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Sources and Cycling of Organic Matter in the Marine Water Column

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Abstract The organic carbon cycle operates on multiple time scales with a only small fraction of the global reservoir actively exchanged. For the marine system, the sources are principally recently synthesized material from autotrophic production which annually contribute 44–50 Pg/year of new organic carbon. This is supplemented by terrestrial carbon arriving from rivers, erosion and the atmosphere which contribute to the complex mixture present on oceanic waters. The focus of this review is to highlight the major sources or organic carbon and describe how the interaction of biological, chemical and physical processes provides an efficient mechanism for its eventual recycling.

Keywords Carbon reservoirs · Diagenesis · DOM · Global carbon cycle · Microbial loop · Particles · POC

1 Introduction

The cycling of organic carbon in the marine environment is a key process in the global carbon cycle. Marine systems are roughly equal to the terrestrial

system as a source of new organic carbon to the biosphere, contributing an estimated 44–50 Pg/year of new production [1]. Over 80% of this amount is in the open ocean [2]. Yet only a small fraction (< 1%) of this material escapes recycling in the water column or active sediments to be ultimately buried and preserved in the sedimentary record [3, 4]. The interaction of biological, chemical and physical processes in oceanic systems thus provides an efficient mechanism for the production of new organic carbon as well as its eventual recycling as part of the global carbon cycle.

The sources of organic matter in the oceans are myriad, and dependent upon the intensity of the autochthonous signal and the proximity and magnitude of inputs from rivers, coastal erosion, and the atmosphere (Fig. 1). Although organic carbon is ultimately a product of biological synthesis, its sources are often viewed as a dichotomy between terrestrial inputs of particles and dissolved fractions, and primary production by phytoplankton in the water column. Primary production by algae is the larger of these two sources to the marine system, but terrestrial material eroded from rivers has received heightened interest in recent years as a recorder of changing coastal systems and increased sea level. The balance between these two end members is highly variable in differing ocean regions, ranging from systems such as the Arctic which receive large freshwater and erosional inputs [5] to the pelagic

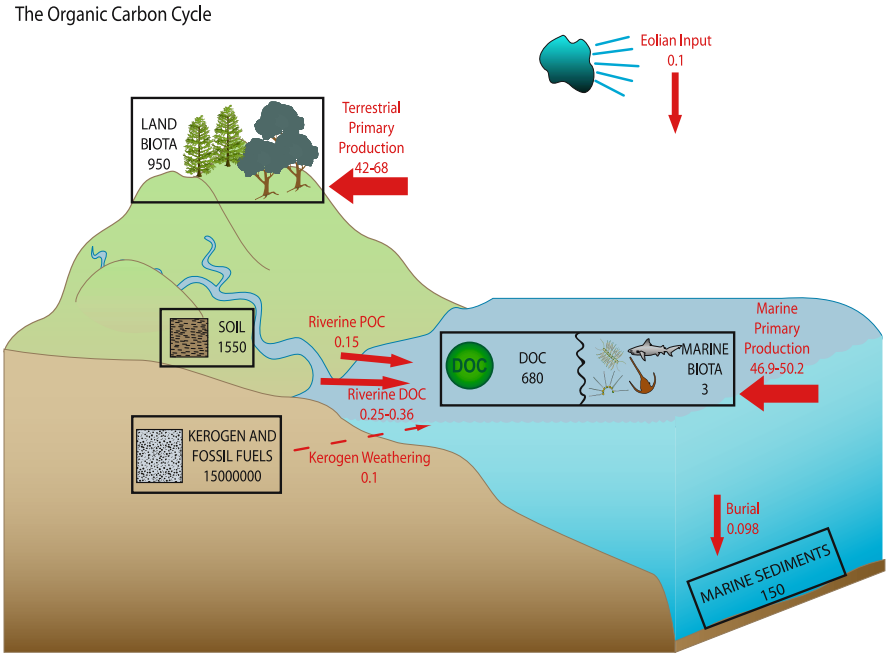

Fig. 1 The global organic carbon cycle. The major reservoirs (10^{15} G C) are shown as boxes with arrows depicting fluxes (10^{15} G C year^{-1}) of the cycle

Pacific, which is dominated by marine-derived material. Atmospheric input is a quantitatively minor fraction from the perspective of total organic input, but has indirect importance for transport of essential trace metals needed for phytoplankton growth [6, 7]. Atmospheric transport may also be of unique consequence, since the organic materials deposited range from soil-derived particles to highly labile dissolved forms of local and remote origins [8, 9].

The intention of this review is not to provide a comprehensive discussion of the processes that alter the organic matter signature, but instead focus on the major sources and how biological processing in the marine water column alters the amount and composition of organic matter in marine systems. Recent reviews of the literature which detail processes and organic character are emphasized. The active carbon cycle is a dynamic environment where single measures of organic carbon content integrate complex mixtures; mixtures that arise from the combined effects of multiple sources and varied reactivity.

2 Global Reservoirs of Organic Carbon

An examination of organic matter cycling in marine systems must begin with the realization that the vast majority of organic carbon does not actively participate in the global carbon cycle, but is retained as finely distributed material in sedimentary rocks (Table 1). Fossil fuel combustion has returned a measurable, albeit minor, fraction of this material back to the active carbon cycle in recent years [10, 11], largely as CO_2. Of the global total, only about 0.1% of the organic reservoir actually cycles through the active pool. Within this active cycle, soils which represent the largest pool, with decreasing amounts of organic matter contained in land biota, dissolved organic matter in seawater, and surficial marine sediments. The smallest fraction includes marine biota and particulate pools, encompassing highly variable

Table 1 Major reservoirs of organic carbon on Earth

Reservoir	Size (Pg C)	References
Kerogen and fossil fuels	15 000 000	Berner, 1989 (3) [115]
Soil	1550	Lal, 2003 [116]
Land biota	950	Olson et al., 1985 [117]
Ocean DOC	680	Hansell and Carlson, 1998 [118]
Marine surface sediments	150	Emerson and Hedges, 1988 [119]
Marine biota	3	Siegenthaler and Sarmiento, 1993 [120]

mixtures ranging from recently synthesized material as intact living cells to heavily degraded detrital substances with little resemblance to their original precursor. Although the particulate organic carbon (POC) reservoir is small, it undergoes rapid exchange and plays a central role in both amount and composition of organic mater which reaches underlying sediments. Over long time scales, the small fraction of organic matter remaining after extensive exposure to degradative processes is transferred to the geological reservoir.

