



What happens to terrestrial organic matter in the ocean?

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Abstract—Each year rivers transport approximately 0.25×10^{15} g of dissolved ($<0.5 \mu\text{m}$) organic carbon (DOC) and 0.15×10^{15} g of particulate ($>0.5 \mu\text{m}$) organic carbon (POC) from continents to the ocean. Global discharge of riverine DOC is sufficient alone to sustain turnover of the entire pool of organic carbon dissolved in seawater. Similarly, the input of terrestrial POC by rivers is adequate to supply all the organic carbon buried in marine sediments. Because riverine organic matter consists of highly degraded, nitrogen-poor remains of terrestrial organisms, it might be expected to suffer minimal respiration in the ocean. One of the biggest mysteries in the global carbon cycle, therefore, is that only a small fraction of the organic matter dissolved in seawater and preserved in marine sediments appears to be land-derived. Either our global budgets and distribution estimates are greatly in error, or both dissolved and particulate organic matter of terrestrial origin suffer rapid and remarkably extensive remineralization at sea. Although many uncertainties remain, recent studies provide growing evidence for destruction of both dissolved and particulate terrestrial organic matter in the ocean. The mechanisms by which these huge masses of organic materials might be so rapidly oxidized following discharge are largely unknown. This report focuses on the transport and transformations of land-derived organic matter in the ocean, highlighting recent research on the patterns and processes involved. © 1997 Elsevier Science Ltd. All rights reserved

Key words—POC, DOC, terrestrial organic matter, terrestrial biomarker, river input, soil, organic matter preservation, partitioning, surface area, pollen, lignin

INTRODUCTION

The question of the fate of terrestrial organic matter (TOM) in the ocean has intrigued scientists for decades (Waksman, 1933; Bader, 1956; Handa, 1977; Deuser, 1988) and is key to understanding the global carbon cycle (Berner, 1989) and its anthropogenic perturbations (Siegenthaler and Sarmiento, 1993). TOM represents a huge source of reduced carbon (approximately 0.4×10^{15} g C yr⁻¹) to the marine environment (Schlesinger and Melack, 1981), integrates drainage basin processes, and incorporates bioactive elements whose cycling modulates the biosphere over geologic time (Meybeck, 1982; Thurman, 1985). Organic remains of terrestrial organisms preserved in marine sediments provide one of the most extensive records of life on the continents, whose continuously eroding surfaces are ephemeral over millennia and seldom preserved (Judson, 1968). Organic substances unique to land plants label continental debris from specific regions, imprinting marine deposits with information concerning proximity to continents, wind strength and other climatically-related variables (Summons, 1993). Successful environmental reconstructions and searches for fossil fuels often hinge on an under-

standing of processes controlling the distributions and destinies of TOM in fluvial/marine systems.

Many circumstances appear to favor efficient dispersion and sensitive detection of TOM in marine environments. Rivers alone discharge sufficient DOC to support the turnover of DOC throughout the ocean (Williams and Druffel, 1987) and enough POC to account for all the organic carbon now being buried in marine sediments (Berner, 1989; Hedges and Keil, 1995). Aeolian inputs of TOM are challenging to determine, but at open ocean sites appear to be comparable to the delivery rate of marine-derived organic matter to the seafloor (Zafriou *et al.*, 1985), and hence are geochemically significant (Peltzer and Gagosian, 1989). The major ultimate source of TOM is vascular plants, which are confined essentially to land and characteristically contain high concentrations of recalcitrant, nitrogen-free biomacromolecules such as lignin, tannin, suberin and cutin (de Leeuw and Largeau, 1993). These “higher” plants have distinctive stable carbon isotope compositions (Fry and Sherr, 1984) and produce a host of unique lipids (Simoneit, 1977; Peltzer and Gagosian, 1989) which can be used as sensitive biomarkers of terrestrial origin (Hedges, 1990; Prahl *et al.*, 1994). Despite its large input, relative resistance to microbial degradation and multiple biomarkers, there is surprisingly little evidence that TOM persists as a major component

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of organic mixtures in sea-water and marine sediments (Hedges and Keil, 1995). Either our global budgets and tracer methods are terribly flawed, or the ocean has remarkable means of ridding itself of TOM while preserving organic matter of planktonic origin. This geochemical conundrum will be reviewed in the following discussion, along with possible methods for its resolution.

RESERVOIRS AND FLUXES OF TERRESTRIAL ORGANIC MATTER

It is helpful to evaluate the question of the marine fate of TOM within the context of the global carbon cycle (Siegenthaler and Sarmiento, 1993; Hedges and Oades, in press). Most organic matter is stored on land within terrestrial biota (570 gigatons C; $1 \text{ Gt} = 1 \times 10^{15} \text{ g}$), plant litter (70 Gt C; Post, 1993) and surface (0–100 cm) soils (1600 Gt C; Eswaran *et al.*, 1993). Assuming that litter and biomass are compositionally similar (Huc, 1980; Goñi and Hedges, 1990a), the total inventory of above-ground terrestrial plant matter corresponds roughly to 250 Gt C in cellulose, 175 Gt lignin C, 150 Gt of C in hemicellulose and other polysaccharide, and 5–10 Gt C each in protein, lipid and cutin. The major reservoirs of reduced carbon in the ocean are organic matter dissolved in sea-water (700 Gt C) and a comparable amount of organic matter within the top meter of marine sediments (Emerson and Hedges, 1988). Relatively short-lived marine biota account for only about 3 Gt C. Overall, approximately two-thirds of all actively cycling organic carbon is stored on land and one-third in the ocean.

The 0.4 Gt of total organic carbon carried each year by rivers to the ocean (Schlesinger and Melack, 1981) corresponds to about 1% of terrestrial photosynthetic production (Siegenthaler and Sarmiento, 1993). At a global average DOC/POC ratio near 1.5 (Meybeck, 1982), rivers discharge about 0.25 Gt of DOC and 0.15 Gt of POC each year. The total riverine organic flux derives largely (approximately 60%) from forested catchments (Fig. 1), which cover over 40% of the Earth surface and export an average of $4\text{--}5 \text{ g m}^{-2} \text{ yr}^{-1}$ of DOC plus POC (Schlesinger and Melack, 1981). Tropical forests export roughly $0.12 \text{ Gt OC yr}^{-1}$, whereas temperate and boreal forests each contribute about half this flux (Schlesinger and Melack, 1981). The remaining TOM flux comes from cultivated land (approximately 15%), wetlands (approximately 15%), grasslands (approximately 5%) tundra and desert (less than 5%). Much of the organic matter borne by larger rivers appears to be soil-derived (Meybeck, 1982; Hedges *et al.*, 1986a,b) and highly degraded (Ittekkot, 1988; Hedges *et al.*, 1994). An appreciable autochthonous fraction, however, can occur in rivers that are impounded or have natu-

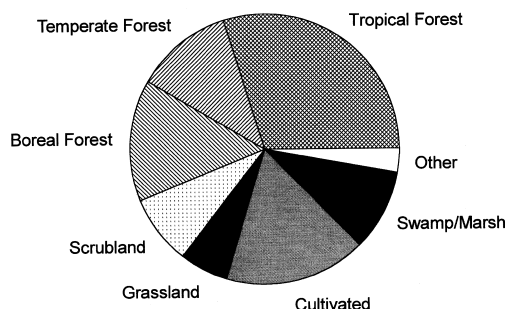


Fig. 1. Fractions of total organic carbon delivered from different watershed types of the world (from Schlesinger and Melack, 1981).

rally low turbidity (e.g. Pocklington and Tan, 1987; Jaffé *et al.*, 1995). The global atmospheric flux of TOM to the surface ocean is difficult to estimate, but may be as large as 0.1 Gt yr^{-1} (Romankevich, 1984; Zafiriou *et al.*, 1985). This input may be particularly important at open ocean sites, where vascular plant lipids are widely observed (Simoneit, 1977; Peltzer and Gagosian, 1989; Santos *et al.*, 1994).

Marine plankton photosynthesize about 50 Gt yr^{-1} of organic carbon (Siegenthaler and Sarmiento, 1993). The resulting particulate material is efficiently recycled throughout the ocean water column and at the water/sediment interface (Wakeham and Lee, 1993). DOC exuded by phytoplankton and released as a consequence of heterotrophic activity is also extremely dynamic in the surface ocean. Active cycling is indicated both by a contemporary ^{14}C content (Williams and Druffel, 1987) and by sharp concentration decreases and composition changes in the upper few hundred meters of the water column (Benner *et al.*, 1992; Peltzer and Hayward, 1996). Most marine DOC resides at about 0.5 mg l^{-1} (ppm) concentration in the deep ocean, where it has a ^{14}C content equivalent to an "age" near 6000 years (Williams and Druffel, 1987; Bauer *et al.*, 1992). Division of the total amount of DOC in sea-water by this crude residence time indicates an overall flux of DOC through the deep ocean (approximately 0.1 Gt yr^{-1}) comparable in magnitude to the global discharge of riverine DOC.

The global burial flux of total organic carbon within modern marine sediments is estimated at $0.1\text{--}0.2 \text{ Gt yr}^{-1}$ (Berner, 1989; Hedges and Keil, 1995). This rate of ultimate preservation is remarkably small (Fig. 2), accounting for roughly 0.1% of global primary production, 0.2% of marine plankton photosynthesis and less than half of the input of total TOM by rivers alone (aeolian TOM sources not included). Unless these budgets are greatly in error, at least 99.5% of marine primary production

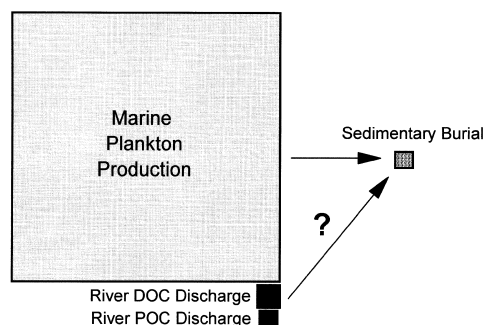


Fig. 2. Relative magnitudes of inputs and sinks of organic carbon to the ocean (from Hedges and Oades, in press). For scale, the areas illustrated for net marine plankton production and for sedimentary burial are 50 and $0.15 \text{ Gt C yr}^{-1}$, respectively. The respiration flux (not shown) is essentially equivalent to plankton production.

and 50% of TOM introduced to the ocean must be completely remineralized (oxidized to CO_2 , H_2O and nutrients). TOM losses actually must be in substantial excess of 50%, a minimum that would require all the organic matter preserved in ocean sediments to be terrigenous. In fact, isotopic and biomarker measurements indicate scant TOM in seawater (Benner *et al.*, 1992; Opsahl and Benner, 1997) or marine sediments (Emerson *et al.*, 1987). Similar characterizations show that sedimentary organic matter accumulating in deltas and along open continental margins (which together account for more than 90% of all marine OC burial; Berner, 1989) is also predominantly marine-derived (Gearing *et al.*, 1977; Hedges and Mann, 1979; Gough *et al.*, 1993). These compositional data support evidence from global mass balances for extensive and rapid destruction of TOM at sea.

COMPOSITIONAL AND MOLECULAR TRACERS OF TOM

A key requirement for defining the marine fate of TOM is to distinguish and quantify this often-small component in complex water and sedimentary mixtures. Discriminating TOM in marine settings usually boils down to identifying isotopic signatures and biochemicals characteristic of vascular plants (Hedges, 1990; Prahl *et al.*, 1994). These almost exclusively terrestrial flora have evolved a variety of physiological adaptations and structural biomacromolecules (e.g. lignin and hemicelluloses) to provide the strength needed to suspend photosynthetic tissues high in the light while exchanging water and solutes with underlying soil. Tannins, resins, cuticular waxes, cutin and suberin also occur uniquely in vascular plants (Fengel and Wegener, 1984). Although many species of nonvascular plants and microorganisms are unique to land, the biochemicals they contain usually occur in marine counterparts, minimizing their usefulness as geographic biomarkers.

Bulk compositional indicators

Vascular plants exhibit many bulk chemical and isotopic properties that distinguish them from marine organisms (Hedges, 1990). For example, the predominance of nitrogen-free biomacromolecules (e.g. lignin, tannin, hemicellulose, cellulose, cutin, and suberin) over proteins ($\text{C/N} \approx 3\text{--}4$) makes higher plant tissues characteristically carbon-rich ($\text{C/N} 20\text{--}500$) versus plankton ($\text{C/N} \approx 7$), bacteria ($\text{C/N} \approx 4$) and fungi ($\text{C/N} \approx 10$) (Hedges *et al.*, 1986a). These original distinctions, however, can be blurred substantially by the tendency of vascular plant tissues to preferentially gain nitrogen during microbial decay, and for degrading marine plankton to lose nitrogen in preference to carbon (Hedges and Oades, in press). The high aromaticity contributed by lignin and tannins also can indicate vascular land plant remains against a low background of aromatic amino acids and simple phenols in other organisms (Reuter and Perdue, 1984; Wilson, 1987).

