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SPECIAL ISSUE-CURRENT EVIDENCE

Interactions between sunlight and microorganisms influence dissolved organic matter degradation along the aquatic continuum

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Scientific Significance Statement

CO_2 emissions from inland surface waters to the atmosphere are almost as large as the net carbon transfer from the atmosphere to Earth's land surface. This large flux is supported by the movement of dissolved organic matter (DOM) from land and its subsequent oxidation to CO_2 in freshwaters as a result of interactions between sunlight and microbes. These interactions are poorly known, but measuring the coupled "photo-bio" degradation of DOM is critical to understanding DOM fate. Changes in inland waters from climate or land-use are affecting the fundamental controls on the processing of DOM by sunlight. Thus, this literature synthesis highlights the approaches and knowledge needed to understand the role of sunlight in DOM processing within aquatic ecosystems and across ecosystems at landscape scales.

Abstract

CO_2 emissions from inland surface waters to the atmosphere are almost as large as the net carbon transfer from the atmosphere to Earth's land surface. This large flux is supported by dissolved organic matter (DOM) from land and its complete oxidation to CO_2 in freshwaters. A critical nexus in the global carbon cycle is the fate of DOM, either complete or partial oxidation. Interactions between sunlight and microbes control DOM degradation, but the relative importance of photodegradation vs. degradation by microbes is poorly known. The knowledge gaps required to advance understanding of key interactions between photochemistry and biology influencing DOM degradation include: (1) the efficiencies and products of DOM photodegradation, (2) how do photo-products control microbial metabolism of photo-altered DOM and on what time scales, and (3) how do water and DOM residence times and light exposure interact to determine the fate of DOM moving across the landscape to oceans?

Dissolved organic matter (DOM) dominates the pool sizes and fluxes in organic carbon and nutrient budgets in most aquatic ecosystems (Wetzel 2001). Because only ~ 0.1% of net primary production on Earth is stored in aquatic sediments (Burdige 2007), tremendous amounts of particulate organic matter (POM) are degraded and pass through the

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DOM pool on different time scales. POM to DOM conversion and DOM processing can be rapid; e.g., Meyers et al. (1984) found > 90% of the photosynthetically formed POM was mineralized annually within the upper 100 m of Lake Michigan. Microbial mineralization of POM begins with degradation into DOM, which can pass through cell membranes. Thus, DOM is a critical intermediate pool between particulate organic and inorganic C, and important in budgets of local to global C cycles. However, limitations in traditional approaches to studying DOM degradation, plus the lack of integration of these approaches, have left gaps in our ability to predict the fate of DOM in inland waters.

Research on DOM fate typically uses one of three approaches. (1) Bottle or bioreactor incubation studies evaluate the biolability (ease of use) of DOM to microbes in the dark to understand the effect of DOM chemistry, temperature, or nutrients on DOM degradation (e.g., Volk et al. 1997; Tranvik and Bertilsson 2001; Fellman et al. 2009; Guillemette and del Giorgio 2011; McCallister and del Giorgio 2012). Such studies often provide rates of DOM processing (e.g., Fellman et al. 2009), but tend to exclude budget information or other processes such as photochemical degradation. (2) In the second approach, chemists provide molecular characterization of DOM, often along a continuum from land to water or river to coast, to infer processes responsible for DOM degradation (Dalzell et al. 2009). A typical finding is that microbial or photochemical degradation could account for observed chemical shifts in DOM (Cory et al. 2007; Minor and Stephens 2008; Abdulla et al. 2010; Goldberg et al. 2015; Kellerman et al. 2015). However, these studies rarely measure rates of DOM processing. (3) The third approach examines DOM budgets directly (Wetzel 2001) or DOM importance is implied based on C budgets quantifying air–water CO_2 exchange (e.g., Kling et al. 1991; Cole et al. 1994; Raymond et al. 2013). Such studies often conclude that most CO_2 emitted is from microbial respiration of terrestrially sourced DOM, but the role or rates of other processes such as photochemical degradation are usually ignored (Biddanda 2017 and therein). Thus, these three approaches (microbial, chemical, and C budgets) have individual strengths but when applied in isolation cannot fill basic knowledge gaps about DOM degradation rates and fate.

A common result or inference in microbial and budgetary approaches is that most DOM processing or CO_2 production in surface waters is from microbial respiration of labile DOM. However, recent research on DOM degradation highlights a major challenge to this assertion, because from a mass balance perspective these biolabile fractions are insufficient to support the uptake rate and levels of DOM consumption by microbial communities (Kaplan and Cory 2016 and therein). Furthermore, based on rates of DOM use by microbes during bottle incubations, most DOM in streams is not susceptible to microbial respiration over time scales equivalent to water residence times (Volk et al. 1997; Wiegner et al. 2005; Fellman et al. 2009). The questions, then, are what causes microbial respiration rates in dark incubations to be too low to support observed rates of DOM degradation, and what other processes might be involved?

Chemical approaches to characterizing DOM degradation show that photodegradation is involved (Cory et al. 2007; Minor and Stephens 2008; Spencer et al. 2009; Stubbins et al. 2010), and we suggest that direct and indirect photochemical effects may account for the gap between microbial respiration rates and observed DOM degradation. Photodegradation by sunlight includes conversion of DOM to CO_2 (photomineralization), and partial oxidation of DOM resulting in altered chemical composition (photo-alteration or partial photooxidation; Andrews et al. 2000; Cory et al. 2007, 2010; Minor and Stephens 2008; Stubbins et al. 2010). Freshwater studies that quantified DOM photodegradation (Amon and Benner 1996; Cory et al. 2014, 2015) show that rapid rates are consistent with rapid photobleaching of the chromophoric fraction of DOM (CDOM) in marshes, wetlands, lakes, and rivers (Wetzel et al. 1995; Graneli et al. 1996; Moran et al. 2000; Tzortziou et al. 2007). In addition, the less labile but more abundant pool of DOM supporting microbial respiration in streams (Cory and Kaplan 2012; Sleighter et al. 2014; Ward et al. 2017) is photolabile, meaning its chemical composition is easily altered by sunlight (Stubbins et al. 2010; Ward et al. 2017). Because DOM chemical composition can control microbial activity and community composition (Wetzel et al. 1995; Bertilsson and Tranvik 1998; Tranvik and Bertilsson 2001; Cory et al. 2010, 2013; Ward et al. 2017), it follows that photo-alteration of DOM is likely a critical, indirect control on microbial DOM uptake and thus DOM fate.

