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Impacts of Polar Changes on the UV-induced Mineralization of Terrigenous Dissolved Organic Matter

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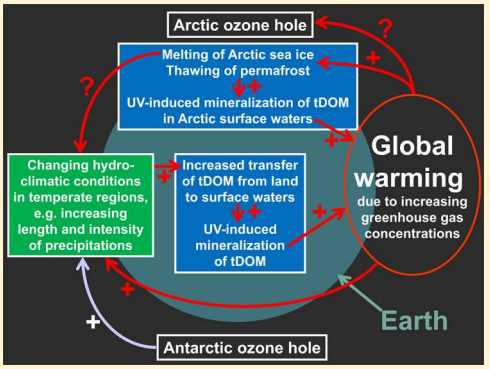
ABSTRACT: Local climates in the Northern and Southern Hemisphere are influenced by Arctic Amplification and by interactions of the Antarctic ozone hole with climate change, respectively. Polar changes may affect hydroclimatic conditions in temperate regions, for example, by increasing the length and intensity of precipitation events at Northern Hemisphere midlatitudes. Additionally, global warming has led to the thawing of ancient permafrost soils, particularly in Arctic regions, due to Arctic Amplification. Both heavy precipitation events and thawing of permafrost are increasing the net transfer of terrestrially derived dissolved organic matter (DOM) from land to surface waters. In aquatic ecosystems, UV-induced oxidation of terrigenous DOM (tDOM) produces atmospheric CO_2 and this process is one of several mechanisms by which natural organic matter in aquatic and soil environments may play an important role in climate feedbacks. The Arctic is particularly affected by these processes: for example, melting of Arctic sea ice allows solar UV radiation to penetrate into the ice-free Arctic Ocean and to cause photochemical reactions that result in bleaching and mineralization of tDOM. Open questions, in addition to those shown in the Graphical Abstract, remain regarding the resulting contributions of tDOM photomineralization to CO_2 production and global warming.



INTRODUCTION

The Montreal Protocol on substances that deplete the ozone layer was signed in 1987 and in 1989 it was ratified and entered into force. The Montreal Protocol, together with the Vienna Convention, became the first treaty in the history of the United Nations to achieve universal ratification in 2009. The Montreal Protocol has been successful in phasing out ozone-depleting chlorofluorocarbons (CFCs) and, as a consequence, the levels of stratospheric ozone outside the polar regions have stopped decreasing since the late 1990s.[1,2] However, springtime ozone depletion is expected to continue over the Antarctic for many decades.[2−4] In the Arctic, climate change-related stratospheric cooling may slow ozone recovery,[4−9] although this hypothesis is a matter of debate.

The Arctic is particularly affected by climate change, due to various feedback mechanisms.[10−12] An important contribution to Arctic Amplification (the fact that the rise in Arctic near-surface air temperatures has been almost twice as large as the global average in recent decades) is the reduced albedo caused by melting of Arctic sea ice and vegetation shifts on land.[10,12] Arctic sea-ice melting may be linked to a higher incidence of high-amplitude jet-stream configurations that favor persistent weather patterns in the Northern Hemisphere such as long-lasting heat waves, droughts, cold spells, and heavy precipitations.[13−21] Also the weather in the Southern Hemisphere is to a large extent determined by atmospheric and ocean circulation, which are changing partly as a result of the interplay between Antarctic stratospheric ozone depletion and climate change. This interplay results in increased incidences of droughts, wildfires, floods, and extreme precipitation events in various regions of the Southern Hemisphere.[2,22,23]

Changing hydroclimatic conditions influence rates of UV-induced mineralization of dissolved organic matter (DOM) to produce atmospheric CO_2.[24] For example, droughts can enhance the UV-induced mineralization of above-ground litter to CO_2, which in turn reinforces the increased radiative forcing of the atmosphere (Erickson et al., 2015[24] and refs cited therein). Similarly, solar UV radiation facilitates the production of CO_2 in surface waters containing terrestrial dissolved organic matter (tDOM) that is being released from thawing permafrost

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soils[25−30] and via increased tDOM transfer from land to water as a consequence of increased frequency of heavy precipitation events.[31−35] Hence UV-induced mineralization of DOM that is enhanced by changing hydroclimatic conditions may result in a positive feedback on climate change.[4,24]

