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DOM in the long arc of environmental science: looking back and thinking ahead

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Abstract Dissolved organic matter (DOM) is a heterogeneous mixture of organic compounds that is produced through both microbial degradation and abiotic leaching of solid phase organic matter, and by a wide range of metabolic processes in algae and higher plants. DOM is ubiquitous throughout the hydrologic cycle and plays an important role in watershed management for drinking water supply as well as many aspects of aquatic ecology and geochemistry. Due to its wide-ranging effects in natural waters and analytical challenges, the focal research questions regarding DOM have varied since the 1920s. A standard catchment-scale model has emerged to describe the environmental controls on DOM concentrations. Modest concentrations of DOM are found in atmospheric deposition, large increases occur in throughfall and shallow soil flow paths, and variable concentrations in surface waters occur largely as a result of the extent to which hydrologic flow paths encounter deeper mineral soils, wetlands or shallow organic-rich riparian soils. Both production and consumption of DOM occur in surface waters but appear to frequently balance, resulting in relatively constant concentrations with distance downstream in most streams and rivers. Across biomes the concentration and composition of DOM in flowing waters is driven largely by soil processes or direct inputs to channels, but high levels can be found in streams and rivers from the tropics to the poles. Seven central challenges and opportunities in the study of DOM should frame ongoing research. These include maintaining or establishing long-term records of changes in concentrations and fluxes over time, capitalizing on the use of sensors to describe short-term DOM dynamics in aquatic systems, integrating the full carbon cycle into understanding of watershed and aquatic DOM dynamics, understanding the role of DOM in evasion of greenhouse gases from inland waters, unraveling the enigma of dissolved organic nitrogen, documenting gross versus net DOM fluxes, and moving beyond an emphasis on functional ecological significance to understanding the evolutionary significance of DOM in a wide range of environments.

Keywords Dissolved organic matter · Dissolved organic carbon · Dissolved organic nitrogen · Watershed · Inland waters · Carbon budget · DOC · DON

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DOM and its role in inland waters and watersheds

Structure

Dissolved organic matter (DOM) is a heterogeneous mixture of organic compounds that is produced by a

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wide range of biological and physical processes. Initial assessment of the composition of DOM in surface waters was based on bulk analysis of evaporated residues into fractions such as protein and carbohydrates (Birge and Juday 1926, 1934), the analysis of specific functional groups such as monomeric and polymeric carbohydrates using wet chemical approaches (Burney and Sieburth 1977), optical properties from which structure is inferred (Coble et al. 1990; McKnight et al. 2001), and various approaches to mass spectrometry such as FT-ICR MS (Stubbins et al. 2010) and TIMS-FT-ICR MS/MS (Levya et al. 2020). Many different analytical approaches to understanding the structural and compositional characteristics of DOM are currently in use (Minor et al. 2014; Nebbioso and Piccolo 2013), but no single method provides a complete accounting of the molecular structure of the entire DOM pool. Most characterization of DOM focuses on smaller molecules (< 1000 daltons), yet ultrafiltration suggests that the total DOM pool is dominated by material > 1000 daltons (e.g. Cole et al. 1984). The composition of dissolved organic matter can also be expressed as the elemental content of its bulk constituents, in particular the concentrations of dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and dissolved organic phosphorus (DOP). These bulk analyses provide a stoichiometric description of the entire pool of DOM, rather than the composition of individual compounds or structures. The stoichiometry of DOM can vary dramatically in response to environmental conditions, with the DOC:DON ratio in stream water, for example, nearly doubling across watersheds with a wide range of soil C:N (Yates et al. 2019).