Another characteristic bulk property of most TOM is its depletion in ^{13}C versus ^{12}C , as measured by the per mil differences ($\delta^{13}\text{C}$) between the $^{13}\text{C}/^{12}\text{C}$ ratio of a sample and standard (Faure, 1986). Most terrestrial plants, including all trees, fix carbon by the Calvin-Benson (C3) pathway and have $\delta^{13}\text{C}$ values of -28 to -25‰ , versus -22 to -19‰ for temperate marine plankton (Fry and Sherr, 1984). In contrast, C4 vascular plants (e.g. maize, sugar cane, cord grass and sea grasses) have "heavier" $\delta^{13}\text{C}$ values near -12‰ , and thus are more enriched in ^{13}C than marine plankton (Smith and Epstein, 1971; Fry and Sherr, 1984; McMillan *et al.*, 1980). Because metabolic fractionation of organic carbon is minimal ($\leq +1\text{‰}$ per trophic level), the carbon isotopic label of locally predominant plants is broadly expressed up food webs and in organic remains (Peterson and Fry, 1987; Rundel *et al.*, 1989).

Applications of stable carbon isotopes in source studies, however, include complexities on several levels. One complication is that different biochemicals in individual organisms exhibit contrasting $\delta^{13}\text{C}$ values. For example, lipids are isotopically "light" and most amino acids are "heavy", with overall ranges often on the order of $5\text{--}10\text{‰}$ (Degens, 1969; Blair *et al.*, 1985; Benner *et al.*, 1987). This internal heterogeneity can lead to confusing compositional offsets when one biochemical type is preferentially assimilated or preserved. A second problem is that equal parts of C4 and C3 plant carbon combine to yield a TOM mixture with a $\delta^{13}\text{C}$ which isotopically resembles marine plankton. Finally, marine plankton vary substantially over space and time in their stable carbon isotopic composition. It has been recognized for decades that marine plankton tend to become "lighter" at higher latitudes (Degens, 1969; Fontugne and Duplessy, 1978). What is becoming increasingly

clear, however, is that carbon isotopic compositions of marine plankton vary complexly with species, CO_2 abundance, growth rate (nutrient availability) and light intensity (e.g. Laws *et al.*, 1995; Thompson and Calvert, 1995). Short-term variations of 5‰ or more have been documented in the $\delta^{13}\text{C}$ of some coastal plankton (e.g. Gearing *et al.*, 1984; Hedges *et al.*, 1988) and kelps (Simenstad *et al.*, 1993).

Stable nitrogen, sulfur and hydrogen compositions of vascular land plants and marine plankton also can be sufficiently different to provide tracer potential (Peterson and Howarth, 1987; Rundel *et al.*, 1989). For example, seawater nitrate has a $\delta^{15}\text{N}$ of about +5 to +7‰, which is incorporated with little alteration if NO_3^- is taken up quantitatively by marine phytoplankton (Liu and Kaplan, 1989; Wada and Hattori, 1978). Fixation of N_2 ($\delta^{15}\text{N} \approx 0$) by bacteria occurs with minimal nitrogen isotopic fractionation (Hoering and Ford, 1960), resulting in organic nitrogen with a $\delta^{15}\text{N}$ near zero. Because of the prevalence of nitrogen fixation on land, "light" organic nitrogen compositions have been suggested as being typical of terrigenous origin (Peters *et al.*, 1978). Substantial variations in the $\delta^{15}\text{N}$ of marine organic materials of different origins (Altebet and Francois, 1994) and stages of degradation (Libes and Deuser, 1988), however, can compromise the use of stable nitrogen isotope compositions in source assignments.

The general relationships that (a) precipitation generally has a lower D/H than its parent water (Faure, 1986), and (b) the stable hydrogen isotope composition of organic matter parallels local precipitation (Estep and Hoering, 1980), make source distinctions based on D/H ratios feasible. It has been shown, for example, that marine versus terrestrial origins of sedimentary fatty acids and humic substances can be distinguished based upon stable hydrogen isotopic compositions (Nissenbaum, 1974; Hoering, 1974). This method is especially useful because precipitation becomes progressively depleted in deuterium as it falls from clouds passing inland and to higher altitudes (Faure, 1986). Thus, the D/H ratios of plant tissues and their sedimentary remains can reflect different source zones within larger catchments (Ziegler, 1988), in addition to indicating more general terrestrial/marine differences. One complication in D/H applications is a positive offset in the D/H of cell water in vascular plant leaves due to evapotranspiration, a process which decreases the δD difference between marine and terrestrial organic materials (Hoering, 1974). Post-photosynthetic exchange of organic hydrogens with environmental water also can be a problem (Epstein *et al.*, 1976), although the effects are minimal for intact algal cells during routine washing and drying procedures (Estep and Hoering, 1980). The full potential of stable hydrogen isotopes as in-

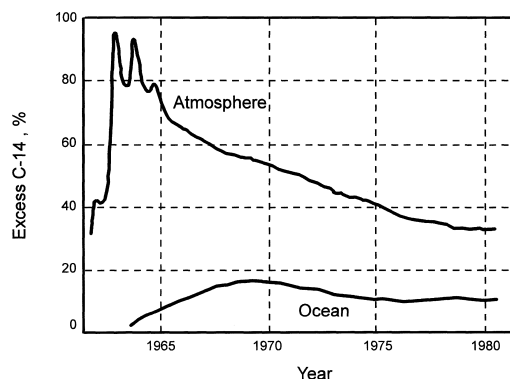


Fig. 3. Record of the $\Delta^{14}\text{C}$ of atmospheric CO_2 and oceanic DIC since atmospheric testing of thermonuclear devices (from Nydal and Lövseth, 1983).

dicators of organic province is largely untapped, especially at the molecular level.

Radiocarbon abundances have become an additional indicator of terrestrial versus marine sources since 1945 when widespread atmospheric detonation of thermonuclear devices increased the $^{14}\text{C}/^{12}\text{C}$ of atmospheric CO_2 (Fig. 3). Atmospheric activities (as measured by $\Delta^{14}\text{C}$ in ‰) reached a maximum of about twice natural levels in the mid-1960s and have since continually decreased due to exchange of atmospheric CO_2 with other carbon reservoirs (Nydal and Lövseth, 1983). Although the ocean has been one of the main sinks for bomb ^{14}C (Druffel and Suess, 1983), mixing with ^{14}C -poor dissolved inorganic carbon (DIC) has diluted this input (Fig. 3). Because the different $\Delta^{14}\text{C}$ signatures of contemporary marine DIC ($\Delta^{14}\text{C} \approx +100$ ‰) and atmospheric CO_2 ($\Delta^{14}\text{C} \approx +300$ ‰) are directly incorporated by photosynthesis, contemporary TOM can be traced into the marine environment based on its enriched ^{14}C signature (Druffel *et al.*, 1986; Bauer and Druffel, submitted). Since the advent of commercial accelerator mass spectrometry (AMS) for directly measuring ^{14}C in microgram amounts of carbonaceous materials, radiocarbon-based characterizations of DOC and POC in ocean samples have proliferated (e.g. Bauer *et al.*, 1995; Santschi *et al.*, 1995). AMS ^{14}C measurements have recently been extended to individual organic compounds isolated chromatographically from complex natural mixtures (Eglinton *et al.*, 1996).

Molecular tracers

Any biochemical that is unique to vascular plants can be used as a sensitive biomarker for TOM in general (Killops and Killops, 1993). The most commonly applied terrestrial biomarkers have been lipids, many of which can be directly extracted from natural samples and are highly source-specific and environmentally persistent. Plant-wax *n*-

alkanes, straight-chain hydrocarbons containing between 25 and 35 carbons per molecule, are among the most broadly distributed and applied terrestrial tracers. The homologues of this suite exhibit a strong predominance (factor of 5–10) of molecules containing odd, versus even, numbers of carbon atoms (Brassell and Eglinton, 1983). Plant-wax *n*-alkanes have been found in marine sediments depositing along coasts (Kennicutt *et al.*, 1987; Prahl *et al.*, 1980, 1994; Yunker *et al.*, 1993), below highly productive upwelling regions (Brassell and Eglinton, 1983; McCaffrey *et al.*, 1991) and at open ocean sites (Prahl *et al.*, 1989; Schubert and Stein, 1996). Three-ring diterpenoid hydrocarbons with 18–20 carbon atoms, and varying extents of ring aromatization, also are characteristic of some vascular land plants (McCrimble and Overton, 1969; Simoneit, 1977). These substances occur in both coastal marine (Barrick and Hedges, 1981; Yunker *et al.*, 1993) and deep-sea sediments (Simoneit, 1977), where they often co-vary in abundance with plant-wax *n*-alkanes, pollen, coal fragments, and other terrestrial-derived material. Pyrogenic aromatic hydrocarbons, various sesquiterpenes (Elias *et al.*, 1996), triterpenes, and thermally rearranged fossil hydrocarbons also have found application as indicators of terrestrial origin (Prahl and Carpenter, 1979; Barrick and Prahl, 1987; Prahl *et al.*, 1984; Yunker *et al.*, 1993).

In addition, a wide variety of oxygenated lipids have been applied as TOM tracers in marine settings. This more polar group includes straight-chain fatty acids with greater than 22 carbons and a strong predominance of molecules with even numbers of carbons. Like the plant-wax *n*-alkanes, high molecular weight *n*-fatty acids are found widely in marine deposits (Prahl *et al.*, 1989; Parrish, 1988) and are concentrated in particles sinking through the water column and accumulating in sediments (Prahl *et al.*, 1980; Wakeham *et al.*, in press-a). Diterpenoid acids also are biosynthesized in appreciable amounts only by higher plants and are useful TOM tracers (Simoneit, 1977). Other oxygenated lipids characteristic of vascular land plant sources include long-chain ($> C_{24}$) *n*-aldehydes (Prahl and Pinto, 1987) and *n*-alcohols (Peltzer and Gagosian, 1989; McCaffrey *et al.*, 1991), 3-oxytriterpenoid compounds such as α - and β -amyrin (Brassell and Eglinton, 1983) and possibly some C_{29} sterols (Wakeham *et al.*, in press-b). Series of ω -oxycarboxylic acids and mid-chain ketocarboxylic acids in marine aerosols appear to result from photolysis of unsaturated lipids (Kawamura *et al.*, 1996) and thus are useful indicators of atmospheric input of terrestrial- and marine-derived materials (Kawamura *et al.*, 1990). A major challenge for the future will be to apply the great diversity and source specificity of lipids to more quantitatively

constrain distributions of terrigenous organic materials in marine waters and sediments.

Two commonly employed non-lipid tracers of TOM in marine settings are methoxylated phenols derived from lignin (Sarkanen and Ludwig, 1971) and internally hydroxylated *n*-C₁₆ and *n*-C₁₈ carboxylic acids, which largely compose cutin (Stark *et al.*, 1989). Both types of tracers must be destructively released from the parent biomacromolecules by hydrolysis, pyrolysis or oxidation (Sjöström, 1981; Kolattukudy, 1980). Lignin and cutin occur abundantly in many vascular plant tissues and are relatively resistant to microbial degradation. In addition, their structural units are produced in extensive suites whose individual constituents carry “embedded” information about the type of plants and tissues from which they are formed (Goñi *et al.*, 1993; Goñi and Hedges, 1990a,b). For example, syringyl phenols and trihydroxy *n*-C₁₈ acids are derived uniquely from angiosperms, whereas cinnamyl phenols and cutin acids characterize nonwoody vascular plant tissues. In addition, elevated acid/aldehyde ratios among lignin-derived phenolic monomers and dimers reflect the extent of some types of fungal degradation (Goñi *et al.*, 1993; Nelson *et al.*, 1995). Lignin phenols have now been measured among the basic CuO reaction products of estuarine (Louchouart *et al.*, in press), coastal (Hedges and Mann, 1979; Prahl, 1985; Prahl *et al.*, 1994) and deep-sea sediments (Gough *et al.*, 1993). Similar methods have been used to trace TOM dissolved in coastal marine (Moran *et al.*, 1991a,b) and open-ocean waters (Meyers-Schulte and Hedges, 1986; Opsahl and Benner, 1997). Both lignin and cutin produce CuO reaction products that can be analyzed simultaneously as complementary terrestrial tracers (Gough *et al.*, 1993; Opsahl and Benner, 1995).

A general consideration in applications of bulk properties versus biomarkers in source studies is that each of these two fundamental approaches has intrinsic strengths and weaknesses. Bulk measurements such as of C/N, spectral properties and stable isotopic compositions, are feasible for major constituents of organic mixtures, among which they usually are comparably sensitive. Bulk techniques, however, often yield limited information and are not particularly sensitive to trace components or shared properties (Hedges, 1990). In contrast, a biomarker that occurs at a known concentration in only one component of a natural mixture can be used to quantify that source with exquisite sensitivity. Common problems here, however, are that biomarker concentrations in different fresh plant materials can be variable and also are susceptible to alteration by selective degradation (Hedges and Prahl, 1993). Multiple bulk chemical characteristics and molecular tracers can be combined, however,

to maximize the potential for accurate source assessments (e.g. Prahl *et al.*, 1994).

