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Key Points:
- Terrestrial loads of dissolved organic matter to lakes are an underappreciated nutrient load to surface waters
- Browning in lakes in the U.S. upper Midwest shows a delayed response compared to other temperate regions

Nitrogen and Phosphorus Loads to Temperate Seepage Lakes Associated With Allochthonous Dissolved Organic Carbon Loads

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Abstract Terrestrial loads of dissolved organic matter (DOM) have increased in recent years in many north temperate lakes. While much of the focus on the "browning" phenomena has been on its consequences for carbon cycling, much less is known about how it influences nutrient loading to lakes. We characterize potential loads of nitrogen and phosphorus to seepage lakes in northern Wisconsin, USA, based on a laboratory soil leaching experiment and a model that includes landscape cover and watershed area. In these seepage lakes, nutrient concentrations are positively correlated with dissolved organic carbon concentrations (nitrogen: $r = 0.68$, phosphorus: $r = 0.54$). Using long-term records of browning, we found that dissolved organic matter-associated nutrient loadings may have resulted in substantial increases in nitrogen and phosphorus in seepage lakes and could account for currently observed nutrient concentrations in the lake. "Silent" nutrient loadings to brown-water lakes may lead to future water-quality concerns.

Plain Language Summary The color of many temperate lakes is changing; some lakes are becoming more darkly stained brown. The tea-colored stain is due to dissolved organic matter from the surrounding landscape. Much of the research related to the causes and consequences of increased staining, or "brownification," relate to its connection to the carbon cycle. However, by examining long-term lake chemical records, analyzing the properties of the organic compounds, and modeling potential flows of the compounds, we find that carbon is not the only element that is influenced by browning. Nitrogen and phosphorus, two nutrients important to growth of organisms at the base of the food web, may also be increasing in lakes due to brownification.

1. Introduction

Dissolved organic carbon (DOC) concentrations are increasing in many lakes across temperate North America and Europe (Clark et al., 2010; Monteith et al., 2007). Increases in lake chromophoric DOC concentration often cause staining, or "browning," of lake water (Monteith et al., 2007; Roulet & Moore, 2006). Browning affects a range of physical and ecological attributes and processes within a lake (Solomon et al., 2015), including water transparency and thermal structure (Read & Rose, 2013), phytoplankton community composition (Brown et al., 2016), bacterial production (Hessen, 1992), and ecosystem respiration (Hanson et al., 2003, 2015; Zwart et al., 2016). The leading hypothesis for the cause of browning is related to acid rain recovery in soils, such that decreases in atmospheric sulfate deposition have caused increases in soil pH and reductions in soil ionic strength that have increased organic matter solubility, and ultimately, DOC flux from soils to receiving waters (Clark et al., 2010; Evans et al., 2012). While this mechanism is debated and other causes have been suggested (e.g., climate change, Oni et al., 2013; shifts in drought or precipitation regimes, Eimers et al., 2008; land-use change, Garnett et al., 2000; and nitrogen deposition, Pregitzer et al., 2004), an impact of the browning process that has been largely ignored is its influence on lake nutrient loading.

Browning typically results from increased flow of dissolved organic matter (DOM) to lakes, and while much attention has been paid to the associated increase in DOC load, browning may also influence nutrient flows. DOM can either contain or complex with nitrogen (N) and phosphorus (P; Dillon & Molot, 1997; Hessen et al., 2009; Kortelainen, 1993), and in some cases, this allochthonous or terrestrially derived material provides the

majority of nutrients to brown lakes (Berggren et al., 2015). However, both the total and relative quantities of nutrients derived from this flux are not well constrained. Studies of leachates from different terrestrial materials illustrate that DOM contains different amounts of N and P (Buckeridge et al., 2016; Lennon & Pfaff, 2005; Wallace et al., 2008). Hence, depending on the source material, increases in DOM input from leachates may greatly impact the total quantity, as well as relative quantity or stoichiometry, of N and P flows to lakes (Dillon & Molot, 2005; Stoddard et al., 2016).

