Lake browning generates a spatiotemporal mismatch between dissolved organic carbon and limiting nutrients

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Scientific Significance Statement

The ecological effects of long-term increases in dissolved organic carbon (DOC) are poorly understood. One hypothesis, developed from surveys and short-term experiments, is that increases in DOC (also known as “browning”) will increase productivity in low DOC systems due to associated increases in limiting nutrients, while productivity will decrease in high DOC lakes due to increased light limitation. A critical assumption of this hypothesis is that the ratio of nutrients or dissolved absorbance to DOC remains constant through time. We find that these ratios change through time, but not space, indicating that space-for-time substitutions are insufficient to fully characterize the ecological consequences of long-term browning observed in many regions. Our results suggest that browning results in increased light limitation without concurrent increases in limiting nutrients.

Abstract

Widespread long-term increases in dissolved organic carbon (DOC) concentrations (i.e., “browning”) have been observed in many lakes, but the ecological consequences are poorly understood. Some studies suggest a unimodal relationship between DOC and primary productivity, with peak productivity at intermediate DOC concentrations. This peak is hypothesized to result from the tradeoff between light absorbing properties of DOC, and increases in limiting nutrients with browning. Nevertheless, it is unclear whether nutrient stoichiometry is constant as lakes brown. Across both regional and national surveys, we found a positive linear relationship between DOC and both total and organic forms of nitrogen and phosphorus. However, long-term data from a suite of browning lakes indicates that total nutrients do not increase as DOC increases through time. Our results show that DOC and limiting nutrients are coupled spatially, but not temporally, and that this temporal mismatch challenges previous conceptualizations of the long-term effects of browning on productivity.

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Data Availability Statement: Data for the 2018 lake and wetland survey along with long-term estimates of light availability and primary productivity potential are available in the environmental data initiative repository at https://doi.org/10.6073/pasta/4872830ed162a6f73817fa9cc6ba286. Long-term Adirondack data are available via the R package “adlkakdata” and online in the Zenodo repository at https://zenodo.org/record/1181754#.YDZ_2uhKhPY. The National Lakes Assessment data are available for download from https://www.epa.gov/national-aquatic-resource-surveys/data-national-aquatic-resource-surveys.

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Dissolved organic matter (DOM), often quantified by dissolved organic carbon (DOC) concentration, is increasing in many inland and coastal waters in several regions, including throughout Northeastern North America and Northern Europe (Monteith et al. 2007; Driscoll et al. 2016; Creed et al. 2018). This phenomenon, referred to as “browning” of aquatic ecosystems, is driven by multiple complex and often co-occurring factors. Browning is widespread in regions recovering from past decades of acidic deposition, but is also occurring in response to climate and land cover changes in some regions (Monteith et al. 2007; De Wit et al. 2016; Kritzberg 2017). Lakes may continue to be susceptible to browning in future decades depending on the direction and magnitude of change in these large-scale drivers (Creed et al. 2018; Meyer-Jacob et al. 2019).

Forecasting the long-term consequences of browning on ecosystem productivity is challenging. Whole-lake primary productivity in lakes is often limited by light and/or nutrients, especially phosphorus (P) and nitrogen (N) (Elser et al. 2007; Karlsson et al. 2009; Leach et al. 2018a). It has been hypothesized that browning may increase primary production at low DOC concentrations, but decrease production at high DOC concentrations, with a unimodal peak in productivity occurring at intermediate DOC concentrations (Jones 1992; Klug 2002; Finstad et al. 2014; Kelly et al. 2018). These contrasting effects are predicted to occur based on the net effect of stimulatory DOC-associated increases in limiting nutrients at low DOC concentrations, vs. the negative effects of decreasing water clarity and increased light limitation. While surface waters may not become light limited, light limitation may still be prevalent due to a decrease in benthic and deep-water habitats in browning waterbodies (Karlsson et al. 2009; Solomon et al. 2015; Creed et al. 2018). With increasing DOC, a unimodal peak in productivity thus implies a shift from nutrient to light limitation. This hypothesis has, in general, been supported across spatial surveys and short-term experiments across various trophic levels such as primary productivity (including both pelagic and benthic productivity), zooplankton, and fish (Ask et al. 2009; Finstad et al. 2014; Kelly et al. 2014).

