



Soothsaying DOM: A Current Perspective on the Future of Oceanic Dissolved Organic Carbon

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The vast majority of freshly produced oceanic dissolved organic carbon (DOC) is derived from marine phytoplankton, then rapidly recycled by heterotrophic microbes. A small fraction of this DOC survives long enough to be routed to the interior ocean, which houses the largest and oldest DOC reservoir. DOC reactivity depends upon its intrinsic chemical composition and extrinsic environmental conditions. Therefore, recalcitrance is an emergent property of DOC that is analytically difficult to constrain. New isotopic techniques that track the flow of carbon through individual organic molecules show promise in unveiling specific biosynthetic or degradation pathways that control the metabolic turnover of DOC and its accumulation in the deep ocean. However, a multivariate approach is required to constrain current carbon fluxes so that we may better predict how the cycling of oceanic DOC will be altered with continued climate change. Ocean warming, acidification, and oxygen depletion may upset the balance between the primary production and heterotrophic reworking of DOC, thus modifying the amount and/or composition of recalcitrant DOC. Climate change and anthropogenic activities may enhance mobilization of terrestrial DOC and/or stimulate DOC production in coastal waters, but it is unclear how this would affect the flux of DOC to the open ocean. Here, we assess current knowledge on the oceanic DOC cycle and identify research gaps that must be addressed to successfully implement its use in global scale carbon models.

Keywords: dissolved organic carbon, global carbon cycle, recalcitrance, isotopic probing, climate change

INTRODUCTION

Containing roughly the same amount of carbon as terrestrial biomass, or CO₂ in the atmosphere, the oceanic dissolved organic matter (DOM) pool represents one of Earth's large organic carbon reservoirs (660 Pg-C; Hansell et al., 2009; Houghton, 2014). Global carbon cycling models generally consider the total ocean split into three "boxes" – the surface ocean (<200 m), the twilight or mesopelagic zone (200–1,000 m) and the interior ocean (>1,000 m). This compartmentalization of oceanic water masses is driven by our current understanding of how carbon is produced, cycled, and stored with depth. Oceanic DOM derives mainly from autochthonous production by phytoplankton in surface waters where it is rapidly recycled and serves as an energy source for heterotrophic microbes. A small portion of DOM produced in surface waters is eventually routed to the ocean's interior, which houses the bulk of the oceanic dissolved organic carbon (DOC) pool and cycles on much longer timescales. However, mechanisms controlling the accumulation of DOM in the interior ocean remain poorly understood. The oceanic DOC cycle is an essential component of the global carbon cycle, thus imbalances among oceanic DOC pools would impact future climate scenarios. However, global scale carbon models lack a coherent implementation of DOC at present.

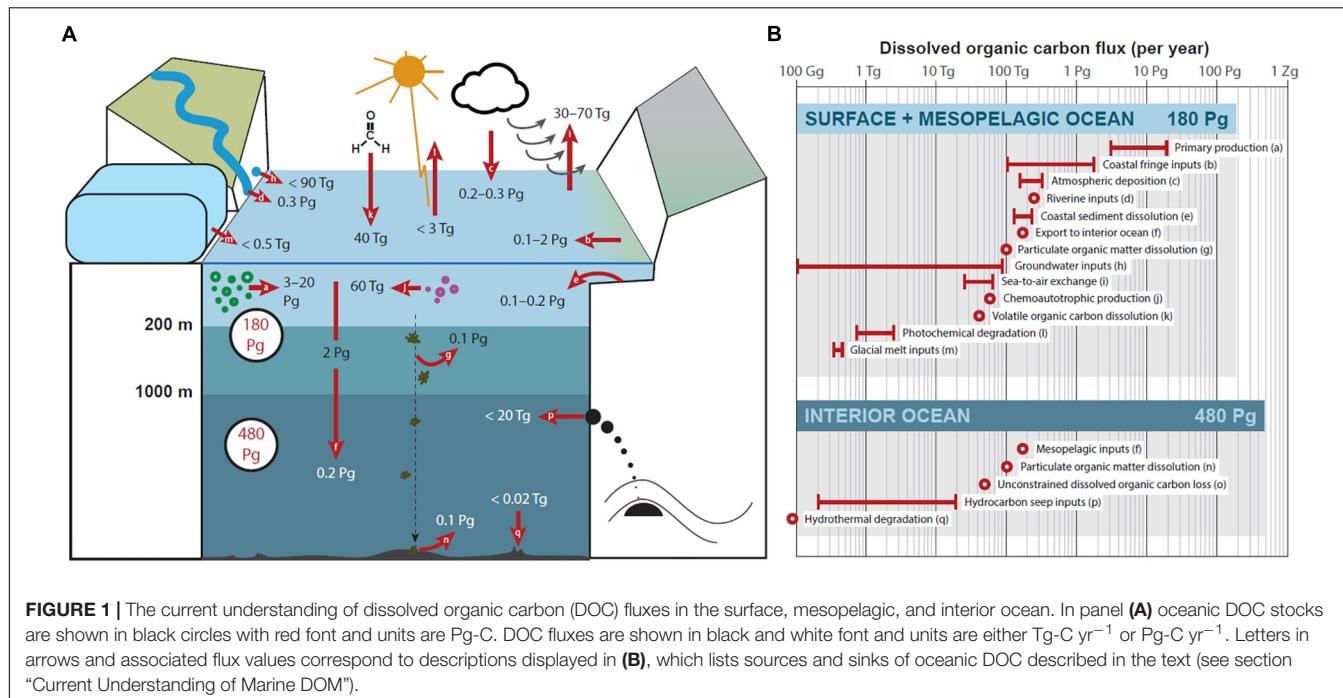
Surface, mesopelagic, and interior ocean DOM each exhibit distinct latitudinal trends (Carlson et al., 2010). The distribution of DOM among these ocean boxes is largely mediated by biological activity. The "biological carbon pump" is a conceptual framework that describes the cumulative processes involved in the transport of biogenic material from the surface to the deeper ocean, including the formation and settling of particulate organic matter (POM), the active migration of zooplankton and other mobile organisms and the physical overturning of ocean water, including its organic constituents (Sarmiento and Gruber, 2006; Lutz et al., 2007; Jiao et al., 2010). Taken together, these mechanisms result in the total export of ca. 0.2 Pg-C yr⁻¹ as DOC from the surface and mesopelagic ocean (<1,000 m; 180 Pg-C) to the interior ocean (>1,000 m), contributing to the large, slowly cycling DOC pool that resides there (480 Pg-C; Hansell et al., 2009). However, balancing oceanic DOC budgets is challenging, particularly in the transitional mesopelagic zone where isopycnal gradients and microbial activity results in a DOM pool with a wide spectrum of reactivity (Carlson and Hansell, 2015). Labile DOM is taken up by heterotrophic organisms within hours to days in shallow ocean depths. Refractory DOM is largely resistant to microbial degradation and therefore cycles on millennial timescales. It is proposed that the continuous and/or repeated reworking of freshly produced DOM in surface waters results in the accumulation of recalcitrant DOM (Jiao et al., 2010), which is comprised of molecular components that fall along a reactivity continuum (Carlson and Hansell, 2015). Radiocarbon and stoichiometric analyses provide evidence for the accumulation of apparently old (~6,000 ¹⁴C-years; Williams and Druffel, 1987) and carbon-enriched (Hopkinson and Vallino, 2005) DOM in the deep ocean. However, the distribution of labile and refractory DOM can also be explained by the

"dilution hypothesis," which argues that the degradation of DOM is controlled by its concentration rather than its intrinsic chemical reactivity (Jannasch, 1967; Arrieta et al., 2015). If the formation of the recalcitrant DOM pool is not strictly dependent upon microbial lability, then a holistic approach, one that considers environmental redox conditions, concentration, time, etc. is needed to further refine current and predict future oceanic carbon cycles (see section "DOM Recalcitrance Is an Emergent Property").

