The Size-Reactivity Continuum of Major Bioelements in the Ocean

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Annu. Rev. Mar. Sci. 2015. 7:185–205

First published online as a Review in Advance on July 25, 2014

The *Annual Review of Marine Science* is online at marine.annualreviews.org

This article's doi: 10.1146/annurev-marine-010213-135126

Keywords

ocean carbon cycle, size-reactivity continuum, dissolved organic matter, molecular size, bioreactivity, chemical complexity

Abstract

Most of the carbon fixed in primary production is rapidly cycled and remineralized, leaving behind various forms of organic carbon that contribute to a vast reservoir of nonliving organic matter in seawater. Most of this carbon resides in dissolved molecules of varying bioavailability and reactivity, and aspects of the cycling of this carbon remain an enigma. The size-reactivity continuum model provides a conceptual framework for understanding the mechanisms governing the formation and mineralization of this carbon. In the seawater bioassay experiments that served as the original basis for this model, investigators observed that larger size classes of organic matter were more bioavailable and more rapidly remineralized by microbes than were smaller size classes. Studies of the chemical composition and radiocarbon content of marine organic matter have further indicated that the complexity and age of organic matter increase with decreasing molecular size. Biodegradation processes appear to shape the size distribution of organic matter and the nature of the small dissolved molecules that persist in the ocean.

INTRODUCTION

Net primary production in the sunlit waters of the ocean is comparable to that on land and accounts for the annual fixation of ~48.5 Pg C (Field et al. 1998). Most of this organic matter cycles rapidly through the food web and is remineralized in the upper ocean. The cycle of global carbon fixation and remineralization is reflected in the annual pattern of atmospheric carbon dioxide concentrations, with maximal concentrations in the Northern Hemisphere in May and minimal concentrations in October (Scripps Inst. Oceanogr. 2014). The small fraction of organic matter that escapes remineralization in the ocean water column and sediments plays a critical role in the global sequestration of carbon from the atmosphere. The efficiency of carbon sequestration in the ocean is, in large part, dependent on the efficiency of organic matter remineralization in the upper ocean.

As originally conceived, the size-reactivity continuum model provided insights about microbial remineralization processes and proposed that the bioreactivity of natural organic matter decreases along a continuum of size, diagenetic alteration, and radiocarbon age (Amon & Benner 1996). This conceptual model was developed from bioassay experiments using different size classes of dissolved organic matter and assemblages of microorganisms collected from marine and freshwater environments. Evidence supporting and expanding on the size-reactivity continuum model has grown substantially in the years since its introduction, and this review synthesizes these observations and provides novel insights about the cycling of major bioelements and the nature of small dissolved molecules that persist in the ocean and sequester carbon for centuries to millennia.

THE SIZE DISTRIBUTION OF ORGANIC MATTER

Gazing into the ocean's depths is an awe-inspiring experience, in large part because of the paucity of particles. The small particle sizes in most regions of the ocean are readily apparent and reflect the diminutive nature of the planktonic organisms responsible for marine productivity. The global ocean reservoir of total organic carbon (TOC) is ~670 Pg C (Ogawa & Tanoue 2003, Hansell 2013) and has a distribution that is heavily skewed toward the nanometer size range (**Figure 1*a***). The ocean harbors tremendous biological diversity that spans more than eight orders of magnitude in size, from the great whales down to bacteria, archaea, and viruses. These organisms orchestrate biogeochemical cycles, but living biomass accounts for only a minor fraction of the TOC in seawater (Buitenhuis et al. 2013). Particulate organic carbon (POC), which includes living and nonliving components of suspended and sinking particles, accounts for <2% of marine TOC (Bishop 1999, Gardner et al. 2006). Submicron particles, gels, and colloids in the size range of 1 nm–1 μm are abundant in seawater but are particularly difficult to identify and quantify (Koike et al. 1990, Wells & Goldberg 1991, Chin et al. 1998, Wells 1998, Verdugo et al. 2004). Varying fractions of these intermediate size classes of TOC pass through the filtration membranes commonly used to separate the operationally defined particulate and dissolved components of TOC.

Ultrafiltration membranes with pore sizes of ~1 nm (molecular weight cutoff of 1 kDa) separate colloids, macromolecules, and other high-molecular-weight (HMW) components of dissolved organic carbon (DOC) from low-molecular-weight (LMW) dissolved molecules (Sharp 1973, Carlson et al. 1985, Benner et al. 1992, Ogawa & Ogura 1992). The HMW size class of DOC includes most colloids and gels and accounts for ~22% of TOC in the ocean (Benner et al. 1992, 1997; Ogawa & Ogura 1992; Guo et al. 1995; Kaiser & Benner 2009). The vast majority (~77%) of TOC in the ocean resides in the LMW size class of dissolved molecules, comprising those less than 1 kDa in mass (**Figure 1*a***). Pore water DOC in marine sediments is also dominated by

