
CHAPTER 23

THE PRODUCTION AND DESTRUCTION OF ORGANIC COMPOUNDS IN THE SEA

INTRODUCTION

Though organic compounds constitute a relatively small reservoir in the crustal-ocean factory, they play a central role in the marine biogeochemical cycles of the biolimiting elements. Except for humic acids, all of these naturally occurring compounds are synthesized by marine organisms. Likewise, all heterotrophs require organic compounds as their source of chemical energy. The molecular structures of the most abundant of these biomolecules were given in the preceding chapter. They are present in seawater as true solutes, colloids, and solids. As shown in Figure 23.1, some of the smaller particles, such as bacteria and adsorbed colloids, are included in the operationally defined DOM fraction.

Most organic matter in the sea is present in dissolved or colloidal form. As shown in Figure 23.2, less than a quarter of the POC is alive, with most being phytoplankton and bacteria. Other marine organisms that contribute significantly to marine biomass include protozoans, fungi, and viruses. With an average concentration of 10^7 cells/ml, viruses appear to be the most numerous, but due to their small size (10^{-18} g C/cell), they account for less than 1 percent of the standing stock of marine biomass.

Because of differences in molecular structure, organic compounds vary in chemical reactivity and hence their susceptibility to transformation by marine organisms. Nevertheless, concentrations tend to be low, due to rapid uptake and release by marine organisms. The mechanisms by which organisms produce and destroy specific organic compounds are discussed below. This chapter also contains a description of the abiogenic processes that are responsible for the formation of the humic substances. This information is used to explain the marine distributions of these compounds.

THE PRODUCTION AND DESTRUCTION OF POM

The riverine transport of terrestrial POM (4.2×10^9 g C/y) is much smaller than the rate of marine primary production (4×10^{16} g C/y). The aeolian

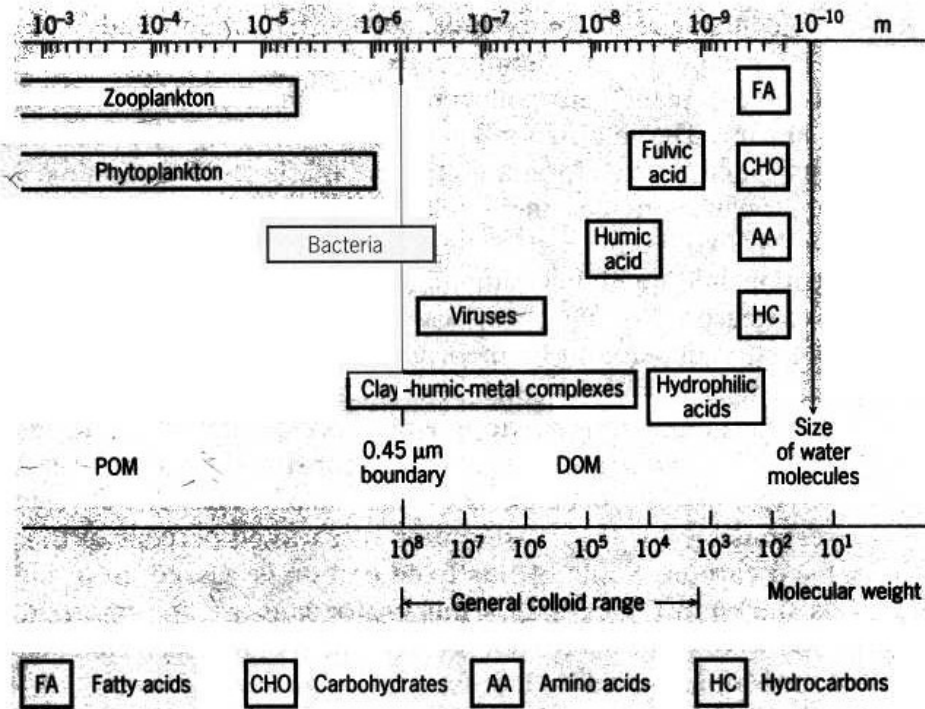


FIGURE 23.1. Continuum of particulate and dissolved organic carbon in natural water. Source: From *Organic Geochemistry of Natural Waters*, E. M. Thurman, copyright © 1985 by Kluwer Academic Publishers, Dordrecht, The Netherlands, p. 3. Reprinted by permission.

transport of POM is also very small. Thus most marine POM is generated in situ by primary producers, such as phytoplankton, macroalgae, and chemoautolithotrophic bacteria. Most primary production is accomplished by photoautotrophic nanoplankton (2.0–20 μ m in diameter) and picoplankton (0.2–2 μ m in diameter). The carbon fixed by these marine autotrophs has several possible fates. Approximately 10 percent is exuded from the plants in the form of low-

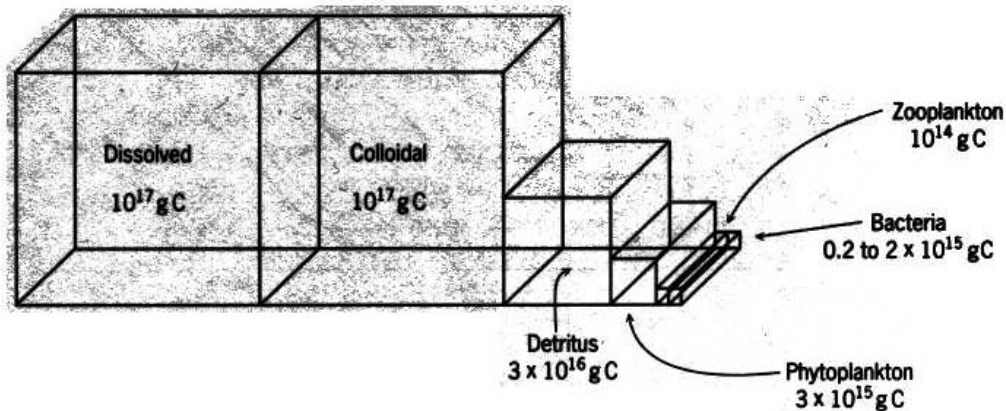


FIGURE 23.2. Distribution of organic carbon in the oceans. Source: After G. Cauwet, reprinted with permission from *Oceanologica Acta*, vol. 1, p. 101, copyright © 1978 by Gauthiers-Villars, Montrouge, France.

molecular-weight compounds, such as free amino acids and tricarboxylic acids. These exudates are rapidly consumed by bacteria.

Most plant cells are consumed by filter-feeding microzooplankton (20–200 μm). The microzooplankton are primarily flagellated and ciliated protozoans, such as the foraminifera, radiolaria, and tintinnids. When the uneaten phytoplankton die, their cells membranes are rapidly lysed. The resulting DOM, like the plant exudates, is rapidly taken up by bacteria. This process is responsible for the consumption of 10 to 50 percent of the photosynthetically fixed carbon. Some of this carbon is returned to seawater as DOC and DIC, but most appears to be incorporated into microbial biomass.

Bacteria and the small phytoplankton are too small to be efficiently grazed by the larger zooplankton, which are primarily copepods, euphausiids, and larvae. Protozoans are able to consume bacteria, as well as the small phytoplankton, because they are also small. As a result, protozoans are responsible for the consumption of 25 to 50 percent of the photosynthetically fixed carbon. Some of this fixed carbon is passed up to higher trophic levels, as shown in Figure 23.3. Thus protozoans are an important link in the marine food web. If they were not present, most of the bacterial, and hence autotrophic production, would be lost from the marine food web.

Not all of the organic matter consumed by protozoans is passed to higher trophic levels. A substantial amount is released as DOM. This process also

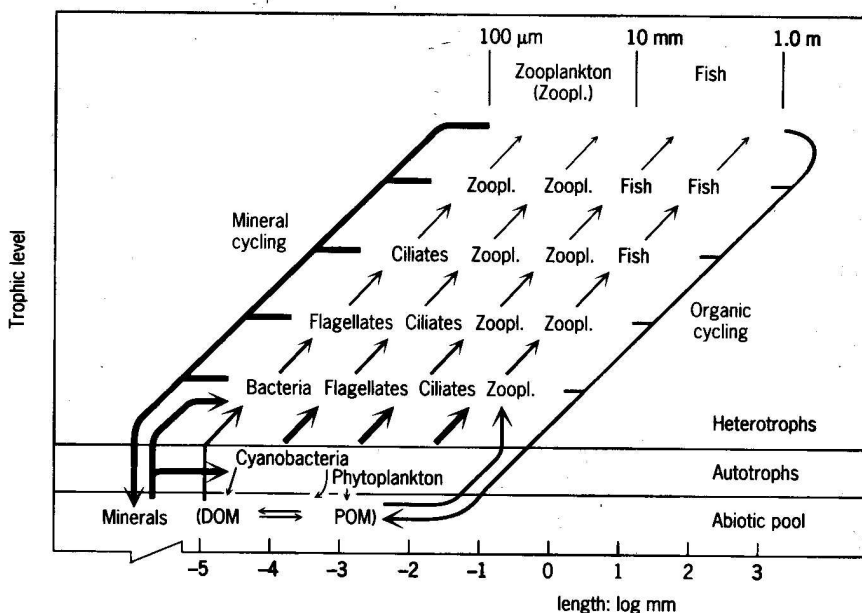


FIGURE 23.3. Marine food web. Source: From F. Azam, J. G. Field, J. S. Gray, L. A. Meyer-Reil, and F. Thingstad, reprinted with permission from *Marine Ecology-Progress Series*, vol. 10, p. 260, copyright © 1983 by Inter-Research, Amelinghausen, Germany.

resolubilizes nitrogen and phosphorus and hence greatly enhances nutrient recycling rates. Though larger zooplankton excrete ammonium and low molecular weight DOM, this release is significant only in ecosystems characterized by high nutrient concentrations. Under these conditions, large-celled plants, such as diatoms, are favored. Hence most of the primary production can be consumed by the larger zooplankton. Regardless, the larger zooplankton are a very important source of detrital POM, including such items as fecal pellets, egg cases, molts, mucus feeding nets, and food fragments.

The detrital pool of POM also includes dead plant and animal tissues, such as fragments of saltmarsh grass and terrestrial plants. Some of these particles aggregate to form flakes called **marine snow**. Some marine snow has been observed to contain large numbers of bacteria and protozoans whose biochemical activities cause the detrital POM to decompose as it sinks. Due to the remineralization of nitrogen and phosphorus, the seawater surrounding marine snow is often characterized by elevated nutrient concentrations and reducing conditions. The importance of these suboxic and anoxic microzones to the biogeochemical cycles of the biolimiting elements is unknown.

Large aggregates are also produced by the bioflocculation of diatoms during plankton blooms. Likewise, POM can also be created by the aggregation and precipitation of DOM from seawater. This process is accelerated by certain types of water motion, such as bubbling. Changes in environmental conditions can also cause precipitation. For example, DOM precipitates from river water in estuaries as a result of colloidal destabilization caused by increasing salinity. DOM also tends to be concentrated at boundaries, such as the sediment-water and air-sea interfaces. The latter is also characterized by enrichments of POM, such as bacteria. Under calm conditions, this organic matter forms a visible surface slick or microlayer. On windy days, the organic matter can be whipped up into an emulsion that has the appearance of a very sturdy foam.