Although contemporary carbon flux estimates have benefited from a two-component model approach involving labile and refractory fractions (Williams and Druffel, 1987; Druffel et al., 1992; Bauer et al., 1998), spatial mapping of DOM throughout the global oceans reveals a more dynamic system at play (Hansell et al., 2009). Oceanic DOC concentrations range from 40 to 80 $\mu\text{M-C}$ where observed gradients are driven by vertical stratification and mixing, biological degradation, and terrigenous inputs (Hansell et al., 2009). Although the formation and degradation of recalcitrant DOM occurs on relatively long timescales, the spatial and temporal variability of this accumulated fraction of DOM has a major impact on the long-term storage of carbon in the ocean's interior, thus affecting global carbon cycles and associated climate change. As our analytical capabilities continue to advance, so should our understanding of the fine-scale processes that govern the global distribution of oceanic DOC. In turn, a clearer view of fine-scale biogeochemistry will allow for improved oceanic representation in global carbon cycling and Earth system models. This review of oceanic fluxes focuses upon DOC only (see section "Current Understanding of Marine DOM"). While some information on the cycling of organic heteroatoms exist (Pohlabeln and Dittmar, 2015; Gomez-Saez et al., 2016; Ksionzek et al., 2016; Pohlabeln et al., 2017; Broek et al., 2019), data available for dissolved organic nitrogen, sulfur, and phosphorous are extremely limited compared to DOC measurements. Here, we synthesize both well and poorly characterized fluxes of oceanic DOC, consider what is meant by DOM "recalcitrance," spotlight new isotopic approaches for probing the oceanic distribution of DOC, and discuss changes to DOM quantity and composition that are expected to occur in response to our changing climate.

CURRENT UNDERSTANDING OF MARINE DOM

Implementing oceanic DOC in the global carbon cycle and associated climate models requires an improved quantitative understanding of marine DOC. Here, we provide an overview of DOC sources and sinks as currently estimated for the surface and interior ocean. These fluxes are summarized in **Figure 1**. The apparent imbalance between sources and sinks can be ascribed to unconstrained loss estimates within the water column by either DOC remineralization or sorption to particles. In this section, we also highlight research gaps that must be addressed for a more accurate view of marine DOC cycling and how it may be altered with future climatic and oceanic change.



Surface Ocean

Biotic Processes

Primary production (about 50 Pg-C yr⁻¹) is the main source of DOC in oceanic surface waters (3–20 Pg-C yr⁻¹) with significantly smaller contributions deriving from chemoautotrophic production (0.06 Pg-C yr⁻¹) (Middelburg, 2011; Carlson and Hansell, 2015). Intracellular organic matter accumulates when cell division is limited. This excess material is subsequently discharged via extracellular release (Fogg, 1966; Engel et al., 2004). Specific mechanisms of release are yet not fully understood, but low molecular weight DOC can leak through the cell membrane directly (Fogg, 1966) and high molecular weight DOC is actively excreted via exocytosis or similar processes (Leppard, 1995). Extracellular release is a cellular overflow mechanism shedding excess carbon, where compounds released are depleted in biolimiting elements (Wood and Van Valen, 1990; Engel et al., 2002; Schartau et al., 2007). Thus, the extracellular release of carbon-enriched DOM represents a significant source for DOC in the upper ocean (Aluwihare et al., 1997) and partly explains seasonal variations observed for Redfield ratios (Williams, 1995; Søndergaard et al., 2000). DOC is also released when zooplankton feed on phytoplankton in surface waters. The production of DOC from "sloppy feeding" ranges from 3 to 70% of the total mass of phytoplankton carbon ingested and is generally a function of predator-to-prey size (Copping and Lorenzen, 1980; Bjørnsen, 1988; Moller, 2005, 2007; Saba et al., 2011). The amount of DOC released during zooplankton grazing ranges from 2 to 10% of the total zooplankton carbon mass (Steinberg et al., 2000, 2002). Similarly, microzooplankton have been shown to ingest 20–50% of algal biomass carbon during grazing, the majority of which is subsequently released as DOC (Nagata et al., 2000). However, given the high degree

of spatiotemporal variability of zooplankton feeding, global DOC flux values for grazing and sloppy feeding have not been adequately constrained (Steinberg and Landry, 2017).

Viral infections are a major cause of marine microbial mortality (Wilhelm and Suttle, 1999; Suttle, 2007) and result in cell lysis and release of DOM during cell death. An estimated 6–26% of annual marine primary production flows through the viral shunt producing 3–13 Pg-C as DOC per year (Wilhelm and Suttle, 1999; Carlson and Hansell, 2015). Compositionally, viral lysates are rich in dissolved amino acids, carbohydrates, and nucleic acids (Weinbauer and Peduzzi, 1995; Middelboe and Jørgensen, 2006; Holmfeldt et al., 2010). Most of the DOC produced in the surface ocean is then routed through microorganisms and remineralized to CO₂ within an annual cycle (Azam et al., 1983). Only a small fraction of autotrophic DOC is converted to recalcitrant forms of DOC and survives long enough to be exported to the interior ocean (Gruber et al., 2006; Brophy and Carlson, 1989). Microbes utilize the diverse pool of organic compounds through direct uptake of small molecules or extracellular enzymatic hydrolysis to initiate decomposition (Weiss et al., 1991; Arnosti, 2004). The degradation of macromolecular structures is thereby linked enzymatic capabilities of the heterotrophic microbes.

Air-Sea Exchange

The transfer of organic matter from the atmosphere to the ocean occurs by dry deposition (settling of organic gases or particles) or by wet deposition (organic molecules dissolved in rainwater). Atmospheric deposition (wet plus dry) delivers 0.25 Pg-C yr⁻¹ to the global surface ocean (Jurado et al., 2008; Kanakidou et al., 2012). However, atmospheric contributions to oceanic DOC depend largely upon the solubility of the deposited organic

matter. Most wet deposition organics are presumed to be water soluble DOC (>90%; Kanakidou et al., 2012). Therefore, a lower limit for atmospheric DOC fluxes can be derived considering only wet deposition, which equates to $0.17 \text{ Pg-C yr}^{-1}$, while an upper limit of $0.25 \text{ Pg-C yr}^{-1}$ implies that all atmospherically deposited organic carbon dissolves within oceanic surface waters. Volatile organic molecules can also be transferred between the surface skin of the ocean and the overlying atmosphere (Liss et al., 2014). The efficiency of this ocean-to-air exchange is dependent upon molecular structure, current regimes, biological productivity, and light availability. Summed across all volatile organic compound classes, the ocean constitutes a net sink of short-lived gases [41 Tg-C yr^{-1} ; (Heikes et al., 2002; Marandino et al., 2005; Shim et al., 2007; Millet et al., 2008; Liss et al., 2014)]. Marine aerosols are produced from both primary (bursting bubbles and breaking waves) and secondary processes (nucleation and oxidative reactions) and are highly enriched in organic matter compared to seawater (Keene et al., 2007; O'Dowd and de Leeuw, 2007; Quinn et al., 2014). Model estimates suggest the ocean-air flux of organic matter from primary marine aerosol production ($8\text{--}50 \text{ Tg-C yr}^{-1}$) (Roelofs, 2008; Spracklen et al., 2008) can exceed that of organic matter transferred during secondary marine aerosol production (18 Tg-C yr^{-1}) (Andreae and Rosenfeld, 2008). Primary marine organic aerosols are also comprised of roughly one third refractory carbon (Kieber et al., 2016; Beaupre et al., 2019). Thus, the atmospheric release of marine aerosols is a significant loss mechanism for recalcitrant DOM in the surface ocean.