The goal of understanding overall controls on DOM fate begs the question of how do rates of microbial and photodegradation compare? The few studies making this direct comparison (Vähätalo et al. 2003; Cory et al. 2013, 2014, 2015) show that DOM photodegradation rates can be substantial, even exceeding rates of microbial DOM respiration in shallow waters. Photodegradation of DOM can exceed microbial respiration and account for more than 90% of the total DOM processed in the water column (Cory et al. 2014), and from 10% to 30% of the CO_2 emitted to the atmosphere (Cory et al. 2014; Koehler et al. 2014; Vachon et al. 2016). What is clear is that in any sunlit water column a coupled, simultaneous "photobio" process degrades DOM (Judd et al. 2007; Cory et al. 2010, 2013; Fasching and Battin 2012; Vachon et al. 2016), suggesting that integration of photochemistry and biology is necessary to advance our understanding of DOM fate.

Here, we highlight research that integrates different approaches to show that interactions between photochemical and microbial processes influence DOM degradation. We introduce key knowledge gaps of (1) interactions between sunlight and microorganisms that feedback to influence DOM degradation in water and sediments, (2) the role of temporal changes in DOM chemistry and microbial community composition, and (3) the landscape-level controls on DOM degradation as determined by the arrangement of lakes and streams and the role of spatial sources and sinks of DOM.

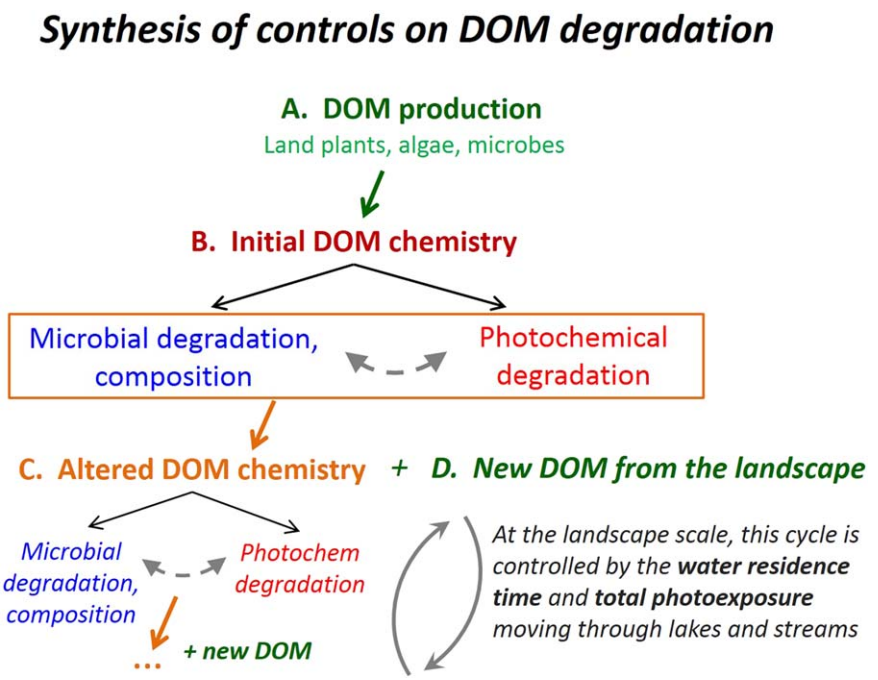

Fig. 1. Synthesis of controls on DOM degradation. (**A**) DOM is produced on land by plants and microorganisms, which shapes the initial biopolymers and DOM chemistry exported to waters. (**B**) This chemical diversity is critical for determining DOM lability and for setting the rates of photo-bio degradation. In surface waters, this chemical diversity constrains photochemical processes as well as microbial activity and community composition, which then interact and feedback (double-headed arrow) to ultimately control DOM degradation. (**C**) Microbial and photochemical DOM degradation leads to altered DOM chemistry, and degradation of this mixture continues for many iterative cycles. (**D**) This altered DOM is continually mixed in with new DOM flushed from soils or other sources to surface waters, highlighting the need for short-term kinetic studies which mimic natural conditions. Experimental studies must be placed in the context of controls at larger, landscape scales—these controls are essentially the water residence time and the total sunlight exposure of the DOM as it moves between lakes and streams on its way to the ocean. Finally, tracking changes in DOM degradation (e.g., by optical metrics, Williamson et al. 2014) can provide information on how degradation affects subsequent biolability and photolability as DOM moves through the landscape (e.g., Fig. 4).

Summary of controls on photodegradation for aquatic C cycling

DOM sources include land plants, soils, algae, aquatic macrophytes, and microbes, and they strongly determine the initial DOM chemistry (Fig. 1A). In turn this chemistry controls DOM photodegradation, and microbial community composition and DOM degradation (Fig. 1B,C). At the landscape scale, the repeated additions of new DOM will affect microbial and photodegradation, and the residence times of water and DOM control the total light exposure and the time available for changes in microbial community composition and rates of processing (Fig. 1C,D). Here, we use DOM as the default term when discussing DOM degradation by microbes and sunlight; dissolved organic carbon refers to carbon concentration, while light-absorbing DOM is quantified as chromophoric (colored) DOM (CDOM).

Quantifying rates of DOM photodegradation

Water column rates of DOM photodegradation (Fig. 2) are governed by three wavelength-dependent processes: (1) sunlight amount reaching the water surface, (2) sunlight absorption rate by CDOM in the water, and (3) the apparent quantum yield (AQY), which quantifies DOM photolability as moles of product formed per moles of photons absorbed by CDOM.

Photon flux ($E_{0,\lambda}$)

Amounts of DOM photodegraded in the water column generally increase with increasing sunlight reaching the water surface (Cory et al. 2015). Sunlight at the water surface, represented as the spectrum of direct and diffuse photons ($E_{0,\lambda}$ in Fig. 2, in mol photons m^{-2} $time^{-1}$ nm^{-1} wavelength) depends on latitude, date, time of day (i.e., the solar zenith angle), elevation (Leifer 1988), and cloud cover (Bernhard 2011). Depending on location and atmospheric composition, spectral distributions of UV and visible light differ from clear-sky conditions because some fraction of downwelling light is diffuse when clouds or particles are present. Large uncertainties can exist when assessing deviations from clear sky conditions, especially for the UVB spectrum (Bernhard 2011), which is important because light absorption by CDOM and efficiency of DOM photodegradation are highest in the UVB range (White et al. 2003; Osburn et al. 2009).

