



How humans alter dissolved organic matter composition in freshwater: relevance for the Earth's biogeochemistry

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Abstract Dissolved organic matter (DOM) is recognized for its importance in freshwater ecosystems, but historical reliance on DOM quantity rather than indicators of DOM composition has led to an incomplete understanding of DOM and an underestimation of its role and importance in biogeochemical processes. A single sample of DOM can be composed of tens of thousands of distinct molecules. Each of these unique DOM molecules has their own chemical properties and reactivity or role in the environment.

Human activities can modify DOM composition and recent research has uncovered distinct DOM pools laced with human markers and footprints. Here we review how land use change, climate change, nutrient pollution, browning, wildfires, and dams can change DOM composition which in turn will affect internal processing of freshwater DOM. We then describe how human-modified DOM can affect biogeochemical processes. Drought, wildfires, cultivated land use, eutrophication, climate change driven permafrost thaw, and other human stressors can shift the composition of DOM in freshwater ecosystems increasing the relative contribution of microbial-like and aliphatic components. In contrast, increases in precipitation may shift DOM towards more relatively humic-rich, allochthonous forms of DOM. These shifts in DOM pools will likely have highly contrasting effects on carbon outgassing and burial, nutrient cycles, ecosystem metabolism, metal toxicity, and the treatments

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needed to produce clean drinking water. A deeper understanding of the links between the chemical properties of DOM and biogeochemical dynamics can help to address important future environmental issues, such as the transfer of organic contaminants through food webs, alterations to nitrogen cycling, impacts on drinking water quality, and biogeochemical effects of global climate change.

Keywords Dissolved organic matter composition · Climate change · Land use change · Biogeochemical processes · Ecosystem function

Introduction

The movement and processing of organic matter within and among terrestrial, freshwater, and oceanic environments has extensive implications for global climate and carbon (C) cycles (Battin et al. 2009; Tranvik et al. 2009). While organic matter pools in freshwater ecosystems are relatively small compared to the marine pool, omission of freshwater organic matter pools leads to > 25% overestimation in terrestrial net ecosystem production (Aufdenkampe et al. 2011; Butman et al. 2016; Cole et al. 2007). One primary pool of organic matter is dissolved organic matter (DOM), which helps control and is shaped by physical, chemical, and biological aspects of freshwater ecosystems. DOM plays an important role in the global C cycle due to its abundance and through its stimulation of microbial metabolism (Battin et al. 2008). The most common analysis to investigate the

DOM pool is the measurement of its concentration in units of C (DOC), but DOM contains other elements in abundance as well (e.g., O, H, N, S and P). Recent changes in DOC loading reported in freshwater ecosystems reflect global ecosystem change (e.g., Evans et al. 2006). Here we are proposing that DOM is sensitive to global change because DOM pools integrate aspects of ecosystem energy and nutrient flows, landscapes, and climate. These changes in DOC and DOM can in turn affect primary production, biodiversity, fish production, biogeochemical processes, and drinking water quality.

When the journal *Biogeochemistry* was founded in 1985 there were only a handful of studies on DOM composition (Fig. 1). Yet, it has long been recognized that not all DOM is chemically equivalent (e.g., Thurman 1985). Over time, this recognition has been solidified by the different means to assess DOM composition including its age (i.e., time since fixation to an organic state), its average molecular weight and size of its molecules, its biochemical composition such as its free amino acid and simple sugar content, and its content of humified terrestrial-derived plant decay products. There are now a wide range of techniques to characterize DOM, varying in complexity such as elemental content, stable isotopic composition, radiocarbon dating, molecular level classification and spectrofluorometric characterization (e.g., Butman et al. 2012; Jaffe et al. 2008; Massicotte et al. 2017; McCallister et al. 2018; Minor et al. 2014). With these approaches, DOM composition has been described using a plethora of terminology (Table 1). The chemical composition, age, color, and molecular size of DOM also varies as it is transformed by biological,

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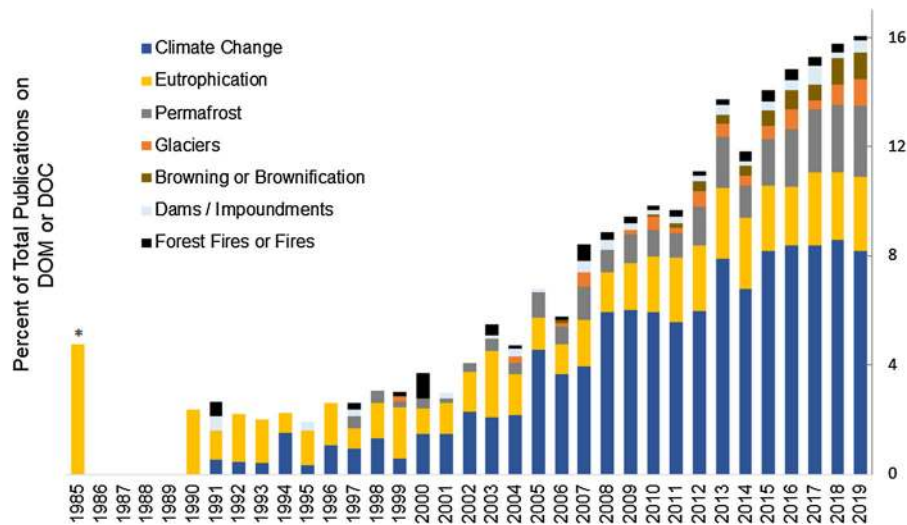


Fig. 1 Evaluation of the percentage of publications with “dissolved organic matter” (DOM) or “dissolved organic carbon” (DOC) and selected global changes over time, starting in 1985, the year *Biogeochemistry* began publishing. Data is

based on searches performed in Web of Science (August 6, 2020). Raw data and search details are available in the supplemental information. *In 1985, 1/25 (or 4.8%) of publications on DOM or DOC were on eutrophication

chemical, and physical processes (Cory et al. 2007; Kothawala et al. 2006). No matter how you slice it, DOM pools echo the health of ecosystems and provide clear signals of how humans have reshaped the Earth’s biogeochemistry.

Considerable uncertainty remains about the processing of freshwater C and its net effect on the ecology and biogeochemistry of lakes and rivers. The nature of chemical changes to DOM is further complicated because this processing is proximally controlled both by the environmental context and by the compositional characteristics of the DOM, such that similar sources processed differently can yield disparate end-products (Moran et al. 2000). Consequently, the source of the DOM and the nature of its processing shape the quantity and quality of DOM present in any freshwater ecosystem at a given time. Across spatial and temporal scales, local scale variation in DOM cycles give way to reliable, long-term DOM quality patterns within biomes and aquatic ecosystems. However, both the dominant sources of DOM to freshwater ecosystems and the environmental conditions under which processing occurs (Fig. 2) have been significantly altered by anthropogenic global changes. The aggregate properties of this DOM are an important indicator of the source and past transformation of this C pool and are a key determinant of current and future ecosystem

processes. While our knowledge of DOM chemistry has progressed rapidly over the past decade, it has not been well integrated into our understanding of C fluxes across landscapes, the ecological functioning of freshwater, and global change.

In the Anthropocene, freshwater ecosystems are experiencing cumulative stress from climate and land use change, among other human impacts. Through connections of river and lake DOM composition to land use, climate and other human activities, recent research discovered distinct DOM pools laced with “human markers and footprints” (Fig. 3). This “human-modified DOM” can in turn profoundly impact the biogeochemical processing and ecological function of aquatic ecosystems (Figs. 2, 4). The various human and natural drivers can also interact with one another and chronically, acutely, and/or synergistically influence DOM composition. Here, we review global changes that can affect DOM composition and in turn impact the transformation and processing of DOM within freshwater ecosystems. We focus on the following extensive global changes: climate change, land use change, nutrient pollution, browning, forest fires and dams. We then present the possible consequences of this variable, “human-transformed” DOM, on the biogeochemistry of freshwater environments.