THE CHEMICAL TRANSFORMATION OF PARTICULATE ORGANIC COMPOUNDS

Living organisms, primarily phytoplankton, make up a significant amount of the surface-water particles. Their chemical composition is somewhat species specific and is also influenced by the physiological state of the organisms. In general, 40 to 60 percent of the carbon in phytoplankton is in the form of protein. Carbohydrates and lipids compose 20 to 40 percent and 5 to 20 percent of the cellular carbon, respectively. The average elemental composition of these classes of organic compounds is given in Table 23.1.

Due to net production, the euphotic zone is characterized by high and variable POM concentrations (10–1000 $\mu\text{g/L}$). The C to N ratio of this surface-water POM ranges from 5 to 7 and is similar to that of the Redfield-Richards Ratio ($C/N = 6.6$). This reflects the influence of phytoplankton on the surface-water pool of POM. Below the euphotic zone, organic matter is respired faster

TABLE 23.1
Average Composition of Organic Materials

Percentage composition ^a				Relative proportions by weight, C = 100 ^b			
Element	Carbohydrates	Lipids	Proteins	Element	Seawater	Lipids	Proteins
O	49.38	17.90	22.4	C	100	100	100
C	44.44	69.05	51.3	P	0.05	3.1	1.4
H	6.18	10.00	6.9	N	0.5	0.88	34.7
P		2.13	0.7	S	3150	0.45	1.6
N		0.61	17.8	Fe	0.07		0.2
S		0.31	0.8				
Fe			0.1				

Source: From *The Oceans*, H. U. Sverdrup, M. W. Johnson, and R. H. Fleming, copyright © 1941 by Prentice Hall, Inc., Englewood Cliffs, NJ, p. 230. Reprinted by permission. Data from *Textbook of Comparative Physiology*, C. G. Rogers 2nd ed., copyright © 1938 by McGraw-Hill, Inc., New York, p. 59. Reprinted by permission.

^aElemental Contribution by Percent Mass.

^bRelative Elemental Contribution Normalized to Carbon.

than it is produced, so POM concentrations decline with increasing depth, as shown in Figure 23.4. In general, concentrations decrease exponentially through the thermocline and reach uniformly low (<10 $\mu\text{g/L}$) levels in the deep zone. Thus, much of the sinking POM appears to be decomposed in the thermocline. This process is partially responsible for maintaining low O_2 concentrations at mid depth. POM concentrations in the deep water exhibit little temporal or geographic variability.

Since most of the living POM is concentrated in the euphotic zone, the relative contribution of detrital POM increases with depth. The C to N ratio of this detrital POM also increases with depth because nitrogen-rich compounds (proteins) degrade faster than the nitrogen-deficient ones (carbohydrates and

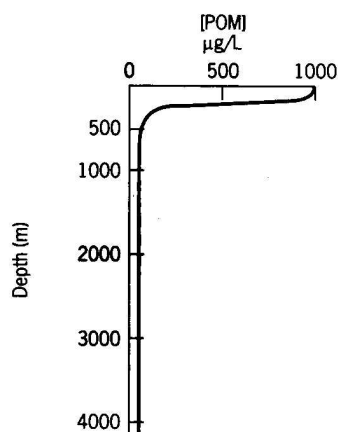


FIGURE 23.4. Depth profile of POM.

lipids). As shown in Figure 23.5, this causes the relative abundance of proteins to decrease with depth, while that of the carbohydrates increases.

In detrital POM, the large biopolymers are the first compounds to degrade. As shown in Table 23.2, this occurs by the breakage of the bonds which hold the monomeric units together. For example, proteins are decomposed into polypeptides, which are then fragmented into free amino acids. These amino acids are then converted into fatty acids and smaller molecules such as CO_2 , CH_4 , NH_4^+ , HPO_4^{2-} , HS^- , phenols, and urea. Nucleotides, such as RNA, DNA, and ATP, are fragmented into their constituent nucleic acids, which are degraded into fragments similar to those resulting from the catabolism of amino acids. The degradation of lipids yields hydrocarbons, carbohydrates, and small carboxylic acids. These, in turn, are decomposed to CO_2 and CH_4 . The polysaccharides, such as cellulose and starch, are initially broken into oligosaccharides and then into monosaccharides. Their complete degradation also yields CO_2 and CH_4 . As with anabolism, the reaction mechanisms, and hence their products, are species specific.

These catabolic reactions are the result of microbial degradation, as well as consumption by higher-order organisms, such as filter-feeding zooplankton. The extent and type of transformations that detrital POM undergoes as it sinks toward the seafloor depends on (1) the types and relative abundance of deep-water heterotrophs, (2) the chemical composition of the particles, and (3) the physical packaging of the particles, as this determines their sinking rates. Most

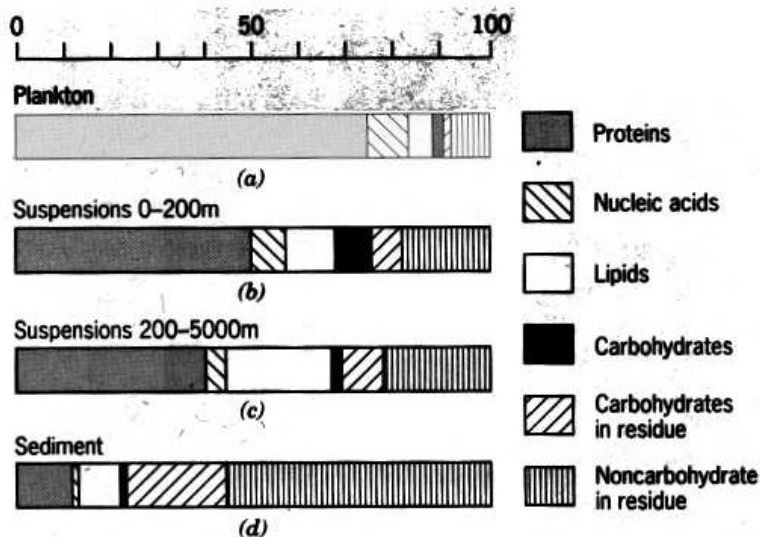


FIGURE 23.5. Biochemical composition of (a) plankton, (b) POM from the euphotic zone, (c) POM from the thermocline and deep waters, and (d) surface sediments. The scale represents the percent by mass contribution of each class of organic compound. *Source:* From G. Cauwet, reprinted with permission from *Oceanologica Acta*, vol. 1, p. 102, copyright © 1978 by Gauthiers-Villars, Montrouge, France. After A. T. Agatova and Y. A. Bogdanov, reprinted with permission from *Okeanologiya*, vol. 12, p. 234, copyright © 1972 by the Academy of Sciences of the USSR Oceanology, Moscow, USSR.

TABLE 23.2
Decomposition Products Produced from Organic Compounds Present in Detrital POM

Life Substances	Decomposition Intermediates	Intermediates and Products Typically Found in Nonpolluted Natural Waters
Proteins	Polypeptides \rightarrow $\left. \begin{array}{l} \text{RCOOH} \\ \text{RCH}_2\text{OHCOOH} \\ \text{RCH}_2\text{OH} \\ \text{RCH}_2\text{NH}_2 \end{array} \right\}$ amino acids	NH_4^+ , CO_2 , HS^- , CH_4 , HPO_4^{2-} , peptides, amino acids, urea, phenols, indole, fatty acids, mercaptans
Polynucleotides	Nucleotides \rightarrow purine and pyrimidine bases	
Lipids		
Fats	$\text{RCH}_2\text{CH}_2\text{COOH} + \text{CH}_2\text{OHCHOHCH}_2\text{OH} \rightarrow$ fatty acids glycerol	$\left. \begin{array}{l} \text{RCH}_2\text{OH} \\ \text{RCOOH} \\ \text{RCH}_3 \\ \text{RH} \end{array} \right\}$ shorter chain acids
Waxes		
Oils		
Carbohydrates		
Cellulose	$\left. \begin{array}{l} \text{C}_x(\text{H}_2\text{O})_y \rightarrow \left\{ \begin{array}{l} \text{monosaccharides} \\ \text{oligosaccharides} \\ \text{chitin} \end{array} \right\}$	CO_2 , CH_4 , aliphatic acids, acetic, lactic, citric, glycolic, malic, palmitic, stearic, and oleic acids, carbohydrates, hydrocarbons
Starch		
Hemicellulose		
Lignin	$(\text{C}_2\text{H}_2\text{O})_x \rightarrow$ unsaturated aromatic alcohols \rightarrow polyhydroxy carboxylic acids	HPO_4^{2-} , CO_2 , CH_4 , glucose, fructose, galactose, arabinose, ribose, xylose
Porphyryns and plant pigments		
Chlorophyll	$\left. \begin{array}{l} \text{Chlorin} \rightarrow \text{phaeophytin} \rightarrow \text{hydrocarbons} \end{array} \right\}$	Pristane, carotenoids
Hemin		
Carotenes and Xanthophylls		
Complex substances formed from breakdown intermediates, e.g.,		
	Phenols + quinones + amino compounds \rightarrow	Melanins, melanoidin, gelbstoffe
	Amino compounds + breakdown products of carbohydrates \rightarrow	Humic acids, fulvic acids, "tannic" substances

Source: From *Aquatic Chemistry*, W. S. Stumm and J. J. Morgan, copyright © 1970 by John Wiley & Sons, Inc., New York, p. 344. Reprinted by permission.

deep-water particles are small ($<20 \mu\text{m}$), so they sink slowly ($\leq 1 \text{ m/d}$) and are subject to microbial attack for extended periods of time. As a result, most small particles are composed of refractory materials, such as plankton cell walls, zooplankton exoskeletons, and precipitated humic substances. The refractory nature of this material is seen in its relatively high C to N ratio (10–13).

A relatively small number of deep-water particles are large ($>20 \mu\text{m}$) and thus sink rapidly (10–100 m/d). Most are fecal pellets produced by surface-water zooplankton. Though low in number, these large particles account for most of the mass flux of organic matter to the seafloor. Due to their rapid sinking rates, the large particles are more likely to reach the seafloor than the smaller size fraction of POM. Since they reach the seafloor relatively intact, the large particles are composed of relatively labile organic matter. Hence, they are the major food source for the benthos.

The sinking rates of small undigested particles, such as algal and microbial cells, are increased by incorporation into fecal pellets. This rapid transport, termed “the fecal pellet express,” is thought to be responsible for maintaining a viable population of bacteria in the deep sea. As illustrated in Figure 23.6, it also enhances the accumulation rates of calcareous and siliceous tests in the sediments, as these particles would otherwise dissolve in transit.

Significant sampling problems are encountered in the study of POM. Because large particles are scarce in the deep sea, large volumes of water must be filtered to collect a representative number. Alternatively, a passive trap can be used to intercept sinking particles. These sediment traps (Figure 16.6) are deployed at a specific depth for times that range from days to months. The collected particles are protected from consumption by poisoning the traps. Unfortunately, these traps do not collect the entire POM flux. The fraction collected has been shown to depend on the design of the trap, particularly on its size and shape. As no standard design is used, data from different traps are not easily compared.