The chemical characteristics of DOM are related both to the processes that influence it during transport to receiving waters and to its source material (Aiken & Cotsaris, 1995; Marin-Spiotta et al., 2014; Thurman, 1986, and references therein), the latter being a focal point of this study. Wetlands in lake catchment areas are well recognized as important sources of DOM to lakes (e.g., Dillon & Molot, 1997; Kortelainen, 1993; Stets & Cotner, 2008), but other sources include upland forest soils (Qualls et al., 1991; Solinger et al., 2001), aerial plant inputs (France & Peters, 1995), groundwater (Einarsdottir et al., 2016), and tributary streams (Cotner et al., 2004). To reduce some of these complexities, we focus on seepage lakes: lakes with no surface inputs or outputs, that are fed primarily by precipitation or runoff, and that typically have limited local groundwater connection (Wetzel, 2001). The simplified hydrology of these systems reduces the number of potential DOM sources needing to be considered (Driscoll et al., 2016; Webster et al., 1990) to those related to runoff or shallow subsurface flows (Hinton et al., 1998); hence, we focus on wetland and forest soils as the main potential DOM sources to seepage lakes.

Our objective is to consider potential nutrient loads of DOM to seepage lakes in northern Wisconsin, a lake-rich region that is recovering from acid rain deposition (Stoddard et al., 1999) and where some lakes are browning (Jane et al., 2017). First, we identify trends in browning using long-term records collected from a wilderness area, the Rainbow Lakes Wilderness (RLW) in the Chequamegon-Nicolet National Forest (CNNF). Then we determine the C, N, and P content of leachates from representative soils in the area. Next, we combine these historical records with laboratory studies to model how leachates, based on different surrounding landscape area extents, can contribute to potential N and P loadings to lakes, both in terms of quantity and stoichiometry. Then we ask, despite the many processes that can influence nutrient fluxes into and within lakes, are modeled leachate N and P fluxes a potential substantial source of nutrients to seepage lakes?

2. Materials and Methods

2.1. Description of Study Region

The CNNF encompasses over 600,000 ha of northern Wisconsin, USA. The soils are mostly sand, sandy or silt loams, or wetland or organic soils (Natural Resources Conservation Service, 2017). The mixed deciduous-coniferous forests contain approximately 2,000 lakes and ponds, many of which are seepage lakes with minimal anthropogenic disturbance. DOM in lakes in this region is almost entirely allochthonous (Wilkinson et al., 2013). Lakes in this region are warming, but probably less than 1–2 °C in the last 30 years (Winslow et al., 2015). Data are included in this study from 17 lakes from across the CNNF, including the RLW area, which the U.S. Forest Service, in collaboration with other agencies and research partners, have been sampling sporadically since 1984 (Ford et al., 1993). Three of the focal lakes, Morgan, Gates, and Jupa, were chosen to span a range of low, medium, and high DOC concentrations (LO-DOC, MED-DOC, and HI-DOC, respectively). Information about all 17 lakes can be found in Table S1 in the supporting information.

2.2. Long-Term Trends in Browning in Northern Wisconsin

We used air and water-quality records to estimate historic shifts in acid rain deposition and terrestrial loads of DOM. Wet deposition records were retrieved from the National Atmospheric Deposition Program (2017); we compared estimates of sulfate and nitrate deposition between 1988–1992 and 2008–2012 at sites WI36 and WI37 to define acid rain reduction in the region. The U.S. Forest Service measured sulfate (SO_4^{2-}), pH, and color from 1984 to 2016 from the RLW lakes. Fourteen years are missing from the data and not all parameters were collected each sampling year (Data Set S1). Based on recommendations within Hirsch et al. (1991) and Helsel and Hirsch (2002), we used a step trend procedure to determine temporal change in each parameter. Samples were grouped into time periods based on large breaks (4 years or more of missing data) in sample collection (with sampled years listed in parentheses): 1990s (1994 or earlier), 2000s (1999–2004), and 2010s (2007 and later); only data from samples collected during summer stratification

(June, July, and August) were used. As the number of sample years differed among time periods, we used the median parameter value of each lake to perform a paired Wilcoxon signed-rank test between each time period (i.e., 1990s–2000s, 2000s–2010s, and 1990s–2010s) and a Hedges-Lehmann estimator to determine differences among time periods.

Historic lake color data were converted to DOC concentrations using linear regression of both parameters from seven lakes in the RLW sampled between 2013 and 2016. In 2016, 14 lakes across the CNNF, including four from the RLW, were sampled for total nitrogen (TN) and total phosphorus (TP) concentrations during summer lake stratification (Table S1). We used correlation analysis to investigate relationships between different historic water-quality parameters and to investigate relationships between DOC concentrations and nutrients based on sampling in 2016. A Shapiro-Wilk test was used to test assumptions of normality between data pairs; when the assumption of normality was not rejected ($p > 0.05$), we report the Pearson correlation's coefficient, when it was, the Spearman's correlation coefficient.

