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# Particulate Organic Carbon Deconstructed: Molecular and Chemical Composition of Particulate Organic Carbon in the Ocean

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The dynamics of the particulate organic carbon (POC) pool in the ocean are central to the marine carbon cycle. POC is the link between surface primary production, the deep ocean, and sediments. The rate at which POC is degraded in the dark ocean can impact atmospheric CO<sub>2</sub> concentration. Therefore, a central focus of marine organic geochemistry studies is to improve our understanding of POC distribution, composition, and cycling. The last few decades have seen improvements in analytical techniques that have greatly expanded what we can measure, both in terms of organic compound structural diversity and isotopic composition, and complementary molecular omics studies. Here we provide a brief overview of the autochthonous, allochthonous, and anthropogenic components comprising POC in the ocean. In addition, we highlight key needs for future research that will enable us to more effectively connect diverse data sources and link the identity and structural diversity of POC to its sources and transformation processes.

**Keywords:** marine particles, water column, phytoplankton, marine microbes, structural analysis, organic matter characterization, biomarkers

## INTRODUCTION

Particulate organic carbon (POC) is operationally defined as all combustible, non-carbonate carbon that can be collected on a filter. The oceanographic community has historically used a variety of filters and pore sizes, most commonly 0.7, 0.8, or 1.0 μm glass or quartz fiber filters. The biomass of living zooplankton is intentionally excluded from POC through the use of a pre-filter or specially designed sampling intakes that repel swimming organisms. Sub-micron particles, including most ocean prokaryotes, which are 0.2–0.8 μm in diameter, are often not captured but should be considered part of POC rather than dissolved organic carbon (DOC, recently reviewed

in Wagner et al., 2020), which is usually operationally defined as  $< 0.2 \mu\text{m}$ . Here, we consider POC to contain suspended and sinking particles  $\geq 0.2 \mu\text{m}$  in size, which therefore includes biomass from living microbial cells, detrital material including dead cells, fecal pellets, other aggregated material, and terrestrially-derived organic matter. Some studies further divide POC operationally based on its sinking rate (Riley et al., 2012) or size, with  $\geq 51 \mu\text{m}$  particles sometimes equated to the sinking fraction (e.g., Lam et al., 2011). Both DOC and POC play major roles in the carbon cycle, but POC is the major pathway by which OC produced by phytoplankton is exported -mainly by gravitational settling - from the surface to the deep ocean and eventually to sediments, and is thus a key component of the biological pump (Eppley and Peterson, 1979; Volk and Hoffert, 1985; Boyd and Trull, 2007; Cavan et al., 2015; Boyd et al., 2019; Le Moigne, 2019).

Accurately modeling the ocean carbon cycle requires both quantitative and qualitative understanding of POC production, composition, transformation, and cycling. Decades of measurements and modeling efforts have made significant progress toward this understanding, but persistent questions remain: How much POC is in the oceans? What determines POC spatial distribution and molecular composition? What is the residence time of POC? What regulates exchange between POC and DOC? What processes control the delivery of POC from surface waters to the mesopelagic? What controls degradation and preservation of POC delivered to marine sediments (Arnosti et al., 2019, this issue)?

Many marine organic geochemical investigations attempt to answer these questions from the bottom up, through characterization and quantification of the molecules that make up POC. Notably, because POC encompasses most living cells in the ocean, a considerable proportion of POC (particularly “fresh” POC collected in the upper ocean) is identifiable at the biomolecular level. This contrasts with DOC and sedimentary organic matter, which are predominantly non-cellular and molecularly uncharacterizable (Hedges et al., 2000; Kujawinski, 2011; Hansell, 2013), and implies that molecular-level understanding of POC can provide both qualitative and quantitative information. Major ocean surveys in the 1980s (VERTEX) and 1990s (JGOFS) demonstrated that the biochemical composition of POC was more dynamic and informative than expected from analysis of bulk POC data alone (Wakeham et al., 1984, 1997, 2000). Since then, improvements in analytical techniques have resulted in increasingly detailed studies of POC components in efforts to unmask what Hedges et al. (2000) called biogeochemical “trump cards” hidden by a lack of detailed structural knowledge. Regardless, structural understanding of POC has yet to be translated into parameterizations for carbon cycle models; global biogeochemical ocean models vary widely in their formulation of POC composition and reactivity (e.g., Bendtsen et al., 2015; Weber et al., 2016).

