

# The role of terrestrially derived organic carbon in the coastal ocean: A changing paradigm and the priming effect

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One of the major conundrums in oceanography for the past 20 y has been that, although the total flux of dissolved organic carbon (OC; DOC) discharged annually to the global ocean can account for the turnover time of all oceanic DOC (ca. 4,000–6,000 y), chemical biomarker and stable isotopic data indicate that there is very little terrestrially derived OC (TerrOC) in the global ocean. Similarly, it has been estimated that only 30% of the TerrOC buried in marine sediments is of terrestrial origin in muddy deltaic regions with high sedimentation rates. If vascular plant material—assumed to be highly resistant to decay—makes up much of the DOC and particulate OC of riverine OC (along with soil OC), why do we not see more TerrOC in coastal and oceanic waters and sediments? An explanation for this “missing” TerrOC in the ocean is critical in our understanding of the global carbon cycle. Here, I consider the origin of vascular plants, the major component of TerrOC, and how their appearance affected the overall cycling of OC on land. I also examine the role vascular plant material plays in soil OC, inland aquatic ecosystems, and the ocean, and how our understanding of TerrOC and “priming” processes in these natural systems has gained considerable interests in the terrestrial literature, but has largely been ignored in the aquatic sciences. Finally, I close by postulating that priming is in fact an important process that needs to be incorporated into global carbon models in the context of climate change.

decomposition | global carbon cycling | terrestrial organic matter

Understanding the alteration of materials flowing from rivers to the ocean has been an increasing area of research over the past few decade(s), and presently global community programs such as the International Geosphere Biosphere Program and its major project, Land Ocean Interaction in the Coastal Zone, are leading the research in this field (1). Natural organic matter (OM), one of the most important components of riverine material, is the largest reactive reservoir of reduced carbon on Earth, with soil containing 1,600 Pg C, sediments 1,000 Pg C, and the ocean 685 Pg C as dissolved OM (DOM), comparable to the global atmospheric CO<sub>2</sub> reservoir (2–6) (Fig. 1). Terrestrially derived organic carbon (OC; TerrOC) is a heterogeneous mix of recent vascular plant detritus, associated soil OC (SOC), older fossil (i.e., petrogenic) OC from carbonate rock erosion, and black carbon (e.g., soil organic charcoals and anthropogenic soots) (refs. 2, 7 and refs. therein). Approximately 90% of the OC (15,000,000 Pg C) on Earth resides in shales and other sedimentary rocks (7). Vascular plant material is believed to spend little time sequestered in intermediate reservoirs such as soils, freshwater sediments, and river deltas and contributes minimally to the old <sup>14</sup>C ages often observed on continental shelves. This results in part from the large contribution of petrogenic relative to vascular plant material found in marine sediments (8). All the aforementioned TerrOC materials are important in regulating the global carbon and oxygen cycles.

It is well known that terrestrial and aquatic biogeochemistry have developed

independently of each other over the years (9). In terrestrial ecosystem studies, more studies are now focusing on priming effect experiments that examine the addition of labile compounds to soils that results in enhanced release of soil-derived carbon and nitrogen—compared with those without additions. The general term to describe this is the “priming effect,” first introduced by Bingemann et al. (10) and later reviewed by Kuzyakov et al. (11). The actual process of priming was first described in agricultural literature by using the decomposition of green manure of legume plants in soils (12). However, it was not until the middle 1940s and 1950s that the priming effect was more formally recognized with renewed interest (13, 14). Although terrestrial studies continue to incorporate priming as an important process in soil carbon cycling, aquatic studies are seriously lagging behind, especially relative to the dramatic increase in the number of priming studies in the past decade in the terrestrial literature (15).

## Evolution of Land Plants and Their Impact on Chemical Ecology of Natural Ecosystems

Vascular plants represent the largest component of living biomass on Earth (570 Pg C). The oldest fossil proven to be a vascular land plant is *Cooksonia*, from the late Silurian Period (ca. 420 Ma) (16). Much of the paleobotanical work in the 1970s suggested that the timeframe for the initial diversification of land plants was between the late Silurian and early Devonian (410 Ma). Later work has suggested a time frame that begins in the Ordovician (ca. 480 Ma) and lasts over a period of more than 100 Myr (24). Lignin, a complex

heterogeneous phenylpropanoid polymer that occurs throughout the cell walls within the xylem tissues of vascular plants, evolved in land plants from their aquatic ancestors approximately 475 Ma (17). Lignin provided structural integrity for the entire plant as well as resistance to cell collapse under tension associated with water transport. Although lignin-like compounds have been identified in green algae (18), the presence of “true” lignin was only recently discovered in the walls of certain intertidal red algae (19). Nevertheless, the overwhelmingly dominant source of vascular plant detritus and the associated moieties of lignin, in both dissolved and particulate OC of natural ecosystems, are terrestrial biomes.

In terrestrial ecosystems, most decomposition studies have traditionally considered lignin to be the most recalcitrant component in the degradation of TerrOC. In fact, lignin is one of the most abundant natural organic compound on earth, second only to cellulose. These compounds have had a significant impact on the biogeochemistry of both terrestrial and aquatic ecosystems, particularly in the context of decomposer evolution. Therefore, how has a molecule like lignin (in both woody and nonwoody plant tissues) affected the overall kinetics of OC cycling on land since its appearance in the mid-Paleozoic (ca. 350 Ma), and what impact has this had on aquatic ecosystems? The fossil record of wood decay reveals fossils that have white-pocket rot fungi and

