

# New Perspectives on the Marine Carbon Cycle—The Marine Dissolved Organic Matter Reactivity Continuum

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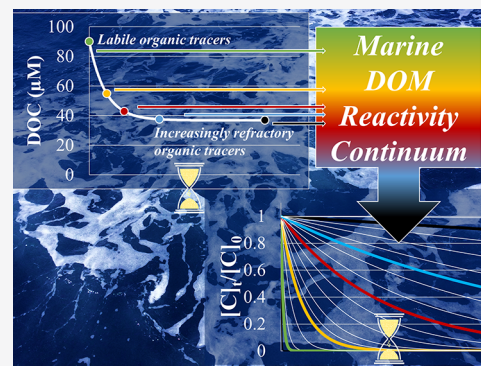
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**ABSTRACT:** This perspective challenges our current understanding of the marine carbon cycle, including an alternative explanation of bulk  $^{14}\text{C}$ -DOM measurements. We propose the adoption of the carbon reactivity continuum concept previously established for lakes and sediments for the oceans using kinetic data and term this the marine DOM reactivity continuum. We need to gain a fundamental understanding of the biogeochemical drivers of surface water DOM concentrations and reactivity, biological carbon pump efficiency, and the autotrophic communities that are the ultimate but variable sources of marine DOM. This perspective is intended to shift our focus to a more inclusive kinetic model and may lead us to a more accurate assessment of the active and dynamic role marine DOM plays in the global carbon cycle. Currently, the kinetic data to establish and validate such a marine DOM reactivity continuum model are still lacking, and their resolution depends on the discovery of new organic tracers that span large differences in reactivity and microbial degradation rates. We may need to refocus our efforts in deciphering the structure and reactivity of marine organic molecules in a kinetic context, including the microbial and physicochemical constraints on molecular reactivity that are present in the deep ocean.

**KEYWORDS:** marine DOM, organic tracers, reactivity continuum, kinetic model



## PERSPECTIVE

The reactivity of marine dissolved organic matter (DOM) remains at the forefront of global carbon research.<sup>1–6</sup> However, our understanding of dissolved organic carbon (DOC) turnover is hampered by its sluggish decomposition, making direct comprehensive decomposition studies prohibitive, given the extremely large time scale from hours to decades or even longer turnover times. Consequently, our current working knowledge is inferred from chemical proxies, metabolic measurements, and C flux budgets that do not take into account DOM sources outside the photic zone. Currently, we compartmentalize the marine DOM pool into broad reactivity brackets of labile, semilabile, and refractory, but here, we argue that we need to introduce the concept of the marine DOM reactivity continuum, not unlike established models for freshwater and sediment organic matter.<sup>7,8</sup> It is more intuitive and plausible that marine DOM reactivity is based on a continuum of compounds that react at different kinetic rates, analogous to the freshwater DOM reactivity continuum established for boreal lake DOM in Sweden.<sup>8</sup> Although one may argue that DOM degradation in sediments may not be comparable to that in the water column, as DOM is exposed to fundamentally different processes due to different redox chemistry, even here the validity of the DOM reactivity continuum approach has been established.<sup>7</sup> We detail below a

hypothetical approach to establish a marine DOM reactivity continuum.

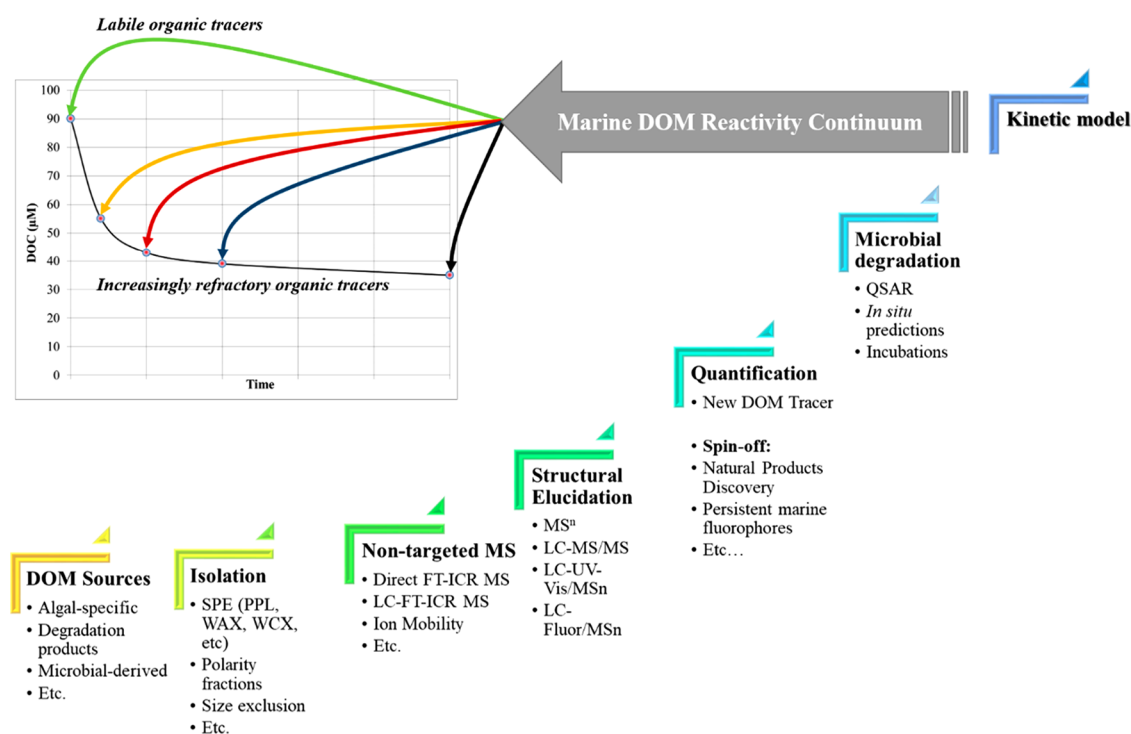
The proposed kinetic model would need to be established at the molecular level (e.g., development of organic tracers), because sufficiently long incubation times required to generate kinetic rates for bulk marine DOM, as undertaken for freshwater and sediment DOM, are unrealistic. A conceptual framework detailing the specific steps for the development of a kinetic model and the associated modern analytical tools employed to achieve this goal are provided in Figure 1. A promising recent study summarized the microbial metabolites currently known to contribute to the DOM pool<sup>9</sup> and potentially provided a starting point to evaluate the stability of these metabolites and their direct degradation products as suitable organic tracers to span portions of the reactivity continuum.

The development and adoption of the marine DOM reactivity and turnover are critical for several reasons: 1) to

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**Figure 1.** Conceptual framework to develop the marine DOM reactivity continuum based on kinetic data of individual organic tracers and their determined and predicted degradation rates in the ocean. Examples for each category are provided; however, the list is by no means comprehensive.

be able to more accurately predict marine carbon sequestration; 2) to explain the microbial carbon demand in the deep ocean; 3) to model global carbon cycling and future climate predictions; and 4) to better understand the marine DOM composition and reactivity.

Interestingly, marine carbon cycle modelers recognized the carbon reactivity controversy emerging in the literature about proposed different pools of refractory DOC and created an updated model incorporating multiple decay functions for DOC that could be easily adapted to the proposed marine DOM reactivity continuum concept.<sup>10</sup> In short, a reactivity continuum model assumes bulk DOM degradation can be described by an integration of first-order exponential decay functions (say for individual compounds) over the reactivity distribution (Figure 2). This reactivity distribution is the

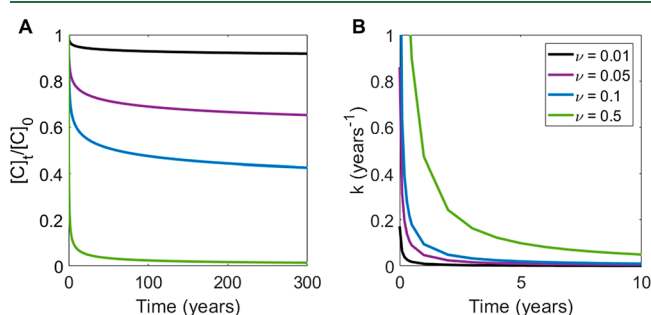
weighted probability of initial reactivity, typically described by a gamma distribution,<sup>8,11</sup> and allows for the following model equation

$$(\text{DOC}_t/\text{DOC}_0) = [\alpha/(\alpha + t)]^\nu \quad (1)$$

where  $\alpha$  is the average lifetime of more reactive compounds, and  $\nu$  (unitless) is the shape parameter. Thus, the apparent decay coefficient,  $k$  ( $\text{years}^{-1}$ ), can be described by eq 2, which highlights that decay is not constant but decreases with time.

