

COMMENTARY

Unifying chemical and biological perspectives of carbon accumulation in the environment

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Heterotrophic microorganisms are fiendishly clever at degrading all shapes and sizes of organic compounds to extract the energy they need to build biomass. Every year marine phytoplankton fix ~50 billion tons of carbon dioxide into organic matter, and every year marine heterotrophs respire nearly all of this organic matter back to carbon dioxide (1). Nearly all, but not all. With each spin of this carbon cycle, a small amount of organic matter escapes respiration and becomes sequestered in seawater, sediments, and soils. Over time, this small “leak” in the system leads to the accumulation of a vast reservoir of carbon; some 5×10^{19} kg of organic matter are thought to be sequestered in sedimentary rocks (2). This carbon sequestration has immense consequences for life on Earth, as illustrated by the change in climate we are now experiencing due in part to the transfer of a minute portion of this inventory from geologic reservoirs into the atmosphere.

The question of why carbon is preserved at all has puzzled geochemists and biogeochemists for well over half a century. Why is organic matter production and consumption not coupled even more tightly? If the organic matter that ultimately accumulates in geologic reservoirs is synthesized by microbes in the first place, why cannot microbes degrade it? In soils and sediments minerals are thought to be an important part of the answer. Adsorption of organic matter onto mineral surfaces imposes a number of penalties on degradation: the extra energy cost of organic matter desorption, impediments to the movement of hydrolytic enzymes through the environment, and irreversible deactivation of enzymes by mineral surfaces, to name a few. Each of these penalties makes degradation less of an energy gain for consumers (3, 4). However, organic matter–mineral surface interactions alone cannot be the whole answer, and nowhere is this more evident than in the ocean. A bit less than 700 Pg of carbon, an amount equal to the organic carbon stored in terrestrial biomass or in soils, persists in the ocean as dissolved organic matter (DOM) (5). Even more surprising, most of this DOM is recalcitrant; it resides in the ocean for several millennia (6). Water

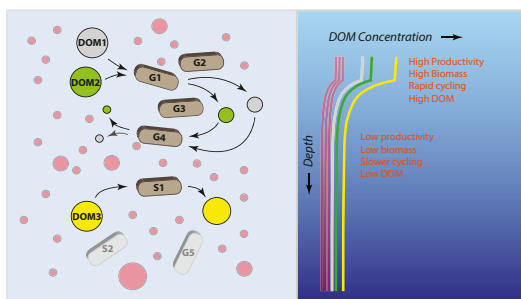


Fig. 1. In Zakem et al.’s model (Left), pools of DOM (DOM1, DOM2, ... DOMn; here depicted as colored circles) are taken up by a diverse community of microbial generalists (G1, G2, ... Gn) and specialist (S1, S2, ... Sn) consumers. DOM pools with high rates of uptake that are consumed by a number of generalists and specialists (green and gray circles) are quickly degraded to their subsistence (less than picomolar to nanomolar) concentrations. Other DOM pools (yellow circles) that have lower uptake rates, or require more complex suites of enzymes for degradation that are expressed by fewer members of the microbial community (here S1) accumulate to higher concentrations in the model. The abundance of microbial consumers is regulated by the mortality of the different populations (S2 and G5). The outcome of these interactions leads to a characteristic profile of DOM in the ocean (Right) with high concentrations of DOM in the surface where DOM supply, microbial cycling, and biomass are all high, and lower concentrations at depth where DOM supply is reduced and rates of cycling decline. The distribution of DOM pools is bimodal, with many pools at low abundance (red profiles) and a fewer number of pools that are present at high abundance (yellow, green, and gray profiles).

circulates through the deep sea about once every thousand years, so DOM appears to take several trips through the ocean before it is removed.