A complication in describing each organic reservoir is that they comprise complex fractions having multiple origins and different turnover times. A recent example is black carbon, which represents a refractory and chemically complex product of incomplete combustion. It includes both ancient fossil fuels and modern biomass, including vegetation burns and forest fires. Operationally defined, the presence of black carbon in particles from the atmosphere, ice, rivers, soils and marine sediments suggests that this material is ubiquitous in the environment [12–14]. Black carbon accumulates in sediments and thus appears refractory, comprising 10–50% of sedimentary organic carbon [15] and having much older ages than other organic fractions [16]. Recent evidence suggests that black carbon also comprises a significant fraction of marine DOM in coastal zones [17]. The widespread presence of this organic component suggests that it represents an important fraction of the ocean's carbon cycle, yet its poorly defined structure and multiple origins complicates interpretation of its cycling and transfer from the active carbon cycle.

3
Defining the Compartments – The Size Continuum

The physical size (or more appropriately the density) of the organic fraction is an important control over where recycling occurs. Given the operational definitions inherent in the collection of samples prior to analysis of organic matter composition, the size distribution from dissolved molecules to large particles is an important influence over the fraction which is sampled and subsequently measured. The distribution of organic matter in the ocean is continuous yet variable, with the overall total abundance decreasing as size increases (Fig. 2). Although particles represent a quantitatively small fraction of the total organic carbon present in marine waters, they have historically attracted much attention, largely due to the ability of oceanographers and geochemists to collect them in traps or filter material from seawater in adequate amounts for chemical characterization.

Traditional collections have used filters having a variety of pore sizes or mesh supports, generally from 0.2 to 1.0 μm which operationally define the particulate fraction before analysis. Particles for organic analysis are often collected on glass fiber filters (e.g. GF/F nominally 0.7 μm pore size) which can be made organic-free through combustion. Depending on the definition

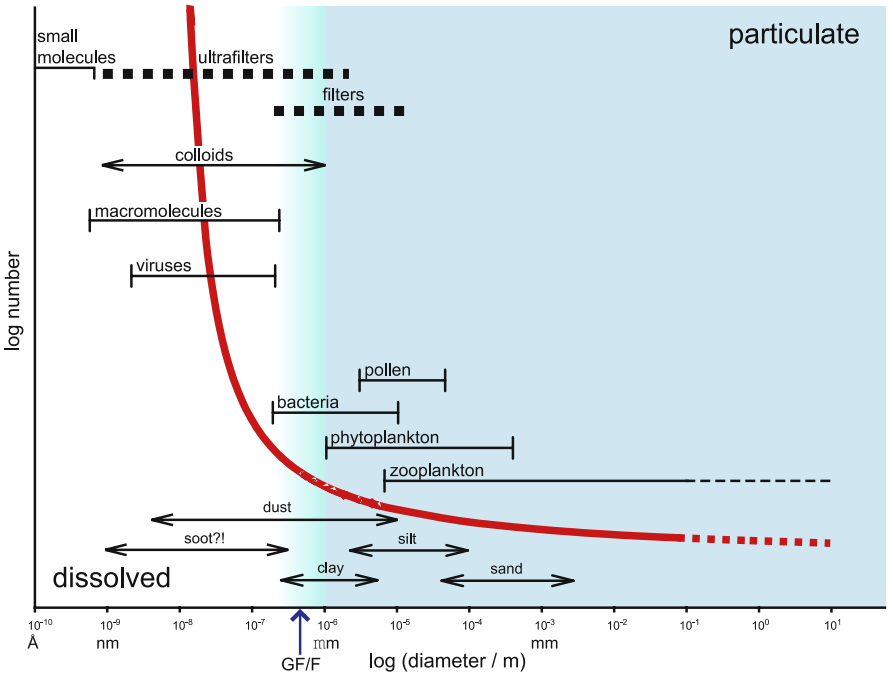

Fig. 2 The log abundance of particles versus log diameter in aquatic environments together with major components and collection ranges. Ranges among varying compartments are shown as well as arrows of major inorganic and soot components. The *vertical shading* shows the major cutoff for commonly used glass fiber filters (GF/F)

of what constitutes a particulate fraction [18], such filters might be considered either quantitative or highly selective (Fig. 2). Comparative measures of the organic composition of differing size fractions have shown important differences suggesting that the context of collection is required to fully interpret the organic signatures observed.

4 The Flux of Organic Carbon in the Ocean

The movement of organic carbon between compartments and its eventual recycling to inorganic phases are illustrated in Fig. 1 and summarized in Table 2. In the ocean the autotrophic production by phytoplankton represents the major source of organic carbon [19], supplemented by terrestrial material supplied by rivers. Most particulate forms of terrestrial matter, however, are rapidly deposited in coastal shelf and slope environments [20], with the general character of particles as seen in molecular biomarkers and isotopic values shifting to one where marine phytoplankton in surface waters

Table 2 Fluxes of organic carbon in the global carbon cycle

Type	Flux (Pg C year^{-1})	References
Terrestrial primary Production	42–68	Potter et al., 2003 [119]; Schimel et al., 2001 [120]
Marine primary Production	44–50	Behrenfeld and Falkowski, 1997 [121]; Antoine et al., 1996 [122]; Longhurst et al., 1995 [27]
Riverine DOC discharge	0.25–0.36	Hedges et al., 1997 [124]; Aitkenhead and McDowell, 2000 [125]
Riverine POC discharge	0.15	Hedges et al., 1997 [126]
Burial in marine Sediments	0.098	Schlunz and Schneider, 2000 [36]
Kerogen weathering	0.1	Berner, 1989 [3]
Eolian input	0.1	Romankevich, 1984 [127]

dominate the organic carbon signal. Although autotrophic production occurs in the lighted surface waters, sinking provides the major pathway for transport of particulate organic carbon (POC) from surface waters to the ocean depths and sediments. Estimates of the transfer of material and losses during sinking have often relied on data from particle (i.e. sediment) traps [21] which have shown that larger particle settling accounts for the majority of the flux, but also show an exponential decrease of surface productivity flux with depth [22, 23]. Such estimates come with the realization that the efficiency of such traps are affected by particle sinking rates, hydrodynamics at the opening, trap design and the nature of the particles themselves [24, 25]. All suggest, however, that in oxic waters most (> 80%) of the particulate organic material originating in surface waters is recycled at depths < 1000 m.