DETERMINING TOM CONCENTRATIONS AND FATES IN THE OCEAN

Rather than attempting a comprehensive review of the literature on TOM in the ocean, we will address two questions: (a) "What is our present understanding of the types, quantities and dynamics of terrestrial organic matter in the World Ocean?" and (b) "How might new methods be applied to improve this knowledge?" This discussion will highlight recent research on dissolved TOM in the ocean and on particulate TOM off the well-studied Washington and northern Brazil coasts. We will begin with dissolved TOM, whose physical pathways are often more evident than for particulate matter.

Dissolved TOM

Approaches that might be applied to characterize TOM dissolved in sea-water must be consistent with compositions and concentrations measured in rivers, as well as with expected dispersal patterns of this material in the ocean. To address the fundamental question of what dissolved TOM looks like, the Amazon provides an excellent reference point. This largest of all rivers supplies 20% of the total freshwater discharge to the ocean (Richey *et al.*, 1990). It also is representative of tropical rivers and rivers draining forested catchments, the two predominant types of terrestrial watersheds in terms of TOC (total organic carbon) discharge (Fig. 1). In addition, the TOC content (approximately 9 mg l⁻¹), DOC/POC ratio (approximately 1.8) and suspended sediment (approximately 200 mg l⁻¹) load of the lower Amazon mainstem (Richey *et al.*, 1986, 1990) are near global averages for large rivers (Meybeck, 1982). The Amazon is now one of the most intensively studied rivers in the world (Richey *et al.*, 1990), and discharges into one of the most comprehensively defined coastal sedimentary zones (Nittrouer and Demaster, 1996).

Because of their comprehensive scope, bulk chemical measurements are good starting points for surveys of TOM in the ocean. DOM isolates from

river water and open ocean seawater are distinctly different in almost all measured bulk properties (Table 1). Only 20–35% of oceanic DOC is recovered by ultrafiltration with 1000-Dalton membrane (Benner *et al.*, 1992; Benner *et al.*, in press), whereas about 70% of the higher molecular weight DOM in the lower Amazon can be isolated by the identical procedure (Benner and Hedges, 1993). The atomic C/N of Amazon DOM (approximately 35) is roughly twice the ratio (15–20) of open ocean DOM (Hedges *et al.*, 1994; Benner *et al.*, 1992; Benner *et al.*, in press), as is its aromaticity (Table 1). As expected from the predominance of forests in its basin, DOM in the Amazon River exhibits quite negative $\delta^{13}\text{C}$ values near -29‰ (Hedges *et al.*, 1994). In comparison, values between -21 and -22‰ are typical of seawater DOM (Williams and Gordon, 1970; Benner *et al.*, 1997). The $\Delta^{14}\text{C}$ values measured for Amazon River DOM are strikingly higher (approximately +250‰) than for DOM in contemporary surface (-200 to -250‰) and deep (-500 to -550‰) ocean waters (Bauer *et al.*, 1992). $\delta^{15}\text{N}$ values near +8‰ are typical of DOM isolated by ultrafiltration from the surface and deep Pacific Ocean (Benner *et al.*, 1997), whereas Amazon counterparts have values of about +4‰ (Benner, unpublished data).

These extreme differences in bulk properties indicate that riverine and sea-water DOM likely do not share a common origin. The broad isotopic contrasts are particularly telling because of their relative insensitivity to chemical and biological alterations. Moreover, all the above contrasts are in the direction, and often to the extent, expected for direct derivation of riverine DOM from local C3 land plants and of sea-water DOM from marine plankton.

In order to obtain sufficient sensitivity to make crude estimates of the fraction of terrestrial matter in the marine DOM pool, a molecular tracer unique to land and representative of the bulk TOM component is needed. Methoxylated phenols produced degradatively from lignin structural units in TOM often have been applied to this task because these characteristic compounds are yielded in amounts and patterns which reflect their vascular plant

Table 1. Comparative bulk chemical properties (means \pm standard deviations) of dissolved organic matter (DOM) from the Amazon River and surface and deep seawater

DOM sample	Depth, m	Recovery, %	(C/N) ^a	$\Delta^{14}\text{C}$, ‰	$\delta^{13}\text{C}$, ‰	$\delta^{15}\text{N}$, ‰	C = C, %
Amazon (Obidos)	< 10	73 \pm 3 ^a	34 ^b	+265 ^c	-29.2 ^b	+4.0 ^d	31 ^e
Surface ocean	< 25	30 \pm 5 ^f	16.5 \pm 0.7 ^f	-263 \pm 23 ^g	-21.7 \pm 0.2 ^f	+7.9 \pm 0.8 ^f	7 ^h
Deep ocean	> 2400	22 \pm 1 ^f	18.6 \pm 0.6 ^f	-546 \pm 14 ^g	-21.7 \pm 0.3 ^f	+8.1 \pm 0.6 ^f	19 ^h

Abbreviations and symbols: Recovery, the percentage of total DOC in the sample recovered as a powder after isolation with a 1000-Dalton ultrafilter; (C/N)^a, the atomic carbon to nitrogen ratio; $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$; the per mil variations of $^{14}\text{C}/^{12}\text{C}$, $^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$ ratios versus corresponding isotopic standards; C = C, the percentage of total carbon in the sample that is unsaturated based on ^{13}C NMR analysis. Standard deviation intervals are not given for individual analyses (typically from the Amazon River at Obidos). Details can be found in the indicated references: ^aBenner and Hedges (1993), ^bHedges *et al.* (1994), ^cHedges *et al.* (1986b), ^dBenner, unpublished data, ^eHedges *et al.* (1992), ^fBenner *et al.* (1997), ^gBauer personal communication, and ^hBenner *et al.* (1992).

sources (Ertel *et al.*, 1984; Ertel and Hedges, 1984; Ertel *et al.*, 1986). For example, lignin-derived phenols such as vanillin and vanillic acid were detected among the CuO reaction products of humic substances isolated by adsorption onto XAD resin from sea-water collected near the surface of the East Equatorial Pacific ocean (Meyers-Schulte and Hedges, 1986). Vanillyl phenol yields averaging approximately 0.15 mg per 100 mg OC were measured, along with elevated weight ratios of vanillic acid to vanillin (1–2) indicative of highly altered lignin. Comparison to an average yield of 1.2 mg 100 mg OC⁻¹ for humic substances similarly isolated from the Amazon mainstem (Ertel *et al.*, 1986), indicated that less than 10% of the humic material isolated from the surface Equatorial Pacific is terrestrially derived. However the efficiency and selectivity with which these “marine humic substances” were isolated were unclear, and only one region in the Pacific Ocean was sampled.

Opsahl and Benner (1997) have just completed a more comprehensive survey of CuO reaction products from DOM in the World Ocean. The sample set includes five surface (0–100 m) waters and six deeper (200–4000 m) samples from the central Equatorial Pacific, as well as a three-depth profile (1–2400 μ m) taken in the north Atlantic off Bermuda. DOM was isolated by ultrafiltration with 1000 Dalton membranes, a method that is milder and more representative than the conventional XAD procedure (Benner *et al.*, 1992). Lignin-derived phenols were sensitively measured by selective ion monitoring of mass spectral traces. Syringyl phenols were detected for the first time in pelagic seawater, indicating the presence of angiosperm-derived lignin. The volume-normalized yields of lignin phenols measured in the open Atlantic (25–30 ng l⁻¹) agreed with a value near 50 ng l⁻¹ determined by Moran *et al.* (1991b) for Gulf Stream seawater. Opsahl and Benner compared these water results to an average yield (approximately 900 μ g 100 mg OC⁻¹) obtained for the lower Amazon and Mississippi Rivers to calculate that 0.2–0.7% of the DOM in the Pacific, and 0.5–2.4% of the DOM in the Atlantic, is terrestrial.

A key finding of Opsahl and Benner's survey is that distinctly higher lignin phenol yields are obtained from waters of the Atlantic (25–30 ng l⁻¹) than the Pacific (5–15 ng l⁻¹). This observation is consistent with the 3.6-fold higher input of river water to the Atlantic on a volume/volume basis. The measured ocean inventories of dissolved lignin were divided by the corresponding lignin discharge rates from rivers to calculate mean residence times for dissolved TOM in both the Atlantic and Pacific Oceans. These average cycling times (20–150 years) are short in comparison to the 500–1000 year mixing rate of the World Ocean (Stuiver *et al.*, 1983). These within-ocean gradients and calculated short

cycling times both indicate that riverine DOM is removed rapidly and efficiently from the ocean.

In spite of this evidence for rapid turnover in the ocean, most studies of the dynamics of TOM along continental margins have not demonstrated pronounced removal on the annual and shorter time scales of estuarine mixing or offshore advection. For example, dissolved TOM mixes almost conservatively in many estuaries (e.g. Mantoura and Woodward, 1983). Fox (1991) estimated an average of 20% of riverine DOC removal in estuaries, with a wide range of 4–60% that depends partly on the type of discharged organic matter. Although many studies indicate that the “humic acid” component of river water is subject to more extensive removal in estuaries (e.g. Sholkovitz, 1976; Fox, 1991), this relatively hydrophobic material usually accounts for a minor fraction of total riverine DOC (Fox, 1983; Ertel *et al.*, 1986).

Attempts to trace riverine organic matter in offshore coastal zones with spectral (Blough *et al.*, 1993; Muller-Karger *et al.*, 1988), isotopic (Santschi *et al.*, 1995; Bauer and Druffel, submitted; Bauer *et al.*, in press) and molecular (Pempkowiak and Pocklington, 1983; Moran *et al.*, 1991a,b) tracers have demonstrated pronounced mixing gradients and high short-term variability (e.g. Moran *et al.*, 1991b). These studies, however, have not provided clear evidence of pronounced TOM removal as indicated by nonconservative concentration variations with salinity. Slow photolysis (Mopper *et al.*, 1991; Miller and Zepp, 1995; Amon and Benner, 1996a) and microbial degradation (Benner *et al.*, 1995; Amon and Benner, 1996b) are both likely removal mechanisms for dissolved TOM, but are difficult to discern in dynamic coastal and surface ocean waters. Concentration gradients that would document ongoing removal of dissolved TOM have not, as yet, been systematically measured along constrained flow paths.

Particulate TOM

Due in part to the ease with which large samples of sediment can be collected and analyzed, there have been many studies of the distribution of particulate TOM in marine deposits (Hedges, 1992; Prahl *et al.*, 1994). As previously discussed, stable carbon isotope compositions have been the measurement of choice for estimating TOM distribution patterns in modern (Sackett and Thompson, 1963; Gearing *et al.*, 1977) and ancient (Rogers and Koons, 1969; Newman *et al.*, 1973) marine sediments. Surveys of deltas and adjacent coastal zones often indicate sharp offshore increases in $\delta^{13}\text{C}$ from values typical of local rivers (–25‰ to –28‰) toward “heavier” values similar to local marine plankton (–19‰ to –22‰) in temperate waters. Even under favorable circumstances of extensive local surveys, the average $\delta^{13}\text{C}$ values of river- and

marine-derived organic matter in a coastal zone are usually uncertain within at least $\pm 0.5\%$, making it difficult to discern less than 10% of carbon from either source within the 5–7‰ mixing range (Hedges, 1990). Surveys on larger space scales become increasingly uncertain owing to multiple TOM sources. This sensitivity limitation is a major impediment to meaningful regional surveys of TOM, which typically accounts for less than half of the total organic carbon in most marine sediments (Gearing *et al.*, 1977; Prahl *et al.*, 1994).

The uncertainty in estimating mixing endmembers and compositions by a single bulk property, such as stable isotope composition, often can be reduced by applying a second comprehensive measurement. For example, C/N is easily determined in elemental analyses and usually is higher for TOM than marine plankton remains. Kennicutt *et al.* (1987) observed generally higher C/N ratios at more negative $\delta^{13}\text{C}$ values, indicating increased percentages of riverine material in Orinoco delta sediments. Although this relationship substantiated a mixing phenomenon, samples with apparently marine $\delta^{13}\text{C}$ values near -22% had C/N ratios near 10 (versus about 7 for plankton) and a wide C/N ratio range of 15–30 was observed for “terrestrial” samples with $\delta^{13}\text{C}$ values near -28% . Pillon *et al.* (1986) also demonstrated parallel increases in C/N, plant-wax *n*-alkanes and fatty acids with increasing grain size in sediments from the Mahakam delta. In a systematic comparison, Prahl *et al.* (1994) found that C/N increased with other bulk and molecular indicators of TOM in sediments off the Washington coast. Direct comparisons in this study to the elemental compositions of organic matter in sediments of the upper Columbia River, however, indicated preferential loss of N versus C from riverine organic matter following discharge. Elemental compositions of TOM, therefore, are sensitive to diagenetic alteration both before and after introduction to the marine environment.