This critical review is divided into two parts. The first part discusses polar changes and how they may affect hydroclimatic conditions in the Northern and Southern Hemisphere. In the second part of this paper we examine how heavy precipitation events and permafrost melting facilitate the UV-induced mineralization of dissolved organic matter (DOM). This section includes molecular-scale consideration of photochemical oxidation of colored dissolved organic matter (CDOM). Biotic processes, particularly primary production, play the most important roles in carbon cycling that is driven by solar radiation.[36] We have not included this topic since it would be beyond the scope of this critical review. In the "Conclusions" section we make a plea for the consideration of UV-mediated positive feedbacks on climate in coupled carbon cycle climate models. This article is inspired by many Comments that Jerald L. Schnoor has written as the Editor-in-Chief of *ES&T* over the years, particularly by those related to climate change, for example by the following publications since 2010: Schnoor, 2010; 2011; 2012a; 2012b; 2013; 2014a; 2014b; 2014c.[37−44] It is also inspired by Jerry's scientific approach that ranges from molecular to regional to global scales. We have also benefitted from other reviews regarding interactive effects of solar UV radiation and climate change on the environment, particularly from the assessment by Erickson and coauthors (2015),[24] and the review by Williamson and coauthors (2014).[4] The present paper is not intended as a comprehensive review. Rather, it is based on selected studies that we think are important with regard to effects of polar changes on UV-induced mineralization of dissolved organic matter.

POLAR CHANGES AND IMPACTS ON LOCAL WEATHER PATTERNS

Arctic Amplification and interactions of the Antarctic ozone hole with climate change affect not only terrestrial and aquatic ecosystems in polar regions[11] but also weather patterns and ecosystems in the Northern and Southern Hemisphere (discussed in the third subsection). Arctic Amplification and consequences for terrestrial and aquatic Arctic ecosystems are discussed in the second subsection. In the first subsection we review some aspects of polar stratospheric ozone depletion. The processes that lead to ozone holes in the Antarctic and the Arctic are complex and have been described, e.g. by Solomon (1999),[45] and by von Hobe and coinvestigators (2013).[9]

The Arctic and Antarctic Ozone Holes. In boreal spring 2011, an unprecedented loss of stratospheric ozone was observed over the Arctic, although the 2011 Arctic ozone hole was not as severe as that in the Antarctic in September 2010.[46] Polar ozone holes result from the coupling of CFCs present in the stratosphere with surface chemistry in polar stratospheric clouds (PSC) that form during extreme cold conditions.[9,45,47] Polar stratospheric ozone depletion involves fast heterogeneous reactions on particle surfaces that activate chlorine from the main reservoir gases HCl and $ClONO_2$.[9,45] A key reaction in the catalytic ozone destruction cycle is photolysis of the ClO dimer (ClOOCl) to yield the Cl atom, which reacts with O_3, when the sun reappears after the polar stratospheric winter.[9,45,48] A prerequisite for the efficient "activation" of reactive chlorine is the removal of HNO_3 via sedimentation of PSC particles (so-called denitrification);[9,45] stratospheric denitrification is associated with temperatures between −80 to −85 °C.[47] Another prerequisite for polar stratospheric ozone depletion to occur efficiently is long-lasting extreme cold conditions.[47] In the Antarctic stratosphere, temperatures below −80 °C have been measured frequently beyond September, which was not the case for the corresponding season, i.e. March, in the Arctic.[47] However, Arctic stratospheric winters seem to have become colder since the start of their measurements in 1958.[8,49,50] The Arctic stratospheric winter 2010/2011 was about 4 K colder than the long-term average, and this may have been one cause for the unprecedented Arctic ozone hole in boreal spring 2011.[9,46,50]

Several factors influence temperatures in the Arctic stratosphere.[2,5−9] One factor is stratospheric water vapor (SWV),[7] which increases with tropospheric temperatures.[51] Maycock and co-workers (2014)[7] reported polar cooling of 0.6 K decade^{-1} at 50 hPa in Arctic winter during the period 1980−2010, in response to increasing SWV. Hence, radiative cooling of the Arctic stratosphere might counteract the dynamical contributions to Arctic stratospheric temperature changes.[5,8,9] Bohlinger and coinvestigators (2014)[5] predicted a continued cooling of the Arctic stratosphere over the coming decades, which could offset the Arctic ozone recovery between 15% and 40%. However, whether or not climate change-related stratospheric cooling will offset ozone recovery in the Arctic stratosphere is a matter of debate.[2,5−9,50,52,53] If climate change does offset ozone recovery in the Arctic, then we might expect an ozone hole in Arctic spring to occur also in the future.[9] The major effect of the Arctic ozone hole is increased levels of solar UV radiation reaching Arctic aquatic and terrestrial ecosystems, as were measured at Arctic ground stations in spring 2011.[54]