To understand the movement of POC, an extensive comparison of organic carbon flux estimates was conducted by Lampitt and Antia [26], who examined a total of 68 data years of trap deployments to provide a global picture of carbon flux to the deep (> 2000 m) ocean and its seasonal variability. Calculations included estimates of total annual primary production derived from long-term satellite observations at the same sites [27]. The annual range was large, with organic carbon flux varying by a factor of 375 when extreme values seen in high latitude environments are included (Table 3). Excluding high latitudes where episodic primary production is common and variable; however, a much narrower range was evident, with organic carbon flux varying by a factor of 11. The estimated range was similar to that estimated for primary production (factor of 5) for the same stations. In comparing the relationship between primary production and flux, they also found organic carbon reaching deep waters to comprise from 0.4 to 2.7% of annual primary production

Table 3 Particle flux and composition compiled from 68 data years of deep (> 1000 m) trap deployments in all major ocean basins by Lampitt and Anita (1997) [26]. Maximum and minimum flux in all ocean basin are shown. Columns include all except polar stations which show large variability. Rates in g m^{-2} $year^{-1}$

	All ocean basins collected			Sites excluding polar oceans		
	Max	Min	Median+SD	Max	Min	Median+SD
Dry weight	147.88	0.259	22.3 ± 22.0	66.26	7.77	22.89 ± 13.66
Organic carbon	5.24	0.014	1.00 ± 0.94	3.07	0.26	1.02 ± 0.74
C_{org} 2000	5.94	0.007	1.37 ± 1.27	4.24	0.38	1.50 ± 1.08
Inorganic carbon	3.64	0.001	1.40 ± 0.90	3.64	0.60	1.68 ± 0.83
Opaline silica	8.92	0.10	1.60 ± 2.02	8.92	0.37	1.91 ± 1.94

(Fig. 3). This suggests that for many ocean basins where primary production is not episodic (i.e. polar oceans) that there is a large scale balance in the fraction of new primary production which is exported from upper ocean waters over annual cycles despite known seasonal variability [28, 29]. Recent models of particulate flux have explored the complex interactions which occur during sedimentation [30, 31] and suggested that mesozooplankton are more important in decreasing particle fluxes than macrozooplankton, particularly in midwater zones where much POC is remineralized. In the context of organic matter cycling, it reinforces the long held belief that the vast majority of organic matter produced in oceanic surface waters as particles are recycled during descent, never to be incorporated into oceanic sediments.

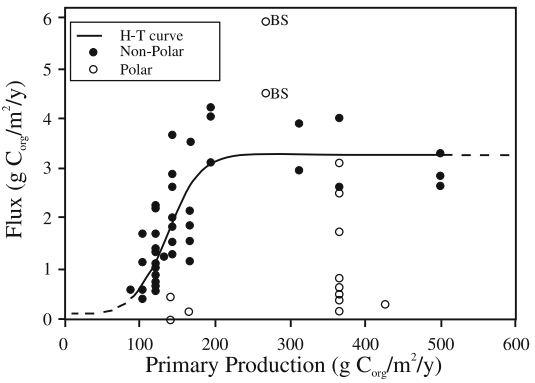

Fig. 3 Relationship between annual primary production and flux of organic carbon at 2000 m depth in the oceans. The line represents hyperbolic tangent fit with polar environments (*open circles*) excluded. Redrawn from Lampitt and Antia (1997) [26] with modifications. BS represents sites in the Bering Sea excluded from the line fit

Recent estimates and modeling have shown that at least part of the variability observed in the flux of organic carbon might also be due to the fraction of mineral ballast associated with sinking particles [32]. The presence of mineral matrices affects the time particles spent in the water column, with organic materials associated with denser minerals having more rapid transit to the ocean floor. In addition, mineral matrices have been suggested to provide direct physical protection of organic material through either adsorptive processes or perhaps as binding agents [33, 34], thus influencing the amount and composition of organic matter that survives descent and is incorporated into sediments.

Among the varied sources of organic carbon to marine systems, terrestrial organic matter is an important component, yet its fate in the ocean is not clear [35]. Much arrives through river transport, with estimates of the flux of organic carbon to the sea ranging from 0.25–0.36 Pg C year for dissolved OC and less for particles (Table 1). The range encompasses much variability, due in part to the lack in uniformity in the estimates themselves. Some of the issues which affect the accuracy of estimates have been discussed by Schlünz and Schneider (2000) [36] in their compilation of published estimates of terrestrial transport by rivers. They noted a lack of uniformity in approaches and assumptions, particularly for flux estimates where data may not include seasonal trends in discharge or measures of both particulate and dissolved components. This appears particularly true for Asian rivers, which account for 40% of the total annual sediment discharge but are poorly documented.

Despite these gaps, it is apparent that terrestrial organic matter represents a large source of reduced organic carbon to marine systems which principally arrives in dissolved form. Much of this terrestrial export by rivers appears to be derived from soils [37] and includes the highly degraded remnants of vascular plants which have been used to provide a detailed suite of molecular structures as tracers of their input (Ittekot, this volume). The primary drainage sources which account for terrestrial discharge are varied, but the majority has been estimated to be from forested catchments, with decreasing contributions from other forests, cultivated lands, wetlands, grasslands, tundra and deserts. Eolian input of terrestrial carbon to the ocean surface has been difficult to quantify, partly due to the highly variable and complex wind patterns. Estimates for total carbon range as high as 0.1 pg C year [38] and is particularly important for terrestrial input to open ocean areas [39, 40].