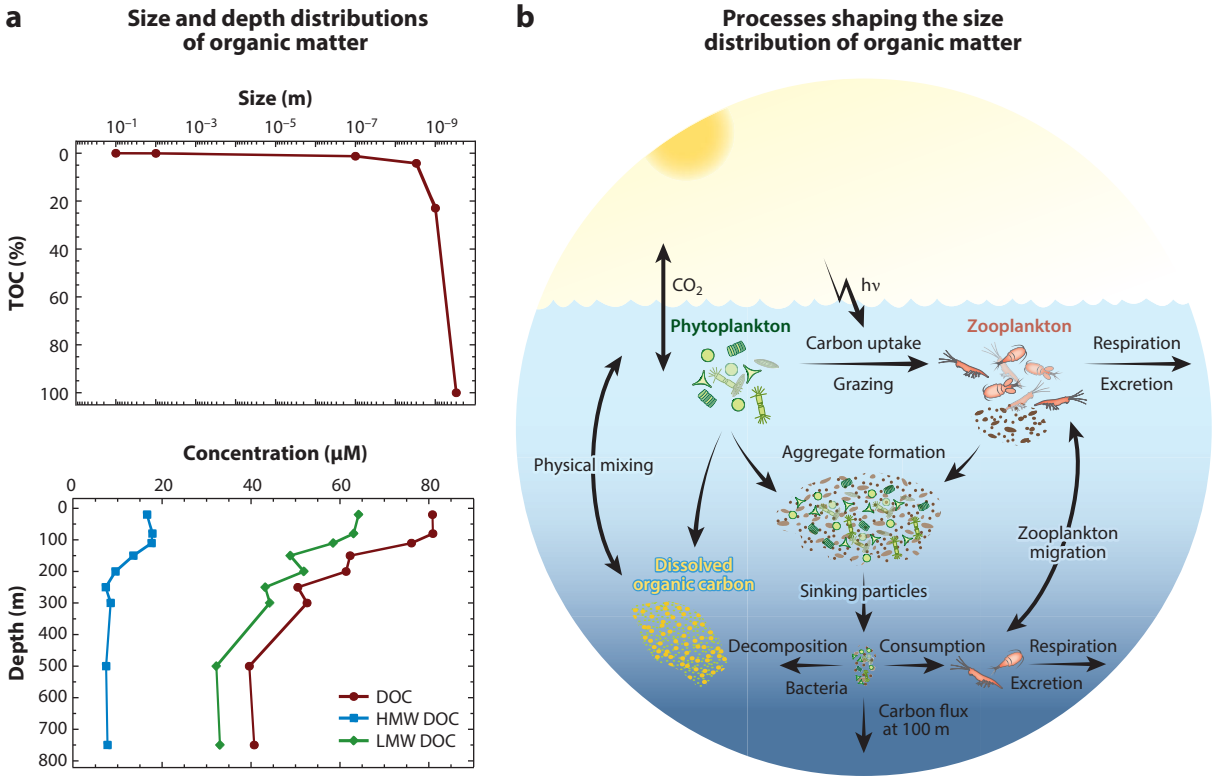

Figure 1

(*a*) Size distribution of organic matter in the ocean as a percentage of total organic carbon (TOC) (*top*) and depth distributions of total dissolved organic carbon (DOC), high-molecular-weight (HMW) DOC, and low-molecular-weight (LMW) DOC (*bottom*) at the Hawaii Ocean Time-Series site. Panel data from Sharp (1973), Benner et al. (1997), and Kaiser & Benner (2009). (*b*) Conceptual diagram of the biological pump and the biological, physicochemical, and photochemical processes shaping the size distribution of organic matter. Panel adapted from Buesseler et al. (2001), US JGOFS brochure.

LMW molecules (Burdige & Gardner 1998). These simple but remarkable observations lead to numerous insights about the pathways of carbon flow and the reactivity of organic matter in the ocean.

The size distributions of organic matter presented in this review are not precise, owing to the variable pore sizes and retention characteristics of commercial membranes and to the different filtration conditions used by the oceanographic community (Benner 1991, Buesseler et al. 1996, Guo & Santschi 1996, Benner et al. 1997, Walker et al. 2011). We have considered this shortcoming and focus on the three broad size classes of organic matter most commonly separated using micro- and ultrafiltration membranes: suspended POC (pore size of 0.1–0.8 μm), HMW DOC (pore size of 1–200 nm), and LMW DOC (pore size of <1 nm).

PROCESSES SHAPING THE SIZE DISTRIBUTION OF ORGANIC MATTER

Biological processes play a dominant role in shaping the size spectrum of organic matter in the ocean. Enzymes mediate the synthesis of macromolecules needed for growth and then disassemble

and remineralize these macromolecules, thereby driving metabolism and the flow of carbon through the food web. Primary production by microalgae and cyanobacteria in the euphotic zone is the major source of particulate and dissolved organic matter (POM and DOM) in the ocean (**Figure 1*b***). Chemoautotrophic archaea and bacteria have more recently been recognized as important primary producers in mesopelagic and deep waters (McCarthy et al. 2011, Swan et al. 2011, Herndl & Reinthaler 2013). Most of the carbon fixed in primary production is rapidly consumed, transformed, and remineralized in the food web. Planktonic organisms have relatively short life spans, and biomass accounts for a minor fraction of the TOC in the ocean, indicating that biodegradation has a greater net effect on the observed size distribution of organic matter in seawater than does biosynthesis.

Approximately 10–15% of phytoplankton production is directly released from cells as DOC (Baines & Pace 1991, Nagata 2000). The size distribution of this DOM varies depending on the community composition, physiological state, and environmental conditions (Hama & Handa 1987, Biddanda & Benner 1997, Nagata 2000). Phytoplankton release HMW and LMW DOM throughout the growth cycle, with HMW DOC typically accounting for 30–60% of the total DOC released (Biddanda & Benner 1997, Hama et al. 2004). Herbivorous zooplankton and protists are major consumers of phytoplankton biomass, and these grazers release cellular debris during feeding and egestion (Strom et al. 1997, Steinberg et al. 2000) (**Figure 1*b***). Grazers release an estimated 25–35% of phytoplankton production as DOC (Nagata 2000), thereby shifting the size distribution of carbon from biomass to dissolved molecules. Zooplankton also transfer organic matter from surface to mesopelagic waters through vertical migration (Steinberg et al. 2000, Hannides et al. 2013). A recent study tracing nitrogen through the food web found that the disaggregation and heterotrophic alteration of sinking particles and fecal pellets produce smaller suspended particles in midwaters (Hannides et al. 2013). Like grazing, viral lysis of cells releases particulate debris and DOM (Suttle 2007).

Microbial degradation of POM and HMW DOM generally requires ectoenzymes that hydrolyze macromolecules to smaller substrates prior to transport and utilization (Arnosti 2011). Various measures of microbial enzyme activity indicate that the hydrolysis of peptide and glycosidic bonds can be rapid in seawater (Hoppe et al. 2002, Baltar et al. 2009, Steen et al. 2010). Particles and aggregates are hot spots of enzyme activity, releasing dissolved molecules that can be rapidly utilized by microbes (Smith et al. 1992, Kähler & Bauerfeind 2001, Ziervogel et al. 2010). The net effect of enzyme activities is a shift in the size distribution of organic matter to smaller dissolved molecules. Biodegradation processes appear to play a major role in shaping the size distribution of DOM in sediment pore waters (Burdige & Gardner 1998) as well as in the water column. Utilization of the products of enzyme activities supports the growth of heterotrophic microbes, thereby incorporating carbon and associated bioelements from small labile molecules into cellular macromolecules. This process counters the biodegradation-driven flow of carbon down the size spectrum from larger to smaller molecules. Overall, decomposition processes lead to the production of small molecules that are resistant to microbial utilization. Some of these small molecules appear to be derived from bacteria and to persist for long periods of time (Ogawa et al. 2001).

Photochemical transformations of organic matter release a variety of small molecules, including carbonyl compounds, carbon monoxide, and carbon dioxide (Kieber et al. 1989, Miller & Zepp 1995). Some of the organic photoproducts are rapidly utilized by microbes and remineralized, whereas others appear to persist in the ocean (Moran & Zepp 1997, Benner & Biddanda 1998, Obernosterer et al. 1999). Experiments with river, estuarine, and coastal water samples indicate that photodegradation shifts the size spectrum of DOM from higher- to lower-molecular-weight molecules (Opsahl & Benner 1998, Helms et al. 2008, Dalzell et al. 2009). The water samples used

in these studies had relatively high concentrations of terrigenous DOM, which includes aromatic molecules, such as lignins, that are highly photoreactive. The observed shifts in DOM size distributions were, in part, due to phototransformations of the abundant terrigenous chromophores in estuarine and coastal waters (Fichot & Benner 2012). The photochemical production of pyruvate from marine DOM with a nominal molecular weight of >500 Da indicates that photochemical transformations likely shift the size spectrum of organic matter to smaller molecules in the ocean (Kieber et al. 1989).