The fate of photons in surface waters

After reflection off the water surface, the fate of most photons is to be absorbed by CDOM (Williamson et al. 1996). Concentrations of CDOM are often high enough to absorb

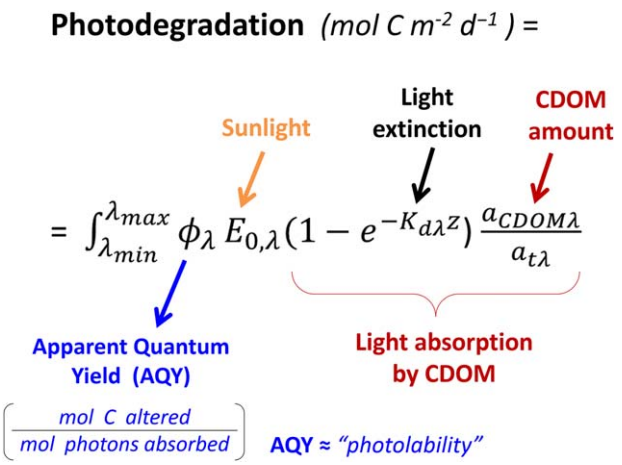

Fig. 2. The water column rate of DOM photodegradation is the integrated product of two spectra: sunlight absorption by CDOM (sunlight = UV plus photosynthetically active radiation (PAR) irradiance; mol photons m^{-2} d^{-1}), which depends on the photon flux to the water surface, the fraction of sunlight absorbed by CDOM in the water column (light extinction times the amount of CDOM absorbing light relative to the total light absorbed, $a_{CDOM,\lambda}/a_{t,\lambda}$), and the AQY for a specific photochemical product (ϕ_λ; e.g., mol CO_2 produced per mol photons absorbed by CDOM for photomineralization). The AQY is a measure of the DOM "photolability," or ease of photochemical alteration; e.g., a high AQY for photomineralization of DOM to CO_2 means high photolability of DOM to be converted to CO_2 by sunlight.

all UV light before it reaches the river or lake bottom, while in low-CDOM waters light reaching the bottom is reflected back into the water column (i.e., upwelling radiation). Rates of light absorption increase with increasing CDOM concentrations and with the fraction of light absorbed by CDOM vs. other aqueous constituents ($a_{CDOM,\lambda}/a_{t,\lambda}$ in Fig. 2; Cory et al. 2015). The fraction of sunlight absorbed by CDOM is often ~ 1.0 for wavelengths between 280 nm and 400 nm (Cory et al. 2014). In waters receiving high loads of terrestrially derived DOM, CDOM can also contribute substantially to absorption of visible light (Williamson et al. 1996; Cory et al. 2015). In contrast, in low CDOM or turbid waters, absorption by CDOM can be lower than absorption by particulate matter, especially in the visible range (Cory et al. 2013, 2014).

Light absorption by CDOM initiates photochemical reactions, and must be quantified to calculate rates of photodegradation and to compare DOM photolability between different conditions or systems. Photolability of DOM is the wavelength-dependent efficiency of any product formed per photon absorbed by CDOM, called the AQY (ϕ_λ, Fig. 2). AQYs for photomineralization of DOM range from approximately < 1 mmol CO_2 mol^{-1} photons to > 3 mmol CO_2 mol^{-1} photons at 350 nm (Vähätalo et al. 2000; Johannessen and Miller 2001; Osburn et al. 2009; White et al. 2010; Cory et al. 2014; Koehler et al. 2014; Vachon et al. 2016), a reaction that is < 0.1% efficient per mol photons absorbed.

Despite the low efficiency for any particular photochemical reaction, CDOM is consumed by absorption of sunlight, referred to as "photobleaching." A common misconception is that only CDOM is degraded by light, but light absorption by CDOM promotes photodegradation of the chromophoric *and* nonchromophoric DOM pools through a range of indirect photochemical reactions likely involving reactive oxygen species (ROS) and radical intermediates (Andrews et al. 2000; White et al. 2003, 2010; Cory et al. 2010; Page et al. 2014). Light absorption can degrade both aromatic CDOM and aliphatic DOM (Gonsior et al. 2009; Cory et al. 2010; Stubbins et al. 2010; Ward et al. 2014; Ward and Cory 2016).

Knowledge gaps on the controls of DOM photodegradation

The three main knowledge gaps in our understanding of DOM photodegradation are how efficiently DOM is (1) completely oxidized (photomineralization), (2) partially oxidized (photooxidation), and (3) how initial and altered DOM chemistry controls the efficiency of photochemical reactions (AQYs).

Photomineralization

Many studies show the photochemical loss of aromatic CDOM and its conversion to CO_2 (Graneli et al. 1996; Lindell et al. 2000; Tzortziou et al. 2007; Osburn et al. 2009; Spencer et al. 2009). There are likely many ways to photomineralize aromatic C, and below we discuss two pathways best supported by the literature. Hydroxyl radical is a strong, unselective ROS made by photochemical reactions and may oxidize DOM to CO_2 (Gao and Zepp 1998; Goldstone et al. 2002; White et al. 2003, 2010; Molot et al. 2005; Page et al. 2014). Hydroxyl radical is implicated in photobleaching (White et al. 2003) and in the oxidation and removal of aromatic (Westerhoff et al. 1999; Waggoner et al. 2017) and aliphatic carbon (Waggoner et al. 2015). Conservative estimates are that oxidation of DOM by hydroxyl radical may account for up to 10% of CO_2 produced during photomineralization (Page et al. 2014 and therein).

The second major pathway proposed to contribute to photomineralization is Ligand-Metal-Charge-Transfer (Miles and Brezonik 1981; Xie et al. 2004; Ward and Cory 2016). Carboxylic acids such as citric or oxalic acids form ligand-metal complexes with iron or other metals (Faust and Zepp 1993). Absorption of sunlight by these complexes results in photodecarboxylation of the organic acid (i.e., loss of carboxyl C; Faust and Zepp 1993), which should produce more CO_2 than O_2 consumed. Consistent with this prediction, high ratios of photochemical CO_2 produced per O_2 consumed by DOM have been observed in high-iron waters (Miles and Brezonik 1981; Xie et al. 2004; Cory et al. 2015; Ward and Cory 2016). Carboxyl C loss accounted for 40–90% of the CO_2 produced during photomineralization of DOM draining permafrost soils, and there was a loss of high O/C aromatic (and aliphatic) DOM (Ward and Cory 2016).

These observations of high photochemical CO_2 produced per O_2 consumed, loss of carboxyl C, and loss of high O/C aromatic DOM suggest that photodecarboxylation may be an important pathway for CO_2 produced by photomineralization (Ward and Cory 2016), especially in mildly acidic, high iron waters (Molot et al. 2005; Cory et al. 2015).

Although the mechanisms and pathways of DOM photomineralization are poorly known, many studies document the same changes in DOM composition during light exposure: loss of CDOM, loss of aromatic C, loss of high molecular weight DOM, loss of carboxyl C, and loss or oxidation of lignin phenols (Hernes and Benner 2003; Spencer et al. 2009). These findings, plus isotopic tracer studies (Opsahl and Zepp 2001), suggest that DOM fractions most susceptible to photomineralization include lignin phenols and tannin-like C.