2.3. Leachate Collection and Analysis

Potential nutrient loads associated with browning were estimated by analyzing the chemical composition of leachates derived from soils. Soils were collected with a 5-cm (internal dimension) stainless steel core from peat soils along the perimeter of HI-DOC and sandy soils along the perimeter of MED-DOC. Five cores were taken at each site, and each core contained the upper 10 cm of soil. While deeper flow paths may influence solute movement to these seepage lakes, work wetland-forest dominated catchments in northern Wisconsin (Elder et al., 2000; Krabbenhoft et al., 1995) and elsewhere suggest flow path importance of DOC to surface waters decreases with depth (Laudon et al., 2007). Leachates were extracted from soils mixed in Nanopure water using an orbital shaker (rpm = 150, time = 4 hr) and analyzed for DOC and total dissolved N and P (TDN and TDP) following standard methods (American Public Health Association, 1998). Details of the leaching procedure and chemical analysis can be found in Text S1.

2.4. Watershed Leachate Potential

We considered potential nutrient loads associated with allochthonous loads of carbon in two ways: first, based on contemporary carbon budgets, and second, based on historical browning trends. Our first method, Model 1, is an index of the relative importance of watershed buffer zone size to nutrient loads in the LO-, MED-, and HI-DOC lakes based on a carbon budget of lakes in northern Wisconsin. Our second method, Model 2, is an index of soil leachate nutrient loads to receiving lakes based on historic increases in DOC described in section 2.2.

2.4.1. Model 1: Potential Leachate Loads to Seepage Lakes

In Model 1, we estimate allochthonous nutrient inputs into seepage lakes based on a model of carbon loads to lakes in northern Wisconsin, similar to Buffam et al. (2011). Buffam et al. (2011) developed a regional C budget for the Northern Highlands Lake District based on major C fluxes into and out of forest, wetlands, and surface waters. In our model, we focus on the hydrological flow paths from Buffam et al. (2011) of prime relevance to DOM loading to seepage lakes: shallow subsurface flows or soil runoff. Therefore, nutrient loads based on this flow path are modeled using forest or wetland cover, watershed area, and leachate stoichiometry.

Estimates of soil carbon leachates were based on the amount of forested or wetland area within each watershed (Buffam et al., 2011). As it is difficult to determine the watershed area of seepage lakes due to subtle topographic relief and relatively low-resolution of current elevational mapping products, we used a range of contributing areas most likely to contribute to DOC loads: 25–1500 m perimeters around a lake (Gergel et al., 1999; Soranno et al., 2015). We determined the proportion of wetland and forested areas in these contributing areas using the Wisconsin Initiative for Statewide Cooperation on Landscape Analysis and Data land cover data. "Forest" includes coniferous, broad-leaf deciduous, and mixed deciduous/coniferous classifications and "wetland" includes emergent/wet meadows, lowland shrub, and forested wetland classifications. Then we used the mean stoichiometric relationships of C to N (C:N) and C to P (C:P) for each leachate source to determine potential N and P loads to the lakes.

To determine nutrient loads into each lake, we used the following equation:

$$I_{i,x} = A_{i,j} * C_{\text{Soil},i,j} * (X : C_{\text{Soil}})_j,$$

where I is the input, x is the nutrient (N or P), A is the area of the land cover type of the buffer zone, C is the carbon content of the soil leachate, $X{:}C$ is the ratio of nutrient x to carbon in the soil leachate, j is the land cover type (forest or wetland), and i is the buffer zone width.

2.4.2. Model 2: Nitrogen and Phosphorus Loading Based on Changes in DOC

The second approach considered potential N and P loading to lakes based on historic browning trends in terms of predicted lake N and P concentrations. First, as described above, we used long-term estimates of lake browning from the RLW to define the increase color between the 1990s and 2010s and a regression equation to model DOC from color. We sampled the latter 10,000 times with replacement to generate a bootstrapped error term (Snedecor & Cochran, 1989; Yanai et al., 2010). Potential nutrient loads to each lake were estimated using the stoichiometric ratios of C, N, and P in the soil leachates as DOC associated with lake browning is thought to be derived solely from soil DOM inputs (Evans et al., 2012). To generate bootstrapped distributions of potential lake TN and TP concentrations, we sampled with replacement from the measured leachate values and multiplied these values by a sample with replacement from the modelled DOC increases. While differential processing of N or P in the watershed along the flow path from soils into the lake or within the lake would mean that actual N and P concentrations would differ from those that this model suggests, we use this model to consider the whether or not the potential magnitude of N and P loading associated with brownification could be a substantial source of nutrients to lakes. We do this by graphically comparing observed TN and TP concentrations to those predicted by our model. All statistical analyses were performed in R (R Core Team, 2017).