$$k = \nu/(\alpha + t) \quad (2)$$

We have built a reasonable estimation of DOC distributions and bulk quantities in the Global Oceans based on tens of thousands of DOC measurements. Bulk global concentrations range between 65 and 80  $\mu\text{mol C kg}^{-1}$ . Deep ocean values are lower and between 38  $\mu\text{mol C kg}^{-1}$  (Pacific) and 42  $\mu\text{mol C kg}^{-1}$  (Atlantic)<sup>13,14</sup> on average, which yields a global ocean DOC inventory of  $662 \pm 32 \text{ Pg C}$ .<sup>14</sup> Based solely on this global DOC inventory and a global marine DOC export rate of 1.8 Pg C  $\text{yr}^{-1}$ , marine DOC would turn over in  $370 \pm 20$  years.<sup>13</sup> This estimate however still does not include additional sources within the water column and the contribution of particulate organic matter (POM) dissolution or DOM arising from chemoautotrophs, which seem to be abundant in the deep ocean.<sup>15</sup> A more recent study evaluated the importance of nitrite oxidizing chemoautotrophs in the dark ocean and estimated that a surprisingly high percentage of 15–45% of dissolved inorganic carbon (DIC) is fixed in the mesopelagic western North Atlantic.<sup>16</sup> It seems that there is a tight relationship between these nitrite-oxidizing *Nitrospinae* chemoautotrophs and the better known ammonium oxidizing archaea.<sup>16</sup> This is an intriguing and presumably large pool of primary producers at depth, but certainly more data is needed to evaluate the quantitative importance of chemoautotrophy on a global scale and what fraction of this biomass may be



**Figure 2.** A: Hypothetical loss of individual compounds ( $[C]$ ) over time (years) according to the reactivity continuum model, where line colors correspond to modeled (or hypothetical) decay coefficients. B: The dependency of  $k$  on different shape parameter values. Note: this hypothetical model has been initiated with an  $\alpha$  value of 0.0588  $\text{yr}^{-1}$  based on the published total dissolved amino acid (TDAA) decay rate and concentration at a 300 m depth at station Aloha, Pacific Ocean.<sup>12</sup>

released as DOM with different reactivity pools. We will revisit below the incorporation of DIC into the DOM pool as a possible pathway to introduce a bias in using radiocarbon age as a proxy for bulk DOC turnover. POM dissolution at depth is another active field of research, and little is known about the derived DOM, its composition, or its reactivity. However, progress is underway, and a recent study classified POM constituents to better constrain its degradability.<sup>17</sup> Further detailed studies are needed to gain a better understanding of DOM arising from POM dissolution and its accumulation and reactivity in the deep ocean.

Interestingly, radiocarbon data finds that bulk DOC ages range from 3780–6,000 yrs before present (BP) and were calculated from  $\Delta^{14}\text{C}$  values ( $-375\text{‰}$  to  $-525\text{‰}$ ),<sup>18–24</sup> which has been used to infer that DOC survives several oceanic overturns.<sup>24</sup> Thus, a two-end-member mixing model has commonly been used to describe marine DOC turnover<sup>25</sup>

$$[\text{DOC}]_t = [\text{DOC}]_L \cdot \text{EXP}(-k_L \cdot t) + [\text{DOC}]_R \cdot \text{EXP}(-k_R \cdot t) \quad (3)$$

where  $[\text{DOC}]_L$  and  $[\text{DOC}]_R$  are the labile and refractory DOC pools, respectively. However, additional  $^{14}\text{C}$ -free sources to the deep ocean have been identified and challenge the age distribution of marine DOM. What if only a small fraction of the deep ocean DOM is  $^{14}\text{C}$ -free and the remainder is turning over on much shorter time scales, as suggested even when DOC is only generated in the photic zone? We will revisit this point, but first, we have to review the current state of knowledge.

The prevailing foundation for our understanding of the marine carbon cycle and its reactivity is based in large on three fundamental pillars: (1) ocean DOC inventories, (2) the radiocarbon age of DOC, and (3) the efficiency of the biological and microbial carbon pumps. Below we review our current knowledge of DOC sources, ages, and reactivity to help reconcile these perceived disparities in DOC turnover and integrate this understanding with the proposed marine DOM reactivity continuum concept. The basis of this perspective is that marine DOM constituents are very complex and span a wide continuum in their turnover times, and conceivably, the pool of refractory DOM molecules that reaches half-lives of thousands of years may not be as large as previously believed. We suggest that kinetic data of a multitude of structurally elucidated DOM molecules and their precisely measured reactivity are needed to more accurately predict DOM sequestration as a whole in the deep ocean. Hence, this perspective highlights suspected fundamental differences in DOM composition and resulting reactivity in the context of these pillars and also emphasizes the need to deviate from a two-end-member DOM age model.

**1. Pillar 1. DOM Composition: Contrasting Sources in Ocean Basins.** We contend that DOM reactivity is highly dependent on the source, is tied to its composition, and changes over time. Accordingly, fundamental differences in DOM reactivity between ocean basins and locale in general must exist, given variations in primary producers and terrestrial inputs. It is well established that the overwhelming majority of marine DOM arises from carbon dioxide fixation by marine photoautotrophs in the sunlit waters of the surface ocean. At depth, chemoautotrophs may also fix potentially substantial amounts of DIC,<sup>16,26</sup> but the rate of DOM production arising from chemoautotrophs remains unknown. Below we discuss examples that underline the expected fundamental and large geographical variations in the DOM composition, which would

result in presumably large differences in the decay coefficients and hence kinetics of the proposed marine DOM reactivity continuum model (eqs 1 and 2). While more eutrophic coastal oceans may be dominated by other species such as diatoms and dinoflagellates,<sup>27,28</sup> picocyanobacteria *Prochlorococcus* and *Synechococcus* are by far the largest primary producers in the oligotrophic subtropical and tropical ocean<sup>29</sup> and therefore are major contributors to the DOM pool. Marine open ocean sediment trap records also show strong cyanobacterial pigment signals in deep-ocean samples well below the mixed layer,<sup>30</sup> suggesting that POC is partially derived from these cells and dissolution of this POC will yield DOM that is ultimately derived from these picocyanobacteria. We do know that picocyanobacteria-derived DOM is very complex, including rather stable fluorophores that resemble fluorescent DOM found in the deep ocean.<sup>31</sup> Further this organic matter is transported relatively quickly to deeper waters as evidenced by intact DNA signatures.<sup>30</sup> The transport mechanism is still under investigation, because it was previously believed that these small cells did not contribute much to the biological pump and did not substantially transport organic matter to the deep ocean.<sup>32</sup> One possibility is the route via fecal pellets from grazers<sup>33</sup> and enhanced aggregation by bacteria.<sup>34</sup> The dissolution of POM to DOM remains poorly constrained, and further research is needed to establish better links.

The surface Arctic Ocean is another example of an ocean basin exhibiting fundamentally different DOM, as a substantial portion is of terrestrial origin, which is largely defined by a very complex polyphenolic composition.<sup>35</sup> Due to the large river discharge of terrigenous DOM from the arctic/subarctic tundra and boreal systems, the surface Arctic Ocean was estimated to contain 14–24% of terrigenous DOM,<sup>35</sup> which also has undergone limited photobleaching due to its rapid supply, the low solar angle, and the long Arctic winter. This polyphenol-rich DOM is then transported into the deep North Atlantic during deep-water formation.<sup>35</sup> As a result, the North Atlantic deep DOM is likely a special case and contains overall greater concentrations of DOC with more lignin/tannin degradation products when compared to other ocean basins. The Southern Ocean is another interesting example, because *Prochlorococcus* and *Synechococcus* cannot survive in such cold waters. Hence, Antarctic surface DOM sources do not contain picocyanobacteria lysates, exudates, or their degradation products and do not receive any terrestrially derived DOM either. As a result, the DOM exported during Antarctic bottom water (AABW) formation contains presumably, not only compositionally different DOM, but also lower DOC concentrations than other oceanic regions.<sup>14</sup> The exported DOC from the Antarctic shelf was estimated to be  $4.0 \pm 0.6$  Tg DOC yr<sup>-1</sup>,<sup>36</sup> but it seemed to be labile and thus did not contribute to newly formed AABW.<sup>36</sup> However, there is much to be learned about Antarctic marine DOM.

