RESEARCH REVIEW

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Global change-driven effects on dissolved organic matter composition: Implications for food webs of northern lakes

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Abstract

Northern ecosystems are experiencing some of the most dramatic impacts of global change on Earth. Rising temperatures, hydrological intensification, changes in atmospheric acid deposition and associated acidification recovery, and changes in vegetative cover are resulting in fundamental changes in terrestrial–aquatic biogeochemical linkages. The effects of global change are readily observed in alterations in the supply of dissolved organic matter (DOM)—the messenger between terrestrial and lake ecosystems—with potentially profound effects on the structure and function of lakes. Northern terrestrial ecosystems contain substantial stores of organic matter and filter or funnel DOM, affecting the timing and magnitude of DOM delivery to surface waters. This terrestrial DOM is processed in streams, rivers, and lakes, ultimately shifting its composition, stoichiometry, and bioavailability. Here, we explore the potential consequences of these global change-driven effects for lake food webs at northern latitudes. Notably, we provide evidence that increased allochthonous DOM supply to lakes is overwhelming increased autochthonous DOM supply that potentially results from earlier ice-out and a longer growing season. Furthermore, we assess the potential implications of this shift for the nutritional quality of autotrophs in terms of their stoichiometry, fatty acid composition, toxin production, and

methylmercury concentration, and therefore, contaminant transfer through the food web. We conclude that global change in northern regions leads not only to reduced primary productivity but also to nutritionally poorer lake food webs, with discernible consequences for the trophic web to fish and humans.

1 | INTRODUCTION

Northern ecosystems (>45°N latitude) are expected to experience the highest rates of change in any category of ecosystems on the planet (Hansen et al., 2006; Kirtman et al., 2013). Higher temperatures, an intensification of hydrology (i.e., wet areas become wetter, dry areas become drier), and increased frequency and magnitude of extreme events (e.g., floods and droughts) are having significant effects on these ecosystems. While the ways in which underlying ecological processes are responding to climate change are hard to gauge, lakes integrate many of these effects and may, therefore, serve as *sentinels* of change—integrating atmospheric, terrestrial, and aquatic processes (Williamson, Dodds, Kratz, & Palmer, 2008; Williamson et al., 2016).

Climate change is altering the relationship between northern terrestrial and aquatic ecosystems in complex ways—with dissolved organic matter (DOM) potentially serving as a signaling catalyst of changes in upstream and downstream processes that influence lake food webs (Figure 1). DOM refers to soluble and colloidal organic material arbitrarily defined by the pore size of the filter it is passing through [ranging between 0.2 and 0.7 μm, but most commonly 0.45 μm (Xu & Guo, 2017)]. DOM represents a rich diversity of organic materials produced by living organisms rivaled only by the diversity of organic molecules that result from the degradation of these organisms (Koch & Dittmar, 2006). DOM in lakes may originate from the surrounding catchment (allochthonous) or be produced within the lake (autochthonous). While the primary component of DOM is carbon (C), it also contains macronutrients such as nitrogen (N) and phosphorus (P), micronutrients such as iron (Fe), as well as toxins and contaminants such as mercury (Hg) (Ged & Boyer, 2013; Maranger & Pullin, 2003; Qualls & Richardson, 2003; Ravichandran, 2004). As DOM is transported in percolating and running waters, climatic and environmental factors operating within watersheds influence its compositional diversity (Battin et al., 2008; Hedin, Armesto, & Johnson, 1995; Manzoni & Porporato, 2011).

There is a strong relationship between the lateral export of organic material from northern forests and the organic matter content in lakes (Gergel, Turner, & Kratz, 1999; Rasmussen, Godbout, & Schallenberg, 1989), which reflects the large proportion of land relative to often-small inland waters. In fact, terrestrial (allochthonous) DOM is considered to be the major fraction of total aquatic DOM in northern lakes (Berggren, Ziegler, St-Gelais, Beisner, & Del Giorgio,

2014; Karlsson et al., 2012; Wilkinson, Pace, & Cole, 2013). Both increased temperature (Weyhenmeyer & Karlsson, 2009) and precipitation-driven runoff (de Wit et al., 2016; Tranvik & Jansson, 2002), together with changes in atmospheric acid deposition (Evans et al., 2012; SanClements, Oelsner, McKnight, Stoddard, & Nelson, 2012), land use, and land cover (Finstad et al., 2016; Kritzberg, 2017; Meyer-Jacob, Tolu, Bigler, Yang, & Bindler, 2015), are likely to lead to fundamental changes in terrestrial ecosystems. The interplay between these changing factors is altering the properties of DOM in lakes. For example, the rates of terrestrial production and decomposition, which determine the potential flux of organic C and nutrients to recipient lakes, are increasing (Hessen, Andersen, Larsen, Skjelkvåle, & de Wit, 2009). The combined effects of changes in the C pool, together with distinct environmental modulators operating on this C pool, are affecting terrestrial–aquatic DOM linkages in three ways: the amount and composition of DOM that reaches freshwaters from land; the timing of these DOM fluxes; and how DOM is processed in rivers and lakes. The responses of lakes to these escalating changes may alter ecosystem structure and function, potentially presenting a risk for people who rely on northern lakes for ecosystem services (Chapin et al., 2004).

Herein, we present a synthesis of the expected effects of climate change on DOM. The effects of changing DOM concentrations on food web carbon subsidies have been extensively studied and debated (e.g., Solomon et al., 2015), often without arriving at firm conclusions. Other consequences of changing DOM, particularly related to other aspects such as the stoichiometry of DOM (and the stoichiometric impact on the biota) have been less explored and require further consideration. These aspects may also explain some of the contrasting findings regarding the effects of DOM on aquatic ecosystems. First, we summarize how changes in climate affect the timing, magnitude, and composition of DOM delivered to lakes benefiting from recent reviews on the topic (e.g., Filella & Rodríguez-Murillo, 2014; Hanson, Pace, Carpenter, Cole, & Stanley, 2015; Pagano, Bida, & Kenny, 2014; Porcal, Koprivnjak, Molot, & Dillon, 2009; Solomon et al., 2015). Second, we build on this summary by considering possible consequences of these changes in DOM for lake productivity and food web structure. Third, we assess the impact of changing DOM on whole-lake production and the "nutritional value" of this production (i.e., essential fatty acids [EFAs], toxins, and contaminants). We pose the following questions: (1) How is the distribution of DOM concentration and composition in northern
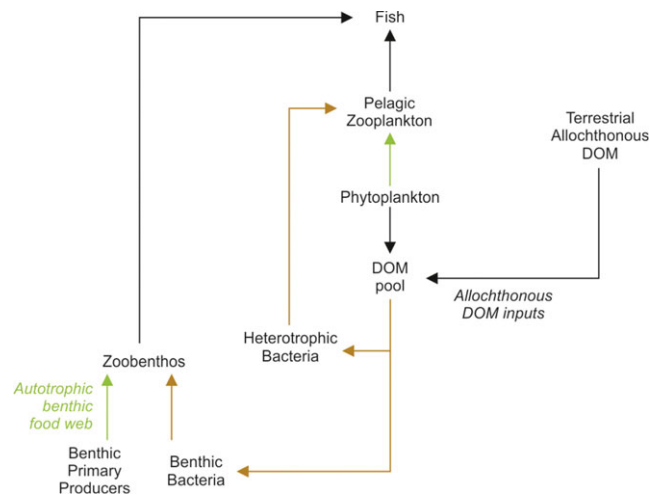
FIGURE 1 Lake food webs represented by the transfer of energy and matter from autotrophic (green) and heterotrophic (brown) sources in the pelagic and benthic environments. The lake dissolved organic matter (DOM) pool is contributed by both terrestrial allochthonous inputs and autochthonous phytoplankton and is used by pelagic and benthic heterotrophic bacteria

lakes affected by changes in climate? and (2) Given changes in DOM concentration and composition, what are the potential consequences for food web functioning? To address these questions, we present several compelling hypotheses, synthesize the current evidence, and advance key knowledge gaps that we view as future research priorities. The insights gathered build a holistic view of the realized and prospective ecological outcomes of changing DOM.

2 | GREATER INPUTS OF DOM TO LAKES

We hypothesize that browning of northern lakes is a product of climate warming, hydrological intensification, terrestrial primary production, and a decline in atmospheric acid deposition, reflecting an increase in the concentration, and a decrease in the biolability of DOM exported to northern lakes (Figure 2).

Many lakes in the boreal regions of northern Europe and northeastern North America are undergoing a "browning" due to rising concentrations of allochthonous DOM (Monteith et al., 2007; Solomon et al., 2015) and associated Fe (Björnerås et al., 2017; Kritzberg & Ekström, 2012). The link between increased DOM and Fe has been found in many regions throughout northern Europe and North America (e.g., Björnerås et al., 2017). Exceptions to lakes undergoing browning include alpine lakes surrounded by talus, northern lakes in watersheds with little terrestrial vegetation (e.g., Preston et al., 2016), and northern lakes experiencing long-term drought (Schindler et al., 1997; Williamson et al., 2016).