Assessment of the structure/composition of DOM has typically been driven by its potential utility as a means of tracking the sources, or quantifying the lability, of DOM. One of the earliest classifications of DOM structure involved quantifying the humic and fulvic acids in surface waters, which provided insights into the mechanisms by which DOM enhances pollutant solubility (Chiou et al. 1986). More recently, the physical separation of DOM into hydrophilic and hydrophobic fractions has provided insights into the transport of DOM through watersheds and its microbial lability (Wickland et al. 2007). Quantification of optical properties beyond color (e.g. $SUVA_{254}$, which generally reflects the aromaticity of DOM; Weishaar et al. 2003) has been used to assess sources and potential lability of DOM. A wide range of fluorescent properties has been used to characterize sources and flow paths of DOM through watersheds (Fellman et al. 2010) and monitor changes in DOM over time (Jaffé et al. 2008). The presence of combustion products (e.g. benzenepolycarboxylic acids) in DOC has been used to quantify the contribution of "black carbon" produced by wildfires to riverine DOC loads (Jaffé et al. 2013; Wagner et al. 2018). Monitoring of specific organic compounds such as geosmin has been used to quantify the contributions of organic matter to objectionable odors in water supplies (Ridal et al. 1999). In short, an extremely wide range of techniques has been used to characterize the naturally occurring dissolved organic matter in freshwaters, with the analytical approach dictated by the fundamental research question being addressed.

Ecological and environmental significance

Dissolved organic matter is found throughout the hydrologic cycle, with measurable concentrations in precipitation, throughfall, soil solution, groundwater, surface waters, estuaries and the ocean. Microbial degradation of organic matter such as terrestrial foliage, aquatic detritus, or soil organic matter are all potentially important sources of the DOM in aquatic ecosystems (e.g. Hernes et al. 2017). Release of DOM by autotrophs is also known to occur widely, from forest canopies in throughfall (McDowell et al. 2020), exudation by roots (Chen et al. 2017), and extracellular release by algae (Mueller et al. 2016). Abiotic leaching of solid phase organic matter (leaf litter, soil organic matter, aquatic detritus) also occurs and can be a significant flux of DOM in aquatic ecosystems (McDowell and Fisher 1976).

The effects of DOM in aquatic ecosystems have been addressed for well over a century, beginning with the large and obvious impacts of the dissolved and particulate organic matter in raw sewage on river oxygen levels (e.g. Mason 2002). These initial concerns associated with sewage treatment are important for public health policy but will not be considered in detail here. Lakes high in DOM have been classified separately since the early 1900s (Hansen 1962) and have frequently been termed "dystrophic" in recognition of the fact that the brown-colored water in these lakes profoundly affects lake biology. DOM in lake waters alters thermal structure and light penetration,

with implications for lake productivity and habitat quality (Rose et al. 2009). The light-absorbing properties of DOM also result in attenuation of UV-B radiation, with important implications for plankton communities (Williamson et al. 1996). DOM is widely known to chelate trace metals, such as copper and aluminum, that may otherwise pose hazards to aquatic biota if they remained in their inorganic, unchelated form (Driscoll et al. 1980). Conversely, DOM chelation of iron enhances iron uptake by cyanobacteria when iron is present at low concentrations, and reduces photosynthesis by algal competitors (Murphy et al. 1976). DOM can serve as both an energy and nutrient source for microbial food webs (Tanentzap et al. 2017). This dual function of DOM is particularly well studied for DON, which responds to both N and C additions in streams (Lutz et al. 2012; Wymore et al. 2015). The chemical reactivity of DOM, in particular the N-rich fraction measured as DON, also plays a dominant role in determining the extent to which disinfection byproducts are produced upon chlorination of drinking water supplies (Dotson et al. 2009).

Research focus in different eras

Over the past century the focal topics and research approaches used to understand DOM dynamics in inland waters have varied dramatically. Initial research largely focused on the yellowish water color that is characteristic of many high-DOM lakes, with analysis by photometer. Termed "Gelbstoff" (yellow matter) in the 1930s, the emphasis in the marine science community was on understanding how riverine and open ocean sources contributed to this organic matter pool (reviewed by Kalle 1966). With the advent of several methods of chemical oxidation, emphasis on DOM dynamics shifted from a focus on light penetration and dystrophy to organic matter dynamics (DOM by dichromate oxidation and titration; Maciolek 1962). With the seminal publication of a method for wet chemical oxidation by persulfate (Menzel and Vacarro 1964) that allowed quantification of DOC, research emphasis shifted more to understanding DOC dynamics rather than those of DOM. This research emphasis on DOC was accelerated by development of various high temperature catalytic oxidation techniques, which ultimately allowed analysis of both DOC and TDN (Merriam et al. 1994). Large numbers of papers in the 1980s and 1990s documented DOC dynamics in various aquatic and terrestrial ecosystems as well as the ocean (McDowell and Likens 1988; Hansell and Carlson 1993; Kalbitz et al. 2000), which has resulted in an explosion of interest in DOC across a wide range of research communities. In the journal Limnology and Oceanography, for example, a virtual special issue assembled in 2016 shows that the top 5 most cited papers published from 2010–2015 were dominated (3 of 5) by those with a significant focus on DOC or DOM (Fellman et al. 2010; Stubbins et al. 2010; Williams et al. 2010). With the advent of remote sensing of water color, refinement of optical proxies to infer molecular structure and composition (e.g. $SUVA_{254}$ and fluorescence excitation-emission spectroscopy), and multiple approaches to direct chemical analysis of molecular structure such as FT-ICR MS, the DOM research community is vast, with echoes of each of these earlier eras still present in current research.