Importantly, there are various scientific motivations for studying POC that determine which organic compounds are characterized in specific studies. For example, biological oceanography or microbial ecology studies examining living

components or biological responses are more likely to target labile compounds and small size classes of POC. Chemical oceanography or carbon cycle studies, on the other hand, often consider POC as a bulk, non-living material sinking through the water column, and are therefore more likely to target compounds that may indicate bulk POC sources and lability, and to sample sinking particles. Paleooceanography or “modern analog” approaches may be unconcerned about the bulk properties of POC and instead focus on specific recalcitrant compounds that can be preserved in sediments and serve as indicators of environmental conditions. Still other studies are focused on anthropogenic impacts, and therefore target anthropogenic compounds like plastics, often without contextualizing their quantity in relation to naturally occurring materials in POC. Though seemingly very different, these applications all fall within the framework of organic geochemistry of POC.

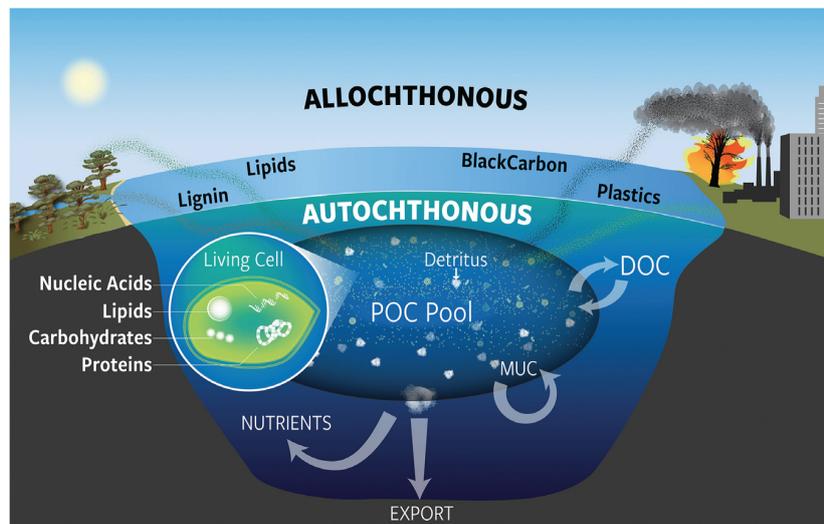
Overall, a molecular-level view of POC enables us to explore the biological, chemical, and metabolic processes that underlie carbon cycling in the ocean (**Figure 1**), in order to better understand OC reactivity, its relationship to food web composition and dynamics, how and why the composition of POC changes with depth in the water column, and the types and quantity of carbon exported to sediments. In this overview based on discussions from a recent workshop<sup>1</sup>, we briefly highlight the current understanding, recent developments, and knowledge gaps for the major components of POC. We discuss autochthonous sources of POC produced mostly by phytoplankton in surface waters as well as allochthonous material exported from terrestrial environments.

## AUTOCHTHONOUS COMPONENTS OF POC

### Lipids

All living cells and many viruses contain lipids, which we define here as molecules that are insoluble in water but extractable by non-polar solvents such as chloroform, dichloromethane, and hexane (McNaught and Wilkinson, 1997; Killips and Killips, 2005; Luo et al., 2019). Under this definition, lipids comprise hundreds of thousands of distinct molecules including photosynthetic pigments, hydrocarbons, and glycerol esters/ethers. Functions range from the foundation of cell membrane structure to energy storage, electron transport, signaling, reactive oxygen species scavenging, and light harvesting. Lipids comprise ~20% of OC in living cells but are usually only a small percentage of sedimentary OC (Wakeham et al., 1997; Wang and Druffel, 2001), and may therefore contribute to the formation of recalcitrant molecularly uncharacterized organic matter (MUC, section “The Molecularly Uncharacterized Component (MUC) of POC”; Hwang and Druffel, 2003). Recent analytical advancements allow us to take advantage of lipid structural diversity to connect organismal ecology and physiology with POC cycling, through both targeted