There is abundant evidence that DOM pools today have been altered by humans. The human impacts on

Table 1 Decoding the DOM composition jargon

Term	What it usually means
Allochthonous, allochthonous-like, terrestrial	Refers to DOM that is derived externally from outside the aquatic ecosystem (e.g., from soils or humified plant material)
Autochthonous, autochthonous-like	DOM that is derived within the aquatic ecosystem produced by microbes, algae or aquatic macrophytes
Aromatic, aromaticity	Property of DOM containing many ring-shaped planar structures that can be measured using a proxy that correlates with proportion of aromatic carbon (e.g., SUVA ₂₅₄)
Aliphatic	Compounds within the DOM pool that are not aromatic
Lignin, lignin-like	Phenolic compound found in terrestrial plants. Some aquatic organisms may contain lignin-like compounds
Humic, humic-like	Chemical class, based on extraction technique or solubility
Fulvic, fulvic-like	Chemical class, based on extraction technique or solubility
Microbial, microbial-like, microbially-derived, protein-like, tryptophan-like, tyrosine-like	Usually refers to DOM that is derived from in situ and whose composition is largely of simple, small, and of proteinaceous compounds
Labile ^a	Easily degraded or easily broken apart through abiotic (e.g., light) and/or biotic transformations
Bioavailable, biolabile	Components of the DOM which are degradable or useable by microbial organisms
Recalcitrant	Not easily degraded, persistent
Refractory	Not degradable
Reactive ^a , reactivity	Usually used to describe abiotic (e.g., light) and chemical effects of DOM (for example DOM acting as a proton and metal ion buffer) but could also be used in reference to biological transformations (e.g., bioreactive)
Chromophoric DOM (CDOM)	Refers to components of the DOM that absorb light or parts of the solar spectrum
Transparent/bleached	Highly photo-processed

In any given DOM sample, one should find components that are “labile” and have very fast turnover rates along with long-lived DOM components that are “recalcitrant”. Because of these different “reactivities”, we have often conceptualized DOM as being composed by a number of fractions and used (sometime confusing) nomenclature to describe the entire DOM pool or the different subcomponents of the DOM. Many of the terms that have been used to describe variable DOM composition are based on the perceived, inferred, or measured properties (recalcitrance, bioavailability, lability, humicity, refractory, aromaticity, size, and/or origin) of the DOM sample

^aSometimes used interchangeably

DOM can be indirect, as in glacial and permafrost thawing and forest fires, or direct as with nutrient pollution, urbanization, agriculture, and dams (Fig. 3). The properties and reactivity of the DOM pool have strong effects on biogeochemical processes, which are mediated by and feedback into the environmental context (physical, chemical, and biological processes; Fig. 2). The environmental impacts of humans are speeding up processes controlling the formation, transformation, burial, and decomposition of DOM. Over the short-term (years to decades), human activities have accelerated terrestrial sourced DOM loading into aquatic ecosystems. Over the long-term (decades

to centuries) human activities provide two contrasting sides: (1) human activities are scattering more stable forms of DOM around the globe in the form of black carbon, formed from incomplete fossil fuel and biomass combustion and (2) human activities are shifting aquatic DOM pools either toward simpler, smaller, and potentially more reactive forms than what is observed in reference “natural” systems, or are increasing the amount of larger more aromatic forms in warmer and hydrologically altered ecosystems. Humans are mixing up aquatic DOM pools and leading to new DOM signatures. At the same concentration, different forms and mixtures of DOM can have

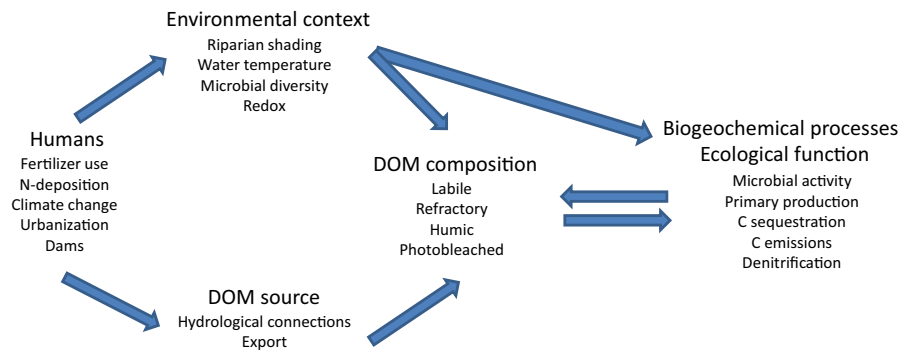


Fig. 2 Flow chart exemplifying how human disturbances can impact environmental context and the source of DOM to inland waters which can potentially shift DOM composition,

biogeochemical processing, ecological functioning, and a feedback back to DOM composition, since altered biogeochemical processing can also result in shifts to DOM composition

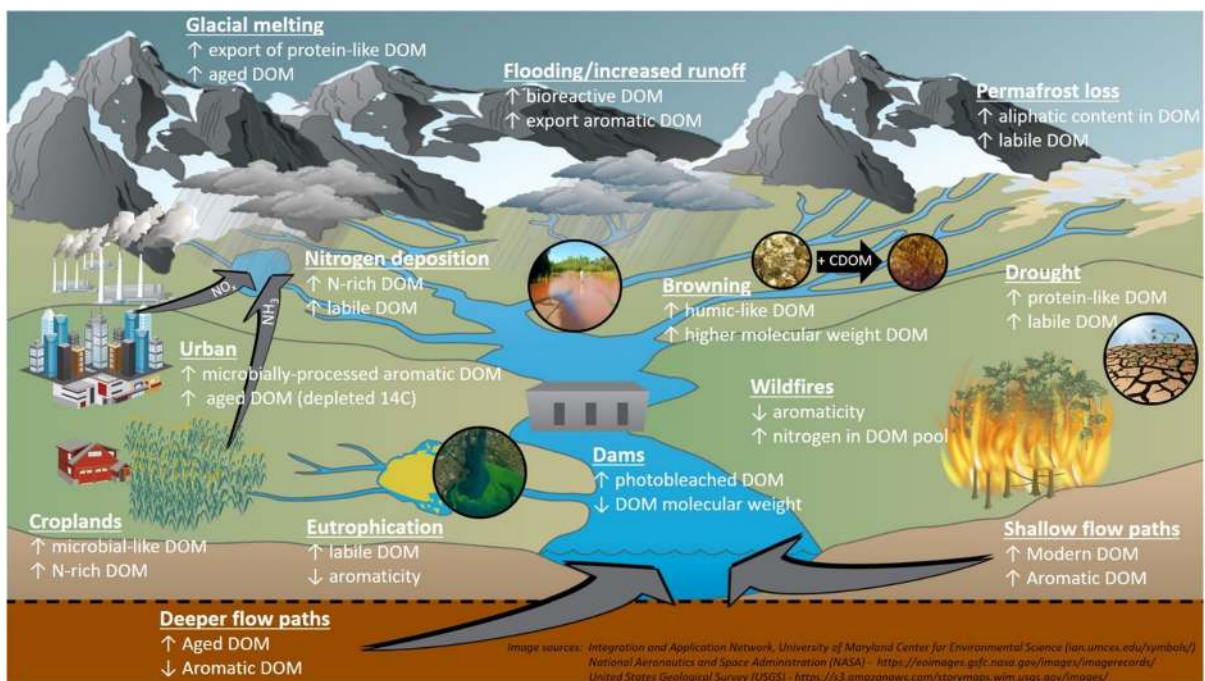


Fig. 3 Selected global changes and associated selected changes to the composition of the DOM pool leading to human fingerprints. These human DOM fingerprints influence biogeochemical processes in differential ways

drastically different effects on C transformations, ecosystem nutrient cycles, ecosystem productivity, metal toxicity, and the treatability of drinking water. Since humans are a major driver of global biogeochemical change, by incorporating human activities into studies of the C cycle and using DOM composition proxies, we can gain a better mechanistic understanding of DOM source, processing, sinks and ultimately the global C-cycle.