A common assumption is that loss of some DOM fraction is due to photomineralization to CO_2. However, aromatic or high molecular weight DOM may also be partially photodegraded into aliphatic or lower molecular weight C, with little or no production of CO_2 (Cory et al. 2010; Ward et al. 2014). This poorly studied partial oxidation of DOM may constitute the bulk of DOM alteration by sunlight because DOM is labile to photooxidation (e.g., AQYs equal to or greater than those for photomineralization; Andrews et al. 2000; Cory et al. 2010, 2014; Ward and Cory 2016).

Partial photooxidation

Partial oxidation is generally indicated when sunlight exposure of DOM consumes more O_2 than the sum of CO and CO_2 produced (Amon and Benner 1996; Cory et al. 2014). High O_2 consumption is consistent with the expectation that DOM photodegradation is foremost an oxidative process, where O_2 is consumed as DOM is oxidized to CO and CO_2. Some photochemical O_2 consumption likely contributes to photochemical CO_2 production (Miles and Brezonik 1981; Xie et al. 2004; Ward and Cory 2016), although a substantial (but unknown) fraction of photochemical O_2 consumption likely produces new O-containing functional groups (Cory et al. 2010, 2014; Ward and Cory 2016).

As with complete oxidation of DOM to CO_2, it is likely that ROS are involved in DOM partial oxidation (Westerhoff et al. 1999; Goldstone et al. 2002; Kaiser and Sulzberger 2004; Cory et al. 2009, 2010; Waggoner et al. 2017). For example, singlet oxygen, a ROS produced by photo-excited CDOM and O_2, may oxidize more DOM than other ROS because of higher concentrations of singlet oxygen associated with hydrophobic components of DOM (Latch and McNeill 2006). Singlet oxygen may oxidize and alter N-rich fractions of DOM such as free and combined amino acids (Lundeen and McNeill 2013), and may produce oxygen-rich aliphatics (Cory et al. 2010; Waggoner et al. 2017), a class of compounds widely observed in freshwater and marine DOM (Lam et al. 2007). Hydroxyl radical may also be involved in the partial photooxidation of DOM (Goldstone et al. 2002; Waggoner et al. 2017), and may react with DOM by addition (i.e., hydroxylation) or hydrogen atom abstraction and produce organic and hydroperoxyl radicals (Sulzberger and Durisch-Kaiser 2009). These radicals may react further with DOM forming partially oxidized aromatic or aliphatic compounds (Westerhoff et al. 1999; Waggoner et al. 2015, 2017) and low molecular weight organic acids (Goldstone et al. 2002).

In general, the photochemical reactions involving ROS or organic radicals that oxidize DOM are poorly known, due to the difficulty of isolating reactions of each ROS with DOM (Andrews et al. 2000; Cory et al. 2009, 2010; Page et al. 2014; Ward and Cory 2016; Waggoner et al. 2017). However, high AQYs for partial photooxidation suggest that a large fraction of DOM is rapidly altered by sunlight (Ward and Cory 2016), and that this photo-altered DOM may be important for aquatic C cycling by influencing microbial processing of DOM (discussed below, Ward et al. 2017).

Controls on AQYs

Because the amount of DOM photodegradation can be very sensitive to the spectral shape and magnitude of the AQYs (e.g., Cory et al. 2015), we need to understand what controls AQYs. AQYs for DOM photodegradation and ROS production likely depend on DOM chemistry (Fasching and Battin 2012; Peterson et al. 2012; Hong et al. 2014), although it is not clear how. For example, for >100 samples, there was no relationship between DOM composition and AQYs for photomineralization and partial photooxidation in arctic surface waters (Cory et al. 2014). In addition to DOM composition, patterns in AQY magnitudes or ROS photoproduction rates along the terrestrial to aquatic continuum have been attributed to changes in pH, iron, or salinity (White et al. 2010; Peterson et al. 2012; Hong et al. 2014; Page et al. 2014).

Finally, we know very little about how AQYs change over time. Exposure of DOM to sunlight alters DOM composition, and changes in composition should feedback to influence AQYs (Andrews et al. 2000; Reader and Miller 2014). As light dosage accumulates, AQYs should decrease as photolabile components of the DOM pool are consumed or altered, leaving behind less labile moieties with a lower capacity to form product per mol photons absorbed (Reader and Miller 2014). Thus, studies that scale in time assuming a constant AQY may overestimate rates of DOM photodegradation. However, in inland waters rich in photolabile DOM, changes in AQY over time may be less important because of a strong subsidy of fresh, light-absorbing CDOM from the riparian zone (Fig. 1; Cory et al. 2015). Therefore, the timescale of changing AQYs as a function of DOM sunlight exposure relative to inputs of fresh CDOM is important to address, but has never been studied.

In summary, we lack a thorough understanding of what controls the efficiency of partial or complete DOM oxidation, which limits our ability to scale rates of DOM photodegradation in space and time. Scaling depends in large part on the product of the three wavelength-dependent factors in Fig. 2, which remain poorly characterized. Furthermore, AQY quantification has been limited to products we expect and can measure; other photo-products are likely, and may be identified by coupling AQY measurements with high-resolution chemical characterization (Ward et al. 2014; Ward and Cory 2016).

Integrating the controls on DOM photodegradation

Given the above review, we can investigate how the variables in Fig. 2 interact to control DOM processing and fate. The first key point is that controls on DOM photodegradation interact to produce relatively high rates of DOM photodegradation even in low-light and low-clarity aquatic environments. The second point is that the interaction of controls on photochemical reactions results in a fundamental competition between light and substrate (CDOM) that must be quantified to understand the limitations on DOM photodegradation in any system.

Photodegradation can be important in low-light systems

UV and visible irradiance reaching the water surface annually is lower at high latitudes compared to mid and tropical latitudes due to lower solar zenith angles (Leifer 1988). Thus, lower rates of DOM photodegradation are expected at high latitudes even accounting for longer summer days (Koehler et al. 2014). However, low photon fluxes can be offset by high rates of light absorption by CDOM and high photolability (i.e., high AQY in Fig. 2); these characteristics are observed in arctic and boreal waters (Cory et al. 2014; Vachon et al. 2016). In addition, shallow, unshaded waters in arctic and boreal zones confine DOM to a thin sunlit layer of the water column, providing more opportunities for photodegradation compared to deeper waters or those shaded at lower latitudes.