The term browning refers to a change in the optical properties of lake water with a shift toward a brown color. This change is caused by an increased presence of humic matter of terrestrial and wetland origin, which absorbs strongly the shorter wavelengths of the visible spectrum of solar radiation (Granéli, 2012; Jones, 1992).
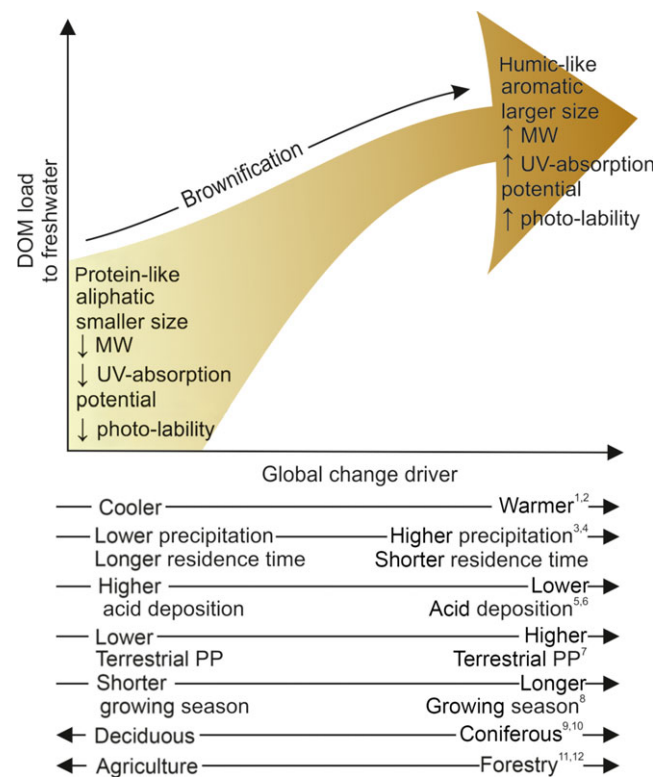

FIGURE 2 Hypothesized effects of global changes on properties of dissolved organic matter (DOM) loads to northern lakes. Previous scientific literature (e.g., [1]Freeman, Evans, Monteith, Reynolds, & Fenner, 2001; [2]Larsen et al., 2011; [3]Laudon et al., 2012; [4]Mattsson et al., 2015; [5]Monteith et al., 2007; [6]Ekström et al., 2011; [7]Jansson et al., 2008; [8]Jeganathan et al., 2014; [9]McKenney et al., 2014; [10]Sittaro et al., 2017; [11]Hansen et al., 2013; [12]Kritzberg, 2017) has established that global change is leading to an increase in the concentration of allochthonous DOM to many northern lakes. However, the global change effects on the composition of allochthonous DOM are unknown. We hypothesize that global change is leading to DOM that is on average more humic-like, aromatic, and with larger molecules entering lakes. Once DOM enters the lakes, in-lake processes further modify DOM molecular structure (e.g., bacterial and photodegradation of humic compounds). The hypothesized effects show the influence of individual global change drivers on DOM loads; the interactive effects of these global change drivers (e.g., a shift to a warmer and drier climate) are important but not shown

The tight coupling between DOM and Fe (which also contributes to the change in the chromophoric properties of DOM, creating an even browner color) is explained in part by: (1) the Fe redox chemistry, since reductive dissolution of iron(oxy)hydroxides can cause a release of associated DOM in soil pore water (Knorr, 2013); and (2) the interactions of DOM with Fe that can prevent its precipitation and sedimentation (Shapiro, 1966; Tipping, 1981). These two processes facilitate the cotransport, via runoff, of DOM and Fe from organic soils into lakes. DOM of different origins varies in Fe-binding capacity (Shapiro, 1964); for instance, wetland-derived DOM has a relatively high Fe-binding capacity (Xiao, Sara-Aho, Hartikainen, & Vähätalo, 2013). Therefore, northern lakes which have a relatively

high proportion of wetlands in their contributing catchments are more vulnerable to browning due to high-DOM–Fe loading potentials.

Several factors drive the browning of surface waters (Figure 2): warming and hydrological shifts due to climate change (Erlandsson et al., 2008; Roulet & Moore, 2006; Sarkkola et al., 2009); reduced atmospheric acid deposition (Clark et al., 2010; Evans, Chapman, Clark, Monteith, & Cresser, 2006; Monteith et al., 2007); a change in the composition of DOM that alters degradation rates (either biodegradation rates or photodegradation rates) (Cory, Ward, Crump, & Kling, 2014); and the "greening" of the northern hemisphere (Finstad et al., 2016). A combination of these factors is the most likely explanation for browning, but interactive effects are complex. Most drivers are changing in a direction that is resulting in further surface water browning, but uncertainties remain. One such uncertainty is the effect of climate change-driven alterations in temperature on loads of allochthonous DOM to surface waters. According to recent studies, the thawing of permafrost and lengthening of growing season in vast areas in the north (Barichivich et al., 2013; Buitenwerf, Rose, & Higgins, 2015) may result in either increases in allochthonous DOM inputs to headwater streams (Spencer et al., 2015) and rivers (Holmes et al., 2008), or decreases in allochthonous DOM export through a deepening of hydrological flow paths (Harms et al., 2016; Walvoord & Striegl, 2007). These contrasting results suggest significant uncertainties related to permafrost degradation and upland hydrology in predicting future DOM export to northern surface waters (Abbott et al., 2016).

Climate change-driven alterations in thermal and hydrological regimes (Andréasson, Bergström, Carlsson, Graham, & Lindström, 2004; Korhonen & Kuusisto, 2010) are affecting DOM loads (e.g., Laudon et al., 2012; Mattsson, Kortelainen, Räike, Lepistö, & Thomas, 2015; Schiff et al., 1998). First, an important direct influence of climate change on northern lakes is the progressively longer ice-free period, with ice-on occurring on average 5.8 ± 1.9 days per century later and ice-out occurring on average 6.5 ± 1.4 days per century earlier (Magnuson et al., 2000). However, while the increase in the duration of the ice-free period may be expected to enhance primary production (Hampton et al., 2017; Smol et al., 2005), the proportion of autochthonous DOM produced by in situ primary production is relatively small (Miller, McKnight, Chapra, & Williams, 2009). Second, a change in precipitation amounts may influence concentration and composition of DOM in lakes. Increasing precipitation and associated shorter hydrological residence times may translate into a larger proportion of DOM to be derived from allochthonous sources (Algesten et al., 2004; Hansson et al., 2013), if the rate of allochthonous DOM loading exceeds the rate of autochthonous DOM production (Kothawala et al., 2014). In contrast, decreasing precipitation and associated longer water residence times are allowing for a larger proportion of allochthonous DOM to be lost from the lake water column by mineralization, flocculation, or sedimentation. Third, a change in the timing of precipitation events may influence in-lake uptake and processing of DOM. Spring melt and autumn storms that flush DOM from forests are important in providing fresh supplies of

allochthonous DOM to lakes. Bacteria preferentially remove amino acids and carbohydrates from this fresh supply of allochthonous DOM (e.g., Berggren, Laudon, Haei, Ström, & Jansson, 2010).

Changes in atmospheric pollution that are evident today—specifically, a reduction in the atmospheric deposition of sulfur and, to some extent, the associated recovery from acidification—are increasing allochthonous inputs of DOM to the majority of surface waters (Ekström et al., 2011; Hagedorn, Schleppi, Waldner, & Fluhler, 2000; Monteith et al., 2007). A return to higher pH results in higher net charge of organic molecules and higher polarity (Ekström et al., 2011). Therefore, reduced soil acidity leads to a decrease in the adsorption capacity of the soil, increased DOM solubility, and higher export of terrestrial DOM (Jardine, McCarthy, & Weber, 1989). The mobilized DOM has high molecular weight and a high sensitivity to ultraviolet (UV) light and photoreactive damage (Lu, Yuan, Tao, & Tang, 2015; SanClements et al., 2012; Timko, Gonsior, & Cooper, 2015). Due to these properties, the mobilized DOM may be less available to bacterial uptake (Figure 2) (Ekström et al., 2016).

Changes caused by a greening of the northern hemisphere result in increased DOM export (Finstad et al., 2016; Larsen, Andersen, & Hessen, 2011), possibly with different composition (Boisvert-Marsh, Perie, & de Blois, 2014). Increased temperature is leading to higher rates of terrestrial net primary production (Jansson, Hickler, Jonsson, & Karlsson, 2008) and ecosystem respiration over a longer growing season (Jeganathan, Dash, & Atkinson, 2014) leading to greater accumulation of organic matter to be exported as DOM to lakes. These changes in the rate and duration of terrestrial primary production (cf. Barichivich et al., 2013) may be coupled with changes in land cover including a shift in tree species. Some suggest that the boundary between the boreal (coniferous) and temperate (deciduous) forests is shifting northward (McKenney et al., 2014), which is resulting in the accumulation and export of DOM of different composition (Boisvert-Marsh et al., 2014). However, others suggest that the rate of northward expansion of tree species is not keeping pace with the rate of increase in air temperature at the northerly limits of the tree species' ranges (Sittaro, Paquette, Messier, & Nock, 2017), which may result in forest decline as tree species experience suboptimal conditions. Furthermore, changes in land use because of deforestation or afforestation in the northern hemisphere (Hansen et al., 2013) are leading to changes in the production of terrestrial organic matter, accumulation of organic matter in the landscape, and ultimately export of DOM into lakes (Kritzberg, 2017). While brownification has already been observed in northern lakes, there are responses that may take long timescales to become evident. For example, effects of changes in forest primary production occur over annual timescales, effects of recovery from acidification occur over decadal timescales, and effects of afforestation occur over longer timescales.

3 | CHANGING ROLE OF DOM IN LAKES

We hypothesize that changed allochthonous DOM is leading to fundamental transformations at the base of the food web by modifying

the physical and chemical properties of the water such as light, temperature, and nutrients. These changes are, in turn, impacting productivity and community composition (Figure 3).