Human-dominated landscapes and effects on DOM composition

Across the relatively short-time scale of years, human modified landscapes create novel environmental conditions that alter biological organization and ecosystem functioning in freshwaters (e.g., Fasching et al. 2020), leading to distinct DOM pools and altered fluxes and processing of DOM. Depending on climate, pollution, hydrology, soil properties, the intensity of

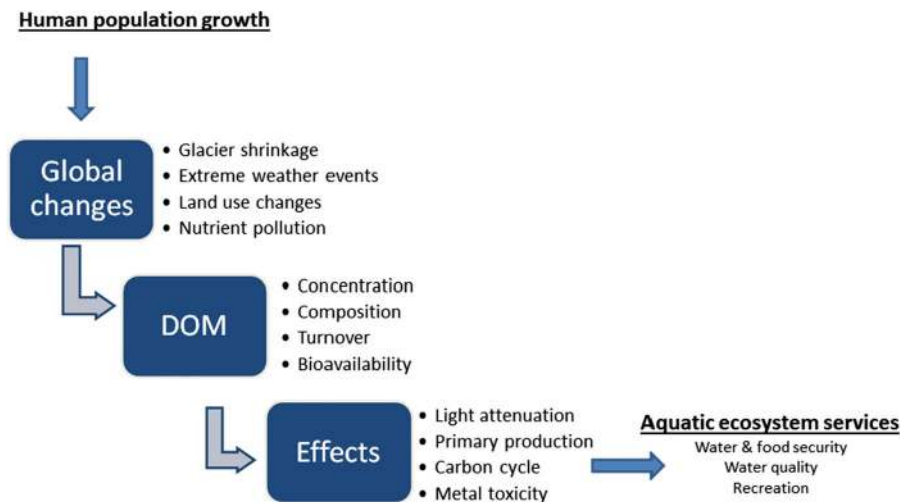


Fig. 4 DOM composition as a sentinel variable that is sensitive to global change. Changes in the DOM pool may significantly alter important ecosystem functions and ecosystem services.

Selected global changes, ecosystem effects and aquatic ecosystem services are shown

human activities, and the extent of natural land covers, human altered landscapes produce DOM pools with diverging characteristics. Human altered landscapes can enrich DOM pools with small-sized, aliphatic, and microbial-sourced components and/or load DOM pools with large-sized, aromatic, and terrestrial-sourced components. Hence, DOM pools are being altered by humans, but the local and regional effects are often context dependent.

Several studies have characterized DOM composition over gradients of land use disturbance. The percent cover of forested riparian areas alters temperature and light regimes through shading (Frost et al. 2006), composition of DOM inputs with differing vegetation and soils disturbance, and rate of groundwater input through increased transpiration (Wilson and Xenopoulos 2013), together placing strong constraints on the rates of photochemical degradation and microbial respiration. Most commonly observed across aquatic systems draining cultivated agricultural landscapes are an increase in microbial-derived DOM, protein-like DOM, and a higher fraction of dissolved organic nitrogen (DON) (Baker and Spencer 2004; Graeber et al. 2019; Lu et al. 2014; Pisani et al. 2020; Williams et al. 2010; Wilson and Xenopoulos 2009). In urban aquatic ecosystems and watersheds with high human population densities, a unique anthropogenic DOM signature has been identified with microbial and autochthonous characteristics (Hosen et al. 2014;

Lambert et al. 2017; Williams et al. 2013, 2016). At the same time, an increase in the average age of DOC (i.e., fossil C) in streams has been observed in anthropogenic landscapes (Butman et al. 2015) because of changes in primary flow paths and loss of organic matter rich surface soils (Barnes et al. 2018; Ekblad and Bastviken 2019; Drake et al. 2019). In contrast, when agricultural activities result in increasing water yield, soil connectivity, surface flow, and DOC export (Graeber et al. 2012) or are associated with grazing animals rather than cropland (Catalán et al. 2013; Shang et al. 2018; Wilson and Xenopoulos 2009), agricultural activities may increase export of modern C (i.e., C recently fixed circa 1950) and high molecular weight material (Butman et al. 2015; Hosen et al. 2014; Lu et al. 2014).

Anthropogenic DOM in human-dominated landscapes is a symptom of the novel chemical cocktails resulting from soil changes, hydrology, light, temperature, nutrient pollution, organic contaminants (e.g., hydrocarbons, pesticides, pharmaceuticals, personal care products), wastewater inputs, and microbial activity (Hosen et al. 2014; Kaushal et al. 2018, 2020; Lambert et al. 2017; McEnroe et al. 2013). Increase in impervious surfaces, soil degradation, and from by-passing of surface flow with subsurface artificial drainage, all typically result in a reduction of aromatic DOM. Afforestation, activities that enhance hydrological connection with organic

matter rich surface soils, and landscape management that leaves crop/vegetation residuals on the land, all typically result in an increase of aromatic DOM. Over the longer term, as landscapes are further degraded by humans and climate change allows for agricultural expansion and intensification, DOM pools will likely resemble anthropogenic rather than natural qualities. Landscape-mediated changes to the DOM pool should ultimately be super-imposed against large-scale changes to landscapes and hydrology resulting from climate change and nutrient pollution (see sections below).

Climate change effects on DOM composition

While considerable attention has focused on the potential changes in DOC loading resulting from a globally changing climate, less is known about whether and how DOM composition will change. Speculatively, some climate change drivers would likely have strong effects on DOM composition in aquatic ecosystems. In particular, the loss of permafrost, and areas of increased precipitation are associated with greater hydrologic connectivity and may receive more terrestrially derived DOM. In contrast, warmer and drier areas may become hydrologically disconnected and eventually be characterized by more internally derived DOM. Further changes in DOM processing factors (temperature, light, and nutrients) and their response to climate change makes simple predictions about how they will alter DOM chemistry challenging. In addition, climate change effects in terrestrial habitats can easily influence the amounts of terrestrial primary production, the quality of litter, water table level, soil temperature and moisture. All of these factors can lead to changes in the quantity and composition of leachable DOM exported from terrestrial systems to inland waters (e.g., brownification see below). Finally, storms and extreme climate events are expected to mobilize the aforementioned anthropogenic chemical cocktails (*sensu* Kaushal et al. 2018), but how this will translate into changes in DOM composition is still emerging. What is clear is that climate change is leading to rapid and large pulses of DOM into aquatic ecosystems, which is shifting the composition and reactivity of the DOM pool.

