corresponding shifts were not observed in the less transparent, browner lake. These observations support previous findings that the vertical temperature and oxygen structure in clearer lakes may be more sensitive than browner lakes to browning and climate change (Snucins and Gunn 2000, Read and Rose 2013).

The oxygen changes in the clearer lake were related to corresponding and marked increases in DOM and corresponding decreases in water transparency. Both water color and DOC concentration have increased while chlorophyll has not changed significantly (Williamson et al. 2015). We predict that 2 main mechanisms link decreases in water transparency and oxygen depletion. First, as light penetration decreases, the compensation depth (i.e., 1% PAR depth) below which respiration exceeds photosynthesis becomes shallower. This in turn will cause net oxygen depletion to occur at a shallower depth and over a larger volume of the lake. Second, previous studies have shown that a reduction in water transparency can increase the strength of thermal stratification due to increased absorption of light in the surface waters (Mazumder and Taylor 1994, Fee et al. 1996,

Houser 2006, Keller et al. 2006, Read and Rose 2013). Increased strength of stratification reduces vertical mixing of well-oxygenated water to deeper depths (Foley et al. 2012, North et al. 2014) and increases the degree of oxygen depletion in deep waters. The data from our clearer lake support these mechanisms as recent work showed trends of a significant reduction in 1% PAR depth (Williamson et al. 2015), and we observed increased water column stability (Fig. 2) coincident with the onset of deep-water oxygen depletion. Minimum dissolved oxygen concentrations were also strongly associated with both 1% PAR and water column stability.

Over the time period of our study we found no significant air temperature changes (Pilla 2015, Williamson et al. 2015), but warming trends in this region are occurring over a longer time scale (Melillo et al. 2014). Note that a warmer climate may influence deep-water oxygen depletion because long-term increases in air temperature can also increase thermal stratification (Livingstone 2003, Kraemer et al. 2015) and, in turn, intensify oxygen depletion (Wilhelm and Adrian 2008, North et al. 2014, Palmer et al. 2014). Warm water also holds less oxygen. Interestingly, a recent modeling study found that water clarity trends and warming air temperatures can play similar roles in determining lake thermal responses to climate change (Rose et al. 2016). The combined effects of warming and increasing DOM thus likely have a dual negative effect on oxygen concentrations in oligotrophic lakes, increasing the likelihood of anoxia (Couture et al. 2015).

Although unlikely, several alternative mechanisms might be invoked to explain our observed long-term oxygen trends. For example, deep-water oxygen consumption would increase with phytoplankton biomass, but we have not observed significant trends in chlorophyll during the study period in the clearer lake (Williamson et al. 2015). Temperature is another important consideration. While dissolved oxygen concentrations are related to water temperature, documented temperature trends in our clearer lake are not consistent with temperature playing a role in the observed increases in anoxia. Dissolved oxygen solubility is higher in cooler waters, and since the late 1980s, summer deep-water temperatures have been decreasing in the clearer lake (Pilla 2015, Williamson et al. 2015) where anoxia has been increasing. Cooler deep-waters would also tend to slow respiration and thus decrease oxygen depletion.

Another factor that could contribute to reductions in deep-water oxygen are long-term trends toward earlier ice breakup dates. With a shorter duration of ice cover and earlier ice breakup, lakes can stratify earlier and for a longer duration, thereby increasing summer anoxia (Fang and Stefan 2009). Ice breakup dates were shown

to be earlier in many New England lakes, a region near but not in our study location (Hodgkins et al. 2002). Although we lack ice duration data, no significant trends in winter air temperature data (defined here as Dec–Mar) over our study period were found, and winter temperature is one of the most important factors in determining ice breakup date (Weyhenmeyer et al. 2004, Jensen et al. 2007). Warming spring air temperatures could also lead to earlier stratification, but no trend was found for spring air temperatures at the location and time period of our study (Williamson et al. 2015). Despite this lack of trends, both warming air temperatures and earlier ice breakup dates should be considered in the future for this region or for other regions experiencing these changes coincident with browning.