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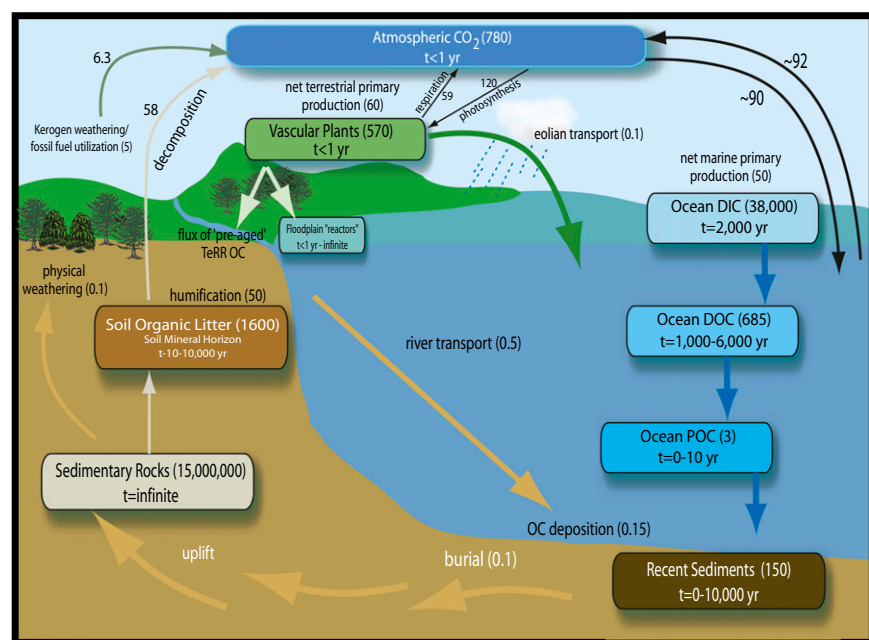


Fig. 1. The global carbon cycle (units are in PgC or Pg C $\cdot$ y $^{-1}$ ). Sources of inventories and fluxes are refs. 2–8, 48, 59, 61; diagram modified from Drenzek (114).

spindle-shaped zones of delignified wood that occur as early as the Triassic (ca. 220 Ma), which, very interestingly, suggests that this decay process has not changed for millions of years.

### Enzyme Dynamics and TerrOC Decay

**Fungal Enzymes.** Fungi are the primary decomposers of woody and nonwoody vascular plant materials in terrestrial ecosystem. The decomposition pathway for some *Basidiomycotina* fungi (i.e., brown-rot fungi) involves an initial decay of wood that begins with an extracellular non-enzymatic attack by generating hydroxyl radicals ( $\cdot$ OH) via the Fenton reaction (20). In a different pathway of decay, other *Basidiomycotina* (i.e., white-rot fungi) simultaneously decompose cellulose and lignin using free radical attack that can break a variety of bonds in the large phenylpropanoid heteropolymer (21).

Wetland systems, which are important transitional zones between terrestrial and aquatic ecosystems, have marine fungi that are important in decomposing vascular plant materials (22) (Fig. 1). Many of the dominant marine fungi [e.g., eumycotic, mitosporic, and chytrids (39)] have enzymes capable of decomposing wetland litter. The primary fungal species in decomposing salt marsh cordgrass (*Spartina alterniflora*) is *Phaeosphaeria spartinicola*, whereas that in mangroves is *Halophytophthora* spp. (23).

**Bacterial Enzymes.** Bacteria that decompose TerrOC are generally divided into two categories: the primary degraders (con-

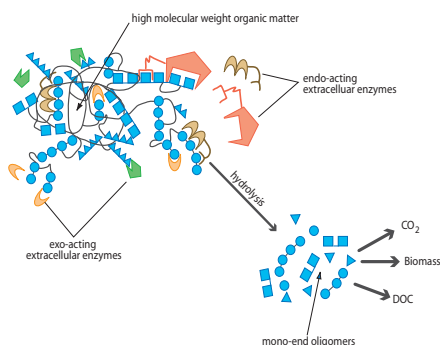
sidered erosional bacteria) and initiate digestion of woody and nonwoody plant material, which allows for the secondary degraders (considered scavenging bacteria), to consume metabolites from the primary degraders. Sulfate reducing bacteria *Desulfovibrio* spp. are an example of scavenging bacteria when considering their role in wood decay (24). Some rate controlling effects on decay are different species of wood, water temperature, oxygen availability, and salinity. The bacteria commonly associated with wood decay are cellulolytic aerobes such as *Cytophaga* and *Cellvibrio* and anaerobic species such as *Clostridium*, *Bacillus*, *Pseudomonas*, *Anthrobacter*, *Flavobacterium*, and *Spirillum*. Under anaerobic conditions, lignin is thought to be well preserved. However, methanogenic degradation of lignin derivatives has been reported (25). In fact, lignin components of softwood and hardwood have been shown to partially degrade to gaseous end products under anaerobic conditions (26).

New molecular techniques that use the 16S rRNA or its encoding gene (rDNA) can be used as molecular biomarkers for the presence of wood-decaying bacteria (28). Identifying the putative genes in gene databases can provide important information on the source of the enzyme and its potential functions (28); this approach is key in our understanding of global carbon cycling. Because not all bacteria found in wood are actually wood-decaying species, in general, the rRNA diversity is typically less than 20 taxa,

particularly in samples from marine sites (27). It has been shown that the enzymes in sediments have a wider range of substrates than their water column analogues (28). Therefore, understanding the genes responsible for the production of enzymes capable of lignin decay is key in our understanding of global carbon cycling.