Alternatively, a bulk chemical property can be matched with a biomarker in mixture analysis, taking advantage of the strong points of both methods. This combined approach has now been used in measurements of lignin phenols with stable carbon isotopes (Hedges and Mann, 1979) and N/C (Hedges *et al.*, 1988), and in correlations of $\delta^{13}\text{C}$ with various lipid tracers (Kennicutt *et al.*, 1987; Jasper and Gagosian, 1990). An example of this general approach is illustrated in a plot of lignin phenol yield versus $\delta^{13}\text{C}$ for surface sediments from the Washington State continental margin (Fig. 4). For these sediments, $\delta^{13}\text{C}$ decreases systematically with increasing carbon-normalized lignin phenol yield (Λ). This trend would be expected for increasing amounts of TOM mixed with lignin-free marine plankton remains (Hedges and Mann, 1979). Extrapolation of the correlation line to $\Lambda = 0$ indi-

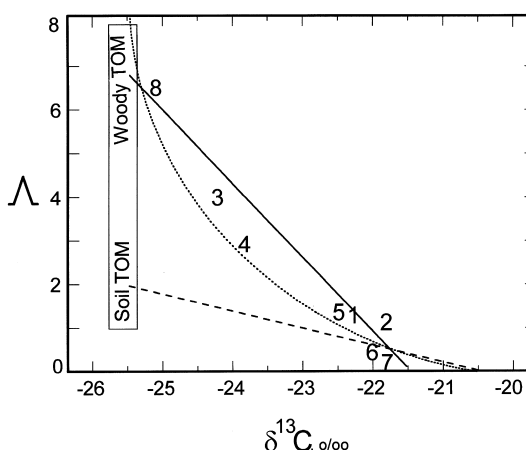


Fig. 4. $\delta^{13}\text{C}$ versus total lignin phenol yield (Λ , mg phenol per 100 mg OC) from surface (0–5 cm) marine sediments of the Washington coast (Hedges and Mann, 1979). Numbers indicate compositional points for individual sediment samples (identified as in the original paper). The solid mixing line corresponds to that initially fitted to data for all eight sediments. The dashed line indicates a possible alternative mixing line that might apply to more offshore samples containing TOM of predominantly soil origin, also mixed with marine plankton (see pivotal paper by Prahl *et al.*, 1994). The dotted curve illustrates the type of compositional trend that might correspond to a ternary mixture of plankton remains with both woody and soil-derived TOM, which becomes more woody in coarser near-shore sediments. The range of Λ values illustrated for woody and soil-derived TOM in this region is based on values measured by Hedges and Mann (1979), Hedges *et al.* (1984) and Ertel and Hedges (1984).

cates an average $\delta^{13}\text{C}$ near -21.5% for local plankton remains (Fig. 4). The correlation line also can be extrapolated to the average $\delta^{13}\text{C}$ of particulate material in the Columbia River (-25.5%) to estimate that TOM in the coastal deposits has a Λ near 7, as is typical of gymnosperm woods (Hedges and Mann, 1979). Once these two endmembers have been, thus, established, the percentage of TOM in each sediment can be approximated by the position of its composition point along the mixing line. Based on this approach, Sample 8 depositing in sands near the mouth of the Columbia River contains more than 90% TOM, whereas Samples 6 and 7 from the silts and clays on the outer shelf and slope appear to include less than 10% terrestrial carbon.

Not all biomarkers, however, give similar estimates of TOM distribution in this region. For example, Prahl and Muehlhausen (1989) compared the average concentrations of high molecular weight *n*-alkanes of vascular plant origin in sediments from the Columbia River with corresponding levels in sediments from the Washington continental margin. Plant-wax *n*-alkane concentrations indicate substantially higher percentages of TOM (20–50%) on the outer continental shelf and slope than obtained from the Λ versus $\delta^{13}\text{C}$ plot in Fig. 4. Prahl *et al.*

(1994) extrapolated a linear decrease in carbon-normalized plant-wax *n*-alkane concentrations with increasing $\delta^{13}\text{C}$ values to estimate that the marine component of organic matter in Washington coastal sediments has a $\delta^{13}\text{C}$ in the vicinity of -20‰ , over 1‰ "heavier" than the lignin-based extrapolation in Fig. 4. How can these estimates be so different, and which parameter(s) are "telling the truth?"

To answer this question it is necessary to reconsider the assumed homogeneity of organic material in these sediments. TOM in the Columbia River and adjacent coastal sediments varies greatly in size and composition from coarse woody material deposited with sands (Harmon, 1972) to nonwoody debris and lipids concentrated in silts and clays of soil origin (Hedges *et al.*, 1984; Prahl, 1985; Prahl *et al.*, 1994). Figure 5 shows a plot of atomic N/C versus $\delta^{13}\text{C}$ for size and density fractions isolated from five Washington coast sediments (Keil *et al.*, 1994). The divergent trend lines in Fig. 5 indicate two distinct types of TOM. The lower correlation line corresponds to sandy samples and trends from a nitrogen-rich "plankton" composition ($\text{N/C} \approx 0.10$, $\delta^{13}\text{C} \approx -20$ to -22‰) toward a nitrogen-poor ($\text{N/C} \approx 0.02$) composition typified by isotopically "light" ($\delta^{13}\text{C} \approx -25$ to -26‰) woody debris (S_0) separated from these samples. The upper trend line is represented by clays and runs from near the same plankton compositional range toward a second terrestrial endmember having a similarly "light" $\delta^{13}\text{C}$, but with an N/C only slightly lower than for plankton remains.

The TOM causing this second trend appears to be nitrogen-rich soil organic matter ($\text{C/N} \approx 12$) similar to that occurring in fine-grain sediments in the Columbia River basin (Hedges *et al.*, 1984; Prahl *et al.*, 1994). This organic matter contains characteristically low concentrations of highly degraded lignin (Prahl *et al.*, 1994; Keil *et al.*, in

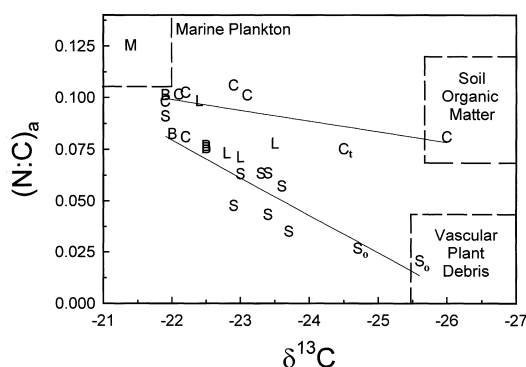


Fig. 5. Atomic N/C ratio versus stable carbon isotopic composition ($\delta^{13}\text{C}$, ‰) of organic matter in size and density fractions isolated from Washington coast sediments (Keil *et al.*, 1994). M is marine material, B is bulk sediment, C is clay-, L is silt- and S is sand-sized sediment. Subscript t is high density ($\rho > 2.6$) fraction and subscript o is low density ($\rho < 1.5$) fraction.

press), characteristics which are typical of soils (Ertel and Hedges, 1984; Hedges *et al.*, 1986a) and become more strongly expressed in smaller particle size fractions of coastal sediments (Fig. 6). This soil organic matter is not separable from dense inorganic particles by hydrodynamic sorting or flotation with heavy liquids and thus appears to be strongly sorbed to mineral grains (Keil *et al.*, 1994). The compositional range of these two major TOM components can be represented by a rectangle extending (at $\delta^{13}\text{C} \approx -25.5 \pm 0.5\text{‰}$) from Λ values of 6–8 for coarse woody debris, down to values of 1–4 for soil organic matter associated with fine-grained minerals (Ertel and Hedges, 1984; Prahl *et al.*, 1994). Which TOM endmember composition is most appropriate for describing samples from this region depends largely upon whether most of the analyzed sediments are wood-rich nearshore sands or offshore silts and clays containing soil organic matter. The most appropriate mixing line for the entire suite of samples may actually be a curve that is bowed down in the center (Fig. 4) and extends asymptotically toward poorly constrained $\delta^{13}\text{C}$ and Λ endmember values.

Another example of the type of complication that can arise in TOM source assessment is evident from contrasting organic distributions among particle size classes (Keil *et al.*, in press). It has been observed (Hedges and Mann, 1979; Prahl, 1985) that finer-grain sediments depositing on the Washington continental slope give elevated yields of cinnamyl versus vanillyl phenols ($\text{C/V} > 0.2$). This pattern has been taken as evidence for selective transport and preservation in offshore regions of

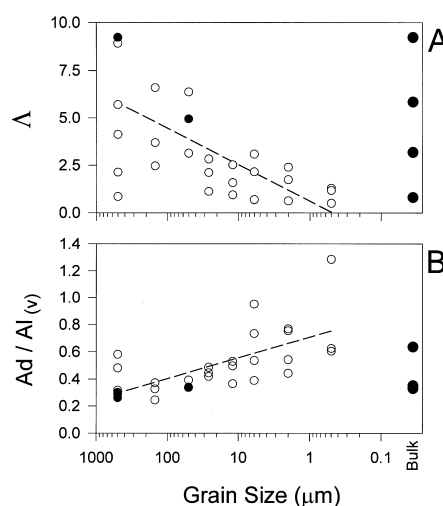


Fig. 6. Trends in (A) total lignin phenol yield (Λ , mg phenol per 100 mg OC) and (B) vanillic acid/vanillin ratios for different size fractions of Washington coast sediments (Keil *et al.*, in press). Filled circles represent distinct organic debris isolated by density fractionation, whereas the filled circles to the right indicate measurements for bulk (unfractionated) sediments.

nonwoody vascular plant tissues, which characteristically produce cinnamyl phenols (Hedges and Mann, 1979; Prahl and Carpenter, 1983). Analyses across the size spectrum of particles in the same Washington coast sediments, however, indicate pronounced maxima in pollen counts and the ratio of *p*-coumaric acid to ferulic acid (Cad/Fad \approx 10) within the 40–100 μm size range (Fig. 7). Local pollen typically gives high Cad/Fad ratios of 10–50 (Hedges, unpublished data) and alone can account for most of the increase of C/V in the more offshore sediments. In this case a third discrete particle type (in addition to woody debris and soil organic matter) contributes toward TOM compositional trends within a narrow size range.

Lipid analyses in sediments from the Washington State region provide independent evidence for other discrete particle types. These carriers include shales containing thermally rearranged *n*-alkanes, coals transporting fossil diterpenoid hydrocarbons and soot or charcoal with associated polynuclear aromatic hydrocarbons (Barrick and Hedges, 1981; Barrick *et al.*, 1984; Prahl and Carpenter, 1983, 1984; Prahl, 1985). Although some of these phases do not contribute strongly to bulk organic carbon, they may be major carriers of fossil, anthropogenic or harmful substances. Clearly, a wide variety of molecular tracers and bulk chemical properties need to be measured across multiple particle size ranges to comprehensively characterize and quantify TOM in marine sediments (e.g. Prahl *et al.*, 1994).

The close association of sedimentary organic matter with clastic mineral grains in rivers and along many continental margins can provide an aid in the daunting task of defining the marine fate of TOM. An example of this application can be drawn from a comparison of organic carbon content/surface area (OC/SA, mg OC per m^2) relationships for suspended particulate material from a number of rivers (Amazon, Mississippi, Columbia, Huange-He,

Johnstone, Sacramento and Fly) and their corresponding deltas (Keil *et al.*, 1997a). Suspended sediments from the Amazon (Fig. 8) and other rivers exhibit strong direct correlations of %OC with SA. The OC/SA ratio of these riverine particles corresponds to organic loading of 0.5–1.0 mg OC m^{-2} that are within the range for most coastal marine areas outside deltas (Mayer, 1994a,b; Keil *et al.*, 1994). Sedimentary particles of corresponding size from the Amazon delta (e.g. Figure 8) and deltas of the other rivers also exhibit a linear OC/SA, but at about half to a third of the total surface loadings typical of these minerals before discharge. The stable carbon isotope compositions of the different samples vary from locally representative terrestrial values ($\delta^{13}\text{C} = -28$ to -26‰) in the rivers to values ($\delta^{13}\text{C} = -26$ to -20‰) approaching marine material in the corresponding deltas (Fig. 8). These isotopic shifts indicate that up to half of the total organic matter associated with the surfaces of river-derived minerals in these deltas is of marine origin. The overall losses of TOM resulting from net removal and replacement on particle surfaces are near 70% for the Amazon and all other rivers tested except the Huange He, which already has a low organic carbon loading upon discharge.