5 The Importance of DOM

Although the dissolved organic phases of carbon which pass through various filters (Fig. 2) have been long studied (see [41]), intense interest did not developed until the late 1980s. In several papers describing new approaches

using high temperature combustion as well as oceanographic surveys of surface and deep waters, Suzuki et al. [42] and Sugimura and Suzuki [43] challenged early observations, stating that previous wet chemical measures of DOC concentration in ocean waters were substantial underestimates. Although this work has subsequently been discounted [44, 45], the initial reports led to a revolution in interest to understand dissolved organic matter (DOM) in aquatic systems and a variety of new analytical approaches were developed to examine both their concentration and chemical character. The outpouring of research on the dynamics and cycling of DOM has led to a much better understanding of its composition and cycling and a greater appreciation of its important role in the global carbon cycle. A number of recent reviews have discussed the chemical composition and cycling of DOM [46, 47] and a comprehensive presentation of sources, character and cycling of marine DOM is now available, reflecting the rapid progress in the field [48]. Its total contribution to the organic carbon pool places it as an essential component of the global cycle (Fig. 1) and a crossroads for many components of organic carbon during recycling.

In the context of global carbon estimates, Del Giorgio and Duarte [49] have argued that present estimates of DOC may not reflect its important role. They noted that DOC also represents a substantial fraction of total primary production which is not captured in satellite estimates of chlorophyll or standard ^{14}C incorporation measures used to quantify particles. By including estimated values for oceanic algal respiration and DOC production together with measures of primary production as seen in particles, they calculated that estimates of gross primary production would be enhanced by up to 48%. Such a correction would elevate the values seen in Table 2 for primary production to 69.4 to 72.3×10^{15} g C year^{-1}. The inclusion of DOC dynamics has the potential to substantially increase the total amounts of new production and export in the open ocean.

Both the chemical character and general distribution of DOM show parallels with that seen for particles. DOM has consistently been found to show highest concentration in surface waters, and compositional analysis suggests that most is derived from biological production [50]. Direct sources are varied, but direct inputs from phytoplankton [51] and sloppy feeding by macrozooplankton are significant sources as well as organic material leached from soils [52]. As with particles, the organic composition of DOM includes a significant portion which cannot be characterized at the molecular level [53, 54]. Much of the DOM as defined by ultrafiltration is low molecular weight (< 1000 Da) [55, 56] and resistant to biological recycling.

The high abundance and refractory nature of this low molecular weight dissolved organic material in the ocean might seem at odds with observation that its major recycler are bacteria which rapidly take up low molecular weight compounds. Amon and Benner [57], proposed that low molecular weight does not equate with lability. They postulated that DOM exists in

a "size-reactivity continuum", suggesting that particulate organic material might follow a transition through dissolved materials, with bioreactivity decreasing in concert with molecular size along the path:

POM → High molecular weight DOM → Low molecular weight DOM

Each size fraction comprises a continuum of organic compositions and reactivities in multiple states of decay. This reactivity continuum would also help explain the relatively old age of deep-water DOM in several ocean basins, with an apparent age of 400–600 years [58], yet relatively young DOM is seen in coastal environments since this is where most appears to be produced [59, 60]. This might also explain recent observations that the fraction of DOM which cannot be easily characterized at the molecular level increases with decreasing molecular weight [61, 62]. In the context of organic matter cycling in the water column, the similarity in many of the processes that affect particles and dissolved fractions reinforces the need for integrated information and detailed composition on multiple organic matter pools to understand the pathways for cycling. A significant avenue for removal of DOM in surface waters is also photooxidation, with exposure leading to significant losses seen for chromophoric dissolved organic matter, and specific molecular markers for vascular plants such as lignins [63] and lipids of phytoplankton [64, 65].

6 Kinetics of Organic Matter Recycling

The majority of organic matter produced in surface waters by autotrophic organisms is not incorporated into surface sediments, but is recycled in the water column or at the sediment-water interface. The same is also true for terrestrial material carried in rivers or deposited across the water-atmosphere interface, although the efficiency of these recycling terms are more poorly constrained. The changes that these mixtures of organic materials undergo are both complex and selective, with the general observation of decreasing concentration with increasing water depth and increasing recalcitrance whether as particles or in dissolved phases. There are notable exceptions, including the rapid deposition of algal blooms to the sea floor [66, 67], or water column discontinuities which impede sedimentation (e.g. Black Sea), but for oxic water columns, the majority of labile compounds are degraded during decent. The fact that a variable, but ultimately very small, fraction of organic matter present in surface waters is ultimately incorporated in sediments illustrates the efficiency at which heterotrophic processes act on material prior to sediment incorporation.

Given the importance of phytoplankton as a dominant source of particles, there has been much effort to understand the liability and turnover

of algal material during water column decent and at the sediment interface. These studies range from unialgal cultures in static incubations to field programs following bloom dynamics. Early work on algal carbon dynamics [68] first suggested that algal carbon might be variable in its degradation. This suggested that while algal carbon measured as POC was often considered as a single compound class during recycling, observed rates of carbon loss represented a composite of rates among the various biochemical classes. Based upon changes in POC seen in algal carbon degradation experiments, Westrich and Berner [69] developed multi-first-order rate equations (the multi-G model) to describe the utilization of multiple pools of algal carbon. Organic carbon loss could be described by a series of exponential decreases in specific components, with a first order rate used to describe the overall decrease observed.