Though the total POM flux decreases with increasing depth, considerable variations are observed among the classes and specific compounds of organic matter, as illustrated in Figure 23.7. Rapid decreases are characteristic of chemically labile molecules. On the other hand, in situ production can produce mid-water maxima. In cases where products are species specific, their presence can be used to identify the types of marine organisms active at the sampling site. Temporal variations in these fluxes can be caused by seasonal shifts in surface productivity and diel migrations of mid-water organisms.

The sediment–water interface is the site of much biological activity. Thus POM that reaches the seafloor is subject to extensive degradation prior to burial. The sediment–water interface is a transitional zone that is best described as a loose floc populated by high concentrations of microbes. Due to high rates of organic matter decomposition, the organic carbon and nitrogen contents of these particles are decreased by an order of magnitude prior to burial. This loss continues after burial, but at much slower rates. As shown in Figure 23.8, this causes the C to N ratio in the sediments to continue to increase with

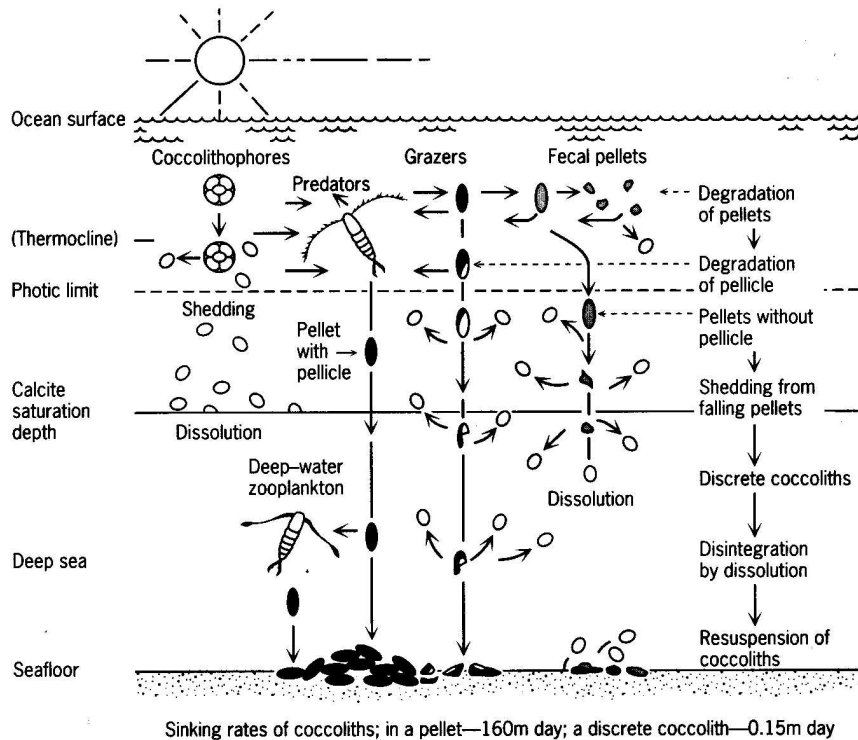


FIGURE 23.6. A schematic diagram of the relationship between the production, transportation, dissolution, and deposition of coccoliths in the ocean, demonstrating the role of fecal pellets. *Source:* From S. Honjo, reprinted with permission from *Marine Micropaleontology*, vol. 1, p. 76, copyright © 1976 by Elsevier Science Publishers, B.V., Amsterdam, The Netherlands.

depth. The chemical homogeneity of the top meter of the sediment column is likely due to bioturbation.

DISSOLVED ORGANIC COMPOUNDS

DOM is the second largest reservoir of carbon in seawater, the first being DIC. As such, DOM could represent an important source of food for heterotrophs and thus have great impact on global rates of O_2 uptake and nutrient recycling. Despite its likely importance, little is known about the quantity or chemical composition of marine DOM. This is due to the analytical difficulties associated with the identification and quantification of specific dissolved organic compounds. The low molecular weight compounds are difficult to detect because of their low concentrations and interference by salt ions. The high molecular weight compounds have proven difficult to study because of their complex and

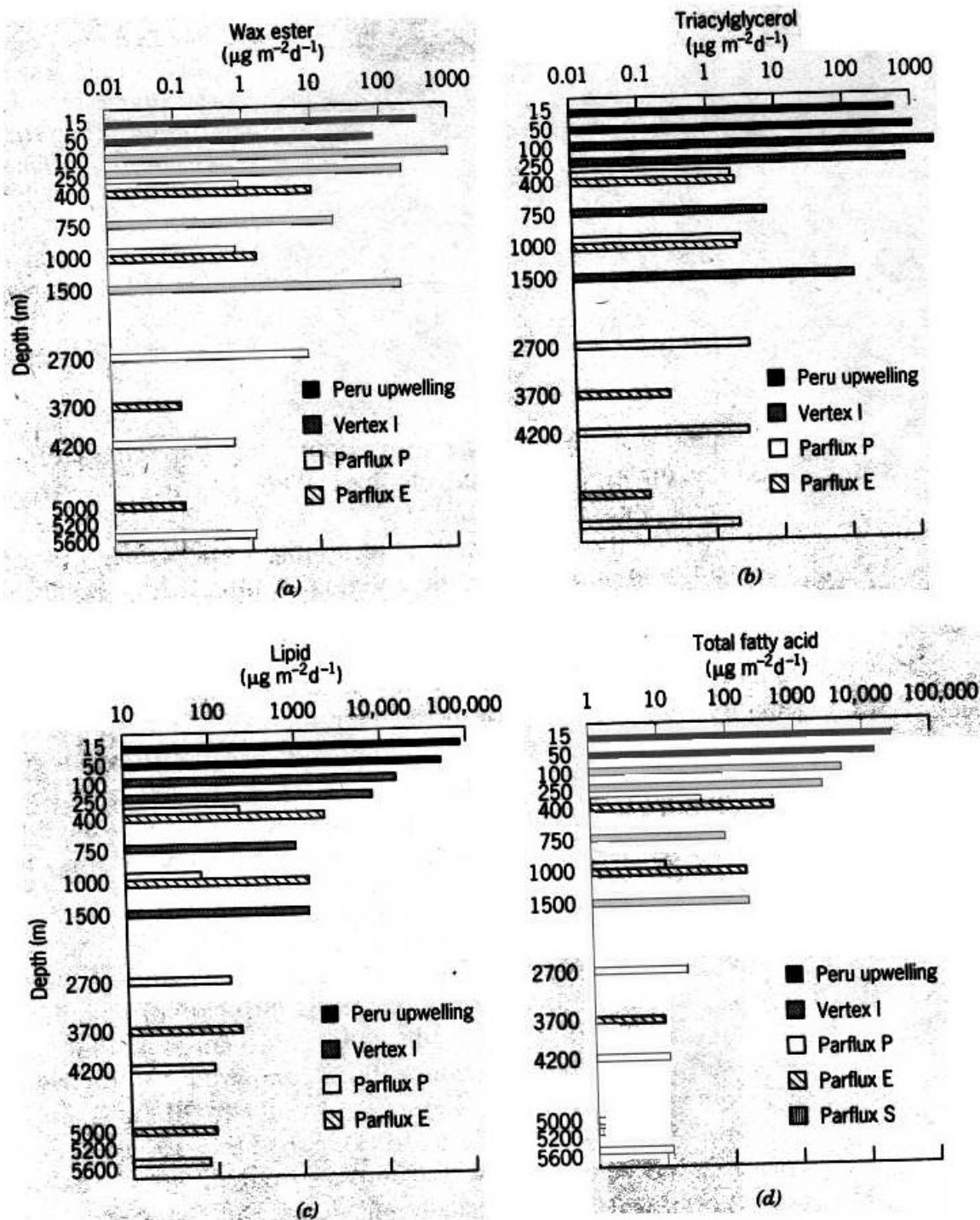


FIGURE 23.7. Fluxes ($\mu\text{g m}^{-2}\text{d}^{-1}$) of organic constituents in POM collected in sediment traps deployed in the Peru upwelling area (15°S), at Vertex I in the California current off Monterey, CA, at Parflux P in the central North Pacific, at Parflux E in the equatorial North Atlantic, and Parflux S in the Sargasso Sea: (a) wax esters, (b) triacylglycerols, (c) lipids, and (d) total fatty acids. Source: From S. G. Wakeham, C. Lee, J. W. Farrington, and R. B. Gagosian, reprinted with permission from *Deep-Sea Research*, vol. 31, p. 514, copyright © 1984 by Pergamon Press, Elmsford, NY.

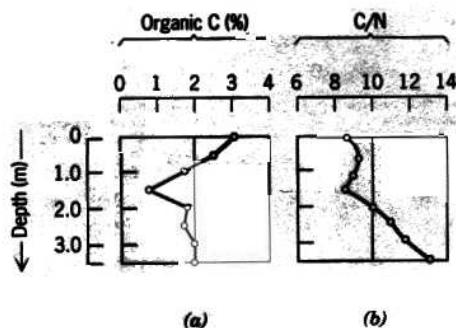


FIGURE 23.8. (a) % organic carbon and (b) C/N ratio of sedimentary organic matter in a core from the Oman Sea. Source: From *Humic Substances in Soil, Sediment and Water*, M. Vanderbroucke, R. Pelet, and Y. Debyser (eds.: G. R. Aiken, D. M. McKnight, R. L. Wershaw, and P. MacCarthy), copyright © 1985 by John Wiley & Sons, Inc., New York, p. 254. Reprinted by permission.

variable structures. Since these compounds are relatively inert, they do not readily undergo chemical changes. This is a necessity for any type of wet-chemical analysis.

Part of the difficulty in determining DOM concentrations also lies in the variable retention of organic colloids on filters. As a result, a variable fraction of organic matter is operationally defined as DOM. This variability is due to differences in filter porosity as well as in filtration conditions, such as in the amount of particle loading and suction applied. The development of new analytical techniques for the measurement of DOM is an active area of research. Recent results using a new method suggest that previous measurements have underestimated DOC concentrations by 50 to 400 percent. If so, our models of the biogeochemical cycling of organic matter will have to be considerably revised. This subject is addressed toward the end of this chapter.

Sources of DOM

Terrestrial DOM is carried to the ocean by winds, rivers, or groundwater runoff. Aeolian transport can occur via diffusion of volatile compounds across the air-sea interface or by adsorption onto aerosols that are deposited on the sea surface. This is a minor flux compared to the riverine input. DOC concentrations in river water range from 1 to 20 mg/L. Its annual global flux is approximately the same as for POC (0.11×10^9 g C). Some of this DOC is precipitated when river water enters estuaries and mixes with seawater. This effect is largest for terrestrial humic acids. Due to the small size of the terrestrial DOM flux, it appears that most marine DOM is produced in situ.

DOM is produced in situ as a result of excretions and exudations from animals, microorganisms, and plants. As mentioned above, phytoplankton "excrete" a significant amount of their fixed carbon in the form of low molecular weight compounds, such as those listed in Table 23.3. Though this process is variable, it is ubiquitous and appears to be associated with dark respiration.