Increases in allochthonous DOM loads to lakes are having a strong effect on internal lake processes. Climate change is warming lake surface waters globally, with many northern lakes warming significantly faster than the global average (O'Reilly et al., 2015). Although increased air temperature is the primary driver of this change, factors such as lake depth, clarity, and mixing regime are also playing an important role in determining whole-lake temperature response (Kraemer et al., 2015; Rose, Winslow, Read, & Hansen, 2016). DOM affects lake warming trends by influencing light attenuation. DOM attenuates light by absorbing photosynthetically active radiation (PAR), and the absorption of PAR creates a positive feedback by initiating a biogeochemical cycle that results in *further* warming of the surface waters of lakes (Porcal et al., 2009; Solomon et al., 2015), and preventing a larger fraction of the deeper waters of lakes to warm up. As a consequence, DOM-rich lakes have a shallower and more stable thermocline, which restricts the photic zone and reduces the mixing of nutrients from deeper layers (Houser, 2006). However, browning of lakes is leading to overall cooler than expected water temperature as the volume of the hypolimnion increases (Read & Rose, 2013; Williamson et al., 2015). DOM also attenuates UV and therefore protects organisms from harmful UV radiation (Schindler et al., 1997; Williamson, Stemberger, Morris, Frost, & Paulsen, 1996; Williamson et al., 2016). Consequently, DOM is a key determinant of lake productivity in northern lakes (Karlsson et al., 2009; Thrane, Hessen, & Andersen, 2014).

Dissolved organic matter absorption of light results in photolysis, promoting a suite of photochemical processes that partially or completely oxidize complex organic molecules into smaller units (Bertilsson & Tranvik, 2000). Sustained photolysis of DOM leads to photomineralization (notably converting some dissolved organic C into dissolved inorganic C), coupled with a loss of photolabile aromatic molecules and a gain of photo-resistant aliphatic molecules (Moran & Zepp, 1997; Vinebrooke & Leavitt, 1998; Wetzel, Hatcher, & Bianchi, 1995). Some studies suggest that up to 10% of the mineralization of DOM in lakes happens through photodegradation (Cory et al., 2014; Koehler, Landelius, Weyhenmeyer, Machida, & Trankvik, 2014). A consequence of photolysis is a loss of the light-absorption properties of the photo-bleached DOM (Del Vecchio & Blough, 2002; Helms et al., 2014; Moran, Sheldon, & Zepp, 2000) and an increase in the biolability of the carbon molecules resulting from photodegradation (Lindell, Granéli, & Tranvik, 1995).

The products of DOM photolysis have different fates and impacts. Many photoproducts of DOM are benign. Some photoproducts of DOM have beneficial effects on microbial communities by providing a source of small organic molecules that may support the metabolism of bacteria and primary producers. However, other photoproducts of DOM have harmful effects on microbial communities by serving as a source of potentially harmful transient byproducts such as reactive oxygen species (i.e., hydrogen peroxide [H_2O_2] and superoxide [O_2^-]) (Hudson, Dillon, & Somers, 2003; Wolf, Andersen,
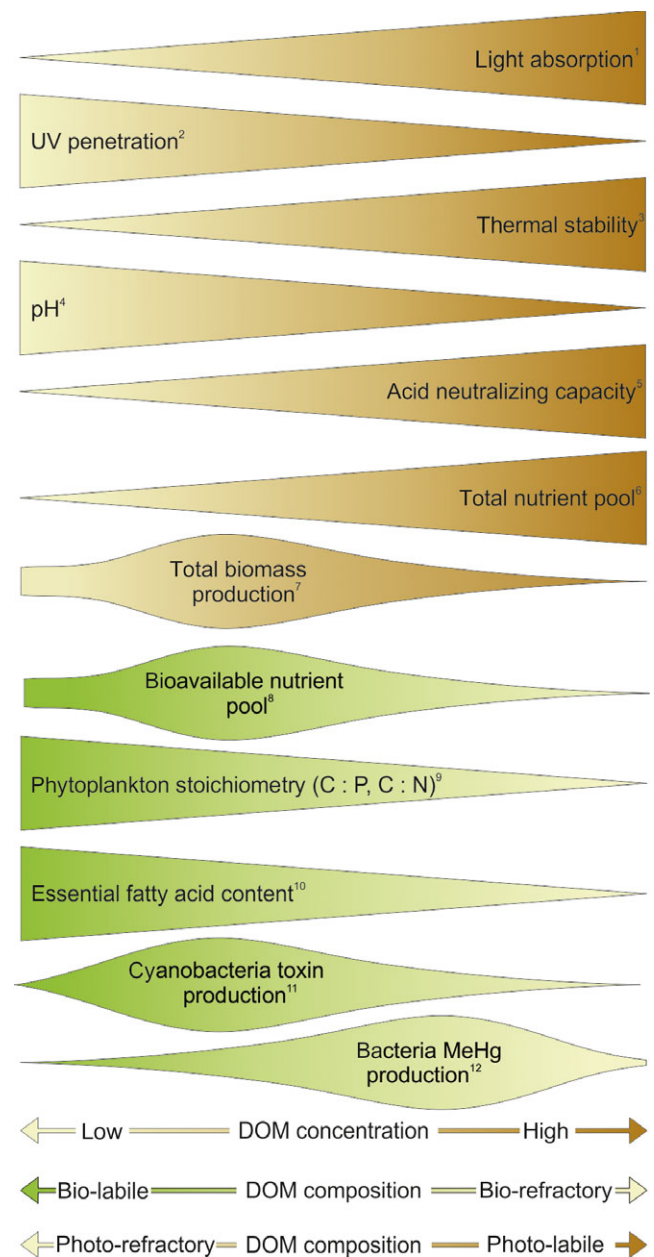

FIGURE 3 Main effects of terrestrial dissolved organic matter (DOM) loading on the chemical, physical, and biological characteristics of DOM into and within a lake. Effects driven by DOM concentration are in brown, with the effects of higher concentrations increasing to the right. Effects driven by DOM composition are in green, with the effects of more refractory composition increasing to the right. The thickness of the shapes represents the magnitude of change. Footnotes reflect published scientific support for the depicted trend: [1]Karlsson et al. (2009), [2]Williamson et al. (1996), [3]Houser (2006), [4]Ekström et al. (2011), [5]Lydersen, Larssen, and Fjeld (2004), [6]Solomon et al. (2015), [7]Kelly et al. (2014), [8]Berggren et al. (2015), [9]Seekell, Lapierre, Ask, et al. (2015), [10]Taipale et al. (2016), [11]Sorichetti et al. (2014), [12]Watras et al. (1998)

Hessen, & Hylland, 2017). DOM may also serve as a sink or scavenger for some reactive oxygen species (e.g., hydroxyl and singlet oxygen radicals) (Vione et al., 2006). Therefore, the relationship

between DOM, light, and reactive oxygen species is complex (Page, Logan, Cory, & McNeill, 2014). Certain organisms may benefit from the harmful effects of UV exposure or reactive oxygen species if their predators, parasites, or competitors have a higher vulnerability to these stressors (Häder et al., 2015; Imlay, 2003). For example, in the surface waters of DOM-rich lakes, the conversion of light energy into heat in oxygenated waters results in the formation of harmful reactive oxygen species that are known disinfecting agents (Lv et al., 2016). Cyanobacteria that aggregate and accumulate in assemblages or mats near the surface may have an advantage over other autotrophs in their ability to neutralize reactive oxygen species through superoxide dismutase and other enzymes (Latifi, Ruiz, & Zhang, 2009; Ross, Santiago-Vázquez, & Paul, 2006). Yet, the photoproducts of DOM generally have a negative impact, particularly on heterotrophic bacteria, viruses, and small phytoplankton (Häder et al., 2015; Kieber, Peake, & Scully, 2003; Yuan, Yin, Harrison, & Zhang, 2011).

Dissolved organic matter and its photo-oxidized products interact with ionic compounds to modulate the pH and oxidative state of a system. These factors may provide microbes with alternative electron donors or acceptors and regulate the overall metabolic potential or metabolic stress affecting both planktonic and benthic species. DOM also influences the chemical matrix of aqueous systems. For example, DOM serves as a carrier and regulator of nutrients and keeps these elements in solution and available for use by plankton in the water column (Jones, 1998). An increase in the concentration of DOM increases the concentration of nutrients in the water column (Findlay, 2003), but the photolability and composition of DOM has an important influence on the *bioavailability* of these nutrients (Figure 4). For example, allochthonous DOM that is more photolabile and aromatic will have enhanced bioavailability following exposure to light (Tranvik & Bertilsson, 2001). In contrast, autochthonous DOM becomes more biorefractory and less bioavailable following exposure to light (Miller, McKnight, & Chapra, 2009; Moran &

Covert, 2003). How, and in what direction, the complexation properties of DOM itself and its linkages to other elements are changing under climate change is unknown, as are the consequences of these changes for lake ecosystem structure and functioning (Berggren, Sponseller, Soares, & Bergström, 2015).

To fully reveal the complexity of these effects—including synergistic and antagonistic interactions—in ecosystems with varying concentrations and compositions of DOM is beyond the reach of most studies. Hence, from an ecological point of view, it may be more fruitful to consider the net effects of these processes on the basis of lake production and lake food webs, which are primary foci of this paper.

4 | LOWER FOOD QUANTITY

The potential outcome of increased terrestrial DOM subsidies on lake food webs is being determined by trade-offs between increased nutrient availability that raises autotrophic biomass and decreased light that lowers it. With increased browning, the balance will trend toward decreased light availability, which is driving a shift from autotrophic-based to heterotrophic-based basal production, with a subsequent decline in energy transfer efficiency and a reduction in biomass of higher trophic levels. We hypothesize that the net outcome is that the food web is becoming increasingly reliant on terrestrial DOM subsidies, which is further constraining the transfer of energy up the food web (Figure 5).