Arctic Amplification. New studies suggest that the Arctic troposphere will continue to warm faster than elsewhere in response to rising greenhouse-gas concentrations.[15] This phenomenon has been called Arctic Amplification (AA) and it arises from a number of processes that result from global warming.[11,55] Key contributions to AA are reduced albedo due to vegetation shifts, Arctic sea-ice melting, and disappearing snow,[10−12,56] and an increase in atmospheric water vapor.[11,56] AA is also due to the inflow of relatively warm Atlantic water into the Arctic Ocean.[57] Spielagen and co-workers (2011)[57] have confirmed a warming of the Arctic Atlantic water layer by ∼2 °C since the end of the little ice age (1850). An important effect of AA is vegetation shifts.[12,58] Settele and coauthors (2014)[58] state: "Continued warming is projected to cause the terrestrial vegetation and lake systems in the Arctic to change substantially (*high confidence*)." Pearson and co-workers (2013)[12] predicted that by 2050 woody cover will increase by as much as 52% in Arctic terrestrial ecosystems. Although vegetation shifts in the Arctic may result in higher rates of primary production and hence increased CO_2 uptake, the overall effect is expected to be a positive feedback on climate change due to reduced albedo from Arctic terrestrial ecosystems.[12]

Other major consequences of AA are melting of Arctic sea ice, thawing of permafrost soils, and enhanced input of tDOM into Arctic surface waters.[58] Since 1980, both the perennial and the multiyear central Arctic sea ice areas have declined by approximately 13% and 15% per decade, respectively (Figure 1).[59] Arctic sea-ice melting might be expected to facilitate the sequestration of CO_2 by way of the biological pump (CO_2 fixation in photosynthesis by phytoplankton and export of dead

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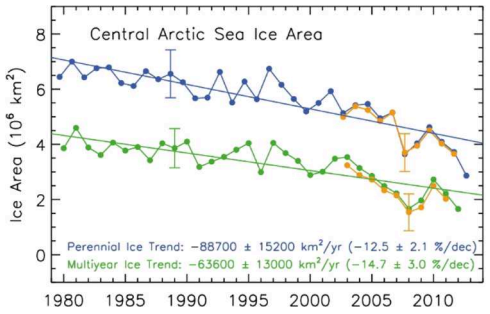

Figure 1. Arctic sea ice loss from 1979 to 2012 as derived from satellite passive microwave data. The yellow lines (after 2002) are from AMSR-E data. Reproduced with permission from 59. Copyright 2013 Intergovernmental Panel on Climate Change (IPCC).

particulate organic matter to the sediment of aquatic ecosystems) in ice-free marine environments.[60] Furthermore, increased tDOM concentrations in Arctic surface waters due to AA[33] could have a positive effect on the biological pump. This is because a large portion of tDOM is colored (referred to as colored dissolved organic matter, CDOM) and CDOM protects phytoplankton from harmful solar UV−B radiation.[4,11,24,36] However, increased inputs of fresh meltwater into Arctic coastal waters likely influences stratification in the water column.[61] Increased stratification of water bodies is expected to enhance UV-induced bleaching of CDOM, thereby decreasing the protective effect of CDOM (Figure 2, left side).[4,24,36]

On the other hand, increased CDOM concentrations may decrease the CO_2 sink strength of Arctic surface waters, due to reduced availability of photosynthetic active radiation (PAR) to phytoplankton and thus reduced primary production,[36] and also due to higher rates of remineralization of organic carbon,[11] as discussed in the second part of this critical review. Therefore, increased CDOM inputs to Arctic coastal waters due to AA may trigger climate feedback mechanisms, in which primary production is lowered due to decreased PAR and in which the rate of remineralization of CDOM to CO_2, which is facilitated by solar UV radiation, is increased. Additionally, increased CDOM inputs into coastal waters likely influences stratification in the water column, by altering the depth at which heat is produced by incoming radiation, and this may lead to further climate feedbacks.[62] However, to our knowledge, the magnitudes of these potential feedbacks have not been quantified or explored thoroughly, and the present paper aims to convince the reader that further research is needed in this area. It remains a matter of debate whether Arctic sea ice melting will increase or decrease the CO_2 sink strength of the Arctic Ocean.[11,61]

Impacts of Polar Changes on Northern and Southern Hemisphere Climate. Polar changes affect weather patterns in the Northern and Southern Hemisphere. Effects on the Northern Hemisphere may be due to Arctic sea ice melting,[13−21] where the extent of the Arctic sea ice usually reaches a minimum in September.[11,59] Whether extreme weather events across the Northern Hemisphere midlatitudes will occur more frequently in response to Artic sea-ice loss is a question of controversy.[63−65,150] In the following paragraph, we focus on studies that showed how Arctic sea-ice melting might affect weather patterns in the Northern Hemisphere.[13−21]

