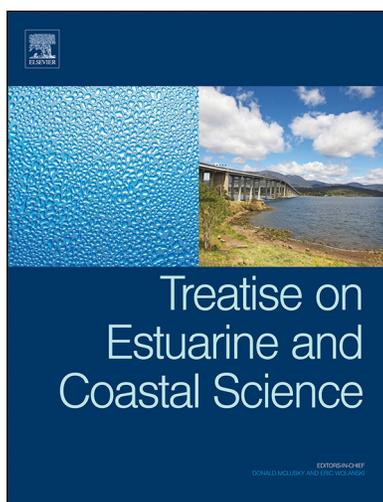


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5.02 Dissolved Organic Carbon Cycling and Transformation

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Abstract

This chapter reviews and synthesizes the current state of knowledge on sources, transformations, cycling, and fluxes of dissolved organic carbon (DOC) in river-estuarine and coastal ocean systems. Because estuarine waters represent a complex interface between terrestrial, marine, seafloor, and even atmospheric environments, significant consideration is given to the diverse sources of organic matter contributing to estuarine and coastal marine DOC pools. Distributions of bulk DOC, its stable ($\delta^{13}\text{C}$) and radioactive ($\Delta^{14}\text{C}$) isotopes, and its biochemical components are reviewed with representative estuaries globally highlighted as examples of the variable types of DOC mixing and processing dynamics in different systems. The significant microbial, photochemical, and physical transformation processes affecting both the amounts and characteristics of DOC during estuarine transport are also evaluated. The chapter concludes by providing some examples of important and compelling recent studies of land-river estuary-coastal ocean DOC fluxes and transfers and their observed long-term changes, both natural and anthropogenically driven.

5.02.1 Introduction

Rivers and estuaries are the primary link between land and oceans, connecting over 87% of the Earth's land surface area to its coasts (Hedges et al., 1997; Ludwig and Probst, 1998). Interactions between land and ocean and their organic carbon (OC) cycles occur via rivers and estuaries, regions of transition ranging from predominantly freshwater to predominantly seawater. Some estuarine systems exist in semi-enclosed basins landward of the coastline, whereas others extend seaward to the shelf break and even beyond as in the case of very large river systems, which transport organic and inorganic materials directly into the interior ocean. River discharge and associated elemental fluxes are directly forced by atmospheric processes such as precipitation and evaporation, as well as by retention and release of moisture in snowpack, and in the forms of both surface and subsurface flows. In a similar sense, estuarine fluxes of materials are controlled not only by physical forcing by river discharge, tidal currents, resuspension, and sedimentation, but also by the often high rates of biological and abiological degradation, alteration, and remineralization that take place there. Estuarine and river plume systems are spatially limited, with lateral dimensions of 1–100 km and relatively shallow depths of up to tens of meters, yet span maximal ranges in basic

physicochemical conditions such as salinity and turbidity. Likewise, extreme gradients in concentrations of bioreactive species (e.g., carbon, nutrients, and trace elements) exist over some fraction of the physical dimensions of the estuary/plume (Hobbie, 2000; Bianchi, 2007). Temporal variability in these systems covers a wide range of scales, given their sensitivity to tidal forcing (timescales of hours), flood and storm events (days), seasonal variability in insolation, precipitation, and snowmelt (months), and long-term climatic variability (e.g., El Niño–Southern Oscillation, Pacific Decadal Oscillation, and North Atlantic Oscillation) that drives changes in precipitation, winds, and temperatures (years to decades).

The major surface reservoirs and fluxes of OC of relevance to estuarine biogeochemical cycles and processes occur at the Earth's surface (Figure 1). These include (1) contemporary terrestrial biomass, (2) noncontemporary terrestrial biomass or soil humus, (3) fossil kerogen from uplifted marine sedimentary rocks, (4) marine organic matter (OM, which itself can be delineated into contemporary and highly aged components), and (5) estuarine primary production itself. Technically speaking, while both river and marine inputs serve as sources of allochthonous OM to estuaries, for purposes of this chapter, we will consider terrestrial and river sources as allochthonous, and estuarine and marine sources as autochthonous in nature.

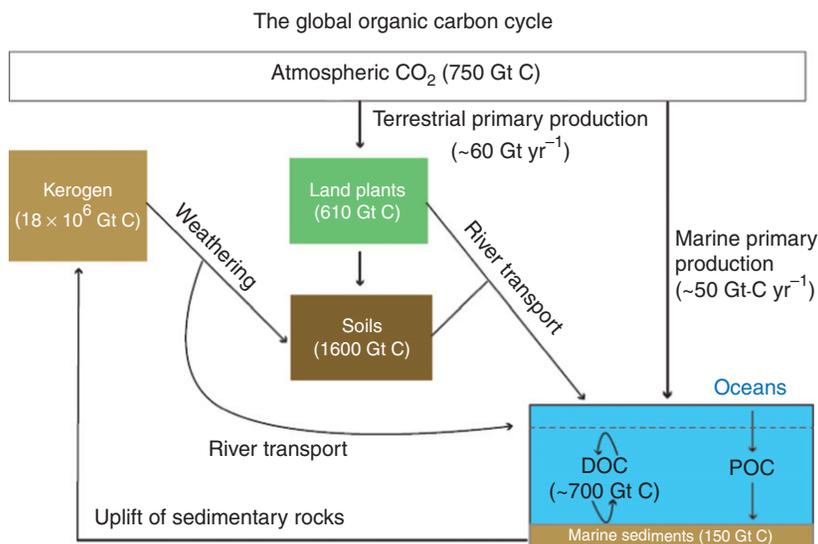


Figure 1 Major reservoirs and fluxes of organic carbon at the Earth's surface relevant to estuarine and coastal ocean biogeochemical processes. 1 Gt = 1 Pg = 10^{15} g. Modified from Hedges, J.I., Hatcher, P.H., Ertel, J.R., Meyers-Schulte, K.J., 1992. A comparison of dissolved humic substances from seawater with Amazon River counterparts by ^{13}C -NMR spectrometry. *Geochimica et Cosmochimica Acta* 56, 1753–1757.

The dominant riverine allochthonous inputs of both dissolved and particulate OC (DOC and POC, respectively) to estuaries include terrestrial plant detritus, mineral soils, resuspended river sediments, and freshwater plankton. Bordering terrestrial freshwater (including tidal freshwaters) and wetland sources (mangroves and freshwater/salt marshes) are also considered to be allochthonous sources of OC. Autochthonous sources of OC typically include estuarine and marine plankton (including benthic and epiphytic micro- and macro-algae) (Laane, 1982), emergent and submergent aquatic vegetation (EAV and SAV, respectively) within the estuary proper, and secondary production (e.g., zooplankton, fishes, and benthic organisms) (Duursma, 1965; Valiela, 1995; Bianchi, 2007; Libes 2009; see Chapter 5.03 for a more complete discussion of autochthonous OM sources in estuaries and coastal waters).

As a result of its ubiquity in biomolecules, carbon (C) is the major biogenic element transported to and found in rivers, estuaries, and other aquatic systems. The dominant forms of this carbon include inorganic, organic, particulate, and dissolved (Table 1). The inorganic forms of C are dominated by carbonates, whereas the organic forms in bulk pools such as DOC and POC may be comprised of up to millions of individual compounds (Holmén, 2000; Kim et al., 2003a, 2003b; Berner, 2004; Bianchi, 2007), each potentially having unique sources and reactivities. As we shall see, an organic substance's behavior, reactivity, and fate in aquatic systems, particularly in estuaries where steep gradients exist in ionic strength, light, turbidity, microbial communities, and other parameters, strongly depend on whether that substance is present in the dissolved and/or particulate phases, whether these phases are from terrestrial or

in situ sources, and how they are altered by biotic and abiotic processes during estuarine transport (Figure 2).

It is also important to recognize that the biogeochemical processes that are often characterized and quantified in estuarine environments are done so against a background of high natural complexity, and one that is rapidly changing due to a number of anthropogenic forces (Figure 3; see also Section 5.02.10). For example, the organic materials entering estuaries from fluvial sources are an integrated function of watershed-based processes such as geomorphological controls, regional and system-specific hydrologic cycles, and climatological effects on vegetation types and soil respiration (Richey, 2004). In addition, nearly every watershed (including its river and estuarine components) in the world has been subjected to some type of damming and other surrounding land-use change (e.g., deforestation, wetland drainage, and land reclamation; Bilby, 1981; Graf, 1999; Meybeck and Vörösmarty, 2005). Therefore, carbon cycling and transformations in modern-day estuarine systems must be assumed to be altered in significant ways over their pre-anthropogenic state.

The general processes controlling the sources and transformations of estuarine DOC will be addressed in this chapter. However, the interactions between dissolved and particulate organic materials are both numerous and inextricable in aquatic systems, and, as a result, the information presented in this chapter will frequently cross-reference its companion chapter on POC cycling and transformation in estuaries (see Chapter 5.03) in this volume.

5.02.2 Methods of DOC Sample Collection, Preparation, and Isolation

5.02.2.1 DOC Sampling and Sample Preparation

A variety of methods have been used historically to separate, extract, and subsequently analyze DOC and POC from aquatic environments (Raymond and Bauer, 2001a; Sobczak et al., 2002; Lawacz, 2006). Nearly all current methods of separation provide operationally defined classes of DOC and POC, and are based on technical limitations of the separation methods available, and, hence, each is subject to limitations and potential artifacts (see, e.g., Moran et al., 1999a; Turnewitsch et al., 2007 and references therein). Simple membrane filtration techniques have dominated, and still do dominate, as the simplest methods for separating DOC and POC. Filter materials include glass, alumina, quartz, polycarbonate, polysulfone, polypropylene, and others (see Hurd and Spencer (1991) for a review of filtration methods and materials) (Table 2). The different compositional materials may be used in the choice of filter, provided they can be precleaned such that no significant blank material is present in the filtrate. Precleaning methods include filter combustion for inorganic filters or chemical cleaning for organic filters. As a cautionary note, the sorption of estuarine DOC to glass filters (and presumably quartz) has been observed (Hullar et al., 1996; Moran et al., 1999a), and the proportion of this sorbed DOC relative to the POC appears to be inversely proportional to the amount of water that has been processed through the filter. Although such artifacts may not necessarily influence the amounts and characteristics of the filtrate DOC, this cannot be ruled out depending on the specific sample concentration and

Table 1 Present-day global estimates of organic and inorganic carbon export from rivers to estuaries and ocean margins

Form	Gt-C yr ⁻¹
DOC	0.22–0.40
POC	0.14–0.40 ^a
TOC	0.36–0.80
DIC	0.38–0.41

^aAccounts for ~50–75% of sediment OC burial in self-slope sediments. From Mulholland, P.J., Watts, J.A., 1982. Transport of organic carbon to the oceans by rivers of North America – A synthesis of existing data. *Tellus* 34, 176–186. Meybeck, M., 1982. Carbon, nitrogen, and phosphorus transport by world rivers. *American Journal of Science* 282, 401–450. Degens, E.T., Kempe, S., Richey, J.E. (Eds.), 1991. *Biogeochemistry of Major Rivers*. Wiley, New York, NY, 382 pp. Spitz, A., Ittekkot, V., 1991. Dissolved and particulate organic matter in rivers. In: Mantoura, R.F.C., Martin, J.M., Wollast, R. (Eds.), *Ocean Margin Processes in Global Change*. Wiley, New York, NY, pp. 5–16. Spitz, A., Leenheer, J., 1991. Dissolved organic carbon in rivers. In: Degens, E.T., Kempe, S., Richey, J.E. (Eds.), *Biogeochemistry of Major World Rivers*. Wiley, New York, NY, pp. 213–232. Hedges, J.I., 1992. Global biogeochemical cycles: progress and problems. *Marine Chemistry* 39, 67–93. Meybeck, M., 1993b. Riverine transport of atmospheric carbon: sources, global typology, and budget. *Water, Air, and Soil Pollution* 70, 443–463. Ludwig, W. J., Probst, L., Kempe, S., 1996. Predicting the oceanic input of organic carbon by continental erosion. *Global Biogeochemical Cycles* 10, 23–41. Hedges, J.I., Keil, R.G., Benner, R., 1997. What happens to terrestrial organic matter in the ocean? *Organic Geochemistry* 27, 195–212. Aitkenhead, J.A., McDowell, W.H., 2000. Soil C/N ratio as a predictor of annual riverine DOC flux at local and global scales. *Global Biogeochemical Cycles* 14, 127–138. Richey, J.E., 2004. Pathways of atmospheric CO₂ through fluvial systems. In: Field, C.B., Raupach, M.R. (Eds.), *The Global Carbon Cycle*, SCOPE. Island Press, Washington, DC, pp. 329–340.