Terrestrial Inputs

Globally, the export of riverine DOC to the coast is estimated to be $0.25 \text{ Pg-C yr}^{-1}$ (Hedges et al., 1997; Raymond and Spencer, 2015). Within the last decade, efforts have been aimed to refine flux estimates from individual rivers. For example, due to increased temporal sampling resolution that now includes periods of high DOC export (spring freshet), estimated DOC fluxes for major Arctic Rivers have increased by $\sim 10 \text{ Tg-C yr}^{-1}$ (Holmes et al., 2012). Rivers with high DOC yields export more carbon per unit area (e.g., the Amazon and Congo; Raymond and Spencer, 2015), and thus represent key targets for research seeking to constrain fluxes of terrestrial carbon to the ocean. Mountain glaciers export 0.58 Tg-C as DOC annually (Hood et al., 2015), but the majority of this glacial melt-derived DOC feeds primarily into fluvial systems and is thus captured by riverine DOC flux estimates and/or is highly bioavailable and degrades before reaching the ocean (Hemingway et al., 2019). At present, glacial melt represents a small source of terrestrial DOC to the coastal ocean ($0.32\text{--}0.46 \text{ Tg-C yr}^{-1}$; Priscu and Christner, 2004; Bamber et al., 2012; Hood et al., 2015). However, continued climate warming could unlock and mobilize a significant portion of the organic carbon currently stored in glacial ice (5.9 Pg-C) (Hood et al., 2015). Although glacial DOC is generally old, it is highly labile (Hood et al., 2009), which suggests the majority of glacier-derived DOC would be rapidly remineralized post-melt. However, more research is needed to estimate this potential loss of terrestrial DOC. In addition, it is unlikely that most riverine DOC would reach the open ocean due to efficient removal in

estuaries and on the shelf (Fichot and Benner, 2014; Kaiser et al., 2017; Sharples et al., 2017).

Submarine groundwater flows from land to sea by gravity and is comprised of both a terrestrial component (meteoric groundwater) and a seawater component that circulates through the coastal aquifer through wave and tidal pumping (Burnett et al., 2003). Terrestrial DOM, which is transported directly by groundwater from inland watersheds, has global average DOC concentrations of 2.7 mg-C L^{-1} (McDonough et al., 2020). Thus, assuming fresh groundwater discharge equates to 0.3–10% of surface runoff, then terrestrial groundwater DOC inputs would account for $0.1\text{--}90 \text{ Tg-C yr}^{-1}$ (Burnett et al., 2003; McDonough et al., 2020). However, coastal peatlands and marsh areas have been shown to spike local groundwater and recirculating seawater with DOC to increase concentrations up to 20-fold higher than the global average (Goñi and Gardner, 2003; Seidel et al., 2014). Therefore, subterranean inputs of terrestrial DOM may be much larger than currently assumed.

Coastal Fringe

Coastal fringe ecosystems are among the highest in productivity on Earth and include mangroves, salt marshes, and seagrass beds (Jennerjahn and Ittekkot, 2002). Intertidal sediments that house these highly productive coastal plant communities and their detritus are permanently flooded, which contributes to consistently high DOC yields. Combined, coastal fringe ecosystems are thought to export an estimated $0.1\text{--}1.9 \text{ Pg-C}$ per year as DOC (Duarte, 2017). Since coastal fringe-derived DOC has been suggested to subsidize respiration in the open ocean (Barrón and Duarte, 2015), much of the DOC exported by these ecosystems may be rapidly remineralized by microbes. However, it is reported that as much as one third of the total DOC flux derived from coastal fringe ecosystems survives degradation and is eventually mobilized to the interior ocean (Krause-Jensen and Duarte, 2016). Further offshore, terrestrial and marine organic matter that is temporarily stored in coastal and continental margin sediments is laterally transported to deliver an additional $0.12\text{--}0.23 \text{ Pg-C yr}^{-1}$ as DOC to open oceanic surface waters (Burdige et al., 1999; Burdige and Komada, 2015).

Photodegradation

The photomineralization of DOC in sunlit surface waters is an important, yet poorly understood, mechanism for the degradation of oceanic organic matter. Estimates currently suggest $0.7\text{--}2.7 \text{ Tg-C}$ DOC is lost annually via photomineralization (Mopper and Kieber, 2002; Stubbins et al., 2006). The photomineralization of DOC depends upon several factors, including DOM composition, prior irradiation history, irradiation conditions, and the model used to fit the photobleaching kinetics (Mopper et al., 2014). DOM compounds exist along a continuum of varying photolability (Stubbins et al., 2010). For example, sulfur-containing compounds from sulfidic sediments are more photosensitive than bulk DOC (Gomez-Saez et al., 2017). Aromatic, refractory DOM is comprised of organic compounds that are most susceptible to photodegradation and have an estimated removal rate of up to 0.5 Tg-C yr^{-1} (Anderson and Williams, 1999; Stubbins et al., 2012). Partially

degraded DOM compounds may be more bioavailable than organic molecules shielded from sunlight, thus coupled photo- and bio- degradation can remineralize more refractory DOC than photodegradation alone (Fichot and Benner, 2014; Shen and Benner, 2018). Degradation of recalcitrant DOC is likely also controlled by physical ocean circulation, specifically the rate at which deep water upwelling returns deep ocean DOC to the photic zone.

Interior Ocean

Net Losses

Of all the DOC that enters or is produced within surface waters each year, only 1.9 Pg-C yr^{-1} is exported to mesopelagic depths and a mere $0.18 \text{ Pg-C yr}^{-1}$ survives long enough to reach the ocean's interior (Carlson and Hansell, 2015). The exponential decrease in DOC export from the surface to deep ocean indicates the majority of exported DOC (~99%) is respired in the water column, is incorporated into microbial biomass, or forms aggregates to sink and ultimately become stored in sediments as particulate organic carbon (POC). Respiration is the primary mode of DOC removal in surface waters, yet the complex cascade of processes that encompass a variety of biotic and abiotic mechanisms that control the formation of the recalcitrant DOM pool remains poorly understood. Upon entering the ocean's interior, there is a net loss of refractory DOC (50 Tg-C yr^{-1}), which cycles on millennial timescales (Hansell et al., 2009). The removal of refractory DOC from the deep ocean is ascribed to heterotrophic remineralization and/or sorption onto sinking particles, however, the relative contributions of these biogeochemical processes are largely unknown (Hansell et al., 2009).