As a consequence of Arctic sea-ice melting, large fluxes of heat and moisture enter the lower atmosphere during fall and winter.[13−15,20] Enhanced high-latitude warming causes 500 hPa heights to rise more at high-latitudes than at midlatitudes, which increases the amplitude of Rossby waves and elongates the peaks of jet stream ridges northward (Figure 3).[14] A strongly meandering Northern Hemisphere jet stream causes cold air to move further to the south and warm air further to the north. With increasing amplitude, the eastward progression of Rossby waves becomes slower (indicated by the arrows in Figure 3).[14] Slowly moving Rossby waves result in blocking of weather patterns and, therefore, in longer lasting extreme weather events such as heat waves, droughts, cold spells, and heavy precipitation events.[13−19,21] For example, during the 2003 European and 2010 Russian heat waves, the Northern Hemisphere jet stream was characterized by a strongly meandering pattern that remained locked in place for several

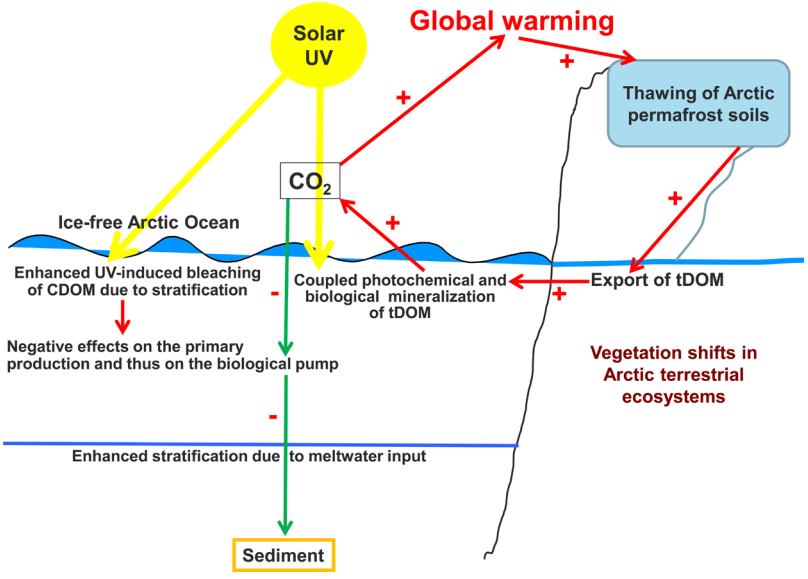

Figure 2. UV-induced mineralization of terrigenous DOM from thawing Arctic permafrost soils, and photobleaching of CDOM in the ice-free Arctic Ocean result potentially in positive feedbacks on global warming. Enhancing and weakening effects are denoted with "+" and "−", respectively.

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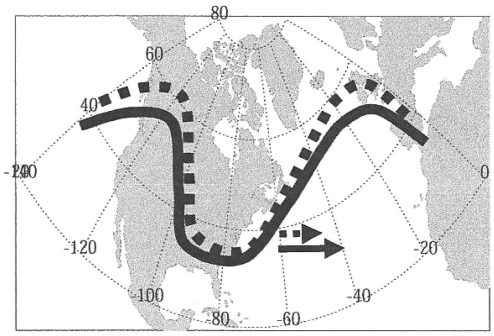

Figure 3. Elongation of the peaks of jet stream ridges northward and augmentation of Rossby wave amplitude (dashed versus solid lines) in the period 1979 to 2010 in the region 140 °W to 0°. Higher amplitude waves progress eastward more slowly, as indicated by arrows. Reproduced with permission from ref 14. Copyright 2012 John Wiley and Sons.

weeks.[18] Furthermore, the enhanced ridging of the jet stream over North America is consistent with recent droughts and heat waves in the western part of North America.[13] Not only droughts and heat waves but also heavy precipitation events may be linked to Arctic sea ice melting. According to Schubert and co-workers (2011),[18] changing Rossby waves accounted for more than 30% of the precipitation variability over several regions of the northern middle and high latitudes, including the US northern Great Plains and parts of Canada, Europe, and Russia. From 2007 to 2013, northern Europe experienced heavy summer precipitations events that were unprecedented in over a century, concomitant with Arctic sea ice loss, which was particularly dramatic in 2008 (see Figure 1).[13,19]

In the Southern Hemisphere, weather patterns have changed as a consequence of the Antarctic ozone hole.[22,23,66−68] The interplay between Antarctic stratospheric ozone depletion and thus decreasing Antarctic stratospheric temperatures and increasing greenhouse gas concentrations in the middle latitudes of the Southern Hemisphere results in an upward trend of the Southern Annular Mode (SAM).[22,69,70] This trend is congruent with a poleward shift of the midlatitude westerly jet during the Antarctic summer.[72] Several studies have shown that the poleward jet shift is linked to increased summer precipitations in the subtropics of the Southern Hemisphere and to drier conditions around 45 °S.[22,23,66−68,71,72] For example, summers in Patagonia have become warmer and drier,[23] while summers over SE S America, S Africa, and SE Australia have become wetter.[22,23,66−68,71,73] In 2010, the highest December total rainfall was recorded in SE Australia since 1900.[73] Effects of the Antarctic ozone hole on Southern Hemisphere climate and ecosystems have been reviewed by Robinson and Erickson (2015).[23]