Browning of lakes is expected to cause substantial changes in the productivity of lake ecosystems (Finstad, Helland, Ugedal, Hesthagen, & Hessen, 2014; Karlsson et al., 2009; Solomon et al., 2015). Fish populations in lakes with low allochthonous inputs of DOM are largely supported by benthic algae (Hecky & Hesslein,
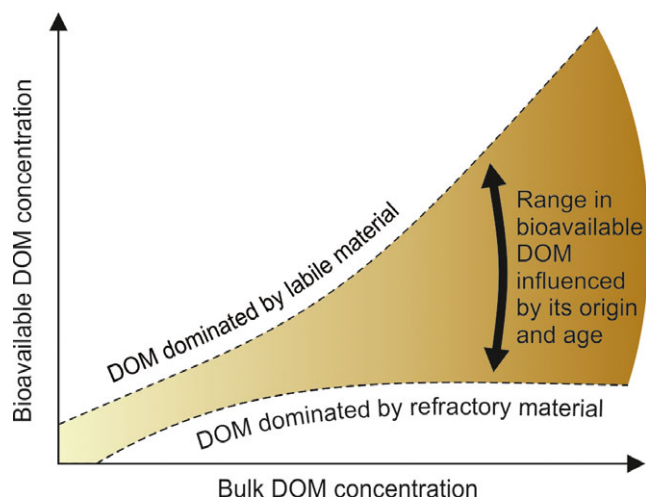

FIGURE 4 Relationship between the bulk concentration of dissolved organic matter (DOM) and the concentration of bioavailable DOM (modified from Findlay, 2003)
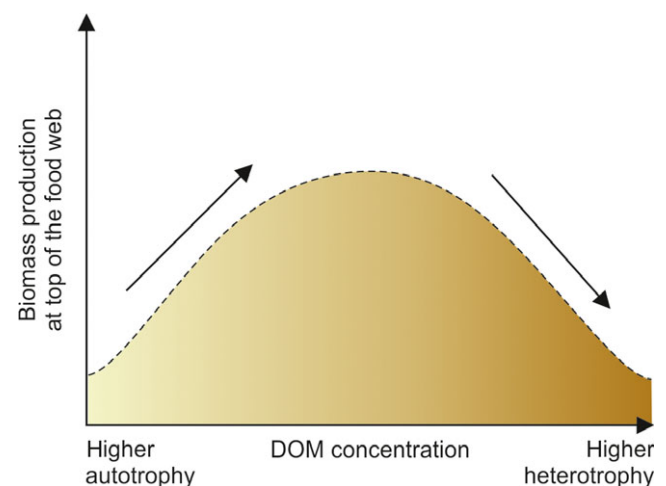

FIGURE 5 Hypothesized relationship between dissolved organic matter (DOM) concentration at the base of the food web, representing the main food source for consumers at the extremes of the *x*-axis (higher autotrophy at low-DOM and high-light conditions, and higher heterotrophy at high-DOM and low-light conditions) and biomass production at the top of the food web on the *y*-axis

1995; Karlsson & Byström, 2005). On the other hand, fish populations in lakes with higher allochthonous DOM inputs, especially those that are hydrologically connected to catchments with large C stocks, are to a larger degree supported by both (in variable proportion) bacterial and pelagic algal production (Karlsson et al., 2012; Solomon et al., 2011). Browning of lakes is leading to changes in basal production that propagate through food webs in lakes, including a shift from food webs dominated by autotrophs to food webs dominated by heterotrophic bacteria, and a shift from benthic to largely pelagic-driven productivity (Ask et al., 2009; Karlsson et al., 2009; Kissman, Williamson, Rose, & Saros, 2017).

Browning of lakes represents an energy input to aquatic ecosystems, yet the ecological trajectory and consequences of this input are not well understood. Allochthonous DOM stimulates bacterial production (Hessen, Andersen, & Lyche, 1990) and can be directly consumed by secondary consumers such as zooplankton (Cole et al., 2011). However, it unclear if this consumption leads to reproduction and growth (Faithfull, Huss, Vrede, & Bergström, 2011; Wenzel, Bergström, Jansson, & Vrede, 2012). Allochthonous DOM may also serve as a nutrient vector as it can supply micronutrients and macronutrients necessary for phytoplankton growth, increasing primary production and favoring the transfer of autochthonous C into the food web (Tanentzap et al., 2014). However, it also serves as a light absorber, limiting primary production in lakes (Karlsson et al., 2009). Therefore, a modest input of DOM into clear, nutrient-poor systems may initially boost primary production because of the nutrient inputs associated with the DOM (Seekell, Lapierre, Ask, et al., 2015; Thrane et al., 2014), but this nutrient subsidy is eventually overridden by the increased light attenuation of DOM (i.e., at dissolved organic C concentrations above 5 mg C L^{-1}) (Finstad et al., 2014; Seekell, Lapierre, & Karlsson, 2015; Thrane et al., 2014).

Browning of lakes may lead to regime shifts from clear-water, autotrophic, benthic-dominated systems to brown-water, heterotrophic, pelagic-dominated systems. These shifts are driven by the dual effect of allochthonous DOM in promoting heterotrophs as an energy source at the base of the food web and suppressing autotrophs via light extinction and intensified nutrient competition (Ask et al., 2009; Hessen et al., 1990). The switch from algal to bacterial dominance is expected to reduce energy transfer efficiency through food webs due to increases in the complexity of the lower levels of the food web (Hessen, 1998). The effects of browning is particularly pronounced for food webs where allochthonous DOM suppresses otherwise dominant benthic primary production (Craig, Jones, Weidel, & Solomon, 2015; Karlsson et al., 2009; Premke et al., 2010).

A rise in allochthonous DOM may have other indirect negative effects on lakes by promoting deep-water anoxia, more- dy-like sediments (i.e., the fluffy sedimented humic matter that provides a poor substrate for benthic plants or animals) and by reducing consumers' habitat availability as well as their ability to see prey in pelagic areas (Brothers et al., 2014; Craig et al., 2015; Karlsson et al., 2015; Stasko, Gunn, & Johnston, 2012). In general, except for clear and shallow lakes with high light availability, a rise in allochthonous DOM is expected to create conditions resulting in lower production

and higher dependence on terrestrial resources by organisms at higher trophic levels (Craig et al., 2015; Jones, Solomon, & Weidel, 2012; Karlsson et al., 2009, 2015; Kelly, Solomon, Weidel, & Jones, 2014).

5 | CHANGES IN STOICHIOMETRY AFFECT FOOD QUALITY

As terrestrial subsidies of DOM increase, we hypothesize that reduced light availability is constraining biomass and primary production of phytoplankton. However, due to the plastic stoichiometry of phytoplankton that allows them to store nutrients supplied by DOM, the remaining phytoplankton biomass is having higher nutrient content (i.e., lower C:N and C:P ratios) (Figure 6). In contrast, heterotrophic bacteria is increasing in biomass but is unaffected in both C:N and C:P ratios due to their less plastic stoichiometry. This stoichiometrically modified food quality is propagating up the pelagic food web via zooplankton to fish (Figure 6).

Increased terrestrial subsidies of DOM to lakes are accompanied by changes in DOM stoichiometry in lakes (Estiarte & Peñuelas, 2015; Hessen, Agren, Anderson, Elser, & De Ruiter, 2004; Mattsson, Kortelainen, & Räike, 2005; Norby et al., 2005). Stoichiometric changes occur in DOM as it flows from headwaters downstream to lakes, rivers, and ultimately oceans (Creed et al., 2015). However, the complex interactions and feedbacks that occur as DOM flows
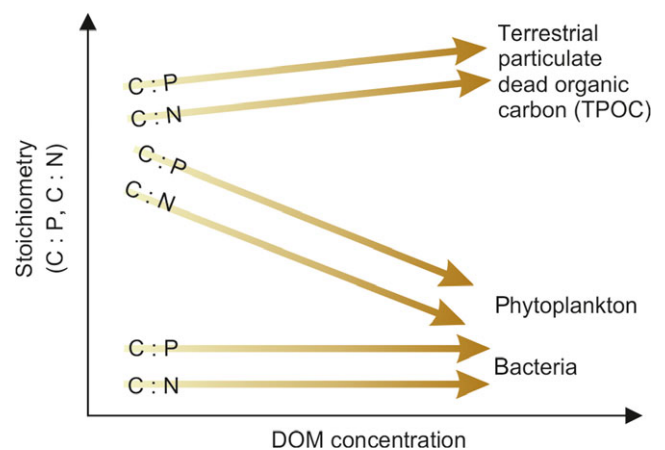
FIGURE 6 Hypothesized relationship between increasing concentration of dissolved organic matter (DOM) and the stoichiometric properties of allochthonous particulate (dead) organic matter (POM), phytoplankton, and bacteria. Since browning is characterized by an increase in allochthonous organic matter with greater proportions of refractory compounds, an increase in the C to nutrient ratios of the particulate fraction (i.e., POM) can be expected due to the higher C content in humic acids (e.g., Allard, 2006). Different C:P and C:N ratios are promoting dominance of particular microbial communities, with the concentration of DOM influencing the biomass of the dominating community. Changes in the quality of allochthonous POM depend on the DOM source and transformations and are, therefore, dependent on the individual characteristics of the catchment

through landscapes make it a challenge to predict compositional changes in the DOM input to lakes (Mattsson et al., 2015). Given the strong focus of previous studies and syntheses on DOM and C, it is timely to draw the attention toward other elements tightly linked to DOM (Hessen et al., 2009).

The browning of lakes is expected to change the total concentration and bioavailability of elements, including macronutrients (C, N, P), as well as micronutrients (e.g., Fe), and how they cycle in freshwaters (Jones & Lennon, 2015; Solomon et al., 2015). Research on the effects of stoichiometry on basal primary and secondary producers (i.e., phytoplankton and bacteria) considers total bioavailable pools of N and P to be their inorganic fractions (Berggren et al., 2015; Jansson, Berggren, Laudon, & Jonsson, 2012; Soares et al., 2017). Yet there is an extensive, but poorly accounted for, range in the degree to which dissolved *organic* nutrients can be used by microorganisms. In fact, the organic N and particularly organic P contents of DOM seem to be much more bioavailable than its organic C content (Berggren et al., 2015). This suggests that the stoichiometry of the in-lake bulk nutrient pool may systematically over-represent the actual supply ratios of C:N:P to bacteria, and likely to phytoplankton (Berggren et al., 2015).