Animals and microbes also excrete low-molecular-weight compounds. Those released by animals tend to be nitrogen-rich (e.g., uric acid, urea, amino acids, and nucleic acids). Fecal material is an indirect source of DOM as the

TABLE 23.3
Excretion Products of Algae

<i>Products</i>	
Glycolic acid	Polysaccharides
Amino acids	Vitamins
Volatile compounds	Polymeric organic acids
Sterols	Fatty acids
Pigments	

Source: From *Organic Geochemistry of Natural Waters*, E. M. Thurman, copyright © 1985 by Kluwer Academic Publishers, Dordrecht, The Netherlands, p. 83. Reprinted by permission. Data from G. E. Fogg, reprinted with permission from *Limnology and Oceanography*, vol. 22, p. 576, copyright © 1977 by the American Society of Limnology and Oceanography, Seattle, WA; and E. Billmire and S. Aaronson, reprinted with permission from *Limnology and Oceanography*, vol. 21, p. 138, copyright © 1976 by the American Society of Limnology and Oceanography, Seattle, WA.

solids are solubilized during microbial degradation. DOM is also released into seawater following the death of organisms due to rapid lysis of their cell membranes. Sloppy feeding breaks cell membranes, thereby releasing DOM into seawater.

The Ecological Role of DOM

Although the low-molecular-weight compounds represent a small fraction of the DOM reservoir, they play an important ecological role in the sea. These compounds have high production rates, but their concentrations tend to be very low due to rapid uptake, primarily by heterotrophic bacteria. As a result, low-molecular-weight compounds tend to have small turnover times and hence function as an important microbial food source, despite their low concentrations.

Some marine organisms release low-molecular-weight compounds in an effort to control some aspect of their environment. For example, some of these compounds act as toxins that repel or kill competitors or predators. Others act to "neutralize" toxins. Some function as attractants and are used for mating purposes. Other types of chemical communication conveyed by dissolved compounds are described in Table 23.4.

The Fate of Low-Molecular-Weight DOM in the Sea

The low-molecular-weight fraction of DOM is rapidly consumed upon introduction into seawater. As a result, the concentrations of these compounds are low

TABLE 23.4
Classes of Interorganismic Chemical Effects^a

-
- I. Allelochemic Effects**
- A. Allomones (+ /), which give adaptive advantage to the producing organism**
1. Repellents (+ /), which provide defense against attack or infection (many secondary plant substances, chemical defenses among animals, probably some toxins of other organisms)
 2. Escape substances (+ /) that are not repellents in the usual sense (inks of cephalopods, tension-swimming substances)
 3. Suppressants (+ -), which inhibit competitors (antibiotics, possibly some allelopathics, and plankton ectocrines)
 4. Venoms (+ -), which poison prey organisms (venoms of predatory animals and myxobacteria, aggressins of parasites, and pathogens)
 5. Inductants (+ /), which modify growth of the second organism (gall, nodule, and mycorrhiza-producing agents)
 6. Counteractants (+ /), which neutralize as a defense the effect of a venom or other agent (antibodies, substances inactivating stinging cells, substances protecting parasites against digestive enzymes)
 7. Attractants (+ /)
 - a. Chemical lures (+ -), which attract prey to a predator (attractants of carnivorous plants and fungi)
 - b. Pollination attractants, which are without (+ 0) or with (+ +) advantage to the organism attracted (flower scents)
- B. Kairomones (/ +), which give adaptive advantage to the receiving organism**
1. Attractants as food location signals (/ +), which attract the organism to its food source, including (- +) those attracting to a food organism (use of secondary substances as signals by plant consumers, of prey scents by predators or chemical cues by parasites), (+ +) pollination attractants when the attracted organism obtains food, and (0 +) those attracting to nonliving food (response to scent by carrion feeder, chemotactic response by motile bacteria and by fungal hyphae)
 2. Inductants (/ +), which stimulate adaptive development in the receiving organism (hyphal loop factor in nematode-trapping fungi, spine-development factor in rotifers)
 3. Signals (/ +) that warn of danger or toxicity to receiver [repellent signals that have adaptive advantage to the receiver; scents and flavors that indicate unpalatability of nonliving food, predator scents]
 4. Stimulants (/ +), such as hormones, that benefit the second organism by inducing growth
- C. Depressants (0 -), wastes and so forth, that inhibit or poison the receiver without adaptive advantage to releaser from this effect (some bacterial and parasite toxins, allelopathics that give no competitive advantage, some plankton ectocrines)**
- II. Intraspecific Chemical Effects**
- A. Autotoxins (- /), repellents, wastes, and so forth, that are toxic or inhibitory to individuals of the releasing populations, with or without selective advantage from detriment to some other species (some bacterial toxins, antibiotics, ectocrines, and accumulated wastes of animals in dense culture)**

TABLE 23.4 (Continued)
Classes of Interorganismic Chemical Effects^a

-
- B. Adaptive autoinhibitors (+ /) that limit the population to numbers that do not destroy the host or produce excessive crowding (staling substance of fungi)
 - C. Pheromones (+ /), chemical messages between members of a species, that are signals for
 1. Reproductive behavior
 2. Social regulation and recognition
 3. Control of caste differentiation
 4. Alarm and defense
 5. Territory and trail marking
 6. Food location
-

Source: From R. H. Whittaker and P. P. Feeny, reprinted with permission from *Science*, vol. 171, p. 767, copyright © 1971 by the American Association for the Advancement of Science, Washington, D.C.

^aAdaptive advantage is indicated by +, detriment by -, and adaptive indifference by 0, for the releasing organism first and the receiving organism second. The virgule (/) indicates that adaptive advantage or detriment is not specified for one side of the relationship.

(<100's $\mu\text{g/L}$). As shown in Figure 23.9, the polypeptides are most abundant. The concentration of free amino acids is much lower due to rapid microbial uptake. Most of the sugars are glucose, which is excreted into seawater by phytoplankton.

Though most of the labile fraction of DOM is consumed and degraded by microbes, some is assimilated by phytoplankton during dark respiration. The degradation products are eventually incorporated into humic substances as described below. A significant amount of DOM is also lost by adsorption onto sinking particles. The bursting of bubbles at the sea surface also causes a small amount of DOM to be volatilized or converted to POM.

The Production and Destruction of High-Molecular-Weight DOM

Forty to 80 percent of DOM is composed of high-molecular-weight compounds that are collectively referred to as **humic substances**. Their contribution is highest in deep waters due to the relative scarcity of low-molecular-weight compounds. They impart a yellow or brown cast to seawater when present at very high concentrations. Humic substances that are insoluble at acidic pH's are termed **humic acids**; those that are soluble at all pH's are termed **fulvic acids**. The latter are more abundant in seawater.

As shown in Figure 23.10, humic substances are thought to be produced by abiogenic chemical reactions that link together relatively low-molecular-weight compounds. Most of these low-molecular-weight compounds are derived from the degradation of biopolymers, such as proteins and carbohydrates.

These reactions include condensations, polymerizations, oxidations, and reductions. As shown in Figure 23.11, the nonaromatic structures tend to form

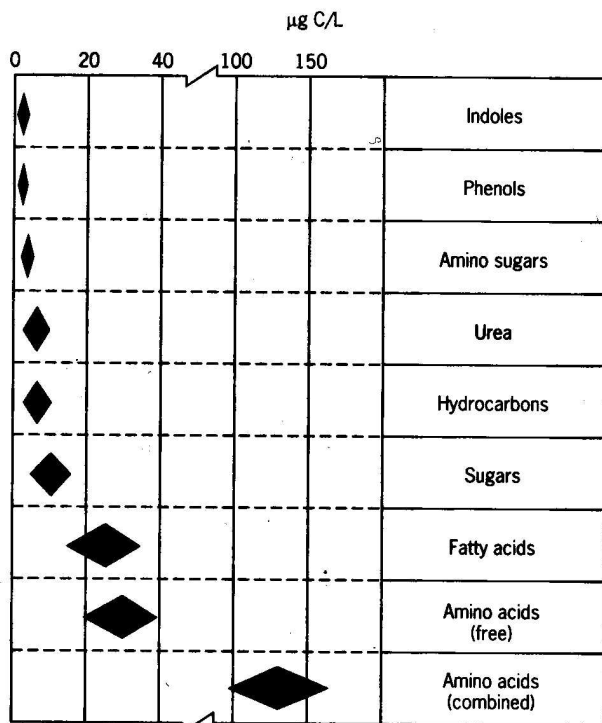


FIGURE 23.9. Range of concentrations of various types of DOC. *Source:* From *Symposium on Organic Matter in Natural Waters*, E. T. Degens (ed.: D. Hood), copyright © 1970 by the Institute of Marine Science, University of Alaska, College, Alaska, p. 79. Reprinted by permission.

highly cross-linked polymers. At the sea surface, photochemical reactions produce O_2 free radicals that accelerate the rates of some of the polymerization reactions.

The molecular structure of the resulting humic substances are very variable, partly as a result of differences in the availability of low-molecular-weight compounds. Nevertheless, they possess similar functional groups, such as aromatic structures, carboxylic acids, and amines, as shown in Figure 23.12a. This example is a likely structure for a humic acid. In comparison, fulvic acids tend to have a greater abundance of acidic functional groups, such as those shown in Figure 23.12b.

As shown in Figure 23.13, terrestrial humic substances compose a significant fraction of the riverine input of DOM to the ocean. Terrestrial humics tend to have more acidic groups and a higher degree of oxidation than marine forms. They also contain more aromatic structures and hence are more susceptible to flocculation when exposed to high concentrations of electrolytes. Other differences between terrestrial and marine humics are described in Table 23.5.

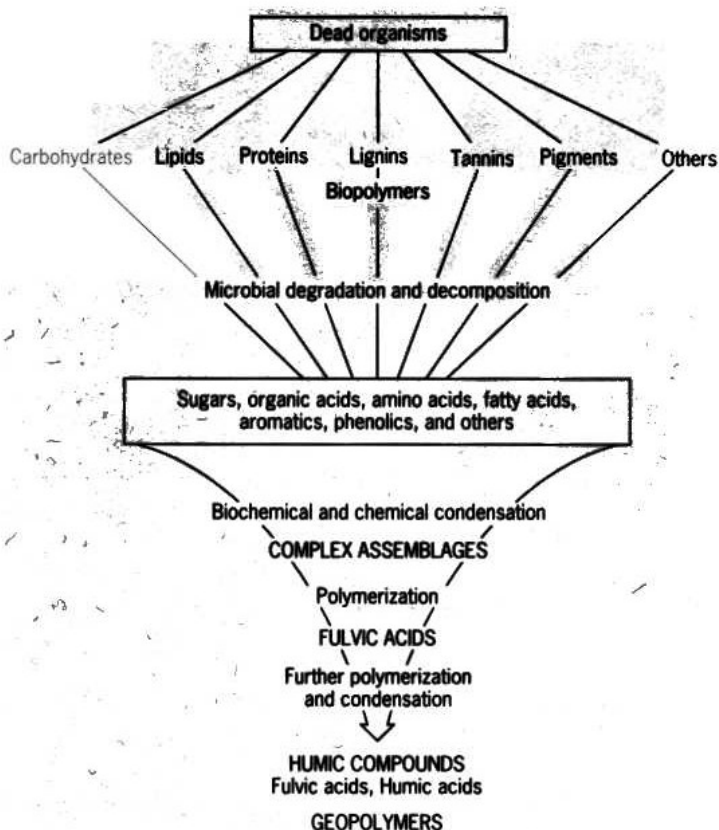


FIGURE 23.10. A simplified scheme of the humification process. *Source:* From *Geochemistry of Marine Humic Compounds*, M. A. Rashid, copyright © 1985 by Springer-Verlag, Heidelberg, Germany, p. 59. Reprinted by permission.