Because the hypothesized effects of long-term browning on limnetic productivity depend on simultaneous increases in nutrients and light absorbance, the response may be regulated by the degree to which DOM quality is constant through time. DOM quality characteristics include nutrient stoichiometry (defined here as the in-lake ratio of P : DOC or N : DOC) and the ratio of dissolved absorbance to DOC (termed DOC specific absorbance or \( a_d : \text{DOC} \)); these characteristics may constrain productivity and the response of surface productivity along a DOC gradient. Therefore, the ratio of nutrient stoichiometry (in-lake P : DOC or N : DOC) to DOC-specific absorbance may be an important characteristic describing how primary production responds to browning. Through time, an implicit prediction of this unimodal hypothesis is that the ratio of limiting nutrients to light absorbance of the DOM pool (i.e., \( P : a_d \) or \( N : a_d \)) remains constant (Kelly et al. 2018).

This important assumption of long-term constant DOM quality has not been tested. Long-term ecosystem data from browning waterbodies are scarce, which makes detecting consequences of decadal-scale changes difficult. Therefore, space for time substitutions (Pickett 1989), experiments, and modeling have been implemented to predict the long-term effects of lake browning (Ask et al. 2009; Finstad et al. 2014; Kelly et al. 2014; Bergström and Karlsson 2019). Spatially, studies have found constant nutrient stoichiometry across a wide range in DOC concentrations (Pérakis and Hedin 2007; Cormack et al. 2018; Thompson and Cotner 2018). However, temporal trends may not be consistent with spatial patterns (e.g., Isles et al. 2018), which may indicate that long-term trends in DOM quality (e.g., \( P : \text{DOC}, N : \text{DOC}, a_d : \text{DOC}, \text{and } P : a_d \text{ or } N : a_d \) are not well understood.

If spatial surveys and shorter-term experiments do not match long-term trends, then a spatiotemporal mismatch has occurred, meaning that the consequences of long-term browning may not be fully explained by hypotheses based on past spatial, experimental, or model studies. Here, we use a combination of long-term data set analyses and large multiregion and continental-scale spatial surveys to assess the ecological impacts of browning on both water color and nutrient status through space and time in lakes. Our results indicate that findings from spatial surveys are inconsistent with long-term trends, suggesting the need for cautious interpretation of projections of longer-term changes in DOM quality from short term experiments or surveys.

**Materials and methods**

We set out to determine if DOM quality is constant over a large DOC concentration gradient both across space and through time in lakes. We investigated changes in DOC concentration and quality characteristics, including DOC to dissolved absorbance and DOC to organic nutrient concentration ratios, and the ratio of dissolved absorbance to organic nutrient concentrations. We conducted this research in three ways: (1) we performed a multiregion spatial survey of limiting nutrients (P and N), DOC concentration, and dissolved absorbance of lakes; (2) we analyzed continental-scale spatial relationships between these endpoints using the US Environmental Protection Agency’s (EPA) National Lakes Assessment (NLA) data base; and (3) we investigated long-term trends in limiting nutrients, DOC concentration, dissolved absorbance, in-lake light availability (light extinction coefficient of photosynthetically active radiation; \( K_d \)), and modeled estimates of the depth of the euphotic zone and whole-lake photosynthetic potential from a long-term data set of browning lakes in the Adirondack region of New York (Leach et al. 2018b).
Regional-scale survey

We performed a field survey of 38 lakes across three US states (New York, Pennsylvania, and Minnesota), with a range of DOC from 1.6 to 11.1 mg L\(^{-1}\) (Stetler et al. 2021). Lakes selected in New York and Pennsylvania were in regions that have experienced substantial recovery from acidification and associated browning in recent decades (Williamson et al. 2015; Leach et al. 2019). Lakes in Minnesota were selected because the region contrasts with the Northeast United States and were not subjected to the same substantial historic acidification. This approach ensured that we sampled a substantial range in potential differences in DOM quality in case major historical acidification had legacy effects on current DOM quantity and quality.