Sorption and Dissolution

Organic matter-mineral interactions can lead to the ballasting and/or removal of DOC throughout the water column (Keil et al., 1994, 1997; Blattmann et al., 2018). The export of sediment from land to the ocean releases terrestrial organic matter, including labile compounds (Keil et al., 1994; Blattmann et al., 2018). The surfaces of terrestrial minerals are then repopulated with marine organic matter (Keil et al., 1997; Kennedy et al., 2002; Blattmann et al., 2018), an exchange process that depends upon sediment mineralogy (Blattmann et al., 2019). Since the degree of sorption is a function of surface area and DOC concentration (Henrichs, 1995; Kennedy et al., 2002), the removal of DOC from the water column likely scales with its concentration as well as availability of reactive sorption sites for organic compounds that persist in the interior ocean. While the loss and replacement of terrestrial and marine organic matter from mineral surfaces might pose no net sink or source of DOC, it may alter the composition and lability of the oceanic DOC pool. However, the abiotic exchange of organic matter between the operational POM and DOM fractions is a process that is not well understood (Carlson, 2002) and is in need of further research.

The imbalance of POM fluxes from the surface to depth and from depth to the seafloor (7.3 Pg-C yr^{-1}) points to a likely source of DOC within the oceanic water column (Carlson and Hansell, 2015). POM loss processes are not well understood,

but it is estimated that half is remineralized (3.6 Pg-C yr^{-1}) and half is taken up by heterotrophic bacteria (3.6 Pg-C yr^{-1}) (Carlson and Hansell, 2015). Sinking particles are enriched in organic and inorganic nutrients, thus representing energy hotspots in the open ocean. Microbes colonize the sinking particles and break down the POM into soluble components, releasing a trail of DOM that serves as a substrate to free floating microbes (Cho and Azam, 1988; Kiørboe, 2011). A small portion of this POM-derived DOC accumulates in the surface ocean at an estimated rate of 0.1 Pg-C yr^{-1} (Hansell, 2013; Carlson and Hansell, 2015). As particle flux decreases with depth, it is therefore unlikely that the flux of POM-derived DOC to the interior ocean is substantial. However, the dissolution of POM accumulated in ocean sediments contributes 0.1 Pg-C yr^{-1} (Dunne et al., 2007; Burdige and Komada, 2015), representing an important carbon and nutrient source to benthic microorganisms (Jones et al., 2014). A fraction of this sediment-derived DOC may also escape degradation and diffuse into deep waters overlying the seafloor, consistent with higher DOC concentrations observed in sediment porewaters compared to bottom waters (Burdige et al., 1992; Schmidt et al., 2011; Rossel et al., 2016). Consequently, sediment-derived DOC may subsidize benthic microbial communities and thus be an important source of the recalcitrant carbon observed in bottom waters (Burdige and Komada, 2015).

Seeps and Vents

Located along continental margins, hydrocarbon seeps represent an external source of DOC to the deep ocean. Current flux estimates ($0.2\text{--}20 \text{ Tg-C yr}^{-1}$) are based only upon data collected from known mud volcano seeps (Pohlman et al., 2010). These values likely underrepresent true DOC fluxes since current estimates omit inputs from other seep types, including seeps that have not yet been discovered. Depending upon the study, seep-derived DOC has been shown to either not accumulate or comprise up to 30% of DOC in the overlying water (Wang et al., 2001; Walker et al., 2017). Investigations that took place after the *Deepwater Horizon* oil spill (Gulf of Mexico) suggest microbial transformations of seep-derived hydrocarbons may result in the production of refractory DOC years after their release (Bianchi et al., 2014; Walker et al., 2017), thus contributing unknown quantities to the ^{14}C -depleted DOC pool that resides in the deep ocean. Overall, hydrocarbon seeps likely represent a minor contribution to DOC in the ocean interior.

Concentrations of DOC in hydrothermal systems vary by an order of magnitude and are generally higher at low temperature diffusive systems compared to high temperature vents (Lang et al., 2006, 2010; Yamanaka et al., 2013; Hawkes et al., 2015). Hydrothermal circulation that exposes fluids to high temperatures ($>400^\circ\text{C}$; Fontaine et al., 2009) is generally considered a sink of deep ocean DOC (Lang et al., 2006; Lin et al., 2012; Hawkes et al., 2015; Rossel et al., 2017), but these fluxes may be somewhat offset by cooler diffuse vent systems which are suggested to be a minor source of deep ocean DOC (Lang et al., 2006). Based upon data collected from DOC isolated by solid phase extraction, which is presumed to represent the less biologically labile fraction of marine DOC, high temperature

fluids remove an estimated 0.02 Tg-C of refractory DOC per year (Hawkes et al., 2015). However, this flux estimate only considers the extractable portion of DOC, which becomes smaller with increased temperature (Hawkes et al., 2015, 2016) and largely excludes low molecular weight compounds (Klevenz et al., 2010; Lang et al., 2010; Fuchida et al., 2014; Reeves et al., 2014; McDermott et al., 2015; Longnecker et al., 2018). Hydrothermal vent-derived DOC may be a source of carbon for the deep ocean microbial communities (Winkel et al., 2014; Rossel et al., 2015), but fluxes have not yet been determined.

DOM RECALCITRANCE IS AN EMERGENT PROPERTY

Dissolved organic matter is a heterogeneous pool of thousands, likely millions, of organic compounds. These compounds differ not only in composition and concentration (from pM to μ M), but also originate from various organisms (phytoplankton, zooplankton, and bacteria) and environments (terrestrial vegetation and soils, coastal fringe ecosystems) and may have been produced recently or thousands of years ago. Moreover, even organic compounds deriving from the same source and of the same age may have been subjected to different processing histories prior to accumulating within the same pool of DOM.

Interior ocean DOM is a highly modified fraction that remains after years of exposure to sunlight, utilization by heterotrophs, flocculation and coagulation, and interaction with particles. Many of these processes within the DOM pool are compound- or class-specific. For example, condensed aromatic compounds are highly photosensitive (Stubbins et al., 2012), whereas proteins, carbohydrates, and their monomers are readily taken up by bacteria (Hodson et al., 1981; Hollibaugh and Azam, 1983; Ferguson and Sunda, 1984). Microbes and other consumers are selective in the type of DOM they utilize and typically prefer certain organic compounds over others. Consequently, DOM becomes less reactive as it is continually reworked. Said another way, the DOM pool becomes less labile and more refractory with degradation. As it is reworked, organic compounds are continually being added to the bulk DOM pool by physical mixing, exchange with particles, and/or production of organic molecules by the consumer community (Ogawa et al., 2001; Kaiser and Benner, 2008; Jiao et al., 2010; Shen and Benner, 2018). As such, the compositional changes that occur during degradation are more complex than the simple removal of more labile components and resultant accumulation of remaining, less labile compounds. The combined effect of the physicochemical and biological reworking of individual molecules on the overall molecular diversity and apparent recalcitrance of bulk interior ocean DOM is illustrated in **Figure 2**.