The documented shift toward anoxia may result in many biogeochemical consequences, including internal phosphorus loading (Mortimer 1942) and reduced organic carbon mineralization rates leading to increased organic carbon burial in lake sediments (Sobek et al. 2009, Fortino et al. 2014). We do not have long-term deep-water phosphorus data to explore potential changes with decreasing clarity and increasing anoxia. In the clearer lake, however, recent high-frequency deep-water dissolved oxygen and soluble reactive phosphorus (SRP) and total phosphorus data show a short-term relationship between the onset of dissolved oxygen depletion and an increase in deep-water phosphorus. For example, after the onset of anoxia, bottom-water SRP concentrations increased by ~2.5-fold in 2014 while they increased by nearly 16-fold in 2015 (Supplemental Fig. S1). Future efforts are needed to explore the long-term significance of our observed short-term trends. These efforts should include examining whether deep-water phosphorus is transferred to shallower depths where the available phosphorus may influence phytoplankton growth, potentially creating a positive feedback loop whereby internal phosphorus loading increases algal biomass and further decreases water transparency. We suggest this area for future research efforts in lakes with long-term datasets similar to our clearer, oligotrophic lake. Future efforts are also needed to establish a mechanistic link between anoxia and increased bottom-water phosphorus because decomposition and remineralization of organic phosphorus may also contribute to phosphorus accumulation.

Browning may continue in lakes in northeastern North America and Europe as lakes continue to recover from acidification and as climate change alters temperature and precipitation patterns (Zhang et al. 2010, Larsen et al. 2011, Couture et al. 2012). Regionally across the United States, the northeast has experienced some of the highest average increases in precipitation (15–20%)

and by far the greatest increase in extreme precipitation events (71%) compared with any other region of the country (Melillo et al. 2014). Further, since 1975 the surface waters are warmer and the strength of thermal stratification is stronger in many lakes in this region of North America (Richardson et al. 2017). A warmer climate may further enhance lake oxygen depletion because long-term increases in air temperature can increase thermal stratification (Livingstone 2003, Kraemer et al. 2015) and, in turn, intensify anoxia (Wilhelm and Adrian 2008, North et al. 2014, Palmer et al. 2014). Thus, increasing terrestrial DOM and increasing anoxia, described here, along with a warming climate could have a synergistic effect on anoxia and related biogeochemical processes in some of the most pristine temperate lakes in the Northern Hemisphere.

Acknowledgements

We thank R. Moeller, B. Hargreaves, D. Morris, E. Overholt, and numerous field assistants for help in collecting long-term limnological data. We thank T. Warner for assistance during early stages of data analysis and discussion. We thank Lacawac Sanctuary for access to Lake Lacawac.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the National Science Foundation under Grant NSF numbers DBI-1318747, DEB-1754265, DEB-1754276.

References

- Brothers S, Köhler J, Attermeyer K, Grossart HP, Mehner T, Meyer N, Scharnweber K, Hilt S. 2014. A feedback loop links brownification and anoxia in a temperate, shallow lake. *Limnol Oceanogr.* 59:1388–1398.
- Christensen DL, Carpenter SR, Cottingham KL, Knight SE, LeBouton JP, Schindler DE, Voichick N, Cole JJ, Pace ML. 1996. Pelagic responses to changes in dissolved organic carbon following division of a seepage lake. *Limnol Oceanogr.* 41:553–559.
- Cole JJ, Prairie YT, Caraco NF, McDowell WH, Tranvik LJ, Striegl RG, Duarte CM, Kortelainen P, Downing JA, Middelburg JJ, et al. 2007. Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems.* 10:172–185.
- Couture R-M, de Wit HA, Tominaga K, Kiuru P, Markelov I. 2015. Oxygen dynamics in a boreal lake responds to long-term changes in climate, ice phenology, and DOC inputs. *J Geophys Res-Biogeosci.* 120:2015JG003065.