Particle aggregation and disaggregation influence the size spectrum of organic matter in seawater and are driven by complex physical, chemical, and biological interactions. Aggregation shifts the size spectrum from colloids and submicron particles to macroscopic particles and can enhance the vertical export of carbon and associated elements from the upper ocean (McCave 1975, Engel et al. 2004, Burd & Jackson 2009). Grazing and microbial degradation contribute to particle disaggregation and shift the size spectrum of organic matter from larger to smaller particles and dissolved molecules, as described above. The balance between aggregation and disaggregation and their net effect on the size distribution of organic matter are not well understood (Burd & Jackson 2009, Verdugo 2012). In the following sections, we review the elemental, chemical, and radiocarbon distributions among the major size classes of organic matter, which provide further insights about the influences of aggregation and disaggregation on the size distribution of seawater TOC.

THE BIOLOGICAL REACTIVITY OF ORGANIC MATTER

The primary data leading to the conceptualization of the size-reactivity continuum model came from seawater incubation experiments with natural DOM that was separated into HMW and LMW size fractions using ultrafiltration membranes (Amon & Benner 1994, 1996). Particularly high rates of microbial activity were observed in experiments with samples collected from coastal waters that experienced a recent diatom bloom. Rates of bacterial production and respiration were substantially higher in the incubations with HMW DOM, as were rates of DOC removal (**Figure 2**). Bacterial growth efficiencies were higher in incubations with LMW DOM, and the regeneration of ammonium and nitrate was observed. By contrast, the net utilization of ammonium and nitrate has been observed during incubations with HMW DOM (Amon & Benner 1994, Gardner et al. 1996). Carbohydrates appear to be preferentially utilized in HMW DOM incubations, which is consistent with studies demonstrating that phytoplankton produce DOM that is rich in polysaccharides (Biddanda & Benner 1997, Biersmith & Benner 1998, Aluwihare & Repeta 1999). In summary, rates of microbial activity and carbon mineralization were consistently higher in incubations with HMW DOM, leading us to propose that "the bulk of HMW DOM is more bioreactive and less diagenetically altered than the bulk of LMW DOM" (Amon & Benner 1996, p. 41).

The experiments described above were conducted with natural DOM of various origins and stages of diagenetic alteration, and they did not examine the reactivity of POM. Hama et al. (2004) conducted an elegant ^{13}C-tracer experiment with coastal water samples collected during a diatom (*Skeletonema costatum*) bloom to directly compare the reactivities of phytoplankton-derived POC, HMW DOC, and LMW DOC. Nutrients and ^{13}C-bicarbonate were added to the water, and the samples were incubated in the light for 12 h to label the phytoplankton. After labeling, the samples were incubated in the dark, and sampling to investigate the decomposition of the ^{13}C-labeled phytoplankton organic matter was initiated on day 3. More than 70% of the labeled organic carbon on this day was associated with POC, with the remaining label distributed between HMW and LMW DOC (**Figure 3**). On day 60, 5% of the ^{13}C-labeled phytoplankton TOC remained, with

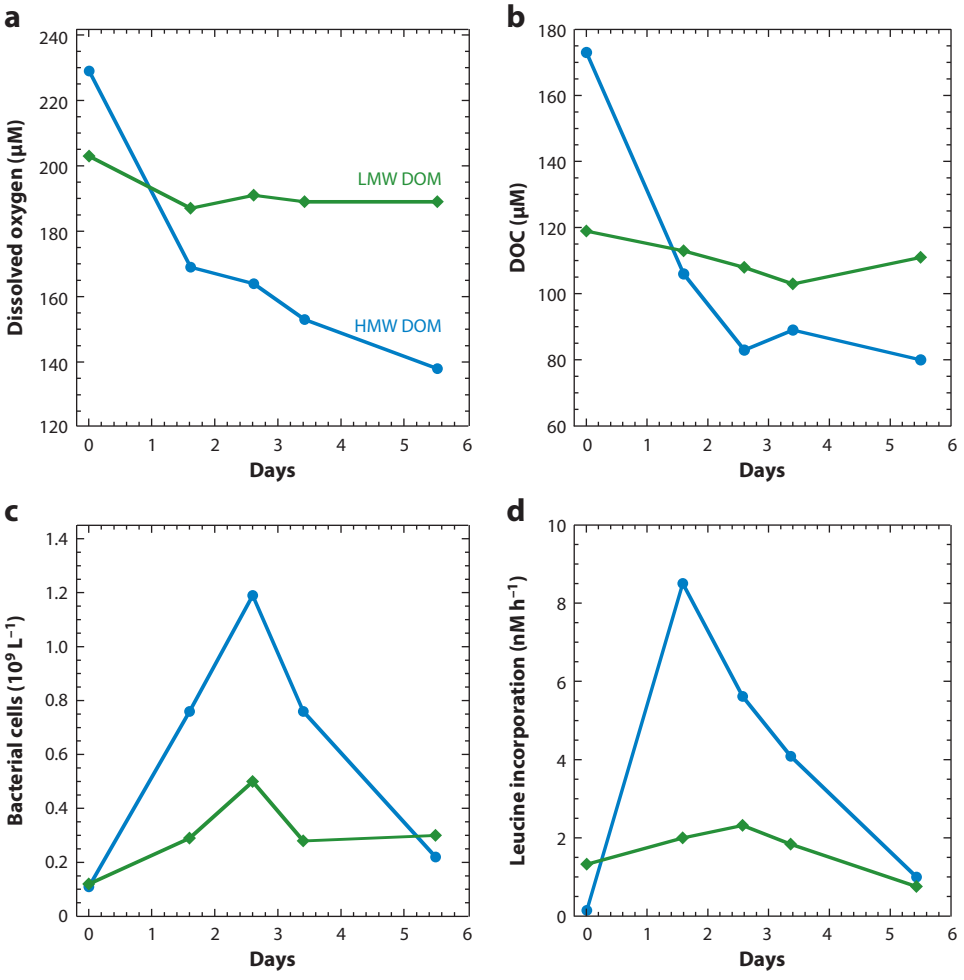

Figure 2

Bacterial consumption of (*a*) dissolved oxygen and (*b*) dissolved organic carbon (DOC), along with (*c*) bacterial abundance and (*d*) bacterial leucine incorporation in coastal seawater incubations with natural dissolved organic matter (DOM) and a seawater inoculum (<0.6-μm pore size). Additional abbreviations: HMW, high molecular weight; LMW, low molecular weight. Figure adapted from Amon & Benner (1994).

only 14% of the label in POC and most (64%) of the label in LMW DOC. The distribution of the label between HMW (25%) and LMW (75%) DOC on day 60 was similar to that observed in the surface ocean. The exponential decay constant (*k*) for POC was 1.8 and 8.6 times higher than those for HMW and LMW DOC, respectively (**Figure 3**). The ratio of the decay constant for HMW DOC to that for LMW DOC (4.8) in the Hama et al. (2004) study was similar to that observed for DOM (4.3) from a coastal diatom bloom (Amon & Benner 1994). The decay constants for fresh, phytoplankton-derived size fractions declined with decreasing size (POM > HMW DOM > LMW DOM), confirming the size-reactivity continuum model for marine organic matter.