In addition to these above-mentioned examples, a DOC anomaly with substantially higher DOC concentrations has been identified in the Western North Atlantic, when compared to Eastern North Atlantic/South Atlantic subtropical gyres,<sup>14</sup> and it may be related to another rather unique source. It has been recently shown that *Sargassum* exudes an incredibly high amount of DOC<sup>37</sup> that contains large quantities of very specific polyphenols (phlorotannins).<sup>37</sup> Hence, *Sargassum* alone can potentially explain this anomaly with a contribution of a rather unique open ocean DOM composition.



Overall the supply of new nutrients is a reasonable predictor for surface DOC concentrations<sup>14</sup> but not necessarily for the degradability time scale of DOM derived from fundamentally different autotrophic sources in the ocean. It has been projected that up to 50% of the photoautotrophically derived organic carbon or  $\sim 25 \text{ Pg C yr}^{-1}$  can pass through the DOC pool.<sup>21</sup> However, it is estimated that only  $2 \text{ Pg C yr}^{-1}$  of the surface-derived DOC is stable enough to be exported to greater depth,<sup>14</sup> but dissolution of particles as well as chemoautotrophically derived DOM have been neglected in these calculations. To date, we do not have sufficient data to estimate these contributions, but they may be substantial as discussed above. Respiration is also not exclusively a surface ocean phenomenon, and surprisingly, respiration in the dark ocean seems comparable to that in the epipelagic zone.<sup>38</sup> It becomes conceivable that DOC concentrations in the world oceans may be largely explained based on vertical transport and differences in its degradability and source. This approach to marine DOM turnover would require a deviation from a two-end-member mixing model based on radiocarbon measurements. This would also mean a departure from the currently accepted marine carbon cycling theory; however, the dilemma of predicting DOM turnover and reactivity over longer time scales still remains. These data are critical for evaluating the validity of the concept of very slow DOM degradation (millennia time scale) along the meridional overturning circulation versus the notion that DOM contribution is largely driven by vertical transport and internal processes, which would not require the DOM exported from the surface waters to be excessively old.

**2. Pillar 2. DOM Radiocarbon Ages:  $^{14}\text{C}$ -Free Sources and New Insights.** DOC age based on radiocarbon ( $^{14}\text{C}$ ) measurements has been established as the second pillar informing our current understanding of the marine carbon cycle.<sup>24</sup> In 1992, Bauer and Druffel published the first data set of  $^{14}\text{C}$ -DOC from the Pacific and Atlantic Oceans.<sup>24</sup> They measured surprisingly old radiocarbon ages of DOC in the deep ocean with values of  $^{14}\text{C}$  that translate into an apparent age of about 6,000 years BP ( $\Delta^{14}\text{C}$ :  $-525\text{‰}$ ) in the Pacific and slightly younger apparent ages in the deep Atlantic of 3,780–4,300 years BP ( $\Delta^{14}\text{C}$ :  $-375\text{‰}$  to  $-414\text{‰}$ ). They concluded that the difference in the apparent DOC age between the two ocean basins was a result of different deep-water circulation patterns and transit times. Since that time, biogeochemists have largely accepted the notion that surface-derived DOM in the deep ocean is thousands of years old and survives several ocean overturns.<sup>39,40</sup> These combined observations led to the two-end-member mixing model for oceanic DOC which identified a labile and semilabile pool derived from contemporary primary production which turns over on time scales of hours to days and weeks to months, respectively, that is superimposed on a recalcitrant DOC pool cycling on time scales of millennia.<sup>25,41</sup> The apparent  $^{14}\text{C}$  age of bulk marine DOM directly contrasts with even early studies from the 1990s showing that recently produced algal DOM was rapidly decomposed and may substantially contribute to the overall marine DOC fluxes.<sup>39,40</sup> While  $^{14}\text{C}$  measurements are likely accurate, alternative explanations for the apparent  $^{14}\text{C}$  age are emerging.

The interpretation of the apparent  $^{14}\text{C}$  age of marine DOM has been challenged, and an increasing number of sources of  $^{14}\text{C}$ -free DOC have been identified.<sup>42,43</sup> The most significant ones are methane seeps<sup>43</sup> and hydrothermal vents, although oil

and carbon dioxide seeps may also be important but remain largely unexplored in this context. Ridge-flank hydrothermal systems are also hot spots for chemosynthetically produced  $^{14}\text{C}$ -depleted DOM.<sup>44</sup> The measured values showed apparent  $^{14}\text{C}$  ages of hydrothermal recirculated water DOM ranging from 11,800 to 14,400 years BP ( $\Delta^{14}\text{C}$ :  $-770\text{‰}$  to  $-835\text{‰}$ ). Current estimates of DOM derived from hydrocarbon seeps range from  $0.2\text{--}20 \text{ Tg C yr}^{-1}$  and are likely underestimated, as they account only for mud volcano seeps and overlook inputs from other known seep types.<sup>43,45</sup> A more recent study also confirmed that hydrothermal vents are a source of  $^{14}\text{C}$ -depleted DOC,<sup>45</sup> but they were also not able to estimate its contribution to the overall DOC pool. Radiocarbon measurements on fractionated DOM are still rare but have illustrated that multiple age groups have to be present in marine DOM,<sup>21,46,47</sup> which is another piece of the puzzle. In fact,  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  results from serial oxidation experiments of DOM from the Central Pacific<sup>42</sup> were used for modeling and predicted that 30% of deep ocean DOM (500–2000 m) could be modern.<sup>42</sup>

On the other hand, while this study suggested that 30% of deep ocean DOM is modern, they further suggest that 30–60% of deep ocean DOM was “highly depleted” with an apparent radiocarbon age of  $\sim 30,000$  years.<sup>42</sup> It also was recently shown that different size fractions within DOM have fundamentally different apparent  $^{14}\text{C}$  values.<sup>46,47</sup> Further, a 12 Pg C fraction of the marine DOC pool (determined using a proxy method for polycyclic aromatic hydrocarbons or dissolved black carbon (DBC) compounds) has been described as “ultrarefractory”.<sup>48</sup> This classification is based on average radiocarbon age measurements of 18,300 ( $\Delta^{14}\text{C}$ :  $-895\text{‰}$ ) (SE Atlantic) and 20,100 ( $\Delta^{14}\text{C}$ :  $-920\text{‰}$ ) (NE Pacific) years BP for open ocean DBC in ultrafiltered DOM (UDOM,  $>1000 \text{ Da}$ ).<sup>49</sup> Ziolkowski and Druffel (2010)<sup>49</sup> stated that DBC could be 4–22% of total deep ocean DOC, although a more recent estimate was only 2% DBC and an apparent  $^{14}\text{C}$  age of 23,000 BP ( $\Delta^{14}\text{C}$ :  $-945\text{‰}$ ).<sup>50</sup> To further complicate the matter, surface DOC apparent  $^{14}\text{C}$  ages of almost 2,000 years BP ( $\Delta^{14}\text{C}$ :  $-220\text{‰}$ ) have also been used to infer the presence of a large refractory DOM pool at the surface, but the possible incorporation of preaged carbon dioxide into primary producer biomass during large scale upwelling has not been considered<sup>14</sup> in this context. Nonetheless, two recent studies showcase large scale upwelling regions across the Global Oceans based on  $\Delta^{14}\text{C}$ -DOC measurements<sup>51,52</sup> confirming the presence of preaged DIC and DOC at the surface. This effect might be of particular importance in coastal upwelling regions but seems to be much larger than previously thought. The established link between DOC and nitrate<sup>14</sup> is a testimony to this idea, and greater variability of carbon dioxide at the surface during upwelling may also further enhance primary production when sufficient nutrients are available. While the controversy of refractory DOC persisting for several meridional overturning circulations is still fueled by strong correlations between deep water masses (e.g., AABW) aging and DOC decrease over time,<sup>19</sup> it is necessary to postulate viable alternative explanations.