There are several assumptions within the model. First, when calculating DOC loads related to browning, we did not account for whether DOC was respired or otherwise processed in the lake between the 1990s and 2010s (Hanson et al., 2011). If allochthonous DOC is respired, then our estimate of loads is conservative while if sedimentation rates decreased or increased between the 1990s and 2010s, our estimates could be exaggerated or conservative, respectively. Second, we did not consider changes, either seasonal or long-term, in lake water levels even though they can influence water chemistry (Marin et al., 1990; Webster, 1993; Webster & Brezonik, 1995). To minimize the potential influence of seasonal water level fluctuations, we only used water-quality information from the summer. We did not account for longer-scale fluctuations, per se, but because calculations of N and P loads are based on DOC shifts, any hydrologic changes that would influence DOC concentrations are implicit. We are unable to bound these uncertainties in this study, so results should be considered for their heuristic value.

3. Results

3.1. Long-term Trends in Browning in Northern Wisconsin

Water-quality records from the RLW are consistent with acid rain recovery. Regional atmospheric sulfate and nitrate deposition rates decreased 60% and 40%, respectively, between the 1990s and 2010s (Figure S1). Lake sulfate concentrations decreased by 42% (median) or 1.39 (95% CI [−2.05, −0.46] mg SO_4^{-2} L^{-1} ($p < 0.05$, V = 27) while the trend in pH was indeterminate (Figure S2 and Table S2). Water color increased by 134% (median) or 44.8 Pt-Co [17.0, 77.2], $p < 0.05$, V = 28, with darkening evident in all lakes (Figure 1a). The greatest increase in browning happened between the 2000s–2010s. Decreases in sulfate were directly related to increases in color ($r = -0.74$, $p = 0.057$; Figure 1b) and increases in color were significantly correlated to the color of the lakes in the 1990s ($r = 0.96$, $p < 0.001$; Figure 1c).

Based on the relationship between water color and DOC (Figure S3), the RLW increase of color correlates with an increase of 9.66 mg C^{-1} L [4.01, 12.90] in lake waters. Across lakes, nutrient concentrations were positively related to DOC concentrations (TN: $r = 0.68$, $p < 0.01$; TP: $r = 0.52$, $p < 0.05$, Figure S4).