Experimental measurements of the turnover of organic matter in the open ocean are challenging owing to low rates of metabolism. We are unaware of any direct determinations of HMW and LMW DOC loss rates for the open ocean, but decomposition rates have been measured in

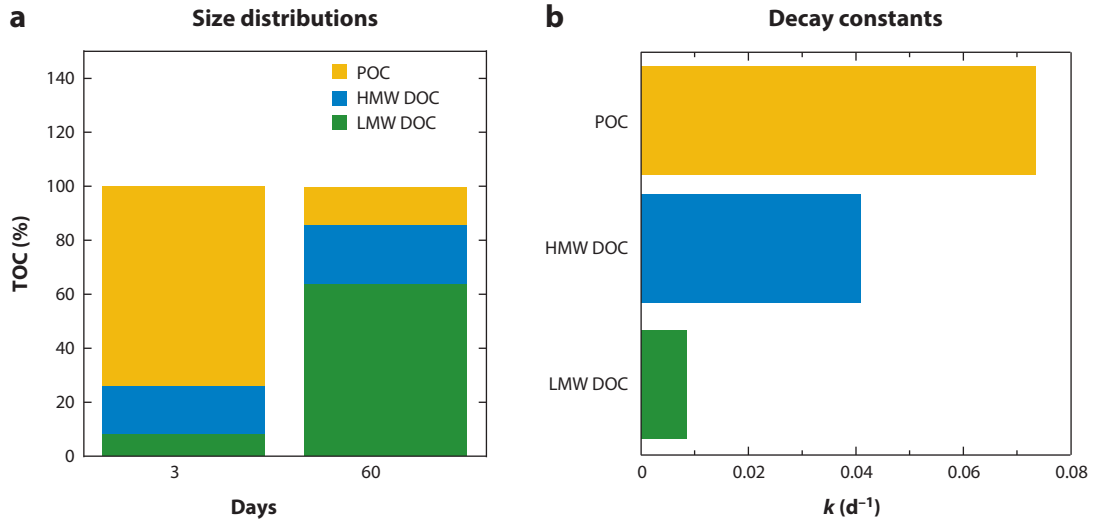

Figure 3

(*a*) Size distributions of total organic carbon (TOC) in coastal seawater that was collected during a diatom (*Skeletonema costatum*) bloom, incubated with added nutrients and ^{13}C-bicarbonate in the light for 12 h, and then incubated in the dark for 60 days. The ^{13}C label was used to trace photosynthetically produced organic carbon. In this study, high-molecular-weight (HMW) dissolved organic carbon (DOC) is >10 kDa, and low-molecular-weight (LMW) DOC is <10 kDa. Concentrations of TOC declined by 95% between days 3 and 60, and the size distribution shifted from predominantly particulate organic carbon (POC) to predominantly LMW DOC. (*b*) Exponential decay constants (*k*) calculated for ^{13}C-labeled size fractions of TOC. Figure data from Hama et al. (2004).

experiments using particles collected from the upper ocean (Sempéré et al. 2000, Panagiotopoulos et al. 2002, Goutx et al. 2007). Exponential decay constants for POC loss from large (>60-μm) particles collected from depths of 30–200 m range from 0.012 to 0.034 d^{-1}, with an average value of 0.024 d^{-1} (Panagiotopoulos et al. 2002). This rate of POC loss is 2–3 times lower than that observed for freshly produced POC from phytoplankton (Harvey et al. 1995, Hama et al. 2004). Particle degradation can lead to increases in HMW DOC concentrations (Panagiotopoulos et al. 2002), presumably through the ectoenzymatic activities of the attached microflora (Karner & Herndl 1992, Smith et al. 1992). The enzymatic release of HMW DOC from sinking particles appears to be an important source of bioavailable DOM for microbial populations in mesopelagic and bathypelagic waters (Tamburini et al. 2003).

It is important to recognize that net losses of carbon from different size classes are due to mineralization and other transformation processes, such as solubilization, that transfer organic carbon from larger to smaller size classes. In addition, heterotrophic organisms grow and assimilate organic carbon during decomposition, resulting in a countercurrent of carbon flow from smaller to larger size classes, with the resulting organic matter having a different biochemical composition compared to the initial organic substrates. However, the growth efficiencies of marine microbes are typically <40% (Cherrier et al. 1996, Carlson et al. 1999, Sempéré et al. 2000), so microbial decomposition is the dominant process shaping the size-reactivity continuum.

Variable reactivities among the chemical components of different size classes of organic matter have been observed during seawater incubation experiments. Exponential decay constants for the major biochemical components of phytoplankton-derived POM varied by more than fourfold during experiments lasting 7–10 weeks (Harvey et al. 1995) (**Figure 4**). The following ranking from highest to lowest decay constant was observed: carbohydrates > proteins > lipids. Biodegradation

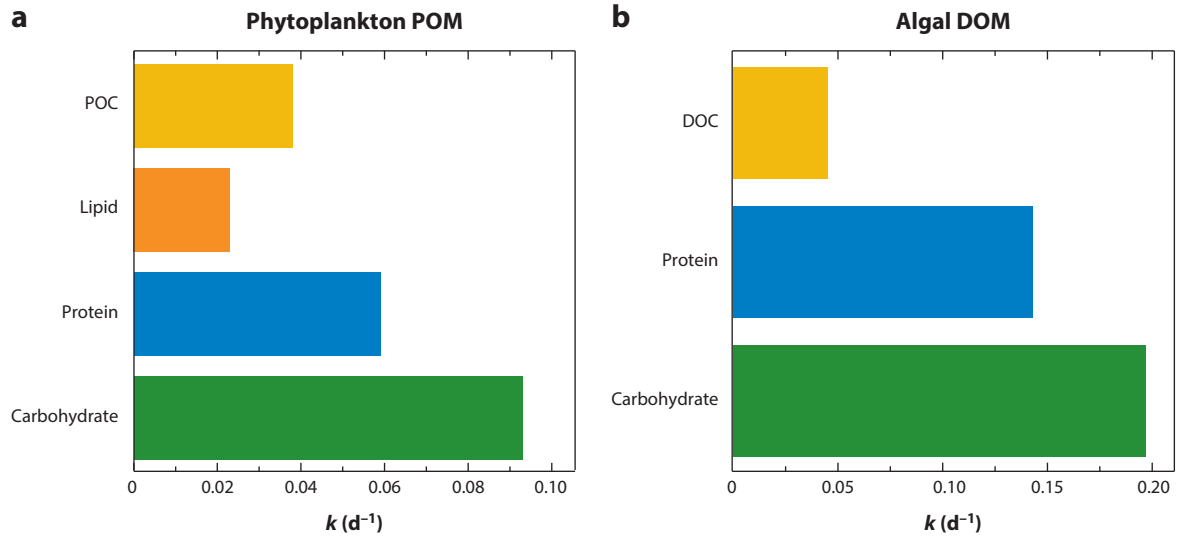

Figure 4

(*a*) Exponential decay constants (*k*) for particulate organic carbon (POC) and major biochemicals during dark incubations in coastal seawater with particulate organic matter (POM) from cultured phytoplankton (average values, using incubations with POM from *Thalassiosira weissflogii* and *Synechococcus* sp.). Panel data from Harvey et al. (1995). (*b*) Exponential decay constants (*k*) for dissolved organic carbon (DOC) and major biochemicals in seawater incubations with algal dissolved organic matter (DOM) in sea-ice meltwater. Panel data from Amon et al. (2001).

experiments using sinking particles collected from seawater revealed a consistent pattern, with higher decay constants for protein than for bulk POC (Panagiotopoulos et al. 2002, Goutx et al. 2007). These studies also indicated that decay constants for carbohydrate and lipid degradation are sometimes higher or lower than those for bulk POC, depending on the source, type, and location of particle collection.