Unified model for DOM production and transport from mountains to the sea

After decades of study a standard catchment-scale model has emerged to describe the environmental controls on DOM concentrations as water moves through terrestrial ecosystems and across the terrestrial-aquatic interface into surface waters. Modest concentrations of DOM are found in atmospheric deposition, large increases occur in throughfall and shallow soil flow paths, and concentrations decline dramatically with depth in the mineral soil (McDowell and Likens 1988; Qualls and Haines 1991). Variable concentrations in surface waters result from the extent to which flow paths encounter deeper mineral soils versus organic-rich riparian soils (Fig. 1). This unified model has been invoked to explain variability between watersheds in the steep, well-drained Hubbard Brook Experimental Forest in New Hampshire USA (McDowell and Likens 1988), variation in DOC concentrations between high- and low-permafrost watersheds in Alaska (MacLean et al. 1999), and the high DOC that is found in wetland-dominated watersheds, which by definition have near-surface flow paths (Moore 2003). Recent work in boreal Sweden shows that riparian zones can be a major source of stream DOC (Fork et al. 2020), but in many other

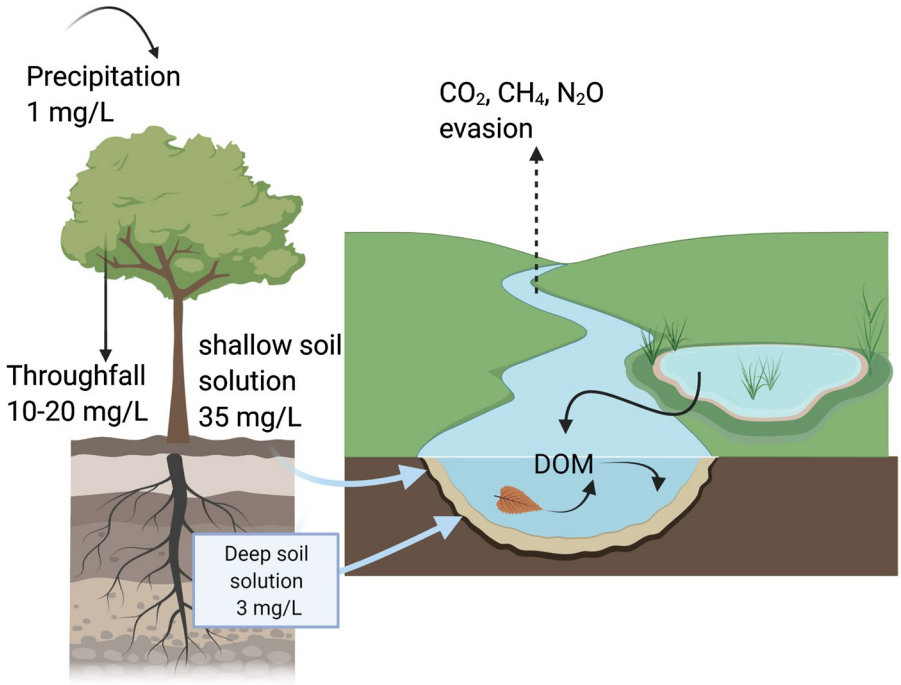

Fig. 1 Unified model of DOM flux from mountains to the sea. Values for concentration are mg/L DOC. Created with Biorender.com

watersheds stream DOC reflects the concentrations found in soil solution of upland mineral horizons rather than shallow, organic-rich riparian horizons (McDowell 1998; Qualls and Haines 1991). Across biomes the concentration and composition of DOM in flowing waters is driven largely by soil processes, but high concentrations can be found in streams and rivers from the tropics to the poles (Aitkenhead and McDowell 2000). The composition of DOM in surface waters, as well as its concentration, can also be dictated by soil processes. Qualls and Haines (1991) showed clear differences in the sorption behavior of different fractions of DOM, a conclusion further verified by Kaiser et al. (2004) and subsequent papers.