- Couture S, Houle D, Gagnon C. 2012. Increases of dissolved organic carbon in temperate and boreal lakes in Quebec, Canada. *Environ Sci Pollut Res.* 19:361–371.
- Diaz RJ, Rosenberg R. 2008. Spreading dead zones and consequences for marine ecosystems. *Science.* 321:926–929.
- Evans CD, Chapman PJ, Clark JM, Monteith DT, Cresser MS. 2006. Alternative explanations for rising dissolved organic carbon export from organic soils. *Glob Change Biol.* 12:2044–2053.
- Fang X, Stefan HG. 2009. Simulations of climate effects on water temperature, dissolved oxygen, and ice and snow covers in lakes of the contiguous U.S. under past and future climate scenarios. *Limnol Oceanogr.* 54:2359–2370.
- Fee EJ, Hecky RE, Kasian SEM, Cruikshank DR. 1996. Effects of lake size, water clarity, and climatic variability on mixing depths in Canadian Shield lakes. *Limnol Oceanogr.* 41:912–920.
- Finstad AG, Andersen T, Larsen S, Tominaga K, Blumentrath S, de Wit HA, Tømmervik H, Hessen DO. 2016. From greening to browning: catchment vegetation development and reduced S-deposition promote organic carbon load on decadal time scales in Nordic lakes. *Sci Rep.* 6:31944.
- Finstad AG, Helland IP, Ugedal O, Hesthagen T, Hessen DO. 2014. Unimodal response of fish yield to dissolved organic carbon. *Ecol Lett.* 17:36–43.
- Foley B, Jones ID, Maberly SC, Rippey B. 2012. Long-term changes in oxygen depletion in a small temperate lake: effects of climate change and eutrophication. *Freshwater Biol.* 57:278–289.
- Fortino K, Whalen SC, Johnson CR. 2014. Relationships between lake transparency, thermocline depth, and sediment oxygen demand in Arctic lakes. *Inland Waters.* 4:79–90.
- Hodgkins GA, James IC, Huntington TG. 2002. Historical changes in lake ice-out dates as indicators of climate change in New England, 1850–2000. *Int J Climatol.* 22:1819–1827.
- Horne AJ, Goldman CR. 1994. *Limnology*. 2nd ed. New York: McGraw-Hill.
- Houser JN. 2006. Water color affects the stratification, surface temperature, heat content, and mean epilimnetic irradiance of small lakes. *Can J Fish Aquat Sci.* 63:2447–2455.
- Hyndman R. 2016. Package “forecast.” [Accessed 2017 Jan 17]. <https://cran.r-project.org/web/packages/forecast/citation.html>
- Idso SB. 1973. On the concept of lake stability1. *Limnol Oceanogr.* 18:681–683.
- Jankowski T, Livingstone DM, Bührer H, Forster R, Niederhauser P. 2006. Consequences of the 2003 European heat wave for lake temperature profiles, thermal stability, and hypolimnetic oxygen depletion: implications for a warmer world. *Limnol Oceanogr.* 51:815–819.
- Jenny J-P, Francus P, Normandeau A, Lapointe F, Perga M-E, Ojala A, Schimmelmänn A, Zolitschka B. 2016. Global spread of hypoxia in freshwater ecosystems during the last three centuries is caused by rising local human pressure. *Glob Change Biol.* 22:1481–1489.
- Jensen OP, Benson BJ, Magnuson JJ, Card VM, Futter MN, Soranno PA, Stewart KM. 2007. Spatial analysis of ice phenology trends across the Laurentian Great Lakes region during a recent warming period. *Limnol Oceanogr.* 52:2013–2026.