A similar pattern of biochemical reactivity was observed during the microbial decomposition of algal-derived DOM during short-term (10-day) incubations (Amon et al. 2001) (**Figure 4**): Decay constants for carbohydrates were highest, followed by those for proteins (i.e., hydrolyzable amino acids) and DOC. Similar dissolved protein decay constants were also measured in surface waters of the Sargasso Sea and Southern Ocean (Keil & Kirchman 1999, Simon & Rosenstock 2007). The relatively rapid turnover of combined forms of amino acids (Keil & Kirchman 1993, Cherrier & Bauer 2004, Davis & Benner 2007) and carbohydrates (Meon & Kirchman 2001, Steen et al. 2008, Davis et al. 2009, Piontek et al. 2011) in diverse marine environments is well documented.

THE ELEMENTAL AND CHEMICAL COMPOSITION OF ORGANIC MATTER

Surface water POM, which includes living and nonliving components, has similar C:N ratios and slightly higher C:P ratios compared with those in cultured phytoplankton (Geider & La Roche 2002, Martiny et al. 2013). By contrast, the C:N and C:P ratios observed in surface water DOM are typically higher than those in phytoplankton and POM (Loh & Bauer 2000, Bronk 2002, Sannigrahi et al. 2006, Yoshimura et al. 2009) (**Figure 5**). The HMW DOM in surface water has similar C:P ratios and slightly higher C:N ratios compared with those in DOM (Benner et al.

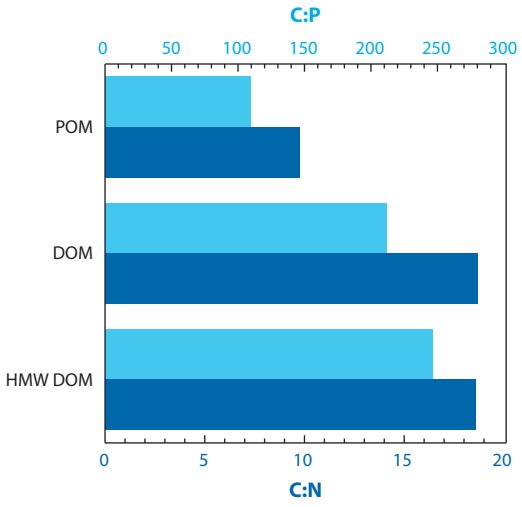

Figure 5

Typical elemental ratios (C:N, C:P) in surface ocean particulate organic matter (POM), dissolved organic matter (DOM), and high-molecular-weight (HMW) DOM. Figure data from Benner et al. (1997), Loh & Bauer (2000), Kolowith et al. (2001), Geider & La Roche (2002), Sannigrahi et al. (2006), Meador et al. (2007), and Martiny et al. (2013).

1997, Kolowith et al. 2001, Sannigrahi et al. 2006, Meador et al. 2007). Phytoplankton exudation and grazing release DOM that is rich in oligo- and polysaccharides (Strom et al. 1997, Biersmith & Benner 1998, Fajon et al. 1999) and has elevated C:N and C:P ratios (Conan et al. 2007), suggesting that these processes could be responsible for the elevated ratios observed in HMW DOM. The C:N ratios of POM and HMW DOM in a coastal upwelling system were lower than those found in less productive waters, but the pattern of increasing C:N ratios with decreasing size was similar from large particles to DOM (Walker & McCarthy 2012). Bulk elemental compositions reflect the biochemical composition of organic matter and indicate that marine POM is relatively enriched in nitrogen- and phosphorus-containing macromolecules, such as proteins and nucleic acids, compared with DOM. The preferential biodegradation of these macromolecules produces smaller dissolved molecules that are relatively depleted in nitrogen and phosphorus and is generally considered the primary reason for the elevated C:N and C:P ratios in DOM (Hopkinson et al. 1997, Lønborg & Álvarez-Salgado 2012).

The size-reactivity continuum indicates that POM and HMW DOM are on average more reactive than LMW DOM, which constitutes the largest reservoir of organic carbon in seawater. However, size per se does not appear to be the primary driver of the size-reactivity continuum. The different size classes of organic matter have distinct chemical compositions that have a strong influence on rates of microbial degradation. The rapid decline in concentrations of oligo- and polysaccharides with depth in the upper ocean demonstrates that these carbohydrates are produced primarily within the sunlit layer of the surface ocean and consumed primarily within the upper mesopelagic zone (Benner et al. 1992, Pakulski & Benner 1994, McCarthy et al. 1996, Kaiser & Benner 2012). Combined forms of amino acids and carbohydrates are among the most reactive components of marine POM and DOM (**Figure 4**), indicating that the chemical composition of organic matter is a major driver of processes shaping the size-reactivity continuum.

Molecular measurements of combined amino acids, neutral sugars, and amino sugars in various size classes of organic matter in surface and deep waters at the Hawaii and Bermuda time-series