Re-cal-ci-trant (ri-kal-sə-trent) *adj.* Hard to manage, deal with, or control

A number of seemingly disconnected hypotheses have been advanced to explain the recalcitrance of marine DOM. One body of work suggests that some organic compounds are intrinsically hard to metabolize. Other

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studies suggest that the metabolic pathways necessary for DOM degradation may have environmental or ecological controls that separate them in space or time from their intended substrates. Still other work suggests that the concentration of individual DOM compounds may be so low that uptake and utilization is no longer an energetically profitable enterprise vis-à-vis microbial metabolism. The paper by Zakem et al. (7) that appears in PNAS uses a stochastic model of microbial–organic matter interactions to illuminate how these hypotheses are in fact interconnected, and how DOM composition, microbial metabolism, environmental, and ecosystem properties interact simultaneously in ways that ultimately lead to carbon accumulation, even in carbon and energy-limited systems. Zakem et al.'s model shows that carbon accumulation is an emergent property of the complex microbial foodwebs that cycle organic matter.

Rates of marine primary production span several orders of magnitude across different ocean locales; however, the concentration of DOM, a by-product of primary production, is surprisingly constant. Surface waters in highly productive coastal upwelling regions that support tremendous rates of carbon fixation, and surface waters of oligotrophic gyres with minimal levels of production, both have DOM concentrations between 0.7 and 1.0 mg C·L⁻¹. Concentrations of DOM in the deep ocean are about half of surface water values and fall within an even narrower range of 0.4 to 0.5 mg C·L⁻¹ (5, 6). This distribution of DOM has long been recognized to imply strong feedbacks between DOM production and consumption, but the mechanistic underpinnings of those feedbacks have never been described. At the molecular level, about half of all DOM consists of an incredibly complex mixture of perhaps 10⁶ different small molecules that individually occur at femtomolar to nanomolar concentrations. These organic matter pools include metabolites (simple sugars, lipids, and amino acids) and more complex humic-like compounds, all of which have molecular weights of only a few hundred daltons (8). The low molecular weight of these pools should allow them to be taken up rapidly by marine microbes, but surprisingly their radiocarbon age is quite old (6, 8). In contrast to the immense structural diversity of low-molecular-weight DOM, another 25–30% of DOM consists of a specific family of polysaccharides that accumulate to very high concentrations (15 to 20 μM C) throughout the water column. The chemical characteristics of these polysaccharides are highly conserved. Polysaccharides isolated from the deep Pacific Ocean are practically indistinguishable from polysaccharides isolated from surface waters of the North Atlantic Ocean (9). This selective preservation of a particular family of polysaccharides suggests they incorporate some as-yet-unidentified structural features that inhibit their degradation. In short, microbial cycling of organic matter can on the one hand lead to the accumulation of a very diverse suite of compounds at low concentrations, while on the other hand also lead to the accumulation of high concentrations of a smaller set of very specific compounds. How to sort this all out?

Managing the Unmanageable

Zakem et al. approached the problem by building a mechanistic model that captures how microbial consumers interact with organic matter (Fig. 1). The complex processes that supply DOM (primary production, grazing, viral lysis, etc.), determine its uptake (hydrolysis of DOM by extracellular enzymes, cross-membrane transport of substrates, respiration and biomass synthesis, etc.), and impact microbial community structure and ecosystem dynamics (number of microbial generalist and specialist, cell mortality, etc.) were parameterized using well-established equations

for microbial growth and respiration. DOM supply was allowed to vary freely across a large number (1,000 to 10,000) of DOM “pools” or compounds, reflecting the stochastic nature of DOM production by producers under a range of environmental conditions. Different organic matter pools are respired or used to synthesize biomass by one or more consumers, each of which takes up that pool with a distinct uptake rate, half saturation constant, and the like. Consumers are removed from the model at a loss rate proportional to their abundance. Some organic matter pools are functionally labile and reach an equilibrium concentration; the supply of the organic pool is sufficient to maintain the community of consumers in the face of population loss. In contrast, other pools of organic matter do not reach equilibrium. The supply of these pools exceeds the ability of the microbial community to consume them. These pools are functionally recalcitrant and are able to accumulate. In the model, functional lability and functional recalcitrance are distinguished by the “recalcitrance indicator” parameter (Q_i). When $Q_i > 1$, the pool is functionally labile and equilibrates. When $Q_i \leq 1$, it is functionally recalcitrant and accumulates.

Much exploration and investigation remain if we are to fully understand why carbon accumulates in the environment, but the roadmap provided by Zakem et al. promises to help keep marine and terrestrial biogeochemists, microbiologists, and ecosystem modelers all headed in the same direction.