Photodegradation can be important in low-clarity systems

Despite the fact that sunlight must be absorbed by CDOM for DOM photodegradation, a common misconception is that DOM photodegradation is unimportant in high CDOM waters (Creed et al. 2015). The underlying assumption is that because all light is rapidly absorbed by CDOM in a thin surface layer, most DOM at depth is protected from photodegradation. However, high light attenuation by CDOM results in high rates of DOM photodegradation, meaning that photochemical processes may be important compared to microbial respiration even if attenuation confines DOM photodegradation to a thin layer at the water surface (Cory et al. 2015). For example, in a high-CDOM beaded stream, most of the CDOM (and thus mass of DOM) was in the bottom waters below the depth of UV light penetration, but rates of DOM photomineralization to CO_2, while limited to the top $\sim$ 45 cm, were $\sim$ 15-fold higher than rates of microbial respiration of DOM to CO_2 occurring over a much larger area (volume) of the water column. In low-CDOM waters such as clear lakes, insufficient CDOM (substrate) limits the rates of sunlight absorption and photochemical reactions, and DOM photodegradation may be relatively less important (Cory et al. 2015). Thus, the critical control is the total amount of light absorption by CDOM, independent of the fraction of the water column exposed to light.

In turbid waters, the fraction of light absorbed by CDOM ($a_{CDOM,\lambda}/a_{t,\lambda}$; Fig. 2) can be low (Osburn et al. 2009; Cory et al. 2013, 2014), and because the rate of DOM photodegradation increases linearly with $a_{CDOM,\lambda}/a_{t,\lambda}$, DOM photodegradation rates may be low in turbid waters. However, even in turbid, glacial-fed rivers or lakes where the ratio of $a_{CDOM,\lambda}/a_{t,\lambda}$ is < 1 in the UV range, DOM photodegradation can still account for a substantial fraction of DOM degradation (photochemical + biological) in the water column (Cory et al. 2013). This is because low rates of light absorption by CDOM can be offset by high AQYs (Fig. 2) for DOM photodegradation.

Light vs. substrate limitation of photodegradation

A major interaction in the photodegradation equation (Fig. 2) is between sunlight available vs. light absorption by CDOM. If the light available is higher than the amount of CDOM to absorb it, then photodegradation in the system is limited by the substrate (CDOM), whereas if CDOM is higher than the available light the system is light limited (Cory et al. 2015). These two terms interact because CDOM absorbs light, and higher light attenuation can result in thermal stratification, which increases water residence times and thus may increase DOM photodegradation due to greater total light exposure (Cory et al. 2015). Thus, light limitation occurs when sunlight is insufficient under conditions of high CDOM and short residence times. In turn, photodegradation is substrate limited when sunlight is excessive under conditions of low CDOM and long residence times. These substrate and light limitations are not absolute (i.e., substrate can limit photodegradation before all CDOM is gone), but are instead relative to one another and can shift over time (Cory et al. 2015). Distinguishing light vs. substrate limitation will increase the robustness of photodegradation estimates, and will help predict how photodegradation rates will respond to changing conditions including shifting AQYs over time.

Microbial DOM degradation and its interactions with light

Our synthesis of microbial controls on DOM degradation (Fig. 3) illustrates that for a heterotrophic microbe, all activity starts with the initial DOM concentration and chemical composition (Fig. 3A). DOM chemistry is altered by light or

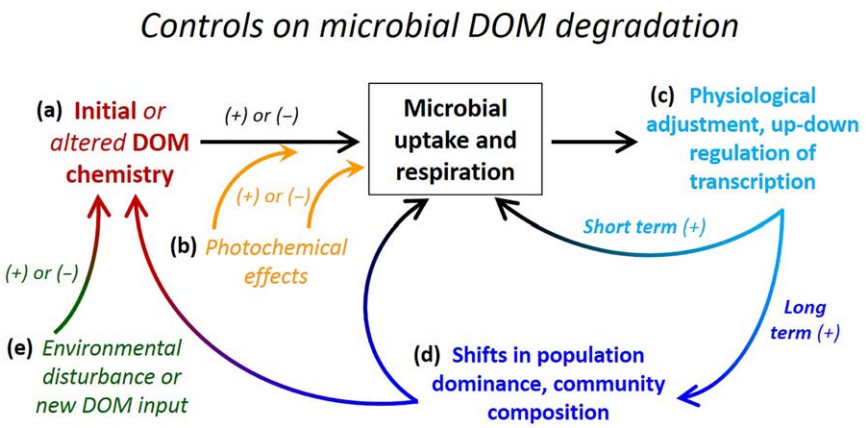

Fig. 3. Proposed synthesis of controls on microbial degradation of DOM, which depends on (**A**) the initial response of microbes to DOM chemistry, (**B**) the photochemical alteration of DOM chemistry (left arrow), and the more direct effect of sunlight on microbes (e.g., UV or ROS damage and loss of CDOM as a "sunscreen" for microbes; right arrow). The short-term physiological adjustment of microbes to DOM (**C**) are followed by the long-term shifts in population dominance that lead to changes in community composition (**D**), documented in response to changes in DOM composition alone (Crump et al. 2009; Logue et al. 2015) and in conjunction with photo-exposure of DOM (Judd et al. 2007; Cory et al. 2013). Especially over longer time scales, microbial communities themselves can alter the chemical composition of DOM through regeneration of CDOM, selective uptake of compounds, or enzymatic degradation of polymeric DOM and POM, which is coupled to (**E**) changes in DOM inputs from shifting environments (e.g., temperature, nutrients) or from inputs of "new" DOM (e.g., rain events washing in DOM from soils). This very dynamic "loop" of controls and interactions operates continuously in time starting at the initial DOM chemistry (**A**), and the various controls can shift in importance on different time scales or as a result of disturbances that can reset the system (**E**) (e.g., Wetzel 2001; Adams et al. 2015). Note that top-down controls such as bacterivory may also affect microbial activity and community composition, but that topic is not addressed in this review.

new DOM inputs, which in turn affects microbial activity and community composition over different time scales (Fig. 3B–E). Although this entire "loop" of controls has yet to be studied in its entirety, in this review, we focus on the specific interactions between microbes and light that affect DOM degradation.

Microbes interact with light in several ways, starting with a direct, harmful effect of intense UV light on microbial cells (Fig. 3B; e.g., Neale et al. 2014). However, it is the indirect interaction between how light influences DOM chemistry, and in turn how DOM chemistry affects microbial activity and function, which is less well understood. Here, we highlight three indirect interactions between light and microbes that influence (1) the activity rates and growth efficiencies of microbes, (2) the molecular controls that explain responses of microbes to photo-altered DOM, and (3) the time scales of interactions between light and microbes.