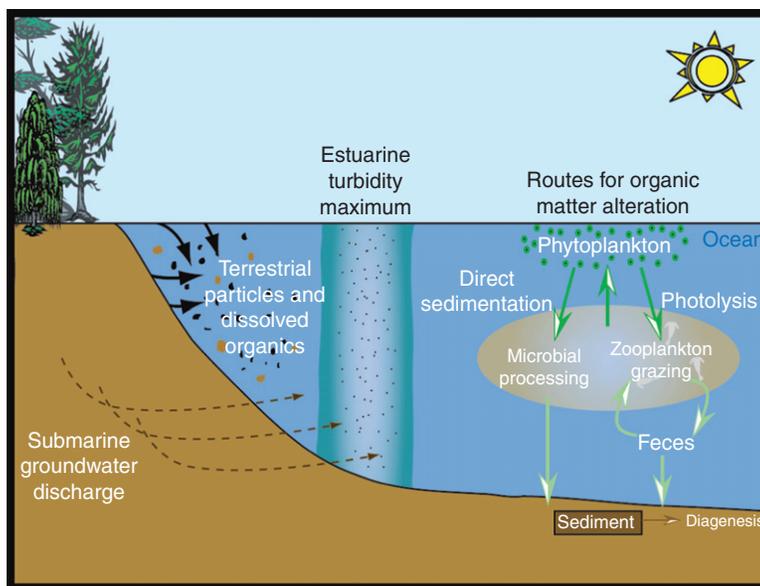


Figure 2 General pathways of autochthonous and allochthonous organic material inputs and fates in estuarine systems.

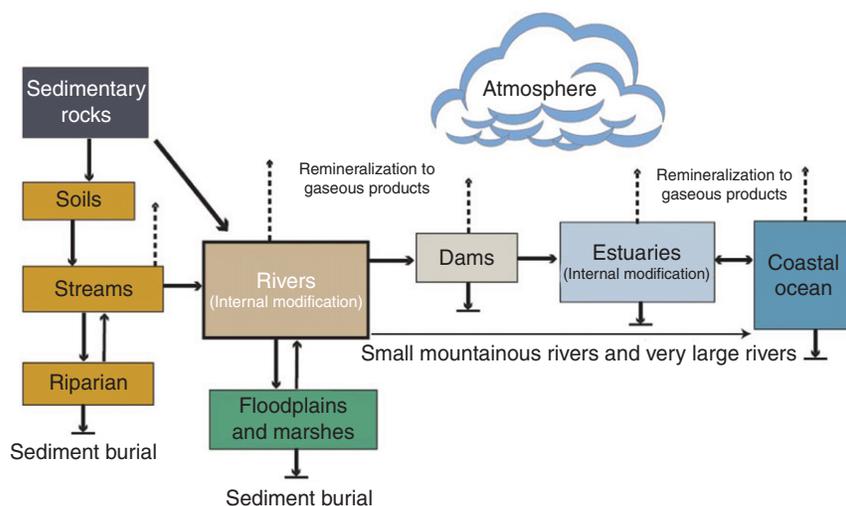


Figure 3 Potential sources and pathways of introduction of terrestrial DOC and POC to the coastal ocean via watersheds, rivers, and estuaries. Also shown are potential losses from natural (e.g., remineralization and sedimentation) and anthropogenic (e.g., damming and watershed modification) factors. Modified from Richey, J.E., 2004., Pathways of atmospheric CO₂ through fluvial systems. In: Field, C.B., Raupach, M.R. (Eds.), *The Global Carbon Cycle*, SCOPE. Island Press, Washington, DC, pp. 329–340.

characteristics (e.g., greater or lesser of hydrophobic vs. hydrophilic materials). By contrast, sorption of sample DOC to glass and quartz filters may contribute a significant component of non-POC blank carbon to filters that will be analyzed for POC (see Chapter 5.03).

Ideally, DOC samples should be processed using membrane filters (e.g., polycarbonate or polysulfone) with a nominal pore size of <0.2 μm in order to eliminate bacteria from the filtrate. However, due to frequent limitations in sample volume and throughput, filters having <0.2 μm nominal pore sizes are not typically used, especially in particle-rich freshwaters and estuarine waters. More often, higher-flow and -capacity glass or quartz fiber filters (GFF and QFF, respectively) are used that allow for the passage of a significant fraction of the free-living bacteria and viruses into a DOC sample. Similarly, a significant portion of the

bacterial (and possibly viral) load is also collected on the filter and characterized as part of the POC. The presence of bacteria in the sample filtrate is potentially problematic for two main reasons. First, if the sample is not preserved rapidly enough with inorganic poisons (HgCl₂, sodium azide, etc.), acids (HCl, H₂SO₄, etc.), or by freezing, bacterial activity may alter the quantity and character of the DOC. Second, the bacterial biomass itself, and its component biomolecules, which may be significantly different from the ambient DOC, will be included in the operationally defined pool of DOC. Although several studies have evaluated changes in DOC due to inadequate sample poisoning, preservation, and storage (Merks and Vlasblom, 1983; Tupas et al., 1994), differences in chemical and isotopic composition due to the inclusion of bacterial biomass in samples have not been rigorously addressed.

Table 2 Selected methods for the collection and isolation of DOC in estuarine and other natural waters

<i>Collection method</i>	<i>DOC fraction(s) collected</i>
Membrane filtration	Total or bulk material
Lyophilization	Total or bulk (fresh or low-S waters only)
XAD resins	Hydrophobic fraction
C ₁₈ stationary phases	Hydrophobic fraction
Gel filtration	Different MW fractions
Gel filtration ultracentrifugation	Different MW fractions
Field-flow fractionation	Different MW fractions
Size-exclusion chromatography	Different MW fractions
High-performance size-exclusion chromatography	Different MW fractions
Ultrafiltration	High MW fraction
Reverse osmosis/electrodialysis	greater than ~75% of total or bulk material

See text for further description and applicable references to studies using these methods. MW, Molecular weight.

5.02.2.2 Techniques for Concentrating DOC and Removal of Interfering Salts

Many different analyses for the chemical and isotopic characterization of estuarine and seawater DOC have historically been difficult, if not impossible, to conduct on salt-containing water samples such as those found in estuaries and coastal seawater (Aiken and Leenheer, 1993; Raymond and Bauer, 2001a; Bauer, 2002). This is because of the often low concentrations of dissolved organic species in estuarine and marine water samples, and the generally very high amounts of dissolved salts in these samples. Freshwater (river, lake, rainwater, etc.) samples can often be distilled using rotary evaporation and related methods to a more concentrated form for aqueous analyses (see, e.g., Moran et al., 1991b; Thacker et al., 2005), or to complete dryness (e.g., by freeze-drying or lyophilization), with the majority of the DOC left as a residue that can be used for any number of dry-phase analyses (see below). Aside from riverine end members, estuarine waters contain significant amounts of salts that will require one or another form of sample concentration and salt removal.

A number of techniques have been developed and employed over the past several decades to isolate DOC (see Hedges (2002); and Benner (2002) for reviews) from both freshwater and marine water (Table 2). These include solid-phase amberlite ion-exchange resins for extraction of humic substances (e.g., XAD-2, XAD-8, and XAD-4; Aiken et al., 1985; Thurman, 1985), gel filtration (Sakugawa and Handa, 1985), gel filtration ultracentrifugation (Wells and Goldberg, 1991; Wells, 2002), flow field-flow fractionation (flow FFF; Beckett et al., 1987; Hassellöv et al., 1999), size-exclusion chromatography (Chin and Gschwend, 1991), ultrafiltration (UF; Benner, 1991; Buffle et al., 1993; Buesseler et al., 1996; Benner et al., 1997; Guo and Santschi, 1997a), silica-based C₁₈ stationary phases (Louchouart et al., 2000; Dittmar et al., 2007; Simjouw et al., 2008), modified styrene divinylbenzene polymer-type sorbents (Dittmar et al., 2008), and high-performance size-exclusion chromatography (Minor et al., 2002). As might be expected, none of these methods is without bias or collects the full complement of DOC (see, e.g., Simjouw et al., 2008; Koprivnjak et al., 2009); hence, the

most appropriate extraction method for the required analyses must be carefully chosen and applied for the system of interest. For example, solid-phase extraction (SPE) procedures (e.g., XAD resins and C₁₈ columns) suffer from the need for DOC molecules to be in their protonated form through pretreatment using acids to pH <~4. This enhances the extraction efficiency (adsorption onto the resin), which is still only ~20% of the total DOC and is dominated by lipophilic or hydrophobic components (Hedges et al., 1992). Concerns also arise that pretreatment may alter certain structural components of DOC through factors such as acid hydrolysis of specific DOC moieties (Benner, 2002).

UF, also known as cross-flow filtration (CFF) or tangential flow filtration (TFF), has become widely used over the last 10–20 years in an attempt to overcome many of the problems noted above, especially for salt-containing samples (Benner, 1991; Benner et al., 1992; Bauer et al., 1996; Buesseler et al., 1996; Guo et al., 1996; Benner et al., 1997; Guo and Santschi, 1997a; see Benner (2002) for review; Table 2). This method can accommodate processing of large (tens to thousands of liters) sample volumes but does not require pretreatment of DOC (Benner et al., 1992). The technique has been found to extract ~20–30% of marine DOC (also known as the UDOC or UDOM fraction) and as much as ~50–60% of freshwater and estuarine DOC using 1-kDa filters (Guo and Santschi, 1996, 1997a; Benner, 2002). Problems include (1) 40–80% of the DOC (presumably lower-molecular-weight (MW) components) is not collected, resulting in potential sample bias and (2) additional loss of the collected DOC resulting from de-salting of the sample and subsequent lyophilization. Nonetheless, this method has the advantage of allowing the dry DOC residue remaining after lyophilization to be subjected to numerous solid-phase chemical analyses, similar to those used for solid-phase materials such as POC or sedimentary OM (e.g., nuclear magnetic resonance (NMR), CHN elemental analysis, gas chromatography-mass spectrometry (GC-MS), high-performance liquid chromatography (HPLC), and sealed-tube combustion; see, for example, Benner, 1991; Santschi et al., 1995; Guo et al., 1996; Benner et al., 1997; Bianchi et al., 1997b; Guo and Santschi, 1997a, 1997b; McCarthy et al., 1997; Opsahl and Benner, 1997; Mitra et al., 2000; Benner, 2002). Other potential problems with UF include variability in the performance of cartridge membranes from different manufacturers on the same samples, raising concerns about findings from different laboratories (Buesseler et al., 1996; Guo and Santschi, 1996). In addition, the performance of system checks on cartridge membrane integrity using, for example, molecular probes has been found to be critical to preventing possible breakthrough, or leakage of even the high MW (HMW) DOC component as it becomes concentrated during UF (Guo et al., 2000).

It has long been established that DOC exists in different size fractions in aquatic systems (Sharp, 1973a) and that a large portion of estuarine DOC is composed of the so-called colloidal OM (Whitehouse et al., 1989; Filella and Buffle, 1993; Guo et al., 1995; Martin et al., 1995; Sempere and Cauwet, 1995; Guo and Santschi, 1997a; Guo et al., 1999; Cauwet, 2002). The characterization of different size classes of DOC is established by physical separation through filters/membranes of differing pore sizes; thus, colloids are an operationally defined fraction of the total DOC in the size range of 0.001–1 μm (Vold and Vold, 1983). Unfortunately, using size as the primary criteria for characterizing colloids can be misleading when considering the biochemical differences associated with these different size

fractions as well as their reactivity (Gustafsson and Gschwend, 1997; Benner, 2002).

A potentially promising new method that may help overcome many of the problems of these earlier DOC isolation and concentration approaches is reverse osmosis/electrodialysis (RO/ED; Table 2). This procedure relies on coupled RO and pulsed electrical current ED for the removal of both salts and water from a sample, and the concomitant concentration of DOC (Koprivnjak et al., 2006, 2009; Vetter et al., 2007; Gurtler et al., 2008). The method has been found to extract greater than ~75% of the total DOC from saline waters with a reduction of residual salts from ~17 500:1 (full-strength seawater) to ~1.5:1, allowing for collection of a more representative fraction of estuarine and seawater DOC than previous methods. With the reduction of residual salts, RO/ED should permit the analysis of lyophilized DOC by methods such as NMR, gas chromatography-isotope ratio mass spectrometry (GC-IRMS), HPLC, and other analytical methods that provide a more comprehensive assessment of its character in estuarine and other saline waters. Not unexpectedly, the chemical characteristics of marine and estuarine DOC collected using RO/ED versus other extraction techniques (e.g., UF, XAD resins, and C18 reverse-phase sorbents; Simjouw et al., 2008; Koprivnjak et al., 2009) have been found to differ significantly owing to bias introduced by different methods of DOC isolation and extraction. With greater recoveries of DOC by methods such as RO/ED, the expectation is that DOC characteristics will reflect the full suite of *in situ* material to a greater extent than lower-recovery methods.