The outcome of all of these complex interactions is an accumulating pool of organic matter that looks very much like what we see in the real ocean (Fig. 1). Rates of organic matter production and consumption are highest in the sunlight surface waters. Here, microbial populations grow and turnover quickly. Below the euphotic zone, rates of organic matter production and consumption decline, and lower concentrations of organic pools are able to sustain the lower growth rates needed to match population loss. Equilibrium concentrations of DOM pools are therefore greater in the surface than at depth, reproducing the characteristic water column profile of marine DOM. At the molecular level, the interaction of DOM supply, microbial uptake and respiration, and microbial community dynamics leads to a bimodal distribution of DOM pools. Most organic pools in the model are functionally labile and equilibrate to very low concentrations, mimicking the complex mixture and low abundances of low-molecular-weight DOM compounds found in the ocean. These pools are consumed until their concentrations fall to subsistence levels, the threshold concentration where the production of microbial biomass just keeps pace with population loss at steady state. A fewer number of organic pools are functionally recalcitrant; the rate of population loss for microbes that have the metabolic capacity to degrade these pools exceeds the rate of biomass synthesis. Microbial consumption cannot keep up with organic matter supply. These pools accumulate to relatively high concentrations as reflected in the high concentrations of specific polysaccharides found throughout the water column. Recalcitrance is not an inherent property of a particular organic pool, but is determined by the chemical, biological, environmental, and ecosystem properties of the system. That is, recalcitrance depends on the context, which can change as environmental and ecological properties

change over time and space. This realization of recalcitrance has been detected in experiments that show enhanced degradation or preservation of heretofore recalcitrant or labile DOM when it is exposed to different communities of microbes (as when surface and deep water mix) (10, 11), or when a community of consumers is exposed to new pools of DOM (12).

The definition of functional recalcitrance, and the explicit description of the factors that underpin it, are two of the most important results of Zakem et al.'s model. In the past, recalcitrance has been defined by the experimental or observational window that bracketed a set of measurements. A laboratory experiment designed to monitor organic matter degradation over a 2-wk period might define recalcitrant organic matter as any material not consumed by the end of the experiment. In contrast, marine chemists who measure DOM profiles in the ocean might define recalcitrant organic matter as material that survives the seasonal to millennial mixing cycles that characterize the upper and deep ocean, respectively. Zakem et al. free the definition of organic matter recalcitrance from these constraints and place it squarely within an ecological framework.

Coping with Climate Change

If carbon accumulation is an emergent property of organic matter cycling by complex microbial networks, what happens if the environment changes? Over the next century, the oceans will likely become warmer, more acidic, and more highly stratified (13). Delivery of nutrients to surface-dwelling communities of microbes may be curtailed, leading to lower overall productivity (14, 15). How might these changes impact carbon accumulation? Zakem et al.'s framing of recalcitrance suggests that, of the factors we can

measure, ocean warming will tend to move organic matter away from functional recalcitrance toward functional lability. Less carbon could be sequestered as DOM, creating a positive-feedback loop. One example of this phenomenon may be the 10-fold higher rate at which recalcitrant DOM reaches equilibrium values in the relatively warm (13 °C) deep Mediterranean Sea compared to the colder (2–3 °C) deep global ocean (16). However, there is much we do not understand about how microbial communities function, and how other climate-driven changes in microbial metabolism or community structure might counterbalance lower DOM values expected from a more slowly spinning carbon cycle. Finally, the model describes only one of several important contemporary reservoirs of carbon on the planet. Zakem et al.'s model was designed to capture some of the dynamics of organic matter cycling in the marine water column, but other important dynamics can be added as more information becomes available. For example, experiments suggest that photochemical transformations of DOM in the sunlit surface ocean might disrupt the coupling between organic matter production and consumption to enhance accumulation (17). Expressions capturing this process could be added to future formulations of the model. Zakem et al.'s framework can also be expanded to include descriptions of how the physicochemical properties of minerals, or changing redox conditions, might impact organic matter cycling in soils and sediments. Much exploration and investigation remain if we are to fully understand why carbon accumulates in the environment, but the roadmap provided by Zakem et al. promises to help keep marine and terrestrial biogeochemists, microbiologists, and ecosystem modelers all headed in the same direction.

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