These results seem robust and have broad implications. The estimate that almost three-quarters of the particulate TOM discharged by the Amazon River is respired in its delta is consistent with a depositional budget for the Amazon continental shelf (Showers and Angle, 1986), and with direct measurements of organic carbon respiration in these sediments (Aller *et al.*, 1996). In the latter study, stable carbon isotope compositions of pore-water DIC indicate extensive remineralization of

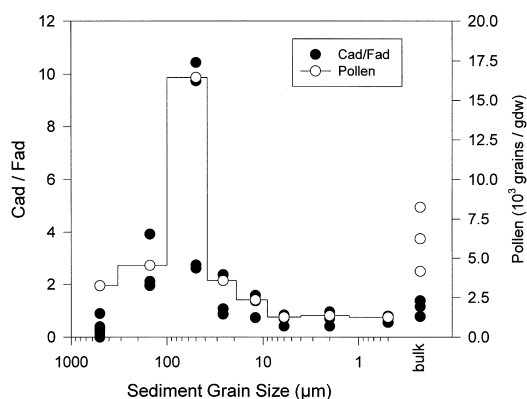


Fig. 7. Trends versus sediment size class for *p*-coumaric acid to ferulic acid ratios (Cad/Fad) and pollen abundances (grains/gdw, slope station only) in Washington coast sediments (Keil *et al.*, in press).

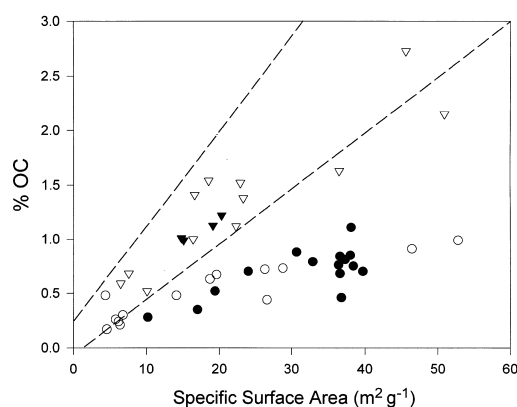


Fig. 8. Weight percentages of organic carbon (%OC) as a function of mineral specific surface area for bulk and hydrodynamically fractionated sediments from the Amazon River and delta (Keil *et al.*, 1997a). Filled triangles indicate bulk river fine suspended sediment (< 63 μm); open triangles indicate size fractions of river suspended sediment, filled circles indicate bulk deltaic sediment, and open circles indicate size fractions of deltaic sediments.

TOM within the upper meter of Amazon Delta sediments (Aller *et al.*, 1996). TOM appears to be co-oxidized with relatively labile marine-derived organics during repeated resuspension/deposition events, during which the sediments oscillate between oxic conditions due to O_2 exposure and suboxic conditions where iron reduction predominates. This is one of the few studies that directly demonstrates ongoing degradation of TOM at a specific rate and location in the marine environment. The survey of Keil *et al.* (1997a) indicates that such extensive losses of TOM are typical of many river/delta systems exhibiting a variety of physical settings, and thus that globally significant fluxes of carbon, and other bioactive elements, are likely involved.

Although this discussion deals primarily with modern ocean settings, it is geochemically pertinent to note that similar patterns appear to have characterized TOM degradation in the Amazon delta/cone system over previous eras. For example, Keil *et al.* (1997b) report OC/SA ratios for sediment horizons deposited on the Amazon cone during various periods of the Quaternary. The pattern observed (Fig. 9) is that directly deposited turbidites with minimal resuspension histories exhibit OC/SA ratios near 0.5. Such values fall in the lower portion of the surface loading range for particles suspended in the modern Amazon River. These relatively carbon-rich deposits all exhibit $\delta^{13}C$ values which are less than -27‰ , which attest to high fractions of preserved TOM. Sediments that evidently were deposited indirectly at other times via resuspension and nepheloid transport have OC/SA ratios which are less than 0.35 and $\delta^{13}C$ values which are greater than -27‰ . These compositions are similar to those for heavily reworked sediments from the modern delta (Fig. 9). Because the compositions of the lignin mixtures are similar between glacial and interglacial deposits, the observed differences in or-

ganic carbon loadings in the ODP cores apparently are not due to past vegetative changes in the Amazon Basin (Goñi, 1997). TOM preservation in the Amazon cone/delta system appears to be favored during much of the Quaternary by conditions of minimal sediment resuspension and redox oscillation (Keil *et al.*, 1997a,b). Strong predominances of TOM also have been observed in the extensive turbidite deposits (Rogers and Koons, 1969) which cover the northern basin of the Gulf of Mexico and originated from the Mississippi Cone during low glacial sea-level stands (Newman *et al.*, 1973). Particulate TOM discharge by rivers constitutes a sufficiently large carbon flux over the millennial time scales of sea-level oscillation to merit serious consideration as an environmental variable in global climate change.

Overall, the physical forms in which TOM is discharged to the ocean appear to be the prime determinant of the ultimate distributions and fates of the component molecules. Particulate TOM is evident chemically and morphologically (e.g. pollen, plant debris and charcoal) in both coastal and open ocean sediments. There is essentially no evidence, however, that marine sediments incorporate riverine DOM beyond the small amounts that are passively buried in interstitial sea-water. The different ultimate fates of particulate and dissolved TOM may result more from separate physical pathways than contrasting chemical compositions. Particulate TOM settles rapidly through the marine water column and typically accumulates to suboxic depths of coastal marine sediments within periods of decades to centuries (Hedges and Keil, 1995). In contrast, dissolved TOM is discharged by rivers directly into lighted, highly oxygenated surface ocean waters where it is subjected to oxic biodegradation and photolysis (Mopper *et al.*, 1991). Dissolved TOM also lacks a physically protective inorganic matrix (Hedges and Keil, 1995) and appears to have little affinity for sorption to mineral surfaces (Mantoura and Woodward, 1983) which could remove it to more benign sedimentary settings. In spite of being discharged in greater amounts (Fig. 2) and more degraded forms, dissolved TOM appears never to escape seawater, where it is rapidly cycled by as yet poorly defined mechanisms (Opsahl and Benner, 1997).

FUTURE RESEARCH DIRECTIONS

Although recent studies involving a variety of measurements and strategies provide consistent evidence that dissolved and particulate TOM are rapidly and extensively remineralized in the ocean, it has been extremely difficult to identify the processes involved and the settings in which they operate. Where do we go from here to better define the fate of TOM in the ocean? This question will be

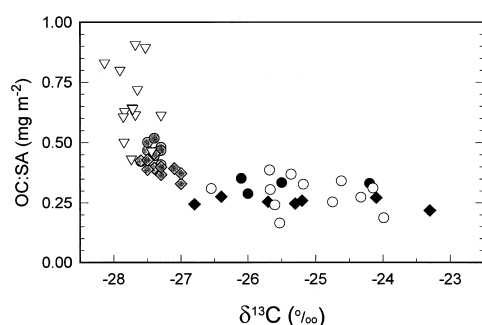


Fig. 9. Organic carbon to mineral surface area ratio (OC:SA) plotted against stable carbon isotopic composition of organic matter for modern Amazon river and delta sediments and sediment size fractions (Keil *et al.*, 1997a), and for ODP cores 932A and 942A from the Amazon fan (Keil *et al.*, 1997b). Open triangles indicate river sediment; open circles indicate deltaic sediment. The filled circles and diamonds represent fan sediments (cores 932 and 942, respectively).

discussed along the themes of improved: (a) measurements of bulk properties, (b) applications of molecular tracers and (c) analytical techniques.

Bulk characterizations

Although insensitive, bulk analyses such as C/N and $\delta^{13}\text{C}$ can be useful for tracing TOM through pronounced nearshore gradients. This is especially true if a large number of measurements can be made rapidly to account (along with salinity and surface area) for physical mixing, *in situ* reactions and variations in endmember composition. One example of an expedient survey tool is the high-temperature combustion system described by Hansell (1993) which simultaneously measures DOC (by nondispersive IR) and total dissolved nitrogen (by chemiluminescence). Dissolved organic nitrogen (DON) can then be calculated as the difference between total dissolved nitrogen and total nitrogenous nutrients ($\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$). Another useful instrument of this type is a DOC analyzer from which the CO_2 can be swept into a ratio mass spectrometer for $\delta^{13}\text{C}$ measurements (e.g. Leckrone and Hayes, 1996). Optical absorption (Blough *et al.*, 1993) and three-dimensional UV/fluorescence spectrometry (Coble *et al.*, 1990) also can help to rapidly discriminate marine and terrestrial DOM in small water samples. In particular, detailed surveys based on these types of synoptic measurements might allow gradual processes, such as photolysis of dissolved TOM, to be monitored in dynamic coastal marine waters.

Many of the bulk chemical characterizations that might potentially be applied to measure particulate TOM in marine sediments are compromised by interference from coexisting minerals. Exceptions are $\delta^{13}\text{C}$ and C/N determinations, which are possible because total carbon and nitrogen are converted to easily separated volatile products. In contrast, the wealth of information that comprehensive analyses of organic elements (CHNSO) and cross polarization/magic angle spinning (CP/MAS) ^{13}C and ^{15}N NMR have provided for DOM isolates from natural waters (e.g. Benner *et al.*, 1992, 1997; McCarthy *et al.*, in press), remains untapped for sedimentary organic matter. This gap is unfortunate because NMR and elemental analyses provide fundamental constraints on total biochemical compositions, aromaticity and acidity (Reuter and Perdue, 1984; Wilson *et al.*, 1987). In particular, a better knowledge of elemental compositions of organic matter in marine deposits would more closely constrain nutrient and oxygen exchanges that could be expected during *in situ* respiration.

One means of getting such fundamentally useful information is to pursue physical and chemical methods for gently separating sedimentary organic matter from its mineral matrix. Large particles such as vascular plant fragments and pollen can be phy-

sically separable by flotation in heavy liquids or with hydrodynamic sorting techniques (e.g. Keil *et al.*, 1994; Christensen, 1996). The key to comprehensive characterization of sedimentary organic matter by NMR and elemental methods, however, is to separate organic materials from minerals with which they are tightly associated. Although marine chemists have not aggressively pursued this problem outside of kerogen isolation applications, soil scientists have (Hedges and Oades, in press). The current method of choice in soil studies is to dissolve away silicate minerals with HF. This procedure greatly concentrates the organic component and substantially reduces interference of NMR by paramagnetic elements, reportedly without causing large losses of soil organic matter or compositional changes (Skjemstad *et al.*, 1994; Schmidt *et al.*, 1997). Parallel HF treatments should be investigated systematically for sedimentary organic matter, as could even milder demineralization of carbonate oozes with HCl or CO_2 .

Biomarker applications

Terrestrial biomarkers will probably continue to be the tracers of choice in studies of small amounts of TOM dispersed in the open ocean. Although high molecular weight *n*-alkanes, fatty acids, and aldehydes are widely distributed in marine sediments, attempts at quantitative tracer studies with such lipids have been relatively limited (see however: Prahl and Muehlhausen, 1989; Prahl *et al.*, 1994; Kennicutt *et al.*, 1987). Lignin-derived phenols have proven useful tracers, but usually have been applied alone. Thus it has been difficult to evaluate the possible selectivity of the isolation method for different TOM components, the extent of preferential degradation in the water column and sediments, and specifically where the molecular tags originate and why they are lost. One clear need is for more types of terrestrial tracers, which offer complementary information on sources, transport pathways and reactions. For solid phases, lignin dimers (Goñi *et al.*, 1993) and cutin acids (Goñi and Hedges, 1990a,b) offer complementary geochemical information from the conventional CuO method (e.g. Gough *et al.*, 1993; Opsahl and Benner, 1995). Other potential terrestrial biomarkers that should receive more quantitative attention include lipids, tannins and suberin. There is a critical need to identify chemical compounds which are the specific products of key TOM reactions such as photolysis, spontaneous condensation and microbial degradation. In particular, a chemical tag should be pursued that would allow previously dissolved TOM to be detected unambiguously within marine sediments. If such reaction indicators can be found and linked to precursor molecules, then it should be possible to evaluate the degradation histories of different TOM components and

to identify where in the ocean specific alterations and transformations occur.

An additional challenge for biomarker-based studies will be, as with bulk chemical properties, to make analytical techniques fast and easy enough for detailed surveys in real time on small samples. Many of the conventional tracer methods, such as for lignin phenols, will have to become considerably easier and more sensitive. Other analytical approaches such as pyrolysis in the presence of tetramethylammonium hydroxide (TMAH), which simultaneously breaks down and methylates small amounts of lignin to form products analogous to those from CuO, may be advantageous (Hatcher *et al.*, 1995; Hatcher and Minard, 1996). Automated methods of sampling, laboratory manipulation and analysis are needed to provide the data densities required for geographically extensive surveys across multiple size and compound classes.