Dissolved organic matter recalcitrance (i.e., its overall reactivity toward degradation and/or utilization) is therefore an emergent property. Thus, the perception of DOM recalcitrance changes during organic matter degradation and in conjunction with any other process that removes or adds organic compounds to the DOM pool under consideration. While it is possible

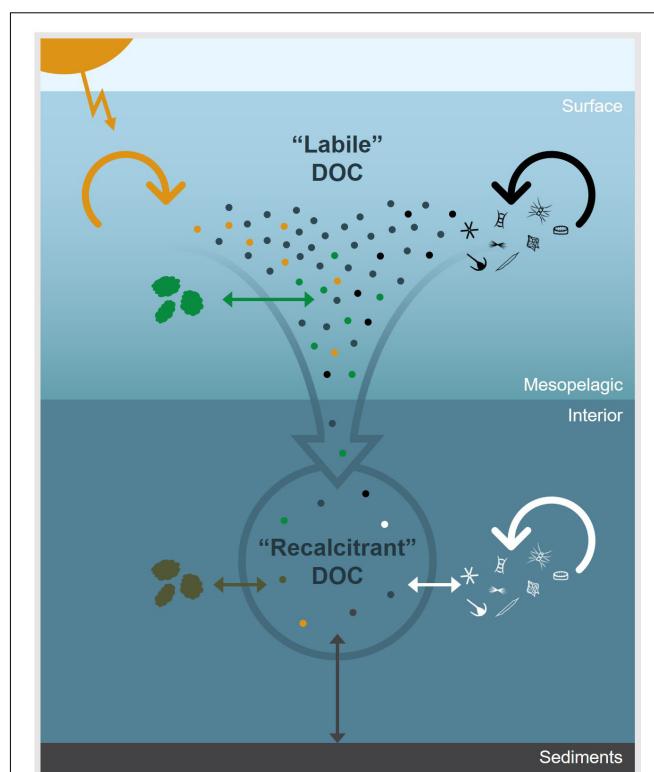


FIGURE 2 | A conceptual diagram of some of the major environmental processes which control the apparent recalcitrance of oceanic DOC. The dots represent DOC molecules and arrows represent physicochemical and biological processes that impact DOC concentration and molecular composition. In the surface ocean, DOC derived from primary production is rapidly remineralized or transformed through microbial degradation (black arrow), photochemical degradation (yellow arrow), or particle exchange (green arrow). Labile components are removed down the water column and DOC becomes diluted by processes, such as particle exchange (brown arrow), sediment dissolution (gray arrow), and microbial reworking (white arrow), which continue to alter, add, and/or remove molecules from the bulk DOC pool. Thus, the apparent recalcitrance of DOC in the ocean's interior is an emergent property that is largely controlled by environmental context.

to experimentally quantify the lability of very reactive, non-recalcitrant material on short time scales (Hodson et al., 1981; Hollibaugh and Azam, 1983; Ferguson and Sunda, 1984), we must infer DOM reactivities from chemical proxies, such as molecular composition, size distribution, and/or radiocarbon ages, for longer experimental temporal domains (i.e., more than 1 year). For example, older (^{14}C -depleted) DOC is considered more refractory than young (^{14}C -enriched) DOC and components with higher molecular mass are more reactive than components with lower molecular mass (Amon and Benner, 1994, 1996; Benner and Amon, 2015; Walker et al., 2016).

The reactivity of DOM is not only dependent upon intrinsic chemical characteristics of the organic compounds, but also depends upon the consumer community composition (e.g., microbes versus metazoans) (de Goeij et al., 2013). The availability of nutrients and biolimiting elements also comes into play, potentially limiting or promoting primary production

and/or microbial consumption of DOM. Consumers must invest in structural or enzymatic machinery for harvesting certain compound classes. If target compound classes persist at very low concentration levels, the energetic gain from taking up these compounds may not be balanced by the cost of constructing the machinery required to utilize them. Consequently, even intrinsically labile DOM may not be readily degraded due to limited availability or access to such molecules (Jannasch, 1967; Arrieta et al., 2015). Thus, the apparent recalcitrance of DOM described by the dilution hypothesis is a property of the consumer or environmental context rather than the intrinsic chemical lability of substrate (Middelburg, 2015), yet provides a coherent explanation for the size and apparent age observed for the marine DOC pool (Mentges et al., 2019).

NEW ISOTOPIC APPROACHES FOR PROBING THE ORIGIN AND FATE OF OCEANIC DOC

The marine DOC pool is molecularly complex, where compounds produced contemporaneously from the same source may have different degradation pathways and compounds that appear to be molecularly identical (i.e., have the same molecular formula or bulk isotopic composition) may have diverse sources and biogeochemical histories. Thus, in addition to analytical challenges, the flow of carbon through different organic molecules is highly convoluted, preventing a clear view of biotic drivers that control the production of recalcitrant DOC and its accumulation in the interior ocean. Natural abundance radiocarbon (^{14}C) measurements are a powerful tool for assessing the age of oceanic DOC that cycles on centennial to millennial timescales (McNichol and Aluwihare, 2007), whereas stable carbon isotopic analyses (^{13}C) supply information on carbon origins, degradation pathways, and transfer through marine food webs. At the bulk scale, radiocarbon data suggests oceanic DOC ranges in age from ca. 4,000 to ca. 6,000 ^{14}C -years with older ages in the interior ocean, although spatiotemporal resolution of these measurements is relatively limited (Beaupre, 2015). The World Ocean Circulation Experiment (WOCE) initiated a systematic increase in the resolution of dissolved inorganic carbon (DIC) ^{14}C analyses, which has led to unprecedented insights into the dynamics of the marine carbon reservoir, particularly in the face of increasing atmospheric CO_2 concentrations (McNichol et al., 2000). Thus, more extensive ^{14}C analyses of DOC across our global oceans is needed to refine our understanding of DOC turnover and assess its role in modulating future climate scenarios. Bulk marine DOC is uniformly ^{13}C -enriched and generally consistent with a marine phytoplankton source (Beaupre, 2015). However, compound-specific ^{13}C analysis is an effective approach for discerning the source and fate of different DOM subcomponents, such as black carbon (Wagner et al., 2019). Similarly, ^{14}C measurements on different DOC molecular fractions has revealed that the apparent age and lability is not evenly distributed throughout the marine DOM pool (Follett et al., 2014; Close, 2019; Ishikawa et al., 2019). Thus,

targeted isotopic analyses are needed to unveil drivers of DOM accumulation and apparent recalcitrance in the interior ocean.

The enzymatic activity of heterotrophic microbes strongly affects the transformation of labile DOC into semi-labile and refractory DOC, thus altering the reactivity of DOC and modulating carbon fluxes in the ocean (Azam et al., 1983; Azam and Malfatti, 2007; Benner and Herndl, 2011). However, microbial activity is limited by both the accessibility of labile DOC components and nutrient availability. It is debated whether the balance between microbial growth and associated remineralization processes controls DOC cycling and whether this balance enhances or weakens the efficiency of the biological carbon pump (Azam and Malfatti, 2007). Biological carbon turnover is typically tracked by feeding molecular substrates (short-chain fatty acids, sugars, and amino acids) that have been uniformly labeled with stable (^{13}C , ^{15}N) or radiogenic (^{14}C , ^{3}H) isotopes (Ducklow et al., 1986; Jørgensen et al., 1993; Boschker et al., 1998; Keil and Kirchman, 1999; Boschker and Middelburg, 2002; Herndl et al., 2005). Some studies have utilized more complex isotopically labeled substrates, such as bacteria- or algae-derived DOC (Bronk and Glibert, 1993; Veuger et al., 2004; Bronk et al., 2007). However, bulk DOC does not permit distinction between the different carbon pools and uniformly labeled substrates omit the understanding of the fate of single carbon atoms within a molecule that are being differently used during uptake, biosynthesis, molecular transformation, and final release of DIC. Therefore, to specifically trace the microbial conversion of DOC to cellular biomolecules and metabolites or microbial remineralization of DOC to CO_2 , novel approaches based on position-specific and dual-isotope stable isotope probing (SIP), lipid radioisotope probing (RIP), and reversed isotope labeling (RIL) have been adapted from routine labeling techniques (Figure 3) (Wegener et al., 2012; Dippold and Kuzyakov, 2013; Kellermann et al., 2016; Dong et al., 2017, 2019; Evans et al., 2018, 2019; Aepfler et al., 2019).