A number of studies have examined the fate of algae in the water column, yielding a range of turnover times of total organic carbon under oxic and anoxic conditions from 3.7 to 256 days ([70] and references therein). As these and other authors have noted, the wide range of reported degradation rates is a likely consequence of both the differing reactivity among specific biochemical pools in concert with differences in the duration of experiments and their environmental conditions. A study by Harvey et al. [71] reported results on the degradation sequence for major biochemical classes (protein, lipid, and carbohydrate) in two diverse marine phytoplankters (a diatom and cyanobacterium). The major biochemical fractions of organic carbon were found to degrade at significantly different rates in both algae, with kinetics following multiple first order kinetics. In these microbial dominated experiments, carbohydrates were most rapidly utilized followed by protein and then lipid (Table 4).

Parallel incubations with oxygen as the major variable showed that substantially lower rates occur when oxygen was absent, even though levels of microbial activity were equal or greater than under oxic conditions. Subsequent work by Nguyen and Harvey [72] observed that dinoflagellates showed similar kinetics of carbon turnover. Perhaps most important for understanding organic carbon cycling is the observation that degradation rates of major biochemical fractions differed by a maximum of 4-fold for all algae despite differences in size, cellular organization and chemical composition (Table 4). The reactivity of algal derived material under oscillating redox conditions [73] and estimated removal near the sediment water interface [74] have often shown rates intermediate between these purely oxic and anoxic laboratory conditions. Although such differences are important for tracing heterotrophic processes and organic matter utilization, it illustrates the rapidity at which most algal POC is removed before sediment incorporation.

Table 4 First order decay constants (k years^{-1}) and corresponding turnover time (τ days^{-1}) for algal cells and various biochemical components during water column degradation of phytoplankton by microbes. Additional rates for individual organic classes are included where available for comparison

Biochemical fraction	Oxic		Anoxic	
	k (year^{-1})	τ	k (year^{-1})	τ
Diatom[a]				
POC	13	28.5	2.9	125
Total lipid	8.3	43.7	2.7	135
Protein	21	17.1	15	24
Carbohydrate	34	10.8	7.2	50
Fatty acids				
Polyunsaturated	34	10.7	13.6	26.8
Monounsaturated	37.7	9.8	9.3	39.5
Saturated	25.7	14.1	8.2	44.4
Sterols	33.4	10.9	2.6	142
Phytol	15–31*	11–29*	3–3.4*	114–120*
Cyanobacteria[b]				
POC	15	23.8	2.5	146
Total lipid	8.2	44.3	2.3	160
Protein	22	16.6	6.2	58
Carbohydrate	34	10.7	4.1	88
Dinoflagellate				
POC	24	15	5.6	65
Protein	34	11	5.2	70
THAA-C	18	21	3.8	96

* Range of rates seen for diatom and cyanobacterium incubations. Algal rates based on Harvey et al., 1995 [93]; Nguyen and Harvey, 1997 [128]. See Canuel and Martens (1996) [129] sediments.

7 Organic Matter Composition During Decay

A difficulty in understanding the sources and processing of organic matter in the water column is its dynamic state, with multiple compartments in various stages of biosynthesis, metabolism and decomposition. Kinetic information obtained from controlled degradation experiments can be used to describe the compositional changes that autotrophic material undergoes during degradation. This approach has been used to illustrate the potential impact of

variable degradation rates of multi-component biomarker mixtures during diagenesis [74].

We can use measured rates for POC and several biochemical compartments to examine how water column degradation alters organic composition even when starting from well characterized material. Just as the overall rate of POC recycling is a composite of many degradative rates, each of these compartments in turn contain a large suite of individual molecules. This undoubtedly is a simplistic explanation of a much more complex process, but can serve to illustrate the compositional changes in POC over time which impacts interpretation.

To represent a typical phytoplankton we first approximate the distribution of major biochemical groups of a phytoplankton cell. Absolute amount are highly variable [75, 76], but a composite value among biochemical classes suggests a composition of 35% protein, 16% lipid and 40% carbohydrate. These values sum to 90% of the total organic matter observed. The final 10% represents material contained within the POC, but which cannot be classified into one of the three biochemical pools. This would include nucleic acids or perhaps mineral-bound material that is not extractable [77]. Using this composite as a "typical cell", we can apply measured removal rates to follow the changing composition of POC during early diagenesis as particulate material sinks through an oxic water column. For this exercise, the three major biochemical components are matched to their respective first order decay constants (Table 4), which vary only slightly among phytoplankton, but do differ between oxic and anoxic environments.

The calculated losses among the major biochemical classes and POC are shown in Fig. 4a. Following their prescribed first-order rate constants, all three classes decrease quickly over the 100 day time frame shown. POC which was quantified independently, follows a first order rate as well, with a loss of $> 94\%$ over the period. What is quickly evident is that while both overall POC and individual biochemical groups are lost as carbon is efficiently recycled, the major biochemical classes are lost more rapidly than the total POC. The unidentified material originally presents as a small component of carbon in algal cells rapidly accounts for the majority of organic matter remaining. As a result, the composition of particles evolves from living cellular material where most components can be assigned to one of three major biochemical groups to one which the bulk of organic material cannot be identified to biochemical class (Fig. 4a). Although the amount of total organic carbon remaining is small given the efficiency of mineralization, the organic composition is less clear than the cellular material from which it originated. These results parallel observations seen for many environments where much of the total organic pool is not amenable to characterization at the molecular level [78].