Changes in precipitation and runoff patterns, floods, and droughts

An increase in flooding and discharge could result in more hydrological connections between C-rich terrestrial ecosystems and downstream aquatic ecosystems and increase DOC export. However, whether such increases in DOC will be of a different DOM composition has only recently been considered (e.g., Fasching et al. 2016, 2019). During extended baseflow conditions (e.g., droughts), DOM inputs derived primarily from groundwater have a more protein-like, biolabile composition (Fasching et al. 2016; Inamdar et al. 2011), with summer low flows linked to the production of in-stream DOM from aquatic primary production (Hosen et al. 2020). The mobile pool of DOM in the soils of most small watersheds is large and usually transport limited. In natural/forested headwater systems during high flow/flood events, higher concentration and export of nutrients and C-rich DOM (higher C:N) with higher molecular weight, and more aromatic DOM properties have frequently been observed (Fasching and Battin 2012; Hood et al. 2006; Nguyen et al. 2010; Vidon et al. 2008; Wilson and Xenopoulos 2009; Wilson et al. 2016). Across agricultural landscapes, flooding events modify DOM composition by disproportionately increasing the export of proteinaceous DOM compared to catchments with relatively more natural land cover (Fasching et al. 2019). In landscapes with very little DOM (e.g., glacial melt, a large snowpack, or rain on impervious surfaces) or where conditions favor flow over or around, rather than through organic rich substrates (e.g., the presence of an ice layer at the soil surface during snowmelt, freshet in big Arctic rivers) initially DOM inputs increase but ultimately dilution of DOM occurs with flow increases (Hornberger et al. 1994; Hood and Scott 2008; Wilson and Xenopoulos 2008). Furthermore, increased overland flow from heavy rainfall, can reduce the contact time with the mineral soils decreasing microbial processing and sorption (Inamdar et al. 2012) and consequently increasing the mobile hydrophilic fraction of DOM exported to streams (Kaiser and Zech 1998). Similar to what is observed around land use, these flood-drought patterns then produce divergent DOM pools depending on hydrologic flow paths, water availability, and soil properties.

Climatic changes may further impact the magnitude, composition and timing of DOM exported to aquatic environments. For instance, most DOC export from terrestrial sources and its downstream transport, takes place during floods (Raymond and Saiers 2010) and during spring snowmelt in northern high-latitude and temperate systems (e.g., Laudon et al. 2004; Spencer et al. 2009). Increased frequency and magnitude of floods due to climate change may cause the temporary depletion of the event transportable terrestrial soil organic C (Butman et al. 2015), while the earlier onset of snowmelt alters the timing of DOM fluxes. Additionally, while reductions in subsurface flow paths through mineral soils remove DOM via sorption, increased overland flow from land use change, can lead to increased export of DOM from the C-rich soil surface (e.g., Hood et al. 2006; Kaiser and Kalbitz 2012). This may consequently increase the mobile hydrophilic fraction of DOM exported to streams (Kaiser and Zech 1998). Altogether, this evidence suggests that in order to predict the impact of humans on DOM composition, we need to understand the hydrology and soil–water connectivity of ecosystems.

The melting of glaciers

Ongoing trends in atmospheric warming, and the reduction in snowfall has led to the shrinking of glaciers globally (Milner et al. 2017). Melting glaciers contribute to the DOM pool in glacial streams and downstream ecosystems. DOM derived from melting glaciers in Alaska has been found to be highly biolabile (Hood et al. 2009) and biogeochemically diverse (Singer et al. 2012). Glaciers accumulate organic C from terrestrial sources, atmospheric deposition and in situ primary production (e.g., Stubbins et al. 2012; Hood et al. 2015; Singer et al. 2012; Smith et al. 2017). Atmospheric deposition can take two forms. The first is anthropogenic aerosols and combustion products which have been detected in glaciers using ultrahigh resolution mass spectrometry and act as a source of pre-aged organic matter (Singer et al. 2012; Spencer et al. 2014; Stubbins et al. 2012). The second form is from N atmospheric deposition, which fuels glacier microbes and leads to autochthonous production that is rich in proteinaceous DOM (Dubnick et al. 2010; Pautler et al. 2012). Ongoing loss of glacial mass implies shifts in the quantity and

composition (Milner et al. 2017; Behnke et al. 2020) of glacial-derived DOM to downstream ecosystems. Continued net glacial melt may initially increase the deliveries of ancient bioavailable DOM to streams, potentially increasing downstream metabolism (Brighenti et al. 2019). As glacial retreat continues, the export of bioavailable DOM may decrease (Huss and Hock 2018), leading instead to the export of ancient stable C (Bardgett et al. 2007), at least until new soil is formed.

Thawing of permafrost

Permafrost soils are expected to contribute to the DOM pool with climate change. In the Arctic, permafrost contains ~ 1700 Pg of organic C, nearly double the amount in the contemporary atmosphere (Schuur et al. 2013; Tarnocai et al. 2009). These permafrost soils have stored organic C frozen in many regions for millennia, and due to ongoing and amplified Arctic warming are projected to release between 41 and 288 Pg-C by 2100 and up to 616 Pg-C by 2300 due to permafrost thaw (Schaefer et al. 2011; Schuur et al. 2013; Zimov et al. 2006). The fate of this liberated organic matter in Arctic fluvial ecosystems remains unclear but despite its ancient age, upon thaw permafrost derived DOM has been shown to be highly biolabile (Drake et al. 2015; Mann et al. 2015; Spencer et al. 2015). High loss of permafrost DOC has been reported in bottle experiments with typically 30–50% loss of DOC in 14–28-day incubations despite the permafrost DOC having radiocarbon ages $> 20,000$ ybp (Spencer et al. 2015; Vonk et al. 2013). Microbial utilization of permafrost DOC in headwater streams may be so rapid that little permafrost derived aged DOC is exported from large Arctic rivers where extensive thaw has been shown (Mann et al. 2015; Spencer et al. 2015).

The high biolability of permafrost DOM is from its unique molecular composition exhibiting a high aliphatic content, and relative enrichment in low molecular weight, saturated, and less-oxidized compounds (Drake et al. 2015; Spencer et al. 2015; Ward and Cory 2015). In comparison to other Arctic surface waters a number of unique molecular formulae have been identified by FT-ICR MS in permafrost thaw streams with relatively high H/C CHO and lower H/C N-containing compounds which are energy-rich and thus highly biolabile (Drake et al. 2018a, b; Spencer

Panel 1. Characterizing the human fingerprint on DOM composition in freshwaters.



Fluorescence coupled with PARAFAC are useful for resolving the unique DOM signature in urban ponds.

Examination of DOM composition in aquatic ecosystems historically incorporated a broad array of measurements including optical (absorbance and fluorescence), bulk chemical, isotopic, and biomarker analyses. Since the turn of the 21st century, due to the low sample volume requirements, ease of methodology, and the relatively inexpensive and high throughput analyses, use of optical measurements has burgeoned, providing insights into the source and reactivity of DOM (e.g., McKnight et al. 2001). Application of standardized statistical techniques such as parallel factor analysis (PARAFAC) and quantitative spectral comparison (OpenFluor) streamlined the interpretation of 3D fluorescence spectra (Stedmon and Bro 2008). In more recent years, advanced analytical approaches including ultrahigh resolution mass spectrometry techniques such as Fourier transform ion cyclotron mass spectrometry (FT-ICR MS) have become more common due to their extreme mass accuracy and precision allowing for assignment of molecular formulae (e.g., Spencer et al. 2019) and thus detailed insights into the DOM pool.