**Enzyme Strategies and Limitations.** The reliance of microbes on extracellular enzymes as an energy acquisition strategy raises a number of questions in ecosystem sciences. When do microbes produce extracellular enzymes? Moreover, at what costs do extracellular enzymes play a central role in the heterotrophic utilization of OC by microbial communities? Particulate substrates usually need to be degraded to a size of approximately 600 Da before they can actively be transported across cell walls by porins (29). Hydrolysis by extracellular enzymes is commonly considered a rate-limiting step in the remineralization of OC (28, 30). Extracellular enzymes are either released freely into solution or may remain tethered to the cell (30). Some enzymes are constitutive (produced regardless of cellular substrate conditions) and others are produced only in response to specific environmental cues (28). Enzymes can also be blocked or inactivated, rendering them ineffective in the process of carbon remineralization (28) (Fig. 2). Substrates may also slow the process of carbon remineralization if they are adsorbed to particles (e.g., clays) or complexed by macromolecules (e.g., humic substances) (28, 31). Not all substrates have to be hydrolyzed to monomers before being transported into the cell, so simply looking at the uptake of monomers as indicators of carbon remineralization may be somewhat restrictive (28, 32). Additionally, exo-acting extracellular enzymes cleave units from the terminal end of a polymer chain, where endo-acting enzymes are specially targeted to certain substrates (32), further complicating the study of monomer uptake.

As extracellular enzymes function outside the cell, the reaction products may diffuse away from the enzyme-secreting microbe (33, 34). Therefore, microbes may benefit by intercepting the products without secreting their own enzymes. This strategy has been referred to as “cheating” and should arise whenever there are multiple organisms that can benefit from the resource investment of a single organism (33). Thus, enzyme diffusion must be extremely slow for producers to compete well in natural environments; such slow diffusion could occur if enzymes were to encounter more tortuous diffusion pathways in soils, sediments, or particles because of pore structures (35). Most natural terrestrial soil systems contain a large



**Fig. 2.** Hydrolysis of high molecular weight OM to mono/oligomers (blue) by a variety of endo-acting (gold and red) and exo-acting (green, orange) extracellular enzymes. The identity of organisms producing enzymes, structural specificity of enzymes, size spectrum of hydrolysis products, and identity of organisms consuming substrates are not specified in this diagram. This highlights some of the major unknown factors in the early steps of carbon transformation in many aquatic systems. Modified from Arnosti (28).

degree of heterogeneity: organism substrates, microbes, and mineral particles form a 3D matrix of aggregates and pore spaces of different sizes. Aggregates have been shown to be “hot spots” for microbial and enzyme activities (e.g., refs. 35, 36); this increase in enzyme activity has been attributed to quorum sensing (system of stimulus and response correlated with population density) (37).

**Other Metazoan Effects on Wood and Lignin Decay.** Perhaps the most well known wood-decomposing organism in marine systems is the shipworm (*Teredo navalis*) (38), which results in extensive biomechanical erosion of the woody material. Biomechanical disruption of soils can certainly affect the distribution of oxygen, surface litter, and enzyme pathways. The scales of habitat utilization in soils depend mainly on the size of the organisms: a few microns for bacteria, less than 100  $\mu\text{m}$  for fungi, between 100  $\mu\text{m}$  and 2 mm for macroarthropods, and between 2 and 20 mm for macroarthropods (39). For example, macrodetritivores such as earthworms are important in processing SOC and wood (e.g., termites, bark beetles), there are macrodetritivores in coastal wetlands (e.g., crabs and amphipods) that are capable of digesting large amounts of vascular plant litter (40). TerrOC residues that have been fragmented and moistened during macrofaunal gut transfer are more easily digested by microflora. For example, macrofauna like earthworms and termites are large enough to develop symbiotic relationships with the microflora in their guts (41), but also allow for more effective breakdown of any remaining TerrOC in their feces. Fresh litter is often mixed down into the soil profiles by mac-

rofaunal organisms such as earthworms, thus injecting less degraded TerrOC at deeper soil horizons. In fact, a quote by Charles Darwin further captures the importance of bioturbation in soils: “...in many parts of England a weight of more than 10,516 kg of dry earth annually passes through the bodies of earthworms and is brought to the surface on an acre of land...” (42).

### Storage and Cycling of TerrOC in Soils

Soils, as the largest active OC pool on earth, contain an estimated 1,600 Pg of OC (43) (Fig. 1). One estimate of the SOC inventory suggests that 250 Pg C is bound within cellulose, 175 Pg in lignin, 150 Pg in hemicellulose and other polysaccharides, and 5 to 10 Pg in protein, lipids, and cutin, in addition to a large fraction that remains unrecognizable (44). Mean residence time of SOC increases with depth from 10 to 10,000 y in the soil mineral horizon (Fig. 1), dramatically increasing at greater than 0.2 m (45).

There are three general mechanisms associated with stabilizing TerrOC in soils: (i) inherent recalcitrance of specific organic molecules that resist decay by microbes and enzymes; (ii) chemical stabilization caused by interactions between organic molecules, like surface condensation (sorption), which results in decreased availability of organic substrates; and (iii) physical protection of organic substrates against decomposers from occlusion of substrates within aggregates (46). Sorption processes are an important mechanism for transforming labile DOC defined in the literature as OC lower than 0.2, 0.45, or 0.7  $\mu\text{m}$  in size) into stable SOC (47). The process of leaching DOC from forest floor litter with subsequent transport and sorption to lower mineral phase horizons has been increasingly recognized as an important mechanism for SOC formation and stabilization. TerrDOC collected within the mineral soil is chemically more similar to soil OC than to fresh litter as a result of sorption and exchange as water percolates through soils (47) (Fig. 2).

### Transport of TerrOC from Soils to Global Ocean

**From Soils to Inland Waters.** Approximately 1.9 Pg C  $\text{y}^{-1}$  is delivered to inland waters from the landscape (48). The distribution of molecules of different charge, weight, and size controls the reactivity of TerrDOC in soils and its release to aquatic environments. Differences in the composition of TerrDOC as it passes through the upper mineral soils are largely as a result of microbial breakdown. Recent work has shown that eroded soil particles can release TerrOC and N when entering rivers and oceans and that as much as 50% of

this OC is available for aquatic metabolism (49). TerrDOC released in summer from soils during high temperature has been shown to be mainly derived from oxidative breakdown of lignin, whereas TerrDOC released in winter and spring is dominated by carbohydrates; the reasons for this are not yet fully understood (50).