EFFECTS OF HEAVY PRECIPITATION EVENTS AND THAWING OF PERMAFROST SOILS ON THE UV-INDUCED MINERALIZATION OF DISSOLVED ORGANIC MATTER

As discussed above, evolving polar processes affect the weather patterns in both the Northern and Southern Hemisphere with the tendency toward longer lasting extreme weather events, such as droughts and heavy precipitations.[13−19,21−23,66−68,74] Furthermore, AA enhances the thawing of Arctic permafrost soils.[58] In the following subsection, we discuss how heavy precipitation events and thawing of permafrost are facilitating increased mineralization of terrestrially derived dissolved organic matter (tDOM) by solar UV radiation. This input to atmospheric CO_2 potentially contributes to positive feedbacks on global warming. Later, we discuss what is known about the molecular-scale mechanisms of UV-induced transformations of tDOM.

UV-Induced Mineralization of Terrestrially Derived Dissolved Organic Matter. In many freshwater ecosystems the input of tDOM through runoff from the catchment has increased,[58] owing in part to changing hydroclimatic conditions.[35] Terrestrial DOM may be processed in inland aquatic ecosystems (via microbial and/or UV-induced transformations or flocculation) or it may reach estuarine and shelf waters as unprocessed tDOM via riverine export.[34,75−80] Heavy precipitation events and enhanced continental runoff and river discharge, as well as thawing of permafrost soils, are likely to increase the net transfer of tDOM from land to surface waters.[25,26,29,31,32,34,35,81] For example, increased concentrations of tDOM were found in Arctic inland waters as a result of Arctic permafrost thaws.[25−28,33]

Surface waters exhibit substantial variability in the ratio of terrestrial DOM to autochthonous DOM, the latter of which is derived from aquatic algal and bacterial biomass. Arctic fresh and marine waters contain a greater proportion of tDOM than other surface waters.[34,82] This phenomenon is due in part to the strong land-water linkage in the Arctic.[11,83] Terrestrially derived DOM generally exhibits a higher specific rate of light absorption than autochthonous DOM, attributed to the high aromaticity of the former.[25,30,76,84] Colored dissolved organic matter (CDOM) absorbs solar radiation reaching the Earth surface (mainly in the UV region) and thus can undergo direct phototransformations.[85−87] In aquatic ecosystems, CDOM undergoes either partial or total UV-induced oxidation (also referred to as photomineralization), releasing CO_2 and to a lesser extent CO.[88−93] However, CDOM photoreactivity and thus the extent of photo-oxidation depends in part on prior light exposure.[25,26,77] Cory and co-workers[25,26] found that 92% of total dissolved organic carbon underwent photomineralization in Arctic headwater streams, whereas in the downstream Sagavanirktak River about 75% of total dissolved organic carbon was subject to only partial photo-oxidation. tDOM present in headwater streams had a low prior light exposure compared to the tDOM measured in the Sagavanirktak River, consistent with the expectation that additional photomineralization decreased with increasing light exposure. Several studies by Cory and co-workers[25,26,83,94] suggest that DOM in Arctic surface waters exhibits a higher photoreactivity compared to DOM in lower-latitude fresh waters. This phenomenon is tentatively explained as the release of tDOM having little prior light exposure, due to the recent thawing of permafrost soils in the Arctic. Thawing of Arctic permafrost soils thus results in a positive feedback on climate change via both photomineralization and microbial mineralization of DOM to release CO_2[25,26,96,97] (Figure 2, right side).

Photomineralization of tDOM is an important source of CO_2 also in river-dominated coastal systems,[98] for example in Arctic shelf waters,[99] and in the Baltic Sea.[100] Based on air-sea CO_2 flux measurements, Laruelle and coauthors (2014)[99] found that the global coastal ocean is a much smaller CO_2 sink (~0.2 PgC yr^{-1}) than was previously thought and that many coastal regions are net sources of CO_2. Interestingly, the distribution of CO_2 sources and sinks does not follow that of primary production. This phenomenon may be rationalized in terms of

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Environ. Sci. Technol. 2016, 50, 6621−6631

(i) the temperature-dependent solubility of CO_2, (ii) geographically varying rates of microbial respiration, and (iii) the extent of upwelling and mixing from deeper water layers.[99,101] In addition, one can speculate that an increasing release of CO_2 via UV-induced mineralization of tDOM, owing to changes in continental hydrology, may add to the source strength of some coastal areas. In order to better understand the underlying processes involved in photo-oxidation of tDOM in surface waters that are affected by high tDOM inputs, in the following subsection we discuss what is known about the molecular-scale mechanisms.