We collected surface grab samples (~ 0.5 m below the surface) in lakes in summer 2018. In most lakes, we collected samples in the pelagic zone, except for two lakes, which were sampled by wading in to the near shore area due to inclement weather. Three lakes in Pennsylvania were sampled twice and chemical parameters were averaged. Lakes were predominately oligotrophic to mesotrophic and covered a wide range in size (Table 1). We also examined the nutrient stoichiometry of wetlands that were adjacent to a subset of lakes (n = 9) in order to assess whether DOM in lakes was associated with known sources of organic matter (see Supporting Information Data S1). In total, we sampled 38 lakes. Sample preservation, lab analyses, and data quality assurance procedures for field samples are described in Supporting Information Data S1.

Continental-scale assessment

To understand the relationships between DOM and limiting nutrients at a continental scale, we used data from the 2012 NLA conducted by the US EPA (2016a). The NLA included measurements of DOC concentration, water color (platinum cobalt units [PCU]), total phosphorus (TP), and total nitrogen (TN). To minimize the impacts of large anthropogenic nutrient sources in our analysis of EPA NLA lakes, we chose to only include lakes that were designated as reference lakes. Reference lakes are defined by the EPA NLA as “a lake, either natural or man-made, with attributes (such as water quality) that come as close as practical to those expected in a natural state, i.e., a least disturbed lake” (US EPA 2016b). We further restricted our selection to include only those lakes with TP concentrations less than 48 \(\mu\)g L\(^{-1}\) corresponding to a Carlson Trophic Status Index of 60 or less (Wetzel 2001), and focused on freshwater lakes that had a specific conductance of less than or equal to 50 \(\mu\)S cm\(^{-1}\) @ 25°C which resulted in 90 total lakes. Standard field and laboratory methods for this survey are provided in previous publications (US EPA 2011, 2012).

Long-term data analysis

We used a publicly available data set of 28 lakes in the Adirondack region of New York (Winslow et al. 2018; Leach et al. 2018b) to determine long-term trends in DOM quality and test for constant nutrient to DOC ratios. Due to its protective status within a state park, Adirondack lake watersheds are predominantly heavily forested and have experienced minimal land use change in recent decades. Data were collected 1994 to 2012, but all lakes were not sampled every year (see Leach et al. 2018b for details, including methods). We calculated annual summer averages for DOC, TP, TN, and water color (PCU) measurements. We estimated and calculated long-term trends in the light extinction coefficient \((K_d)\) by converting from average summer DOC concentrations using a coefficient of 0.22 * DOC (Morris et al. 1995; Read and Rose 2013). We then used the light extinction coefficient to estimate the euphotic zone and whole-lake photosynthetic potential using a generic photosynthetic irradiance curve (Kirk 1994). Further details describing this modeling are described in Supplemental Information Data S1.

Table 1. Descriptive information for the 38 lakes included in the 2018 summer field survey from the Northeastern United States (NE: New York and Pennsylvania) and Minnesota (MN).

| Region  | NE | MN |
|---------|----|----|
| **Trophic state** | | |
| Oligotrophic | 25 | 5 |
| Mesotrophic | 3 | 2 |
| Eutrophic | 0 | 3 |
| **Maximum depth (m)** | | |
| ≤ 5 | 2 | 2 |
| > 5 and ≤ 15 | 19 | 3 |
| > 15 and ≤ 30 | 5 | 4 |
| > 30 | 2 | 1 |
| **Surface area (ha)** | | |
| ≤ 25 | 10 | 4 |
| > 25 and ≤ 50 | 7 | 0 |
| > 50 and ≤ 100 | 5 | 4 |
| > 100 | 6 | 2 |

Statistical analyses

We performed all statistical analyses in R version 3.6.2 (R Core Team 2019). To determine whether the ratio of DOC to limiting nutrients was constant across space, we tested for significant linear relationships between DOC concentration and different limiting nutrient forms in both spatial surveys (our regional survey and the EPA NLA continental survey). We tested if linear regression assumptions were met using the “gvlma” R package (Peña and Slate 2006). When assumptions were not met, we used Kendall’s rank correlation to test for significant correlations. For all statistical tests, \(\alpha = 0.05\). We also report linear slopes. To test if nutrient stoichiometry significantly varied between the Northeast lake region and
Minnesota lake region, we performed a Welch’s t-test of the average nutrient to DOC ratio (e.g., log-transformed [TP/DOC]), which accounts for uneven sample sizes. We tested for normality using the Shapiro–Wilk test.