<sup>1</sup>“Future Directions in Marine Organic Biogeochemistry” held at the Hanse Institute for Advanced Study, Delmenhorst, Germany; April 27–30, 2019.



**FIGURE 1** | Conceptual overview of marine particulate organic carbon (POC) in the ocean. POC includes components of living cells as well as dead material (detritus), and originates from both allochthonous and autochthonous sources. The POC pool can also exchange material with the dissolved OC (DOC) pool through aggregation and disaggregation of particles. This process and others may be involved in the formation of the molecularly uncharacterized component (MUC), which may incorporate both autochthonous and allochthonous OC.

studies of specific lipid biomarkers and untargeted surveys of the entire POC lipidome (Kharbush et al., 2016; Becker et al., 2018; Sollai et al., 2019).

Lipids and pigments are commonly employed as biomarkers because many of them are synthesized by specific organisms, allowing their sources to be traced within POC pools. Recalcitrant lipid biomarkers have been heavily pursued within POC as indicators that can be exported to sediments and therefore preserve a geologic snapshot of water column metabolisms. For example, pigments like chlorophylls, carotenoids, and their degradation products are used to track phytoplankton-derived POC through the water column (Repeta and Gagosian, 1984; Llewellyn and Mantoura, 1996). Sterol lipid biomarkers exist for a range of planktonic organisms (Wakeham and Beier, 1991; Volkman, 2016). Ladderane lipids are specific to anaerobic ammonia-oxidizing bacteria and thus identify the presence of this metabolism (Sinninghe Damsté et al., 2002). Fatty acids are the non-polar core components of glycerol-based membrane lipids in bacteria and eukaryotes and have long been characterized in POC, and isoprenoid biphytane lipids compose the non-polar core of archaeal membranes. Core lipids are relatively recalcitrant, and some are structurally distinct enough to be used as biomarkers, especially when combined with compound-specific isotope analysis (CSIA, Ingalls et al., 2006; Pependorf et al., 2011; Close et al., 2014). Preserved core lipids in sediments can also be proxies for past environmental conditions (Prah and Wakeham, 1987; Schouten et al., 2002; Belt et al., 2007), but interpreting these proxies requires thoroughly understanding lipid production, transformation, and diagenesis processes (e.g., Hurley et al., 2016; Ding et al., 2019).

Studying the living components of POC often involves sampling microbial size classes ( $>0.2 \mu\text{m}$ ) and targeting more specific, labile structures. For instance, analyzing

glycerolipids with their polar headgroups still intact (i.e., intact polar lipids, IPLs) using high-resolution mass spectrometry added a new dimension to the development of lipidomic “fingerprints” for specific microbes and their metabolic status. The microbial lipidome can reflect adjustments made in response to changes in external variables like temperature, pH, or nutrient concentrations. Under low phosphorus (P) conditions, sulfur or nitrogen-containing lipids can be used in place of phospholipids (Van Mooy et al., 2009), making these non-P-containing IPLs useful for studying carbon cycling under P-limitation (Kharbush et al., 2016; Schubotz et al., 2018). The molecular distribution of glycerol-dialkyl(dibiphytane)-glycerol tetraethers (GDGTs) produced by pelagic archaea also appear to reflect environmental factors, including temperature (Elling et al., 2015; Zhou et al., 2020). It is often assumed that IPLs degrade rapidly upon cell death and that they can be used to study *in situ* activity of the living microbial component separately from non-living detrital POC. This assumption, however, rests on limited experimental evidence (White et al., 1979; Harvey et al., 1986) and should be revisited (e.g., Logemann et al., 2011), as defining the fraction of living and detrital POC is of urgent importance for understanding POC export to the deep-sea and sediment.