Irrespective of the source or sources of radiocarbon free DOC, their input is significant for our interpretation of marine DOM age and turnover. Evidence is mounting about these ancient DOC sources, but the lability and incorporation of  $^{14}\text{C}$ -free atoms into the complex pool of marine DOM are at

best anecdotal. Even less is known as to whether or not labile DOM sources exist that have a very old appearance due to the incorporation of  $^{14}\text{C}$ -free organic or inorganic carbon. Examples could be the utilization of mantle-derived carbon dioxide and the production of contemporary but  $^{14}\text{C}$ -free DOM released by chemoautotrophs or microbial oxidation of geogenic methane. Based on model-derived residence times, Lechtenfeld et al.<sup>53</sup> found compound ages substantially higher than those accessible by radiocarbon dating methods suggesting a background pool of “radiocarbon dead” DOC. This is not a hypothetical pathway, and the incorporation of  $^{14}\text{C}$ -free material into the marine DOC pool has been previously demonstrated.<sup>43</sup> A recent publication by Druffel et al. also confirmed the importance of  $^{14}\text{C}$ -free DOC sources and the acknowledgment that the deep ocean DOM might be turning over faster than previously believed.<sup>18</sup>

In addition to newly recognized sources of ancient DOC to the deep ocean pool, there are also potential removal mechanisms for deep ocean DOC, even if one assumes biodegradation is prohibitively slow. Before export to the deep ocean, photochemistry has long been considered a major “refractory” DOM sink in the surface ocean. This assumption is largely based on work that measured photoproduction rates of low molecular weight (LMW) carbonyl compounds and carbon monoxide in the North Atlantic Ocean.<sup>54</sup> Since rates were higher in deep water relative to surface water, it was estimated that the photochemical sink for refractory DOC was 500–2,100 years,<sup>54</sup> well below its apparent  $^{14}\text{C}$  age. While other ocean basins were not considered, there have been a number of studies evaluating the photochemical sink for marine DOM. For instance, DBC in samples collected from the deep (3000 m) North Atlantic were very photoreactive, decreasing by 95% in a 28-day irradiation.<sup>55</sup> However, photoproducts were not quantified, so it is still unclear how much of the “BC” pool can be directly remineralized by sunlight.

A number of studies have also used large-scale modeling approaches to evaluate marine DOM photochemistry and, in particular, focused on products that would serve as proxies for DOM removal or remineralization. While constrained to surface waters, these models are simply based on the fact that photochemical rates are controlled by the rate of photon absorption ( $Q_a(\lambda, z)$ ) at a given wavelength ( $\lambda$ ) and depth ( $z$ ) and the probability that the absorption of solar radiation will lead to a photochemical product. This photochemical efficiency is typically quantified as the spectral apparent quantum yield (AQY;  $\phi(\lambda, z)$ ), defined as the ratio of rate of moles product produced to the rate of moles of photons absorbed by the sample ( $Q_a(\lambda, z)$ ).<sup>56</sup> Fichot and Miller<sup>56</sup> used this approach to develop a method to estimate photochemical rates on a global scale using  $Q_a(\lambda, z)$  derived from satellite data and modeled solar irradiances. Using carbon monoxide as an example, they estimated that surface ocean marine carbon monoxide fluxes amounted to 41 Tg C yr<sup>-1</sup>, in line with previous estimates of 30 to 84 Tg C yr<sup>-1</sup>.<sup>57,58</sup> More recently, this approach was used with temperature-dependent AQY spectra for acetaldehyde and glyoxal to estimate their annual surface ocean production,<sup>59</sup> and it was found that photoproduction of carbonyl carbon (i.e., glyoxal, methylglyoxal, formaldehyde, acetaldehyde) amounts to 110 Tg C yr<sup>-1</sup>. Since these LMW compounds (and CO) are known biological substrates<sup>60</sup> or lost to the atmosphere, their production should also be considered a sink for marine DOM. It has also been

estimated that the photoproduction rates of known biolabile products (BLPs) are about 13 times higher than that for CO.<sup>60</sup> The production of BLPs that could be utilized and respired ranges from 0.4 to 1.2 Pg C yr<sup>-1</sup> and, hence, is comparable to the annual export flux of 1.8 Pg C yr<sup>-1</sup>.

Of course, mineralization to  $\text{CO}_2$  is the proposed largest photochemical sink for DOM, but direct measurements in open ocean seawater are limited. It was reported that  $\text{CO}_2$  photoproduction was on average 15 times higher than CO photoproduction in river-impacted coastal waters.<sup>61–63</sup> Assuming this relationship and temperature-corrected CO production rates,<sup>62,63</sup>  $\text{CO}_2$  photoproduction could amount to 0.5 to 1.4 Pg C yr<sup>-1</sup>. Summing these sinks (CO, BLPs, and  $\text{CO}_2$ ), photochemistry could remove 1.0 to 2.7 Pg C yr<sup>-1</sup>. This estimate is highly speculative, especially since the relationship between photoproduced  $\text{CO}_2$ :CO can range anywhere between 2 and >60.<sup>64–67</sup>  $\text{H}_2\text{O}_2$  was proposed as a better proxy for  $\text{CO}_2$  photoproduction,<sup>67</sup> which appears to have a more constrained relationship from coastal to offshore waters ( $\text{CO}_2$ : $\text{H}_2\text{O}_2$  =  $7 \pm 1$ ). Using this relationship and the global photoproduction rates of  $\text{H}_2\text{O}_2$ ,<sup>68</sup> the photoproduction of  $\text{CO}_2$  alone could account for the removal of 2.8 Pg C yr<sup>-1</sup> from the DOM pool, well above the annual export flux of 1.8 Pg C yr<sup>-1</sup>. These estimates also do not include the production of primary marine aerosols (PMAs), which may contain 20–40% refractory DOM. Beaupre et al.<sup>69</sup> further estimated that formation of PMAs can remove 2 to 20 Tg C yr<sup>-1</sup> from the “refractory” DOM pool and, with subsequent photochemical oxidation in the atmosphere, should be another important loss mechanism.<sup>70</sup> While these estimates indicate that photochemistry is a significant removal mechanism of marine DOM, they, like many DOM flux estimates, are confounded in uncertainty.

**3. Pillar 3. The Efficiency of the Biological and Microbial Pump.** As the foundations of our current theory are becoming more uncertain, incredibly rapid and revolutionary progress has been made in other disciplines and, more specifically, microbiology. Hence, the third and increasingly important pillar is based on the efficiency of the biological and microbial pump as fundamental sources of DOM and advancing our knowledge about the production, vertical transport, and dissolution of organic matter. Understanding these interplays and connecting them more inclusively with DOM composition research is likely the key to understanding the dynamics of marine DOM turnover and the effectiveness of marine carbon sequestration. John Hedges once acknowledged, “*The future of oceanographic research belongs in large part to those who can learn to read these molecular messages.*”<sup>71</sup> In recent years, the dissolution of POM at great depths has become a focal research area as large DOC concentrations have been measured inside marine flocs or “snow”.<sup>72</sup> Partitioning between POM and DOM may not be straightforward, and for example, gel formation of biopolymers may be an important phase that facilitates the transport of otherwise very labile polysaccharides and other gel forming molecules.<sup>73</sup> Regardless of the mechanisms by which POM is transformed to DOM, overall very little POM reaches the seafloor. The global POM flux has been estimated to be 9.7 Pg C yr<sup>-1</sup>,<sup>74</sup> and if only 3–5% reaches the seafloor, about 9.3 Pg C yr<sup>-1</sup> would need to be either mineralized or released as DOM. The microbial carbon pump concept<sup>1,3,75</sup> and the size-reactivity continuum model<sup>1,75</sup> have gained popularity in the past decade and provide an interesting mechanism to explain the

accumulation of refractory DOM in the deep ocean. Using ultrafiltration to separate DOM at 1 kDa, it was found that DOM utilization was 1–4-fold times greater in the >1 kDa fraction.<sup>75</sup> From this study and others, the size-reactivity continuum concept was introduced, suggesting that marine DOM complexity and age increase with decreasing molecular size.<sup>1</sup> Interestingly, substantial changes in the apparent <sup>14</sup>C age of DOM seem also to correspond to molecular size.<sup>47,76</sup> It should be noted here that the proposed marine DOM reactivity continuum concept is much broader than the previously described size-reactivity continuum and includes the degradation of molecules of comparable size but that are degraded on drastically different time scales.

Laboratory and mesocosm experiments have provided insight into the production of more stable DOM through microbial degradation.<sup>2,77–79</sup> These experiments indeed show that bacteria produce DOM that is biologically recalcitrant on time scales of months to a few years; however, we have no knowledge if this material may be degraded on slightly longer time scales. Under the right conditions, deep ocean DOM can degrade on time scales appropriate for laboratory experiments. It was found that 7–13% of “refractory” Atlantic Ocean DOM can be removed in 1.5 years<sup>80</sup> when exposed to different treatments that could enhance its loss, i.e., coastal microbial communities, addition of labile substrates (priming), photo-degradation, and photoenhanced biodegradation. Thus, it appears that deep ocean DOM remineralization can be quite rapid under the right conditions. We also are still in the dark as to whether this “refractory” DOM is derived directly from bacterially synthesized exudates fueling the microbial carbon pump or bacterially modified metabolites from autotrophs. Both mechanisms are likely, but the contribution of each pathway at any given location will determine the fate and degradation kinetics of the DOM. The overall appearance of homogeneity of deep ocean DOM, when looked through the lenses of ultrahigh resolution mass spectrometry (MS) would suggest a convergence to a rather common pool of organic compounds and argue against fundamental differences in composition and reactivity. However, a recent study points to a more structurally diverse DOM composition in different water masses.<sup>81</sup> As with all analytical tools, trying to describe the overall composition, broad overlap of signals will likely dampen and mask small to moderate molecular changes, and hence, close attention needs to be paid to small but consistent differences observed using high resolution analytical techniques that describe the “fingerprint” of DOM. To further complicate the DOM fingerprinting, only a fraction of DOM is visible through this analytical window, and the “dark” DOM may be equally important to that what we currently observe, whether it is biased by extraction techniques (NMR and MS) or simply by ionization efficiency (MS) or broad overlap of incredibly structurally complex DOM (NMR, fluorescence, and UV–vis spectroscopy).