5.02.3 DOC Quantification and Characterization

5.02.3.1 Bulk Concentration Analysis

Analysis of DOC concentration is a fundamental parameter in aquatic organic geochemical studies. Measurements of DOC concentration are generally carried out by either high-temperature catalytic (generally using Pt-impregnated alumina) combustion or low-temperature chemical (generally using $K_2S_2O_4$ under acidic conditions) or photochemical (using a combination of ultraviolet (UV) and $K_2S_2O_4$ oxidation (see Statham and Williams (1999) and Wangersky (2000) for reviews). Attempts to accurately measure DOC in freshwater and saline natural water span nearly a century (Krogh, 1934; Plunkett and Rakestraw, 1955; Duursma, 1961; Armstrong et al., 1966; Williams et al., 1969; Sharp, 1973b; Williams, 1992; Sharp, 2002), and have gone through several instances of critical evaluation and reassessment by the community as new techniques have been developed (see, e.g., Sugimura and Suzuki, 1988; Williams and Druffel, 1988; Chen and Wangersky, 1993; Hedges et al., 1993; Suzuki, 1993; Wangersky, 1993). The actual quantification of DOC is carried out by the detection of the evolved CO_2 gas resulting from DOC oxidation, typically by the principle of its absorption in the infrared (IR) portion of the electromagnetic spectrum using nondispersive IR detection. The sample CO_2 signal is compared to that generated by oxidation of a known standard (typically potassium phthalate, glucose, etc.). Both high-temperature catalytic and low-temperature chemical oxidation methods have been examined through a number of methodological studies and intercomparisons, and both methods appear to perform quantitatively and similarly when employed properly. Methods such as sealed-tube combustion

(e.g., Peterson et al., 1994) and elemental analysis (CHN) have been used to quantify DOC. However, these methods either are difficult and time consuming (in the case of sealed-tube combustion), or only measure a fraction of the total DOC (in the case of CHN analysis of lyophilized DOC from UF and other methods – see below). The reader is referred to reviews by Wangersky (2000) and Sharp (2002) for further details on analyses and intercomparison studies of DOC quantification.

5.02.3.2 DOC Characterization

Although an exhaustive treatment of the different characterization techniques for DOC in river, estuarine, and coastal waters is beyond the scope of this chapter, the reader is referred to excellent recent edited volumes by Hansell and Carlson (2002) and Findlay and Sinsabaugh (2003a) and review by Perdue and Ritchie (2004) for a comprehensive and up-to-date accounting of the methods and findings from the latest analytical techniques applied to the study of river and estuarine DOC. Additional description of current analytical techniques related to OM characterization in general is also provided in Chapter 5.03. Below, we highlight a selection of some of the most commonly used analytical methods for river, estuarine, and coastal DOC characterization (Table 3).

5.02.3.2.1 Isotopic analyses stable carbon isotopes

The use of stable isotopes in natural ecosystems is based on two main factors: (1) the relatively higher natural abundances of lighter isotopes in the Earth system due to nucleosynthesis (Faure, 1986; Hoefs, 2009) and (2) the selection during chemical and biochemical processes and reactions of the lighter isotope(s) compared to the heavier isotope(s) of a given element. As a result of (2), reaction products in nature tend to become relatively enriched in the lighter isotope. These fractionation processes can be complex but have proved to be useful in assessing the sources of organic materials to bulk DOC pools in estuarine studies.

There are three naturally occurring isotopes of carbon: ^{12}C , ^{13}C , and ^{14}C (Figure 4). The application of ^{13}C and other light stable isotopes (most commonly ^{18}O , 2H , ^{15}N , and ^{34}S) in ecological and biogeochemical studies is related to their

Table 3 Selected methods for the characterization of DOC in estuarine and other natural waters

Analytical method	DOC component(s) characterized
High- and low-temperature oxidation	Total or bulk C content
Nuclear magnetic resonance (NMR)	Major structural groups
Isotope ratio mass spectrometry (IRMS)	Natural ^{13}C abundance
Accelerator mass spectrometry	Natural ^{14}C abundance
Gas and liquid chromatography	Specific molecular composition
Compound-specific IRMS	^{13}C abundance of specific biomolecules
Compound-specific accelerator mass spectrometry (AMS)	^{14}C abundance of specific biomolecules
Pyrolysis	Macromolecular composition
Excitation/emission fluorescence	Chromophoric component
UV/vis absorbance	Chromophoric component

See text for further description and applicable references to studies using these methods.

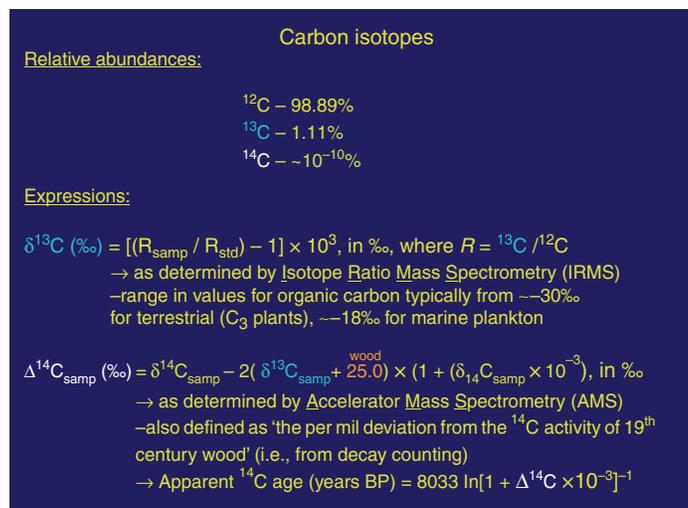


Figure 4 Relative abundances of naturally occurring carbon isotopes at the Earth's surface, commonly used in studies of coastal and estuarine C-cycle studies. Also shown are the equations used for stable carbon isotopic signatures ($\delta^{13}\text{C}$) and radiocarbon isotopic signatures ($\Delta^{14}\text{C}$) (see text for additional information).

biological nature (i.e., they can be incorporated into organic materials through various cellular-level biochemical reactions), low atomic mass, significant mass differences in isotopes, covalent character in bonding, multiple oxidation states, and sufficient abundance of the rare isotope. In particular, studies focusing on natural abundances of C and N isotopes have been successfully used in river, estuarine, and coastal systems to trace source inputs of terrestrial and aquatic OM (Peterson et al., 1985; Cifuentes et al., 1988; Horrigan et al., 1990; Westerhausen et al., 1993), sewage, and nutrients (Voss and Struck, 1997; Caraco et al., 1998; Holmes et al., 2000; Hughes et al., 2000). The conventions used in the expression of carbon isotopic ratios are summarized in Figure 4.

The most commonly used methods for the $\delta^{13}\text{C}$ analysis of DOC have traditionally relied on the oxidation of DOC to CO_2 using high-temperature combustion or low-temperature chemical or photo-oxidation techniques (for reviews, see Raymond and Bauer (2001a) and Bauer (2002)), followed by purification and collection of the CO_2 and stable isotope ratio mass spectrometry (IRMS; for details, see Boutton (1991) and Sulzman (2007)). Promising and reliable on-line techniques that couple low-temperature chemical oxidation of DOC to IRMS have recently been developed (Figure 5; Osburn and St-Jean, 2007) that offer a number of advantages such as higher sample throughput, reduced sample handling and manipulation, and lower blanks.

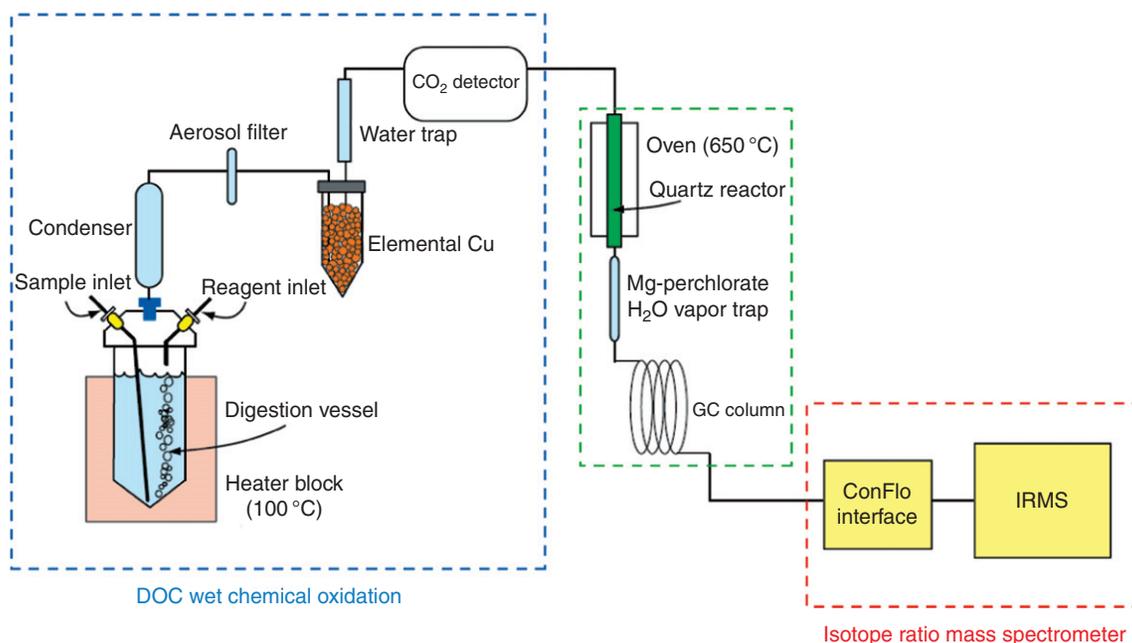


Figure 5 Components of an on-line DOC oxidation–isotope ratio mass spectrometry (IRMS) system for analysis of $\delta^{13}\text{C}$ in river, estuarine, and seawater samples. Modified from Osburn, C.L., St-Jean, G., 2007. The use of wet chemical oxidation with high amplification isotope ratio mass spectrometry (WC-IRMS) to measure stable isotope values of dissolved organic carbon in seawater. *Limnology and Oceanography Methods* 5, 296–308.

Radiocarbon. While the relative natural abundance of ^{14}C is diminishingly small ($10^{-10}\%$; **Figure 4**), it is radioactive, thus historically allowing it to be detected by β -decay-counting techniques. Natural or cosmogenic ^{14}C is produced by reaction of cosmic rays with atmospheric ^{14}N (as N_2 gas) to produce nuclear spallation products (Suess, 1958, 1968; Broecker and Peng, 1982). The dominant mechanism for the formation of ^{14}C in the atmosphere is the reaction between neutrons and nitrogen ($^{14}\text{N} + n \rightarrow ^{14}\text{C} + p$). Once formed, ^{14}C decay occurs as $^{14}\text{C} \rightarrow ^{14}\text{N} + \beta^- + \text{neutrino}$, with a half-life of 5730 ± 40 years. The free ^{14}C atoms formed in the atmosphere then undergo oxidation to $^{14}\text{CO}_2$, which is rapidly mixed throughout the atmosphere (Libby, 1955). This $^{14}\text{CO}_2$ then becomes incorporated into various biospheric reservoirs of biologically fixed C such as plants which reduce the $^{14}\text{CO}_2$ during photosynthesis. The exchange of $^{14}\text{CO}_2$ between the atmosphere and the surface ocean is estimated to take approximately 5 years (Broecker and Peng, 1982), but, for all practical purposes, the ^{14}C signatures of surface marine plants (namely, phytoplankton) can be assumed to be the same as the ^{14}C signature of surface ocean DIC, which is about the same as the ^{14}C signature of atmospheric CO_2 . Note that this may not always be the case for phytoplankton and submersed vegetation in rivers and estuaries where the ^{14}C signature of dissolved inorganic carbon (DIC) may be

significantly lower than the atmosphere owing to respiration of aged organic materials in these systems (Raymond et al., 2004).

The radiological nature of ^{14}C provides the basis for establishing ages, as well as potential sources, of carbon-containing materials. Short-lived (months to years) plants and animals in the biosphere contain a relatively constant level of ^{14}C . As noted below, this is not necessarily the case with extremely long-lived plants over hundreds to thousands of years when secular and anthropogenic changes in atmospheric ^{14}C content will be recorded in different parts of their biomass (e.g., annual tree rings). When plants and animals die, there is no further exchange with the atmosphere and the activity of ^{14}C decreases with a half-life of 5730 ± 40 years. The two assumptions associated with radiocarbon dating of materials are (1) the initial activity of ^{14}C in plants and animals is a known constant and is independent of geographic location and (2) the sample has not been contaminated with either modern or aged ^{14}C (Faure, 1986).