Effects of light on rates and efficiencies of microbial DOM degradation

The reason light alters DOM biolability and microbial metabolism is due primarily to light-induced changes in substrate chemistry (Wetzel et al. 1995; Moran et al. 2000; Tranvik and Bertilsson 2001; Cory et al. 2010, 2013; Mostovaya et al. 2016). This view is supported by substantial changes in rates of microbial respiration or production (Moran et al. 2000; Tranvik and Bertilsson 2001; Cory et al. 2010, 2013, 2014), or by changes in growth efficiencies (Moran et al. 2000; Tranvik and Bertilsson 2001; Pullin et al. 2004; Fasching and Battin 2012) for microbes consuming photo-altered DOM compared to dark controls. Increased growth efficiency for microbes consuming photo-altered DOM indicates more labile substrates for microbes to convert to biomass. In addition, the bacterial respiratory quotient (CO_2 produced per O_2 consumed) on photo-altered DOM may increase compared to dark controls (four boreal lakes, Allesson et al. 2016) or may not change (55 arctic rivers and lakes, Cory et al. 2014). Any substantial change in respiratory quotients after DOM light exposure may indicate that bacteria are shifting to degrade new or altered substrates spanning chemical compositions and oxidation states (Cory et al. 2014; Allesson et al. 2016; Ward et al. 2017).

Molecular controls on biological and photochemical interactions

There is a large literature on what molecules microbes and light may degrade, and how photo-alteration of DOM can increase or decrease its lability to microbes (reviewed in Kaplan and Cory 2016). The contrasting effects of sunlight on DOM biolability are thought to depend on the source and chemical composition of DOM (Wetzel et al. 1995; Tranvik and Bertilsson 2001). A general observation is that photo-alteration of terrestrial DOM produces low molecular weight acids and releases bound nutrients (N and P) that increase biolability (Cotner and Heath 1990; Wetzel et al. 1995; Bertilsson and Tranvik 1998; Goldstone et al. 2002; Amado et al. 2007), while photo-alteration of DOM derived from algal and microbial matter reduces lability to microbes

(Tranvik and Bertilsson 2001). While this general dichotomy has been useful, advances using new tools are beginning to explain, from a molecular standpoint, how the effect of light exposure depends on DOM source and composition, and why specific shifts in molecules of the DOM pool determine the overall interactions and response of light and microbes in DOM degradation.

Abundant fractions of C within terrestrially derived DOM include higher molecular weight, aromatic compounds rich in O-containing functional groups that are generally low lability substrates derived from lignin and tannins (Ward et al. 2013, 2017). Despite lower lability, these relatively abundant substrates are degraded by aquatic microbes (Cory and Kaplan 2012; Fasching et al. 2014; Mann et al. 2014; Sleighter et al. 2014), and are likely more important from a mass balance standpoint in fueling microbial respiration than are small pools of labile C (Wetzel 2001; Cory and Kaplan 2012). Pure culture studies suggest that microbial degradation of low-lability aromatic monomers comprising lignin and other vascular plant components (e.g., vanillate) occurs through limited metabolic pathways (Buchan et al. 2000). In these degradation pathways, most aromatic compounds are first converted to one of several di- or trihydroxylated aromatics that are then enzymatically cleaved by dioxygenases. However, there are other ways to hydroxylate aromatic compounds, such as photochemical oxidation by hydroxyl radical.

Reactions of hydroxyl radical with DOM may create hydroxylated aromatics that feed into microbial metabolic pathways. Therefore, photochemical oxidation of aromatic DOM by hydroxyl radical may bypass key steps in the microbial metabolic pathways of lignin decomposition, thereby increasing rates of microbial respiration or growth efficiencies by producing substrates that can be metabolized by a broad diversity of organisms. Photo-production of substrates that microbial communities are already equipped to consume should increase rates of respiration, the effect generally observed for photo-alteration of terrestrial DOM (Tranvik and Bertilsson 2001; Kaiser and Sulzberger 2004; Cory et al. 2013, 2014). Thus, we suggest that microbes generally respond positively to photo-altered DOM of terrestrial origin because light is degrading DOM to compounds similar to the abundant substrates the microbial communities are already degrading (e.g., hydroxylated aromatics). Photo-production of substrates related to those already fueling native microbial communities is also consistent with similar or increased bacterial growth efficiencies observed on photo-altered terrestrial DOM compared to dark controls (Tranvik and Bertilsson 2001; Fasching and Battin 2012; Cory et al. 2013).

In addition to the response of microbes to photo-alteration of terrestrial DOM, there is evidence that negative responses of aquatic microbes to photo-altered algal or microbial DOM are due to modification or removal of abundant substrates fueling respiration. For example, aquatic DOM of algal or microbial origin is enriched in organic nitrogen (Brown et al. 2004), present as free or combined amino acids or peptides (Goldberg et al. 2015). This N-rich fraction of amino acid-like DOM in aquatic systems can be rapidly taken up by microbes (Cory and Kaplan 2012; Guillemette et al. 2013; Sleighter et al. 2014; Stubbins et al. 2014). Because amino acids are susceptible to degradation by singlet oxygen and other ROS (see above), photo-alteration of this labile pool of C may remove these substrates or make them less biolabile (Amado et al. 2007). The accumulation of protein-like DOM in Lake Tahoe was suggested to result from DOM photo-alteration (Goldberg et al. 2015), rendering this fraction of C more difficult for microbes to degrade. Thus, photochemical removal or alteration of N-rich DOM by singlet oxygen may contribute to the negative response of microbes to photo-altered algal or microbial DOM.

Singlet oxygen may also convert substrates fueling microbial respiration into oxygen-rich aliphatics of lower biolability (see above; Cory et al. 2010; Waggoner et al. 2017). Exposing DOM to singlet oxygen slowed microbial growth (Cory et al. 2010), and produced compounds least labile to microbial degradation (Sleighter et al. 2014). In addition, photo-alteration of autochthonous DOM generally decreases bacterial growth efficiencies (Tranvik and Bertilsson 2001; Pullin et al. 2004; Fasching and Battin 2012), suggesting that biolabile substrates were removed or altered by singlet oxygen or other photochemical processes (Cory et al. 2010).

Almost all research to date on the effects of sunlight on DOM photo-bio degradation has focused on the water column. However, photochemical alteration of DOM may also affect rates and efficiencies of microbial processing of DOM in sediments. Given the potential for substantial exchange of DOM between the water column and sediments, especially in rivers, rapid photochemical alterations could impact how sediment microbes degrade DOM (Sleighter et al. 2014). Examining the extent of DOM photo-alteration in the water column relative to the timescales of DOM residence and microbial processing in the sediments, should advance our knowledge of DOM cycling.

Time scales of interactions

Photochemical transformations of DOM in the water column can be similar to water transit times in stream reaches (Cory et al. 2015), depending on rates of sunlight absorption and AQYs. This rapid photodegradation continually modifies DOM, leaving behind chemically altered compounds relative to the original DOM source. The mixture of original and altered DOM shifts as water moves downstream, and creates the milieu in which microbes operate (Fig. 1C,D).