The presence of lignin degradation products causes the terrestrial humic substances to have a relatively high degree of acidity and aromaticity. Most of these fragments are phenolic acids (Figure 23.14b), which are liberated during the degradation of lignin (Figure 23.14a). These compounds react with other forms of degraded organic matter to generate terrestrial humic substances. Since lignin is unique to land plants, these phenolic moieties can be used as a biomarker indicating the presence of terrestrial organic matter. Their low abundances in open ocean sediments supports the hypothesis that most riverborne POM is deposited in the coastal zone.

A Proposed Cycle for Marine DOM

DOM concentrations are highest in the surface water as this is where most organic matter is synthesized. As illustrated in Figure 23.15, concentrations decrease exponentially through the thermocline. The deep waters are characterized by low and uniform concentrations. Surface-water concentrations are

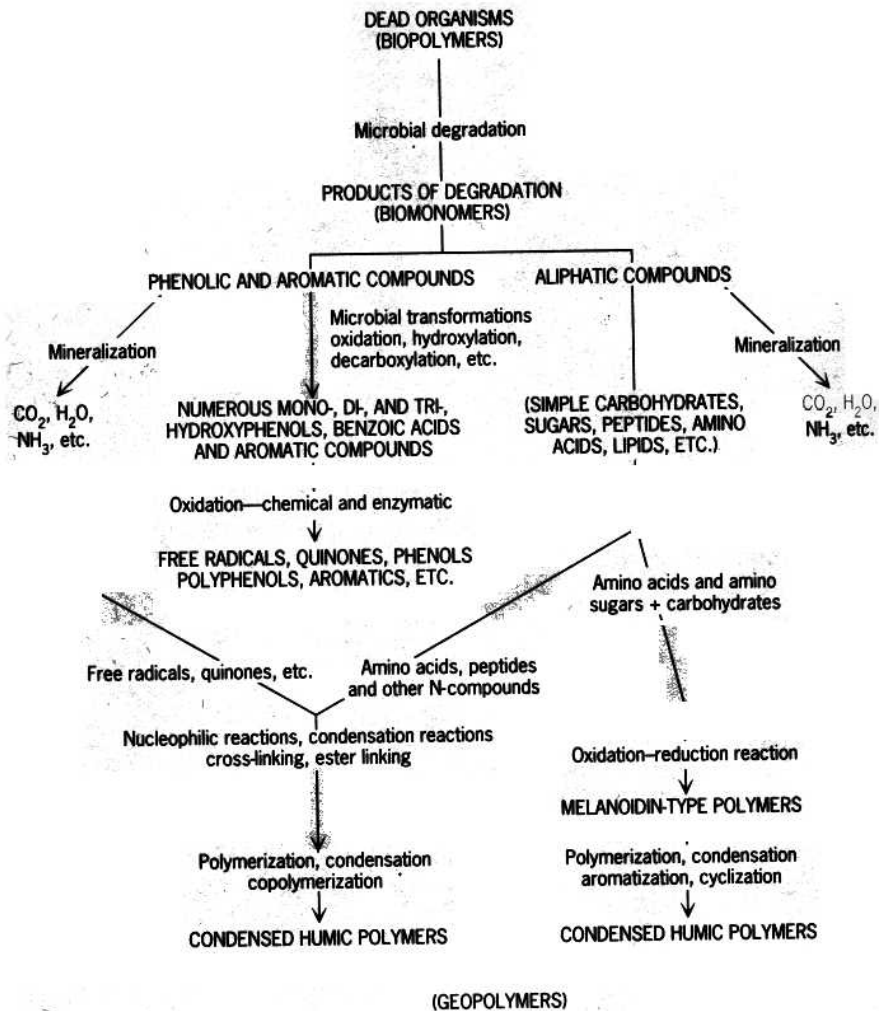
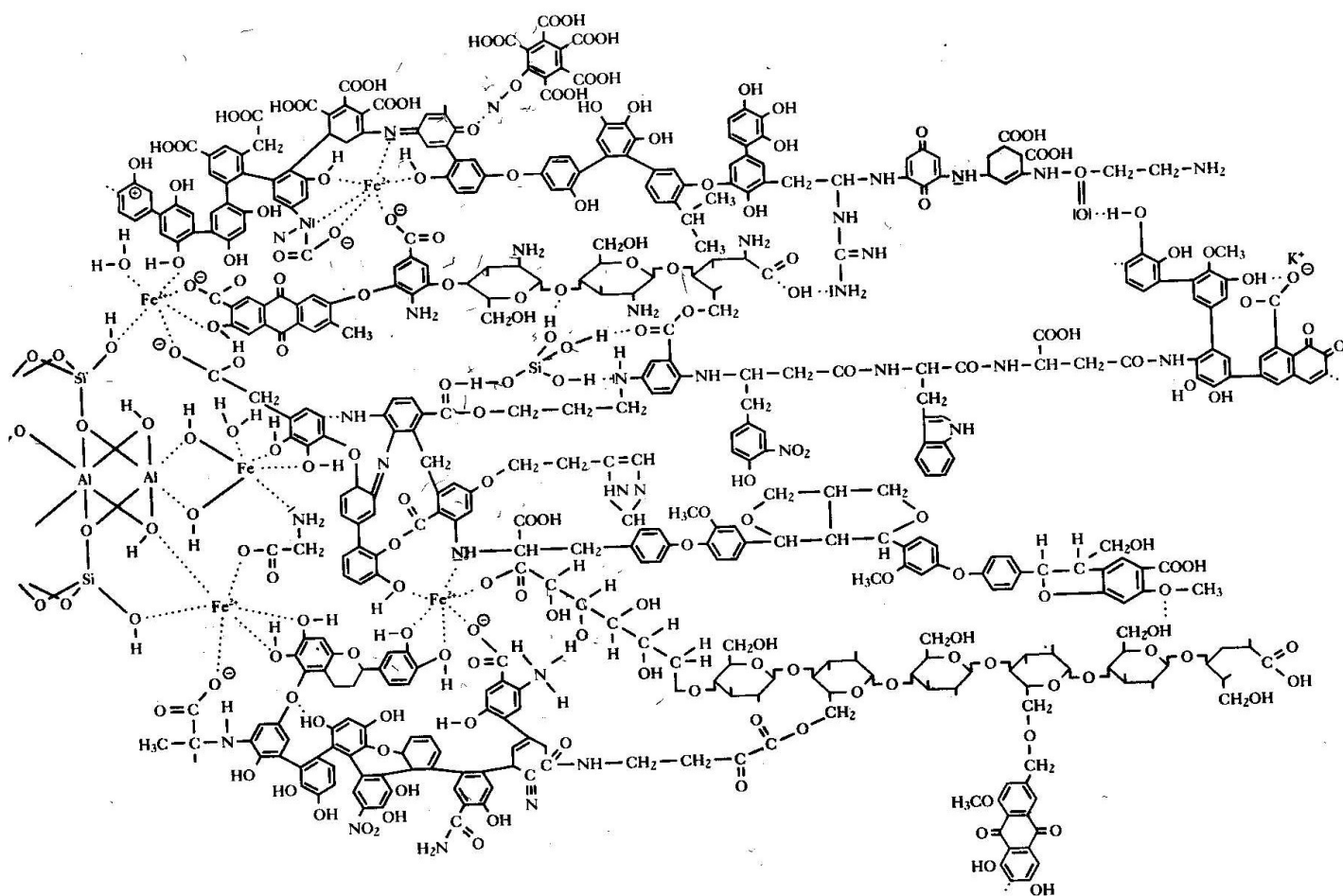
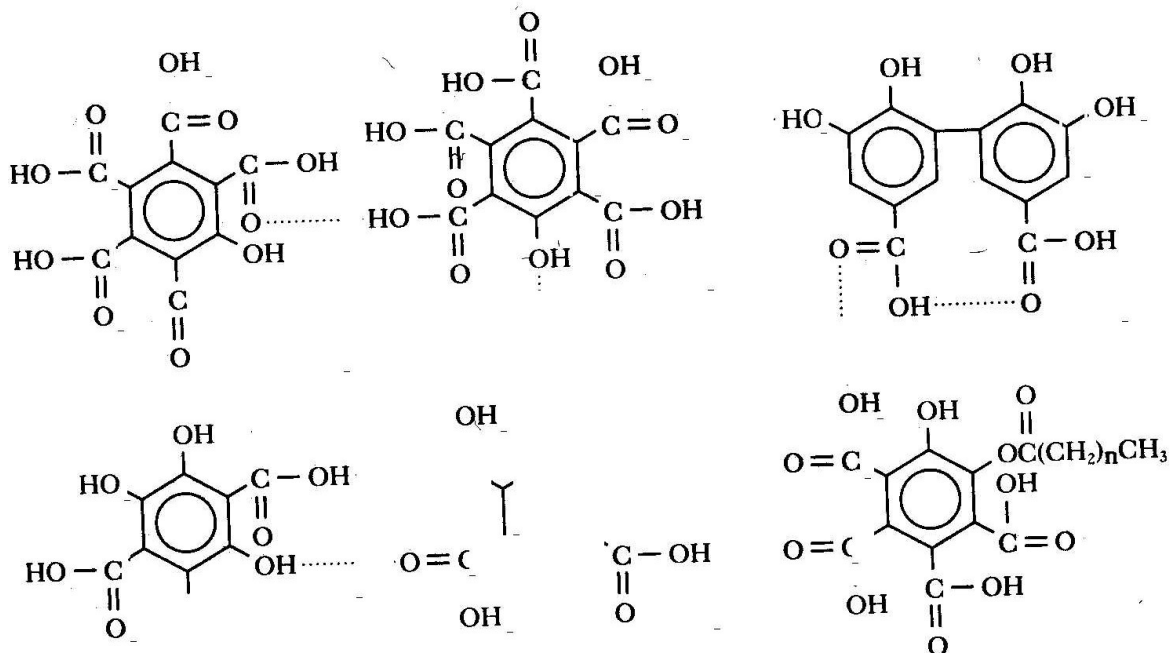


FIGURE 23.11. Major processes involved in the synthesis of humic compounds. Source: From *Geochemistry of Marine Humic Compounds*, M. A. Rashid, copyright © 1985 by Springer-Verlag, Heidelberg, Germany, p. 58. Reprinted by permission.