Lipid biomarkers are especially useful in investigating oceanographic processes that impact POC and the biological pump; for example, as indicators for the degradation state of POC, or which microbial groups are contributing to POC production, degradation, or export. The development and increased access to high-resolution mass spectrometry has resulted in the identification of many more biomarker structures, providing increased statistical power in lipidomics studies (e.g., Becker et al., 2018). An additional frontier is devising approaches to rigorously link lipidomics and other types of data. For example, lipid and genetic biomarkers were recently combined

with satellite data to show that viral infection of coccolithophore blooms enhances vertical flux and export of POC (Laber et al., 2018). Becker et al. (2018) discovered that daily oscillations in triacylglycerol concentrations accounted for about 6% of primary production, and used metatranscriptomics to implicate specific lineages of phytoplankton as sources of these lipids. These examples show that although lipids make up a minor component of total biomass and POC, their source-specificity can be capitalized upon to elucidate novel POC cycling and export pathways, particularly when lipid data are combined with other omics data.

## Amino Acids and Proteins

Hydrolyzable amino acids (AAs) are the most abundant identifiable component of marine POC (Wakeham et al., 1997) and have been studied for decades. AA sources in POC include living autotrophic and heterotrophic cells, as well as detritus, and the relative contribution of each of these varies with depth (Kawasaki et al., 2011). While the same protein-forming L-amino acids are found in all living things, heterotrophic organisms both remineralize AAs and alter the relative concentration of individual AAs during export to depth (Van Mooy et al., 2002; Engel et al., 2017). These compositional changes have been developed into “degradation indices” (e.g., Dauwe et al., 1999) that are used as indicators of OC freshness. Similarly, the enantiomeric (D/L) AA composition of POC is used to estimate the heterotrophic bacterial contribution to POC, as certain D-AA derive exclusively from bacterial cell walls. Using this method, the total contribution from living and detrital bacterial cells in open-ocean surface waters was estimated to be between 15 and 25% of suspended POC (Kaiser and Benner, 2008; Kawasaki et al., 2011; Tremblay et al., 2015).

The stable isotope ratios of C and N in different AAs form patterns related to the biosynthetic source and/or history of passage through heterotrophic metabolisms. Compound specific isotope analysis of AAs (CSIA-AA) thus is beginning to provide unique insights into the cycling of POC and sedimentary AAs (Batista et al., 2014; Sabadel et al., 2019). Nitrogen CSIA-AA is frequently used to estimate trophic position (e.g., Chikaraishi et al., 2009), and alongside other AA degradation indices can trace heterotrophic bacterial activity (Calleja et al., 2013). Carbon CSIA-AA has been used to differentiate various phytoplankton, heterotrophic bacterial, and allochthonous terrigenous sources within POC and sediments (Hannides et al., 2013; Larsen et al., 2015; McMahan et al., 2015). However, our understanding of the mechanisms that influence isotope fractionation patterns of AA is still incomplete. Of particular interest is elucidating how various microbial processes affect amino acid isotope values. For instance, heterotrophic bacteria acquire AAs in several ways, including *de novo* synthesis, extracellular uptake, or “re-synthesizing” them from other AAs (Ohkouchi et al., 2017). Each may have different isotope fractionation patterns, and unless these are robustly known it could complicate interpretation of CSIA-AA patterns.

POC also contains identifiable proteins, as components of living cells or preserved in detrital material (Dong et al., 2010; Moore et al., 2012). Marine metaproteomics is an

emerging technique that links genetic potential with metabolic function, including in particle-associated microbial communities (Bridoux et al., 2015), although challenges remain for data analysis and interpretation (Saito et al., 2019). Although not yet widely applied in marine systems, protein stable isotope probing approaches could further pinpoint *in situ* metabolic activity, yielding simultaneous determination of both phylogeny and metabolic function of specific organisms. This could be useful in determining the role of heterotrophic microbes in degradation and cycling of phytoplankton-derived POC, or in the formation of MUC.