In crop-growing regions, the major factors controlling TerrOC export are land use and drainage associated with agricultural practices. Recent metadata analysis further supports that event-based fluxes of TerrDOC in streams and rivers are very important in forested watersheds (51). More specifically, the majority (70%) of event-based TerrDOC flux occurs during the rising hydrograph and during large events. TerrOC quantity, source, and degradation state are dramatically altered under flooding conditions (52).

**TerrOC Cycling in Inland Waters.** Twice the amount of C is delivered to inland waters than is delivered to the ocean (1.9 Pg C  $\text{y}^{-1}$  vs. 0.9 Pg C  $\text{y}^{-1}$ ), suggesting that TerrOC in these systems is more actively consumed than previously thought. Heterotrophy is a condition in which respiration (R) exceeds production (P; i.e.,  $P/R < 1$ ), and can be inferred for many aquatic systems based on high partial pressure of  $\text{CO}_2$  (53). Recent estimates of  $\text{CO}_2$  efflux from streams and rivers suggests that TerrOC is not as recalcitrant as previously thought (54). Net heterotrophy of global fluvial respiration from headwaters through estuaries is approximately 2.1 Pg C  $\text{y}^{-1}$ , representing a global net heterotrophy of 0.6 Pg C  $\text{y}^{-1}$  (55). This high annual turnover contradicts the paradigm that TerrOC cycles over longer timescales (48). Respiration and net ecosystem production increases from headwaters through rivers to estuaries as the respiration of OC declines relative to gross primary production (55). This supports the River Continuum Concept (RCC) (56) (discussed later) with further extension into estuaries, where metabolic performance is highest in headwaters where most of the microbial biomass and metabolic processes are associated with stream-bed surface, which allows for excellent exchange of nutrients and oxygen and removal of wastes.

The longitudinal change from heterotrophic headwaters, to more autotrophic midorder streams and small rivers, and finally to heterotrophic large rivers is a fundamental property of the RCC (56). There is a gradual succession in the microbial community composition along this longitudinal gradient from headwaters to large rivers and even further out to estuaries (57). TerrDOC and terrestrially derived particulate OC (TerrPOC) produced within small channels are considered to be recalcitrant and thus difficult



to assimilate in the riverine productivity model (58). More specifically, the riverine productivity model suggests that highly and moderately labile autochthonous OC are subsidies from the riparian zone. Moreover, these subsidies compensate for the typically greater abundance of recalcitrant TerrOC from upstream leakage and floodplain inputs (58). In contrast, the RCC suggested that terrestrially derived fine particulate OM leaking from headwaters was the most important source of carbon for food webs in large rivers, although the increased abundance of phytoplankton in larger rivers was acknowledged (56).

#### Riverine Inputs of TerrOC to Global Ocean.

Rivers play a major role in exporting TerrOC from the continents to the oceans (1, 3). Approximately  $0.3 \text{ Pg C} \cdot \text{y}^{-1}$  of DOC and  $0.2 \text{ Pg C} \cdot \text{y}^{-1}$  of POC are discharged by rivers to the global ocean (59); these OC fractions represent approximately 50% of total C (organic and inorganic inputs;  $0.9 \text{ Pg C}$ ) export by rivers (48) (Fig. 1). Before reaching the open ocean, many of these rivers enter into estuarine zones and shelves that have also been shown to be new sources of  $\text{CO}_2$  to the atmosphere (refs. 6, 48 and refs. therein). In particular, the water-to-air flux of  $\text{CO}_2$  in estuaries has been shown to be  $0.3 \text{ Pg C} \cdot \text{y}^{-1}$  (6). In contrast, there can be rapid and efficient delivery of fossil OC to the coast with little degradation in regions of highly erosive steep mountain building areas such as Taiwan (60).

#### Changing Paradigm in Aquatic Ecosystems

**Freshwaters.** Based on a sample of 85 rivers and 2,000 lakes, it has been established that many inland freshwater systems are net heterotrophic, based on supersaturation of  $\text{CO}_2$  (61). Moreover, linkages between upper pelagic phytoplankton and bacterial biomass only explain approximately 20% of bacterial production; once again, this implies the importance of allochthonous sources in fueling ecosystem stability in these freshwater systems. Another widely held paradigm is that riverine OC represents highly degraded remnants of vascular plant sources aged in soils. However, recent work has shown that riverine DOC in most systems is modern and much younger than POC, and therefore not likely aged in soils (54, 62). In fact, lignin compositional differences lignin in soils versus coastal sediments may be entirely caused by selective fractionation of OC during leaching phases and not degradation. Such fractionation processes have already been observed for free amino acids (63) and peptides (64). This may suggest that riverine DOM is less degraded than previously thought, and thus is more labile,

allowing for more rapid mineralization in coastal waters. There are many anthropogenic factors that are contributing to observed changes in river and coastal OC, such as damming and land-use changes in farming (ref. 65 and refs. therein). For example, the Amazon mainstream has very low rates of algal production (66), whereas more than 50% of the POC in the upper Mississippi River is algal-derived (67).