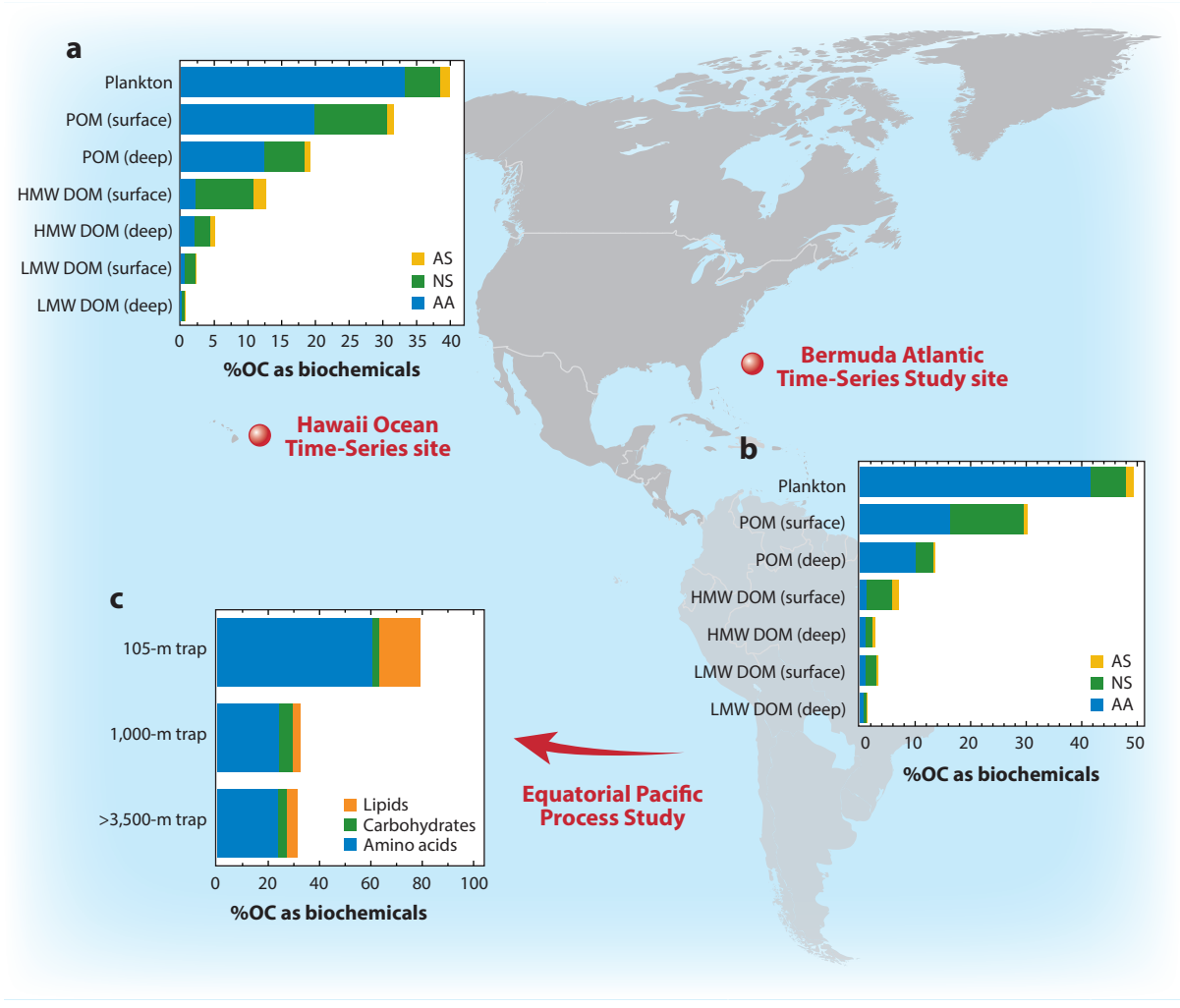

Figure 6

(*a*,*b*) Percentages of organic carbon (%OC) in the form of major biochemicals [hydrolyzable amino acids (AA), neutral sugars (NS), and amino sugars (AS)] in particulate organic matter (POM), high-molecular-weight (HMW) dissolved organic matter (DOM), and low-molecular-weight (LMW) DOM from surface and deep waters at the Hawaii Ocean Time-Series site (panel *a*) and the Bermuda Atlantic Time-Series Study site (panel *b*). Panels adapted from Kaiser & Benner (2009). (*c*) Percentages of organic carbon (%OC) in the form of major biochemicals in sinking particles collected in sediment traps during the Equatorial Pacific Process Study. Panel adapted from Wakeham et al. (1997). Background adapted from Buesseler et al. (2001), US JGOFS brochure.

stations indicate a strong linkage between the size and chemical composition of marine organic matter (Kaiser & Benner 2009) (**Figure 6**). These common biochemicals account for nearly half of the carbon in plankton and declining percentages of carbon in POM, HMW DOM, and LMW DOM. The deepwater counterparts of these size classes have lower percentages of organic carbon in combined amino acids and carbohydrates compared with those in surface water. These compounds account for a surprisingly low percentage (<2%) of LMW DOC in deep waters of the North Pacific and North Atlantic.

The chemical composition of sinking particles collected from sediment traps in the equatorial Pacific also changes dramatically with depth (Wakeham et al. 1997) (**Figure 6**). Amino acids, carbohydrates (neutral sugars), and lipids account for more than 70% of the POC in trap samples from 105-m depth and only ~30% of the POC from deepwater traps. Biological and physicochemical processes alter the size distribution and chemical composition of sinking particles during transit from the surface to the deep ocean. The percentage of amino acid carbon in sinking POM reaching the seabed is similar to that in suspended POM in the surface ocean (**Figure 6**), indicating that sinking POM in the deep ocean includes bioavailable and reactive forms of organic matter.

Observations of the distributions, compositions, and concentrations of major biochemicals in the ocean have provided independent confirmation of the relative reactivities of different size classes of organic matter gleaned from bioassay experiments. Patterns in the alterations of molecular composition among size classes of organic matter are indicative of their diagenetic pathways, and generally demonstrate that smaller size classes of organic matter include decomposition products derived from larger size classes (Mannino & Harvey 1999, 2000; Benner 2002; Kaiser & Benner 2009; Landry & Tremblay 2012; Zhang et al. 2012). The relative abundance of specific D- and L-enantiomers of amino acids provides insights about living and nonliving bacterial contributions to organic matter size classes and the extent of their diagenetic alterations (Jørgensen et al. 1999, Amon et al. 2001, Kawasaki et al. 2011). Combined forms of the D-enantiomers of alanine, aspartic acid, and glutamic acid occur in a variety of biomolecules that are found only in bacteria (McCarthy et al. 1998, Kaiser & Benner 2008). The D:L ratio of these amino acid enantiomers increases in smaller size classes of organic matter, as indicated in surface water samples from the North Pacific (**Figure 7**). The high D:L ratios observed in LMW DOM indicate that remnants of bacterial cells are abundant and that the DOM is highly altered (Kaiser & Benner 2009). Linking the size distribution of organic matter to its chemical composition provides a molecular basis for understanding the size-reactivity continuum and the cycling of major bioelements in the ocean.