Position-specific SIP, where only one carbon position within a particular substrate molecule is labeled with ^{13}C , has been applied extensively for revealing terrestrial carbon pathways (Kuzyakov and Galitsa, 1993; Fischer and Kuzyakov, 2010; Dijkstra et al., 2011; Dippold and Kuzyakov, 2013), but less so in the marine environment. Amino acids are one of the main substrates for heterotrophic bacteria and constitute a large fraction of their carbon demand (Jørgensen et al., 1993). Thus, the amino acids that occur as part of bulk DOC can be isotopically exploited to reveal key biosynthetic and metabolic pathways that link marine carbon and nitrogen cycles. Position-specific SIP has been used to reconstruct metabolic pathways of bacteria, identify substrate specificity of bacterial fatty acid biosynthesis, and quantify the release of metabolic products (e.g., short-chain fatty acids and DIC) (Aepfler et al., 2019). Dual-isotope lipid SIP, which combines D_2O with ^{13}C -labeled DIC, enables the direct quantitative tracking of both autotrophic carbon fixation and heterotrophic lipid production without having to provide an additional energy source in the form of excess carbon substrates (Wegener et al., 2016). This dual-isotopic approach has been utilized to investigate the metabolic activity of microbes in marine sediments, specifically for sulfate

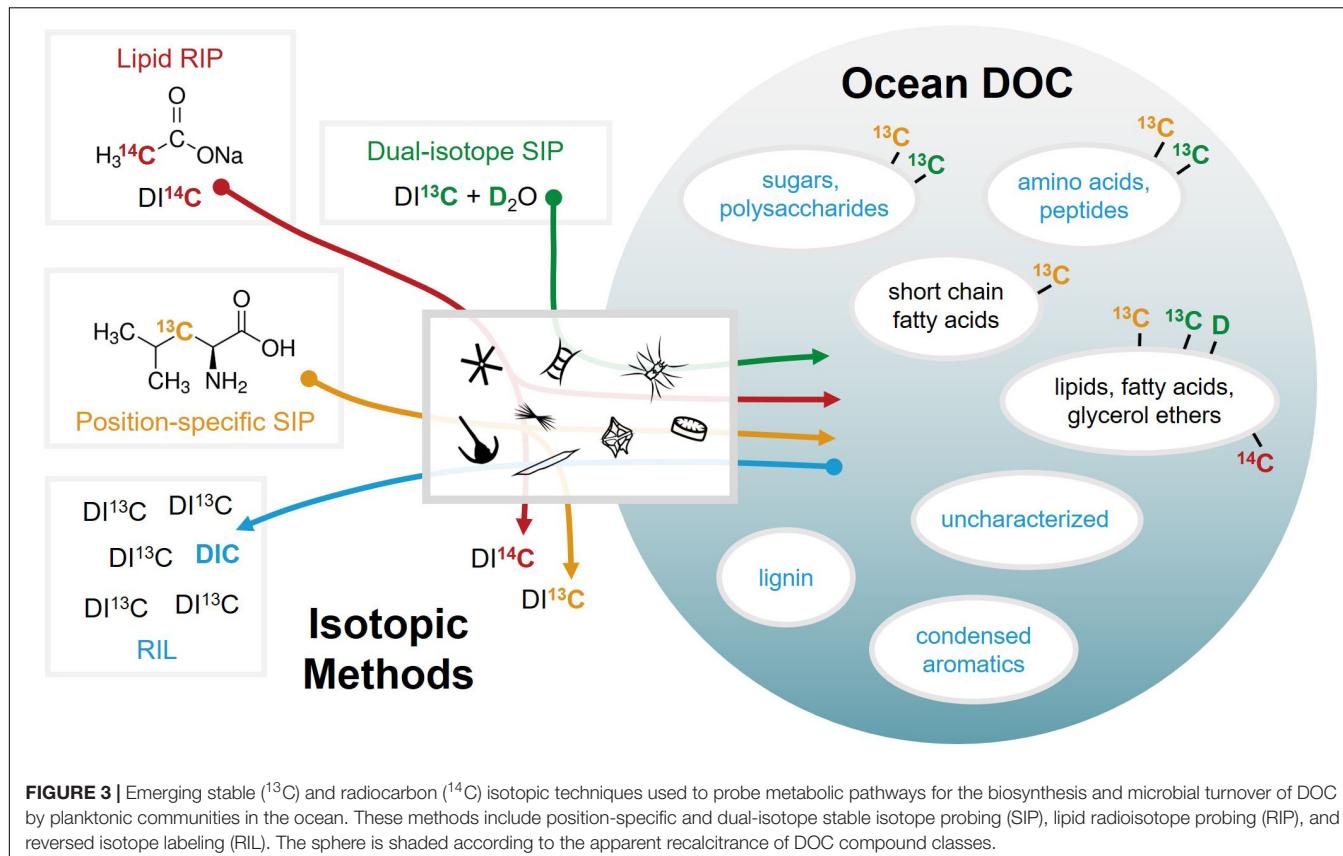


FIGURE 3 | Emerging stable (^{13}C) and radiocarbon (^{14}C) isotopic techniques used to probe metabolic pathways for the biosynthesis and microbial turnover of DOC by planktonic communities in the ocean. These methods include position-specific and dual-isotope stable isotope probing (SIP), lipid radioisotope probing (RIP), and reversed isotope labeling (RIL). The sphere is shaded according to the apparent recalcitrance of DOC compound classes.

reducing bacteria (Wegener et al., 2012), the anaerobic oxidation of methane (Kellermann et al., 2012), and lipid biosynthesis therein (Kellermann et al., 2016). Lipid radioisotope probing has been similarly applied to better understand lipid biosynthetic pathways in marine planktonic archaea (Evans et al., 2018). Natural DOM and environmental organic compounds that are not available in a stable isotope or radiolabeled form are accessible to turnover studies using RIL, in which a pool of ^{13}C -labeled DIC is continuously diluted during microbial degradation of a specific organic substrate or DOM at natural carbon isotope abundance (Dong et al., 2017, 2019). Thus, the change in the isotopic composition of DIC enables quantification of microbial remineralization by mass balance calculations.