- Keller WB, Heneberry J, Leduc J, Gunn J, Yan N. 2006. Variations in epilimnion thickness in small boreal shield lakes: relationships with transparency, weather and acidification. *Environ Monit Assess.* 115:419–431.
- Kemp WM, Boynton WR, Adolf JE, Boesch DF, Boicourt WC, Brush G, Cornwell JC, Fisher TR, Glibert PM, Hagy JD, et al. 2005. Eutrophication of Chesapeake Bay: historical trends and ecological interactions. *Mar Ecol Prog Ser.* 303:1–29.
- Kraemer BM, Anneville O, Chandra S, Dix M, Kuusisto E, Livingstone DM, Rimmer A, Schladow SG, Silow E, Sitoki LM, et al. 2015. Morphometry and average temperature affect lake stratification responses to climate change. *Geophys Res Lett.* 42:2015GL064097.
- Kritzberg ES, Ekström SM. 2012. Increasing iron concentrations in surface waters – a factor behind brownification? *Biogeosciences.* 9:1465–1478.
- Larsen S, Andersen T, Hessen DO. 2011. Climate change predicted to cause severe increase of organic carbon in lakes. *Glob Change Biol.* 17:1186–1192.
- Livingstone DM. 2003. Impact of secular climate change on the thermal structure of a large temperate central European lake. *Clim Change.* 57:205–225.
- Mazumder A, Taylor WD. 1994. Thermal structure of lakes varying in size and water clarity. *Limnol Oceanogr.* 39:968–976.
- Melillo JM, Richmond T, Yohe G. 2014. Climate change impacts in the United States: the third national climate assessment. Washington (DC): US Global Change Research Program. <https://doi.org/10.7930/J0Z31WJ2>
- Moeller RE, Williamson CE, Hargreaves BR, Morris DP. 1995. *Limnology of Lakes Lacawac, Giles, and Waynewood 1989–1993: an introduction to the core lakes of the Pocono Comparative Lakes Program*. Available from Lehigh University Library by Interlibrary Loan System, Bethlehem, PA, USA.
- Monteith DT, Stoddard JL, Evans CD, de Wit HA, Forsius M, Høgåsen T, Wilander A, Skjelkvåle BL, Jeffries DS, Vuorenmaa J, et al. 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature.* 450:537–540.
- Montgomery D, Jennings C, Kulahci M. 2008. *Introduction to time series analysis and forecasting*. Hoboken (NJ): John Wiley and Sons (Wiley Series in Probability and Statistics).
- Morris DP, Zagarese H, Williamson CE, Balseiro EG, Hargreaves BR, Modenutti B, Moeller R, Queimalinos C. 1995. The attenuation of solar UV radiation in lakes and the role of dissolved organic carbon. *Limnol Oceanogr.* 40:1381–1391.
- Mortimer CH. 1942. The exchange of dissolved substances between mud and water in lakes. *J. Ecol.* 30:147–201.
- North RP, North RL, Livingstone DM, Köster O, Kipfer R. 2014. Long-term changes in hypoxia and soluble reactive phosphorus in the hypolimnion of a large temperate lake: consequences of a climate regime shift. *Glob Change Biol.* 20:811–823.
- Nürnberg GK. 1995. Quantifying anoxia in lakes. *Limnol Oceanogr.* 40:1100–1111.
- Nürnberg GK, Shaw M. 1998. Productivity of clear and humic lakes: nutrients, phytoplankton, bacteria. *Hydrobiologia.* 382:97–112.
- Palmer ME, Yan ND, Somers KM. 2014. Climate change drives coherent trends in physics and oxygen content in North American lakes. *Clim Change* 124:285–299.