## Carbohydrates

Carbohydrates are important structural components and energy storage compounds in photosynthetic organisms, constituting ~21–50% of phytoplankton biomass (Biersmith and Benner, 1998), >50% of macroalgal biomass (Mabeau and Kloareg, 1987), and 8–10% of suspended POC and 3–18% of sinking POC (Panagiotopoulos and Sempéré, 2005). A significant fraction of carbohydrates biosynthesized by primary producers is thus transformed and remineralized, but some is preserved as detrital components of OC (Wakeham et al., 1997). What production and transformation processes govern carbohydrate dynamics? What factors distinguish carbohydrates that fuel the food web from carbohydrates that are part of the detrital POM pool? These simple questions have complex answers (Arnosti et al., In press), starting with consideration of carbohydrate structures.

Carbohydrates are structurally highly diverse: individual sugars are monosaccharides, mostly either hexoses or pentoses. Monosaccharides are polymerized into disaccharides (two units), oligosaccharides (~10 units), and polysaccharides (>10 units). Monosaccharides are linked via hydroxyl groups in a vast diversity of linkage conformations; in theory, three different hexoses could lead to 128 different disaccharides (Laine, 1994). Oligo- and polysaccharides are often branched or contain sulfate, methyl, or amino groups, adding further structural complexity and frequently requiring “matching” enzymes to remove the sulfate, methyl, or amino groups prior to degradation of the polysaccharide backbone (e.g., Reisky et al., 2019). The structural diversity of carbohydrates thus could be used to link detrital components back to their sources, but only recently has progress been made in analytical techniques to begin to characterize these structures with sufficient resolution.

Carbohydrates are frequently measured using colorimetric techniques, providing bulk quantitative measurements but little structural information. Analysis of carbohydrate monomers that break carbohydrate polymers into monomers is more informative, but, like a collection of bricks without the blueprint of the building, leaves us wondering about the original structure. In addition, polysaccharide hydrolysis can destroy some component monosaccharides and fail to hydrolyze others. A paradox remains: the reactivity of carbohydrates ranges from very rapid, as for glucose or energy storage polysaccharides like laminarin, to very slow, as evidenced by the presence of carbohydrates in turbidites over 140,000 years old (Cowie et al., 1995). Carbohydrates constitute a substantial fraction of POC, but without the techniques to determine

specific structures, we have few means to read the messages they could convey. Fortunately, emerging analytical approaches may provide additional structural information: for example, improved chromatographic separations allow compound-specific isotope analysis of individual carbohydrates (Nouara et al., 2019), and specific polysaccharide-hydrolyzing enzymes enable quantification of laminarin in POC (Becker et al., 2017, 2020). Use of carbohydrate microarrays provides new insights into the presence and structure of specific complex carbohydrates in marine samples (Salmeán et al., 2018; Koch et al., 2019). Such techniques can enable us to decipher the specific structures – and therefore the origins, transformations, and relative reactivity – of more of the substantial carbohydrate-containing fraction of POC.

## Nucleic Acids

Nucleic acids are the ultimate biomarkers for the living or recently living components of POC, as they can reveal the taxonomic identities and metabolic potential of both photosynthetic producers of POC and heterotrophic organisms that transform POC. Free-living microbial communities are captured as small particles and particle-attached communities are associated with larger suspended and sinking particles (DeLong et al., 1993); investigating these communities can provide critical insight into POC production, export, and attenuation processes. RNA and DNA can distinguish between living, active cells and dead or dormant material, respectively, and enable identification of organisms that are difficult to culture or observe microscopically. Studies can focus on specific genes or use untargeted omics approaches. Commonly applied phylogenetic markers are the 16S (prokaryotic) and 18S (eukaryotic) rRNA genes, used to examine the phylogenetic composition of POC-associated communities and how they change with depth, environmental conditions, and over time (DeLong et al., 2006; Duret et al., 2019; Thiele et al., 2019; Preston et al., 2020).