DOM FUTURE PROJECTIONS

Concentrations of DOC in marine surface waters are closely linked to biogeochemical cycles and physical forcings. The oligotrophic subtropical gyres typically show higher concentrations (65–80 $\mu\text{M-C}$) of DOC than subpolar regions and the circumpolar Southern Ocean (40–50 $\mu\text{M-C}$) (Hansell, 2013). The accumulation and export of DOC in the subtropical gyres contributes to organic carbon flux from surface waters and supports the metabolic demand of heterotrophic microbes in the upper mesopelagic zone (Carlson et al., 2004). Ultimately, the production of DOC in the surface ocean is limited by the

magnitude of primary production, which in turn depends on nutrient supply (Carlson and Hansell, 2015; Romera-Castillo et al., 2016). Within these constraints, an intimate feedback between climate systems, nutrient regimes, and community structure can modulate surface DOC inventories on seasonal and decadal time scales. A multiyear net increase of DOC inventories ($\sim 300 \text{ mmol-C m}^{-2} \text{ yr}^{-1}$) has been reported within the North Pacific Subtropical Gyre, primarily driven by decadal climate variations, along with concurrent shifts in the plankton community and transition from nitrogen- to phosphorus-limitation (Church et al., 2002). The majority of DOC accumulating in the surface ocean is rapidly remineralized in the upper mesopelagic zone (Abell et al., 2000; Kaiser and Benner, 2012). Since a large portion of net primary production is routed through active microbial food webs, the production of recalcitrant DOC should scale proportionally with DOC production (Karl, 1999; Jiao et al., 2010). Heterotrophic microbes transform $\sim 0.02\%$ of primary production carbon into recalcitrant DOC (Benner and Herndl, 2011). Subtropical gyres cover $\sim 60\%$ of the total ocean area (Eppley and Peterson, 1979) and may be expanding in size (Polovina et al., 2008; Sharma et al., 2019). Therefore, small changes to DOC concentrations in these regions can significantly change the size of ocean DOC inventories and funnel a greater fraction to the interior ocean as refractory DOC. Given the multivariate approach required, it is unclear how current oceanic DOC inventories may be altered in response to continued climate change. Here, we

review predictions of how climate change will impact microbial and terrestrial DOC fluxes to the ocean and point out gaps in the current knowledge needed to refine our view of future oceanic DOM cycling.

Ocean Warming and Acidification

As a result of climate change, a concomitant rise in atmospheric temperatures and CO₂ levels have directly contributed to the warming and acidification of global oceans (Doney et al., 2009; Legendre et al., 2015). Controlled experiments have consistently demonstrated enhanced primary production and release of DOC in response to elevated ambient temperatures and CO₂ levels (Egge et al., 2009; Wohlers et al., 2009; Engel et al., 2011, 2013; Kim et al., 2011; Liu et al., 2017; Novak et al., 2018; Sugie et al., 2018). However, enhanced primary productivity may ultimately be balanced or exceeded by respiration rates in a warmer, more acidic ocean (Pomeroy and Wiebe, 2001; Vaquer-Sunyer et al., 2010). Enhanced DOC production under high CO₂ conditions was often accompanied by increased activity of microbial consumers (Engel et al., 2013; Endres et al., 2014), thus counteracting DOC accumulation. Higher DOM degradation rates may be related to extracellular hydrolytic enzymes, which exhibit optimum activity rates under more acidic conditions (Piontek et al., 2010; Endres et al., 2013). However, recent findings suggest that DOC production and quality does not substantially change in the long-term, because either the local phytoplankton communities become nutrient-depleted or the newly produced organic matter is utilized by fast-adapting heterotrophic microbial communities (Zark et al., 2015, 2017; Aparicio et al., 2016; Moran et al., 2016; Kim et al., 2018; Viviani et al., 2018). Regardless of the future balance between production and respiration, modeling of oceanic DOC decay rates suggests that a uniform 1°C warming of the ocean would decrease the global DOC reservoir by ~7 Pg-C (Lønborg et al., 2018). Given higher activation energies for refractory DOC compared to labile DOC, increased temperatures would also disproportionately impact the degradation of recalcitrant DOC presumed to accumulate in the interior ocean.

Thermohaline circulation in the Atlantic and Pacific Oceans is predicted to decrease within the next century (McPhaden and Zhang, 2002; Stocker et al., 2013). Modeling efforts that seek to couple biogeochemical fluxes to ocean circulation patterns suggest that density stratification will be strengthened as a result of ocean warming (Capotondi et al., 2012). It is unknown whether these combined effects would significantly affect losses of DOM by abiotic processes, such as photodegradation or outgassing (Legendre et al., 2015). However, a reduction in the rate at which deep waters are returned to the surface ocean would significantly impact nutrient availability and primary production and could therefore alter the amount and/or quality of DOM that accumulates at shallower depths or is shunted to the interior ocean. Based upon satellite data, warmer surface ocean temperatures have been shown to diminish the supply of nutrients needed to carry out photosynthesis, and thus reduce oceanic biomass and primary productivity (Behrenfeld et al., 2006; Doney, 2006). These observations are in opposition with results from controlled experiments

described previously, which generally show warming and acidification to enhance primary production. This discrepancy spotlights the interdisciplinary and multivariate approach needed to accurately predict DOC production and turnover in the surface ocean.

Oxygen Minimum Zone Expansion

The persistence of organic carbon in the ocean is effectively regulated by O₂ exposure time (Hartnett et al., 1998), which has been linked to the low density of metazoans (Jessen et al., 2017; Middelburg, 2018) and the oxidation reaction energetics of organic matter, which predict the persistence of complex, reduced organic molecules in anoxic settings (LaRowe and Van Cappellen, 2011). As oxygen minimum zones expand in the ocean due to decreased ventilation and increased temperature (Breitburg et al., 2018), the limited catabolic potential under such conditions could render specific molecular structures recalcitrant. Anoxia may have led to larger marine DOC reservoirs in the geological past, as tentatively suggested for the Precambrian and Eocene oceans (Rothman et al., 2003; Sexton et al., 2011; Ridgwell and Arndt, 2015). The deep waters of the Black Sea exhibit DOC concentrations that are 2.5-fold higher than DOC concentrations in the deep ocean (Ducklow et al., 2007; Margolin et al., 2016). It remains unclear whether the DOC accumulation is directly linked to terrestrial DOC inputs to this anoxic basin (Margolin et al., 2016) or is derived from a mixture of terrestrial, marine, and autochthonous DOC (Margolin et al., 2018). The East Japan Sea is a semi-enclosed marginal sea where DOC accumulation is attributed to decreased reactivity resulting from low bottom water temperatures (<1°C) (Kim et al., 2015). Therefore, although these two basins are imperfect modern analogs for future oxygen minimum zone expansion in the global ocean, the Black and East Japan Seas provide contrasting insights as to how the accumulation of marine DOC may increase under reduced O₂ conditions. At present, DOC concentrations in oxygen minimum zones of the Eastern Tropical North Pacific and Eastern Tropical South Pacific Oceans are similar to concentrations observed for the open ocean and are consistent with general water circulation patterns¹. However, rapid utilization of semi-labile DOM has been observed for the upper oxycline in waters of the Eastern Tropical South Pacific (Loginova et al., 2019), suggesting a high degree of diagenetic DOM alteration at shallow oxygen minimum zone depths compared to the open ocean and to deeper oxic waters. This may be explained by the upwelling of altered DOM and/or extensive heterotrophic DOM utilization. Based upon these observations it is unclear how changing O₂ concentrations in the ocean would affect the size of DOC reservoirs and highlights a need for further research in this area.