Measurements of ^{14}C in wood samples dated by dendrochronology indicate that changes in the initial atmospheric ^{14}C content occur over time (Anderson and Libby, 1951). Secular variations in the atmospheric ratio of $^{14}\text{C}/^{12}\text{C}$ in CO_2 (expressed in Δ notation; **Figure 4**) over the last ~1000 years are shown in **Figure 6(a)** (Stuiver and Quay, 1981a). This variation is believed to result from changes in cosmic ray fluxes from the Sun, shifts in

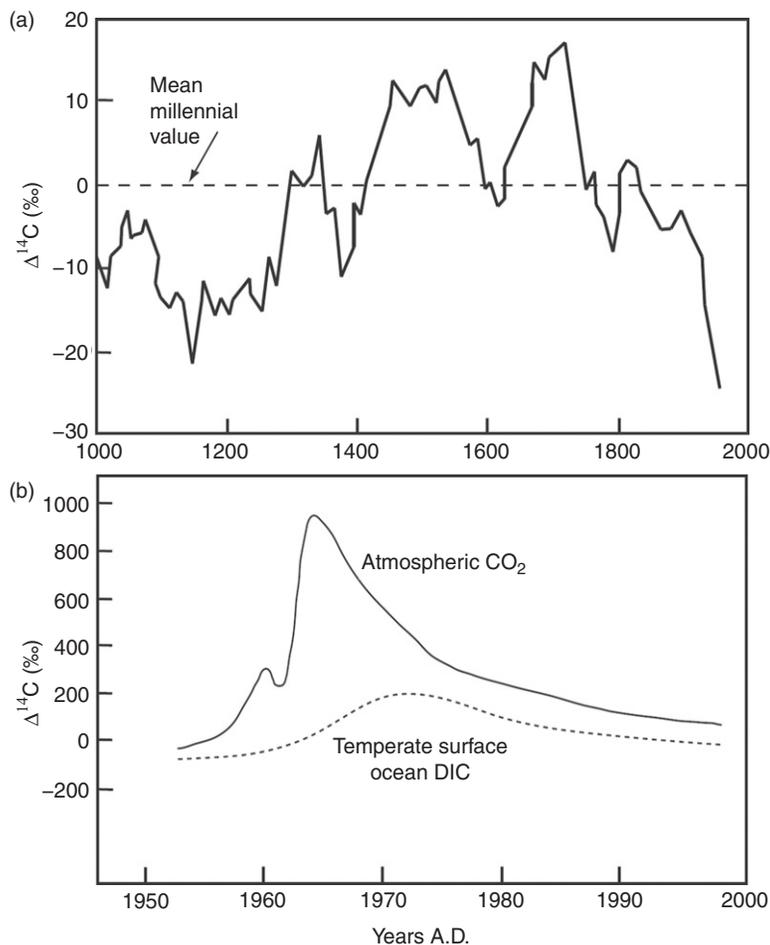


Figure 6 (a) Natural, or secular, changes in the radiocarbon content ($\Delta^{14}\text{C}$) of atmospheric CO_2 over the last millennium and prior to thermonuclear weapons testing and (b) changes following thermonuclear weapons testing since the 1950s in the Northern Hemisphere. Also shown for comparison in (b) is the $\Delta^{14}\text{C}$ signature of dissolved inorganic carbon (DIC) in the temperate surface ocean. Note different scales for $\Delta^{14}\text{C}$ and time in (a) and (b).

the Earth's magnetic field, and to variations in the total amounts of atmospheric CO₂ over geologically relevant timescales (Stuiver and Quay, 1981b; Faure, 1986).

In addition to natural secular variations, anthropogenic effects have both decreased and increased (by almost double) the atmospheric content of ¹⁴C due to combustion of fossil fuels over the past 100 years and nuclear weapons testing, respectively. The dilution, or Suess, effect from inputs of fossil fuel combustion, which are devoid of ¹⁴C, becomes obvious after about 1850 in the early stages of the Industrial Revolution. This same effect has also diluted the atmospheric δ¹³C signature through the injection of isotopically light CO₂ from fossil fuel combustion (Suess, 1958, 1968; Broecker and Peng, 1982). By contrast, during the height of thermonuclear weapons testing in the 1950s and 1960s, the Δ¹⁴C of atmospheric CO₂ increased from ~-70‰ to as much as +900‰ (~-70‰ to +200‰ in surface seawater DIC; Figure 6(b)), injecting large amounts of ¹⁴C into surface Earth reservoirs that have allowed it to be used effectively as a decadal-age tracer of terrestrial, freshwater, and marine C and OM sources and cycling.

Measurements of Δ¹⁴C can therefore provide information on the relative ages of the materials analyzed (Figure 7) provided changes in the natural abundance of ¹⁴C of the reactant (i.e., atmospheric CO₂) can be accounted for (see below). It should also be noted that, in addition to age information, the dynamic range of Δ¹⁴C values in natural systems (~-1000‰ to +200‰) is significantly greater than that for δ¹³C (~-30‰ to -13‰), making Δ¹⁴C a powerful potential source indicator (Bauer, 2002; McNichol and Aluwihare, 2007).

For ¹⁴C standards, it is necessary to use wood from trees harvested prior to industrialization (i.e., before about 1850) to avoid the Suess effect (Stuiver and Polach, 1977). The generally accepted value for pre-industrialized atmospheric CO₂ in the Northern Hemisphere is 13.56 dpm g⁻¹ or ¹⁴C/¹²C = 1.176 × 10⁻¹² (Broecker and Peng, 1982). The National Bureau of Standards (NBS) now provides a secondary oxalic acid ¹⁴C standard (known as OX-II).

The use of ¹⁴C measurements in OC cycling studies, while relatively extensive over the past 30–40 years in pelagic marine environments (Williams and Gordon, 1970; Williams and

Druffel, 1987; Druffel et al., 1992; Bauer and Druffel, 1998; Bauer et al., 1998a, 1998b; see Bauer (2002) and McNichol and Aluwihare (2007) for reviews), has taken longer to receive wider application in river, estuarine, and coastal studies (Spiker and Rubin, 1975; Hedges et al., 1986b). Nonetheless, there has been a considerable increase in recent years in the use of natural abundance ¹⁴C in nearshore and estuarine systems (Santschi et al., 1995; Guo et al., 1996; Guo and Santschi, 1997b; Cherrier et al., 1999; Mitra et al., 2000; Raymond and Bauer, 2001a, 2001b, 2001c; Bauer et al., 2002). The most common methods of Δ¹⁴C–DOC sample preparation are, similar to δ¹³C–DOC, high-temperature combustion or low-temperature photo- or chemical oxidation (for reviews see Bauer (2002), McNichol and Aluwihare (2007), and Tanaka et al. (2009)), followed by cryogenic purification of the evolved CO₂, reduction of CO₂ to elemental graphite targets, and analysis by accelerator mass spectrometry (AMS).

An important caveat of the application of natural ¹⁴C in studies of DOC and OM sources and cycling is that its measurement, particularly of bulk OM pools (though the same argument may also be used even at the compound-specific level), provides a weighted mean Δ¹⁴C value based on the relative abundances of all the materials in a given sample, and having any of a number of potential Δ¹⁴C distributions in the sample (Figure 8). Thus, one must take care not to overinterpret the age information being conveyed by Δ¹⁴C measurements. Recently developed methods, such as automated preparative capillary gas chromatography (PCGC), allow for separation of specific targeted compounds for ¹⁴C analysis based on AMS (Eglinton et al., 1996, 1997; McNichol et al., 2000). These compound-specific radiocarbon analyses (CSRA) may allow for more accurate determination of the ages of organic compounds specific to a particular source (e.g., phytoplankton) within the heterogeneous matrix of other carbon compounds commonly found in bulk DOC (e.g., terrigenous sources).

5.02.3.2.2 NMR analyses

The molecular structural characteristics of aquatic DOC, including that from estuaries, have benefitted tremendously from the use of NMR spectroscopic analysis. ¹H- and ¹³C-NMR have been

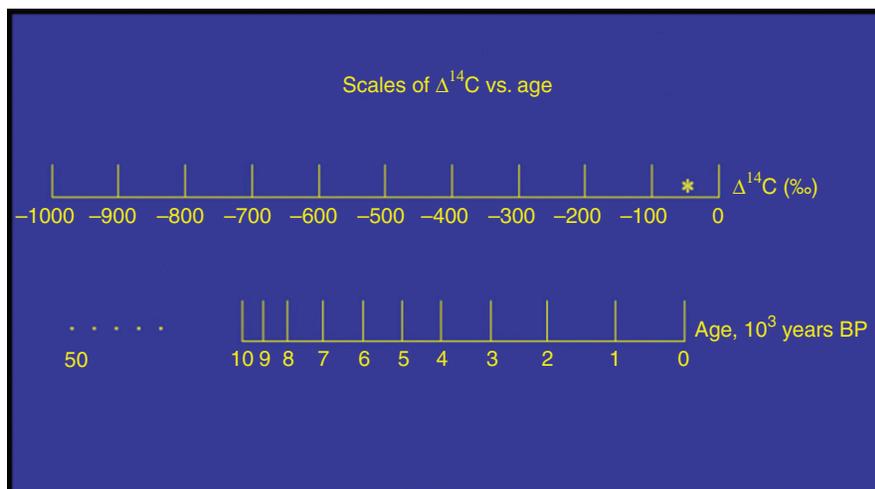


Figure 7 Relationship between Δ¹⁴C values and ¹⁴C-based ages of carbon-containing materials. The asterisk symbol (*) indicates that anything having Δ¹⁴C > ~-70‰ to -50‰ contains bomb ¹⁴C and is said to be modern in age, i.e., formed over the past few decades.

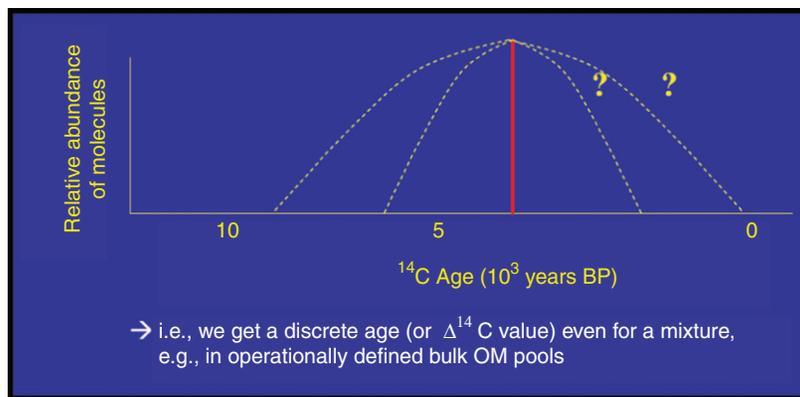


Figure 8 Two potential hypothetical distributions of the ^{14}C ages of materials in a bulk or undifferentiated pool of organic matter having a weighted mean age of ~4 000 years B.P. Vertical red line indicates the actual mean weighted radiocarbon age obtained by the analysis of such a sample. Dashed lines represent potential age distributions of individual compounds or compound classes in the bulk sample.

the most commonly used forms of NMR for the nondestructive assessment of the dominant molecular features and structure functional groups in terrestrial and aquatic biopolymers (Hatcher, 1987; Orem and Hatcher, 1987; Benner et al., 1992; Hedges et al., 1992, 2002; Perdue and Ritchie, 2004). Details on the principles and analytical aspects of this method are provided in Chapter 5.03. Two major advantages of ^{13}C -NMR are that it allows the relative abundances of carbon associated with the major functional groups of organic compounds to be established, and that it is nondestructive (i.e., the sample is not altered or degraded) and can therefore be analyzed again by similar or different methods. While chemical biomarkers (see below) offer greater detail on OM sample composition and structure, ^{13}C -NMR provides a first-order understanding of a larger fraction of the bulk OC. As a result, NMR is most useful as a primary analytical tool that permits an overview of major functional group features of DOC, and is often used in conjunction with more detailed organic and isotopic analyses. Two dimensional (2D) ^{15}N ^{13}C -NMR approaches have also been recently developed that allow N-containing functional groups (e.g., proteins and other polymers) to be evaluated at the same time as C-containing moieties (Zang et al., 2001).

Although an exhaustive review of the use of ^{13}C -NMR is beyond the scope of the chapter, the method has been used for decades to evaluate purified aquatic DOC extracts using XAD, C18, and UF separation methods (Hatcher, 1987; Orem and Hatcher, 1987; Benner et al., 1992; Hedges et al., 1992, 2002; for reviews see Benner (2003), Perdue and Ritchie (2004), and Mopper et al. (2007)). As with other analyses of DOC separated and extracted using these methods (see Section 5.02.2 above), significant (often low MW (LMW)) components of the DOC are typically excluded from ^{13}C -NMR analysis, and, hence, our view of DOC character and composition is often limited to the HMW and/or hydrophobic fractions.

5.02.3.2.3 Optically based analyses

A related operationally defined component of river and estuarine DOC is its humic content. Humic substances are typically defined as complex assemblages of molecules that have a yellow-to-brown color and are derived from plants and soils (Hatcher et al., 2001). Humic substances represent a large fraction of what is termed 'chromophoric dissolved OM' (CDOM) in aquatic systems around the world (Blough and Green, 1995), and, as a

result, lends itself to a variety of absorbance and fluorescence analytical techniques (Stedmon et al., 2003; Fellman et al., 2009). CDOM as a distinct component of bulk DOC is discussed in more detail later in this chapter. Aquatic humic substances can further be categorized as fulvic acids, humic acids, and humin based on the solubility in acid and base solutions (Schnitzer and Khan, 1972; Aiken, 1988; Parson, 1988; McKnight and Aiken, 1998). More specifically, humic acids typically have an MW of greater than 100 000 Da and are soluble above a pH of 2; fulvic acids, which are smaller molecules (~500 Da), are soluble at any pH, and humin is not soluble across a full pH range (McKnight and Aiken, 1998). For reasons of simplification, we use the term high-MW dissolved OM (HMW DOC) to describe DOC greater than 1 kDa and less than 0.45 μm as being inclusive of colloidal and humic acid-type substances and low-MW compounds (LMW DOC) as being less than 1 kDa, unless further distinctions are otherwise required. Detailed mapping of the fluorescence properties of DOC produces excitation emission matrices (EEMs), which are amenable to multiway data chemometric analysis techniques. Techniques such as parallel factor analysis (PARAFAC) are increasingly being applied to characterize DOC fluorescence properties (Zepp and Moran, 2004; Stedmon and Markager, 2005; Stedmon and Bro, 2008). Other recent enhancements in optically based approaches used to characterize coastal and estuarine DOC include assessing spectral slope regions (275–295 nm and 350–400 nm) within log-transformed absorption spectra for comparing DOC from different water types (Helms et al., 2008) and coupled optical and acoustical methods that have been used to establish DOC fluxes and dynamics in coastal environments such as San Francisco Bay Estuary (California, USA) (Downing et al., 2009). For further information on application of optical techniques currently available for measuring and assessing the cycling of CDOM in marine and estuarine waters, the reader is referred to the review by Coble (2007).