The influence of DOM stoichiometry on primary production must also be considered in the context of micronutrients, such as Fe. Fe availability may constrain phytoplankton growth in oligotrophic, clear-water lakes (Vrede & Tranvik, 2006), and is an important element for cyanobacteria (given its role in the nitrogenase enzyme) either in its inorganic forms (Hyenstrand, Rydin, & Gunnerhed, 1999), or as part of DOM complexes (Sorichetti, Creed, & Trick, 2014, 2016). Fe bioavailability may offset the negative effects of Fe on light attenuation for phytoplankton growth (Thrane et al., 2014). Therefore, DOM-induced changes in phytoplankton structure and function may be considerable, not only through changes in light availability (Jones, 1998) but also through changes in access to limiting elements such as N, P, and Fe (Elser et al., 2009; Hessen et al., 2009; Molot et al., 2014; Vrede & Tranvik, 2006). Furthermore, the N:P stoichiometry requirements in phytoplankton are affected by light availability, implying that browning influences not only the *available* nutrient pool but also the *required* pool; that is, that are necessary for phytoplankton growth (Thrane, Hessen, & Andersen, 2016).

Changes in DOM stoichiometry are changing the relative availability of nutrients per available light unit, in turn affecting nutrient cycling and primary and secondary production (Hessen, 2013; Sterner, Elser, Fee, Guildford, & Chrzanowski, 1997). In phytoplankton-dominated pelagic food webs, the expectation is that phytoplankton will have a higher C to nutrient ratio in low-DOM lakes (high light: low nutrient) compared to high-DOM lakes (low light: high nutrient) (cf. Sterner et al., 1997). In contrast, heterotrophic bacteria will have a higher P content than phytoplankton (Vadstein, 2000; but see Godwin & Cotner, 2015) (Figure 6). Based on their C to nutrient stoichiometry, heterotrophic bacteria can be considered high-quality food items for P-demanding zooplankton, but, in the context of cell wall properties (digestibility) and fatty acid profiles, they will be less rewarding food (Martin-Creuzburg, Sperfeld, & Wacker, 2009; Zelles, 1999).

The implications of browning for food webs via nutrient stoichiometry, therefore, vary as DOM loads increase. Higher DOM concentrations in clear oligotrophic lakes will provide nutrients that, in addition to promoting biomass production, will increase the nutrient content of phytoplankton, thereby decreasing C to nutrient ratios at the basal level in the pelagic food web. During the shift from an autotrophic, phytoplankton-dominated basal production to a heterotrophic, bacteria-dominated basal production (as described in Figure 5), higher DOM concentrations may result in a continued decline of C to nutrient ratios at the basal trophic level. Even though brown lakes have phytoplankton species adapted to high-DOM conditions, the already bacteria-dominated food web will shift toward even greater bacterial dominance (Faithfull, Mathisen, Wenzel, Bergström, & Vrede, 2015). Accompanying this increase in bacterial biomass are declines in C:N and C:P ratios of the food for consumers as well as a decrease in food web transfer efficiency (Deininger, Faithfull, Karlsson, Klaus, & Bergstrom, 2017; Jansson, Karlsson, & Blomqvist, 2003) (Figure 6). Currently, we do not know what threshold in DOM concentration marks this fundamental food web shift from reliance on autotrophic production to reliance on heterotrophic bacterial production supported by terrestrial DOM.

6 | GREATER RISK OF LIMITING SUPPLY OF ESSENTIAL FATTY ACIDS

As terrestrial subsidies of DOM increase—provoking a shift from autotrophic to heterotrophic-basal productions—we hypothesize there is a reduction in the production and transfer of high-quality EFA, especially polyunsaturated fatty acids (PUFAs). This decline in EFA is being caused by one or more of three drivers: a reduction in phytoplankton biomass, an associated dilution of the remaining EFA caused by an increase in bacterial biomass, or an increase in the proportion of cyanobacteria (Figure 7).

Ecosystem shifts in the relative importance of allochthonous C due to changes in DOM fluxes may change the quality and quantity of food resources for higher trophic levels. The efficiency of energy transfer in food webs depends both on food quantity and food quality (Müller-Navarra, 2008), the interactions between the two (Persson, Brett, Vrede, & Ravet, 2007), and the pathways by which energy and biochemicals are transferred (Jansson, Persson, De Roos, Jones, & Tranvik, 2007; Müller-Navarra, 2008). Current food quality research examines not only elemental stoichiometry (cf. above) but also the importance of other biochemicals such as PUFAs (Arts, Brett, & Kainz, 2009).

Dissolved organic matter resources that support biomass production in lakes differ substantially in the concentration of high-quality PUFAs, which are important EFAs. The lipids produced by autotrophs are a major component of the dietary needs of primary consumers (Guschina & Harwood, 2009). Autotrophs synthesize PUFAs de novo and contain important long-chained PUFAs, such as
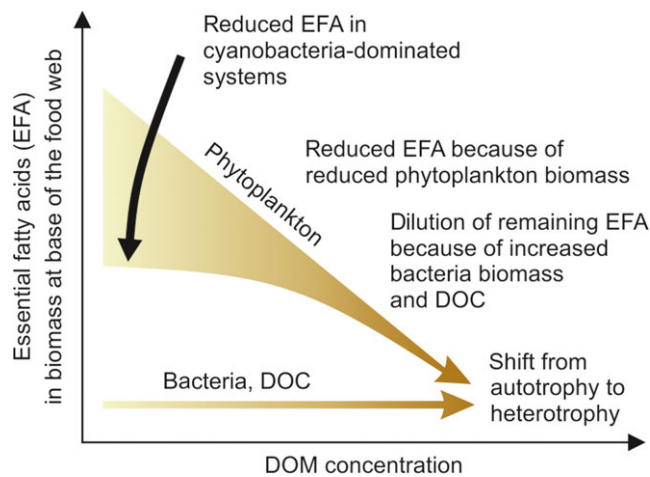
FIGURE 7 Hypothesized relationship between dissolved organic matter (DOM) concentration and biomass quality, based on essential fatty acid (EFA) content. The broad range in EFA at low-DOM concentrations is a function of differences in EFA among phytoplankton species (i.e., food quality), whereas at increased DOM concentrations, reduced EFA is a consequence of reduced primary production (i.e., food quantity) and the subsequent shift to heterotrophic-based production

eicosapentaenoic acid (EPA 20:5ω3) and docosahexaenoic acid (DHA, 22:6ω3) (Lau, Sundh, Vrede, Pickova, & Goedkopp, 2014; Müller-Navarra, 2008). EPA and DHA are absent in most terrestrial autotrophs and therefore also in allochthonous particulate organic matter (POM) (Brett, Taipale, & Heshan, 2009; Wenzel et al., 2012), and are either absent or present in low quantities in aquatic heterotrophs and cyanobacteria (Müller-Navarra, 2008). Therefore, aquatic algae are the principal source of EPA and DHA for aquatic consumers (Gladyshev, Sushchik, & Makhutova, 2013). EPA and DHA are structurally integral for cell membranes and for growth and reproduction in consumers (Parrish, 2009; Sargent, Bell, Hendersen, & Tocher, 1995). As primary consumers are unable to synthesize PUFA themselves, consumers rely on their food for the provision of these lipids (Müller-Navarra, 2008).

Polyunsaturated fatty acids are a major determinant of energy transfer efficiency (Müller-Navarra, Brett, Liston, & Goldman, 2000), with transfer efficiencies twice those of other C compounds that are primarily consumed and respired (Gladyshev et al., 2011). This results in the preferential retention and progressive enrichment of PUFAs at each successive trophic level (Brett, Muller-Navarra, & Presson, 2009; Persson & Vrede, 2006). The concentration of PUFAs in phytoplankton is linked to nutrient status (Galloway & Winder, 2015), with lower concentrations found in phytoplankton under N limitation (Ahlgren & Hyenstrand, 2003) or in lakes with low N content (Gutseit, Berglund, & Granéli, 2007). The composition of PUFAs is also linked to the nutrient status of phytoplankton, with the concentration of EPA reduced in phytoplankton under P limitation (Gulati & DeMott, 1997; Sundbom & Vrede, 1997). Terrestrial subsidies of DOM to northern clear oligotrophic lakes are increasing nutrient availability associated with the DOM, stimulating primary

production, and therefore increasing the concentration of PUFAs (cf. Lau, Goedkoop, & Vrede, 2013) as long as light is not limiting. The composition of PUFAs is further affected by increasing water temperature, which reduces high-quality PUFA production by phytoplankton (Hixson & Arts, 2016).

A shift from benthic and algal basal production dominated lake ecosystems to pelagic and bacterial basal production dominated lake ecosystems will be expected to have consequences in the transfer of PUFAs to higher trophic levels. First, the lower transfer efficiency of bacterial compared to algal basal production will reduce the resources available for most consumers, reducing the transfer of PUFAs. Second, a shift from PUFA-rich autotrophs to comparatively PUFA-poor heterotrophs will further reduce the pool of PUFAs. Both the decrease in biomass and its nutritional content will induce a shift from PUFA-rich food webs in oligotrophic, clear-water lakes to PUFA-poorer food webs in humic lakes (Figure 7). Terrestrial inputs of DOM to brown-water lakes are unlikely to increase the concentration of PUFAs, as phytoplankton and therefore PUFA availability to consumers, are heavily diluted by high concentrations of PUFA-poor allochthonous POM and heterotrophic bacteria (Wenzel et al., 2012) (Figure 7). Evidence for this is the declining proportions of EPA and DHA found in perch muscle with increasing lake DOM content (Taipale et al., 2016).