Terrestrial Inputs

Riverine DOC fluxes will be closely tied to the effects of climate change within the watershed, particularly via enhanced warming and the increased frequency and severity of hydrological events. Climate change impacts will be enhanced in high latitude

¹www.clivar.org

regions, where warming occurs at a rate twice that of the global average (Jeffries and Richter-Menge, 2012; Stocker et al., 2013). Glacial melt will not only increase freshwater runoff, but continued warming would also release the ~6 Pg-C currently stored as DOC in glaciers globally (Hood et al., 2015). Most of the Earth's soil organic carbon is stored in the Arctic, including permafrost (1,300 Pg-C of POC plus DOC) (Hugelius et al., 2014). Increased temperatures will unlock organic matter preserved in these soils, resulting in enhanced DOC export via rivers draining Arctic landscapes (Freeman et al., 2001; de Wit et al., 2016; Wild et al., 2019). In regions where permafrost carbon is a major contributor, riverine DOC may be quickly remineralized to CO₂ before reaching the open ocean (Mann et al., 2015), potentially furthering climate change feedback. In areas of increased runoff, higher DOC concentrations paired with higher discharge will result in concomitantly higher DOC fluxes (Raymond et al., 2016). As such, decreased water residence times during hydrological events will quickly export sediment- and DOC-enriched river water to the coastal ocean. In conjunction with landscape alteration, hydrological events may also result in the enhanced mobilization of aged terrestrial carbon reservoirs (Marwick et al., 2015; Barnes et al., 2018).

The fate of terrestrial DOC also relies upon estuarine behavior and the resilience of coastal fringe ecosystems. These regions are among the highest in productivity on Earth and face increased pressure from anthropogenic and climatic forces (Erwin, 2009; Mitsch and Hernandez, 2013). With continued sea level rise, it is unknown how the migration and/or collapse of these coastal vegetation communities will impact the relative stability of organic matter stored in sediments (Kirwan et al., 2013; Sjøgaard et al., 2017; Ruiz-Fernández et al., 2018; Macreadie et al., 2019). Thus, the net flux of DOC from fringe ecosystems, particularly in tropical regions, is not well constrained. At high latitudes, long-term increases in DOC concentration in coastal surface waters have been observed (Worrall et al., 2004; Filella and Rodríguez-Murillo, 2014). However, when other factors, such as rainfall, land management, and salinity, are also considered, a net decrease in low latitude DOC concentrations is indicated (Regier et al., 2016). Large uncertainties associated with estimating the regional distribution and total land area for sea grasses, salt marshes, and mangrove forests is a major obstacle in constraining global DOC flux values for these coastal ecosystems (Duarte, 2017). These habitats face the fastest loss rates of any ecosystem (1–3% per year), largely as a result of anthropogenic impacts (Duarte, 2017). Therefore, spatial resolution of these ecosystems is critical for enhancing our current and future understanding of their role as an oceanic DOC source.

Anthropogenic Inputs

Poor spatiotemporal resolution of atmospherically deposited organic carbon prevents accurate global ocean flux estimates and highlights a critical area for future research. However, perhaps even more importantly, atmospheric deposition is also a major source of nutrients, such as nitrogen and phosphorus. Ocean stratification driven by a warming climate is expected to further enhance the relative impacts of atmospheric inputs

(Kanakidou et al., 2012). Roughly half of all deposited organic nitrogen is derived from human activities (Kanakidou et al., 2012) and primary production has been shown to correlate with anthropogenic aerosol deposition globally (Wang et al., 2015). Paired with riverine export, the deposition of industrial aerosols in northwestern Pacific Ocean has converted surface waters from being nitrogen-limited to phosphorus-limited (Kim et al., 2011). The interplay of atmospheric deposition, ocean warming, and stratification is complex. However, net gains in primary production with continued industrialization and climate change would probably be significant (St-Laurent et al., 2017) and may enhance local DOC export.

Although wildfires are naturally occurring and have punctuated Earth's history since the emergence of land plants (Scott and Glasspool, 2006), anthropogenic climate change, land use change, and fire suppression practices are enhancing the frequency and severity of vegetation fires (Flannigan et al., 2009; Krawchuk et al., 2009). Although the production of refractory charcoal during wildfires may help mitigate the release of CO₂ globally during burn events (Jones et al., 2019), a considerable portion of the charred organic matter is carried by wind to coastal and offshore surface waters (Jurado et al., 2008). Studies investigating the composition of deposited pyrogenic aerosols are limited but appear to be enriched in nitrogen (Bauters et al., 2018), which may fuel primary production or alter local microbial communities. Despite increased occurrence of wildfire in coastal areas, little is known regarding the short- and long-term impacts and fluxes of deposited ash and smoke in oceanic surface waters.

Increased riverine nutrient concentrations resulting from agricultural development and urbanization contribute to coastal eutrophication and hypoxia (Rabalais et al., 2009; Gilbert et al., 2010). Increased primary productivity paired with O₂ depletion in coastal waters may result in favorable conditions for the accumulation of excess organic matter in sediments. However, predicted increases in the frequency and severity of storm events (e.g., hurricanes), which oxygenate surface waters via mixing and freshwater inputs, could temporarily offset sedimentary organic matter storage. Given that coastal sediments are an intermediate reservoir for organic matter, lateral transport of accumulated carbon to the open ocean could increase as a result of nutrient inputs, but research is needed to confirm this. Finally, the input of microplastics to the ocean is estimated to be 1–4 Tg-C yr⁻¹ (Jambeck et al., 2015). Exposure to sunlight can degrade microplastics, which undergo photodissolution to produce DOC, although photochemical conversion rates are very low (Zhu et al., 2020). Thus, contributions of plastic-derived DOM to the total oceanic DOC pool are likely negligible.

CONCLUSION

The total DOC flux from external sources is similar to the export of DOC to the mesopelagic and an order of magnitude greater than the export of DOC to the interior ocean. Therefore, even small variations in the amount or composition of external

DOC exported to the ocean could ultimately impact the sum of DOC transferred from the surface to the interior ocean each year. However, at present, the slight imbalance between primary production and respiration in surface waters is the driver of recalcitrant DOC accumulation. Therefore, constraining oceanic DOC fluxes through the microbial food web relies upon both a comprehensive understanding of metabolic pathways and the spatiotemporally refined mapping of plankton and bacterial communities. Broad application of novel stable and radiocarbon isotopic techniques will pave the way for a coherent understanding of marine organic carbon cycling by revealing predominant biosynthetic and degradation pathways that control DOM production and turnover. Isotopic analyses, particularly compound-specific measurements, can be expensive and require large sample sizes in order to obtain robust isotopic signatures. An increased demand for DOC stable and radiocarbon isotopic measurements would continue to fuel ongoing analytical innovations that allow for lower analysis cost and sample size requirements. As we continue to accumulate isotopic measurements, these data should also be paired with less expensive, high throughput analyses (e.g., fluorescence spectroscopy) to allow for the extrapolation of stable and radiocarbon signatures more broadly throughout the global ocean. At present, the limited resolution of surface water plankton and bacterial populations, which vary significantly with latitude and coastal proximity (Fuhrman et al., 2008; Zinger et al., 2011; Sunagawa et al., 2015; Arteaga et al., 2016), prevents a globally relevant view of DOC production. Therefore, research efforts should also focus upon the *in situ* variability and activity of marine microbial communities, particularly in surface waters. A fine-scale approach, both molecularly and spatiotemporally, is necessary to refine the current view of oceanic DOC cycling so that we may accurately gauge the response of this major carbon store to anthropogenic perturbations and global climate change.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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