FIGURE 23.12. Model chemical structure of (a) a humic acid and (b) part of a fulvic acid. Source: From (a) D. Kleinhempel, reprinted with permission from *Albrecht Thaer Archiv*, vol. 16, p. 8, copyright © 1970 by Aus dem Institut für Acker- und Pflanzenbau Müncheberg der Deutschen Akademie der Landwirtschaftswissenschaften, Berlin, Germany, and (b) *Geochemistry of Marine Humic Compounds*, M. A. Rashid, copyright © 1985 by Springer-Verlag, Heidelberg, Germany, p. 75. Reprinted by permission.



(a)



(b)

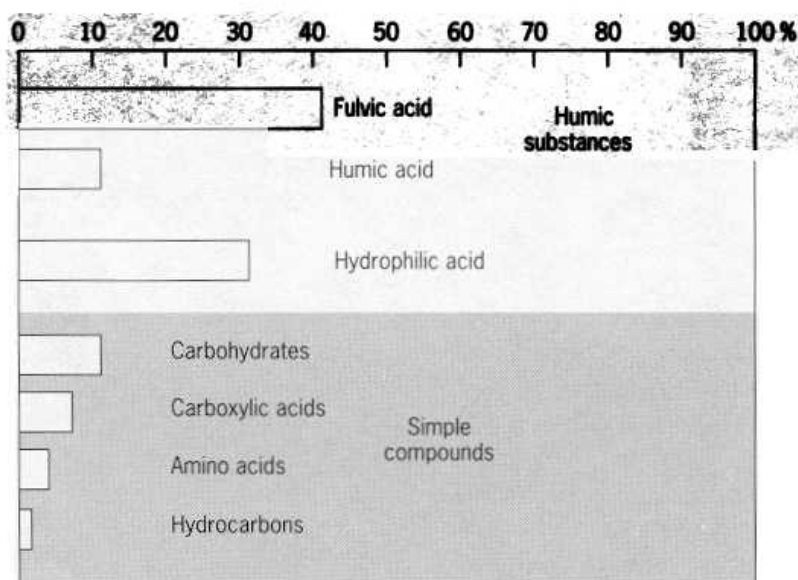


FIGURE 23.13. Composition of dissolved organic carbon in average river water with a DOC concentration of 5 mg/L. *Source:* From *Organic Geochemistry of Natural Waters*, E. M. Thurman, copyright © 1985 by Kluwer Academic Publishers, Dordrecht, The Netherlands. Reprinted by permission.

TABLE 23.5

Certain Striking Differences in the Chemical Nature and Geochemical Behavior of Marine and Soil Humic Compounds^a

<i>Marine Humic Compounds</i>	<i>Soil Humic Compounds</i>
<i>General Composition</i>	
Marine humic compounds are rich in aliphatic substances; the concentration of aliphatic carbon is almost twice that of aromatic carbon	A strong aromatic core is generally the characteristic feature of soil humic compounds; aromatic carbon is predominant in the molecule
Aromatic compounds are present but do not constitute a predominant part of the molecule; the polyphenolic and polyaromatic components are low in concentration and exhibit low degrees of substitution	Aliphatic side chains are attached to the aromatic core, but due to the participation of lignin degradation products, aromatic moieties are more abundant
Anaerobic conditions do not favor the development of highly condensed organic molecules	The molecules contain more polycyclic and polyphenolic constituents
	A high degree of oxidation leads to a high degree of condensation in humic molecules
<i>Elemental Composition</i>	
The carbon contents in fulvic and humic acids are 45–50% and 50–55%, respectively	The carbon content shows broader variations; because of the strong carbon lattice, the concentration of carbon is as high as 65%
Aquatic conditions favor greater hydrogen contents	Terrestrial humic compounds have generally low concentrations of hydrogen

TABLE 23.5 (Continued)
 Certain Striking Differences in the Chemical Nature and Geochemical Behavior of Marine and Soil Humic Compounds^a

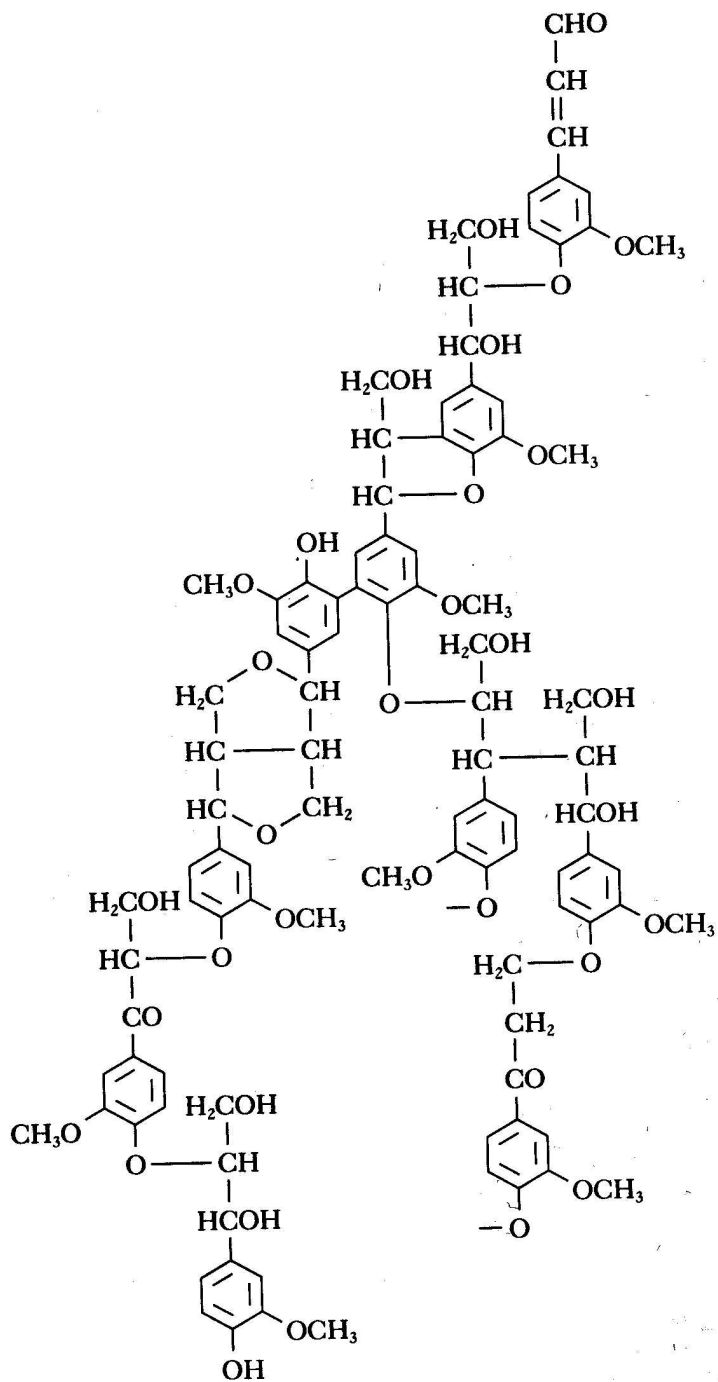
<i>Marine Humic Compounds</i>	<i>Soil Humic Compounds</i>
<i>Elemental Composition (Continued)</i>	
Marine organisms are rich in nitrogen and therefore the humic compounds originating from them contain high amounts of nitrogen; some sedimentary humic compounds contain up to ten times as much sulfur as the soil humic acids	The nitrogen content of soil humic compounds is generally low
<i>Isotopic Composition</i>	
The carbon isotopic composition of marine humic compounds is heavy; $\delta^{13}\text{C}$ values ranging from $\approx -20\text{‰}$ to -23‰	Lighter carbon isotopic composition ($\delta^{13}\text{C} = -25$ to -28‰) is characteristic of terrestrially derived humus
$\delta^{15}\text{N}$ is generally about $+9\text{‰}$ and reflects nitrate as a nitrogen source	Terrestrial plants use atmospheric nitrogen fixed by bacteria; $\delta^{15}\text{N}$ is about $+2\text{‰}$
$\delta^2\text{H}$ values do not show much spread; the average is about -105‰	The $\delta^2\text{H}$ of soil humic compounds show much broader values ranging from -50‰ to -100‰
<i>Functional Groups</i>	
The total acidity is highly variable but in general it is lower than that of soil humic matter; acidity in marine humic compounds is largely a function of carboxyl groups; the phenolic hydroxyl content is generally low; the restricted aeration of bottom sediments favors greater accumulations of carbonyl groups	Soil humic compounds generally possess higher degrees of total acidity; the acidic characteristics arise from the participation of carboxyl as well as phenolic hydroxyl groups
Alcoholic hydroxyl contents are generally high	Because of the high degree of aeration, soil humic material contains more carboxyl groups and fewer carbonyl groups
Functional groups constitute about 20–30% of the humic molecules	Alcoholic hydroxyl contents are low
	About 25% of soil humic acids and about 50–60% of a fulvic acid molecule consist of functional groups

Source: From *Geochemistry of Marine Humic Compounds*, M. A. Rashid, copyright © 1985 by Springer-Verlag, Heidelberg, Germany, p. 105. Reprinted by permission.

^aSee Chapter 29 for an explanation of δ values that are used to describe the stable isotope composition of humic substances.

highest in the coastal zone and in the surface microlayer due to the presence of large numbers of organisms.

DOM concentrations are several orders of magnitude larger than those of the POM. The high concentration of deep-water DOM suggests that this pool of organic matter is relatively refractory and hence remains in seawater. This conclusion is also supported by the advanced age of deep-water DOM as established by its ^{14}C content (6000 y at 5700 m in the north central Pacific Ocean) and the increase in its C to N ratio with increasing depth.