To determine if nutrient stoichiometry was constant through time, we calculated the Sen’s slope trend of the nutrient (TP or TN) to DOC and \(a_{440}\) to DOC ratio for each lake \((n = 28)\) using the “zyp” R package (Bronaugh and Arellia 2019). We also calculated long-term trends in DOC, \(a_{440}\), nutrients, \(K_d\), and light availability in each lake by determining the Sen’s Slope. Summer average ratios were log-transformed before analysis (e.g., Isles et al. 2020). We determined trend significance using a Mann-Kendall test. We converted water color (PCU) to \(a_{440}\) based on established relationships described in Cuthbert and Del Giorgio (1992).

**Results**

Across our regional survey of 38 lakes, TP, DOP, TN, and DON were all significantly and linearly correlated with DOC concentrations (Fig. 1, Table S2). TP and DOP had slope coefficients of 2.52 \(\mu g \text{ TP mg DOC}^{-1}\) and 0.97 \(\mu g \text{ DOP mg DOC}^{-1}\). TN and DON had slope coefficients of 0.09 mg TN mg DOC\(^{-1}\) and 0.06 mg DON mg DOC\(^{-1}\), respectively (Table S2). Both total and dissolved organic P and N forms were also positively correlated with DOC concentration or dissolved absorbance (Fig. 1).

**Fig 1.** Relationships between total phosphorus (TP, a), dissolved organic phosphorus (DOP, b), total nitrogen (TN, c), dissolved organic nitrogen (DON, d), with DOC concentration or dissolved absorbance (\(a_{440}\)) from a survey of 38 lakes in the Northeastern United States (New York and Pennsylvania: Blue) and Minnesota (maroon). Statistics are reported in text and Table S2. Gray line denotes linear trend line.

**Fig 2.** Relationships between total phosphorus (a,c) or total nitrogen (b,d) with DOC (a,b) or \(a_{440}\) (c,d) from the 2012 \((n = 90)\) NLA survey. Statistics are reported in text and Table S2. Gray line denotes linear trend line.
linearly correlated with $a_{440}$ (Fig. 1, Table S2). $a_{440}$ was also significantly correlated with DOC concentrations (Fig. S1a, $p < 0.001$, Table S2). At a continental scale, TP and TN were positively correlated with DOC concentrations with linear slopes of 1.15 $\mu$g TP mg DOC$^{-1}$ and 0.04 mg TN mg DOC$^{-1}$ (Fig. 2, Table S2). While TP and TN were correlated with $a_{440}$, we found stronger relationships between TP and TN with DOC (Table S2). Ratios between DOP, DON, or TN, and DOC did not regionally differ between waterbodies in the Northeast and Minnesota (minimum $p = 0.06$). However, the (log-transformed) ratio between TP and DOC was higher in Minnesota lakes than the northeast ($p = 0.02$; Fig. S2; Table S3).

Our long-term data set analysis showed that over the period 1994–2012, DOC concentrations increased at a median rate of 0.56 mg L$^{-1}$ decade$^{-1}$ (Fig. S4a, 17 of 28 lakes with significant trends) and $a_{440}$ also increased (Fig. S4b, 22 of 28 lakes significant). Over the same period, TP declined at a median rate of $-0.24$ $\mu$gL$^{-1}$ decade$^{-1}$ (Fig. S4c, 4 of 28 significant) and TN declined at a median rate of $-1$ mg L$^{-1}$ decade$^{-1}$ (Fig. S4d, 12 of 28 significant). The $K_d$ increased at a median rate of 0.12 m$^{-1}$ decade$^{-1}$ throughout the study period (Fig. S4e, 17 of 28 lakes significant), indicating a general trend toward reduced light penetration into the water column through time (Fig. S4e). Accounting for surface light availability, light attenuation, and the relationship between photosynthesis and irradiance, we found that the proportion of the water column in the euphotic zone significantly declined in 15 of 28 lakes (Fig. S7) and whole-lake photosynthetic potential significantly declined in 17 of 28 lakes (Fig. 4). We also found that ratios (log transformed) of TP : DOC (11 of 28 significant) and TN : DOC (20 of 28 significant) both decreased through time (Figs. 3b,c, S5, S6). In contrast, DOC specific absorbance increased through time (Fig. 3a), with significant trends in 16 of 28 lakes, and the ratios of TP or TN to $a_{440}$ decreased through time (Figs. 3d,e, S5, S6) with significant trends in 13 of 28 lakes and 18 of 28 lakes, respectively. The TP : TN ratio generally increased through time (Fig. 3f, 5 of 28 lakes significant).