#### Coastal and Open Ocean

**"Missing" TerrPOC.** There is at least twice as much TerrPOC delivered by rivers each year than can be accounted for by burial of OC in marine sediments (68). Assuming a river POC ( $\text{OC} > 0.2, 0.45, \text{ or } 0.7 \mu\text{m}$  in size) discharge of approximately  $0.2 \text{ Pg C} \cdot \text{y}^{-1}$  (69) and a TerrOC burial in sediments of approximately  $0.1 \text{ Pg C} \cdot \text{y}^{-1}$ , there is greater than  $0.1 \text{ Pg C}$  of TerrOC that is remineralized every year between river discharge and marine sediment burial (Fig. 1). More recent calculations estimated that 30% of the TerrOC being buried in marine sediments is of terrestrial origin (3). Ninety percent of the OC burial in the ocean occurs in deltaic and margin sediments and is associated with mineral particles largely of clay-silt sizes (68). This TerrOC associated with minerals can be exchanged with marine OM as it enters the coastal ocean, which also may be why we do not see as much as expected from riverine inputs. OC preservation is significantly enhanced by the formation of microaggregates and has recently been shown to encapsulate colloidal sized particles of OC with minerals, creating pores that are filled with OC (70). More specifically, this has reaffirmed that OC is not protected by small mesopores on clay particles ( $2\text{--}10 \text{ nm}$ ) too small to exclude exoenzymes that degrade OC (68). Resuspension of highly fluidized muds in deltaic regions results in greater oxygen exposure compared with most other fine-grained sediments in shelf environments (71). Although low oxygen concentration is generally assumed to limit microbial processes in sediments, it should also be noted that the lack of availability of labile OM (LOM) limits bacterial heterotrophic activity in aquatic ecosystems even in the presence of adequate oxygen levels (72). The "missing" TerrPOC in coastal sediments suggests that this material is being remineralized faster than previously thought and/or is being transported to other regions offshore.

**"Missing" TerrDOC.** Although the  $0.3 \text{ Pg}$  of DOC (which has been defined in the literature as  $\text{OC} < 0.2, 0.45, \text{ or } 0.7 \mu\text{m}$  in size) that is discharged annually to the global ocean can be accounted for in the turnover time of all oceanic DOC

(ca. 4,000–6,000 y) (73), chemical bio-marker and stable isotopic data (74, 75) indicate that there is very little TerrOC in the global ocean. The average residence time of TerrDOC in the open ocean is less than 100 y (76), suggesting the removal can be as short as decadal time scales. The Arctic Ocean receives approximately 10% of the global river discharge, with Arctic rivers delivering approximately  $0.03 \text{ Pg C} \cdot \text{y}^{-1}$  TerrDOC to shelf waters (77). The aging of deepwater in the ocean may in part be related to processes that occur in coastal regions. Rivers that empty into the North Atlantic have been found to have old (i.e.,  $^{14}\text{C}$ -depleted) and young (i.e.,  $^{14}\text{C}$ -enriched) TerrDOC with predominantly old POC (62). Selective degradation over the residence time of the estuarine and river systems may leave more recalcitrant material OM, resulting in preaging material before reaching the oceans (62).

There is growing evidence that photochemical transformations enhance the loss of TerrDOC in the coastal ocean (78). In fact, in a mesocosm experiment, as much as 75% and 72% of dissolved lignin was removed after 28 d and 10 d, respectively, of exposure to sunlight in Mississippi River waters (79). Recent work in the Congo River, which delivers 5% of the global riverine DOC to the ocean (80), has shown that the DOC has molecular signatures similar to carboxyl-rich alicyclic molecules [CRAM; a complex mixture of carboxylated and fused alicyclic structures with a carboxyl-C-to-aliphatic-C ratio of 1:2 to 1:7 (81)], and was highly photolabile (82). Many of these studies have shown molecular signatures of CRAM derived from lignin, suggesting a linkage in part with TerrOC. CRAM also represents the most abundant component of very old DOC in the deep ocean (81). Moreover, this work showed that some of the missing riverine-derived DOC in the global ocean is, in part, being removed at the river/ocean boundary in river plume environments by photochemical processes. Linkages between the formation of CRAM (82) in shallow coastal waters via photochemical reactions, and possibly microbial decay, may prove to be critical in resolving the absence of TerrOC biomarkers in the open ocean, as well as the "old" recalcitrant pool observed in the ocean deepwaters.

Finally, it should be noted that other in situ open ocean processes, not related to coastal photochemical transformations of river-derived DOM, can form recalcitrant DOM via (i) production of recalcitrant DOM from phytoplankton (e.g., acylheteropolysaccharides); (ii) formation of melanoidins through condensation reactions; (iii) contribution from cell wall-derived material; (iv) adsorption of labile DOC to colloidal material; (v) formation

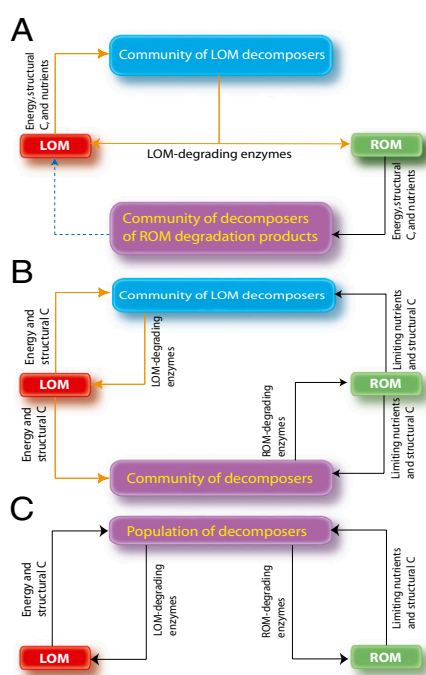
of colloids from microzooplankton grazing; (iv) release of metabolites; and (vii) the microbial carbon pump (ref. 83 and references therein).

### Priming Effect: Bridging the Gap Between Terrestrial and Aquatic Sciences

Priming is formally defined by Kuzyakov et al. (11) as “strong short-term changes in the turnover of soil organic matter caused by comparatively moderate treatments of soil.” Such treatments might include input of organic and mineral fertilizer, exudation of organic substance by roots, mechanical treatment of soil, and rewetting and drying effects on soils. Horvath (84) defined co-metabolism, a subcomponent of priming, as “degradation of a recalcitrant substance by microorganisms in the presence of a readily degradable substrate without the ability for these microorganisms to utilize the products of recalcitrant OC oxidation.” Priming is typically divided into “real” priming, whereby soil OM is decomposed, and “apparent” priming, whereby there are changes in microbial biomass turnover but no effects on SOC decomposition (15).