Molecular-Scale Mechanisms of Photochemical Oxidation of Terrestrial CDOM. Terrestrial CDOM is believed to originate principally from partly oxidized lignins from vascular plants, with a lesser contribution from tannins and other polyphenols.[33,76,86,102−111] Lignin is estimated to constitute 30% of the carbon sequestered in plants annually.[112] Upon partial microbial-induced or photoinduced degradation, partly oxidized lignins exhibit broad UV/visible absorbance spectra that resemble those of terrestrially derived humic material.[76,103,113,114] The interpretation of terrestrial CDOM as partly oxidized lignin is supported by spectroscopic, mass spectrum, and electrochemical data that indicate that the principal chromophores (i.e., structures that absorb solar radiation) are aromatic groups that include substituted phenols, alkoxy-substituted aromatic groups, quinones, other aromatic ketones, and aromatic aldehydes.[86,87,103,111,115−119] Partly degraded, ancient lignin is thus plausibly the principal light-absorbing component in tDOM released from the melting permafrost.[83]

What is the nature of light absorption by terrestrial CDOM? Results from absorbance and fluorescence experiments suggest that CDOM cannot be described as a collection of independently acting chromophores.[87,102,103,120] One conceptual model proposes that absorption and fluorescence spectra of terrestrial CDOM are explainable as a mixed population of charge-transfer (CT) states and isolated excited states.[87,102,103,111,121] A CT state refers to an electronic excited state involving two or more interacting chromophores, whereas an isolated excited state involves only a single chromophore.[122] In this model, the CT states are attributed to intramolecular interactions between electron donor and acceptor groups in partly oxidized substructures of lignin, tannin, and other natural polyphenol molecules.[87,102,111] This interpretation is consistent with classical molecular dynamics studies and small-angle neutron scattering measurements that indicate that aqueously dissolved lignin polymers are hydrophobic, compactly folded molecules exhibiting a high degree of intramolecular contacts.[123] Photoinduced oxidations would progressively disrupt these CT interactions, which would explain the preferential decrease in lower-wavelength absorption bands upon photobleaching.[86] However, to create a CT interaction, a donor and acceptor pair must have a particular distance and orientation that allows neither a complete electron transfer nor a pair of isolated (noninteracting) excited states. Given the relatively small size of most DOM molecules,[124] it remains unclear whether candidate donor and acceptor groups could sufficiently populate the special orientation(s) needed for CT interactions. Further studies are needed to confirm the mechanism of light absorption by terrestrial CDOM.

Solar radiation causes photobleaching of CDOM, in which chromophores are inactivated by photodegradation reactions, thus decreasing the ability of DOM to absorb light.[86,88,103,119,120,125,126] Direct and/or indirect photodegradation processes rapidly break down the lignin, tannin, and CRAM (carboxylic-rich alicyclic molecule) fractions that are abundant in tDOM, according to results from absorbance and fluorescence spectroscopy, mass spectroscopy, nuclear magnetic resonance, and stable isotope methods.[105,108,110,127−130] This is paralleled by the finding that lignin plays a central role in the photochemical degradation of terrestrial plant litter in sunlight.[113] However, tDOM is more susceptible to photodegradation than are either soil organic matter or microbially derived DOM. In recent work, absorbance spectroscopy and electrochemical data showed that terrestrially derived aquatic fulvic acids were more susceptible to photobleaching and photoinduced redox changes than a soil humic acid.[86] This interpretation is supported by the fact that tDOM exhibits a greater electron donor capacity than either soil organic matter or microbially derived DOM.[115] Photochemical oxidation has been found to destroy irreversibly the principal electron donor groups, interpreted as lignin phenols, in tDOM.[86,130] These findings are consistent with previous reports that solar irradiation leads to decreased total aromatic content of tDOM.[83,119,125,128,129] Finally, hydroxyl radical yields of tDOM from Arctic surface waters are higher than the yields typically measured for other freshwater DOM sources.[131] In summary, high aromatic content and low prior light exposure are believed to explain why tDOM currently draining to surface waters in the Arctic is an especially photolabile carbon pool.[25]

What reactions are responsible for the photoproduction of CO_2 from tDOM released from the permafrost? We have limited insights into the mechanisms involved, however one proposed process is summarized in Figure 4. In photo-