**Discussion**

Our results indicate that the ratio of DOC to limiting nutrients was constant across space at both regional and continental scales, but not-constant through time. Changing ratios (in-lake TP : DOC, TN : DOC, and $a_{440}$ : DOC) through time indicates that space-for-time substitutions are likely insufficient to fully characterize the ecological consequences of long-term browning observed in many regions. While our spatial surveys indicate that nutrients are associated with DOM, our results indicate that long-term browning is not associated with increases in-lake nutrient concentrations. This observation is contrary to the implications of past studies that identify long-term browning as a factor that would contribute to long-term increases in nutrient loading (e.g., Corman et al. 2018).
However, our results are consistent with long-term studies from other regions. For example, in a study of Swedish lakes, researchers found tight spatial coupling of nutrients and DOC, but no correlation between changes in DOC and changes in P or N through time (Isles et al. 2018). Thus, a unimodal relationship between DOC concentration and measures of productivity, with peak productivity at intermediate concentrations of DOC, likely does not fully represent the response of many lakes undergoing browning.

Across space, we observed that DOC and nutrients were tightly correlated, with organically bound nutrients comprising approximately 38% of TP and 67% of TN, and few differences in nutrient stoichiometry between regions. Our results build on past spatial studies that have demonstrated tight regional coupling between DOC concentration and nutrient concentration (e.g., Perakis and Hedin 2007; Corman et al. 2018; Thompson and Cotner 2018; Isles 2020). However, our results also show that the ratio of TP : DOC decreased.
through time, as has also been observed in lakes in Sweden (Huser et al. 2018).

While our results demonstrate that long-term browning is not associated with increases in nutrient concentrations, it was associated with increasing dissolved absorbance and light attenuation. Thus, absent nutrient enrichment via other mechanisms, the primary effect of long-term browning is likely to be a reduction in whole-lake production. Indeed, a majority of our study lakes ($n = 17, 61\%$) exhibited a long-term decrease in whole-lake photosynthetic potential, and 15 (54%) lakes exhibited a long-term reduction in the proportion of the water column in the euphotic zone. This estimate of light availability (and limitation) is likely conservative since it was calculated based on the brightest time of year (i.e., the summer solstice). At other times of year, light limitation in deep-water column layers is likely to be much greater. Over time, increases in light limitation may shift the depth distribution of production toward surface waters and away from benthic and meta-metric or hypolimnetic sources (e.g., Vadeboncoeur et al. 2003). However, our model implicitly assumes a static primary producer community and excludes the possibility for species turnover and adaptation to perform better in low-light environments.

Our findings highlight the potential negative effects of browning on lake productivity. Similar implications have been suggested by others including Thrane et al. (2014) who found a negative relationship between DOC and pelagic lake productivity across 75 boreal lakes. While light limitation may decrease primary production, if organisms such as zooplankton can utilize terrestrial resources as DOC increases (e.g., Solomon et al. 2011), they may offset some primary production losses in aquatic food webs. Browning may also increase productivity in some oligotrophic waterbodies where reduced light attenuation may increase primary production by reducing the penetration of damaging solar radiation (Bernhard et al. 2020).