Although decades of study support the contention of McDowell and Wood (1984) that soil processes control stream and river DOM at the landscape scale, it is equally clear that both production and removal of DOM also occur within the channel itself (Lock and Hynes 1976; McDowell and Fisher 1976) through some combination of abiotic sorption (McDowell 1985; Groeneveld et al. 2020); biotic uptake (Fellman et al. 2009); or photodegradation (Cory et al. 2014). Because DOC is relatively constant in concentration with distance downstream in most drainage networks beyond the smallest tributaries (e.g. Coble et al. 2019) the rates of in-channel production and consumption of DOM thus appear to be in balance, or of small magnitude. This results in a fundamental conundrum: the rates of DOC uptake (as fraction removed per time; *Vf*) for specific organic compounds such as acetate are much higher than those that appear to be occurring in situ for bulk DOC in stream channels (Mineau et al. 2016). Thus, one might expect that labile inputs of organic matter will have exceedingly short half lives in streams, and the remaining DOM pool is composed of relatively refractory materials.

Current opportunities and challenges

Long-term records

Because DOM can alter food webs, thermal structure, and other aspects of inland waters, documenting the trajectory of DOM over time is essential for understanding the ecology of inland waters in a changing world (Kritzberg et al. 2020). Various assessments have documented long-term increases in DOC in northern hemisphere lakes, running waters and remote ponds in response to improved air quality and decreased atmospheric deposition of many solutes

(e.g. Monteith et al. 2007; Hruška et al. 2009; Nelson et al. 2021). Recent work also shows that the nitrogen-rich fraction of DOM (DON) often behaves differently over time than does DOC (Rodríguez-Cardona et al. 2021). In addition to documenting the "press" effects of potential drivers such as temperature, CO_2, and atmospheric deposition, long-term records are also essential for understanding the impacts of significant "pulse" events such as wildfires, which for example have been shown to reduce stream DOC concentrations for up to 10 years in continuous permafrost terrain (Parham et al. 2013).

Inclusion of DOC, DON and DOP in biogeochemical analysis of long-term study watersheds is crucial to understanding the drivers of change in DOM concentrations. Monitoring of stream and river chemistry without also understanding the role of watershed processes in driving change will limit the ability to generalize across sites and regions. Broad international networks such as the Critical Zone Observatory network or International Long-Term Ecological Research network (Brantley et al. 2016; Mirtl et al. 2018) provide excellent opportunities to link understanding of watershed-scale processes to changes in DOC and DON, but maintenance of the networks themselves is essential. The U.S. experience with Critical Zone Observatories, which were originally established as long-term sites but were disbanded after little more than a decade, speaks to the difficulty in maintaining long-term sites that can capture important biogeochemical changes occurring over decades. Without such networks, it will be very difficult to understand when, where, and why DOC concentrations are increasing, and whether the increases will continue for decades, will plateau, or will return to some lower "baseline" level after reaching peak levels.

Short-term dynamics: capitalizing on the use of sensors in aquatic systems

Optical sensors provide an unparalleled opportunity to expand understanding of controls on DOM in inland waters, as DOM concentrations can now be followed in rivers through the entire hydrograph at the same frequency as discharge. Because the optical properties of organic matter (absorption or fluorescence) provide only proxies for concentrations of DOC, DON and the structural properties of DOM, the sensors must be coupled with direct measurements. Directly coupling data from in situ fluorescent sensors with full laboratory-based excitation-emission scans (EEMS) shows that the in situ sensors provide as good a proxy for DOC and DON as any of the commonly proposed optical metrics for DOM, with consistently better predictions of in situ DOC concentrations than DON concentrations (Wymore et al. 2018; Fig. 2). Furthermore, the relationship between optical properties and DOC can vary dramatically in streams across a region. For example, Wymore et al. (2018) found that most streams draining largely forested watersheds in New Hampshire had DOC concentrations that could be predicted reasonably well by fDOM and a variety of other optical parameters (33–76% of variance explained). Yet in a single