16S/18S rRNA and other single functional gene approaches reveal “who” is there, but not much insight into “what” they are doing or “how.” Metagenomics/transcriptomics can provide focused insight into the metabolic capabilities of the whole community, and also of distinct community members using metagenomics-assembled genomes (Krüger et al., 2019). Major progress has been made through concerted study of spring phytoplankton blooms (Teeling et al., 2012, 2016) as well as global ocean surveys of microbial communities (e.g., Tara Oceans, Bork et al., 2015), and patterns pertaining to POC cycling are beginning to emerge (Guidi et al., 2016). Future advances depend on continuing these international sampling efforts to incorporate biological and chemical measurements across multiple temporal and spatial scales (e.g., Biogeosciences)<sup>2</sup>.

Though challenging, integrating molecular omics approaches with organic geochemistry is important to link the chemical composition of POC with biological processes, which are likely very important in regulating exchange between POC and DOC pools, and in determining the amount of POC ultimately delivered to marine sediments vs. remineralized vs. sequestered as refractory DOC (the “microbial carbon pump,” Jiao et al., 2010;

Legendre et al., 2015). However, so far we lack sufficient data on both biological as well as chemical composition of different types of particles across varying temporal and spatial scales. To address this knowledge gap some recent studies have begun to examine the relationship of particle size/type with microbial community composition and metabolism using next-generation omics techniques. For example, metagenomics and transcriptomics were recently used to infer the metabolic activities of prokaryotic and eukaryotic communities on sinking particles in the deep sea, which indicated considerable mid-water trophic processing of sinking POC by deep water protists and animals (Boeuf et al., 2019). Additionally, distinct prokaryotic assemblages were associated with suspended vs. sinking particles (Duret et al., 2019), and between different particle size classes (Mestre et al., 2017, 2018). This may suggest that particle compositions foster different metabolisms or modes of colonization, but remains hypothetical without concurrent chemical data.

## ALLOCHTHONOUS COMPONENTS OF POC

### Lignin and Terrestrial Plant Biomarkers

Vascular-plant derived molecules are used as quantitative tracers of terrestrially derived OC. Long-chain *n*-alkanes and fatty acids are synthesized by vascular plants as a component of leaf waxes, which are most abundant in coastal areas, but can be transported into the ocean with atmospheric dust or through riverine inputs. Lignin, a group of phenolic polymers, is probably the most well-studied terrestrial biomarker, as it is only produced by vascular plants and comprises one third of their biomass on average. Lignin is relatively stable in marine environments and has been used to quantify the amount of POC and DOC derived from plants and to determine plant tissue type and degradation state (Gordon and Goñi, 2004; Hernes and Benner, 2006). In the open ocean lignin is usually a minor component of POC, possibly because it is photo-oxidized, microbially degraded, or transformed into refractory molecules such as chromophoric DOC (CDOM, e.g., McDonald et al., 2019). However, higher concentrations of lignin and lignin phenols have been observed in POM in deep water masses, suggesting that terrestrial OM may be a quantitatively important component of POM in the bathypelagic (Hernes and Benner, 2002, 2006). Lignin-derived molecules are also important for tracing and quantifying terrestrial carbon import and export in coastal ecosystems, especially “blue carbon” ecosystems like salt marshes, mangrove forests and seagrass meadows. So far it has been difficult to quantify how much different sources of terrestrial carbon contribute to marine POC and DOC pools, and how much is sequestered in estuaries and coastal sediments (reviewed in Cragg et al., 2020). Recent studies are making progress in separating distinct terrestrial contributions to POC by combining <sup>13</sup>C and radiocarbon CSIA of lignin and other biomarkers (e.g., Tao et al., 2015), and in identifying biological degradation pathways (Woo and Hazen, 2018).