(a)

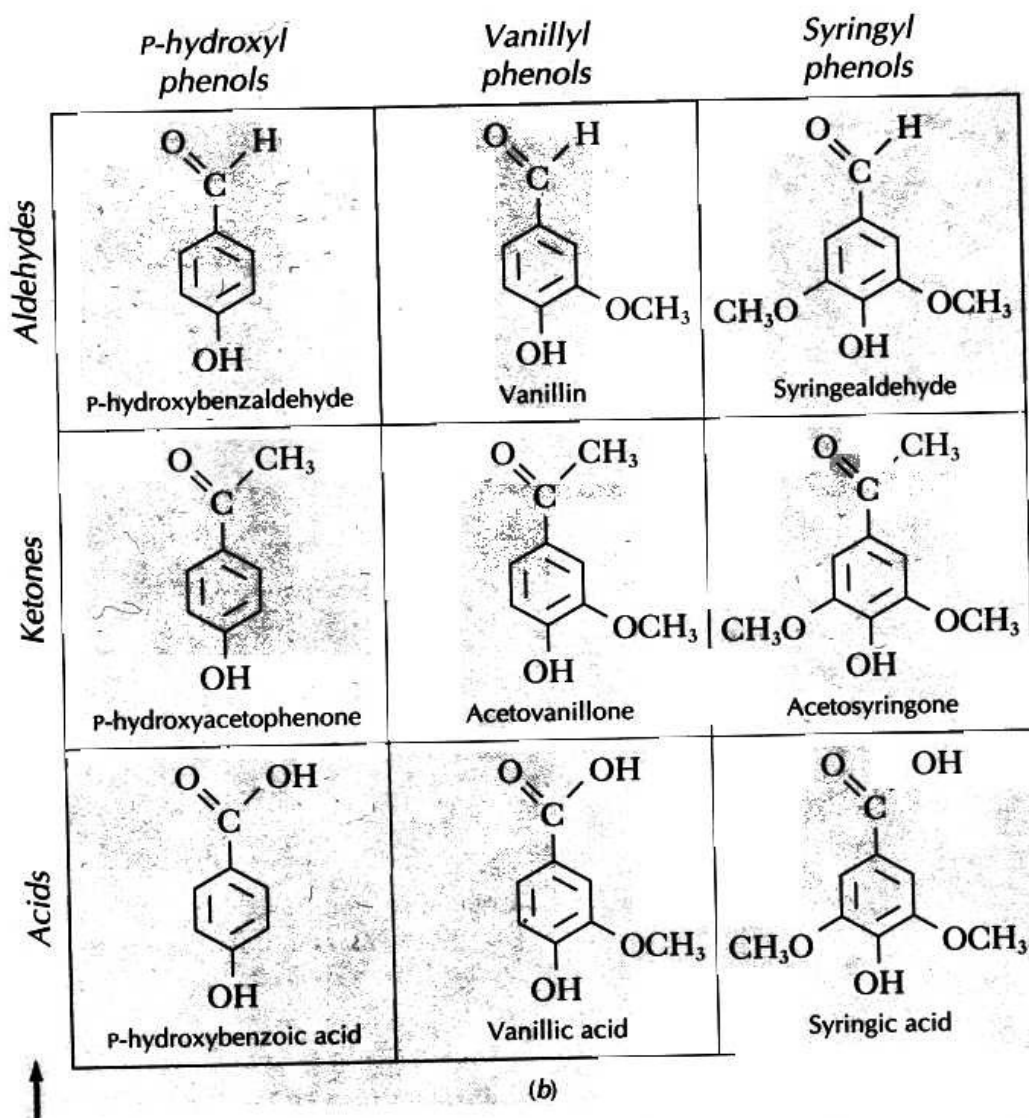


FIGURE 23.14. (a) The structure of a model lignin molecule. (b) Aromatic acids and phenols derived from lignin which are used as indicators of terrestrial plant matter. Source: From *Geochemistry of Marine Humic Compounds*, M. A. Rashid, copyright © 1985 by Springer-Verlag, Heidelberg, Germany, p. 47 (reprinted by permission); and J. I. Hedges and P. L. Parker, reprinted with permission from *Geochimica et Cosmochimica Acta*, vol. 40, p. 1021, copyright © 1976 by Pergamon Press, Elmsford, New York.

The radiocarbon age of surface-water DOM (1300 y) suggests that a significant fraction (approximately 50 percent) of this organic matter is also refractory. These "old" ages have also been observed in the surface-water humics. Thus it appears that labile DOM, produced by biological activity in the surface waters, is degraded into fragments that combine to form a large pool of relatively refractory DOM. The latter is then cycled somewhat conservatively through the ocean. As a result, deep-water DOM is not as vertically or horizontally segregated as is POM, O₂, or the nutrients.

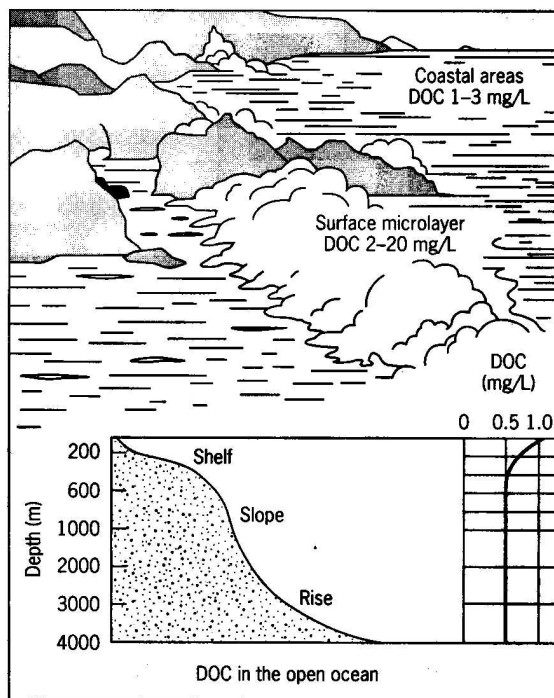


FIGURE 23.15. Dissolved organic carbon in seawater. Source: From *Organic Geochemistry of Natural Waters*, E. M. Thurman, copyright © 1985 by Kluwer Academic Publishers, Dordrecht, The Netherlands, p. 25. Reprinted by permission.

This characterization of the marine DOM cycle may have to be substantially revised in light of recent methodological developments in the measurement of DOM. Substantially higher concentrations of DOC and DON have been detected when filtered seawater is combusted at 680°C in the presence of a platinum catalyst. As shown in Figure 23.16, depth variations in these elevated concentrations correlate closely with those observed in such biologically controlled species as AOU and nitrate.

The strong correlations suggest that the "extra" DOM is biologically labile. This observation is somewhat perplexing as this same organic matter is unreactive in the standard lab procedures formerly used to measure DOM. Elemental analysis has shown that the "extra" DOM is relatively nitrogen enriched ($C/N = 6-7$) and high in molecular weight (4000–22,000 daltons). These compounds are thought to be highly cross-linked polymers derived from proteinaceous precursors by a process similar to that which produces humic substances. Diurnal variations in the concentration of this DOM suggest that the precursors are components of phytoplankton cell walls.

If this "extra" DOM truly exists, our understanding of several other major features of marine chemistry will have to be considerably revised. For example,

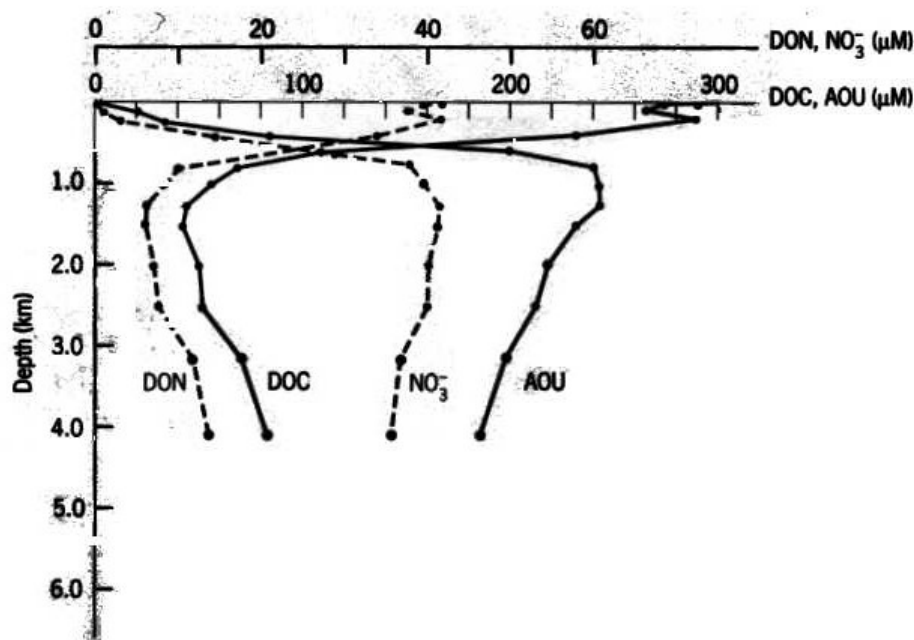


FIGURE 23.16. Depth Profiles of DOC, DON, AOU, and NO₃⁻ Concentrations at 20°N 137°E. Source: From P. M. Williams and E. R. M. Druffel, reprinted with permission from *Oceanography*, vol. 1, p. 16, copyright © 1988 by The Oceanography Society, Washington, DC. Data from Y. Sugimura and Y. Suzuki, reprinted with permission from *Marine Chemistry*, vol. 24, p. 125, copyright © 1988 by Elsevier Science Publishers, B.V., Amsterdam, The Netherlands.

if this “extra” DOM is produced from the degradation of POM that has a chemical composition close to that of detrital phytoplankton, a large pool of as-yet-undiscovered dissolved phosphorus must also be present. The vertical profiles indicate that a significant amount of this DOM is respired. Thus respiration must constitute a large sink for dissolved O₂ that has also not heretofore been detected. Due to its evidently high concentrations, this DOM could be responsible for the complexation of a large amount of dissolved metals. This has also not been considered in current models of ion speciation.

GLOBAL DISTRIBUTION OF ORGANIC CARBON

The geographic distribution of DOM, POM, and sedimentary organic carbon is closely related to that of primary production. As shown in Figure 23.17, primary production is highest in coastal waters and lowest in the open ocean. Biological activity in the coastal zone is supported by large amounts of nutrients supplied by rivers, coastal upwelling, and eddy diffusion. Because of shallow depths, coastal waters are not well stratified and hence vertical mixing is able to return regenerated nutrients to the euphotic zone. Production is lowest in the open ocean due to nutrient limitation.

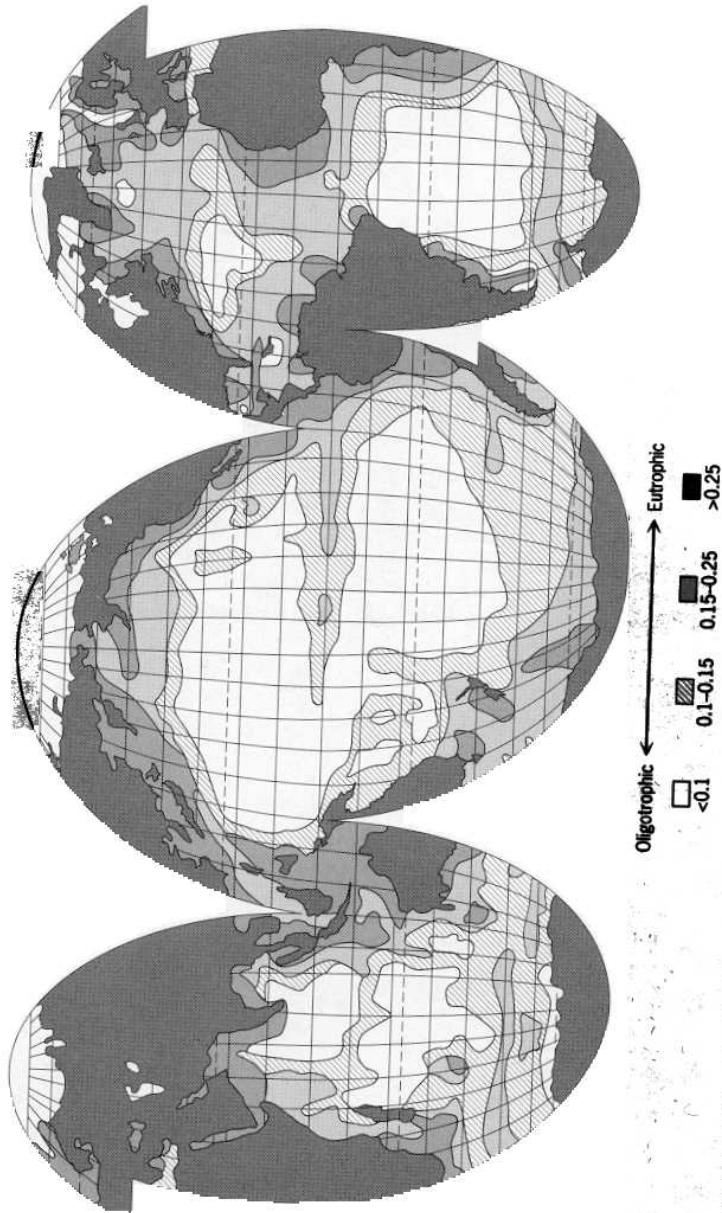


FIGURE 23.17. Distribution of photosynthetic primary productivity ($\text{g C m}^{-2} \text{d}^{-1}$). Source: From *Introductory Oceanography*, 5th ed., H. V. Thurman, copyright © 1988 by Merrill Publishing Company, Columbus, OH, p. 365. After *Scientific Exploration of the South Pacific*, O. J. Koblenz-Mishke, V. V. Volkovinsky, and J. G. Kabanova, (ed.: W. S. Wooster), copyright © 1970 by the National Academy of Sciences, Washington, DC, p. 185. Reprinted by permission.