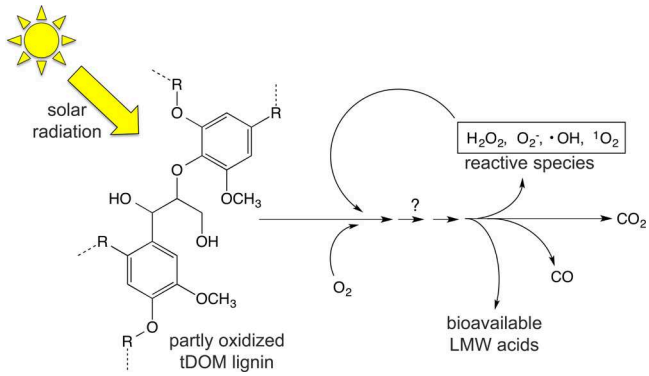

Figure 4. A proposed scheme for the photomineralization of tDOM. Solar radiation converts tDOM to CO_2 principally by the direct photodegradation of partly degraded lignin: however, the relevant mechanisms and intermediates are not known well. This leads to the production of CO_2 and carbon monoxide (CO), bioavailable low-molecular-weight (LMW) acids, and the photoproduced reactive species H_2O_2, $O_2^{\cdot-}$, $OH^{\cdot}$, and $^1O_2$. Further reactions of tDOM with these reactive species are considered responsible for a lesser contribution to the photoproduction of CO_2.

degradation experiments with diverse humic substances (HS), the apparent quantum yield of dissolved inorganic carbon (DIC) correlated well with HS aromaticity (r^2 = 0.81) as measured by solid state NMR, whereas it did not correlate well with HS carboxyl content.[87,98] Experimental evidence suggests that photoproduced charge-separated species ($DOM^{+\cdot/-\cdot}$) involving aromatic groups are a prevalent intermediate responsible for direct photodegradation of DOM, photo-

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production of H_2O_2, and associated consumption of dissolved O_2.[87,98,104,111] Based on this and other evidence, photoproduction of CO_2 from tDOM has been proposed to result primarily from direct photodegradation of aromatic groups (see references in the chapter by Mopper et al., 2015[98]), particularly lignin phenols (Figure 4).[87,98,130] By comparison, oxidation of tDOM by photoproduced oxidants such as H_2O_2, $O_2^{\cdot-}$, $^1O_2$, and $OH^{\cdot}$ (i.e., indirect photodegradation)[132] are considered likely to have a less important role for both photobleaching and CO_2 production from DOM.[87,98] Other proposed mechanisms of photoinduced production of CO_2 from DOM are reviewed recently by Mopper et al. (2015).[98] Finally, the above discussion does not include black carbon, which also may be an important contributor to photoproduction of CO_2 from organic matter in fresh water and marine systems.[98]

Other observations suggest that future changes in UV−B radiation reaching polar regions could influence net rates of photobleaching and photoinduced mineralization of tDOM. In a study of several Swedish lakes, increased UV−B radiation was found to increase DIC production from DOM.[133] UV−B radiation is also responsible for the photoproduction of small biolabile carbonyl compounds from DOM.[134] Additionally, short-wavelength solar radiation is more efficient at photobleaching than long-wavelength radiation,[86,120,126,135] and the quantum yields of important reactive transients (^{3}CDOM*, $^1O_2$, and $OH^{\cdot}$) produced by DOM are higher for UV−B than for longer-wavelength light.[136] Taken together, these results provide further evidence that solar UV radiation plays a key role in the production of CO_2 from tDOM in Arctic and other surface waters (Figure 2).

UV-Induced Increase in the Bioavailability of DOM. Mineralization of DOM to release CO_2 occurs not only via photodegradation processes but also via microbial respiration.[91] A recent study suggests that DOM photomineralization contributes only ∼10% of total CO_2 emission from lakes and reservoirs on a global scale.[95] However, not all chemical forms of DOM are available to bacterioplankton. The bioavailability of DOM depends on its age, size, and chemical composition.[119] For terrestrially derived DOM (tDOM), bioavailability is negatively correlated with the age of the material. According to Amon and Benner's (1996)[137] continuum model, tDOM originating from recently fixed carbon present in leaf litter and soils exhibits a higher bioreactivity than aged tDOM. For example, Letscher and co-workers (2011)[78] reported a tDOM removal rate constant for the eastern Arctic that was 2.5−4 times higher than had been observed for the western Arctic, which they rationalized in terms of microbial mineralization of relatively young plant material over the expansive shelf area of the eastern Arctic. The bioavailability of DOM also depends on its molecular size. Heterotrophic bacteria preferentially utilize the low-molecular-weight (LMW) and hydrophilic fraction of DOM derived from algal and bacterial biomass and from fresh plants or from ancient permafrost soils.[81,96,138,139] Drake and co-workers (2015)[96] demonstrated that mainly the low-molecular-weight fraction of ancient DOM (35′800 y B.P.) from permafrost soils was bioavailable. Furthermore, an important factor that controls the availability of tDOM to bacterioplankton is the lignin content of tDOM. It has been shown[113] that the mass loss of tDOM via biotic and photochemical degradation decreased and increased, respectively, with increasing lignin content (see also the previous subsection).