Microbial ecology can also inform biogeochemists in profound ways, and it is truly time to synthesize existing data on marine microbial processing within the overall concept of the marine carbon cycle. The following quote from Moran et al.<sup>6</sup> highlights this need: “When the question of why deep ocean DOM persists is finally resolved, the answer is likely to be a combination of concentration, chemical structure, bioenergetics, and microbial diversity.”. Take, for example, the observed average prokaryotic abundance in the deep North Pacific of  $1 \times 10^5$  cell mL<sup>-1</sup>, which is substantially greater than the  $0.3 \times$

$10^5$  cells mL<sup>-1</sup> measured in the deep North Atlantic,<sup>82</sup> although this is based on very limited data and not directly comparable regions within the ocean basins. Another study not only showed much more detailed prokaryotic abundances ranging from about  $0.1\text{--}0.4 \times 10^5$  cells mL<sup>-1</sup> in the bathypelagic Pacific Ocean but also underlined substantial geographical differences.<sup>83</sup> This highlights the need for further research on bacterial abundances in the deep ocean of an even larger geographical scale. Microbial respiration rates in the deep interior (>1000 m) oligotrophic core of the Pacific Ocean were found to be more than double those determined for the Atlantic Ocean,<sup>84</sup> but again the sampling locations may not be directly comparable, fueling the need to also extend our data set on microbial respiration across the World’s Oceans.

These above findings seem to be a stark contradiction given the lower DOC concentration in the deep Central Pacific relative to the Atlantic, but if a fundamentally different DOM quality is assumed, then it becomes feasible that deep Pacific DOM is concurrently more accessible, supports greater microbial populations, and is depleted in a steady state equilibrium to a lower concentration than observed in the Atlantic. The observed average DOC concentration difference in the subtropics and tropics (30° N to 30° S) between the Pacific and the Atlantic is only 2 μM (~5%), based on the global DOC data set,<sup>85</sup> and could be easily explained by differences in the DOM pool and its reactivity. Similarly, if we assume that the <sup>14</sup>C-free constituents of deep ocean DOM are similar in concentration between the Pacific and Atlantic, then the Pacific deep ocean DOM would also appear older simply due to lower DOC concentrations in the Pacific. Recently, the term “refractory DOM” has been critically evaluated,<sup>86–88</sup> highlighting that particle fluxes within the biological pump might be severely underestimated.<sup>87,88</sup> The major suggestion of this perspective was that refractory DOM should be operationally defined and tied to the specific analytical window used, because the persistence of DOM is ultimately defined by its chemical composition and the physicochemical and biological matrix in which it exists. Our perspective demonstrates reasonable doubts in the stability of the three pillars upholding our current framework of marine carbon cycling. This review and perspective is not meant to provoke controversy but to catalyze a collaborative effort to re-evaluate our current understanding of the marine carbon cycle and the marine DOM reactivity continuum. This pursuit is also an opportunity to reimagine the conceptualization of the marine carbon dynamics in a logically accessible way.

In one notable study, which sought to estimate the decay rate of marine DOC rather than bin DOC into decomposition categories, Carlson et al. (2010)<sup>89</sup> combined high resolution DOC data from basin-scale meridional transects across the North Atlantic with chlorofluorocarbon ventilation ages to estimate DOC decomposition rates within the mesopelagic and bathypelagic zones of the North Atlantic. Calculated decay rates of exported DOC derived from Model II regression and multiple linear regression models ranged from 0.13 to 0.94 μmol kg<sup>-1</sup> y<sup>-1</sup> and associated DOC turnover times of 6 to 33 y and 30 to 46 y in the thermocline and North Atlantic deep water, respectively. These turnover times are significantly faster than 3,970 y, the mean <sup>14</sup>C age of North Atlantic deep DOC. Nevertheless, these modeled decay rates raise the question as to the true decay coefficients for marine DOM. Another modeling attempt using neural networks could show that marine DOC production and export rates are drastically



different geographically. Rather than compartmentalize DOM solely into vaguely defined reactivity brackets such as labile, semilabile, refractory, or ultrarefractory DOM, we argue that it is time to apply the DOM reactivity continuum concept to the marine carbon pool and to begin to establish the slope of the marine DOM reactivity continuum defined by presumably multiple decay coefficients. This perspective has sought to provide abundant evidence as to why we should question the assumption that all deep ocean DOM is thousands of years old and essentially biologically inert. To fundamentally understand the marine DOM reactivity continuum, we must identify and quantify exact organic compounds from a range of potential sources and test their bio and photoreactivity across short (hours to days), medium (days to months), and long (decades) degradation time scales. This seems to be a daunting task, but small steps in this direction are underway. For example, fluorophores, with a presumably long half-life, derived from picocyanobacteria have already been identified, although their structures are still not fully resolved.<sup>78</sup> Sea surface based temperature projections, as a result of increased concentrations of greenhouse gases at the end of the 21st century, predicted increases in photosynthetic cyanobacterial cell numbers by 29% and 14% for *Prochlorococcus* and *Synechococcus*, respectively.<sup>29</sup> These forecasted increases at the base of the oceanic food web suggest complex and interdependent changes in ocean ecosystems and concomitant increases in the biological and microbial carbon pumps that will have significant implications for global biogeochemical cycles. The projected climate driven changes will be geographically distinct and will vary widely in effect across different biological and physicochemical environments. To overcome the large overall uncertainties in C sources and sinks, we suggest the identification of new and unique biomarkers to be used as model compounds not only to constrain the overall turnover of marine DOM and to define the DOM reactivity continuum but also to evaluate photochemical and microbial degradation pathways and processes both now and in the future.

## ■ FINAL REMARKS

Robust predictions of the marine carbon cycle, and its turnover in particular, are critical to quantify anthropogenic alterations to the global carbon cycle. Resolving the kinetics of the proposed marine DOM reactivity continuum requires an interdisciplinary approach. By working together and across research disciplines, we can better constrain the turnover time of marine DOM and thus gain invaluable knowledge of global marine carbon cycling and oceanic carbon storage capacity as our planet continues to change.

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## Notes

The authors declare no competing financial interest.

## Biography



Dr. Michael Gonsior is currently a tenured associate professor at the University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory. He undertook his Ph.D. in aquatic biogeochemistry at Otago University in New Zealand, before he became a postdoctoral scholar at the University of California, Irvine and later at the Linköping University, Sweden. He joined the University of Maryland Center for Environmental Science in 2012 as a tenure-track assistant professor, and he was promoted to associate professor in 2018. His research is largely centered on analytical chemistry and marine biogeochemistry. His interest is in characterizing complex dissolved organic matter (DOM) not only in the open ocean but also in engineered systems using modern approaches such as ultrahigh resolution mass spectrometry and optical properties characterization. He also has developed a unique photodegradation system for DOM, and he was awarded for this development the Honorable Mentioning to the Masao Horiba Award in Kyoto in 2017. Recently, he also has developed approaches to discover new marine DOM tracers. Dr. Gonsior has published over 75 peer-reviewed publications in highly ranked journals and was a featured scientist in the award-winning documentary “A Plastic Ocean”.

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## ■ REFERENCES

- (1) Benner, R.; Amon, R. M. W. The Size-Reactivity Continuum of Major Bioelements in the Ocean. *Annual Review of Marine Science* **2015**, *7* (1), 185–205.
- (2) Koch, B. P.; Kattner, G.; Witt, M.; Passow, U. Molecular insights into the microbial formation of marine dissolved organic matter: recalcitrant or labile? *Biogeosciences* **2014**, *11* (15), 4173–4190.