**Priming in Soils.** A review by Jenkinson et al. (85) on priming sparked the beginning of many new publications on priming in the soil literature that continues today. In general, there are three different hypotheses explaining the priming effect (86) (Fig. 3). In one case, LOM-degrading enzymes are produced by LOM decomposers that are also capable of degrading recalcitrant OM (ROM) into intermediate catabolites, which could not otherwise be used by LOM decomposers (Fig. 3A). In another situation, a community of decomposers mineralizes catabolites (i.e., cometabolism), whereby LOM degradation by LOM decomposers brings energy to the ROM decomposers. This energy allows the ROM decomposers to produce ROM-degrading enzymes, releasing nutrients for both ROM and LOM decomposers, creating a net mutualism between these two microbial communities (Fig. 3B). Finally, there may be a single population capable of producing enzymes able to degrade LOM and ROM; LOM degradation provides energy for the synthesis of ROM-degrading enzymes (Fig. 3C). All the aforementioned scenarios represent the simplified pathways established for priming in soil types. Similar ones may exist in aquatic systems, but further work is needed for such comparisons.

Many priming experiments in soils have showed that CO<sub>2</sub> evolution could be increased from four- to 11-fold higher after the addition of labeled <sup>13</sup>C-plant residues (ref. 15 and refs. therein). Some of the common priming substrates in soils are simple sugars and amino acids, with com-



**Fig. 3.** Three different priming effects involving LOM and ROM, respectively. These proposed priming effects are mainly derived from work in soils. Modified from Guenet et al. (86).

bined additions having synergistic effects on priming (87). Other common substrates in soils making up a significant fraction of DOC are oxalic acid, acetate, and catechol (88). Deep SOC persists because it is bound to soil minerals and is in a chemical form that is not easily assimilated by microbes (89), and perhaps lacks contact with priming substrates from root tips in the upper soils (Fig. 4).

According to Kuzyakov et al. (17), what is needed to quantify priming effects is the application of both <sup>14</sup>C and <sup>15</sup>N labeling of soil OM or soil microorganisms; simultaneous monitoring of nitrogen-gross mineralization and CO<sub>2</sub> efflux; experiments that examine interactions of plants, microflora, and soil fauna; and quantification of nutrients mobilized or immobilized in priming effects (Fig. 4). The mineralization of charcoal, a very recalcitrant form of OC, was shown to increase between 36% and 600% (vs. control) when primed with glucose (87). Priming has been shown to increase the loss of soil carbon by 169% after priming by sucrose, 44% following chopped maize, and 67% following ground maize additions (90). In another priming experiment, soil samples from deep horizons (0.6–0.8 m) were incubated with <sup>14</sup>C-labeled cellulose at amounts reflecting a rate representing approximately 25% of the annual fresh plant litter carbon deposition into the surface layer by plant roots; the results showed an increase in decomposition of SOC, as indicated by an

increase the amount unlabeled of soil-originated CO<sub>2</sub> (87).

**Priming in Aquatic Systems.** Benzoic acid has been shown to act as a priming substance for the assimilation of fulvic acids by the bacteria *Arthrobacter* spp. in lake waters (91). In one of the few examples of priming in marine sediments, it was shown that algal OC additions induced levels of background remineralization (i.e., priming) by as much as 31% (92), suggesting that OC priming in marine sediments is likely to be more important than previously thought. Earlier work in marine sediments only implied the importance of co-metabolism (a component of priming; Fig. 3) as a mechanism in breaking down recalcitrant material (93). Other studies have shown that sediments can be primed with fresh substrates, typically from algal sources (94) (Fig. 4). It has also been argued that the enhanced remineralization of OC observed in sediments as a result of bioturbation, and the downward transport of oxygen is also likely linked with the injection of fresh surface substrates (92). Although bioassays are still considered perhaps the best method for predicting the biological utilization of OC in ecosystems when combined with proper formulation of biodegradation kinetics (ref. 95 and refs. therein), it is important to include the priming potential. In sediments, bulk POC characterization (e.g., C/N molar ratio) does not reflect the actual reactivity and availability for substrates to the microbial community; it is likely fueled by a small fraction of POC that is not detected by bulk measurements because it is rapidly cycled through the DOC pool in pore waters (28).

Although the majority of DOC produced in the surface ocean is used very quickly by microbes, approximately 20% of the annual net community respiration in the global ocean escapes the euphotic zone and enters into the large pool of recalcitrant DOC in deepwaters (97). This may be an excellent location in which to look for priming effects between these two important global pools of OC, and does have relevance in part to TerrOC because some of the deeper OC pool has been shown to have TerrOC material (e.g., CRAM). Dissolved free amino acids can turn over on the order of hours to days, and therefore contribute to the rapid turnover of open ocean DOC (97). By-products from zooplankton grazing on primary production are an important source of DOC to bacterial production in the open ocean; this labile fraction may turnover as quickly as 2 to 6 d. This young, labile fraction can mix with the semilabile and recalcitrant components in the open ocean, resulting in possible priming effects (Fig. 4). By using nucleic acids as a bacterial