Therefore, photochemical transformations may increase the bioavailability of tDOM with a high lignin content, while decreasing the bioavailability of autochthonous DOM, in both marine and freshwater systems.[91,98,138,140−148] For example, Kaiser and Sulzberger (2004)[138] investigated the effects of light-induced transformation of various DOM fractions on bacterial DOM utilization in water samples from the River Tagliamento, the last large natural river in Europe (northeast Italy). Their studies combined field and laboratory experiments to show that the bioavailability of hydrophobic DOM, which was found to be biorecalcitrant in the River Tagliamento, increased upon exposure to simulated sunlight, whereas hydrophilic DOM, which was most abundant and strongly supported bacterial activity in Tagliamento surface waters, became biorecalcitrant upon irradiation with simulated sunlight.

Regarding the Arctic, Schuur and co-workers (2015)[97] found an exponential increase in microbial DOM mineralization over time following permafrost thawing, which means that the initial decades after thaw will be the most important for greenhouse gas release from thawed soils. This exponential nature of microbial mineralization of DOM from permafrost soils may be explained by UV-induced enhancement of DOM bioavailability in surface waters.[94] Cory and coinvestigators (2013)[94] found that Arctic permafrost DOM was >40% more labile to bacteria after exposure to UV light, compared with the same DOM kept in the dark. From the discussion in this subsection it follows that the coupling of photochemical and biological processes plays a key role for the fate of tDOM in surface waters.

■ CONCLUSIONS

Polar changes affect the climates in the Northern and Southern Hemisphere. Northern Hemisphere weather patterns may be linked to Arctic sea-ice melting.[13,14,18,19,74] On the other hand, interactions between the Antarctic ozone hole and increasing greenhouse gas concentrations in the middle southern latitudes influence weather patterns in the Southern Hemisphere.[23,66−68] Resulting changes in weather patterns include increased frequency and/or intensity of precipitations in some areas of the Earth.[13,14,18,19,23,66,68,72,74] As a result of increased heavy precipitation events and of permafrost thawing, the transfer of terrestrial dissolved organic matter (tDOM) from land to water may increase, both in inland and in coastal waters.[25,26,31,32,34,35,81] In addition to tDOM, also phytoplankton macro- and micronutrients are transported from land to water. However, to include possible effects of changing hydroclimatic conditions on phytoplankton macro- and micronutrient cycling would be beyond the scope of this critical review. Roles of the light-induced redox cycling of the micronutrient iron for CO_2 uptake and release by aquatic ecosystems have been discussed in a recent paper by Sulzberger (2015).[151]

Terrestrially derived dissolved organic matter is subject to UV-induced mineralization, which is an important source of CO_2 in river-dominated coastal systems.[98−100] Additionally, dissolved organic matter draining from thawing permafrost soils is highly photoreactive[25,26] and becomes bioreactive after exposure to sunlight.[94,97] Terrestrial permafrost contains ∼1700 Pg (1 Pg = 10^{15}g) carbon.[149] Schuur and co-workers (2015)[97] estimated that ∼5−15% of the global terrestrial permafrost carbon pool is vulnerable to release as greenhouse gases, mainly as CO_2, during this century, based on the current warming trajectory.

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Environ. Sci. Technol. 2016, 50, 6621−6631

Coupled photochemical and biological mineralization of DOM is expected to be an important process in the Arctic carbon cycle, as the Arctic continues to warm and as permafrost soils continue to thaw.[83] The release of CO_2 from thawing permafrost soils in the Arctic has been proposed as a major positive feedback on global warming.[83,97,149] However, the magnitudes of these feedbacks are not known. In the 2013 IPCC Assessment Report, Ciais and co-workers (2013)[149] state: "... current models do not include the full complexity of Arctic processes that occur when permafrost thaws, such as the formation of lakes and ponds." Although the elucidation of the molecular level mechanisms of light absorption and photodegradation of Arctic tDOM is an active area of research,[25,26,87] there is a need for models that span the range from the molecular to the regional scale. Furthermore, models are needed to describe basin-scale releases of inorganic carbon that result from increased warming and changes in solar radiation at the surface.[25,26] Finally, the magnitudes of UV-mediated positive feedbacks on climate change need to be determined using coupled climate-carbon cycle models.

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Notes

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