While these results illustrate that the overall character of organic matter can show rapid changes in composition during its recycling, such measures

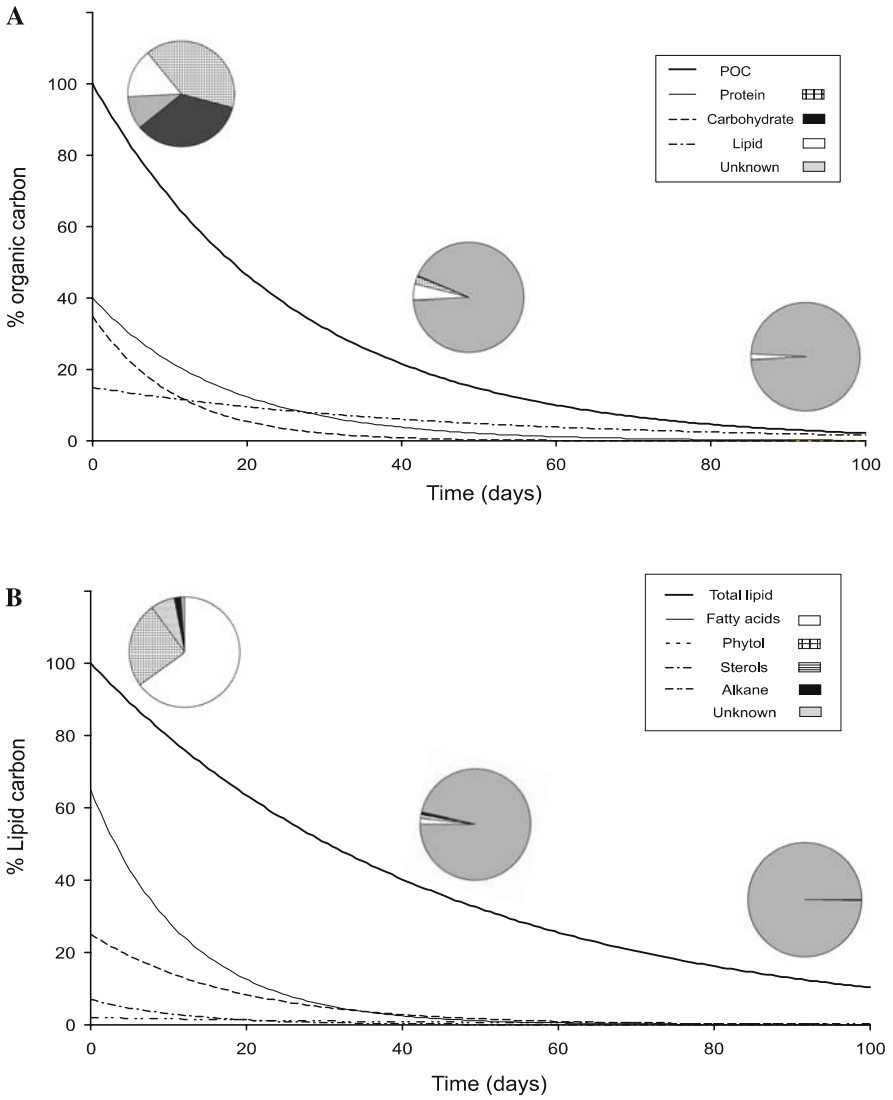

Fig. 4 The changes in amount and distribution of organic carbon and major biochemical components during degradation of "typical" algal material. *Panel A* shows changes in major biochemical components and POC over a 100 day decomposition sequence in oxic waters. *Panel B* shows the lipid fraction of the same algal material and changes in lipid composition over the same time frame. Although most organic matter is efficiently recycled, both major biochemical groups and specific fractions reveal an increasing fraction of unidentified composition over time

are not the norm. More often, either total POC or individual chemical classes are followed. Lipid biomarkers in particular have shown to be very valuable in a host of environments to detail both the sources and processing of organic materials [79], but represent a small fraction of the total organic pool.

We can use a similar scheme as above to compare the distribution of lipids during a decomposition sequence of a typical phytoplankton. Again, each compartment encompasses a suite of individual compounds, but the one might postulate that the more constrained structures would impart greater similarity in degradative rates. In this case, the total lipid pool used above (16% of POC) can be further defined by the major lipid classes. These include fatty acids as the dominant form (65% of lipid carbon) followed by phytol (25%) sterols (7%) and alkanes (2%). The remaining 1% is considered unidentified. Again, exponential first order rate constants obtained from controlled lab experiments can be employed to follow the changes in lipid distribution during the decomposition process. Although these rates may not reflect widespread field conditions, they are nevertheless reasonable approximations which more importantly allow comparative measures among different lipid fractions to be examined.

Tracing the changes in lipid composition during such a degradative sequence is shown in Fig. 4b. Similar to that for the case of broadly defined biochemical fractions, an increasing percentage of the residual organic matter is composed of compounds that elude standard methods for structural analysis. In this case over 83% of the total lipid is lost by 100 days. More importantly, by 50 days the total lipid content of POC has decreased by 60% with the fraction which is identified as lipids by traditional structural approaches constitutes only 4% of the total extractable lipid. The unidentified fraction, originally accounting for only 1% of the total, is now the majority of the extractable lipid observed.

Although such laboratory experiments have all the usual caveats concerning extrapolation to the real world, they do provide an explanation for the varied composition often seen in POC collections [80]. Under idealized conditions of largely synchronous growth and death, organic composition might be reflected by the decreasing content of particulate carbon presented by the differential losses among the various biochemical components. Yet in the environment, POC dominated by algal carbon shows varied composition, depending upon the balance between recently produced organic materials and those which have already been subject to the degradative process.

Such changes in major biochemical groups and lipid biomarker composition parallel that seen for sedimenting material, where the majority of organic matter cannot be identified at the molecular level (Wakeham and Canuel this volume, [81]). As mentioned previously for black carbon, the source in this material is often unclear. It has been suggested that a fraction of the original material may have evaded decomposition through selective preservation. Others have noted the increased presence of bacteria-specific markers in

detrital material [82] and argued that it represents the replacement of carbon derived through autotrophic processes with microbial remains [83]. Depending on location, this includes a variable amount of terrestrial carbon, altering the composition and further complicating measures of its original and turnover. For the utilization of various organic biomarkers commonly used as process markers, it demonstrates that organic composition can change rapidly during decomposition, and thus assignment of source information based on organic biomarker information must be judged in the context of their temporal state – a condition which can rarely be determined with accuracy.