New analytical approaches

Along these same lines, new types of instrumentation and techniques for measuring bulk properties and molecular distributions indicative of TOM are now available or should soon be feasible. One example of an extremely useful analytical innovation is irm-GC/MS (Freeman *et al.*, 1990, 1994). By allowing $\delta^{13}\text{C}$ measurements on specific compounds, this method has been particularly useful for discerning the origin of molecules whose biological or regional sources are not structurally evident. For example, Prahl *et al.* (1992) were able to determine that the pentacyclic triterpene, diploptene, in sediments of the Washington coast has a $\delta^{13}\text{C}$ indicative of a soil origin. This assignment was supported by direct correlation of diploptene and plant-wax *n*-alkane concentrations. Goñi and Eglinton (1996) have shown that stable carbon isotopic composition of phenolic products of the CuO oxidation of C3 and C4 plant tissues preserve the characteristic $\delta^{13}\text{C}$ labels of these precursors. With irm-GC/MS, it is possible to discern the percent contribution of the two plant types to each phenolic product. This information can be obtained without demineralization of the sample and should be particularly useful for detecting contributions of C4 plant carbon from salt marshes or arid terrestrial catchment, which otherwise could lead to a large underestimate of TOM. Finally, a chromatographic procedure similar to that worked out by Eglinton *et al.* (1996) for isolating individual compounds for accelerator mass spectrometry (AMS) analysis might be used to identify and trace ^{14}C -rich terrestrial components of sea-water DOM. It may, thus, be possible to determine the relative turnover times of specific compound types that could then be related to structurally-dependent removal mechanisms. Preparative gas chromatography also might be applied for isolation of individual compounds

for D/H analysis, possibly as a stepping stone toward development of an irm-GC/MS method for stable hydrogen isotopes. The key, as in most geochemical studies, will be to identify the processes controlling TOM distributions in the ocean so that well chosen measurements can accurately describe relatively complex systems, and predict their future states.

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REFERENCES

- Aller, R. C., Blair, N. E., Xai, Q. and Rude, P. D. (1996) Remineralization rates, recycling, and storage of carbon in Amazon shelf sediments. *Continental Shelf Research* **16**, 753–786.
- Altebet, M. A. and Francois, R. (1994) Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization. *Global Biogeochemical Cycles* **8**, 103–116.
- Amon, R. M. W. and Benner, R. (1996a) Photochemical and microbial consumption of dissolved organic carbon and dissolved oxygen in the Amazon River system. *Geochimica et Cosmochimica Acta* **60**, 1783–1792.
- Amon, R. M. W. and Benner, R. (1996b) Bacterial utilization of different size classes of dissolved organic matter. *Limnology and Oceanography* **41**, 41–51.
- Bader, R. G. (1956) The lignin fraction of marine sediments. *Deep-Sea Research* **4**, 15–22.
- Barrick, R. C. and Hedges, J. I. (1981) Hydrocarbon geochemistry of the Puget Sound region II. Sedimentary diterpenoid, steroid and triterpenoid hydrocarbons. *Geochimica et Cosmochimica Acta* **45**, 381–392.
- Barrick, R. C. and Prahl, F. G. (1987) Hydrocarbon geochemistry of the Puget Sound Region III. Polycyclic aromatic hydrocarbons in sediments. *Estuarine, Coastal and Shelf Science* **25**, 175–191.
- Barrick, R. C., Furlong, E. T. and Carpenter, R. (1984) Hydrocarbon and azaarene markers of coal transport to aquatic sediments. *Environmental Science and Technology* **18**, 846–854.
- Bauer, J. E. and Druffel, E. R. M. (submitted) Ocean margins as sources of ^{14}C -depleted organic matter to the open ocean. *Nature*.
- Bauer, J. E., Williams, P. M. and Druffel, E. R. M. (1992) ^{14}C activity of dissolved organic carbon fractions in the north central Pacific and Sargasso Sea. *Nature* **357**, 667–670.
- Bauer, J. E., Reimers, C. E., Druffel, E. R. M. and Williams, P. M. (1995) Isotopic constraints on carbon exchange between deep ocean sediments and seawater. *Nature* **373**, 686–689.
- Bauer, J. E., Druffel, E. R. M., Williams, P. M., Wolgast, D. M. and Griffin, S. (in press) Temporal variability in dissolved organic carbon and radiocarbon in the eastern North Pacific Ocean. *Journal of Geophysical Research*.
- Benner, R. and Hedges, J. I. (1993) A test of the accuracy of freshwater DOC measurements by high-temperature

- catalytic oxidation and UV-promoted persulfate oxidation. *Marine Chemistry* **41**, 161–165.
- Benner, R., Fogel, M. L., Sprague, E. K. and Hodson, R. E. (1987) Depletion of ^{13}C in lignin and its implications for stable carbon isotope studies. *Nature* **329**, 708–710.
- Benner, R., Opsahl, S., Chin-Leo, G., Richey, J. E. and Forsberg, B. (1995) Bacterial carbon metabolism in the Amazon River system. *Limnology and Oceanography* **40**, 1262–1270.
- Benner, R., Biddanda, B., Black, B. and McCarthy, M. (1997) Abundance, size distribution and stable carbon and nitrogen isotopic compositions of marine organic matter isolated by tangential-flow ultrafiltration. *Marine Chemistry* **57**, 243–263.
- Benner, R., Pakulski, J. D., McCarthy, M., Hedges, J. I. and Hatcher, P. G. (1992) Bulk chemical characteristics of dissolved organic matter in the ocean. *Science* **255**, 1561–1564.
- Berner, R. A. (1989) Biogeochemical cycles of carbon and sulfur and their effect on atmospheric oxygen over Phanerozoic time. *Palaeogeography, Palaeoclimatology, Palaeoecology* **73**, 97–122.
- Blair, N., Leu, A., Muñoz, E., Olsen, J., Kwong, E. and Des Marais, D. (1985) Carbon isotopic fractionation in heterotrophic microbial metabolism. *Applied Environmental Microbiology* **50**, 996–1001.
- Blough, N. V., Zafriou, O. and Bonilla, J. (1993) Optical absorption spectra of waters from the Orinoco River outflow: Terrestrial input of colored organic matter to the Caribbean. *Journal of Geophysical Research* **98**, 2271–2278.
- Brassell, S. C. and Eglinton, G. (1983) The potential of organic geochemical compounds as sedimentary indicators of upwelling. In *Coastal Upwelling, Its Sedimentary Record*, eds. E. Suess and J. Thiede, pp. 545–571. Plenum Press, New York.
- Christensen, B. T. (1996) Carbon in primary and secondary organomineral complexes. *Advances in Soil Science* **24**, 97–165.
- Coble, P. C., Green, S., Blough, N. V. and Gagosian, R. B. (1990) Characterization of dissolved organic matter in the Black Sea by fluorescence spectroscopy. *Nature* **348**, 432–435.
- Degens, E. T. (1969) Biogeochemistry of stable carbon isotopes. In *Organic Geochemistry*, eds. G. Eglinton and M. T. J. Murphy, pp. 304–329. Springer, New York.
- Deuser, W. G. (1988) Whither organic carbon? *Nature* **332**, 396–397.
- Druffel, E. M. and Suess, H. E. (1983) On the radiocarbon record in banded corals: Exchange parameters and net transport of $^{14}\text{CO}_2$ between atmosphere and surface ocean. *Journal of Geophysical Research* **88**, 1271–1280.
- Druffel, E. R. M., Honjo, S. and Griffin, S. (1986) Radiocarbon in particulate matter from the eastern Sub-Arctic Pacific Ocean: Evidence of a source of terrestrial carbon to the deep sea. *Radiocarbon* **28**, 397–407.
- Eglinton, T. I., Aluwihare, L. I., Bauer, J. E., Druffel, E. R. M. and McNichol, A. P. (1996) Gas chromatographic isolation of individual compounds from complex matrices for radiocarbon dating. *Analytical Chemistry* **68**, 904–912.
- Elias, V. O., Cardoso, J. N. and Simoneit, B. R. T. (1996) Sesquiterpenoids in Amazon shelf waters. *Organic Geochemistry* **25**, 241–250.
- Emerson, S. and Hedges, J. I. (1988) Processes controlling the organic carbon content of open ocean sediments. *Paleoceanography* **3**, 621–634.
- Emerson, S., Stump, C., Grootes, P. M., Stuiver, M., Farwell, G. W. and Schmidt, F. H. (1987) Estimates of degradable organic carbon in deep-sea sediments from ^{14}C concentrations. *Nature* **329**, 51–53.
- Epstein, S., Yapp, C. J. and Hall, J. H. (1976) The determination of the D/H ratio of non-exchangeable hydrogens in cellulose extracted from aquatic and land plants. *Earth and Planetary Science Letters* **30**, 241–251.
- Ertel, J. R., Hedges, J. I. and Perdue, E. M. (1984) Lignin signature of aquatic humic substances. *Science* **223**, 485–487.
- Ertel, J. R. and Hedges, J. I. (1984) The lignin component of humic substances: Distribution among soil and sedimentary humic, fulvic, and base-insoluble fractions. *Geochimica et Cosmochimica Acta* **48**, 2065–2074.
- Ertel, J. R., Hedges, J. I., Devol, A. H., Richey, J. E. and Ribeiro, M. N. G. (1986) Dissolved humic substances of the Amazon river system. *Geochimica et Cosmochimica Acta* **50**, 739–754.
- Estep, M. F. and Hoering, T. C. (1980) Biogeochemistry of the stable hydrogen isotopes. *Geochimica et Cosmochimica Acta* **44**, 1197–1206.
- Eswaran, H., Van den Berg, E. and Reich, P. (1993) Organic carbon in soils of the world. *Journal of the Soil Science Society of America* **57**, 192–194.
- Faure, G. (1986) *Principle of Isotope Geology*, 2nd edn. John Wiley and Sons, New York.
- Fengel, D. and Wegener, G. (1984) *Wood: Chemistry, Ultrastructure Reactions*. Walter de Gruyter and Co., Berlin.
- Fontugne, M. and Duplessy, J. C. (1978) Carbon isotope ratio of marine plankton related to surface water masses. *Earth and Planetary Science Letters* **41**, 365–371.
- Fox, L. E. (1983) The removal of dissolved humic acid during estuarine mixing. *Estuarine, Coastal and Shelf Science* **16**, 431–440.
- Fox, L. E. (1991) The transport and composition of humic substances in estuaries. In *Organic Substances and Sediments in Water, Vol. 1, Humics and Soils*, ed. R. A. Baker, pp. 129–162. Lewis Publishing, Chelsea, MI.
- Freeman, K. H., Hayes, J. M., Trendel, J.-M. and Albrecht, P. (1990) Evidence from carbon isotope measurements for diverse origins of sedimentary hydrocarbons. *Nature* **343**, 254–256.
- Freeman, K. H., Wakeham, S. G. and Hayes, J. M. (1994) Predictive isotopic biogeochemistry: Hydrocarbons from anoxic marine basins. *Organic Geochemistry* **21**, 629–644.
- Fry, B. and Sherr, E. B. (1984) $\delta^{13}\text{C}$ measurements as indicators of carbon flow in marine and freshwater ecosystems. *Contributions to Marine Science* **27**, 13–47.
- Gearing, P. J., Plucker, F. E. and Parker, P. L. (1977) Organic carbon stable isotope ratios of continental margin sediments. *Marine Chemistry* **5**, 251–266.
- Gearing, J. N., Gearing, P. J., Rudnick, D. T., Requejo, A. G. and Hutchins, M. J. (1984) Isotopic variability of organic carbon in a phytoplankton-based temperate estuary. *Geochimica et Cosmochimica Acta* **48**, 1089–1098.
- Goñi, M. A. (1997) Record of terrestrial organic matter composition in Amazon Fan sediments. In *Proceedings of ODP, Scientific Results*, Vol. 155, eds. R. D. Flood, D. J. W. Piper, A. Klaus and L. C. Peterson, Ocean Drilling Program, College Station, TX.
- Goñi, M. A. and Eglinton, T. I. (1996) Stable carbon isotopic analyses of lignin-derived CuO oxidation products by isotope ratio-monitoring gas-chromatography mass spectrometry (irm-GC-MS). *Organic Geochemistry* **24**, 601–615.
- Goñi, M. A. and Hedges, J. I. (1990a) Potential applications of cutin-derived CuO reaction products for discriminating vascular plant sources in natural environments. *Geochimica et Cosmochimica Acta* **54**, 3073–3081.