- Pilla R. 2015. Lake temperatures as sentinel responses to climate change [master's thesis]. Oxford (OH): Miami University.
- R Development Core Team. 2015. R: a language and environment for statistical computing. Vienna (Austria): R Foundation for Statistical Computing.
- Read JS, Hamilton DP, Jones ID, Muraoka K, Winslow LA, Kroiss R, Wu CH, Gaiser E. 2011. Derivation of lake mixing and stratification indices from high-resolution lake buoy data. *Environ Model Softw.* 26:1325–1336.
- Read JS, Rose KC. 2013. Physical responses of small temperate lakes to variation in dissolved organic carbon concentrations. *Limnol Oceanogr.* 58:921–931.
- Richardson DC, Melles SJ, Pilla RM, Hetherington AL, Knoll LB, Williamson CE, Kraemer BM, Jackson JR, Long EC, Moore K, et al. 2017. Transparency, geomorphology and mixing regime explain variability in trends in lake temperature and stratification across northeastern North America (1975–2014). *Water.* 9:442.
- Rose KC, Winslow LA, Read JS, Hansen GJA. 2016. Climate-induced warming of lakes can be either amplified or suppressed by trends in water clarity. *Limnol Oceanogr Lett.* 1:44–53.
- Roulet N, Moore TR. 2006. Environmental chemistry: browning the waters. *Nature.* 444:283–284.
- Schindler DW. 2006. Recent advances in the understanding and management of eutrophication. *Limnol Oceanogr.* 51:356–363.
- Schmidtko S, Stramma L, Visbeck M. 2017. Decline in global oceanic oxygen content during the past five decades. *Nature.* 542:335–339.
- Seekell DA, Lapierre J-F, Ask J, Bergström A-K, Deininger A, Rodríguez P, Karlsson J. 2015. The influence of dissolved organic carbon on primary production in northern lakes. *Limnol Oceanogr.* 60:1276–1285.
- Smith VH. 2003. Eutrophication of freshwater and coastal marine ecosystems a global problem. *Environ Sci Pollut Res.* 10:126–139.
- Snucins E, Gunn J. 2000. Interannual variation in the thermal structure of clear and colored lakes. *Limnol Oceanogr.* 45:1639–1646.
- Sobek S, Durisch-Kaiser E, Zurbrugg R, Wongfun N, Wessels M, Pasche N, Wehrli B. 2009. Organic carbon burial efficiency in lake sediments controlled by oxygen exposure time and sediment source. *Limnol Oceanogr.* 54:2243–2254.
- Solomon CT, Jones SE, Weidel BC, Buffam I, Fork ML, Karlsson J, Larsen S, Lennon JT, Read JS, Sadro S, et al. 2015. Ecosystem consequences of changing inputs of terrestrial dissolved organic matter to lakes: current knowledge and future challenges. *Ecosystems.* 18:376–389.
- Tranvik LJ, Downing JA, Cotner JB, Loiselle SA, Striegl RG, Ballatore TJ, Dillon P, Finlay K, Fortino K, Knoll LB, et al. 2009. Lakes and reservoirs as regulators of carbon cycling and climate. *Limnol Oceanogr.* 54:2298–2314.
- Vanderploeg HA, Ludsin SA, Ruberg SA, Höök TO, Pothoven SA, Brandt SB, Lang GA, Liebig JR, Cavaletto JF. 2009a. Hypoxia affects spatial distributions and overlap of pelagic fish, zooplankton, and phytoplankton in Lake Erie. *J Exp Mar Biol Ecol.* 381(Suppl.):S92–S107.
- Vanderploeg HA, Ludsin SA, Cavaletto JF, Höök TO, Pothoven SA, Brandt SB, Liebig JR, Lang GA. 2009b. Hypoxic zones as habitat for zooplankton in Lake Erie: refuges from predation or exclusion zones? *J Exp Mar Biol Ecol.* 381(Suppl.):S108–S120.
- Wetzel R. 2001. Limnology: lake and river ecosystems. San Diego (CA): Academic Press.
- Weyhenmeyer GA, Meili M, Livingstone DM. 2004. Nonlinear temperature response of lake ice breakup. *Geophys Res Lett.* 31:L07203.
- Weyhenmeyer GA, Prairie YT, Tranvik LJ. 2014. Browning of boreal freshwaters coupled to carbon-iron interactions along the aquatic continuum. *PLOS ONE* 9:e88104.
- Wilhelm S, Adrian R. 2008. Impact of summer warming on the thermal characteristics of a polymictic lake and consequences for oxygen, nutrients and phytoplankton. *Freshwater Biol.* 53:226–237.
- Wilkinson GM, Cole JJ, Pace ML, Johnson RA, Kleinhans MJ. 2015. Physical and biological contributions to metalimnetic oxygen maxima in lakes. *Limnol Oceanogr.* 60:242–251.
- Williamson CE, Morris DP, Pace ML, Olson OG. 1999. Dissolved organic carbon and nutrients as regulators of lake ecosystems: resurrection of a more integrated paradigm. *Limnol Oceanogr.* 44:795–803.
- Williamson CE, Overholt EP, Pilla RM, Leach TH, Brentrup JA, Knoll LB, Mette EM, Moeller RE. 2015. Ecological consequences of long-term browning in lakes. *Sci Rep.* 5:18666.
- Williamson CE, Stemberger RS, Morris DP, Frost TM, Paulsen SG. 1996. Ultraviolet radiation in North American lakes: attenuation estimates from DOC measurements and implications for plankton communities. *Limnol Oceanogr.* 41:1024–1034.
- Winslow LA, Read JS, Woolway R, Brentrup JA, Leach TH, Zwart JA. 2014. rLakeAnalyzer: package for the analysis of lake physics. R package version 1.4. <http://cran.r-project.org/package=rLakeAnalyzer>
- Wright D, Shapiro J. 1990. Refuge availability: a key to understanding the summer disappearance of *Daphnia*. *Freshwater Biol.* 24:43–62.
- Zhang J, Hudson J, Neal R, Sereda J, Clair T, Turner M, Jeffries D, Dillon P, Molot L, Somers K, et al. 2010. Long-term patterns of dissolved organic carbon in lakes across eastern Canada: evidence of a pronounced climate effect. *Limnol Oceanogr.* 55:30–42.