With these rapidly developing methods, a common question prevails regarding the level of redundancy in information generated by these techniques, and the level of complexity required to address most biogeochemical questions. In some cases, tracing changes to the composition of DOM with simple optical parameters can be highly effective; for example, examining the effects of agriculture land use on DOM composition via fluorescence indices (e.g., Wilson and Xenopoulos 2009). In other cases, such as urban ponds (pictured above), complete 3D fluorescence spectra and PARAFAC can be useful to quantify the human signature on the DOM pool. Naturally, to assess if aged DOM has been mobilized from human-dominated landscapes, or to assess how heteroatom content may be changing, analyses such as radiocarbon and FT-ICR MS would be brought to bear (e.g., Butman et al. 2015; Spencer et al. 2019).

Easy-to-measure optical proxies for DOM composition typically link to the more detailed molecular signatures of DOM (Kellerman et al. 2018), but simple proxies may miss detail that is often important for understanding the fate of DOM and its environmental role. For example, observations of the selective processing of DOM during a long-term mineralization study required full fluorescence spectra, changes that would have remained undetected, if based solely on SUVA₂₅₄ (Kothawala et al. 2012). As another example, in Arctic rivers draining from permafrost (pictured right), FT-ICR MS provides clear insights into the unique molecular signatures, particularly high levels of aliphatic compounds that are rapidly utilized by microbes (Spencer et al. 2015).



Permafrost thaw stream rich in aliphatic material and thus incredibly energy rich for microbes.

Striking a balance to improve both spatial and temporal resolution with easy-to-measure analyses, coupled to greater application of biomarkers and more advanced methods will revolutionize our knowledge and understanding of the sources, transformations, and composition of DOM and its effects on the environment.

et al. 2015). Permafrost thaw DOM is rapidly lost via microbial respiration (i.e., Drake et al. 2018a, b) in small stream networks. Concurrent with large inputs of modern DOM, permafrost thaw DOM does not currently persist to be exported by large Arctic rivers, which are therefore dominated by modern DOC export (Raymond et al. 2007; Wild et al. 2019). Moving forward as permafrost thaw continues into deeper layers, studies have suggested even greater biolability as permafrost DOM at depth has been shown to contain even higher relative contributions of aliphatic compounds and low molecular weight organic acids (Ewing et al. 2015; Heslop et al. 2019) ultimately resulting in the transfer of this long-term C store to the atmosphere with ramifications for climate.

Increased nutrient export and deposition impacts on DOM composition

A major aspect of global change involves the alteration to most biologically important elements, which are closely connected to DOM compositional impacts from landscape change and associated human activities. In particular, perturbations to the cycles of N and phosphorus (P) proportionally exceed changes to the C cycle (Rockström et al. 2009). Human land use disturbances through direct fertilizer application, fossil fuel and biomass burning, and/or landscape destabilisation increase N and P loading in freshwaters, potentially leading to eutrophication. These increases in nutrient loading can strongly influence DOM cycling and transformation through altered microbial processing. Increases in algal biomass and resulting hypoxia from eutrophication can also influence DOM composition. Algal-derived DOM has distinct chemistry; it is aliphatic, proteinaceous, rich in polysaccharides, moderately humic with low C:N stoichiometry and low C/H compounds (Cory et al. 2007; Jaffe et al. 2008; McKnight et al. 2001). Hypoxia and anoxia can directly affect the oxidation state of quinones (Fulton et al. 2004) and enhance the re-suspension of aromatic DOM from sediments (Peter et al. 2016). With eutrophication-induced hypoxia, an accumulation of labile DOM derived from surface phytoplankton blooms is expected (Jessen et al. 2017). Hypoxia and anoxia can also lead to changes in DOM composition because of microbial community changes, the inhibition of fauna and microorganisms responsible for remineralization

and the increase of anaerobic processes that favor sulfurization of organic matter (Jessen et al. 2017). The role of redox conditions in both the formation and degradation of organic matter is also an active area of research (e.g., Macalady and Walton-Day 2011).

Atmospheric N deposition from fossil fuel combustion and agricultural activities is a chronic input of reactive N to terrestrial ecosystems that can shift terrestrial productivity, soil organic matter pools and thus water quality. Enhanced N deposition can affect DOM exports by either shifting the composition and stability of soil DOM from changing humification (e.g., Aitkenhead-Peterson and Kalbitz 2005; Whittinghill et al. 2012) or altering the production and consumption of soil organic matter. Elevated N deposition is expected to be associated with mobilization of DOM, but this is predicated on the form of N and the subsequent changes in acidity (Evans et al. 2008). In temperate watersheds, soil N pools increase, and stream DOM tends to become more N rich reflecting a shift in terrestrial processing (Brookshire et al. 2007). Similarly, experimental N additions to grassland ecosystems have resulted in greater soil organic matter bioavailability due to increased soil microbial activity and a larger pool of labile organic matter in surface soils (Fang et al. 2014). Enhanced decomposition rates have also been observed in peat bogs (Bragazza et al. 2006) and temperate forests (Magill and Aber 2000) that are receiving elevated N deposition. These shifts in organic matter processing have led to greater losses of CO₂ from both systems and DOC from peatlands (Bragazza et al. 2006; Magill and Aber 2000). The fate of this exported DOC remains unclear, in some cases it becomes less reactive over time (Findlay 2005) with continued N loading.

Brownification

DOM loads to, and concentrations in many temperate inland waters have been increasing in recent decades, in response to recovery from anthropogenic acidification, climate change, afforestation, and other drivers (Kritzberg et al. 2020; Monteith et al. 2007; Solomon et al. 2015). This phenomenon is often referred to as “browning”. While most of the work on this topic has focused on DOC quantity, there has been less work documenting long-term changes in DOM composition. Jane et al. (2017) examined trends in both the

DOC and DOM composition (as indicated by absorbance-based indices) in seven Wisconsin lakes over 24 years. Their results suggest that trends in DOC and DOM composition may sometimes be decoupled. They observed variable trends in DOC and found that DOM composition varied with a drought severity index, suggesting greater inputs of complex terrestrial molecules during wet periods. In contrast, two other recent studies found more consistent linkages between long-term increases in DOC and a shift towards more complex, terrestrially derived molecular structures (SanClements et al. 2012; Williamson et al. 2015). In general, it is expected that increases in terrestrial DOC loads should shift the DOM pools in inland waters towards a more “terrestrial” composition, including large, humic-like molecules with high molecular weight and aromatic structures (Creed et al. 2018). This shift should be most pronounced where residence time is short and soil organic matter is well connected to hydrologic flow paths. Where residence time is long, biological and photochemical degradation have more opportunity to alter the composition of the DOM pool relative to the DOM inputs and result in the preferential removal of oxidized, aromatic compounds, with greater humic-like fluorescence while more reduced aliphatic, N-containing and protein-like DOM persists (Kellerman et al. 2014; Kothawala et al. 2015).

Forest fires

Although not all forest fires are caused by humans, climate change and agricultural activities have been key factors in increasing the number and extent of wildfires. Changes in vegetative cover and soil properties following fire tend to increase the amount of water exported from a catchment; reflecting decreases in evapotranspiration and increases in surface runoff (e.g., Hallema et al. 2017). These same drivers alter allochthonous C and nutrient inputs and change in-stream conditions and thus organic matter processing. The DOC exported by burned watersheds is a product of C stock combustion during fire and subsequent alterations to organic matter remaining (Rhoades et al. 2019). A large fraction of the charcoal (black carbon) produced by fires is mobilized from soils and transported to the oceans in rivers (Wagner et al. 2018) although decreases in stream DOC from fire (Rodríguez-Cardona et al. 2020) have also been

reported, often associated with fire severity and extent (Rhoades et al. 2019) and degree of landscape recovery (Rodríguez-Cardona et al. 2020).