3.2. Leachate Chemistry and Watershed Leachate Potential

Wetland soil was a greater source of leachate C and P in terms of both potential quantity (μg nutrient g^{-1} soil) and lower stoichiometric ratios of C:P$_{atomic}$ (185 versus 459, respectively) and N:P$_{atomic}$ (7 versus 31, respectively) than forest soil. The wetland soil was also a greater source of leachate N in terms of quantity, but wetland soil leachate had a higher C:N ratio than that of forest soil leachate (25 versus 17, respectively). The stoichiometry of soil leachates varied based on watershed boundary size, reflecting proportions of forest or wetland area (Figure 2). Overall, larger watershed resulted in P-rich leachates (i.e., N:P ratios lower than 16:1, "Redfield ratio" indicative of N:P balance in aquatic ecosystems, Redfield, 1958).
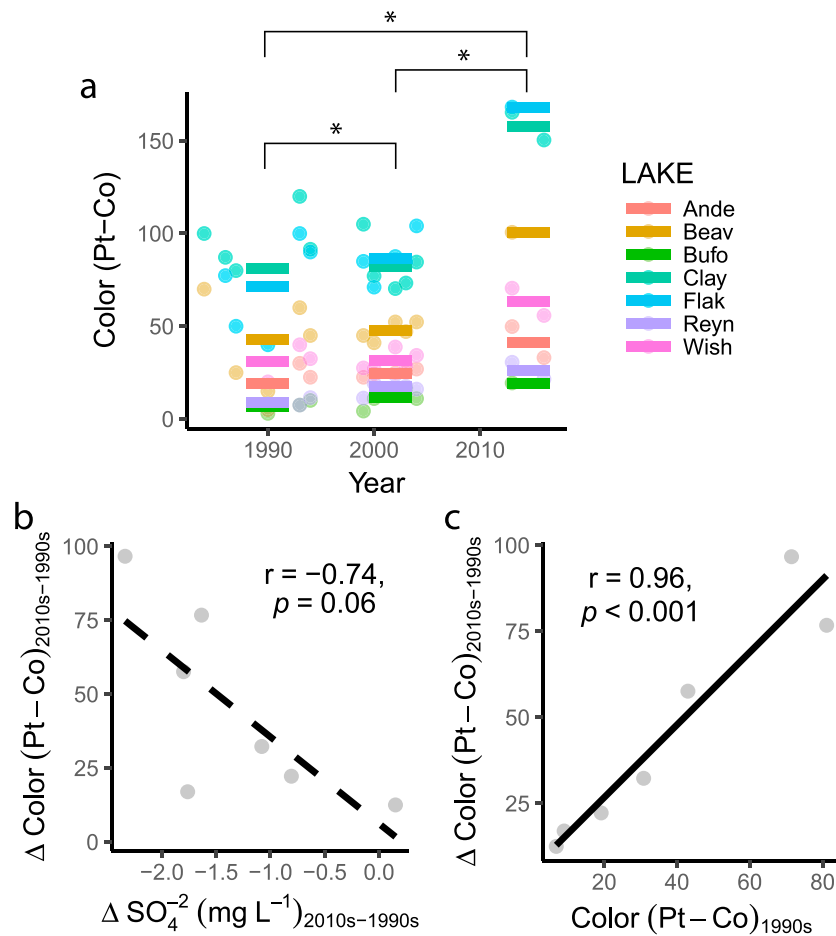
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Figure 1. (a) Water color in lakes from the Rainbow Lakes Wilderness area in the Chequamegon-Nicolet National Forest, WI, from 1984 to 2016. Bars represent lake median values for each time group (1990s [1994 or earlier], 2000s [1999–2004], and 2010s [2007 and later]). Brackets with asterisks indicate significant differences between time periods ($p < 0.05$). Changes in browning are related to (b) decreases in lake sulfate concentrations and (c) water color in the 1990s.

3.3. Lake Browning and Leachates

Based on our model of potential allochthonous nutrient loads associated with browning, we found that median lake nutrient concentrations could have risen between 336 and 563 µg N L^{-1} and 42–105 µg P L^{-1} across the 14 lakes between 1990 and 2016 (Figures 3a–3b). In most lakes, leachate-derived values for nutrient concentrations were greater than contemporary concentrations of TN and TP. However, lake N concentrations due to potential allochthonous N loadings are more similar to current lake N concentration than lake P
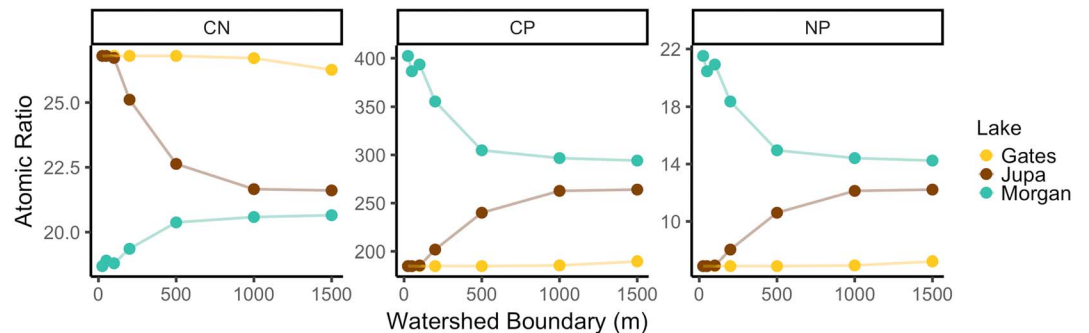