- Goñi, M. A. and Hedges, J. I. (1990b) The diagenetic behavior of cutin acids in buried conifer needles and sediments from a coastal marine environment. *Geochimica et Cosmochimica Acta* **54**, 3083–3093.
- Goñi, M. A., Nelson, B., Blanchette, R. A. and Hedges, J. I. (1993) Fungal degradation of wood lignins: Geochemical perspectives from CuO-derived phenolic dimers and monomers. *Geochimica et Cosmochimica Acta* **57**, 3985–4002.
- Gough, M. A., Mantoura, R. F. C. and Preston, M. (1993) Terrestrial plant biopolymers in marine sediments. *Geochimica et Cosmochimica Acta* **57**, 945–964.
- Handa, N. (1977) Land sources of marine organic matter. *Marine Chemistry* **5**, 341–359.
- Hansell, D. A. (1993) Results and observations from the measurement of DOC and DON in seawater using a high-temperature catalytic oxidation technique. *Marine Chemistry* **41**, 195–202.
- Harmon, R. A. (1972) The distribution of microbiogenic sediment near the mouth of the Columbia River. In *The Columbia River Estuary and Adjacent Ocean Waters*, eds. A. T. Pruther and D. L. Alverson, pp. 265–278. University of Washington Press, Washington.
- Hatcher, P. G. and Minard, R. D. (1996) Comparison of dehydrogenase polymer (DHP) lignin with native lignin from gymnosperm wood by thermochemolysis using tetramethylammonium hydroxide (TMAH). *Organic Geochemistry* **24**, 593–600.
- Hatcher, P. G., Nanny, M. A., Minard, R. D., Dible, S. D. and Carson, D. M. (1995) Comparison of two thermochemolytic methods for the analysis of lignin in decomposing wood: the CuO oxidation method and the method of thermochemolysis with tetramethylammonium hydroxide (TMAH). *Organic Geochemistry* **23**, 881–888.
- Hedges, J. I. (1990) Compositional indicators of organic acid sources and reactions in natural environments. In *Organic Acids in Aquatic Environments*, eds. E. M. Perdue and E. T. Gjessing, pp. 43–63. Wiley and Sons, New York.
- Hedges, J. I. (1992) Global biogeochemical cycles: Progress and problems. *Marine Chemistry* **39**, 67–93.
- Hedges, J. I. and Keil, R. G. (1995) Sedimentary organic matter preservation: an assessment and speculative synthesis. *Marine Chemistry* **49**, 81–115.
- Hedges, J. I. and Mann, D. C. (1979) The lignin geochemistry of marine sediments from the southern Washington coast. *Geochimica et Cosmochimica Acta* **43**, 1809–1818.
- Hedges, J. I. and Oades, J. M. (in press) Comparative organic geochemistries of soils and sediments. *Organic Geochemistry*.
- Hedges, J. I. and Prahl, F. G. (1993) Early diagenesis, consequences for applications of molecular biomarkers. In *Organic Geochemistry*, eds. M. H. Engel and S. A. Macko, pp. 237–253. Plenum, New York.
- Hedges, J. I., Clark, W. A. and Cowie, G. L. (1988) Organic matter sources to the water column and surficial sediments of a marine bay. *Limnology and Oceanography* **33**, 1116–1136.
- Hedges, J. I., Turin, H. J. and Ertel, J. R. (1984) Sources and distributions of sedimentary organic matter in the Columbia River drainage basin, Washington and Oregon. *Limnology and Oceanography* **29**, 35–46.
- Hedges, J. I., Hatcher, P. G., Ertel, J. R. and Meyers-Schulte, K. J. (1992) A comparison of dissolved humic substances from seawater with Amazon River counterparts by ¹³C-NMR spectrometry. *Geochimica et Cosmochimica Acta* **56**, 1753–1757.
- Hedges, J. I., Clark, W. A., Quay, P. D., Richey, J. E., Devol, A. H. and Santos, U. M. (1986a) Composition and fluxes of particulate organic material in the Amazon River. *Limnology and Oceanography* **31**, 717–738.
- Hedges, J. I., Cowie, G. L., Quay, P. D., Grootes, P. M., Richey, J. E., Devol, A. H., Farwell, G. W., Schmidt, F. W. and Salati, E. (1986b) Organic carbon-14 in the Amazon river system. *Nature* **231**, 1129–1131.
- Hedges, J. I., Ertel, J. R., Richey, J. E., Quay, P. D., Benner, R., Strom, M. and Forsberg, B. (1994) Origin and processing of organic matter in the Amazon River as indicated by carbohydrates and amino acids. *Limnology and Oceanography* **39**, 743–761.
- Hoering, T. C. and Ford, H. T. (1960) Isotope effect in the fixation of nitrogen by *Azotobacter*. *Journal of the American Chemical Society* **82**, 376–778.
- Hoering, T. C. (1974) The isotopic composition of the carbon and hydrogen in organic matter of recent sediments. *Carnegie Institute of Washington Yearbook* **73**, 590–595.
- Huc, A. Y. (1980) Origin and formation of organic matter in recent sediments and its relation to kerogen. In *Kerogen*, ed. B. Durand, pp. 445–474. Éditions Technip.
- Ittekkot, V. (1988) Global trends in the nature of organic matter in river suspensions. *Nature* **332**, 436–438.
- Jaffé, R., Wolff, G. A., Cabrera, A. C. and Chitty, H. C. (1995) The biogeochemistry of lipids in rivers of the Orinoco Basin. *Geochimica et Cosmochimica Acta* **59**, 4507–4522.
- Jasper, J. P. and Gagosian, R. B. (1990) The sources and deposition of organic matter in the Late Quaternary Pigmy Basin, Gulf of Mexico. *Geochimica et Cosmochimica Acta* **54**, 1117–1132.
- Judson, S. (1968) Erosion of the land. *American Scientist* **56**, 356–374.
- Kawamura, K., Handa, N. and Nozaki, Y. (1990) Omega-oxocarboxylic acids in the sediment trap and sediment samples from the North Pacific; implication for the transport of photo-oxidation products to deep-sea environments. *Geochemical Journal* **24**, 217–222.
- Kawamura, K., Yanase, A., Eguchi, T., Mikami, T. and Barrie, L. A. (1996) Enhanced atmospheric transport of soil derived organic matter in spring over the high Arctic. *Geophysical Research Letters* **23**, 3735–3738.
- Keil, R. G., Tsamakis, E., Giddings, J. C. and Hedges, J. I. (in press) Biochemical distributions (amino acids, neutral sugars and lignin phenols) among size classes of marine sediments. *Geochimica et Cosmochimica Acta*.
- Keil, R. G., Tsamakis, E., Fuh, C. B., Giddings, J. C. and Hedges, J. I. (1994) Mineralogical and textural controls on organic composition of coastal marine sediments: Hydrodynamic separation using SPLITT fractionation. *Geochimica et Cosmochimica Acta* **57**, 879–893.
- Keil, R. G., Mayer, L. M., Quay, P. D., Richey, J. E. and Hedges, J. I. (1997a) Loss of organic matter from riverine particles in deltas. *Geochimica et Cosmochimica Acta* **61**, 1507–1511.
- Keil, R. G., Tsamakis, E., Wolf, N., Hedges, J. I. and Goñi, M. A. (1997b) Relationships between organic carbon preservation and mineral surface area in Amazon Fan sediments (Sites 932A and 942A). In *Proceedings of ODP, Scientific Results*, Vol. 155, ed. R. D. Flood, D. J. W. Piper, A. Klaus and L. C. Peterson. Ocean Drilling Program, College Station, TX.
- Kennicutt, M. C., Barker, C., Brooks, J. M., DeFreitas, D. A. and Zhu, G. H. (1987) Selected organic matter source indicators in the Orinoco, Nile and Changjiang deltas. *Organic Geochemistry* **11**, 41–51.
- Killops, S. D. and Killops, V. J. (1993) *An Introduction to Organic Geochemistry*. Wiley and Sons, New York.
- Kolattukudy, P. E. (1980) Biopolyester membranes in plants: Cutin and suberin. *Science* **208**, 990–1000.
- Laws, E. A., Popp, B. N., Bidigare, R. R., Kennicutt, M. C. and Macko, S. A. (1995) Dependence of phytoplank-

- ton carbon isotopic composition on growth rate and $[\text{CO}_2]_{\text{aq}}$: Theoretical considerations and experimental results. *Geochimica et Cosmochimica Acta* **59**, 1131–1138.
- Leckrone, K. J. and Hayes, J. M. (1996) A continuous-flow inlet for carbon isotopic analysis of submicromole samples of non-volatile organic matter. Abstract, 1996 Ocean Sciences Meeting, San Diego.
- de Leeuw, J. W. and Largeau, C. (1993) A review of macromolecular organic compounds that comprise living organisms and their role in kerogen, coal, and petroleum formation. In *Organic Geochemistry*, eds. M. H. Engle and S. Macko, pp. 23–72. Plenum, New York.
- Libes, S. M. and Deuser, W. G. (1988) The isotope geochemistry of particulate nitrogen in the Peru Upwelling Area and the Gulf of Maine. *Deep-Sea Research* **35**, 517–533.
- Liu, K.-K. and Kaplan, I. R. (1989) The eastern tropical Pacific as a source of ^{15}N -enriched nitrate in seawater off southern California. *Limnology and Oceanography* **34**, 820–830.
- Louchouart, P., Lucotte, M., Canuel, R., Gagné, J. P. and Richard, L. P. (in press) Sources and early diagenesis of lignin and bulk organic matter in the sediments of the lower St. Lawrence Estuary and the Saguenay Fjord. *Marine Chemistry*.
- Mantoura, R. F. C. and Woodward, E. M. S. (1983) Conservative behaviour of riverine dissolved organic carbon in the Severn Estuary: chemical and geochemical implications. *Geochimica et Cosmochimica Acta* **47**, 1293–1309.
- Mayer, L. M. (1994a) Surface area control of organic carbon accumulation in continental shelf sediments. *Geochimica et Cosmochimica Acta* **58**, 1271–1284.
- Mayer, L. M. (1994b) Relationships between mineral surfaces and organic carbon concentrations in soils and sediments. *Chemical Geology* **114**, 347–363.
- McCaffrey, M. A., Farrington, J. W. and Repeta, D. J. (1991) The organic geochemistry of Peru margin surface sediments: II. Paleoenvironmental implications of hydrocarbon and alcohol profiles. *Geochimica et Cosmochimica Acta* **55**, 483–498.
- McCarthy, M., Pratum, T., Hedges, J. I. and Benner, R. (in press) Chemical composition of dissolved organic nitrogen in the ocean. *Nature*.
- McCrimble, R. and Overton, K. H. (1969) The chemistry of the diterpenoids. In *Advances in Organic Chemistry, Methods and Results*, ed. R. A. Raphael, Vol. 5, pp. 47–113. Interscience.
- McMillan, C., Parker, P. L. and Fry, B. (1980) $^{13}\text{C}/^{12}\text{C}$ ratios in seagrasses. *Aquatic Botany* **9**, 237–249.
- Meybeck, M. (1982) Carbon, nitrogen, and phosphorous transport by world rivers. *American Journal of Science* **282**, 401–450.
- Meyers-Schulte, K. J. and Hedges, J. I. (1986) Molecular evidence for a terrestrial component of organic matter dissolved in ocean water. *Nature* **321**, 61–63.
- Miller, W. L. and Zepp, R. G. (1995) Photochemical production of dissolved inorganic carbon from terrestrial organic matter: Significance to the oceanic organic carbon cycle. *Geophysical Research Letters* **22**, 417–420.
- Mopper, K., Zhou, X., Kieber, R. J., Kieber, D. J., Sikorski, R. J. and Jones, R. D. (1991) Photochemical degradation of dissolved organic carbon and its impact on the oceanic carbon cycle. *Nature* **353**, 60–62.
- Moran, M. A., Wicks, R. J. and Hodson, R. E. (1991a) Export of dissolved organic matter from a mangrove swamp ecosystem: evidence from natural fluorescence, dissolved lignin phenols, and bacterial secondary production. *Marine Ecology Progress Series* **76**, 175–184.
- Moran, M. A., Pomeroy, L. R., Sheppard, E. S., Atkinson, L. P. and Hodson, R. E. (1991b) Distribution of terrestrially derived dissolved organic matter on the southeastern U.S. continental shelf. *Limnology and Oceanography* **36**, 1134–1149.
- Muller-Karger, F. E., McClain, C. R. and Richardson, P. L. (1988) The dispersal of the Amazon's water. *Nature* **333**, 56–59.
- Nelson, B. C., Goñi, M. A., Hedges, J. I. and Blanchette, R. A. (1995) Soft-rot fungal degradation of lignin in 2700 year old archaeological woods. *Holzforschung* **49**, 1–10.
- Newman, J. W., Parker, P. L. and Behrens, E. W. (1973) Organic carbon isotope ratios in Quaternary cores from the Gulf of Mexico. *Geochimica et Cosmochimica Acta* **37**, 225–238.
- Nissenbaum, A. (1974) The organic geochemistry of marine and terrestrial humic substances: Implications of carbon and hydrogen isotope studies. In *Advances in Organic Geochemistry, 1973*, eds. B. Tissot and F. Biennier, pp. 39–52. Editions Technip.
- Nittrouer, C. A. and Demaster, D. (1996) Oceanography of the Amazon continental shelf. *Continental Shelf Research* **16**, 553–841.
- Nydal, R. and Lövseth, K. (1983) Tracing bomb ^{14}C in the atmosphere 1962–1980. *Journal of Geophysical Research* **88**, 3621–3642.
- Opsahl, S. and Benner, R. (1995) Early diagenesis of vascular plant tissues: Lignin and cutin decomposition and biogeochemical implications. *Geochimica et Cosmochimica Acta* **59**, 4889–4904.
- Opsahl, S. and Benner, R. (1997) Distribution and cycling of terrigenous dissolved organic matter in the ocean. *Nature* **386**, 480–482.
- Parrish, C. C. (1988) Dissolved and particulate marine lipid classes: a review. *Marine Chemistry* **23**, 17–40.
- Peltzer, E. T. and Gagosian, R. B. (1989) Organic geochemistry of aerosols over the Pacific Ocean. *Chemical Oceanography* **10**, 281–338.
- Peltzer, E. T. and Hayward, N. A. (1996) Spatial and temporal variability of total organic carbon along 140°W in the equatorial Pacific Ocean in 1992. *Deep-Sea Research* **43**, 1155–1180.
- Pempkowiak, J. and Pocklington, R. (1983) Phenolic aldehydes as indicators of the origin of humic substances in marine environments. In *Aquatic and Terrestrial Humic Materials*, eds. R. F. Christman and E. T. Gjessing, pp. 371–386. Ann Arbor Science, Ann Arbor.
- Peters, K. E., Sweeney, R. E. and Kaplan, I. R. (1978) Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. *Limnology and Oceanography* **23**, 598–604.
- Peterson, B. J. and Fry, B. (1987) Stable isotopes in ecosystem studies. *Annual Review of Ecological Systems* **18**, 293–320.
- Peterson, B. J. and Howarth, R. W. (1987) Sulfur, carbon, and nitrogen isotopes used to trace organic matter flow in the salt-marsh estuaries of Sapelo Island, Georgia. *Limnology and Oceanography* **32**, 1195–1213.
- Pillon, P., Jocteur-Monrozier, L., Gonzalez, C. and Salot, A. (1986) Organic geochemistry of Recent equatorial deltaic sediments. *Organic Geochemistry* **10**, 711–716.
- Pocklington, R. and Tan, F. C. (1987) Seasonal and annual variations in the organic matter contributed by the St. Lawrence River to the Gulf of St. Lawrence. *Geochimica et Cosmochimica Acta* **51**, 2579–2586.
- Post, W. M. (1993) Organic carbon in soil and the global carbon cycle. In *The Global Carbon Cycle*, ed. M. Heimann, pp. 277–302. Springer, New York.
- Prahl, F. G. (1985) Chemical evidence of differential particle dispersal in the southern Washington coastal environment. *Geochimica et Cosmochimica Acta* **49**, 2533–2539.