The framework of these interactions between light exposure, DOM chemistry, rates of microbial degradation, and community composition (Fig. 3A–D) is structured such that substrate amount and chemistry set the initial rates of microbial DOM degradation, and alterations of substrate chemistry

by light initially cause short-term (minutes to hours) physiological shifts and adaptation by the cells present (Wetzel et al. 1995), including up- or down-regulation of transcription to better assimilate the DOM available (Fig. 3C; McCarren et al. 2010; Satinsky et al. 2014; Ward et al. 2017). While chemical alterations to DOM may result in positive or negative effects on microbes (Fig. 3A,B,E), both short-term and long-term adaptations have positive effects on microbial activity (Fig. 3C,D). As populations better adapted to new substrates outcompete others the community composition shifts, often in a matter of days (Crump et al. 2003; Judd et al. 2006, 2007; Adams et al. 2014, 2015). Because the potential activity of microbial communities is set by the species present, as community composition shifts so do rates of DOM degradation (Crump et al. 2003; Kaiser and Sulzberger 2004; Judd et al. 2006, 2007; Cory et al. 2010, 2013). This last shift in DOM degradation occurs only *after* there is a shift in community composition (Judd et al. 2006, 2007; Adams et al. 2014). The fact that community shifts must precede major increases in microbial activity helps resolve the long-standing and seemingly contradictory observations of positive vs. negative influences of DOM photo-alteration on microbial activity. That is, short-term light exposure experiments tend to show negative effects on microbial activity, and longer-term experiments tend to show positive effects because the community had time to adapt (Kaiser and Sulzberger 2004; reviewed in Judd et al. 2007). Therefore, it appears that both photo-alterations of specific substrates in the DOM pool (described above), and temporal shifts in microbial community composition, help explain the variable responses of microbes to photo-exposed DOM. Especially over longer time scales, microbial communities themselves can alter the chemical composition of DOM (Fig. 3D), either through regeneration of CDOM, selective uptake of compounds, or enzymatic degradation of polymeric DOM and POM.

Given this dynamic system of codependent interactions (Fig. 3), and because no sunlit waters on Earth are microbe free for long and few are isolated from rapid changes in DOM, we infer that to advance understanding of DOM cycling we must first characterize the net result of interactions between light and microbes. Second, we must match our tools and approaches to the appropriate time scales of photochemical and microbial reactions. For example, short-term studies (hours to days) that mimic natural conditions have the advantages of (1) using isotopic labels to identifying sources and sinks of labile DOM before pools are mixed, (2) using natural communities that are unbiased by bottle effects and long-term incubations, and (3) measuring metabolic and turnover rates under natural conditions (Cory and Kaplan 2012). In contrast, the longer the incubation period the more time for DOM to degrade in a system without fresh inputs, and the greater the disparity between the experimental results and natural system function.

Landscape controls and scaling up of photo-bio DOM transformations

In larger-scale comparisons of DOM degradation among systems (Guillemette et al. 2013; Lapierre et al. 2013; Lu et al. 2013; Creed et al. 2015; Kellerman et al. 2015; Catalán et al. 2017), one of the strongest patterns is that DOM degradation increases with water residence time (Kothawala et al. 2014; Catalán et al. 2016). It is intuitive to relate the amount of DOM degradation to water residence time, but the total light exposure of DOM drives photodegradation. Increased light exposure and "history" affect specific photo-products; e.g., DOM leached from soils into headwater streams has little prior light exposure and was labile to photomineralization (Hong et al. 2014; Ward and Cory 2016). Along a terrestrial-aquatic continuum, longer light exposure increased DOM partial photooxidation (Cory et al. 2014), possibly due to a successive loss over time of "antioxidants" within DOM (Ward and Cory 2016). Light history is difficult to quantify because the complex physical structures of surface waters can decouple water residence time and light history by transient storage in rivers and isolation of water masses by stratification in lakes or stream pools, and thus lower rates of photo-bio DOM degradation (Cory et al. 2015). These results imply that scaling-up local measurements of DOM degradation must include physical factors such as morphometry and stratification that differentially affect water residence time and total light exposure.

Scaling-up DOM degradation

Quantifying carbon budgets at larger spatial and longer temporal scales is done by multiplying measurements at shorter time scales at specific locations by time and space to arrive at values representing the scales of interest. Given the discussion above, it is clear that such "static" scaling ignores (1) the rapid shifts in DOM lability and microbial community composition, and (2) variable sources and sinks of DOM as water moves across a landscape. Unfortunately, our knowledge of these two components at a landscape level is exceedingly sparse, leaving us with more hypotheses than data.

Variability in DOM sources and sinks, and DOM lability and microbial communities, is due in part to photo-bio degradation rates relative to rates of downstream transport, and in part to the presence and landscape arrangement of lakes and streams (Fig. 4; Kling et al. 2000; Larson et al. 2007). Along the terrestrial-aquatic continuum, DOM leaching from soils has high photolability but may have initially low biolability to microbes (Fig. 4A), and the photolability of terrestrial DOM decreases with increasing light dosage moving downstream (Fig. 4A). Photodegradation of DOM can produce biolabile compounds, a process that may peak near the headwaters of a catchment (Fig. 4A).

The shapes of these lability curves moving downstream are determined by the likely loss in photolability as light history increases (i.e., lowering AQY with time), balanced against fresh DOM inputs from land or protection from sunlight in hyporheic sediments (Fig. 4A). Therefore, if inputs of fresh photolabile