- (3) Jiao, N.; Herndl, G. J.; Hansell, D. A.; Benner, R.; Kattner, G.; Wilhelm, S. W.; Kirchman, D. L.; Weinbauer, M. G.; Luo, T. W.; Chen, F.; Azam, F. Microbial production of recalcitrant dissolved organic matter: long-term carbon storage in the global ocean. *Nature Reviews Microbiology* **2010**, *8* (8), 593–599.
- (4) Wagner, S.; Schubotz, F.; Kaiser, K.; Hallmann, C.; Waska, H.; Rossel, P. E.; Hansman, R.; Elvert, M.; Middelburg, J. J.; Engel, A.; Blattmann, T. M.; Catalá, T. S.; Lennartz, S. T.; Gomez-Saez, G. V.; Pantoja-Gutiérrez, S.; Bao, R.; Galy, V. Soothsaying DOM: A Current Perspective on the Future of Oceanic Dissolved Organic Carbon. *Frontiers in Marine Science* **2020**, *7*, 341.
- (5) Catalá, T. S.; Shorte, S.; Dittmar, T. Marine dissolved organic matter: a vast and unexplored molecular space. *Appl. Microbiol. Biotechnol.* **2021**, *105* (19), 7225–7239.
- (6) Moran, M. A.; Kujawinski, E. B.; Stubbins, A.; Fatland, R.; Aluwihare, L. I.; Buchan, A.; Crump, B. C.; Dorrestein, P. C.; Dyhrman, S. T.; Hess, N. J.; Howe, B.; Longnecker, K.; Medeiros, P. M.; Niggemann, J.; Obernosterer, I.; Repeta, D. J.; Waldbauer, J. R. Deciphering ocean carbon in a changing world. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113* (12), 3143–3151.
- (7) Boudreau, B. P.; Ruddick, B. R. On a reactive continuum representation of organic matter diagenesis. *Am. J. Sci.* **1991**, *291* (5), 507–538.
- (8) Koehler, B.; von Wachenfeldt, E.; Kothawala, D.; Tranvik, L. J. Reactivity continuum of dissolved organic carbon decomposition in lake water. *Journal of Geophysical Research-Biogeosciences* **2012**, *117*, G01024.
- (9) Moran, M. A.; Kujawinski, E. B.; Schroer, W. F.; Amin, S. A.; Bates, N. R.; Bertrand, E. M.; Braakman, R.; Brown, C. T.; Covert, M. W.; Doney, S. C.; Dyhrman, S. T.; Edison, A. S.; Eren, A. M.; Levine, N. M.; Li, L.; Ross, A. C.; Saito, M. A.; Santoro, A. E.; Segrè, D.; Shade, A.; Sullivan, M. B.; Vardi, A. Microbial metabolites in the marine carbon cycle. *Nature Microbiology* **2022**, *7* (4), 508–523.
- (10) Polimene, L.; Rivkin, R. B.; Luo, Y.-W.; Kwon, E. Y.; Gehlen, M.; Peña, M. A.; Wang, N.; Liang, Y.; Kaartokallio, H.; Jiao, N. Modelling marine DOC degradation time scales. *National Science Review* **2018**, *5* (4), 468–474.
- (11) Mostovaya, A.; Hawkes, J. A.; Koehler, B.; Dittmar, T.; Tranvik, L. J. Emergence of the Reactivity Continuum of Organic Matter from Kinetics of a Multitude of Individual Molecular Constituents. *Environ. Sci. Technol.* **2017**, *51* (20), 11571–11579.
- (12) Kaiser, K.; Benner, R. Organic matter transformations in the upper mesopelagic zone of the North Pacific: Chemical composition and linkages to microbial community structure. *Journal of Geophysical Research: Oceans* **2012**, *117*, C01023.
- (13) Hansell, D. A.; Carlson, C. A.; Repeta, D. J.; Schlitzer, R. Dissolved organic matter in the ocean: A controversy stimulates new insights. *Oceanography* **2009**, *22* (4), 202–211.
- (14) Romera-Castillo, C.; Letscher, R. T.; Hansell, D. A. New nutrients exert fundamental control on dissolved organic carbon accumulation in the surface Atlantic Ocean. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113* (38), 10497–10502.
- (15) Herndl, G. J.; Reinthaler, T. Microbial control of the dark end of the biological pump. *Nature Geoscience* **2013**, *6* (9), 718–724.
- (16) Pachiadaki, M. G.; Sintès, E.; Bergauer, K.; Brown, J. M.; Record, N. R.; Swan, B. K.; Mathyer, M. E.; Hallam, S. J.; Lopez-Garcia, P.; Takaki, Y.; Nunoura, T.; Woyke, T.; Herndl, G. J.; Stepanauskas, R. Major role of nitrite-oxidizing bacteria in dark ocean carbon fixation. *Science* **2017**, *358* (6366), 1046–1051.
- (17) Kharbush, J. J.; Close, H. G.; Van Mooy, B. A. S.; Arnosti, C.; Smittenberg, R. H.; Le Moigne, F. A. C.; Mollenhauer, G.; Scholz-Böttcher, B.; Obrecht, I.; Koch, B. P.; Becker, K. W.; Iversen, M. H.; Mohr, W. Particulate Organic Carbon Deconstructed: Molecular and Chemical Composition of Particulate Organic Carbon in the Ocean. *Frontiers in Marine Science* **2020**, *7*, 518.
- (18) Druffel, E. R. M.; Griffin, S.; Lewis, C. B.; Rudresh, M.; Garcia, N. G.; Key, R. M.; McNichol, A. P.; Hauksson, N. E.; Walker, B. D. Dissolved Organic Radiocarbon in the Eastern Pacific and Southern Oceans. *Geophys. Res. Lett.* **2021**, *48* (10), e2021GL092904.
- (19) Druffel, E. R. M.; Griffin, S.; Wang, N.; Garcia, N. G.; McNichol, A. P.; Key, R. M.; Walker, B. D. Dissolved Organic Radiocarbon in the Central Pacific Ocean. *Geophys. Res. Lett.* **2019**, *46* (10), 5396–5403.
- (20) Druffel, E. R. M.; Griffin, S.; Coppola, A. I.; Walker, B. D. Radiocarbon in dissolved organic carbon of the Atlantic Ocean. *Geophys. Res. Lett.* **2016**, *43* (10), 5279–5286.
- (21) McNichol, A. P.; Aluwihare, L. I. The Power of Radiocarbon in Biogeochemical Studies of the Marine Carbon Cycle: Insights from Studies of Dissolved and Particulate Organic Carbon (DOC and POC). *Chem. Rev. (Washington, DC, U. S.)* **2007**, *107*, 443–466.
- (22) Druffel, E. R. M.; Bauer, J. E. Radiocarbon distributions in Southern Ocean dissolved and particulate organic matter. *Geophys. Res. Lett.* **2000**, *27*, 1495–1498.
- (23) Bauer, J. E.; Druffel, E. R. M.; Wolgast, D. M.; Griffin, S.; Masiello, C. A. Distributions of dissolved organic and inorganic carbon and radiocarbon in the eastern North Pacific continental margin. *Deep-Sea Res. Pt II* **1998**, *45* (4–5), 689–713.
- (24) Bauer, J. E.; Williams, P. M.; Druffel, E. R. M. <sup>14</sup>C activity of dissolved organic carbon fractions in the north-central Pacific and Sargasso Sea. *Nature* **1992**, *357* (6380), 667–670.
- (25) Williams, P. M.; Druffel, E. R. M. Radiocarbon in dissolved organic matter in the central North Pacific Ocean. *Nature* **1987**, *330* (6145), 246–248.
- (26) Reinthaler, T.; van Aken, H. M.; Herndl, G. J. Major contribution of autotrophy to microbial carbon cycling in the deep North Atlantic's interior. *Deep-Sea Res. Pt II* **2010**, *57* (16), 1572–1580.
- (27) Taylor, F. J. R.; Hoppenrath, M.; Saldarriaga, J. F. Dinoflagellate diversity and distribution. *Biodiversity and Conservation* **2008**, *17* (2), 407–418.
- (28) Bopp, L.; Aumont, O.; Cadule, P.; Alvain, S.; Gehlen, M. Response of diatoms distribution to global warming and potential implications: A global model study. *Geophys. Res. Lett.* **2005**, *32* (19), L19606.
- (29) Flombaum, P.; Gallegos, J. L.; Gordillo, R. A.; Rincon, J.; Zabala, L. L.; Jiao, N.; Karl, D. M.; Li, W. K. W.; Lomas, M. W.; Veneziano, D.; Vera, C. S.; Vrugt, J. A.; Martiny, A. C. Present and future global distributions of the marine Cyanobacteria *Prochlorococcus* and *Synechococcus*. *Proceedings of the National Academy of Sciences, USA* **2013**, *110* (24), 9824–9829.
- (30) Jiao, N.; Luo, T.; Zhang, R.; Yan, W.; Lin, Y.; Johnson, Z. I.; Tian, J.; Yuan, D.; Yang, Q.; Zheng, Q.; Sun, J.; Hu, D.; Wang, P. Presence of *Prochlorococcus* in the aphotic waters of the western Pacific Ocean. *Biogeosciences* **2014**, *11* (8), 2391–2400.
- (31) Zhao, Z.; Gonsior, M.; Lueck, J.; Timko, S.; Ianiri, H.; Hertkorn, N.; Schmitt-Kopplin, P.; Fang, X.; Zeng, Q.; Jiao, N.; Chen, F. Picocyanobacteria and deep-ocean fluorescent dissolved organic matter share similar optical properties. *Nat. Commun.* **2017**, *8*, 15284.
- (32) Michaels, A. F.; Silver, M. W. Primary production, sinking fluxes and the microbial food web. *Deep Sea Research Part A. Oceanographic Research Papers* **1988**, *35* (4), 473–490.
- (33) Richardson, T. L. Mechanisms and Pathways of Small-Phytoplankton Export from the Surface Ocean. *Annual Review of Marine Science* **2019**, *11* (1), 57–74.
- (34) Cruz, B. N.; Neuer, S. Heterotrophic Bacteria Enhance the Aggregation of the Marine Picocyanobacteria *Prochlorococcus* and *Synechococcus*. *Frontiers in Microbiology* **2019**, *10*, 1864.
- (35) Benner, R.; Louchouart, P.; Amon, R. M. W. Terrigenous dissolved organic matter in the Arctic Ocean and its transport to surface and deep waters of the North Atlantic. *Global Biogeochem. Cycles* **2005**, *19* (2), GB2025.
- (36) Bercovici, S. K.; Huber, B. A.; DeJong, H. B.; Dunbar, R. B.; Hansell, D. A. Dissolved organic carbon in the Ross Sea: Deep enrichment and export. *Limnology and Oceanography* **2017**, *62* (6), 2593–2603.
- (37) Powers, L. C.; Hertkorn, N.; McDonald, N.; Schmitt-Kopplin, P.; Del Vecchio, R.; Blough, N. V.; Gonsior, M. Sargassum sp. Act as a