- Prahl, F. G. and Carpenter, R. (1979) The role of zooplankton fecal pellets in the sedimentation of polycyclic aromatic hydrocarbons in Dabob Bay, Washington. *Geochimica et Cosmochimica Acta* **43**, 1959–1972.
- Prahl, F. G. and Carpenter, R. (1983) Polycyclic aromatic hydrocarbon (PAH)-phase associations in Washington Coastal Sediments. *Geochimica et Cosmochimica Acta* **47**, 1013–1024.
- Prahl, F. G. and Carpenter, R. (1984) Hydrocarbons in Washington coastal sediments. *Estuarine, Coastal and Shelf Science* **18**, 703–720.
- Prahl, F. G. and Muehlhausen, L. A. (1989) Lipid biomarkers as geochemical tools for paleoceanographic study. In *Productivity of the Ocean: Present and Past*, eds. W. H. Berger, V. S. Smetacek and G. Wefer, pp. 271–289. Wiley and Sons, New York.
- Prahl, F. G. and Pinto, L. A. (1987) A geochemical study of long-chain *n*-aldehydes in Washington coastal sediments. *Geochimica et Cosmochimica Acta* **51**, 1573–1582.
- Prahl, F. G., Bennett, J. T. and Carpenter, R. (1980) The early diagenesis of aliphatic hydrocarbons and organic matter in sedimentary particulates from Dabob Bay, Washington. *Geochimica et Cosmochimica Acta* **44**, 1967–1976.
- Prahl, F. G., Crecelius, E. A. and Carpenter, R. (1984) Polycyclic aromatic hydrocarbons in Washington coastal sediments: an evaluation of atmospheric and riverine routes of introduction. *Environmental Science and Technology* **18**, 687–693.
- Prahl, F. G., Hayes, J. M. and Xie, T.-M. (1992) Diploptene: An indicator of soil organic carbon in Washington coastal sediments. *Limnology and Oceanography* **37**, 1290–1300.
- Prahl, F. G., Muehlhausen, L. A. and Lyle, M. (1989) An organic geochemical assessment of oceanographic conditions at MANOP Site C over the past 26,000 years. *Paleoceanography* **4**, 495–510.
- Prahl, F. G., Ertel, J. R., Goñi, M. A., Sparrow, M. A. and Eversmeyer, B. (1994) An assessment of terrestrial organic carbon contributions to Washington coastal sediments. *Geochimica et Cosmochimica Acta* **58**, 3035–3048.
- Reuter, J. H. and Perdue, E. M. (1984) A chemical structural model of early diagenesis of sedimentary humus/proto-kerogens. *Mitt. Geol.-Paläont. Inst. Univ. Hamburg* **56**, 249–262.
- Richey, J. E., Hedges, J. I., Devol, A. H., Quay, P. D., Victoria, R., Martinelli, L. and Forsberg, B. R. (1990) Biogeochemistry of carbon in the Amazon River. *Limnology and Oceanography* **35**, 352–371.
- Richey, J. E., Meade, R. H., Salati, E., Devol, A. H., Nordin, C. F. and Dos Santos, U. (1986) Water discharge and suspended sediment concentrations in the Amazon River: 1982–1984. *Water Resources Research* **22**, 756–764.
- Rogers, M. A. and Koons, C. B. (1969) Organic carbon $\delta^{13}\text{C}$ values from Quaternary marine sequences in the Gulf of Mexico: a reflection of paleotemperature changes. *Transactions of the Gulf Coast Association Geological Society* **19**, 529–534.
- Romankevich, E. A. (1984) *Geochemistry of Organic Matter in the Ocean*. Springer, Berlin.
- Rundel, P. W., Ehleringer, J. R. and Nagy, K. A. (1989) *Stable Isotopes in Ecological Research*. Springer, New York.
- Sackett, W. M. and Thompson, R. R. (1963) Isotopic organic carbon composition of recent continental derived clastic sediments of eastern gulf coast, Gulf of Mexico. *Bulletin of the American Association of Petroleum Geologists* **47**, 525–531.
- Santos, V., Billett, D. S. M., Rice, A. L. and Wolff, G. A. (1994) Organic matter in deep-sea sediments from the Porcupine Abyssal Plain in the North-east Atlantic Ocean. I. Lipids. *Deep-Sea Research* **41**, 787–819.
- Santschi, P. H., Guo, L., Baskaran, M., Trumbore, S., Southon, J., Bianchi, T. S., Honeyman, B. and Cifuentes, L. (1995) Isotopic evidence for the contemporary origin of high-molecular weight organic matter in oceanic environments. *Geochimica et Cosmochimica Acta* **59**, 625–631.
- Sarkanen, K. V. and Ludwig, C. H. (1971) *Lignins*. Wiley-Interscience.
- Schlesinger, W. H. and Melack, J. M. (1981) Transport of organic carbon in the world's rivers. *Tellus* **33**, 172–187.
- Schmidt, M. W. I., Knicker, H., Hatcher, P. G. and Kögel-Knabner, I. (1997) Improvement of ^{13}C and ^{15}N CP/MAS NMR spectra of bulk soils, particle size fractions and organic material by treatment with hydrofluoric acid (10%). *European Journal of Soil Science* **48**, 1997.
- Schubert, C. J. and Stein, R. (1996) Deposition of organic carbon in Arctic Ocean sediments: terrigenous supply vs marine productivity. *Organic Geochemistry* **24**, 421–436.
- Sholkovitz, E. R. (1976) Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. *Geochimica et Cosmochimica Acta* **40**, 831–845.
- Showers, W. J. and Angle, D. G. (1986) Stable isotopic characterization of organic carbon accumulation on the Amazon continental shelf. *Continental Shelf Research* **6**, 227–244.
- Siegenthaler, U. and Sarmiento, J. L. (1993) Atmospheric carbon dioxide and the ocean. *Nature* **365**, 119–125.
- Simenstad, C. A., Duggins, D. O. and Quay, P. D. (1993) High turnover of inorganic carbon in kelp habitats as a cause of $\delta^{13}\text{C}$ variability in marine food webs. *Marine Biology* **116**, 147–160.
- Simoneit, B. R. T. (1977) Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. *Geochimica et Cosmochimica Acta* **41**, 463–476.
- Sjöström, E. (1981) *Wood Chemistry, Fundamentals and Applications*. Academic Press, New York.
- Skjemstad, J. O., Clarke, P., Taylor, J. A., Oades, J. M. and Newman, R. H. (1994) The removal of magnetic materials from surface soils. A solid state ^{13}C CP/MAS n.m.r. study. *Australian Journal of Soil Research* **32**, 1215–1229.
- Smith, B. N. and Epstein, S. (1971) Two categories of $^{13}\text{C}/^{12}\text{C}$ ratios for higher plants. *Plant Physiology* **47**, 380–384.
- Stark, R. E., Zlotnik-Mazori, T., Ferrantello, L. M. and Garbow, J. R. (1989) Molecular structure and dynamics of intact plant polyesters. *American Chemical Society Symposium Series* **399**, 214–229.
- Stuiver, M., Quay, P. D. and Ostlund, H. G. (1983) Abyssal water carbon-14 distribution and the age of the world ocean. *Science* **219**, 849–851.
- Summons, R. E. (1993) Biogeochemical cycles: A review of fundamental aspects of organic matter formation, preservation and composition. In *Organic Geochemistry*, eds. M. H. Engel and S. A. Macko, pp. 3–21. Plenum, New York.
- Thompson, P. A. and Calvert, S. E. (1995) Carbon isotope fractionation by *Emiliania huxleyi*. *Limnology and Oceanography* **40**, 673–679.
- Thurman, E. M. (1985) *Organic Geochemistry of Natural Waters*. Martinus Nijhoff/Dr. W. Junk.
- Wada, E. and Hattori, A. (1978) Nitrogen isotope effects in the assimilation of inorganic nitrogenous compounds by marine diatoms. *Geomicrobiological Journal* **1**, 85–101.
- Wakeham, S. G. and Lee, C. (1993) Production, transport, and alteration of particulate organic matter in the mar-

- ine water column. In *Organic Geochemistry*, eds. M. H. Engel and S. A. Macko, pp. 145–169. Plenum, New York.
- Wakeham, S. G., Hedges, J. I. and Lee, C. (in press-a) Molecular indicators of diagenetic status in marine organic matter. *Geochimica et Cosmochimica Acta*.
- Wakeham, S. G., Lee, C., Hedges, J. I., Hernes, P. J. and Peterson, M. L. (in press-b) Fate of major biochemicals in water column particles and sediments of the central Equatorial Pacific Ocean. *Deep-Sea Research*.
- Waksman, S. A. (1933) On the distribution of organic matter in the sea bottom and the chemical nature and origin of marine humus. *Soil Science* **36**, 125–147.
- Williams, P. M. and Druffel, E. R. M. (1987) Radiocarbon in dissolved organic matter in the central North Pacific Ocean. *Nature* **330**, 246–248.
- Williams, P. M. and Gordon, L. (1970) Carbon-13:carbon-12 ratios in dissolved and particulate organic matter in the sea. *Deep-Sea Research* **17**, 19–27.
- Wilson, M. A. (1987) *NMR Techniques and Applications in Geochemistry and Soil Chemistry*. Pergamon Press, Oxford.
- Wilson, M. A., Vassallo, A. M., Perdue, E. M. and Reuter, J. H. (1987) Compositional and solid-state nuclear magnetic resonance study of humic and fulvic acid fractions of soil organic matter. *Analytical Chemistry* **59**, 551–558.
- Yunker, M. B., MacDonald, R. W., Cretney, W. J., Fowler, B. R. and McLaughlin, F. A. (1993) Alkene, terpene, and polycyclic aromatic hydrocarbon geochemistry of the Mackenzie River and Mackenzie Shelf: Riverine contributions to Beaufort Sea coastal sediment. *Geochimica et Cosmochimica Acta* **57**, 3041–3061.
- Zafiriou, O. C., Gagosian, R. B., Peltzer, E. T. and Alford, J. B. (1985) Air-to-sea fluxes of lipids at Enewetak Atoll. *Journal of Geophysical Research* **90**(D1), 2409–2423.
- Ziegler, H. (1988) Hydrogen isotope fractionation in plant tissues. In *Stable Isotopes in Ecological Research*, eds. P. W. Rundel, J. R. Ehleringer and K. A. Nagy, pp. 105–125. Springer, New York.