The extent to which allochthonous DOM supports the growth of consumers has been debated in the scientific literature. One perspective is that allochthonous DOM and POM do not support production of aquatic consumers; instead, the higher quality autochthonous POM (i.e., algae) that contains EPA and DHA is required to support zooplankton production (Brett, Taipale, et al., 2009). A contrasting perspective is that allochthonous POM and DOM can support zooplankton and fish production (Cole et al., 2006, 2011; Tanentzap et al., 2017). Both radiotracer (Hessen et al., 1990) and stable isotope analysis (Grey, Jones, & Sleep, 2001; Karlsson et al., 2015; Solomon et al., 2011; Tanentzap et al., 2017) studies clearly demonstrate that allochthonous DOM can be a substantial source of C. An emerging perspective is that both organic matter sources support zooplankton production, with allochthonous DOM contributions ranging from a few percent to the majority of zooplankton biomass (Tanentzap et al., 2017; Wilkinson, Carpenter, Cole, Pace, & Yang, 2013). Brett et al. (2017) reconciled these differing perspectives by arguing that it is the PUFA composition of a C resource, which differs between terrestrial and aquatic primary producers, rather than its origin or concentration that is the key determinant of C uptake rate and growth efficiency by consumers. When autochthonous resources are in ample supply, uptake of autochthonous resources enhances uptake of allochthonous C (Guillemette, Leigh, & Del, 2016). In contrast, when autochthonous resources are in low supply, autochthonous DOM is preferentially allocated to anabolic processes rather than catabolic processes, allowing consumers to survive periods of low nutrient availability (Wetzel et al., 1995). Interestingly, in bacteria, the opposite may be true, with autochthonous DOM preferentially allocated to catabolic processes and allochthonous DOM preferentially allocated to anabolic processes (Guillemette et al., 2016).

The community composition of zooplankton may determine how efficiently PUFAs are transferred to fish (cf. Jansson et al., 2007). Zooplankton differ in their feeding modes (Berggren et al., 2014), and there is evidence that suggests that EPA and DHA content may be taxon-specific, reflecting these different feeding modes (Persson & Vrede, 2006). For example, a significant decrease in biomass production in the filter-feeder *Daphnia* has been linked to the lack of PUFAs when terrestrial DOM subsidies are their major C source (Brett, Taipale, et al., 2009). EPA has been found to be limiting for *Daphnia* both in nutrient-poor lakes (total P < 4 μg/L) where phytoplankton biomass is small, as well as in nutrient-rich lakes (total P > 25 μg/L) when cyanobacteria make up a large proportion of the phytoplankton (Persson et al., 2007). However, an increase in terrestrial DOM subsidies may *not* compromise the transfer of PUFAs to consumers, unless phytoplankton represent a negligible proportion of their diets (Brett, Taipale, et al., 2009), or if cyanobacteria with small concentrations of EPA make up a large proportion of the phytoplankton.

FIGURE 8 Hypothesized relationship between dissolved organic matter (DOM) composition and contaminant (toxin and Hg) content in food webs. Biolabile DOM supplies Fe that is available for cyanobacteria growth (thereby exposing toxins to the food web). Refractory DOM supplies Hg that must be removed primarily by bacteria through methylation to access C for growth (thereby providing methyl-Hg to the food web)

7 | GREATER RISK OF INCREASED EXPOSURE TO CYANOBACTERIA TOXINS

As terrestrial contributions of DOM increase—reflecting a shift from biolabile DOM (with weak metal-binding capacity) to refractory DOM (with strong metal-binding capacity)—we hypothesize that these differences in DOM characteristics will initiate shifts in phytoplankton community composition. Changes are favoring cyanobacteria that can access nutrients bound to DOM in oligotrophic lakes that experience increases in relatively biolabile DOM, promoting their dominance and toxin production (Figure 8).

Changes in DOM are implicated in changes in phytoplankton community composition (Sterner, Elser, & Hessen, 1992). In many northern regions, the prevalence of cyanobacteria in lakes is occurring more frequently and with increasing intensity (Winter et al., 2011). While the presence of cyanobacteria in nutrient-rich, eutrophic lakes is well known (Chorus, Falconer, Salas, & Bartram, 2000), the drivers initiating cyanobacteria blooms in these nutrient-poor, oligotrophic lakes are not known. High temperatures are known to promote toxin-producing cyanobacteria blooms (Davis, Berry, Boyer, & Gobler, 2009); however, despite the rates of increase in surface water temperature of about 1.3°C per decade (O'Reilly et al., 2015), the relatively low temperatures of northern lakes are not expected to reach the high (20°C) temperature optimum that is conferring a significant advantage to bloom-forming cyanobacterial species (Jöhnk et al., 2008; Paerl & Huisman, 2008). Given that many of these northern regions have low direct inputs of N and P, we focus on the less well-understood change in DOM as a potential initiator of cyanobacteria blooms and the production of toxins in these blooms (Sorichetti et al., 2014). While our focus is on cyanobacteria due to their toxin-formation potential, there is evidence that other members of the phytoplankton community that are capable of producing noxious metabolites (including chrysophytes
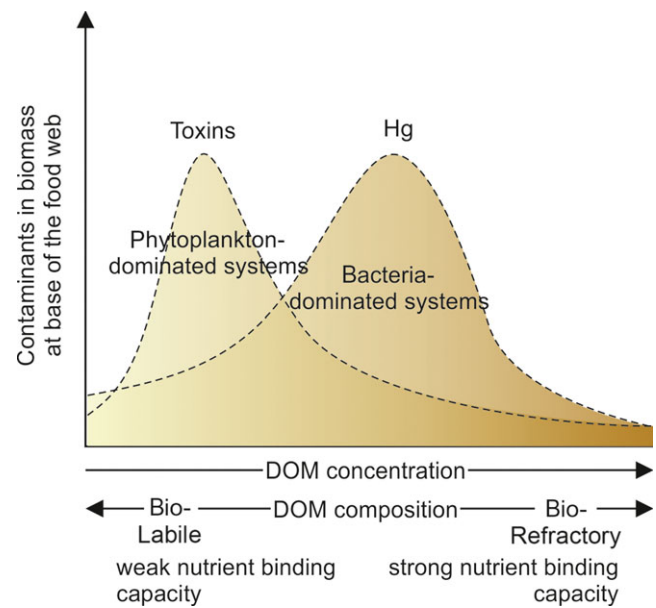
and raphidophytes) also benefit from increases in DOM loading (Paterson, Cumming, Smol, & Hall, 2004; Trigal, Hallstan, Johansson, & Johnson, 2013).

Changes in DOM may alter competition between phytoplankton species, resulting in a change in phytoplankton community structure. An increase in DOM alters the light regime of surface waters (Pattanaik, Wulff, Roleda, Garde, & Mohlin, 2010) by absorbing potentially damaging UV, and creating a shallow zone for PAR that benefits positively buoyant cells. An euphotic zone with these characteristics is highly selective for cyanobacteria. Furthermore, a large input of N-rich DOM, followed by a substantial drawdown of N, may create a nutrient environment beneficial to N_2-fixing cyanobacteria (Rolff, Almesjö, & Elmgren, 2007). Finally, the metal-binding properties of DOM can either increase or decrease the availability of trace metals required for cyanobacterial growth. In the simplest model, DOM can provide required metals from terrestrial sources to the lake (e.g., Fe or copper) that may become available by dissociation from the organic ligand once in surface waters, particularly during photolysis of DOM (Shiller, Duan, van Erp, & Bianchi, 2006). In the case of Fe, DOM could be supplying a potentially growth-limiting metal, but in the case of copper, DOM may be elevating copper to potentially toxic concentrations. Both processes may select for cyanobacteria, given their high Fe requirement and, at least for some species, high tolerance of metals (Sorichetti et al., 2014; Twiss, Welbourn, & Schwärtzel, 1993). In contrast, copper is unaffected, but Fe becomes increasingly growth limiting as phytoplankton biomass increases. This increase in Fe limitation is enhancing the competitive

advantage of cyanobacteria, as these cells respond to low Fe stress by secreting their own Fe-binding organic ligands (i.e., siderophores) (Wilhelm, 1995). Ultimately, cyanobacteria may produce sidero-phores to outcompete other algae for a "pirated" pool of Fe (Rudolf et al., 2015). This DOM–siderophore–Fe cycle is further supported if photoreduction of Fe and formation of reactive oxygen species occurs simultaneously.

In addition to these direct and indirect influences of DOM on the growth of cyanobacteria, DOM may stimulate the formation of cyanobacterial toxins, which in turn confers an ecological advantage to the cyanobacteria population (O'Neil, Davis, Burford, & Gobler, 2012). Several hypotheses exist about the role of these toxins. For example, it has been hypothesized that microcystins, the primary human health concern from some cyanobacteria blooms, may act as oxygen radical scavengers, protecting cyanobacteria cells from pho-todegradation (Huguet, Henri, Petitpas, Hogeveen, & Fessard, 2013; Puerto et al., 2010; Wörmer, Huerta-Fontela, Cirés, Carrasco, & Quesada, 2010; Zilliges et al., 2011). Therefore, elevated DOM in combination with warmer and more stable lake waters—characteris-tics associated with a changing climate—may accelerate toxin pro-duction in prolonged cyanobacteria blooms (Dziallas & Grossart, 2011; Zilliges et al., 2011). It has also been hypothesized that toxins are produced to access resources not available to competitors. Microcystin may serve as an Fe chelator of moderate strength (Li, 2011; Saito, Sei, Miki, & Yamaguchi, 2008), binding Fe but without the strength and specificity of a siderophore (Klein, Baldwin, & Sil-vester, 2013). Fe limitation up-regulates the transcription of genes involved in cyclic heptapeptide synthesis and the production of microcystin (Lyck, Gjølme, & Utkilen, 1996; Neilan, Pearson, Muenchhoff, Moffitt, & Dittmann, 2013; Utkilen & Gjølme, 1995). With such a strong link between low Fe availability and microcystin production, it is possible that microcystin serves to modulate Fe–or-ganic complexes in situ, reducing the Fe transport or scavenging ability of competing cells, and enhancing the success of cyanobacte-ria that can use complexed Fe. Both DOM and microcystin can serve as a temporary Fe buffer, resulting in the release of low levels of Fe that is best obtained by small cells with a high affinity for free Fe (i.e., cyanobacteria). An alternative hypothesis is that toxins are not related to a physiological function, but instead are simply pro-duced as metabolic waste products that result from unbalanced incorporation of nutrients (Van de Waal, Smith, Declerck, Stam, & Elser, 2014). If so, changes in DOM concentration and composition, including the supply of bioavailable macro- and micronutrients, are having unpredictable consequences in terms of toxin levels, as many factors can lead to unbalanced growth.