5.02.3.2.4 Compound-class and compound-specific analyses

Analysis of individual organic molecules in any form of bulk organic material (e.g., DOC, POC, and sedimentary OM) can provide an unprecedented level of detail about the composition of that organic material, including information on its potential sources and degradation history. An enormous variety of compound-specific analytical tools is now available to the aquatic

biogeochemist, and the choice of the exact method(s) to be used depends on the form (dissolved vs. particulate) of OM to be analyzed, and the compounds one wishes to analyze (Engel and Macko, 1993; Killops and Killops, 2005). Organic biomarker compounds have been defined as “[a] compound(s) that characterize certain biotic sources and that retain their source information..., even after some alteration” (Meyers, 2003). While biomarker approaches were originally developed using sediments and POC, their application has recently evolved to include different forms of river and estuarine dissolved OM as well (see, e.g., Mannino and Harvey, 1999, 2000; Loh et al., 2004). This molecular information is more specific and sensitive than bulk elemental and isotopic techniques in characterizing sources of OM, and further allows for identification of multiple sources (Meyers, 1997, 2003). The complexity of DOC sources in estuaries therefore makes application of chemical biomarkers widespread in estuarine research (see review by Bianchi and Canuel (2001)). Earlier biomarker approaches were developed for analysis of dissolved substances in the aqueous phase (see, e.g., Burney and Sieburth, 1977; Lindroth and Mopper, 1979; Burney et al., 1981; Johnson et al., 1981; Mopper and Lindroth, 1982), and, as a result, provided information presumably on the total amounts of those substances in the dissolved phase. However, recent analyses of biomarker compounds and compound classes have largely relied on one or more of the various DOC collection and isolation techniques listed in Table 2, thus limiting interpretation of such findings to those fractions isolated, rather than the total dissolved organic phase.

Specific molecular characterization methods of DOC are also now being combined with natural abundance ^{13}C and ^{14}C measurements to provide information on compound-class and compound specific isotope analyses (CSIA) (Loh et al., 2006; McCallister et al., 2006a, 2006b). The information yielded from such an approach is even more detailed than an isotopic or biomarker approach alone. In addition to source and diagenetic information on DOC, the use of ^{14}C also provides an age element to help constrain the ages of various substrates to the DOC pool. Studies of this type, although still relatively few in number, are becoming more common as methods are worked out for separations and isotopic analyses, as well as for dealing with the often very dilute amounts of compound classes and specific molecules in the DOC pool. The reader is also referred to Chapter 5.03 and to Bianchi (2007) for more detailed treatments of the specific analytical methods used for detailed characterization of estuarine OM in general.

5.02.4 Sources and Mechanisms of DOC Input to Estuaries

Estuarine DOC is comprised of organic materials from a vast array of both allochthonous and autochthonous sources (Figures 2, 3, and 9) (see reviews by Cloern (1996), Raymond and Bauer (2001a), Cauwet (2002), Aitkenhead-Peterson et al. (2003), and Bertilsson and Jones (2003)). In fact, even without unique estuarine sources, admixtures of the two dominant end-member sources alone (i.e., terrestrial and

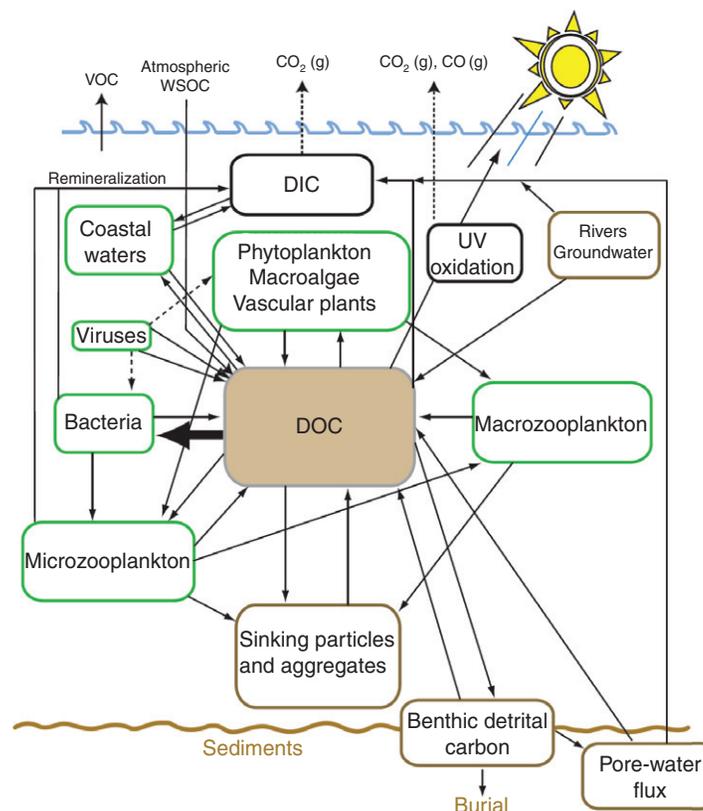


Figure 9 Potential sources, fates, and transformations of DOC in estuarine and coastal ocean waters. WSOC, water-soluble organic carbon; VOC, volatile organic carbon; DIC, dissolved inorganic carbon. Modified from Bianchi, T.S., 2007. *Biogeochemistry of Estuaries*. Oxford University Press, Oxford, 702 pp.

marine) would be predicted to make estuaries among the most complex aquatic systems with respect to OM characterization and biogeochemistry. All of the allochthonous and autochthonous sources of estuarine DOC are ultimately derived from terrestrial and aquatic autotrophs (including unicellular and multicellular algae and vascular plants) and heterotrophs (including bacteria, fungi, and higher multicellular organisms), and result from myriad processes extending from the level of the individual cell, all the way to higher food-web interactions. The characterization and cycling of these diverse pools of DOC in estuaries have been examined in numerous studies using a variety of approaches and analytical techniques.

5.02.4.1 Terrestrial DOC Sources to Rivers and Estuaries

To a significant extent, the DOC in river and estuarine systems is derived from terrestrial vegetation and soils (Malcolm, 1990; Opsahl and Benner, 1997). For example, estuaries bordering the Gulf of Mexico have been found to have among the highest DOC concentrations (Guo et al., 1999; Engelhaupt and Bianchi, 2001) as well as some of the highest rates of fresh litter decomposition in soils (Meentemeyer, 1977). Recent work has shown that DOC concentrations in groundwater near the forest recharge area of North Inlet (South Carolina, USA) range from 50 to 140 mg CL⁻¹, however, much of this DOC is lost within the freshwater portion of the aquifer through sorption and heterotrophic decay (Goni and Gardner, 2003). Despite these

losses during transport to the coast, DOC discharged from saline groundwaters are high and can contribute as much as 600 mg-C m⁻² d⁻¹ to the annual DOC budget of North Inlet (Goni and Gardner, 2003).

For the most part, terrestrial organic material as a source of DOC to rivers and estuaries has largely been deduced from the similarities in OM composition between soils and their water-soluble components (see Kalbitz et al. (2000); Neff and Asner (2001); Chantigne 2003 for reviews) and the presence of unequivocal biomolecules in river, estuarine, and coastal marine waters (Hedges et al., 1997; Opsahl and Benner, 1997; Mannino and Harvey, 2000; Cole and Caraco, 2001). While soils are undoubtedly the major source of organic materials to most rivers, the complexity of soils and soil hydrology and the variables controlling the mobilization of soil organic materials make studies of their direct linkage of this material to streams and rivers extremely difficult (Figure 10; Schulze and Freibauer, 2005). Direct evidence for the hydrological control of DOC inputs to rivers from soils is relatively rare (see Neff and Asner (2001) for review) owing to the difficulty in measuring soil and river components on simultaneous timescales relevant to groundwater and surface water flows and inputs. Synergistic effects of factors such as soil N-limitation may also have a profound effect on the degradational losses of mobile phases (i.e., DOC) of soil organic material relative to sorbed mineral phases (Neff et al., 2002), which may have large impacts on the inputs of soil DOC to rivers.

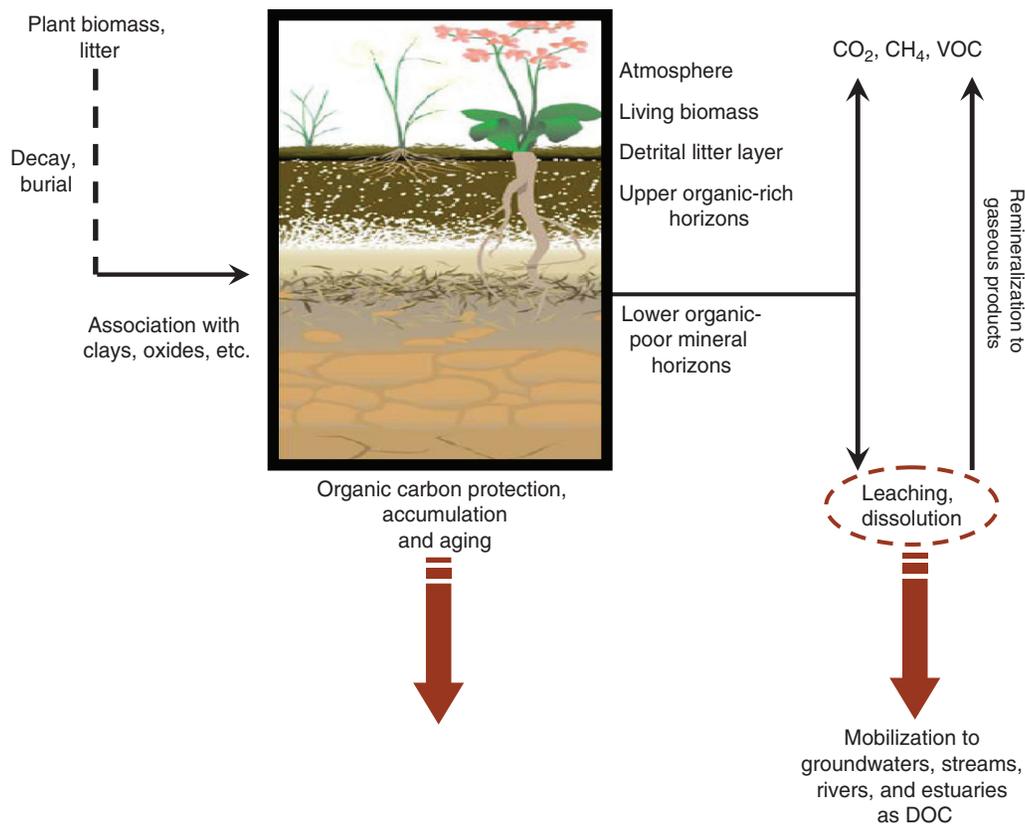


Figure 10 Potential inputs, reservoirs, and exports of organic materials from soils and watersheds to rivers and estuaries. The leached component in the dashed brown oval is the component most likely to be exported as DOC to streams and rivers, though the time frame of this export may vary greatly between watersheds. VOC, volatile organic carbon. Modified from Schulze, E.D., Freibauer, A., 2005. Environmental science – carbon unlocked from soils. *Nature* 437, 205–206.

Large-scale observations of net soil OM losses over decadal timescales (e.g., Bellamy et al., 2005) also provide evidence that at least some of this material may be lost as DOC export to rivers (Freeman et al., 2004; Findlay, 2005; also see Section 5.02.10 below). In addition, although land-use changes are suspected to have profound effects on the character of river and estuarine DOC derived from soils, comprehensive studies confirming the impacts of land-use change and hydrological interactions on river–estuary DOC are relatively rare (see, e.g., Stedmon et al., 2006). However, those few that have examined such changes confirm that land-use alterations can change (e.g., Findlay et al., 2001; Chantigne, 2003; Stedmon et al., 2006) not only the amounts of DOC exported from land to river and estuaries, but also its character (e.g., chromophoric properties), all of which may influence both biogeochemical cycles (e.g., hypoxia and anoxia) as well as food-web structure.

Many watersheds also have relatively low hydrologic gradients, and DOC fluxes from these systems to rivers and estuaries are consequently difficult to estimate due to long water transport times. In addition, these long transport times can also lead to significant modification of the DOC due to both abiotic (e.g., soil mineral sorption–desorption) and soil microbiological processes. To date, the majority of these efforts has been experimental (Ohno et al., 2007a, 2007b; Stutter et al., 2007a, 2007b) or predictive and model-based (e.g., Michalzik et al., 2003) approaches. New approaches focusing on simultaneous measurements of soil OM, soil water DOC, and stream DOC have met with some success, particularly in small watersheds with steep hydrologic gradients where the time frame between soil source materials and runoff waters is much shorter (Figure 11; Sanderman et al., 2009).