As shown in Table 23.6, low-productivity provinces cover most of the surface area of the ocean. Despite low rates, their extensive surface areas cause the open ocean waters to support most of the organic matter production in the sea.

DOM and POM concentrations are highest in coastal upwelling areas and the lowest in the open ocean, particularly in the middle of geostrophic gyres. Because of large seasonal fluctuations in productivity, surface-water concentrations are temporally variable. Seasonal changes in the deep-water flux of large organic particles have also been observed but are relatively small compared to those in the surface waters. Due to the large concentration of refractory compounds, seasonal variations in deep-water DOM concentrations are not observed.

Because of bioturbation, benthic respiration, and slow sedimentation rates, seasonal changes in the POM flux are not well preserved in the sediments. Instead, the organic carbon composition of marine sediments reflects only long-term changes in the rates of primary production in the overlying waters. This record is somewhat altered by changes in oceanographic factors, such as water depth and redox potential, which affect the degree to which sinking POM is preserved prior to its burial in the sediments.

As shown in Figure 23.18, the organic carbon content of oceanic sediments is ≤ 1 percent by mass. In comparison, the organic carbon content in the sediments underlying coastal upwelling areas and estuaries is often greater than 10 percent. The higher organic content of these sediments reflects both higher rates of biological production in the overlying waters and the effect of a relatively short water column. The latter ensures that the sinking POM reaches the seafloor rapidly. The large supply of sinking POM also enhances preservation on the seafloor as it aids in rapid burial and creates suboxic conditions that inhibit the activities of heterotrophic organisms.

TABLE 23.6
Division of the Ocean into Provinces According to Their Level of Primary Organic Production

<i>Province</i>	<i>%Ocean</i>	<i>Area (km²)</i>	<i>Mean Productivity (g C/m²/y)</i>	<i>Total Productivity (10³ tons of C/y)</i>
Open ocean	90.0	326.0×10^6	50	16.3
Coastal zone	9.9	36.0×10^6	100	3.6
Upwelling areas	0.1	3.6×10^5	300	0.1
Total				20.0

Source: From *The Handbook of Marine Science*, vol. II, F. G. Smith and F. A. Kalber, copyright © 1974 by CRC Press, Boca Raton, FL, p. 12. Reprinted by permission.

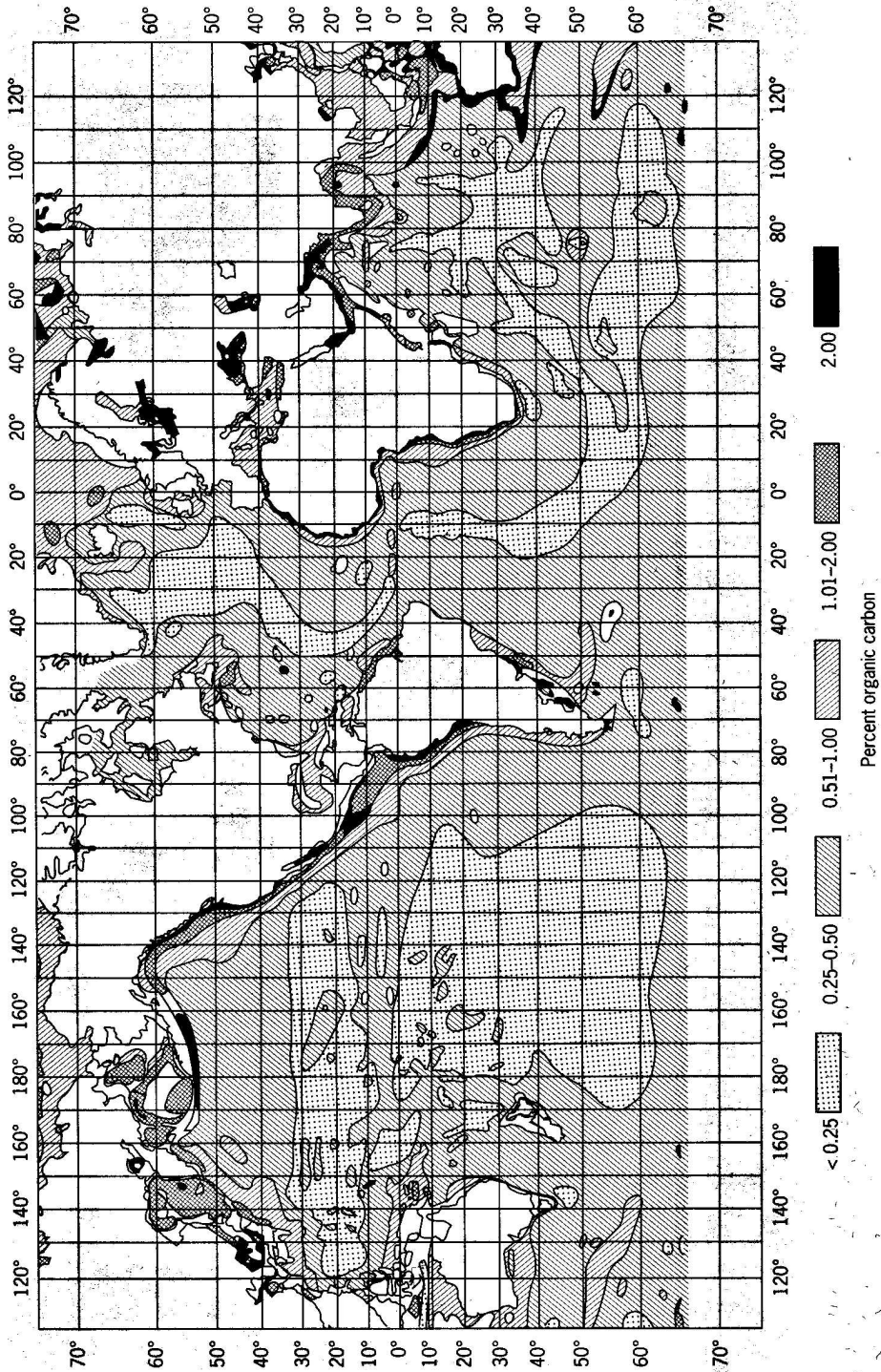


FIGURE 23.18. Distribution of organic carbon in surficial sediments of the world ocean. Source: From E. T. Premuzic, C. M. Benkovitz, J. S. Gaffney, and J. J. Walsh, reprinted with permission from *Organic Geochemistry*, vol. 4, p. 65, copyright © 1982 by Pergamon Press, Elmsford, NY.

SUMMARY

The atmospheric and riverine inputs of organic matter to the ocean are relatively small. Thus most marine organic matter is produced in situ as a result of biological activity. Though living organisms account for a small fraction of the POM, they are responsible for all of its production. Phytoplankton form the base of the marine web. The carbon that they fix is passed to higher trophic levels, though much is lost to excretion and exudation. Many marine organisms exude organic compounds in an effort to modify their environment (e.g., to repel or kill predators and competitors). Most POM is detrital and is composed of particles such as fecal pellets, dead tissues, molts, and aggregates, termed **marine snow**.

Because nitrogen-rich compounds are more labile, the C to N ratio of POM increases with depth, though its overall concentration declines. The steepest gradients coincide with the thermocline. The decomposition of the majority of the sinking POM in these depths is partially responsible for the presence of an O₂ minimum in the thermocline. Some POM is consumed and transformed into other compounds, causing mid-depth concentration maxima for select biomolecules.

A small fraction of the POM synthesized in the euphotic zone reaches the seafloor. Most is in the form of large particles, such as fecal pellets, which have fast sinking rates. The POM that reaches the seafloor is subject to extensive degradation at the sediment–water interface. This causes a decrease in its carbon and nitrogen content, as well as an increase in C to N ratio. These same trends are exhibited to a lesser degree after burial as benthic organisms continue to decompose the organic matter. As a result, the organic matter content of the sediments is usually low, ranging from 1 to 10 percent.

DOM represents the second largest pool of carbon in seawater. Most is produced by the degradation of detrital POM as it sinks through the water column. Most of this DOM is low in molecular weight and relatively labile. These compounds are rapidly assimilated by bacteria, so their concentrations are usually less than 100's µg/L. The most abundant of the low-molecular-weight compounds are polypeptides and free amino acids. The relative abundance of the various compounds reflects their susceptibility to microbial attack, which is determined by their molecular structure.

Some of these compounds combine to form complex macromolecules, termed **humic substances**. Their chemical composition is variable and tends to be unreactive. As a result, their molecular structure has not been well characterized. Those that are insoluble in acid are termed **humic acids**, while those that are soluble at all pH's are termed **fulvic acids**. Most humic substances in seawater are fulvic acids.

Humic substances are also produced in terrestrial waters as a result of similar reactions that occur between molecular fragments derived from land plants. As a result, terrestrial humics are structurally distinct from marine forms and exhibit different chemical behavior. For example, a substantial

fraction of terrestrial humic acids are removed in estuaries by precipitation reactions caused by increasing ionic strength.

In comparison to POM, DOM concentration profiles exhibit less vertical segregation. This is thought to reflect the presence of a large pool of refractory compounds that are primarily humic substances. This hypothesis may have to be modified in light of recent developments in the method by which DOM is measured. If valid, the results from this technique suggest the presence of a large and heretofore unrecognized pool of high-molecular-weight DOM that is also biologically labile.

The global distributions of POM, DOM, and sedimentary organic matter generally follow that of primary production, with highest concentrations in coastal waters and the lowest in open ocean areas, especially in the middle of geostrophic gyres. These patterns are reflected in the concentrations of organic matter in the underlying sediments. The relationship is not always direct, as other oceanographic factors, such as water depth and redox potential, also influence the degree to which POM is preserved prior to burial in the sediments.