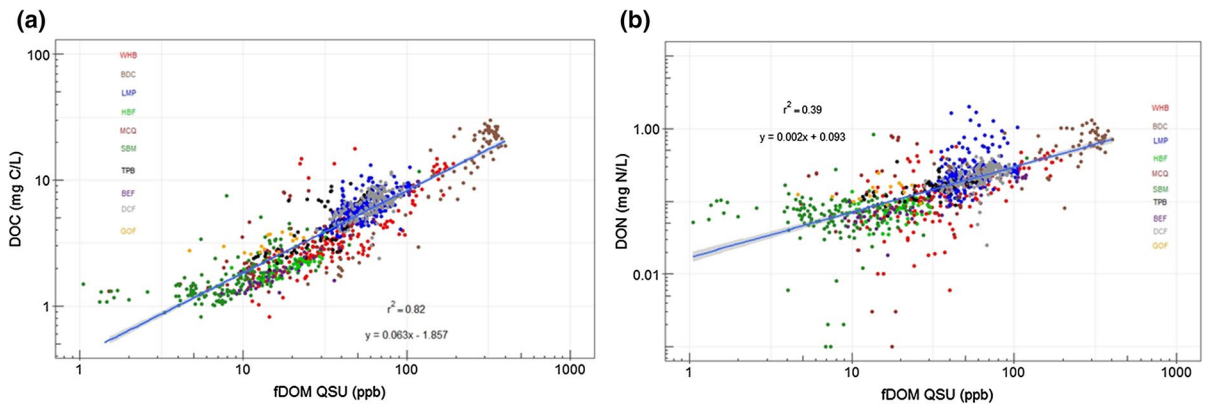

Fig. 2 Relationship between (**A**) dissolved organic carbon concentration (DOC, mg/L) and fluorescent organic matter (fDOM; quinine sulfate units); (**B**) dissolved organic nitrogen concentration (DON, mg/L) and fluorescent organic matter (fDOM; quinine sulfate units). From Wymore et al. (2018)

stream (Albany Brook), the relationships were dramatically stronger (98% of variance explained), and fDOM was also a remarkably good predictor of DON (93% of variance explained). The differences among these streams in optical properties are striking, and unrelated to land use. This suggests that relationships between optical properties and concentrations of DOC and DON are watershed-scale properties with as yet uncertain drivers over time and space.

The use of sensors to provide continuous assessments of bioavailable DOM is largely unexplored but shows considerable promise (Fellman et al. 2010). In developed catchments with a range of site conditions and organic matter inputs, Knapik et al. (2015) showed that microbial degradation of BDOC was associated with removal of tryptophan-like material from solution. In a large catchment with rural and urban areas, Hosen et al. (2014) found that variability in BDOC concentrations across sub-catchments could be effectively predicted by both $SUVA_{254}$ and tryptophan-like peaks in EEMS. The extent to which these results from urbanized watersheds can be applied to other systems is unclear. Development of sensors to provide continuous assessment of BDOM in real time is an important priority, and might be accomplished with specific fluorescence pairs, full EEMS in a sensor, or by using the full wavelength scan of UV and visible light absorbance that is already available in multiple commercial sensors.

Obtaining funding to maintain a sensor network can be difficult once the initial period of installation and operation is completed, as most ongoing funding is tied to explicit hypothesis testing in many parts of the world. Aquatic sites within the U.S. National Ecological Observatory Network (NEON) provide the only ongoing research funding for aquatic sensor infrastructure in the US. NEON is now beginning to provide the data needed to meet the promise of integrating metabolism with coupled measurements of dissolved oxygen, nitrate, and fluorescent DOM (e.g., Appling and Heffernan 2014; Hensley and Cohen 2016). Integrating DOM dynamics into a whole-system metabolic framework such as provided by NEON shows considerable promise in better understanding the dynamics of DOM in stream and river channels. Because many of the NEON aquatic sites are not co-located with ongoing watershed studies, however, there is still a pressing need to develop aquatic sensor networks embedded in broader watershed-scale studies of vegetation, soils, and hydrologic flow paths (McDowell 2015).