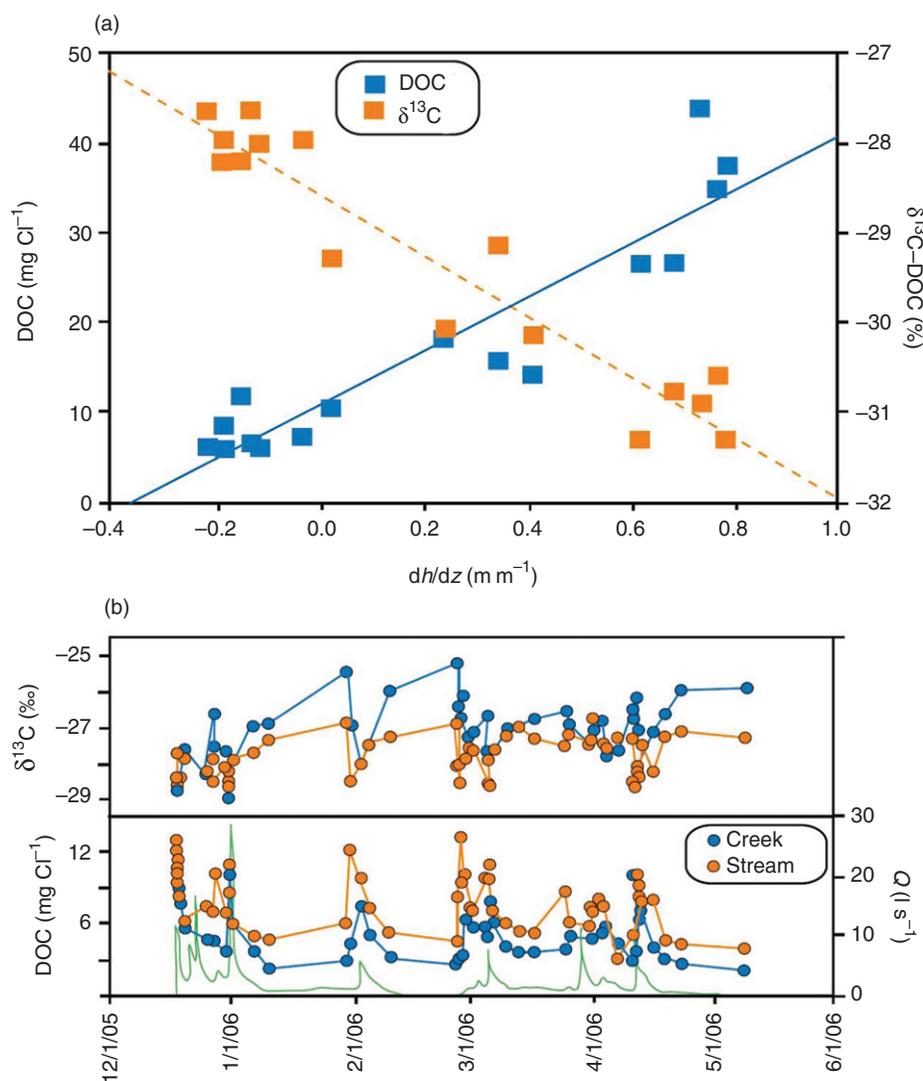


Figure 11 Relationships between soil hydrology and export of soil DOC to creek and stream sand streams of a small coastal watershed in northern California. (a) Correlation plots of DOC concentration and $\delta^{13}C-DOC$ vs. the vertical hydrologic pressure head gradient (dh/dz) in soil waters at one of the sampling sites. (b) Time series of $\delta^{13}C-DOC$ and DOC concentration at creek and stream sampling stations, and creek discharge Q (solid green line; also directly related to dh/dz) showing similar relationships as measured in soil waters in (a). Modified from Sanderman, J., Lohse, K.A., Baldock, J.A., Amundson, R., 2009. Linking soils and streams: sources and chemistry of dissolved organic matter in a small coastal watershed. *Water Resources Research*, W03418, doi:10.1029/2008WR006977.

Riverine DOC has historically been considered to be recalcitrant and transported conservatively to the ocean (Moore et al., 1979; Mantoura and Woodward, 1983; Prahl and Coble, 1994; Van Heemst et al., 2000a, 2000b). However, as we shall see, the biogeochemical complexity of estuaries makes them far from passive transit corridors for DOC and other forms of organic materials. Spatial variability in estuaries, the utilization and degradation of DOC by bacteria (Findlay et al., 1992; Gardner et al., 1996; Zweifel, 1999; Pakulski et al., 2000), chemical removal processes (e.g., flocculation, deflocculation, adsorption, aggregation, and precipitation) (Sholkovitz, 1976; Sholkovitz et al., 1978; Ertel et al., 1986; Lisitzin, 1995), production of phytoplankton exudates (Aminot et al., 1990; Fukushima et al., 2001), inputs from pore waters during resuspension events (Burdige and Homstead, 1994; Middelburg et al., 1997), and atmospheric deposition (Velinsky et al., 1986; Willey et al., 2000; Raymond, 2005; Wozniak et al., 2008) can all contribute to nonconservative behavior in estuaries.

5.02.4.2 The River Input Term

On a global basis, rivers discharge approximately 1 Gt of allochthonous carbon annually to estuaries and ocean margins (Table 1), about 40% in the form of DIC, with the remainder delivered as DOC and POC (Bernier, 1982; Degens et al., 1991; Ittekkot and Laane, 1991; Spitzzy and Ittekkot, 1991; Spitzzy and Leenheer, 1991; Hedges and Keil, 1995; Hedges et al., 1997; Meybeck and Vörösmarty, 1999; Aitkenhead and McDowell, 2000). Discharge of DOC dominates over POC by, on average, about a factor of 4 (Meybeck, 1982; Mulholland and Watts, 1982; Meybeck, 1993a, 1993b; Ludwig et al., 1996; Aitkenhead

and McDowell, 2000 and references therein). In addition, rivers deliver nutrients, from both natural and pollution sources, which can fuel photosynthetic production of OC in both the river and its associated estuary, as well as in the coastal ocean beyond (Bierman et al., 1994; Hickey and Banas, 2003; Carmack et al., 2004; Davies, 2004; Wysocki et al., 2006). The input of OM by rivers to the oceans is a significant term in the global and oceanic carbon budgets (Schlesinger and Melack, 1981; Hedges, 1992; Berner and Berner, 1996; Hedges et al., 1997; Wetzel, 2001) and occurs primarily via estuaries. The ~0.25 Gt of DOC discharged from rivers annually can account for the mean radiocarbon-based turnover times of oceanic DOC (~4000–6000 years). While the global flux of DOC and POC from rivers is small relative to other global carbon fluxes (Figure 12) (Sarmiento and Gruber, 2002), a major question is what the net flux of this riverine term is. If the gross and net fluxes are the same or similar, then the river term rivals the net fluxes of a number of other important global carbon exchanges. Alternately, if, as is believed, most riverine DOC and POC are reactive and removed through respiration and burial on relatively short timescales, then the net term may be relatively small. Thus, estuaries play a key potential role in controlling the net land-to-ocean OC flux. Analysis of global DOC data sets by Mulholland (2003) has shown that DOC inputs from terrestrial systems to streams and rivers appear to scale to several large-scale features, including the proportion of wetlands, forms of stored OM (e.g., peatlands), precipitation, terrestrial primary production, and catchment slope.

Characterization of DOC using ^{13}C -NMR indicates that river and marsh-derived DOC is largely composed of aromatic carbon – reflective of lignin inputs from vascular plant materials (Lobartini et al., 1991; Hedges et al., 1992; Engelhaupt and

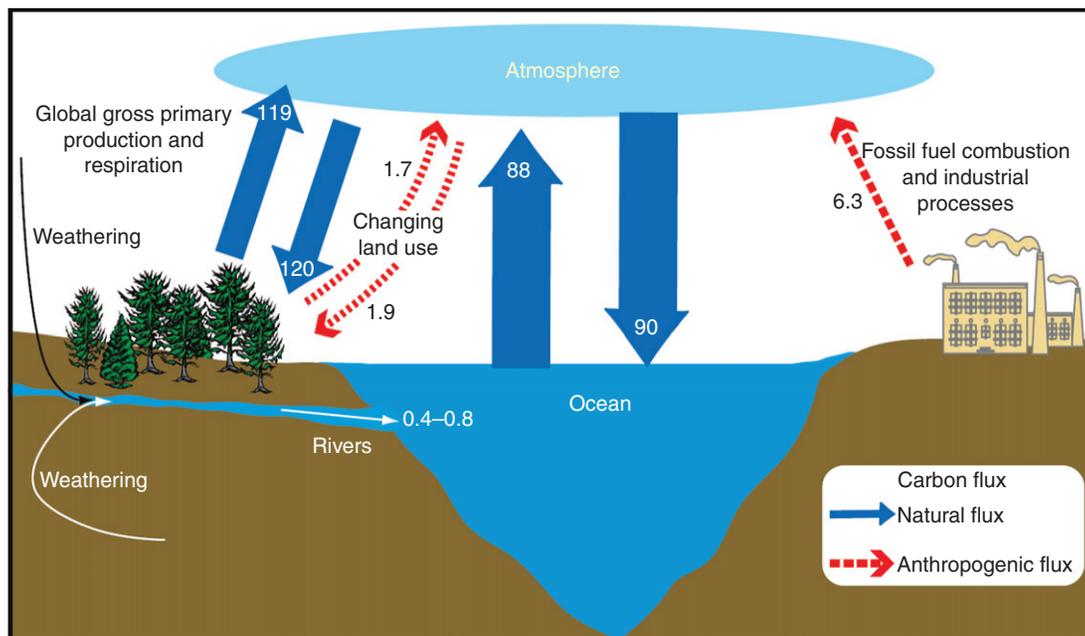


Figure 12 The river flux term of organic carbon to the world ocean relative to other major global carbon fluxes, in units of Gt C yr^{-1} . The river term is presently estimated at between 0.4 and 0.8 Gt C yr^{-1} , with the global river flux of DOC being ~4 times greater than POC. Estuaries likely play a key potential role in regulating the net efflux of riverine DOC and POC from land and rivers to the coastal and open oceans. One of the major questions is what is the net flux of river DOC to the oceans – that is, how much is oxidized to CO_2 vs. how much persists following export. If the majority of this terrestrial material persists in the ocean, it is a significant net flux relative to other globally relevant net fluxes of carbon and has profound implications for ocean carbon sources and budgets.

Bianchi, 2001). Conversely, DOC in the Mississippi River was found to be primarily composed of aliphatic versus aromatic compounds and is believed to be largely derived from freshwater diatoms growing under high-nutrient low-light conditions (Bianchi et al., 2004). Other sources of DOC to estuaries that can significantly affect bulk carbon composition are derived from sediment pore-water fluxes and local runoff from soils. For example, ^{13}C -NMR work indicated that under anoxic conditions pore waters were dominated by DOC primarily composed of carbohydrates and paraffinic structures derived from the decay of algal/bacterial cellulose and other unknown materials, with minimal degradation of lignin (Orem and Hatcher, 1987). Under aerobic conditions, pore-water DOC had lower carbohydrate and higher abundance of aromatic structures. Recent work by Engelhaupt and Bianchi (2001) further supported that lignin was not degraded efficiently under low-oxygen conditions in a tidal stream, adjacent to Lake Pontchartrain Estuary (USA).

Only very small amounts of terrestrial OM, however, have been identified in seawater using organic biomarker and stable carbon isotopic approaches (Williams and Gordon, 1970; Meyers-Schulte and Hedges, 1986; Moran et al., 1991a; Moran and Hodson, 1994; Benner et al., 1997; Opsahl and Benner, 1997). Estuarine processes (chemical, photochemical, and microbial) can significantly alter the molecular composition, isotopic signatures, reactivity, and optical properties of river-transported terrestrial and autochthonous DOC before it discharges to the coastal zone (Mayer, 1985; Fox 1991; Moran et al., 2000; Benner and Opsahl, 2001; Opsahl and Zepp, 2001; Minor et al., 2001; Mopper and Kieber, 2002). Past estimates of terrestrial DOC contributions to the oceans have been based on comparisons of the biochemical and isotopic compositions of open ocean DOC to freshwater riverine end-member counterparts (Meyers-Schulte and Hedges, 1986; Hedges et al., 1992; Hedges et al., 1997; Opsahl and Benner, 1997). However, these estimates have not typically accounted for changes during transit within rivers themselves (Cole and Caraco, 2001), in estuaries (Raymond and Bauer, 2000, 2001a, 2001b, 2001c; Benner, 2002; Raymond and Hopkinson, 2003), or in ocean margins (Kieber et al., 1990; Bauer and Druffel, 1998; Bauer et al., 2001, 2002). Thus, without a better understanding of the types and magnitudes of modifications that components of riverine DOC undergo in estuaries, we may be misinterpreting the effective chemical and isotopic signatures (i.e., source specificity), optical properties, and bioavailability of riverine DOC discharged to the coastal ocean and exported to the ocean interior.

It is increasingly recognized that rivers transport DOC and POC of highly variable age, and presumably reactivity, depending upon the specific river and the characteristics of the surrounding watershed. For example, while tropical rivers, such as the Amazon, transport organic materials that are largely modern in nature (i.e., have been fixed on timescales of no more than a few decades), and derived from vegetation in the significant flood plains in the lower mainstem (Hedges et al., 1986b), they are also imprinted with materials having significantly different geochemical signatures and reactivities from their upland tributaries (Hedges et al., 2000; Mayorga et al., 2005). By contrast, temperate and Arctic rivers have so far been found to contain up to millennial-aged POC, and variably aged DOC, ranging from completely modern to several hundred years in age (Raymond and Bauer, 2001a; Raymond et al.,

2004; Striegl et al., 2005; Neff et al., 2006). The general consensus that seems to be arising, however, is that riverine DOC ages are modern or only slightly aged (decades to centuries), whereas POC is almost always much more highly aged than DOC (Raymond and Bauer, unpublished data; see Chapter 5.03). This finding may have profound implications not only for riverine sources to estuaries, but in how estuaries process variably aged pools of DOC and POC.