Figure 2. The stoichiometry of potential watershed leachates to the three study lakes.
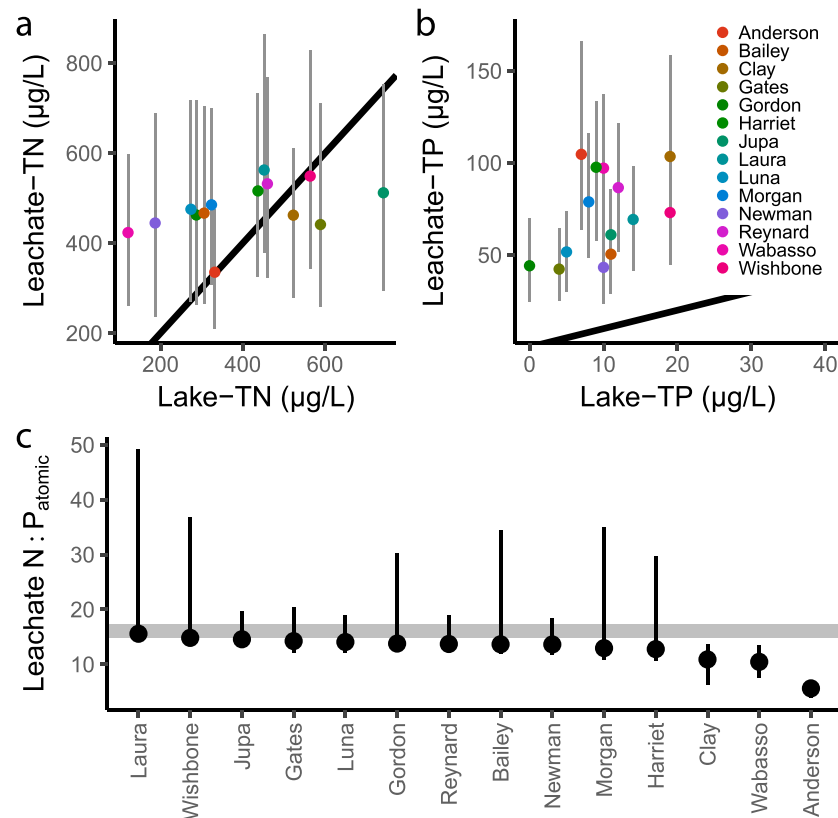
Figure 3. Comparison of potential increases in (a) lake total nitrogen (TN; "Leachate-TN") and (b) lake total phosphorus (TP; "Leachate-TP") based on increases of dissolved organic carbon (DOC) from Rainbow Lakes Wilderness area with lake TN and TP concentrations in 2016. For leachate-associated values, error bars represent the 25% and 75% quantiles of the data and points represent the medians ($n = 10,000$). The black line on each graph represents the 1:1 line. (c) Nitrogen to phosphorus (N:P) ratios of potential loads of allochthonous soil leachates associated with lake browning. Error bars represent the 25% and 75% quantiles of the data and points represent the medians ($n = 10,000$). The gray line represents an N:P ratio of 16.

concentrations due to potential allochthonous P loadings. Current lake P concentrations are ca. 14% of what allochthonous P loadings from browning would suggest. Leachate N:P ratios tend to be less than 16 and less than current mean lake N:P ratios (63 ± 21; Figure 3c).

4. Discussion

Our results show that browning trends observed in other parts of North America and Europe (Monteith et al., 2007) are also found in seepage lakes in northern Wisconsin. Since the 1990s, soils may have leached substantial loads of N and P, in addition to organic C, to receiving lakes; these nutrients could completely account for N and P concentrations in the lakes. If lake browning eventually subsides, either if soils leach less DOM or lake ecosystems become more efficient at mineralizing DOM (Hanson et al., 2011), nutrients associated with the stain may remain in the lakes and could spur algal or bacterial growth.

4.1. Increased Browning in Northern Wisconsin

Our step trend analysis suggests that DOM increases in Wisconsin seepage lakes are offset by approximately a decade relative to those increases observed in the Adirondacks (NY, USA) and Northeast (USA) from the U.S. Environmental Protection Agency Temporally Integrated Monitoring of Ecosystems project (Strock et al., 2014). Lakes in the upper Midwest may be exhibiting a delayed response to acid rain recovery compared to other regions, or are responsive to other drivers of environmental change (e.g., shifts in precipitation regimes, Eimers et al., 2008).

Interestingly, in a study considering long-term trends in browning in Wisconsin, others found little evidence of widespread browning or increases in DOC concentrations in seepage lakes (Jane et al., 2017).

However, five of the six lakes included in their study had low concentrations of DOC (5 mg C L^{-1} or less); the lake with the highest DOC concentrations (5–20 mg C L^{-1}), comparable to lakes in our study, did show significant increases in DOC between 1990 and 2015. Indeed, our work suggests that browning trends may be stronger in lakes that were already stained in the 1990s—hence, historical data sets that do not include brown lakes may not adequately sample regional trends. A larger historical data set from the upper Midwest lakes would allow for a better understanding of how the observed changes in seepage lake chemical properties are related to environmental change, whether these changes are more dramatic for seepage lakes influenced by peatlands, and how these lakes may be sensitive to future environmental change.