Integrating DOM into the full C cycle

It is imperative that the research community does a better job integrating the full carbon cycle into our understanding of watershed and aquatic DOM dynamics. The links between vegetation, soils and streams are built from coupled biotic and abiotic reactions playing out on the lithological template in a given watershed. Weathering, for example, is a major Earth surface process that shapes global C balance at the million-year time scale during cycles of volcanic uplift (Gaillardet et al. 1999). Respiration by roots and their mycorrhizal symbionts is an important source of the CO_2 in soil air that regulates carbonic acid levels at the weathering front. DOC released to the rhizosphere thus can play a crucial role in weathering. There is also compelling evidence that organic acid production by roots directly facilitates weathering as seen in increased etch pits on primary minerals (Landeweert et al. 2001). Because the net products of the weathering reactions typically include large amounts of bicarbonate, measurement of links between DOC and DIC can provide important insights into C dynamics in a watershed. In permafrost terrain of Siberia, for example, riverine fluxes of both DOC and DIC show comparable increases with discharge during periods of modest flow, but diverge at high flow, with much greater DOC than DIC fluxes (Fig. 3). In many well-drained watersheds in non-permafrost terrain, however, DOC concentrations typically increase at high flow but DIC shows strong dilution (McDowell and Asbury 1994). Because direct connections may exist between bicarbonate production during weathering and DOC inputs to the soil environment, more emphasis should be placed on examining the full carbon cycle (DOC, dissolved inorganic carbon, particulate organic carbon) in a watershed rather than simply the DOM.

Greenhouse gases

An important aspect of fully integrating DOM into global biogeochemical cycles is an improved understanding of the role of DOM in production of greenhouse gases (GHGs; CO_2, CH_4, and N_2O) from inland waters, particularly given the increased DOC

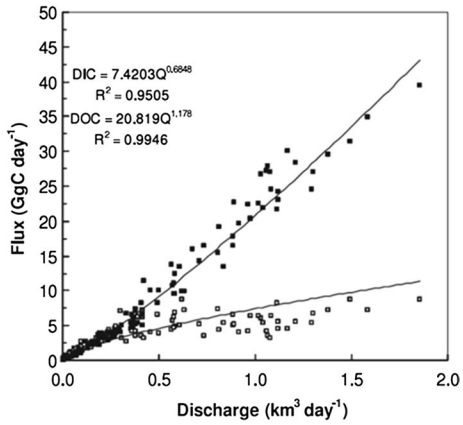

Fig. 3 Relationship between fluxes of DOC (filled squares) and DIC (open squares) in individual grab samples taken across the full flow regime from 2005 to 2010 on the Nizhnyaya Tunguska River, near Tura, Siberia. From Prokushkin et al. (2011)

concentrations reported for many regions. Recent assessments show that aquatic ecosystems serve as net sources of these important gases to the atmosphere (Stanley et al. 2016; Herreid et al. 2020). The links between DOC and greenhouse gases are complex and may not be readily apparent when comparing ambient DOC and GHG concentrations (Schade et al. 2016). Rapid consumption of labile DOC may drive the production of GHGs, but removal of this labile DOC from solution may thereby obscure the relationships between DOC availability and concentrations of GHGs. Likewise, production of CH_4 may be followed by subsequent CH_4 consumption, and production of N_2O may be limited in favor of N_2 production in highly reduced environments. This complex situation is summarized by Stanley et al. (2016), who eloquently argue the need for further study of controls on GHG production within aquatic systems, rather than simply focusing on the role of inland waters as vents for GHGs from the terrestrial landscape. In their global summary of inland water CH_4, Stanley et al. (2016) found that among the predictive variables they considered (temperature, DOC, NH_4, NO_3, and soluble reactive P), DOC is the most informative, even though its predictive power is relatively weak (explaining 19% of variation in CH_4 concentration; Fig. 4). A similar global summary is not available for drivers of variation in N_2O concentrations and fluxes in inland waters.

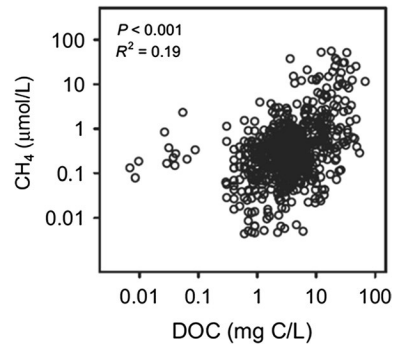

Fig. 4 Relationship between and CH_4 (µmol/L) and DOC (mg/L) concentrations in a global compilation of inland waters. Modified from Stanley et al. (2016)

Such a summary is clearly needed to assess whether ongoing increases in DOC are likely to result in altered production and evasion of N_2O.