It is important to note that virtually all of the discharge estimates for rivers are based on data collected at gauging sites upstream of tidal influences. In large rivers, these sites can be located hundreds of kilometers from the river mouth and do not take into account large regions of lowland rivers and associated floodplains. Thus, important questions remain on the exact magnitude and composition of the materials being delivered to the ocean by river/estuary systems. However, it is clear that a large fraction of the fluvial organic material is degraded or altered in estuaries, the coastal ocean, and beyond. Little is known about how these tidal reaches of rivers influence the magnitude and composition of the sediment, POC/DOC, and nutrient discharges (e.g., Meybeck and Vörösmarty, 1999, 2005; Hoffman and Bronk, 2006), but they clearly are significant zones of modification that need to be much better studied in order to constrain fluxes to the ocean. Extensive reworking of marine-source nutrients and carbon also occurs in these regions (e.g., Aller et al., 2004; Dagg et al., 2004, 2005; Gordon and Goni, 2004; Goni et al., 2005a). Unfortunately, the net rates of any of these processes within estuarine systems are largely unconstrained, let alone differentiated between those that affect river- and ocean-source materials. Ultimately, carbon cycling in estuaries is a poorly constrained and complicated sum of many processes, each of which may rise and fall in relative importance as tides, discharge conditions, and seasons change.

5.02.4.3 Estuarine Sources

In addition to riverine inputs, DOC in estuaries contains significant components from autochthonous production by algal and vascular plant communities unique to estuarine environments themselves (Figure 9) (see Cloern (1996) for review). For additional description of the different sources of autochthonous OM in general to estuarine DOC and POC, the reader is referred to Chapter 5.03 and to Bianchi (2007).

Annual rates of primary production of different estuarine communities (Table 4) may be used as a starting point to examine the main autochthonous sources of OM to estuarine waters. In general, phytoplankton production ($7\text{--}875\text{ g-C m}^{-2}\text{ yr}^{-1}$) is estimated to dominate microalgal OM production in estuaries, with microphytobenthos (see Kromkamp et al., 2006) generally contributing somewhat less ($29\text{--}234\text{ g-C m}^{-2}\text{ yr}^{-1}$) (summarized in Underwood and Kromkamp (1999)). Because of the shallow nature of many rivers and estuaries, submergent and emergent macrophytic production ($150\text{--}15\,000\text{ g-C m}^{-2}\text{ yr}^{-1}$; Moss, 1988; Bertilsson and Jones, 2003) can be a major, if not dominant, source of OM produced in these systems. However, translation of these overall rates of primary production by different groups into net sources of autochthonous estuarine DOC is not easily established (see also Section 5.02.4) and may depend on factors such as (1) the relative inputs of DOC versus POC from different primary producers, (2) abiotic interactions between DOC and

Table 4 Annual rates of primary production in selected estuaries

	$g\ C\ m^{-2}\ yr^{-1}$	References
<i>Phytoplanktonic production</i>		
North America		
San Francisco Bay (California)	93–150	Cole and Cloern (1984,1987), Cloern (1996)
Neuse River Estuary (North Carolina)	360–530	Paerl et al. (1998); Pinckney et al. (1998)
Tomales Bay (California)	60–810	Cole (1989)
Europe		
EMS–Dollart (Netherlands)	26–408	Colijn (1983)
Westerschelde (Netherlands)	75–230	Kromkamp et al. (1995)
Oosterschelde (Netherlands)	223–540	Wetsteyn and Kromkamp (1994)
Bristol Channel (United Kingdom)	50–165	Joint and Pomeroy (1981)
<i>Microphytobenthic production</i>		
North America		
North Inlet (South Carolina)	56–234	Pinckney and Zingmark (1993), Pinckney (1994)
Weeks Bay (Alabama)	~90	Schreiber and Pennock (1995)
Falmouth Bay (Massachusetts)	106	van Raalte et al. (1976)
False Bay (Washington)	143–226	Pamatmat (1968)
Europe		
Ems–Dollard (Netherlands)	69–314	van Es(1982)
Westerschelde (Netherlands)	136	de Jong and de Jonge (1995)
Oosterschelde (Netherlands)	105–242	Nienhuis and Daemen (1985), de Jong et al. (1994)
Lynher (United Kingdom)	143	Joint (1978)
Ythan (United Kingdom)	116	Leach (1971)
Ria de Arosa (Spain)	54	Varela and Penas(1985)
Tagus (Portugal)	47–178	Brotas and Catarino (1995)

Adapted from Heip, C.H., Goosen, N.K., Herman, P.M.J., Kromkamp, J., Middelburg, J.J., Soetaert, K., 1995. Production and consumption of biological particles in temperate tidal estuaries. In: Ansell, A.D., Gibson, R.N., Barnes, M. (Eds.), *Oceanography and Marine Biology: An Annual Review*. UCL Press, London, vol. 33, pp. 1–149. MacIntyre, H.L., Geider, R.J., Miller, D.C., 1996. Microphytobenthos: the ecological role of the "secret garden" of unvegetated, shallow-water marine habitats. 1. Distribution, abundance and primary production. *Estuaries* 19, 186–201. Underwood, G.J.C., Kromkamp, J., 1999. Primary production by phytoplankton and microphytobenthos in estuaries. In: Nedwell, N.D., Raffaelli, D.G. (Eds.), *Estuaries, Volume 29, Advances in Ecological Research*. Academic Press, New York, NY, pp. 93–153.

POC following their production, and (3) the turnover and reactivity of different components of autochthonous estuarine DOC.

In general, it has been found that cellular constituents are released to the surrounding water either following microalgal and macrophytic cell death and senescence (Camilleri and Ribí, 1986; Borsheim et al., 2005; Maie et al., 2006), as a result of cellular (both microalgal and bacterial) lysis due to viral infection (Middelboe and Lyck, 2002; Suttle, 2005), or from physical breakage of cells during grazing processes (so-called 'sloppy feeding'; Jumars et al., 1989; Moller 2005) (Figure 13). Estimates of extracellular release of DOC from cell cultures as well as river, freshwater, and marine systems range from nil to nearly 100% of primary production (Bertilsson and Jones, 2003, and references therein). For macrophytes, similarly high percentage releases of DOC (~30–75% of net primary production) have been reported (Bertilsson and Jones, 2003). For example, in a series of leaching experiments using a variety of estuarine plants, Maie et al. (2006) found that 60–85% of the total amount of DOC was leached during the first 2 weeks, with the leaching rates being represented by exponential decay models. The sugar and phenolic content of the leached DOC was plant dependent (range: 1.1–7.2 and 0.4–12.4 g-C kg⁻¹ dry weight, respectively), and comprised 8–34% and 4–28% of the total DOC, respectively, with the latter being an important potential source of CDOM from estuarine wetlands. These workers (Maie et al., 2006) also found the relative abundances of alkyl

and carbonyl C to be consistently lower in UDOC leached from plants than UDOC in natural waters, suggesting that these constituents increase in relative abundance during diagenetic processing. Thus, variations in primary producer types will likely affect the quantity and quality of DOC leached to estuarine waters.

In coastal and open ocean waters, DOC is generally positively correlated with phytoplankton biomass (Guo et al., 1994; Santschi et al., 1995; Hansell and Carlson, 2002). It has been estimated that phytoplankton release approximately 12% of total primary production as dissolved organics over a range of freshwater to marine environments (Baines and Pace, 1991). However, not surprisingly, water-column DOC in many estuarine systems does not show positive correlations with phytoplankton biomass as a result of the numerous additional allochthonous inputs from soils and vascular plants that are hydrologically coupled to watershed and wetland systems (Hedges et al., 1994; Argyrou et al., 1997; Guo and Santschi, 1997b; Harvey and Mannino, 2001; Hernes et al., 2001; Jaffé et al., 2004). Recent findings on the roles of changing and evolving ecosystems in estuarine waters, due to factors such as climate change, pollution, etc., also emphasize that major shifts may be occurring in some estuaries such as the Chesapeake Bay and its tributaries where increasing populations of gelatinous zooplankton may be transforming food webs from POC-based to DOC-based ones (Condon and Steinberg, 2008).

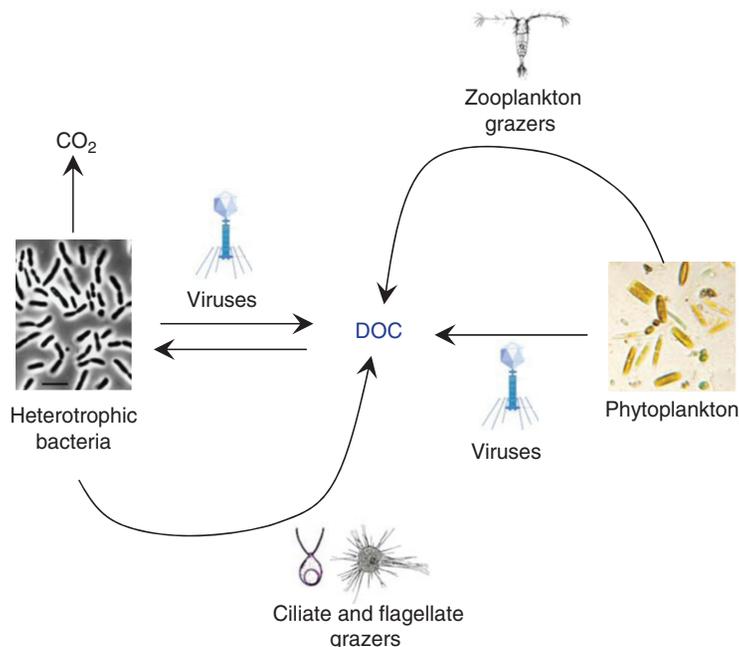


Figure 13 Role of grazing processes and viral lysis of bacteria and phytoplankton populations in the production of autochthonous DOC in estuarine and marine systems.

5.02.4.4 Marine Sources to Estuaries

The input of marine-derived DOC to estuaries (Figures 2 and 9) may be more straightforward than river and estuarine sources owing to the relatively more limited range in the isotopic and molecular signatures of purely marine-derived materials (Bauer, 2002; Killops and Killops, 2005). However, inputs of marine-derived organic materials to estuaries are not *per se* purely oceanic in origin, but, instead, are comprised of a mixture of oceanic and coastal influences (Guo et al., 1999; Bauer et al., 2002). In fact, coastal (i.e., shelf and slope) DOC has been deduced to be comprised of various combinations of (1) upwelled deep ocean DOC, (2) recently produced surface ocean DOC, (3) shelf/slope primary production, and (4) undifferentiated material from rivers, estuaries, and bays (Bauer et al., 1998a, 1998b, 2002). As a result, the marine end-member input term for estuarine OM may be considerably more complex, consisting of a background of high-salinity oceanic materials, unique shelf and slope sources, and riverine and estuarine materials that have escaped degradation and sedimentation in the estuary proper. Thus, the most appropriate marine DOC end member to an estuary is likely to be region specific and depend on the dominant coastal marine sources as well as their relative abundances, reactivities, etc. The reader is referred to Hansell and Carlson (2002) for the most recent and comprehensive synthesis on sources, characterization, and cycling of marine DOC.

5.02.4.5 Other Sources and Mechanisms of DOC Input

5.02.4.5.1 Particle desorption

The strong gradients in chemical parameters, such as salinity and ionic strength in estuaries, have been well documented to remove DOC, particularly HMW and humic components, by mechanisms such as flocculation, which in general varies as a function of factors such as temperature, pH, light availability and wavelength,

concentration of metallic cations, microbial reactivity, and ionic strength (Sholkovitz, 1976; Volk et al., 2000; von Wachenfeldt et al., 2008; see Chapter 5.03), conditions that can vary significantly throughout estuaries. There is also evidence that flocs may involve the CDOM component of DOC disproportionately (von Wachenfeldt et al., 2009). In these cases, there is an effective transformation of DOC to particulate organic flocs (i.e., POC). Interestingly, salinity and ionic strength effects may also have the opposite effect – that is, transferring OC from the particulate to the dissolved phases (Figure 9; see also Section 5.02.8.3). This process has been demonstrated most convincingly for riverine mineral particles, especially clays, where OC sorbed to clay mineral surfaces (Mayer, 1999) is displaced at the increasing ionic strengths encountered in estuaries and coastal waters (Keil et al., 1997; Burns et al., 2008), providing a kind of terrestrial DOC bypass that protects sorbed OC until its release to estuarine waters.