4.2. N and P Dynamics Related to Lake Browning

Our results demonstrate the nutrients associated with DOM may substantially influence N and P concentrations in lakes, supporting short-term experimental results by Zwart et al. (2016) and present-day correlations between DOC and TN and TP (Figure S4). The low N:P ratio (<16) of soil leachates suggests a potential consequence for primary production given that lakes in northern Wisconsin are generally thought to be P-limited (Hanson et al., 2003). Phytoplankton biomass should be monitored in these and other seepage lakes with surrounding peatlands.

Low primary production rates can occur despite potentially high nutrient loading in lakes when photoautotrophs are light limited (Deininger et al., 2017). Current concentrations of DOC in lakes included in this study range from 3.8 to 35.3 mg/L (Data Set S1), concentrations that flank those used by Seekell et al. (2015) to demonstrate a shift from nutrient limitation to light limitation. Hence, if the same cutoffs apply in Wisconsin lakes, browning in the upper Midwest may have shifted primary production in these lakes from primarily nutrient limited to light limited. Any shift in DOM inputs or decrease in stain through photo-oxidation or bacterial processing may increase light availability to prebrowning levels (Graneli et al., 1996; Molot & Dillon, 1997; Vahatalo & Wetzel, 2008); nutrient demand by photoautotrophs may quickly be met by nutrients now present in the lake.

Calculations from our model of potential N and P loading suggest that browning may account for all of the N and P in the water column in seepage lakes in the CNNF. The greater discrepancy among modeled and actual P concentrations versus N concentrations also suggests differential processing of leachate N and P either in the watershed or in the lake (Figure 3). Leached DOM may be adsorbed or chemical altered as it is transported downward through mineral soils (Kalbitz et al., 2000). Hence, soils may retain more P than N and the N:P ratio of the loads into the lake may be greater than the N:P ratio of the soil leachates used in our model. Likewise, in lakes, greater sedimentation rates of P than N is common (Oliver, 2017) and could lead to higher N:P ratios in the water column that the N:P ratio of the soil leachates. Future work examining soil porewater chemical properties and flow paths and/or lake sediment cores could help to differentiate these possibilities.

4.3. Model Assumptions and Limitations

Our results, and their applicability to other lakes, should be considered in light of several of the limitations of our models. We did not consider alternative sources of N or P to the lakes, for example, aerial leaf inputs, pollen, weathering, or atmospheric deposition (Eimers et al., 2017; Selbig, 2016). However, despite this, we found that browning could have led to substantial increases in nutrients in the lakes. Second, we focused on the two main soil types in the region. Further sampling on more soil types is warranted to better constrain the estimates of allochthonous loads into these and other lakes. Yet results from similar leaching experiments support the trends that we found in wetland versus forest soils. Kissman et al. (2017) recorded C:N:P ratios of leachates from bog soils in montane forests ~167:11:1, supporting our conclusion that P enrichment relative to N may be more likely in wetland-dominated landscapes. Qualls et al. (1991) found C:N:P ratios of soil leachates from the organic horizon in montane forests ~3601:76:1, supporting our conclusion that forest soils are relatively P poor. And finally, we were unable to constrain the watershed area that contributes leachates to the lakes. Although this added uncertainty to our estimates of N and P loadings, it is a realistic representation of seepage lakes, where watershed influence varies both among different watersheds and temporally within a watershed (Gergel et al., 1999; Webster et al., 1996). Despite the aforementioned caveats, our heuristic and empirical modeling approaches establish that browning-associated

loading of N and P may have ecological relevance and, therefore, should be further considered in the context of lake browning.

5. Conclusions

Leachates that brown seepage lakes also contribute nutrients to those lakes. As leachate source is important to understanding the absolute and relative quantities of N or P that are leachable, it is necessary to understand watershed characteristics in other lakes to predict nutrient load responses to lake browning. In lakes that are highly colored, but have not yet reached light-limitation, browning could stimulate phytoplankton or bacterial growth. Conversely, in lakes that are brown and phytoplankton growth is light limited, allochthonous nutrient loads may lead to unexpected shifts in water-quality or ecological processes if/when browning attenuates.

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