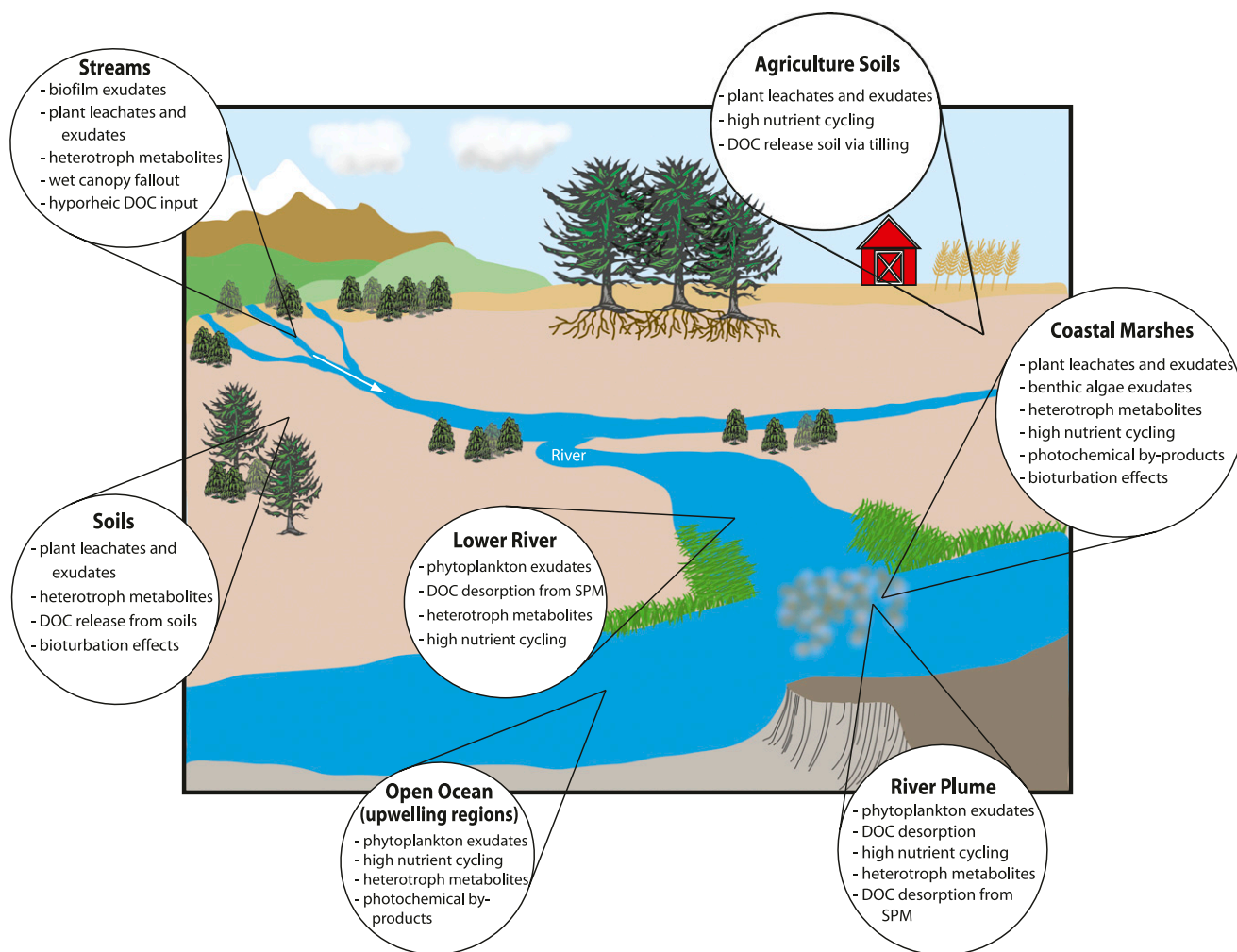


Fig. 4. Sources of possible priming substrates in different terrestrial and aquatic environments. Modified from Raymond et al. (114).

biomarker and compound specific-radio-carbon measurements, it was speculated that the older, more recalcitrant component of the DOC pool in the North Pacific was made available for bacterial utilization and assimilation via co-metabolism and/or photooxidation (98). Surface water from the Sargasso Sea showed that bacterial growth only occurred when the DOC exceeded ambient background levels of DOC; in fact, only the surplus DOC, which represented approximately 6% to 7% of the total DOC, was used by bacteria (99). Other work showed that bacteria serve as remineralizers of a small fraction of bulk DOM during short periods when labile DOM becomes available (97).

Making better linkages among ecosystem science, analytical chemistry, molecular microbiology, and computer informatics has recently been espoused as something that is needed to fill the gaps in our knowledge of OM cycling in aquatic systems (83). One avenue that is very promising in addressing the issue of what microbes are investing into enzymes and

what the return is in a complex mixture of POC and DOC is the use of transporter genes (100). In this process, random libraries of expressed genes from coastal bacteria communities have been used to identify sequences reflective of DOC-transporting proteins (i.e., mRNAs). Many of the transport genes showed that carboxylic acids, polyamines, and lipids were key substrates in the biologically active pool of coastal DOC. Many bacteria had genes for DOC components commonly found in DOC such as amino acids, whereas other bacteria (e.g., Roseobacter, SAR11, Flavobacteriales, and  $\gamma$ -Proteobacteria clades) had genes that were used for specific components of DOC. Recent work has also shown that a greater number of genes are produced for polysaccharide degradation by microbial populations living in deep oceanic water than in surface waters (101). The role of Archaea and Bacteria also remains an interesting question with regard to possible priming effects and utilization of different fractions of OC in the coastal and open ocean (102)

(Fig. 4). For example, *Crenarchaeota* have been shown to be less active in assimilating amino acids and glucose, yet twice as active as bacteria in assimilating protein and diatom exudates (102).