RADIOCARBON AGE OF ORGANIC MATTER

Initial observations of the relationship between the size and reactivity of organic matter indicated that larger size classes were of recent origin and smaller size classes were more altered and older

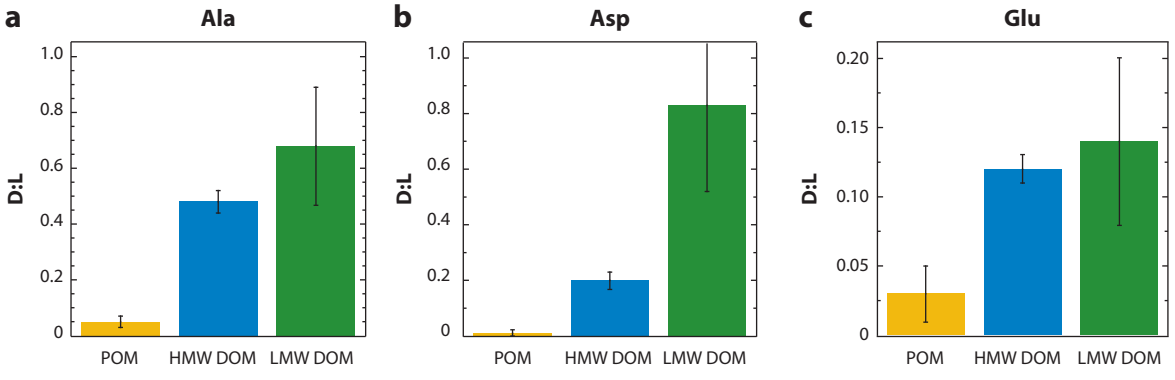

Figure 7

Ratios of D- to L-enantiomers of (*a*) alanine (Ala), (*b*) aspartic acid (Asp), and (*c*) glutamic acid (Glu) in surface waters at the Hawaii Ocean Time-Series site. Error bars represent one standard deviation ($n = 3$). Additional abbreviations: DOM, dissolved organic matter; HMW, high molecular weight; LMW, low molecular weight; POM, particulate organic matter. Figure data from Kaiser & Benner (2009).

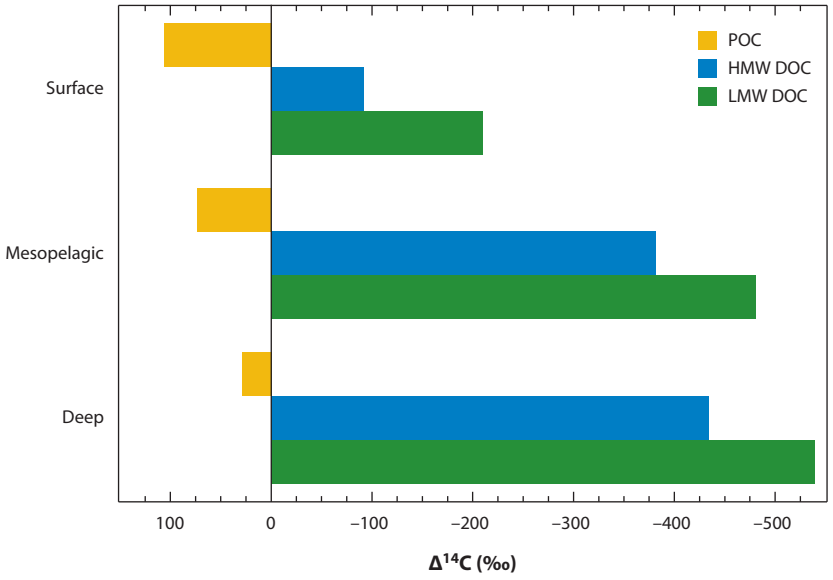

Figure 8

Natural-abundance radiocarbon content ($\Delta^{14}C‰$) in suspended particulate organic carbon (POC), high-molecular-weight (HMW) dissolved organic carbon (DOC), and low-molecular weight (LMW) DOC collected from surface, mesopelagic, and deep waters of the central North Pacific. Figure data from Druffel et al. (2003) and Loh et al. (2004).

(Amon & Benner 1996). These observations were consistent with the average contemporary radiocarbon ages of POC and the average millennial ages of DOC in the ocean (Williams & Druffel 1987, Bauer et al. 1992, Druffel et al. 1992). The size-reactivity continuum further indicates a continuum of increasing radiocarbon age with decreasing size. Analyses of the radiocarbon content of various HMW DOC size fractions were consistent with the continuum concept, indicating decadal to centennial ages for macromolecular size fractions (>10 kDa and >3 kDa), which account for a small percentage (<10%) of DOC (Santschi et al. 1995, Guo et al. 1996).

The radiocarbon content of the major size classes of organic matter has been measured in the water column of the central North Pacific. The radiocarbon content of all size classes decreases with increasing depth, indicating that most of the carbon is fixed in the surface ocean and ages in the ocean interior (**Figure 8**). The distribution of radiocarbon among the three size fractions is consistent with the size-reactivity continuum, with contemporary to decadal ages for suspended POC, centennial to millennial ages for HMW DOC, and millennial ages throughout the water column for LMW DOC (Druffel et al. 2003, Loh et al. 2004). The protein-like and carbohydrate-like components of the DOM had contemporary ages in the surface ocean, indicating that they are relatively reactive components of DOM (Loh et al. 2004). Similar radiocarbon ages of HMW and LMW DOC were observed in the water column off Hawaii, confirming the increasing age of organic matter as it passes through the size-reactivity continuum from particulate matter to small dissolved molecules (Walker et al. 2011).

Contemporary ages of neutral sugars in HMW DOM were observed in the North Pacific, indicating that sinking POM along with its subsequent solubilization is an important source of HMW carbohydrates in mesopelagic waters (Repeta & Aluwihare 2006). Patterns of radiocarbon content among size class of TOC in the North Atlantic are similar to those observed in the North Pacific, further demonstrating the global nature of the size-age continuum (Loh et al. 2004).

Quantitative relationships among the size, age, and C:N ratio of organic matter were recently observed in a coastal upwelling system, suggesting the potential for new modeling approaches to study the carbon and nitrogen cycles in these systems (Walker et al. 2014).

INSIGHTS ABOUT BIOGEOCHEMICAL CYCLES

Biological processes predominantly control the size distribution of organic matter in the ocean. Biosynthesis builds the macromolecular structure of cells, and biodegradation disassembles and alters molecular structures and returns elements to their mineral forms. Common biochemicals comprise most of the biomass, but the fraction of nonliving organic matter identified as these common biochemicals declines rapidly with decreasing size. As indicated by their chemical complexity and age, most of the dissolved molecules that dominate the vast ocean reservoir of organic matter appear to be the remnants of metabolism, which leads to extensive alteration and transformation.

The size-reactivity continuum model synthesizes these and other observations about the size, reactivity, composition, and age of organic matter in the ocean (**Figure 9**). This model indicates that the predominant flow of organic matter follows a continuum from a highly structured cellular state to a seemingly random and complex molecular state. The growth and production of heterotrophic organisms, particle aggregation, and gel formation assemble smaller particles and