<sup>2</sup>www.biogeosciences.org

## Black Carbon

Black carbon (BC) is produced from incomplete combustion during wildfires and burning fossil fuels, and is found in both dissolved (DBC) and particulate (PBC) pools in the ocean (see Wagner et al., 2018 for detailed review of DBC). Marine PBC is primarily attributed to the absorption of DBC to POC. It spans a range of forms and reactivities, from slightly charred plant material to highly refractory, graphitized soot (the “combustion continuum,” Hedges et al., 2000). PBC is enriched in carbon relative to its biological sources and is difficult to characterize structurally because it is dominated by polyaromatic structures, is insoluble, and resists chemical degradations. This is likely why PBC is refractory and decomposes slowly; radiocarbon data show that marine PBC can be tens of thousands of years old (Coppola et al., 2018). PBC represents a significant part of global carbon budgets, and in some locations comprises up to 20% of total POC and up to 50% of the MUC pool in POC (e.g., Gulf of Maine, Flores-Cervantes et al., 2009).

Because of its recalcitrance, PBC may contribute significantly to OC sequestration in marine sediments, however, this quantity is difficult to estimate because PBC reactivity and loss processes are poorly known. Recent work suggests that DBC in the open ocean may not originate from riverine transport, but from another, unidentified source, as its  $\delta^{13}\text{C}$  values differ from riverine DBC (Wagner et al., 2019), and there are low concentrations of other terrigenous compounds in the open ocean (Hedges et al., 1997). Further isotopic studies could constrain potential sources (e.g., aerosols, autochthonous OC, hydrothermal vents) and reveal photo-oxidative or other degradative alteration processes.

## Microplastics

Plastics are a recent but now widespread anthropogenic addition to marine POC (Law, 2017). Plastic particles between 1  $\mu\text{m}$  and 5 mm in size are termed microplastics (MPs). MPs > 100  $\mu\text{m}$  are the most commonly studied; however, the number of plastic particles increases exponentially with decreasing particle size. Because most POC is also < 100  $\mu\text{m}$  in size, the contribution of MP to total POC is poorly known.

Physical forms of MPs include pellets, fragments, fibers, and foils, representing either their originally manufactured size range or alteration during physical and photochemical processes that fragment larger into smaller pieces. Depending on polymer density, MPs may float, sink, or be suspended at intermediate depths. Over time the physical and chemical properties of MPs can also be altered by weathering, embrittlement, fragmentation, and microbial colonization (Bryant et al., 2016).

MPs have been found across all oceans, from the surface to deep sea trenches (Peng et al., 2020). In sediments MPs are accumulating at rates that may leave a stratigraphic signal of the Anthropocene in the geological record (Zalasiewicz et al., 2016). However, the abundance of MPs throughout the marine environment is heterogeneous and inadequately quantified across varying spatial scales, and the processes that distribute MPs among surface, water column, and sediments are poorly understood. Many plastics also contain chemical additives, and their effects on marine species are not well studied.

These knowledge gaps will need to be addressed before we can assess the effects of MPs on marine ecosystems, but new research suggests that MPs could affect the biological pump. For example, laboratory experiments showed that MPs could be ingested by zooplankton, changing the density and sinking rates of their fecal pellets (Cole et al., 2016). In addition, incorporation of MPs can alter particle structure and density, and affect sinking and remineralization rates or influence POC aggregation/disaggregation (Chen et al., 2018; Porter et al., 2018).