### Recalcitrance and Lability: It's All in the Word

In the context of the aforementioned pools of labile and recalcitrant OC in soils, sediments, freshwaters, and oceanic waters, there appears to be an emerging consensus that may modify our meaning of the words "recalcitrant" and "labile." That is, these terms, which are commonly used to describe differences in the "quality" of OC (particularly TerrOC) as food resources for heterotrophs, may only be valid in the context of the ambient environment. Moreover, the potential assimilation capability of the local microbial community, where such substrates may reside, also needs to be considered. To date, these terms have been defined largely based on a chemocentric and anthropocentric view that is in part based on our



view of the chemical composition of TerrOC and/or petrogenic OC. Although this topic has been mentioned previously in the literature (e.g., see reviews in refs. 28, 83 and refs. therein), it was not in the broader context of TerrOC and its origins. Consider for a moment that recent experimental work has shown that cultured prokaryotes were  $^{14}\text{C}$ -dead, illustrating that they were living off of "recalcitrant" OC from 365-Myr-old black shale (103). Similarly, functional exoenzymes of metabolically active bacteria have been found in 124,000-y-old sapropel of the eastern Mediterranean (104). Viable bacteria have also been found in some of the oldest permafrost layers in the Northern hemisphere (105). In addition to the "power" of the ever-evolving enzyme capability of microbial communities, there are physical gradients (e.g., photochemical examples mentioned previously) that also control the availability of "labile" and "recalcitrant" OC substrates. Finally, many of the incubation experiments in aquatic studies typically exclude light when examining the efficiency of uptake of added or natural concentrations of TerrPOC and/or TerrDOC by heterotrophs, which prevents the possible interactive effects of priming between algal exudates on TerrOC uptake.

I propose that future carbon cycling studies in aquatic ecosystems need to be more cognizant of the importance of the priming effect potential (PEP) in designing TerrOC utilization experiments and modeling efforts. For example, regions such as coastal deltaic region, where there are high inputs of TerrOC, as well as, in many cases, high primary production; steep nutrient, light, and salinity gradients; and microbial communities that are highly adaptable to changing physicochemical gradients, will have a high PEP (Fig. 4). Similarly, upwelling regions, whether it be at the equator or along coastal margins, are locations where "old" deepwater DOC comes in contact with surface waters that have some of the highest primary production rates in the global ocean, and hence a high PEP because of the presence of phytoplankton exudates (Fig. 4).

### Impact of Global Change on Role of TerrOC in Aquatic Ecosystems

The Arctic has and will remain one of the focal points in climate change research as a result of the visibility of its rapid ecosystem changes. For example, because of global warming, Arctic rivers have all shown trends of increasing water discharge, as well as total DOC and TerrDOC to the Arctic Ocean (106). TerrDOC has been shown to be correlated with summer sea-

ice retreat in certain years in the Arctic. Increasing freshwater inputs will decrease residence time of TerrOC (both POC and DOC) to the Arctic Ocean, likely increasing inputs to the northern Atlantic; understanding the consequence of such changes will be a key part in understanding the changing global carbon cycle (72, 107).

In Arctic sediments, approximately 40% to 50% of the OC being buried is derived from petrogenic OC, likely derived from weathering of ancient sedimentary rocks in the region (108). This is likely to be enhanced with greater overland flow patterns, as described earlier for the DOC and POC pools with ensuing climate change. Although significant changes are occurring with enhanced ice-melting in the Arctic, there was little evidence for the transport of TerrOC in Hudson Bay (109). The release of labile DOC from estuaries to the coast has been shown to be in part related to changing temperatures over different seasons and not to the inherent "recalcitrance" of the material (62). The Arctic is likely to be an excellent location for observing the PEP on rapidly changing inputs and export of TerrOC in the advent of climate change. Unlike temperate and tropical systems, the Arctic is a place with greater inputs of freshwater and TerrOC, and also where bacterial activity is slower as a result of lower temperatures and photochemical reactions reduced by the light/dark cycle (106). Bacterial diversity has been shown to decline with increased climatic severity, so many of the aforementioned changes in the flux of TerrOC to the Arctic are also likely to be impacted by such changes in microbial communities with a high PEP.

Globally, wetland loss rates are increasing with sea-level rise (65), which will result in greater inputs of both TerrPOC and TerrDOC to the coastal ocean. Recent work has also shown that the role of TerrOC in coastal marine sediments is likely more important than previously thought for the long-term sequestration of atmospheric  $\text{CO}_2$  (65). For example, land-use changes were found to be more important than changes in climate and plant  $\text{CO}_2$  fertilization to increases in Mississippi River water and carbon export from the watershed over the past 50 y (111). Similarly, with the changing view of more efficient consumption of TerrOC in inland freshwater systems (61), it is likely these systems will continue to see greater consumption and  $\text{CO}_2$  efflux with increasing global temperature.

Carbon leaching (i.e., biogenic TerrDOC and DIC) can increase the net losses from croplands by as much as 24% to 105%

in United Kingdom soils (112). These differences between natural forested and cropland regions have important implications for the cycling of TerrOC with the advent of expanding land-use changes in world. Future methods in soil spectral properties using remote sensing such as the cellulose absorption index, the lignin-cellulose absorption index, the normalized difference senescent vegetation index, and normalized difference vegetation indices 5 and 7, will prove to be extremely useful with the rapidly occurring land-use changes in the world (113).

### Conclusions

In summary, I propose that, if we are examine the role of PEP on the utilization of TerrOC in global ecosystems, we need to develop (i) an understanding between the evolution of terrestrial organisms (e.g., fungi) that evolved biochemical pathways to consume recalcitrant molecules (e.g., lignin) TerrOC on land with the pathways for consuming TerrOC in aquatic systems; (ii) a greater understanding of the complex role of enzyme kinetics as it relates to OM cycling in natural systems; (iii) a broader view of the terminology used to define the "quality" of TerrOC; (iv) better experimental design that allows for primary producer exudates to interact with TerrOC; (v) better incorporation of molecular microbiological techniques to understand the role of short-term strategies used by microbial populations to use TerrOC in different environments; (vi) more integrative thinking among classic analytical chemistry, molecular microbiology, and evolutionary ecology; (vii) more cross-breeding of ideas between terrestrial and aquatic ecosystems; and (viii) models that allow for the inclusion of priming effects in the global carbon cycling and climate change. The integration of the foundations of ecological/evolutionary theory in the context of priming combined with the new analytical advancements in the chemical characterization OC and molecular microbiology will prove vital in our understanding of OC cycling in a changing climate.

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