The discrepancy between short-term experiments or surveys and our long-term results suggest that space-for-time substitutions are not a suitable replacement for examining long-term trends. These substitutions inaccurately predict future conditions when the drivers of variability across space are different from the drivers of variability through time (Pickett 1989). Variation in DOC concentrations in the Northeastern United States through time is driven predominately by recovery from acid deposition (Monteith et al. 2007; Leach et al. 2019) and, likely to a lesser extent, precipitation increases (De Wit et al. 2016). In contrast, spatial variability in DOC is driven more by individual lake and watershed characteristics, such as percent wetlands coverage (Solomon et al. 2015).

We observed that nutrients were not increasing with increasing DOC through time. Widespread decreases in TN have been reported and attributed to reductions in anthropogenic emissions and associated deposition (Driscoll et al. 2016). Drivers of P dynamics through time are likely complex. Though a mechanistic explanation has not yet been verified, we offer three potential explanations to explain the lack of P increases as DOC increased through time. First, delays in soil pH recovery from acidification can delay P mobilization (e.g., Kopáček et al. 2015). Thus, as lakes and watersheds continue to respond to decreased acidic deposition, P concentrations may indeed increase in future decades. In less acidified regions such as Wisconsin, USA, lags in P liberation may be minimal (e.g., Kopáček et al. 2015), which may explain the discrepancy between our work and that of Cormann et al. (2018). Cormann et al. (2018) assumed DOM soil quality to be constant through time, which could be true in Wisconsin, but is not true in the Adirondacks, a region that was strongly acidified by acid deposition (Shao et al. 2020). Since browning is largely driven by recovery from acidification (Monteith et al. 2007), the degree to which browning has the potential to contribute P through time may be largely driven by the amount of historical acidification and current soil recovery rates. Alternatively, terrestrial plants are experiencing longer growing seasons in response to climatic warming (Linderholm 2006). This can increase terrestrial nutrient demand (Jonard 2015) and P limitation (Goswami et al. 2018), thereby reducing nutrient export to lakes while also increasing the amount of terrestrial carbon available for export (Groffman et al. 2018). Finally, as lake DOC concentrations increase under browning in response to environmental drivers such as recovery from acidification, the character of the DOM pool may be changing in ways that alter DOM solubility (e.g., De Wit et al. 2007) and nutrient stoichiometry. For example, increases in solubility may be associated with increases in inputs of older and more nutrient-poor DOM from soils (e.g., Tipping et al. 2016), or increases in the proportion of allochthonously derived DOM, which is typically more nutrient depleted than autochthonous DOM (e.g., SanClements et al. 2012). Of these three mechanisms, only the third would actually impact DOM stoichiometry, while all three would depress the $P : DOC$ ratio. The above potential explanations are not mutually exclusive and it is possible that a combination of factors are acting simultaneously (e.g., Huser et al. 2018).

Patterns in the ratio of limiting nutrients to DOC at the continental scale appeared more variable than our regional survey, but still indicated that DOC likely serves as an important source of nutrients across inland waterbodies. Furthermore, substantial variability existed between $a_{440}$ and total nutrients especially at low $a_{440}$ values. Given the broad geographic diversity, it is likely that only a small proportion of lakes in the NLA are undergoing browning. Variation in a wide suite of lake characteristics such as land use and land cover, water residence time, lake morphometry, food web composition, and underlying geology likely contribute to the large variation in DOC, $a_{440}$, and nutrients at the national scale. We calculated that each mg of DOC contributes $1.15 \mu g$
TP and 0.04 mg TN, and about 37.6% and 55.9% of the total TP and TN pool, respectively. Past research has shown that DOP represents over 75% of lake TP in forested watersheds and that while DOP is often bound in complex molecules, it is still a readily bioavailable nutrient supporting aquatic food webs (Thompson and Cotner 2018).

Our results demonstrate that long-term browning leads to light limitation, and although DOC and nutrients were correlated across space, nutrient levels are not increasing through time as lakes brown. Together, our results indicate that browning is likely to result in a reduction in whole-lake productivity, especially in oligotrophic lakes where the majority of productivity occurs in benthic and other deep-water habitats (e.g., Vadeboncoeur et al. 2003; Leach et al. 2018a). Caution is therefore warranted when applying space-for-time substitutions to understand lake browning.

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