Large Regional Source of Marine Dissolved Organic Carbon and Polyphenols. *Global Biogeochemical Cycles* **2019**, 33 (11), 1423–1439.

(38) Aristegui, J.; Gasol, J. M.; Duarte, C. M.; Herndl, G. J. Microbial oceanography of the dark ocean's pelagic realm. *Limnology and Oceanography* **2009**, 54 (5), 1501–1529.

(39) Berger, W. H.; Smetacek, V. S.; Wefer, G., Eds.; *Productivity of the oceans: Present and past. Report on the Dahlem Workshop on Productivity of the Oceans*, Berlin 1988; John Wiley and Sons: 1989; 471pp.

(40) Kirchman, D. L.; Suzuki, Y.; Garside, C.; Ducklow, H. W. High turnover rates of dissolved organic carbon during a spring phytoplankton bloom. *Nature* **1991**, 352 (6336), 612–614.

(41) Carlson, C. A. Production and removal processes. In *Biogeochemistry of Marine Dissolved Organic Matter*; Hansell, D. A., Carlson, C. A., Eds.; Academic Press: 2002; pp 91–151, DOI: 10.1016/B978-012323841-2/50006-3.

(42) Follett, C. L.; Repeta, D. J.; Rothman, D. H.; Xu, L.; Santinelli, C. Hidden cycle of dissolved organic carbon in the deep ocean. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, 111 (47), 16706–16711.

(43) Pohlman, J. W.; Bauer, J. E.; Waite, W. F.; Osburn, C. L.; Chapman, N. R. Methane hydrate-bearing seeps as a source of aged dissolved organic carbon to the oceans. *Nature Geosci* **2011**, 4 (1), 37–41.

(44) McCarthy, M. D.; Beupre, S. R.; Walker, B. D.; Voparil, I.; Guilderson, T. P.; Druffel, E. R. M. Chemosynthetic origin of  $^{14}\text{C}$ -depleted dissolved organic matter in a ridge-flank hydrothermal system. *Nature Geosci* **2011**, 4 (1), 32–36.

(45) Luther, G. W., III Hydrothermal Vents Are a Source of Old Refractory Organic Carbon to the Deep Ocean. *Geophys. Res. Lett.* **2021**, 48 (17), e2021GL094869.

(46) Walker, B. D.; Primeau, F. W.; Beupré, S. R.; Guilderson, T. P.; Druffel, E. R. M.; McCarthy, M. D. Linked changes in marine dissolved organic carbon molecular size and radiocarbon age. *Geophys. Res. Lett.* **2016**, 43 (19), 10385–10393.

(47) Walker, B. D.; Beupré, S. R.; Guilderson, T. P.; McCarthy, M. D.; Druffel, E. R. M. Pacific carbon cycling constrained by organic matter size, age and composition relationships. *Nature Geoscience* **2016**, 9, 888.

(48) Hansell, D. A. Recalcitrant Dissolved Organic Carbon Fractions. *Annual Review of Marine Science*, Vol 5 **2013**, 5, 421–445.

(49) Ziolkowski, L. A.; Druffel, E. R. M. Aged black carbon identified in marine dissolved organic carbon. *Geophys. Res. Lett.* **2010**, 37 (16), L16601.

(50) Coppola, A. I.; Druffel, E. R. M. Cycling of black carbon in the ocean. *Geophys. Res. Lett.* **2016**, 43 (9), 4477–4482.

(51) Toggweiler, J. R.; Druffel, E. R. M.; Key, R. M.; Galbraith, E. D. Upwelling in the Ocean Basins North of the ACC: 1. On the Upwelling Exposed by the Surface Distribution of  $\Delta^{14}\text{C}$ . *Journal of Geophysical Research: Oceans* **2019**, 124 (4), 2591–2608.

(52) Toggweiler, J. R.; Druffel, E. R. M.; Key, R. M.; Galbraith, E. D. Upwelling in the Ocean Basins North of the ACC: 2. How Cool Subantarctic Water Reaches the Surface in the Tropics. *Journal of Geophysical Research: Oceans* **2019**, 124 (4), 2609–2625.

(53) Lechtenfeld, O. J.; Kattner, G.; Flerus, R.; McCallister, S. L.; Schmitt-Kopplin, P.; Koch, B. P. Molecular transformation and degradation of refractory dissolved organic matter in the Atlantic and Southern Ocean. *Geochim. Cosmochim. Acta* **2014**, 126 (0), 321–337.

(54) Mopper, K.; Zhou, X. L.; Kieber, R. J.; Kieber, D. J.; Sikorski, R. J.; Jones, R. D. Photochemical degradation of dissolved organic carbon and its impact on the oceanic carbon cycle. *Nature* **1991**, 353 (6339), 60–62.

(55) Stubbins, A.; Niggemann, J.; Dittmar, T. Photo-lability of deep ocean dissolved black carbon. *Biogeosciences Discussion* **2012**, 9 (5), 1661–1670.

(56) Fichot, C. G.; Miller, W. L. An approach to quantify depth-resolved marine photochemical fluxes using remote sensing: Application to carbon monoxide ( $\text{CO}$ ) photoproduction. *Remote Sensing of Environment* **2010**, 114 (7), 1363–1377.

(57) Stubbins, A.; Uher, G.; Law, C. S.; Mopper, K.; Robinson, C.; Upstill-Goddard, R. C. Open-ocean carbon monoxide photoproduction. *Deep-Sea Res. Pt II* **2006**, 53 (14–16), 1695–1705.

(58) Zafriou, O. C.; Andrews, S. S.; Wang, W. Concordant estimates of oceanic carbon monoxide source and sink processes in the Pacific yield a balanced global "blue-water"  $\text{CO}$  budget. *Global Biogeochemical Cycles* **2003**, 17 (1), 1015.

(59) Zhu, Y.; Kieber, D. J. Global Model for Depth-Dependent Carbonyl Photochemical Production Rates in Seawater. *Global Biogeochemical Cycles* **2020**, 34 (4), e2019GB006431.

(60) Miller, W. L.; Moran, M. A.; Sheldon, W. M.; Zepp, R. G.; Opsahl, S. Determination of apparent quantum yield spectra for the formation of biologically labile photoproducts. *Limnol. Oceanogr.* **2002**, 47, 343–352.

(61) Miller, W. L.; Zepp, R. G. Photochemical production of dissolved inorganic carbon from terrestrial organic matter: significance to the oceanic organic carbon cycle. *Geophys. Res. Lett.* **1995**, 22 (4), 417–20.