8 Pathways for Preservation

The changing palette of organic composition during the degradative process has often complicated the determination of organic sources, with multiple hypotheses used to explain the loss of recognizable organic structures. Based on the distributions of materials found in deep waters and often in sediments, several hypotheses and their subsequent models have attempted to explain the major diagenetic pathway that leads to organic stabilization into the macromolecular matrices that remain beyond current analytical abilities to define their molecular structure. The now classic "depolymerization – recondensation" hypothesis considers macromolecular organic matter largely as a unique material, formed after the microbial breakdown of cellular components while the remaining residues recombine into new substances only distantly related to their biological precursors [84]. This explanation requires that naturally occurring macromolecules such as polysaccharide and proteins are enzymatically depolymerized to oligo- and monomers, with the remaining fraction left to condense or polymerize through chemical or photochemical initiated cross-linking.

It is important that the classic model does not exclude the occasional biomolecules being incorporated, but the preservation of organic molecules in their native form is generally thought to be an exception rather than a common occurrence. Recent observations have suggested that most material observed in sediments and heavily degraded organic materials show similar function group arrangements for carbon and nitrogen as seen in native materials [85] suggesting that abiotic formation is not a dominant process.

In contrast, the "selective preservation" hypothesis takes essentially the opposite view, predicting that macromolecular organic matter in sediments and particles is not a new product, but rather remnant biosynthetic material which has not been degraded due to its inherent resistance to enzymatic or chemical attack [86]. Selective preservation models have gained acceptance in recent years as more sophisticated analytical techniques have made

inroads into the linkages between individual components in preserved organic matter with their likely contemporary precursors. One of the better examples is the number of hydrolysis-resistant biomolecules (e.g. algaenans, suberans and cutans) which have been identified in recent years in both marine and terrestrial plants [87, 88] and in older sediments and soils. These results lend support to the idea that the winnowing of organic material during diagenesis is largely the continual loss of labile material. Recently the encapsulation of organic material within organic matrices themselves have also been suggested [89, 90] as an important mechanism as have hydrophobic interactions [91].

Hedges et al. [92] suggested that perhaps preservation does not have to be selective for the sequestration of organic matter to occur in particles (Fig. 5). Using solid-state NMR analysis of particles collected at multiple depths in sediment traps, they examined the changes in carbon linkages of particles with increasing water depth. Signal intensities of the five major carbon linkages (alkyl, amino, O-alkyl, C = C, and carboxyl) were then used to calculate the contribution of major biochemicals, allotting carbon among amino acids, lipids or carbohydrates. They then estimated the major changes occurring in biochemical composition during the most active phase of diagenesis when the majority of organic matter is recycled. Although carbohydrates showed a significant decrease, amino acids and lipids increased as a fraction of carbon in lower traps. Overall, they concluded that there were no dramatic changes in preservation potential, a point previously observed among major biochemical groups in phytoplankton in laboratory experiments [94].

An important modifier which undoubtedly impacts the preservation of organic matter as well as previously mention flux is chemisorptive attachment

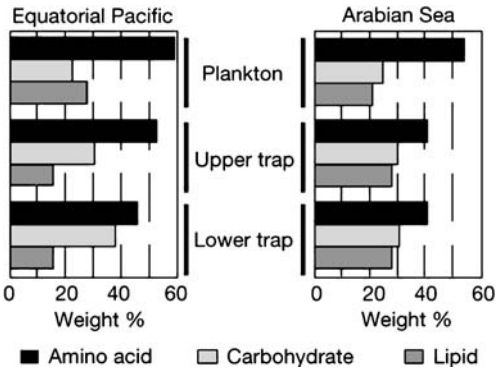

Fig. 5 Calculated weight percentages of biochemicals from sedimenting particles in the Equatorial Pacific and Arabian Sea seen by Hedges et al., (2001) [92]. Contributions of major biochemical were calculated from NMR intensities of particles collected at various depths. Although some changes were evident, overall composition showed little change with depth

to mineral surfaces. Although the emphasis on preservation has been on long term storage in sediments [94, 95], Keil et al. [96] have shown that mineral surface can be an important modifier of organic matter transport from rivers and deltas. Armstrong et al. [97] have suggest that sorption may also be an important process in the water column, with ballast minerals (including silicate and carbonate biominerals and dust) providing a critical mechanism for controlling organic matter transport. Multiple organic pools have been postulated; one tightly associated with the mineral itself and a second fraction which can be accessed and degraded in the water column. This partitioning is thought to account for the variety of degradation rates often seen in water column collections of sedimenting material as well as the variability mentioned previously on organic carbon flux estimates.

9
The Role of Microbes in Organic Matter Cycling

The important role of microbes as a key catalyst of organic matter cycling is firmly established. The concept that an unrecognized and largely unculturable group of organisms' plays a central role in the recycling of organic materials has been the subject of intense interest among microbial ecologists and biogeochemists for the last several decades [98–102]. The foundation for a central role for microbes in organic matter cycling arose from the seminal work of Pomoroy [102], who revised the paradigm of microbes as more than simple decomposers. In tandem was the observation that large phytoplankton (those typically caught in plankton nets) were not the major primary producers in the oceans, but rather smaller, autotrophic organisms less than 60 μm. This smaller size group accounted for the bulk of new organic carbon produced in euphotic waters. Furthermore, these smaller organisms than typical net plankton were also responsible for the bulk of respiration, and thus recycling of organic materials in aquatic systems was driven by microbes.

Perhaps most important for the geochemical community was that nonliving dissolved and particulate organic matter was now an important food source, and this organic material is primarily consumed by small heterotrophic microbes with diverse metabolism [101]. Although the classic idea of direct grazing on phytoplankton by herbivorous zooplankton as the major route for carbon recycling remained, the inclusion of microbes provides a mechanism for a significant fraction of both particulate and dissolved material to flow through microbial processes. Successive work solidified the concept of the "microbial loop" as an important pathway for reincorporation of dissolved organic matter into microbes as well as a path for transfer of material to higher trophic levels. The major components are shown in Fig. 6. Although this pathway is not highly efficient (with bacterial production accounting for only 10–50% of consumed carbon), it provides a mechanism

for efficient recycling. In recent years it has been expanded to include the "microbial food web" with many participants and feedbacks which control organic matter recycling. Bacteria remain major consumers of dissolved materials, but are in turn consumed by bacterivorous protists, lysed by viruses or perhaps die and contribute directly to the POM pool [103].