The enigma of dissolved organic nitrogen

Dissolved organic matter is most commonly measured by analysis of its C content, despite the fact that it contains nitrogen, phosphorus, and sulfur that may be significant in biogeochemical cycles or provide important nutrient sources upon mineralization. Analysis of DOS and DOP has lagged behind that of DON (McDowell 2003), for which some broad generalizations are starting to emerge. One conclusion from recent work is that the stoichiometry of DOM (C/N ratio) can vary over decadal time scales at a given site (Rodríguez-Cardona et al. 2021), across a range of watershed soil conditions (mirroring soil C/N; Yates

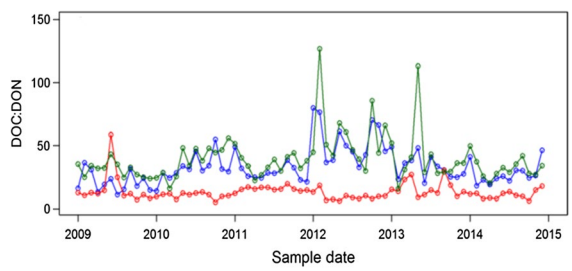

Fig. 5 Monthly variation in dissolved organic matter stoichiometry (molar ratio of DOC:DON) in river water over 6 years of weekly sampling for three study watersheds in Puerto Rico, the urban Río Piedras (RP) and forested Río Mameyes (MPR) and Quebrada Sonadora (QS). From McDowell et al. (2019)

et al. 2019), and due to introduction of waste materials such as untreated sewage leaking directly into streams from sewer mains (McDowell et al. 2019; Fig. 5). More attention should be given to the role of the DON fraction of DOM in overall watershed biogeochemistry and nutrient availability to plants and microbes (Jilling et al. 2018). Much less is known about drivers of variability in the stoichiometric ratios of DOS or DOP in DOM, but the stoichiometry of DOM can change in response to environmental drivers. The DOS content of DOM as measured by FT-ICR MS is higher in Everglades sawgrass sites with higher sulfate levels (Poulin et al. 2017), and both the N and S content of DOM vary by water source in rivers and springs of Florida (Kurek et al. 2020).

One promising research avenue regarding DON is to examine when and where the N-rich fraction of DOM serves largely as a source of energy, or source of nitrogen, to aquatic microflora. This has been addressed by inference (Lutz et al. 2011) and more recently by direct experimental manipulations of the inorganic N pool in streams (Wymore et al. 2015). By adding nitrate to low-N streams, they were able to elicit both increases and decreases in DON, with nitrate addition generally resulting in increasing DON concentrations (Fig. 6). From this observation, Wymore et al. (2015) concluded that DON is largely serving as a nitrogen source in streams. When additional inorganic nitrogen was available, the observed increase in DON concentrations suggests that it was used preferentially to DON as a nutrient source. Wymore et al. (2015) also found that the role of DON in streams may vary over seasonal time frames, serving as an energy source under some conditions and nitrogen source under others. Further work is needed to assess the broader applicability of these observations, and to provide independent verification that changes in ambient DON concentrations during manipulations are indeed the result of changes in the net rates of DON production and consumption by the microflora.

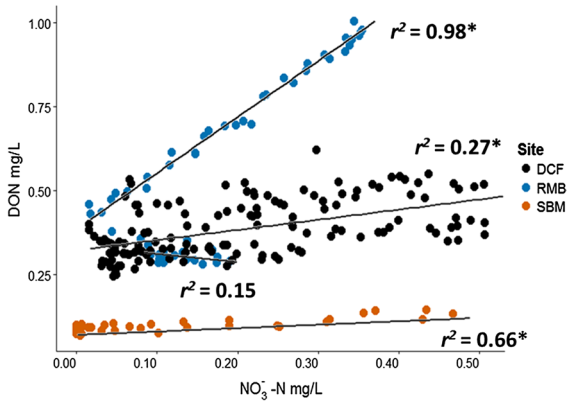

Fig. 6 The relationship between NO_3 and DON concentrations when NO_3 alone is added to stream water during whole-stream manipulations. From Wymore et al. (2015)