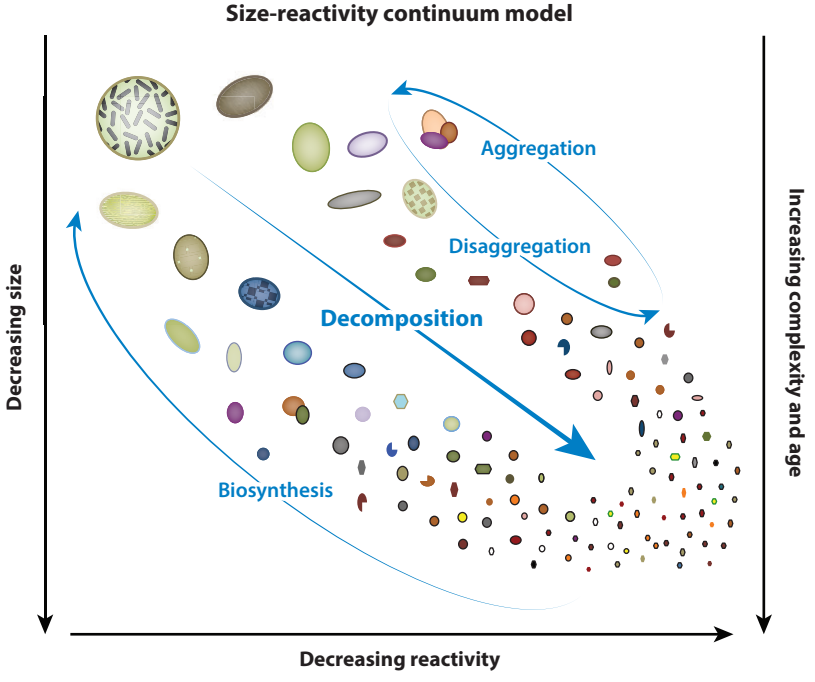

Figure 9

A conceptual model of the size-reactivity continuum, showing the net flow of organic carbon from larger to smaller size classes with increasing decomposition. As decomposition proceeds, the chemical complexity of organic matter increases, biological reactivity declines, and the radiocarbon ages of molecules increase. Biosynthesis by heterotrophic and mixotrophic microorganisms transforms and repackages organic carbon into larger size classes. The net effect of aggregation and disaggregation processes on the size, reactivity, and composition of organic matter is not well understood. Figure adapted from Amon & Benner (1996).

organic molecules into larger ones, but these processes are very different with regard to the compositions of the products. Microbial utilization of DOM results in biomass that is enriched in newly synthesized common biochemicals, whereas aggregation and gel formation do not incorporate novel molecules into the assembled particles and colloids. The products of aggregation and gel formation apparently do not account for a substantial fraction of the TOC in seawater, as they would have a measurable effect on the elemental and chemical compositions of marine organic matter and thereby blur the relationships between the size and composition of organic matter.

The relationships among the size, reactivity, and chemical composition of marine organic matter depicted in the size-reactivity continuum model indicate the possibility of developing chemical proxies for the reactivity and bioavailability of organic matter, which have been classically determined using bioassay experiments (Søndergaard & Middelboe 1995, Lønborg & Álvarez-Salgado 2012). These experiments are labor intensive and typically require weeks of incubation, and are therefore not conducive to broad spatial and temporal coverage. Several chemical indicators of organic matter bioavailability have been developed and tested in a variety of marine waters. Most applications use elemental ratios (Loh & Bauer 2000, Hopkinson & Vallino 2005, Walker & McCarthy 2012) or biochemical characteristics as qualitative indicators to establish the relative reactivities of different samples (Skoog & Benner 1997, Mannino & Harvey 2000, Meon & Kirchman 2001, Davis & Benner 2005, Goldberg et al. 2009, Kaiser & Benner 2009). The C-normalized yields (%OC) of neutral sugars and amino acids have been further developed into quantitative tracers of two forms of bioavailable organic matter: labile DOC and semilabile DOC (Amon & Benner 2003, Davis & Benner 2007). Chemical indicators of bioavailable DOM have the potential to dramatically expand our understanding of factors controlling the microbial utilization of organic matter. This approach was recently used to establish DOM bioavailability as an ecosystem property that reflects the productivity of different oceanic regions in the Arctic (Shen et al. 2012).

One of the major conundrums of the ocean carbon cycle is the occurrence of old and apparently refractory DOC (Barber 1968, Williams & Druffel 1987, Hansell & Carlson 1998). The processes responsible for the formation and removal of refractory DOC and the factors regulating them are poorly understood but critical for maintaining this large carbon reservoir, which sequesters carbon in the ocean for centuries to millennia. The size-reactivity continuum model provides insights about the processes and pathways for refractory DOC formation that can help solve this riddle. As depicted in this model, most refractory DOC resides in LMW molecules, which constitute the largest fraction of TOC in the ocean. Ultra-high-resolution mass spectrometry and NMR spectroscopy have revealed astonishing variety and chemical complexity among the dissolved molecules in the ocean (Koch et al. 2005; Hertkorn et al. 2006, 2013; Kujawinski 2011). These characteristics are consistent with the size-reactivity continuum model, which suggests that the molecular diversity and chemical complexity of LMW DOM have an important influence on its limited bioreactivity.

Enzymes are primary drivers of decomposition processes and carbon flow in the size-reactivity continuum model, so enzymatic processes are likely responsible for much of the molecular diversity and chemical complexity observed in LMW DOM. There is considerable variability in the fidelity of gene maintenance and expression, with error rates ranging from 10^{-8} for DNA replication to 10^{-4} for mRNA translation (Reynolds et al. 2010). Quality control in protein synthesis is quite high, but mistranslation occurs regularly and can affect enzyme specificity. Many enzymes catalyze multiple reactions and transform different substrates, and these so-called promiscuous enzymes are thought to play an important role in protein evolution (O'Brien & Herschlag 1999, Khersonsky & Tawfik 2010). It is possible that nonspecific enzymatic transformations contribute to the molecular diversity and chemical complexity of LMW DOC (Ogawa et al. 2001). Abiotic transformations of organic matter, including photochemical and thermal alterations, also contribute to the diversity,

complexity, and refractory nature of dissolved molecules in seawater (Benner & Biddanda 1998, Tranvik & Kokalj 1998, Dittmar & Koch 2006, Ziolkowski & Druffel 2010).

Early studies of marine bacterial growth at limiting concentrations of substrates indicated that growth ceased when concentrations fell below certain threshold values (Jannasch 1967). These studies led to the hypothesis that concentrations of dissolved organic molecules in the deep ocean are maintained near threshold concentrations by the resident microflora (Jannasch 1995). It was further proposed that refractory molecules might be co-oxidized in the presence of bioavailable substrates, but this process also ceases when concentrations of bioavailable substrates fall below threshold values (Jannasch 1995). A test of the threshold concentration hypothesis failed to stimulate microbial degradation of deep ocean DOM after concentration by ultrafiltration (Barber 1968), but the low concentration factors (three- to fivefold) and low precision of the DOC analyses leave doubts about whether these results were definitive (Kattner et al. 2011). Recent observations of the molecular diversity and chemical complexity of dissolved molecules in seawater indicate that most of these molecules persist at extremely low concentrations that are unable to support microbial growth because they rarely encounter a transporter protein or enzyme that facilitates microbial utilization. Microbial utilization is further complicated by the incredible structural complexity of dissolved molecules. The refractory nature of LMW DOM remains an enigma, but it appears that microbes are simply "out of touch" with many of the dissolved organic molecules that persist in the ocean.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

We thank Karl Kaiser, Matt McCarthy, and Brett Walker for valuable discussions and contributions to our understanding of the size-reactivity continuum model. We each received funding from the National Science Foundation in support of the research described in this review.

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Annual Review of
Marine Science

Volume 7, 2015

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Errata

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