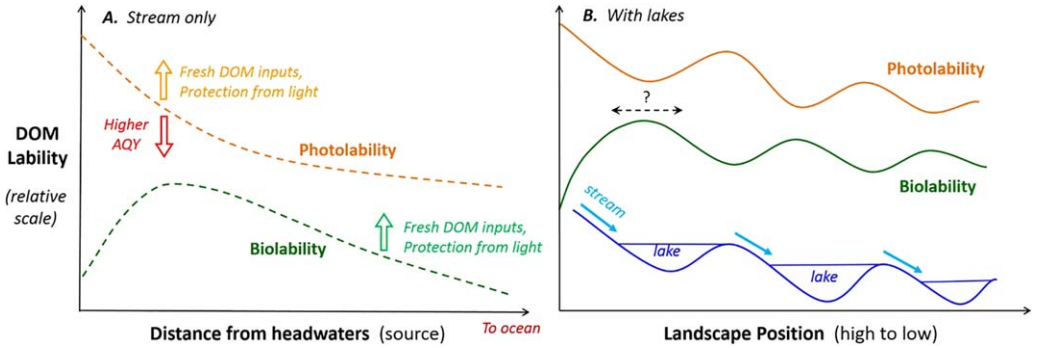

Fig. 4. Hypothesized changes in biolability (defined as microbial growth rates) and photolability (defined as the efficiency of photochemical reactions, AQY) moving from upland terrestrial environments to the ocean. Curve shapes assume no additional inputs of water moving downstream, and curve placement relative to the Y axis does not imply an absolute difference in photolability vs. biolability. (**A**) In streams, the photolability of DOM is highest when fresh inputs of DOM with no prior light exposure are high (left of graph), and photolability is reduced moving downstream. The slope of DOM photolability moving downstream will be shallower if there are fresh DOM inputs or protection from sunlight in transient storage zones (orange up arrow), and will be steeper if the AQY is higher (red down arrow). Biolability is predicted to initially increase moving downstream by additions of photo-products labile to microbes, but after reaching a peak the biolability decreases moving downstream. Additional inputs of fresh DOM or protection from light would make the slope of DOM biolability shallower moving downstream (green up arrow). (**B**) In a catchment of connected lakes and streams, both photolability and biolability decrease downstream (similar to the stream-only case). The peaks and troughs of photo and biolability are aligned with the occurrence of lakes and streams, but the short-dashed line and question mark indicate that there are few data to constrain the exact placement of the curve peaks and troughs. The balance of (1) new inputs of DOM from land moving through a basin, (2) photodegradation in the lake surface vs. replenishing photolabile DOM by mixing deeper water to the surface during storm events or turnover, and (3) the arrangement and number of lakes in a basin influencing landscape-level residence time and light history, will determine the shapes of these curves. Overall, DOM lability is predicted to be higher moving downstream when the landscape configuration contains lakes compared to water moving only through streams and rivers (shallower slope moving downstream compared to panel).

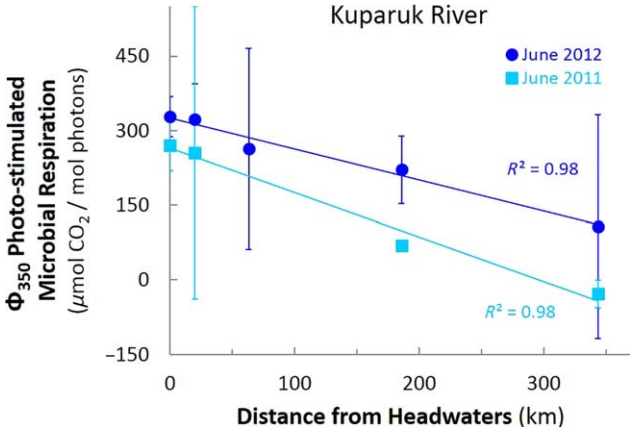

Fig. 5. Downstream changes in the Kuparuk River for the AQY of photo-stimulated microbial respiration, defined as the amount of respiration stimulated by photo-exposed DOM above the background dark microbial respiration (*see* Cory et al. 2014; Cory 2017).

DOM are high and the efficiency of photo-degradation (AQY) is low, photolability may actually increase downstream. The biolability curve shape would respond similarly; e.g., the decrease downstream would be shallower if there was protection from light or high inputs of fresh DOM.

In landscapes with lakes and streams (Fig. 4B), inputs of fresh DOM and AQYs are still important (Fig. 1), but the protection of DOM from sunlight by deep mixing in lakes becomes an additional control. In this case, partially photodegraded DOM in streams enters a lake and is protected from further photodegradation by deep mixing. The lake DOM is less photolabile due to its partial degradation upstream and its longer water residence time in the lake surface than in the stream (low point in photolability curve in Fig. 4B), but the DOM is still taken up by microbes and in the process can be "colored" (production of CDOM; Amado et al. 2007; Guillemette and del Giorgio 2012; Kothawala et al. 2014). Determining the light absorption of this colored microbial matter and the AQYs for its degradation will help determine the importance of microbial coloring in DOM cycling.

Along with microbial coloring, DOM is added from algae or aquatic macrophytes in the lake, increasing the biolability of DOM in and exported from the lake (Fig. 4B; e.g., Creed et al. 2015). This oscillation of DOM lability from stream into lake may restart with new DOM inputs along the next stream bank, but the overall hypothesized pattern is that both photo and biolability decrease moving down the catchment and with increased water residence time (Fig. 4B).

Determining DOM fate requires an analysis of water residence time compared to DOM residence time (i.e., degradation rate). If DOM is transported downstream to a light-protecting environment such as a lake or ocean faster than it is degraded to CO_2, then downstream ecosystems (coastal oceans) will receive more DOM labile to further degradation (*see* Cory et al. 2014). If the degradation sink is strong and DOM residence time in light-protected environments is short, then more DOM will be degraded and released to the atmosphere as CO_2 and oceans will receive less and less-labile DOM. Because the

landscape configuration of lakes and streams affects residence time, light protection, and the source-sink strengths of DOM, in basins with lakes the photo and biolability of DOM will decrease relatively less than in basins with only streams (Fig. 4A,B), although the total amount of DOM degradation will still be governed by residence time and light exposure. These predictions need testing, although preliminary data from an arctic river indicate that the AQY of photo-stimulated microbial respiration decreases moving ~ 300 km downstream from the headwaters (Fig. 5).

Conclusions

DOM degradation is controlled by the interactions between biology, photochemistry, and DOM chemistry. Specifically, (1) DOM photodegradation is important for DOM fate even for waters high in CDOM, high in turbidity, and at high latitudes. (2) The contrasting effects of sunlight on DOM microbial degradation are due to shifts in microbial community composition over time and to production and removal of specific substrates during light exposure. ROS likely contribute to the production, alteration, or removal of substrates fueling microbial respiration. Advances are made by combining DOM molecular characterization with rate measurements of DOM photodegradation, microbial activity, and shifts in gene expression and microbial community composition during the transitions from dark to light conditions. (3) A critical knowledge gap is AQY spectra, especially for (a) partial oxidation (O_2 consumption), (b) key products of DOM photodegradation such as CO_2 and ROS (hydroxyl radical and singlet oxygen), and (c) for the production or alteration of substrates fueling microbial respiration. This information is critical given substantial and widespread shifts in controls on DOM photodegradation, such as changes in rates of CDOM light absorption in browning waters (Lapierre et al. 2013; Williamson et al. 2015), and increases in AQYs from inputs of photolabile DOM from thawing permafrost (Cory et al. 2013; Ward and Cory 2016). (4) Short-term kinetic studies that mimic natural conditions are key, because rates of DOM photochemical alteration and rates of microbial responses to altered DOM are typically rapid (minutes to days). (5) At larger scales, we must understand how inputs of fresh DOM in time and space affect the amount and fate of DOM degradation (Figs. 1D, 4), and how controls on water residence time, DOM residence time, and total light exposure interact to determine the fate of DOM moving from land through lakes and streams to oceans.

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