## THE MOLECULARLY UNCHARACTERIZED COMPONENT (MUC) OF POC

A large fraction of POC is considered “uncharacterizable” because it cannot be separated and identified using traditional chromatography-based molecular analyses. This appropriately abbreviated “MUC” increases in concentration relative to characterizable POC components with increasing depth in the water column, even as the overall flux of POC decreases (Wakeham et al., 1997, 2000; Hedges et al., 2000). This observation suggests that MUC is either produced from transformation of characterizable surface-derived material during export (possibly lipids, Hwang and Druffel, 2003) or from incorporation of DOC deeper in the water column, or, alternatively, that our analytical methods do not adequately identify biomolecules whose presence is obscured in some manner (Hedges et al., 2001). Despite the analytical advancements of the last two decades, the formation and sources of MUC are still poorly understood; hypothesized mechanisms include degradative formation of geo- or bio-macromolecules, incorporation of detrital material and/or black carbon, and interactions with inorganic mineral material. Other analytical methods applied to characterize bulk chemical features of MUC include advanced solid-state NMR and infrared spectroscopy techniques (e.g., Liu et al., 2009; Tremblay et al., 2011). In addition, bulk isotope ratios of POC are one of the few measurements that capture the entire POC pool, including MUC. Some studies have found spatial variations in bulk  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  values of POC that suggest a substantial contribution to POC from  $^{14}\text{C}$ -depleted material not immediately derived from surface primary production, possibly from resuspended sediment, black carbon, or incorporation of “old” water column DOC (Roland et al., 2008; Hwang et al., 2010).

Identifying MUC sources and cycling is an area that merits further attention, but may be better addressed in the future through application of high-resolution or ultra-high-resolution mass spectrometry, as well as high-resolution solid-state NMR (Mao et al., 2011), which have the potential to expand the analytical window to simultaneously examine the molecular diversity of important compound classes (e.g., lipids), and also to identify novel structures or functional groups. Within DOC, new analytical tools and workflows are enabling structural information to be assigned for a growing number of molecular features (e.g., Petras et al., 2017), and metabolomics approaches also are beginning to be applied to POC (Johnson et al., 2020).

## CONCLUDING REMARKS

The development of new and improved analytical techniques now enables analysis of marine POC in greater molecular detail than ever before, with the potential to greatly expand our current catalog of organic biomarkers and other organic proxies and gain insight into the big questions about POC. However, studies of POC cycling in the ocean are fundamentally challenged by a long-standing limitation of established organic geochemical approaches: the most information-rich compounds or proxies tend to compose only tiny fractions of the bulk POC pool. In other words, using biomarkers to infer sources or cycling of more significant portions of POC necessarily involves making many assumptions about the consistencies of the relative initial ratios of biomarker to POC, and their relative reactivity. These assumptions become increasingly tenuous as POC is cycled and distanced from its source. Overcoming this tension between POC chemotaxonomy and biogeochemistry will mark a new era in the use of biomarkers to study POC.

The VERTEX (Martin et al., 1987) and JGOFS (Bowles and Livingston, 1997) ocean surveys were important first steps in understanding the nature and variability of POC composition but predated oceanographic omics data. On the other hand, the Tara Oceans expedition (Bork et al., 2015) successfully assembled a global metagenome of upper ocean biology but with the exception of pigments did not analyze molecular composition. In order to mechanistically tie together organic compositional information with the fate of the bulk POC pool we need more studies that make simultaneous omics, geochemical, and molecular measurements. Still in the planning stage, Biogeoscapes<sup>2</sup> is one new global effort that proposes to do this across multiple temporal and spatial scales, with the ultimate goal of understanding how metabolic feedbacks and interactions underpin biogeochemistry and structure ocean ecosystems. A multi-dimensional global dataset of POC, analyzed using improved analytical methods and integrated with omics, physiological, and nutrient data, would be invaluable for addressing many of the still-unanswered questions about POC,

including how to integrate POC composition into new modeling platforms or even machine learning approaches.

In summary, several areas are promising frontiers for the study of POC: (1) Leveraging the power of structural diversity to identify sources and metabolic processes, (2) Effectively integrating omics and geochemical techniques, (3) Improving methods to characterize unidentified components of POC, (4) coupling isotopic ( $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$ ) and molecular investigations of POC and DOC. While future work aimed at these issues will undoubtedly require field surveys, we also emphasize that controlled laboratory and mesocosm experiments are essential to construct mechanistic interpretations of environmental observations and should not be neglected.

## AUTHOR CONTRIBUTIONS

JK, BV, HC, CA, and RS wrote the manuscript based on the discussions and notes taken at the workshop, with input from all co-authors. All authors contributed to the article and approved the submitted version.

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

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