The composition of stream DOM pools also shifts following fire, reflecting new flow paths and sources of organic matter within the landscape. Lower C:N in burned soils is the result of increased mineralization and nitrification of soil organic matter, increasing inorganic N availability (e.g., Knicker 2007). The associated tightening of C and N cycling results in decreased soil C sequestration and in a greater export of N (Bond-Lamberty et al. 2004; Rhoades et al. 2019) from the combustion of N soil pools and the acceleration of N cycling combined with reduced plant uptake (e.g., Rhoades et al. 2011). Reduced aromaticity of DOM pools with increased burned extent in a slowly recovering landscape reflects the reduction in new organic matter inputs to soil and dominance of microbial-derived, more bioavailable soil organic matter (Barnes et al. personal communication). As landscapes recover, the composition of the DOM pools shifts accordingly, reflecting the increased aromaticity of surficial, relatively organic-rich flow paths (Mann et al. 2012) with higher molecular weight and greater amounts of aliphatic compounds (Rodríguez-Cardona et al. 2020).

River flow alterations, dams, and impoundments

Hydropower and storage dams, in addition to the alteration of river channel morphology, impact stream C dynamics, affecting the storage, transformation and export of DOM from inland waters (Wohl et al. 2017). Dams and impoundments alter river hydrodynamics (mixing of DOM source waters and residence times), influencing the composition and timing of DOM transported to downstream ecosystems. The timing of dam filling/releases, determining DOM residence times and upstream source origins, can determine whether dams act as a source or sink of DOM to downstream ecosystems (Knoll et al. 2013; Kraus et al. 2011). For example, longer residence times and increased opportunity for photodegradation may be associated with export of lower molecular weight (Chen et al. 2016; Kraus et al. 2011) and higher levels of autochthonous DOM (Nguyen et al. 2002). Longer residence times, as well as releases during high flows from dams, result in a shift in peak DOM

concentration from preceding peak discharge, to coinciding with peak stream discharge (Ulseth and Hall Jr. 2015).

While some studies have found that hydropower and storage dams may not significantly alter the DOM composition between upstream and downstream flows in a river (e.g., Nadon et al. 2015), others highlight a significant reduction in downstream DOM bioavailability and shift in DOM composition in terms of aromaticity and molecular weight (Ulseth and Hall Jr. 2015). Tailwaters, located directly downstream of dams have been found to be sites of increased primary production (Davis et al. 2011), leading to increased production and downstream export of autochthonous, and likely biolabile, DOC (Lieberman and Burke 1993; Ulseth and Hall Jr. 2015). Similarly, the removal of natural structures, like established beaver and debris dams, and gravel bars may impact DOM concentration and composition. These structures are associated with export of autochthonous and more processed DOM of high biodegradability and range of reactivities (Catalán et al. 2017), transforming and removing DOM in streams (Boodoo et al. 2020; Findlay and Sobczak 1996). Changes in river morphology and connectivity to their surrounding environment (channelization, impervious riverbeds and embankments, and beaver dams) can have consequences for DOM source, export and biodegradation dynamics within streams (Wohl et al. 2017; Harvey and Gooseff 2015). Decreased residence times and stream-riparian zone hyporheic mixing via river straightening and channelization, leads to decreased opportunity for DOM degradation via in-stream and hyporheic microbial processing (Griffiths et al. 2012). Furthermore, the burial of streams has been linked to lower levels of humic DOM as well as a reduction in DOM complexity and lability (e.g., Pennino et al. 2014; Arango et al. 2017).

Consequences and effects of human-altered DOM on biogeochemical processes

DOM can be highly reactive and strongly affect the functioning of freshwaters. Humans are changing DOM composition, directly and indirectly, with important ecological and biogeochemical consequences that are not yet well understood. The prospects for addressing this research gap is no longer daunting as the scientific community is increasingly

using innovative ways to address biogeochemistry questions with DOM composition proxies. The proxies that can be used vary along a spectrum of complexity between simple optical parameters such as specific UV absorptivity (e.g., $SUV_{A_{254}}$, ϵ_{280}) to more detailed molecular and chemical diversity assessments using ultrahigh resolution mass spectrometry (e.g., McCallister et al. 2018). Each methodology used provides unique insights into different aspects of C dynamics and biogeochemical processes (Panel 1). Below we highlight some of the known consequences of human-altered DOM composition on selected biogeochemical processes and ecosystem services.

The dynamic composition of the DOM pool will impact the global C cycle of inland water

There is now a growing recognition that freshwaters are important modifiers of C. They receive large amounts of C despite their small geographic footprint, sequester organic and inorganic C in their sediments and emit large quantities of C to the atmosphere. DOM composition can influence each of these budget compartments but to date no study has fully integrated DOM composition into local, regional, or global C budgets (Hanson et al. 2015).

Large fluxes of C are exported to inland waters from their surrounding terrestrial environment approximately $5.1 \text{ Pg C year}^{-1}$ (Drake et al. 2018a, b; Raymond et al. 2016), which is processed and transported to downstream ecosystems. In general, DOM pools become more autochthonous-like as one moves along the aquatic continuum from land to oceans (e.g., Larson et al. 2014; Xenopoulos et al. 2017). In addition, increases in the export of autochthonous, bioavailable fractions of the DOM pool are expected in human-influenced ecosystems. For glaciers, the amount of DOC exported ($1.04 \text{ Tg C year}^{-1}$; Hood et al. 2015) is small compared to non-glaciated catchments (Bhatia et al. 2010) but the relatively higher bioavailability of glacier-derived DOM compared to forested, agricultural and wetland dominated catchments (Fasching et al. 2016; Risse-Buhl et al. 2013) supports heterotrophic metabolism in proglacial streams (Hood et al. 2009; Singer et al. 2012; Spencer et al. 2014). It follows that one consequence of an increase in microbial-like, N-rich, aliphatic DOM from human activities is an increase in

microbial metabolism in downstream ecosystems (see below). This increase in microbial metabolism can result into more DOM buried and/or respired and lost into the atmosphere before reaching the ocean. This is complicated by estimates that show that CO₂ emissions from small streams are largely from terrestrial DOM whereas the percentage of CO₂ emissions from autochthonous metabolism increases in large rivers (Hotchkiss et al. 2015).

Changes in the composition of the DOM will likely further lead to changed rates of carbon uptake, retention, and out-gassing in freshwater ecosystems. In relation to out-gassing, DOM composition can impact the relative production of greenhouse gases (CO₂ and CH₄) from freshwaters compared to the amount that is buried in sediment. Several studies have related CO₂ and CH₄ production in freshwaters to DOM composition, with studies linking greater CO₂ and CH₄ production to more terrestrial, aromatic DOM (e.g., D'Amario and Xenopoulos 2015; West et al. 2012; Zhou et al. 2018). However, DOM composition alone is not enough to determine greenhouse gas production and other factors, such as nutrient levels or temperature (e.g., Jane and Rose 2018), also need to be considered. For example, eutrophic lakes with more autochthonous and less humic DOM were associated with CO₂ influx at high phytoplankton biomass and lakes with high amounts of N and more wetland cover were associated with CO₂ efflux (Morales-Williams et al. 2020). Nonlinearity may further complicate the relationships between DOM composition and C emissions (D'Amario and Xenopoulos 2015).