Urrutia-Cordero, Ekvall, and Hansson (2016) considered the impact of temperature and brownification on cyanobacteria presence and toxin levels in a northern Swedish lake. Using both experimental and modeling approaches, they determined that the synergistic inter-action of temperature and brownification results in an increase in cyanobacteria and microcystin toxin levels. While the mechanisms for cyanobacteria and toxin stimulation were not investigated, the multistressor approach reveals the complexity of ecological interac-tions that are associated with brownification.

The preceding discussion suggests that the combination of cli-mate change-driven temperature changes and the shift to more allochthonous DOM are likely to result in an increase in cyanobac-teria biomass in lakes. Increases in DOM load, with associated increases in energy and macro- (organic N and P) and micronutri-ents (Fe), favor cyanobacteria with their mixotrophic capacities (Maranger & Pullin, 2003). A subgroup of phytoplankton (primarily phytoflagellates, mixotrophic flagellates, and cyanobacteria) that benefit from the mixotrophic potential that DOM provides, popu-lates DOM-rich waters. Their ability to use this alternate form of energy will enable these cells to outcompete strict autotrophs in waters with low concentrations of inorganic nutrients (Beamud, Karrasch, & Diaz, 2014; Flynn et al., 2013; Glibert & Legrand, 2006; Granéli, Carlsson, & Legrand, 1999; Monchamp, Pick, Beisner, & Maranger, 2014; Ou, Lundgren, Lu, & Granéli, 2014), or to use alternative sources of N such as DON to satiate the N needs of the otherwise autotrophic cells. DON-containing organic materials as simple as urea have been recently implicated as an alternative source of N linked to an increase in cyanobacteria blooms over the past decade (O'Neil et al., 2012). These changes may also result in higher rates of production of toxins in toxin-producing cyanobacte-ria, either to access these macro-/micronutrients (via intracellular or extracellular ligands) or to outcompete other algae (Van de Waal et al., 2014).

Given the expected ascendance of cyanobacteria, climate change-driven changes in cyanotoxin exposure in food webs of northern lakes are expected. Cyanotoxins are a chemically diverse group of metabolites that may enter and traverse a food web through a variety of pathways. These pathways are complex. Direct exposure to cyanotoxins has been known to exert negative effects on species from every trophic level (Drobac et al., 2016; Ferrão-Filho & Kozlowsky-Suzuki, 2011). Toxin exposure within the food web could occur through: (1) absorption of toxins directly from water (Karjalainen, Reinkainen, Lindvall, Spoof, & Meriluoto, 2003; Miller et al., 2010); (2) consumption of toxin-containing particulate matter (de Maagd, Hendriks, Seinen, & Sijm, 1999); (3) consumption of cyanobacteria (Lance, Neffling, Gerard, Meriluto, & Bormans, 2010; Rohrlack et al., 2005); and (4) consumption of consumers of cyanobacteria (Berry, Lee, Walton, Wilson, & Bernal-brooks, 2011). Due to the water-soluble nature of the most common cyanotoxins, there is a general trend of biodilution in food webs (i.e., a decrease in toxins with each increase in trophic level) (Berry, 2013; Ferrão-Filho & Kozlowsky-Suzuki, 2011; Kozlowsky-Suzuki, Wilson, & Ferrão-Filho, 2012). Despite this trend of biodilution, there is evi-dence of bioconcentration at lower trophic levels (Poste & Ozersky, 2013; Umehara et al., 2017; Zhang, Xie, & Wang, 2016) and trophic transfer of toxins (Berry, 2013; Ferrão-Filho & Kozlowsky-Suzuki, 2011; Kozlowsky-Suzuki et al., 2012; Sotton et al., 2014). The potential consequences of food web-scale chronic exposure to cyan-otoxins remain unknown (Berry, 2013).

8 | GREATER RISK OF MERCURY CONTAMINATION

As terrestrial subsidies of DOM increase, accompanied by a shift from biolabile DOM (with lower aromaticity and therefore sulfur content) to refractory DOM (with higher aromaticity and sulfur content), we hypothesize that methylation and methyl-Hg uptake by heterotrophic bacteria is increasing. This trend will continue until the binding-strength threshold is reached in which DOM effectively sequesters Hg, preventing its release to the food web (Figure 8).

Mercury has both geological and anthropogenic sources and is present in the environment mainly as elementary Hg (Obrist et al., 2017), inorganic (Hg(II)), and organic (methyl-Hg) forms. Both latter forms of Hg can complex to DOM (Haitzer, Aiken, & Ryan, 2002; Ravichandran, 2004), but methyl-Hg is more toxic to organisms (Wiener, Krabbenhoft, Heinz, & Scheuhammer, 2003). Once the complexes are formed, DOM influences the fate of Hg in aquatic systems by controlling its transport through the catchment, cycling within the lake, and chelating the Hg for photolysis and photoreduction (Haitzer et al., 2002). All these factors influence the speciation, mobility, bioavailability, and toxicity of Hg (Sobczak & Raymond, 2015). Therefore, lakes that are predicted to experience an increase in DOM loads may be at greater risk of higher methyl-Hg bioconcentration and biomagnification in their food webs (Lavoie, Jardine, Chumchal, Kidd, & Campbell, 2013; Wiener et al., 2003).

In catchments, transport of DOM-complexed Hg is highest under warmer and wetter conditions (Dittman et al., 2010; Kirtman et al., 2013; Mierle & Ingram, 1991; Shanley et al., 2008), when the upper soil horizon is saturated, and the landscape is hydrologically connected to the aquatic network (Dittman et al., 2010; Shanley et al., 2008). Hg methylation by sulfate-reducing bacteria from bioavailable Hg(II) occurs when DOM-Hg(II) complexes reach reducing zones (Gilmour, Henry, & Mitchell, 1992). Hg methylation occurs on the landscape (in wetland sediments and stream riparian soils) as well as in anoxic lake sediments. It has been shown that allochthonous methyl-Hg represents a higher proportion of bioconcentrated Hg due to higher inputs of DOM-bound Hg in comparison to in-lake methylated Hg (Jonsson et al., 2014). This is partly due to the enhanced solubility of methyl-Hg bound to the sulfur-containing thiol groups of DOM (Watras et al., 1998). Allochthonous methyl-Hg is reported to be taken up at faster rates than in situ methylated Hg both in lakes and estuaries (Bravo et al., 2017; Jonsson et al., 2017). However, highly aromatic (i.e., refractory) fractions of allochthonous DOM bind Hg strongly in its thiol groups, keeping it in solution but reducing its availability for subsequent reactions or uptake (Haitzer et al., 2002; Ravichandran, 2004).

Northern lakes may be at greater risk of higher trophic transfer of methyl-Hg, due to cooler temperatures that reduce growth of organisms leading to the bioconcentration of mercury, and a decrease in the complexity of northern food webs which can increase biomagnification (Lavoie et al., 2013). Methyl-Hg bioconcentrates in lower trophic levels and biomagnifies through food webs (Wiener et al., 2003). Higher Hg is generally found in greater concentrations in fish and invertebrates from systems with greater DOM concentrations (Driscoll et al., 1995; Rennie, Collins, Purchase, & Tremblay, 2005). This is likely due to the effects of DOM on increasing Hg(II) availability to methylating bacteria (Graham, Aiken, & Gilmour, 2013; Hsu-Kim, Kucharzyk, Zhang, & Deshusses, 2013) and increasing methyl-Hg uptake by algae (Le Faucheur, Campbell, Fortin, & Slaveykova, 2014), with subsequent transfer to higher trophic levels (Hall, Bodaly, Fudge, Rudd, & Rosenberg, 1997).

Three main factors are likely increasing the concentrations of methyl-Hg in the base of the food web. *First*, increased allochthonous DOM inputs may result in increased methyl-Hg loading and production (e.g., Graham, Aiken, & Gilmour, 2012) due to increased dissolution of Hg at higher DOM concentrations (Brigham, Wentz, Aiken, & Krabbenhoft, 2009; Gerbig, Ryan, & Aiken, 2012). *Second*, DOM-stimulated heterotrophic bacteria may increase their methyl-Hg uptake (Ravichandran, 2004). The low growth efficiency of heterotrophic bacteria in oligotrophic lakes increases the number of C transfers through the microbial food web (Cotner & Biddanda, 2002) and, although speculative, may affect the fate of Hg. The aromatic nature of DOM is a key predictor of Hg methylation (Graham et al., 2013; Moreau et al., 2015). Methyl-Hg uptake may increase with DOM inputs of increasing aromaticity, sulfur content, and molecular weight, which are related to the greatest methylation of Hg by bacteria and subsequent formation of DOM–Hg complexes (Graham et al., 2013; Moreau et al., 2015). However, reductions in Hg uptake by bacteria and primary producers may occur if there is a shift to even larger and more refractory allochthonous DOM in lakes (Luengen, Fisher, & Bergamasch, 2012), either because the molecules are too large to pass through cell membranes (Ravichandran, 2004; Schartup, Ndu, Balcom, Mason, & Sunderland, 2015), or due to reduced DOM bioavailability and increased binding strength (French et al., 2014). This implies a "sweet spot" for Hg uptake, wherein DOM is refractory enough such that methylation can occur, and the molecular composition of the DOM-Hg complex does not inhibit its uptake. *Third*, the greening of the northern hemisphere, with changes in forest composition from coniferous species with more refractory litter to deciduous species with more biolabile litter, may result in greater methyl-Hg production and uptake at the base of the food web in aquatic systems because of higher rates of microbial activity with biolabile C (see previous point, and Morel, Kraepiel, & Amyot, 1998; Benoit, Gilmour, Heyes, Mason, & Miller, 2003).