Documenting gross versus net DOM flux

A central challenge in understanding DOM dynamics is to develop better ways to discriminate between gross and net DOM fluxes. Studies of DON have benefitted considerably from the use of ^{15}N isotopes. For example, bulk DON concentrations were unchanged with distance downstream in a tropical rain forest stream, suggesting that little production or consumption of DON was occurring. Yet tracer level additions of $^{15}NH_4$ revealed that considerable DON was being produced in the stream reach (Merriam et al. 2002), and similar production of DON from inorganic N occurred in streams throughout North America (Johnson et al. 2013). Elegant isotopic experiments using ^{13}C from labelled leaves to track DOM through aquatic ecosystems have been conducted by Wiegner et al. (2005). This approach shows promise but is highly labor intensive. Use of labelled individual organic compounds that can be purchased commercially is much more practical, yet is hampered by the wide range of compounds that might be used and the fact that the ambient pool of DOC in streams and rivers is not nearly as metabolically active as individual organic compounds (Mineau et al. 2016). The development of a more systematic approach to measuring individual organic compounds or functional groups in known DOC inputs to aquatic ecosystems (e.g., leaching leaves) that can then be labelled may provide promise in separating gross and net fluxes of the most metabolically active fractions of DOM. Linking microbial activity (e.g. incorporation of tritiated thymidine) and metabolomics to whole-ecosystem metabolism and DOC fluxes also shows promise (Sobczak and Findlay 2002; Yeh et al. 2020).

Moving from functional ecological significance to evolutionary significance

Dissolved organic matter is ubiquitous, has been studied in soils and inland waters for almost 100 years, and is a fundamental product of life on earth. Despite this long history, most of the work on DOC has focused on its functional significance (blocking light, chelating metals, fueling food webs) rather than the evolutionary drivers that have resulted in its ubiquity as well as its variability in concentration, composition, and flux. The fundamental difficulty is one of ascribing "purpose" or "meaning" to this variability. Organic matter lost to solution could represent either an unfortunate but unavoidable loss of a valuable resource, or its production could be driven by evolutionary pressures.

Is DOM a waste product or end product? The underlying assumption in most areas of DOM research appears to be that DOM is a waste product. This is perhaps best exemplified by the contention that organic matter (e.g., DON) in streams and rivers is a largely refractory form of N that dominates in surface waters when more valuable inorganic nitrogen is unavailable. It thus represents a "leak" in the otherwise efficient N cycle (Hedin et al. 1995). Yet tantalizing clues have been available for decades to suggest otherwise; that DOM may in fact be an end product of some ecological significance that is thus subject to evolutionary pressures. In terrestrial systems, for example, throughfall has been known since the 1970s to have the potential to influence plant community structure and competition (e.g., walnut trees producing juglone; summarized by McDowell et al. 2020). Root exudates and decomposition of plant residues are additional pathways by which this sort of allelopathy is expressed (Zhang et al. 2021). Salmon homing and return to natal rivers has been known for 50 years (Scholz et al. 1976), with recent work suggesting that in the low-nutrient systems that existed prior to the industrial era, the return of marine derived N and P can provide significant nutrient subsidies to both aquatic and terrestrial ecosystems that produce the DOM that results in a homing signal (Hocking and Reynolds 2011). The production of DOM during algal photosynthesis has been noted since the 1950s (Tolbert and Zill 1956), and its ecological significance puzzled over in the decades since (Fogg 1983). Recent work on kelp shows that on an annual basis, 16% of the carbon fixed during photosynthesis is released as DOC, and DOC production was higher under ambient low nitrate conditions than with nitrate added (Weigel and Pfister 2021). In coral reefs of French Polynesia, Wegley Kelly et al. (2022) observed that distinctive sets of individual DOM compounds were found in water sampled above coral and different algal species. The role of this DOM in coral reef ecology is uncertain, but the authors emphasize that each primary producer can alter both the nutrient stoichiometry and energetic content of the DOM in its immediate vicinity. Each of these examples suggests that the production of DOC may not be a haphazard byproduct of cellular metabolism or decomposition. Understanding the ways in which functional and evolutionary significance of DOM intersect is thus a major research challenge.

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Declarations

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