Among the primary factors influencing the loss of DOM is water residence time, with a general negative relationship between organic C degradation rates and water residence time across different types of freshwater ecosystems (Catalán et al. 2016). DOM composition plays a role as components with higher molecular weight and longer emission fluorescent wavelengths (i.e., DOM with more oxidised polyphenolic aromatic compounds with low H:C) have been found to degrade faster than DOM fluorescing at shorter emission wavelengths (i.e., DOM with more aliphatic and enriched in N-containing compounds; Kellerman et al. 2015; Köhler et al. 2013; Kothawala et al. 2014). This leads to a progressive loss of color with longer water residence time, which corresponds to losses in the terrestrial-like properties of DOM

(Köhler et al. 2013; Weyhenmeyer et al. 2012). With climate change, areas which will experience lower precipitation and lower resulting runoff (thus longer water residence time) could be expected to have lower degradation rates but still degrade a larger portion of incoming terrestrial DOM (Catalán et al. 2016; Jones et al. 2018), potentially resulting in the prevalence of DOM with lower fluorescence and molecular weight, and more N-containing aliphatic compounds. On the other hand, in regions with predicted runoff increase with strong soil–water connectivity (i.e., wetter, thus shorter water residence time) degradation rates will be faster and we will find an apparent increase in terrestrially derived, aromatic DOM.

Sediment burial and storage of organic matter is also affected by DOM composition. Freshwater sediments have accumulated large quantities of organic C during the Holocene (Tranvik et al. 2009; Mendonça et al. 2017a, b) and DOM characteristics change with depth (Xu et al. 2016). The C buried in the sediments is mainly comprised of flocculated DOM compounds of terrestrial origin (Von Wachenfeldt and Tranvik 2008), as autochthonous DOM present in settling particles are preferentially degraded before burial (Guillemette et al. 2017). DOM flocculation may be stimulated by sunlight (von Wachenfeldt et al. 2008) but is also mediated by bacterial respiration (von Wachenfeldt et al. 2009) and in both cases, colored DOM appears as the main precursor of the flocs. Another major contributor to floc formation is the presence of transparent exopolymer particles (Grossart et al. 1998) which are usually related to phytoplankton (de Vicente et al. 2010), but also highly correlated to aromatic and terrestrial DOM (Attermeier et al. 2019).

Carbon sedimentation is affected by the potential of DOM to adsorb onto inorganic surfaces (Kothawala et al. 2012). Although adsorption also depends on the sorbent and the water chemistry, DOM composition analyzed by different spectroscopic methods show that highly aromatic DOM compounds are preferentially adsorbed, whereas a high degree of saturation reduces DOM's susceptibility to adsorption (Groeneveld et al. 2020; Kalbitz et al. 2005; Kothawala et al. 2012). Finally, once buried, lakes with highly aromatic and terrestrial DOM are negatively correlated with sediment bacterial metabolism, while in lakes with significant autochthonous DOM production, mineralization is higher (Gudasz et al. 2012). An increase of

aromatic DOM in aquatic ecosystems (e.g., through soil erosion, floods) may initially stimulate preferential adsorption, flocculation, and preservation of C of terrestrial origin and may therefore result in greater C sequestration initially. However, increased inputs of nutrients into aquatic ecosystems leads to more microbial-like DOM, which while also having high burial rates (e.g., Heathcote and Downing 2012; Mendonça et al. 2017a, b), is more prone to be preferentially metabolised and lost from sediments. Finally, these eutrophic ecosystems, prone to anoxia, lead to an increase in CH₄ emissions (Mendonça et al. 2017a, b), effectively resulting in very little of autochthonous freshwater DOM being transported to the oceans (Regnier et al. 2013).

The heterogeneous nature of the DOM pool will influence aquatic metabolism, microbial biogeochemistry and food webs

Heterotroph and autotroph microbes mediate global biogeochemical cycles through their metabolism by using and producing the heterogeneous mixture of compounds that constitute DOM. DOM fuels the majority of in-stream and in-lake microbial processes which is dictated by the timing and composition of DOM fluxes (e.g., Battin et al. 2008; Williams et al. 2010). Typically, biolabile DOM fuels heterotrophic metabolism (e.g., Kaplan and Bott 1989) and high concentrations of protein-like DOM and dissolved free amino acids found in human-dominated catchments are often associated with high biological activity in surface waters (Duan and Bianchi 2007; Williams et al. 2010, 2013; Yamashita and Tanoue 2003). Beyond the microbial food web, DOM composition can also affect primary and secondary producers, and fish (e.g., Creed et al. 2018).

Specific DOM constituents can determine microbial community composition, microbial function and DOM degradation processes (Logue et al. 2016; Osterholz et al. 2016). Distinct microbial functions have been correlated with more biolabile, less complex, protein-like DOM, and nutrients in agricultural landscapes, likely reflecting functional adaptation to biolabile DOM and higher nutrient inputs (Fasching et al. 2020; Ruiz-González et al. 2015; Wilhelm et al. 2014). Accordingly, functional diversity was found to be reduced in these agricultural landscapes (Fasching et al. 2020), while increased litter inputs to the littoral

sediment translated into greater DOM chemical diversity and was associated with higher microbial diversity and function (Tanentzap et al. 2019). However, the links between individual DOM constituents and the metabolic potential of the microbiota remain poorly understood. The identification of such links might improve our understanding of how changes in the concentration of certain compounds in response to anthropogenic and climatic drivers will impact the microbial community composition and function.

DOM composition influences both the primary production and respiration terms of ecosystem metabolism. Primary production in lakes is controlled not only by the magnitude of DOC loads, but also by their specific light absorptivity and nutrient:C stoichiometry (Bergström and Karlsson 2019; Kelly et al. 2018; Olson et al. 2020). DOM composition also interacts with water residence time and lake thermal structure to control rates of ecosystem respiration (e.g., Berggren et al. 2010; Jones et al. 2018; Mostovaya et al. 2016). Slightly different patterns exist for temperate streams dominated by colored, aromatic, terrestrial-derived DOM and higher ecosystem respiration compared to semi-arid streams dominated by protein-like DOM (Catalán et al. 2018). The response of ecosystem respiration to DOM composition is likely complicated by the simultaneous effects of other variables (e.g., temperature) and appears to be nonlinear (Jane and Rose 2018).

The chemical composition of the DOM pool can modify nutrient cycles

The stoichiometry of DOM to nutrients plays a crucial role in regulating nutrient cycling (Berggren et al. 2015; Stutter et al. 2018; Yates et al. 2019). The DON and DOP contributions to the DOM pool are dependent on its source and composition (Pisani et al. 2020; Yates et al. 2019) and have been shown to be positively correlated to DOM bioavailability (Jansson et al. 2012; Pisani et al. 2017; Thompson and Cotner 2018). The amount of bioavailable material can range from 10 to 70% of riverine DON (Pisani et al. 2017) and 0 to 90% of DOP (Li and Brett 2013) with quantities dependant on inputs and sources of terrestrial runoff and photodegradation processes (Moran and Zepp 1997).

Changes in DOM composition will likely affect the bioavailability of N and P in aquatic ecosystems but

the factors influencing mineralization and bioavailability of elements associated with DOM (N, P, and S) remains unclear. One important role of DOM in nutrient cycling is its use as a microbial substrate for the removal of reactive N (nitrate) via denitrification. In one stream study, denitrification rates were positively related to protein-like fluorophores and negatively related to more aromatic and oxidized fractions of the DOM pool (Barnes et al. 2012). In north Florida rivers, terrestrial-derived DOM has been shown to indirectly inhibit denitrification rates via decreased autochthonous production (Fork and Heffernan 2014). In hyporheic zones, biolabile DOC supply limits denitrification (Zarnetske et al. 2011). Although few studies have directly linked DOM composition with denitrification rates, it is expected that a shift in DOM composition towards microbial-derived, low molecular weight material brought about by changes in land use may ultimately increase the microbial processing and utilization of N. Indeed, in catchments with high urban and agricultural land use, increases in DOM concentration and nutrient richness have affected both autotrophic and heterotrophic pathways of nutrient processing (Stutter et al. 2018; Juckers et al. 2013).