9 | RESEARCH PRIORITIES

Major technological advances have been recently made in the characterization of DOM, laying the groundwork for scientists to cross-disciplinary boundaries and adopt a systems approach to improve understanding the effects of DOM on the physical, chemical, and biological processes in lakes and their implications for human health and well-being.

Improved understanding of how DOM is being influenced by our changing world is needed to enhance the effectiveness of lake

management. Key advances in understanding will require interdisciplinary efforts that lead to process-based knowledge of DOM dynamics in heterogeneous landscapes, that explore the role of changing climate, atmospheric pollution, and terrestrial ecosystems, and that consider internal interactions and feedbacks in elemental cycles and food web dynamics. At stake are social and economic activities such as fishing, swimming, and recreation, as well as the safety of drinking water supplies.

At the core of these interdisciplinary efforts is the need to link DOM *composition* to ecosystem structure and function. Beyond the much-studied impacts of greater inputs of DOM to lakes, issues of nutrient availability for the production base (whether algal or bacterial), stoichiometry, essential biochemicals for consumers, toxins, and Hg bioaccumulation, are related to DOM composition. DOM as a complex mixture of molecules that vary with origin and age, are notoriously difficult to fully characterize (Kellerman, Dittmar, Kothawala, & Tranvik, 2014), although there has been recent progress in this context (Minor, Swenson, Mattson, & Oyler, 2014). For example, simple spectroscopic analysis of whole water samples has proved to be a quick and reliable method that can provide interpretable information about average *chromophoric* DOM source and reactivity (Jaffé et al., 2008). An understanding of nonchromophoric fractions of the DOM pool has been advanced by isolation methods employing size fractionation. For example, ultrafiltration or chromatographic separation based on hydrophobicity and acid/base properties allow for a finer fractionation of DOM and yield quantities of distinct DOM fractions that can be studied by spectroscopic methods such as ^{13}C-NMR spectroscopy and by elemental and isotopic analysis (Matilainen et al., 2011). Furthermore, elemental and structural characterization of some of the myriad organic molecules comprising these DOM fractions, or the DOM in whole water, is now possible through advancements in mass spectrometry (Osterholz et al., 2016; Woods, Simpson, Koerner, Napoli, & Simpson, 2011).

Unraveling DOM chemical characteristics will not in itself be enough to understand the role of DOM in lake ecosystems. The variation in the chemical composition of allochthonous DOM may lead to dissimilarities in the influence of DOM on aquatic organisms, with potential alterations at the organismal level. Even when we have detailed information on DOM chemistry, we do not know how to interpret detailed differences in composition in terms of effect on organisms (e.g., Rue et al., 2017). There is a need for improved process-based knowledge that links DOM quantity and composition to cellular process rates (e.g., stimulation, reduction, and bioaccumulation) in different components of the food web. We envision a three-pronged approach to address this challenge by conducting (1) laboratory experiments in which the DOM is characterized at a detailed level (e.g., FT-ICR-MS), and (2) field comparisons to evaluate potential differences in the effects of allochthonous DOM on organisms. By attacking these questions first from laboratory and field approaches, we will be more successful to then develop testable hypotheses that could be further evaluated in (3) lake-scale manipulative experiments. This improved process-based knowledge must be

scaled to larger spatial scales (catchments to regions) and time scales (days to decades to centuries).

Process-based knowledge of landscape controls on the fate of DOM is needed, tracking changes in DOM concentration and composition as it moves from land to lakes. Several papers suggest a predominantly recent origin of DOM (Butman, Raymond, Butler, & Aiken, 2012; Marwick et al., 2015), pointing to strong temporal coupling of terrestrial C-fixation and aquatic DOM (Finstad et al., 2016). Fresh DOM is inherently less recalcitrant to microbial mineralization as well as more susceptible to photo-oxidation. It, therefore, serves as a major source of CO_2 outgassing from freshwater ecosystems (Mayorga et al., 2005). A deeper understanding of this terrestrial–aquatic coupling on multiple temporal scales is important because changes in temperature and precipitation are affecting all drivers of DOM dynamics from landscape to organismal scales. For example, how changes in vegetation structure of upland ecosystems are affecting DOM composition reaching lakes, eventually cascading through food webs, is poorly known. Similarly, although work on permafrost degradation has suggested likely impacts on DOM transport, changes in the composition of released DOM and how it is affecting recipient ecosystems is poorly known.

Global change effects on DOM in northern lakes are likely more about hydrologic change (e.g., changes in precipitation, the frequency and magnitude of extreme events, and the seasonality of rainfall, snow melt, or droughts and floods) and increased hydrologic connectivity, than about direct effects of temperature change (cf. de Wit et al., 2016). These global change-driven hydrologic changes are altering not only how DOM enters via hydrologic pathways, but also its fate, which are influenced by water and nutrient retention times, the location and occurrence of hotspots and hot moments, and food web dynamics (Grimm et al., 2013; Groffman et al., 2014; Woodward, Perkins, & Brown, 2010; Zwart, Sebestyen, Solomon, & Jones, 2017). Recent studies have confirmed that intensification of the hydrologic cycle affects DOM transport and loading (Raymond & Saiers, 2010), including both enhanced inputs to lakes during extreme precipitation events with subsequent impacts on food webs (Zwart et al., 2017) and reduced connectivity during droughts (Szkokan-Emilson et al., 2017). However, while we know at least some of the impacts of changing hydrology on DOM content, we know less about the consequences on DOM composition and even less about consequences for bioavailability in lakes. More work is needed to link climate-driven changes in hydrology with the composition, stoichiometry, and reactivity of DOM.

The role of allochthonous inputs of DOM as the trophic basis of lake productivity remains contested, and our review has pointed to some conflicting literature findings. Survey results indicate that browning tends to reduce productivity at primary and higher trophic levels (e.g., Craig, Jones, Weidel, & Solomon, 2017; Kelly et al., 2014), but recent experimental manipulations of DOM inputs (albeit a smaller concentration increase than the surveys encompassed) showed a positive impact on both phytoplankton and zooplankton productivity (Kelly et al., 2016; Zwart et al., 2017). Conflicting results highlight the need for more experimental studies, improved

understanding of the link between DOM and changes in light and nutrient availability, and documentation of contexts that may condition the response to DOM inputs. In other words, we need to do more than document the pattern of change in food webs with browning; we need to understand the processes behind these patterns, which entails work in both source and recipient ecosystems.

Although challenging, process-based understanding of the effects of terrestrial organic matter inputs on whole-lake ecosystems calls for large-scale experimentation, integrating abiotic and biotic processes in benthic and pelagic habitats. Also, progress should be focused on improving understanding of the bioavailability of specific essential elements (e.g., N, P, Fe) and pollutants (e.g., Hg) complexed to or contained within DOM, especially under changing environmental conditions like pH and redox (Bravo et al., 2017). For example, if aromatic DOM binds Hg strongly to its thiol groups, then the bacterial uptake of (and perhaps growth efficiency on) aromatic DOM is important for understanding bioaccumulation of DOM-bound Hg. Yet, there is no consensus on the use of allochthonous aromatic DOM by bacteria. Some studies report very low immediate bioavailability of allochthonous DOM (e.g., 2% in Soares et al., 2017), but interactions with sunlight and a variety of other extrinsic factors can prime the bioavailability. Improved understanding of these interactions is needed.

There is also a need to improve understanding of the microbial competition for nutrients and EFAs that are incorporated into organic molecules within the DOM pool, and how the outcome of this competition may influence their accumulation in the food web (Brett et al., 2017)—as well as lead to selection of phytoplankton species that produce toxins that may be accumulated in the food web. At stake is not only the structure and functioning of lakes, but the safety and security of drinking water and freshwater fish resources.

10 | CONCLUSION

Climate change variations in northern terrestrial ecosystems are appreciable—from lengthening growing seasons, to changes in species composition from coniferous to deciduous, to changes in growth stoichiometry associated with elevated levels of CO_2. These changes to the forest biome are accompanied by changes in the hydrologic cycle that are affecting the delivery of water, particulate and dissolved organic material, and nutrients to surface waters. Increased delivery of DOM is further leading to region-wide browning of freshwaters. The freshwater issue of browning introduces substantial uncertainty in projecting future productivity of lakes under climate change. The climate-driven shift to greater predominance of terrestrially derived DOM that is more biorefractory, aromatic, larger in size, and higher in molecular weight than lake-derived DOM is having substantial effects on physiochemical properties of lakes, further influencing lake productivity and the nutritional quality of production. It also means reduced water quality for human consumption. The consequence of these changes at the ecosystem level is uncertain at present, but we have outlined several

pathways of likely impact, given our current state of knowledge. Changes in DOM sources and inputs to northern lakes is initiating a cascade of altered biological outcomes, including lakes with food webs that are likely to be nutritionally poorer (lower EFAs, higher toxins, and higher contaminants such as mercury). While these changes are summarized by the term "browning," real and realized changes are altering the ecology and ecosystem services of northern lakes.

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