The microbial mediation of organic matter cycling has become an important theme for geochemists interested in better defining the routes for organic mater alteration and the suite of compounds present. Although direct grazing of phytoplankton by macro zooplankton shows substantial changes in organic character, including specific biomarkers [104, 105], it appears to be a less important source (a maximum of perhaps 25%) of carbon production in

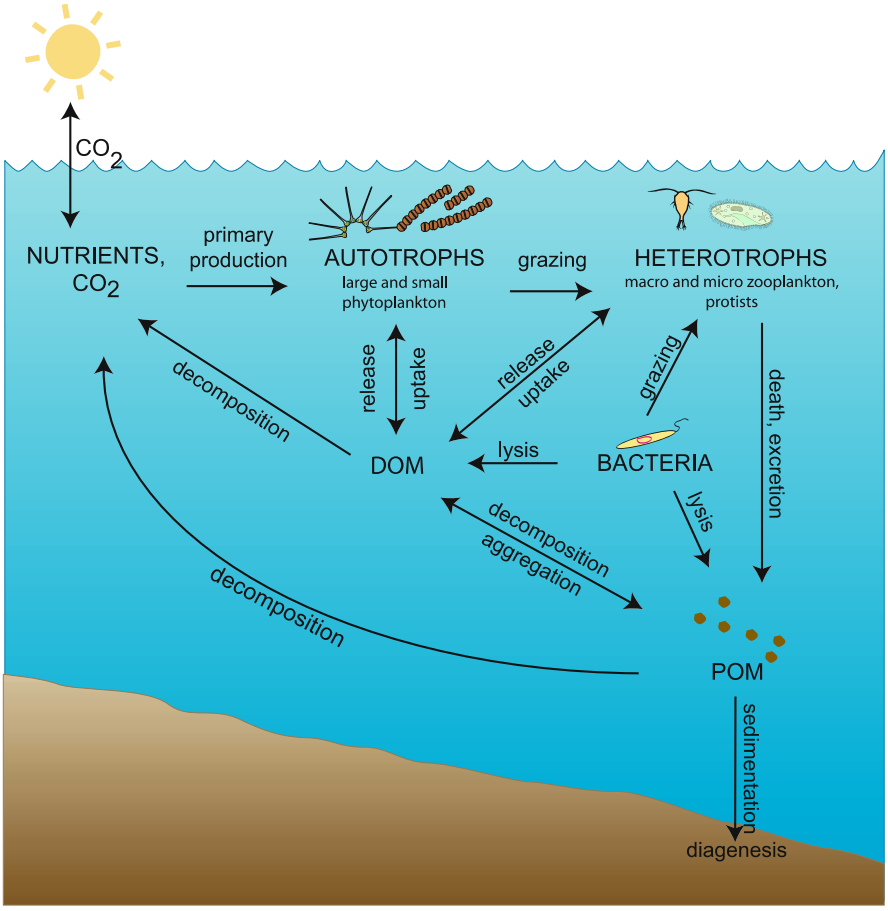

Fig. 6 Conceptual diagram of the microbial food web illustrating the major pathways for carbon recycling and transfer. The microbial food web includes both autotrophic and heterotrophic microbes, with dissolved organic matter playing a central role on the transfer of material and carbon recycling

Table 5 Number and biomass of prokaryotes in various habitats (after Whitman et al., 1998) [106]

Environment	No. of prokaryotic cells, X 10^{26}	Pentagrams of carbon as prokaryotes*
Continental shelves	1.0	0.02
Ocean waters upper 200 m	360	0.72
Ocean waters below 200 m	650	1.3
Surface sediments (0–10 cm)	170	0.3
Oceanic subsurface	35 500	303
Soil	2600	26
Terrestrial subsurface	2500–25 000	22–215
Total	417–640	353–546

* calculated with the assumption of 20 fg carbon/cell for aquatic habitats and 10 fg/cell for sediments and soils. The subsurface compartments are defined as below 8 m in terrestrial systems and below 10 cm in ocean sediments.

pelagic waters, with the majority cycled either directly or indirectly through the microbial food web. Although bacteria possess a suite of specific structures which allow their presence to be identified in the organic matter pool, the question of microbes as contributors to organic matter verses role as the primary catalysts for organic matter recycling remains uncertain. Yet bacteria have the potential to provide an enormous fraction of the total organic matter in both aquatic systems and soils despite their diminutive size (Table 5). Although a wide range of densities have been reported (10^4–10^7 ml^{-1}), the mean values for many aquatic environments are similar [107] and represent a significant reservoir of carbon (Table 5).

A challenge in the next decade will be to better quantify the potential of the fraction of the microbial biomass which is not observed as intact cells to be a significant contributor to organic material in both dissolved and particulate organic fractions. Advances in analytical techniques have a major role to play and recent observations have already detailed the present of potentially important bacterial groups in marine systems [108–110]. An important future direction will be to link the activities of such unculturable groups of bacteria with the cycling of organic materials in the ocean.

10 Concluding Remarks

Although the reactivities of many organic compounds seem similar, closer examination reveals many subtlilities due to chemical structure, environ-

mental conditions and physical matrix. The microbial food web and upper trophic levels are highly efficient at recycling the vast majority of carbon produced, yet some compounds escape to reach underlying sediments or are transported as dissolved material to deep ocean waters. Carbon age as seen in radiocarbon measurements suggest that a portion of both dissolved and particles along the size continuum are retained and recycled over long time periods, yet these fractions of organic carbon are typically those with complex or heterogenous structures which continue to elude detailed structural determination.

Much progress has been made in recent years, particularly by taking advantage of multiple approaches which can be used to constrain the age (radiocarbon), biosynthesis (isotopic) and origin (biomarker) of at least a fraction of the organic carbon pool [111, 112]. A better understanding of the contributors to the organic carbon pool together with evidence of the microbial catalysts responsible for its processing can help discern the path that organic carbon follows in the marine environment.

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