DOM plays a role in the transport and toxicity of metals and this varies based on its chemical composition

DOM is a complexing agent in natural waters, plays a role in the transport of metals and hydrophobic compounds (e.g., pesticides) and as such is an important factor mitigating water-borne metal toxicity. Toxicity measures (e.g., LC50) vary substantially among different DOM sources even for similar DOC concentrations (e.g., Haitzer et al. 1998; Conine et al. 2017). DOM properties measured using fluorescent fractions explain considerable variability in the protective effects against metal toxicity (e.g., Al-Reasi et al. 2012). DOM can alleviate metal toxicity differentially and both DOM composition and DOC should be considered in studies of metal toxicity.

The role of DOM in metal toxicity is best known for how it regulates mercury (Hg) dynamics. DOM composition plays an important role on the regulation of Hg bioavailability and the formation of the toxic methylmercury (MeHg) (Kim et al. 2011; Schartup et al. 2013). Organic compounds act as an electron donor during bacteria-mediated methylation and therefore

DOM composition strongly affects the process (Bravo and Cosio 2020). Accordingly, in sediments from boreal lakes, phytoplankton-derived organic compounds enhanced methylation rates mediated by an increase of bacterial activity (Bravo et al. 2017). Similar results have been found in ponds, where higher methylation rates have been related to newly exported humic DOM substances and an increased production of algal-derived organic matter triggered by enhanced nutrient availability (Herrero Ortega et al. 2018) and in rivers, where autochthonous DOM was linked to higher total % of MeHg in water (Bravo et al. 2018). However, methylation rates and concentrations of MeHg are not necessarily coupled, thus in lakes dominated by terrigenous organic matter inputs the main source and driver of MeHg concentrations are in catchment sources (Bravo et al. 2017). In rivers, total Hg concentrations have been linked to streams with highly terrestrial soil-derived DOM (Bravo et al. 2017). Taken altogether, while increases in terrestrial DOM might translate into inputs of MeHg in freshwaters, increases in autochthonous and freshly exported DOM might lead to increases in methylation rates in freshwaters.

DOM composition is related to ease of treatability for drinking water utilities

The combined effects of land use change, human activities, and climate change on DOM pools pose a challenge to the production of affordable, safe, and reliable drinking water (e.g., Gagliano et al. 2020; Solomon et al. 2015). The quantity and composition of DOM in raw and finished drinking water can contribute to poor taste, odor and color, as well as the formation of potentially carcinogenic halogenated by-products (Lavonen et al. 2013, 2015; Williams et al. 2019). To avoid these problems a variety of methods are used to remove DOM from drinking water (Matilainen et al. 2010), and new methods are being developed such as granulated or powdered active carbon, anion exchange resins, and membranes of different pores sizes to remove DOM with more hydrophobic and aliphatic properties.

The efficiency with which drinking water plants can remove DOM from water supplies is variable, and depends not only on the methods employed, but also on the composition of the DOM and on other chemical and biochemical characteristics of the water. Thus, understanding the composition of the DOM can be important

for supplying quality drinking water. The level of complexity at which the DOM composition needs to be characterized seems to be related to the kinds of human impacts that influence the water supply. When the human impact is browning, simple measurements of SUVA may be sufficient, with $SUVA > 4$ suggesting high removal efficiency and $SUVA < 2$ indicating DOM difficult to remove by coagulation and flocculation (Edzwald and Tobiason 1999). When the human impact is something like eutrophication or urbanization, more complex characterization of the DOM may be necessary. Typically, the most difficult to remove DOM is colorless and hydrophilic from algal and microbially-derived DOM produced within aquatic ecosystems (Liao et al. 2017), rather than the darker DOM that is of terrestrial origin (Golea et al. 2017; Lavonen et al. 2013; Yang et al. 2015). During algal blooms, in systems with higher levels of autochthonous DOM (i.e., low SUVA), and/or with chloramine treatments, N-containing and regulated by-products can be produced above what are considered safe levels even when ambient DOC are low (e.g., Golea et al. 2017; Lavonen et al. 2013; Liao et al. 2017; Yang et al. 2015).

From a societal perspective, there is a growing need to continuously monitor DOM quality in source water with techniques such as absorbance and fluorescence. To effectively remove organic contaminants from drinking water an increased knowledge of the complexity and composition of the DOM pool is needed. In eutrophic systems a molecular level understanding of the source and treated-water DOM pool are necessary to effectively remove both aliphatic DOM and cyanotoxins (Merel et al. 2013; Westrick et al. 2010). Detailed DOM characterization is also useful for identifying compounds in source water with the potential to form harmful disinfection by-products (Beggs and Summers 2011; Lavonen et al. 2013). Finally, a more thorough examination of DOM characteristics may be useful for the development of early warning indicators able to detect the contamination of drinking water with wastewater (Stedmon et al. 2011).

Concluding thoughts

There is a growing opportunity to use advanced chemical techniques to study DOM composition and gain a better mechanistic understanding of DOM

sources and its processing in the environment. Striking a balance between studies that consider simple C fluxes to those that use easy-to-measure DOM composition analyses, with greater application of advanced molecular methods to better recognize underlying mechanisms will revolutionize our knowledge and understanding of the sources, transformations, and composition of DOM, its role in the global C cycle and its effects on the environment (Panel 1).

Using information on detailed DOM composition will allow us to predict and better prepare for future global changes. For example, with prolonged drought and increases in the amount and severity of forest fires, post-fire aquatic DOM will be more N-rich and higher in carbohydrate content. Similarly, in regions that become too arid and experience desertification an increase in microbial-like DOM is expected due to the loss of hydrological connections. In both scenarios and based on current observations and short-term trends, the evidence suggests DOM pools of the future will not look like what they look like today. This human derived DOM cocktail will be rich in aliphatic, polysaccharide, and N-containing compounds, but poor in the humic, aromatic, terrestrial produced compounds found in more natural DOM pools. This will increase DOM photoreactivity in aquatic ecosystems, reduce the amount of carbon buried in aquatic ecosystems, and shift how DOM is processed from the land to the ocean.

Climate change, alterations of the landscape and other global changes can impact biological, physical, and chemical properties of ecosystems. Together, these changes interact, often in nonlinear ways (e.g., D'Amario et al. 2019), to alter DOC and DOM composition, trigger significant changes to freshwater ecosystem function and, relatedly, the services they provide (e.g., nutrient cycling, primary production, provision of clean water). Advances in aquatic biogeochemistry have now made it possible to tackle questions on the effects of human population growth using DOM composition proxies so that the underlying principles in biogeochemistry can be applied to emerging global changes. But with human population growth also comes a greater detection of a human-laced DOM signature. We may be quickly losing opportunities to understand the dynamics of DOM in pristine environments. There are also very few studies examining long-term changes in DOM composition, an important undertaking to accurately document the effects of global change (Xenopoulos 2019).

DOM characterization is changing rapidly and being applied to a greater range of biogeochemical questions. New approaches to better examine DOM composition are continuously being developed and rapidly changing our view of its chemistry and reactivity in the environment. Signals of human-induced changes in the composition of DOM using multiple proxies can be used to gain a better mechanistic understanding of DOM sources, processing and sinks in the environment. The results emerging from the advancing field of DOM characterization are provoking a reconsideration of the conceptual approach to DOM in biogeochemistry.

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Data availability Data for Fig. 1 is available in the supplementary information.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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