(62) Hong, J.; Xie, H.; Guo, L.; Song, G. Carbon Monoxide Photoproduction: Implications for Photoreactivity of Arctic Permafrost-Derived Soil Dissolved Organic Matter. *Environ. Sci. Technol.* **2014**, 48 (16), 9113–9121.

(63) Zhang, Y.; Xie, H.; Chen, G. Factors Affecting the Efficiency of Carbon Monoxide Photoproduction in the St. Lawrence Estuarine System (Canada). *Environ. Sci. Technol.* **2006**, 40 (24), 7771–7777.

(64) Powers, L. C.; Miller, W. L. Photochemical production of  $\text{CO}$  and  $\text{CO}_2$  in the Northern Gulf of Mexico: Estimates and challenges for quantifying the impact of photochemistry on carbon cycles. *Marine Chemistry* **2015**, 171, 21–35.

(65) Reader, H. E.; Miller, W. L. Variability of carbon monoxide and carbon dioxide apparent quantum yield spectra in three coastal estuaries of the South Atlantic Bight. *Biogeosciences* **2012**, 9 (11), 4279–4294.

(66) White, E. M.; Kieber, D. J.; Sherrard, J.; Miller, W. L.; Mopper, K. Carbon dioxide and carbon monoxide photoproduction quantum yields in the Delaware Estuary. *Marine Chemistry* **2010**, 118 (1), 11–21.

(67) Powers, L. C.; Miller, W. L. Hydrogen peroxide and superoxide photoproduction in diverse marine waters: A simple proxy for estimating direct  $\text{CO}_2$  photochemical fluxes. *Geophys. Res. Lett.* **2015**, 42 (18), 7696–7704.

(68) Powers, L. C.; Miller, W. L. Blending remote sensing data products to estimate photochemical production of hydrogen peroxide and superoxide in the surface ocean. *Environmental Science: Processes & Impacts* **2014**, 16 (4), 792–806.

(69) Beupré, S. R.; Kieber, D. J.; Keene, W. C.; Long, M. S.; Maben, J. R.; Lu, X.; Zhu, Y.; Frossard, A. A.; Kinsey, J. D.; Duplessis, P.; Chang, R. Y.-W.; Bisgrove, J. Oceanic efflux of ancient marine dissolved organic carbon in primary marine aerosol. *Science Advances* **2019**, 5 (10), eaax6535.

(70) Kieber, D. J.; Keene, W. C.; Frossard, A. A.; Long, M. S.; Maben, J. R.; Russell, L. M.; Kinsey, J. D.; Tyssebotn, I. M. B.; Quinn, P. K.; Bates, T. S. Coupled ocean-atmosphere loss of marine refractory dissolved organic carbon. *Geophys. Res. Lett.* **2016**, 43 (6), 2765–2772.

(71) Hedges, J. I. Why dissolved organics matter. In *Biogeochemistry of Marine Dissolved Organic Matter*; Hansell, D. A., Carlson, C. A., Eds.; Academic Press: 2002; pp 1–33, DOI: 10.1016/B978-012323841-2/50003-8.

(72) Alldredge, A. L. Interstitial dissolved organic carbon (DOC) concentrations within sinking marine aggregates and their potential contribution to carbon flux. *Limnology and Oceanography* **2000**, 45 (6), 1245–1253.

(73) Verdugo, P.; Alldredge, A. L.; Azam, F.; Kirchman, D. L.; Passow, U.; Santschi, P. H. The oceanic gel phase: a bridge in the DOM-POM continuum. *Mar. Chem.* **2004**, 92, 67–85.

(74) Zui, T.; Tingting, L.; Xiang, Z.; Sheng, M.; Xiangbing, K. Monitoring of sinking flux of ocean particulate organic carbon using remote sensing methods. In *2016 IEEE International Geoscience and*

*Remote Sensing Symposium (IGARSS)*, 10–15 July 2016; 2016; pp 3788–3791, DOI: 10.1109/IGARSS.2016.7729982.

(75) Amon, R. M. W.; Benner, R. Bacterial utilization of different size classes of dissolved organic matter. *Limnology and Oceanography* **1996**, 41 (1), 41–51.

(76) Walker, B. D.; Guilderson, T. P.; Okimura, K. M.; Peacock, M. B.; McCarthy, M. D. Radiocarbon signatures and size-age-composition relationships of major organic matter pools within a unique California upwelling system. *Geochim. Cosmochim. Acta* **2014**, 126, 1–17.

(77) Lonborg, C.; Alvarez-Salgado, X. A.; Davidson, K.; Miller, A. E. J. Production of bioavailable and refractory dissolved organic matter by coastal heterotrophic microbial populations. *Estuar Coast Shelf S* **2009**, 82 (4), 682–688.

(78) Zhao, Z.; Gonsior, M.; Schmitt-Kopplin, P.; Zhan, Y.; Zhang, R.; Jiao, N.; Chen, F. Microbial transformation of virus-induced dissolved organic matter from picocyanobacteria: coupling of bacterial diversity and DOM chemodiversity. *ISME Journal* **2019**, 13 (10), 2551–2565.

(79) Ogawa, H.; Amagai, Y.; Koike, I.; Kaiser, K.; Benner, R. Production of refractory dissolved organic matter by bacteria. *Science* **2001**, 292 (5518), 917–920.

(80) Shen, Y.; Benner, R. Mixing it up in the ocean carbon cycle and the removal of refractory dissolved organic carbon. *Sci. Rep.* **2018**, 8 (1), 2542.

(81) Seidel, M.; Vemulapalli, S. P. B.; Mathieu, D.; Dittmar, T. Marine Dissolved Organic Matter Shares Thousands of Molecular Formulae Yet Differs Structurally across Major Water Masses. *Environ. Sci. Technol.* **2022**, 56 (6), 3758–3769.

(82) Pernice, M. C.; Forn, I.; Gomes, A.; Lara, E.; Alonso-Sáez, L.; Arrieta, J. M.; del Carmen Garcia, F.; Hernando-Morales, V.; MacKenzie, R.; Mestre, M.; Sintes, E.; Teira, E.; Valencia, J.; Varela, M. M.; Vaqué, D.; Duarte, C. M.; Gasol, J. M.; Massana, R. Global abundance of planktonic heterotrophic protists in the deep ocean. *Isme Journal* **2015**, 9 (3), 782–792.

(83) Yokokawa, T.; Yang, Y.; Motegi, C.; Nagata, T. Large-scale geographical variation in prokaryotic abundance and production in meso- and bathypelagic zones of the central Pacific and Southern Ocean. *Limnology and Oceanography* **2013**, 58 (1), 61–73.

(84) Packard, T. T.; Denis, M.; Rodier, M.; Garfield, P. Deep-ocean metabolic CO<sub>2</sub> production: calculations from ETS activity. *Deep Sea Research Part A. Oceanographic Research Papers* **1988**, 35 (3), 371–382.

(85) Hansell, D. A.; Carlson, C. A.; Amon, R. M. W.; Álvarez-Salgado, X. A.; Yamashita, Y.; Romera-Castillo, C.; Bif, M. B. Compilation of dissolved organic matter (DOM) data obtained from global ocean observations from 1994 to 2020 (NCEI Accession 0227166). In *NOAA National Centers for Environmental Information. Dataset*; 2021; DOI: 10.25921/s4f4-ye35.

(86) Baltar, F.; Alvarez-Salgado, X. A.; Aristegui, J.; Benner, R.; Hansell, D. A.; Herndl, G. J.; Lønborg, C. What Is Refractory Organic Matter in the Ocean? *Frontiers in Marine Science* **2021**, 8 (327), 642637.

(87) Buesseler, K. O.; Boyd, P. W.; Black, E. E.; Siegel, D. A. Metrics that matter for assessing the ocean biological carbon pump. *Proc. Natl. Acad. Sci. U. S. A.* **2020**, 117 (18), 9679–9687.

(88) Boyd, P. W.; Claustre, H.; Levy, M.; Siegel, D. A.; Weber, T. Multi-faceted particle pumps drive carbon sequestration in the ocean. *Nature* **2019**, 568 (7752), 327–335.

(89) Carlson, C. A.; Hansell, D. A.; Nelson, N. B.; Siegel, D. A.; Smethie, W. M.; Khatiwala, S.; Meyers, M. M.; Halewood, E. Dissolved organic carbon export and subsequent remineralization in the mesopelagic and bathypelagic realms of the North Atlantic basin. *Deep-Sea Res., Part II* **2010**, 57, 1433–1445.