5.02.4.5.2 Sediment efflux

Sediments may also represent an important source of DOC to the water column of shallow estuarine systems (Figure 9; see Burdige (2002) for review). The accumulation of DOC in pore waters results from the diagenesis of sedimentary OC into a complex mixture of macromolecules (e.g., humic substances) and smaller monomeric forms (e.g., amino acids) (Orem et al., 1986; Burdige, 2002). The flux of pore-water DOC across the sediment–water interface has also been shown to represent an important source to the total DOC pool in estuaries (Alperin et al., 1992a, 1992b; Burdige et al., 1992; Martens et al., 1992; Burdige and Homstead, 1994; Argyrou et al., 1997; Middelburg et al., 1997; Burdige, 2001, 2002; Maher and Eyre, 2011). It has been suggested that benthic fluxes are a significant source of DOC to coastal and estuarine systems (as much as $-0.09 \times 10^{15} \text{ g-C yr}^{-1}$), which is similar in magnitude to riverine DOC fluxes to the ocean ($-0.2\text{--}0.4 \times 10^{15} \text{ g-C yr}^{-1}$) (Table 1).

The role of pore-water DOC that gets entrained in the benthic nepheloid layer (BNL), from resuspension events of estuarine and shelf sediments, may also be important in affecting DOC composition and age in shelf and deeper slope waters (Bauer et al., 1995, 2002; Guo and Santschi, 2000; Mitra et al., 2000) that may be entrained in estuarine waters during circulation. Similarly, pore waters contribute to the protein or amino acid-like fluorescence signature of the water column; maxima in these signals have been observed at the sediment–water interface (Chen and Bada, 1994; Coble, 1996; Burdige et al., 2004).

5.02.4.5.3 Groundwater transport

Although the majority of water discharged from land to the oceans has historically been thought to be dominated by surface water inputs, recent studies suggest that inputs of both freshwater and recirculated groundwater may be highly significant to elemental (including DOC) mass balances in estuaries and other shallow coastal systems (Figure 9). Fresh groundwater aquifers may contain significant amounts of terrestrial-derived DOC (Goni and Gardner, 2003; Aravena et al., 2004), and submarine groundwater discharge (SGD) into estuaries and coastal waters is more significant than previously thought and may have important impacts on the cycling of estuarine DOC as well as other materials, for example, nutrients (Freeze and Cherry, 1979; Valiela and D'Elia, 1990; Moore, 1996, 1999; Burnett et al., 2001; Kelly and Moran, 2002; Burnett et al., 2003). Burnett et al. (2003) recently defined SGD as “any and all flow of water on continental margins from the seabed to the coastal ocean, regardless of fluid composition or driving force”. Assuming a mean river flow of $37\,500\text{ km}^3\text{ yr}^{-1}$, SGD represents approximately 0.3–16% of the global river discharge (Burnett et al., 2003).

Determining groundwater discharge into estuarine and coastal systems remains a difficult task because of the diffuse flow and overall heterogeneous character of groundwater flow. The chemical composition of emerging SGD in coastal waters is generally distinct between river and marine end members; interactions between major ions' solid phases during transport are likely responsible for these differences (Burnett et al., 2003, and references therein). It has been suggested that the chemical interactions between SGD and solid phases at the coastal boundary are similar to what occurs in estuarine systems, and that these coastal aquifers are serving as subterranean estuaries, in a biogeochemical sense (Moore, 1999). Recent work on freshwater SGD inputs of DOC as high as 25% of total DOC inputs has been found for Gulf of Mexico estuaries (Santos et al., 2008, 2009), and the recycled (i.e., saline) component, which essentially represents an advective component of estuarine pore-water DOC flux, could be at least equal to this. Tidal pumping has also been found to be significant to the lateral fluxes of DOC and other pore-water constituents from marshes and other littoral environments to estuaries (Neubauer, 2000; Tobias et al., 2001; Neubauer and Anderson, 2003). These sources often have optically unique CDOM characteristics compared to other autochthonous sources of estuarine DOC (Tzortziou et al., 2008). While studies of fresh versus recycled SGD inputs of DOC to coastal zones are still relatively new, evidence thus far points to quantitatively significant fluxes of possibly unique forms of terrestrial, marsh, and estuarine sedimentary forms of DOC by these mechanisms.

5.02.4.5.4 Atmospheric deposition

Deposition of organic and inorganic materials from the atmosphere to land and aquatic systems has increasingly been found to be important for biogeochemical processes and for quantifying elemental and energy budgets of aerosol-impacted systems (e.g., Likens et al., 1983; Velinsky et al., 1986; Bond et al., 2004; Jurado et al., 2008). Although quantitatively significant atmospheric depositional fluxes of nitrogen to coastal waters have been demonstrated convincingly (Paerl, 2002; Paerl et al., 2002; see Chapter 5.08), less attention has been given to atmospheric forms and deposition of OC. Aerosols are generally highly carbonaceous in nature, with as much as 10–30% by weight being classified as OC (e.g., Wolff et al., 1986; Jacobson et al., 2000; Tanner et al., 2004; Liu et al., 2005). Both natural (e.g., plant emissions) and anthropogenic (e.g., biomass burning and fossil fuel combustion) sources contribute to aerosols, aerosol OC, and aerosol black carbon (BC). Emission-based estimates suggest that up to 93% of the 30–90 Gt of total aerosol OC (Koch, 2001; Bond et al., 2004; and references therein) and 100% of the 8–24 Gt aerosol BC (Penner et al., 1993; Bond et al., 2004) deposited globally each year may be attributed to anthropogenic fossil fuel sources alone. For comparison, riverine export of OC constitutes an input between 0.4 and 0.8 Gt OC to the coastal ocean annually (Table 1; Richey, 2004). Thus, atmospheric OC deposition has the potential to significantly impact C and OM budgets of coastal watersheds, rivers, and estuaries (Figure 9).

The aerosol OC deposited to land has been assumed to remain largely in soils, but given the magnitude of aerosol OC and BC deposition, it is likely that some component of this material is transported from land through watersheds to aquatic systems (e.g., lakes, rivers, estuaries, and coastal ocean) (Wozniak, 2009). In addition, recent findings on the rapid (minutes) and significant solubilization (20–70%) of aerosol OC (Krivacsy et al., 2001; Kleefeld et al., 2002; Yang et al., 2004; Decesari et al., 2007; Wozniak et al., 2008, (submitted)) suggest that much of this material may become mobilized into the DOC pools of watersheds, surface runoff, groundwaters, rivers, and estuaries on timescales relevant to carbon and OC biogeochemical cycling. Aerosol OC may become solubilized either predepositionally in rainwater (Velinsky et al., 1986; Willey et al., 2000; Avery et al., 2004; Raymond, 2005) or postdepositionally in surface waters (Wozniak et al., 2008; Altieri et al., 2009).

Both the atmospheric concentrations and deposition of aerosol OC and aerosol-derived water-soluble organic carbon (WSOC) to watersheds may be considerably higher post-industrially than preindustrially. Globally, ~8.4 Gt C (largely as CO_2) are released to the atmosphere via fossil fuel combustion on an annual basis (Canadell et al., 2007). Approximately 1% of fossil fuel combusted C (~0.084 Gt C) is not fully oxidized to CO_2 , but rather is released as OC by-products (USEPA, 2004). Natural-abundance radiocarbon measurements have been employed in a number of studies to estimate the relative contributions of contemporary and fossil-fuel-derived OC to aerosols. These studies reveal that fossil OC can account for as much as 80% (e.g., Hildemann et al., 1994a, 1994b; Klinedinst and Currie, 1999; Bench and Herckes, 2004; Zheng et al., 2006; Ding et al., 2008) of aerosol OC depending on location. Among the by-products are various hydrocarbons including polycyclic aromatic hydrocarbons (PAHs), *n*-alkanes, *n*-alkanoic acids, benzoic acids, and other compounds (Rogge et al. 1993; Bond et al., 2006). This incompletely combusted fossil OC may potentially

account for as much as 10–20% of the ~0.4–0.8 Gt of total OC (Table 1; Richey, 2004), or up to ~56% of the ~0.15–0.40 Gt POC (Table 1; Richey, 2004), exported globally by rivers to the coastal ocean on an annual basis.

Quantitative and qualitative studies of atmospheric OC deposition to watersheds and their associated rivers and estuaries are still in an early stage of development. However, the evidence to date suggests that the magnitudes of these fluxes alone are a significant term relative to other relevant fluxes such as riverine DOC transport. For example, annual mean aerosol total OC depositional fluxes scaled to the Hudson and York River (USA) watersheds were 6.8×10^{10} and 11.3×10^9 g-C yr⁻¹, respectively, and were similar in magnitude to the mean annual river OC export for these two systems (7.2×10^{10} g-C yr⁻¹ for the Hudson, and 8.4×10^9 g-C yr⁻¹ for the York) (Wozniak, 2009). Further studies on aerosol OC and WSOC components should shed new light on how best to account for these terms in regional watershed–river–estuary carbon and OC budgets.

5.02.5 Bulk DOC Distributions in Estuarine Waters

5.02.5.1 Potential Behavior of Organic Solutes in Estuaries

Because the major dissolved salt ions in seawater are generally nonreactive, their concentrations may be used as a conservative tracer of water mass mixing. In estuaries and other coastal waters, sources or sinks of a dissolved constituent may therefore be deduced relative to salinity. As shown by Wen et al. (1999), the simplest distribution in a 1D two end-member steady-state system is when DOC concentration behaves conservatively (i.e., no sources or sinks on time frames of estuarine mixing) and changes linearly as a function of salinity between marine and river end members (C_s and C_r respectively; Figure 14). However, because of the numerous potential DOC sources (see Section 5.02.4) and sinks (see Section 5.02.8) in estuarine systems, we may also predict that it may behave nonconservatively. For a nonconservative constituent such as DOC, when there is net loss or gain across a salinity gradient, linear extrapolation from high salinities can yield an effective river DOC concentration (C^*). This effective concentration can be used to infer DOC reactivity as well as the total flux of DOC to the ocean. The three potential scenarios are (Figure 14): (1) $C^* = C_r$ and DOC is behaving conservatively, (2) $C^* > C_r$ (case of C_1^* in Figure 14), and there is net DOC addition within the estuary, and (3) $C^* < C_r$ (case of C_2^* in Figure 14), and there is a net sink of DOC within the estuary. River flux (F_r) of DOC to the estuary and ultimately to the ocean are commonly estimated using this simplified mixing model. The riverine flux of DOC into an estuary is $F_r = RC_r$, where R is the river water flux or discharge (volume/time). Similarly, DOC flux from the estuary to the ocean (F_{ocean}) can be estimated by $F_{\text{ocean}} = RC^*$. Finally, the overall net internal flux (F_{int}) of DOC from net input minus removal terms can be estimated by $F_{\text{int}} = R(C^* - C_r)$.

Despite widespread application of this standard mixing model in estuarine systems, there are numerous problems when invoking these simple steady-state mixing assumptions for DOC and especially for POC (see Chapter 5.03). Early work has shown that the even relatively nonreactive OC constituents may display non-conservative mixing plots due to timescale differences in river concentrations of the constituent relative to estuarine mixing timescales (Officer and Lynch, 1981). In addition, biological

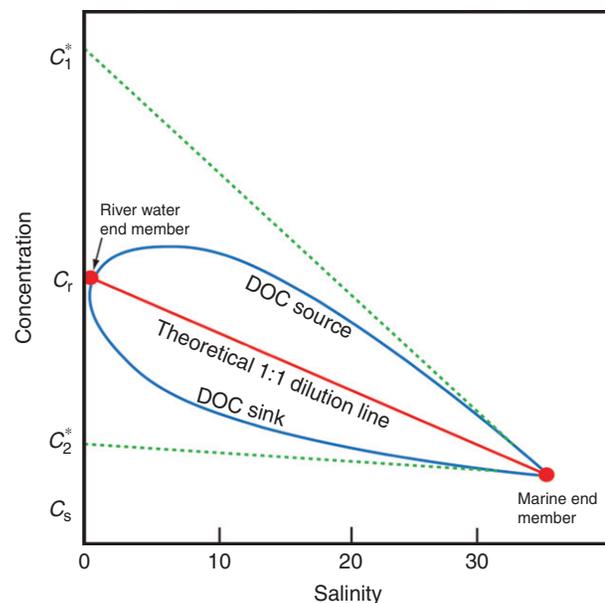


Figure 14 Theoretical distributions for DOC concentration as a function of salinity (mixing curves) across an estuarine salinity gradient. C_r is the riverine end-member concentration, while C_s is the seawater end-member concentration. A linear distribution suggests conservative mixing where DOC is either nonreactive on estuarine mixing times, or sinks of DOC are balanced by equivalent sources in different parts of the estuary. A concave downward distribution suggests net addition(s) of DOC throughout the estuary, while a concave upward distribution suggests net removal(s) of DOC throughout the estuary. C_1^* and C_2^* are effective DOC concentrations that can be used to infer the reactivity and total flux of DOC (see text for additional details). Modified from Wen, L., Shiller, A., Santschi, P.H., Gill, G., 1999. Trace element behavior in Gulf of Mexico estuaries. In: Bianchi, T.S., Pennock, J.R., Twilley, R.R. (Eds.), *Biogeochemistry of Gulf of Mexico Estuaries*. Wiley, New York, NY, pp. 303–346; and Bianchi, T.S., 2007. *Biogeochemistry of Estuaries*. Oxford University Press, Oxford, 702 pp.

(e.g., microbial) versus physicochemical (e.g., desorption, flocculation, and photochemical oxidation) removal mechanisms in estuaries cannot be discerned using these steady-state mixing models, as they only provide information on net additions or removals. Similarly, as pointed out in Section 5.02.4.5.3, groundwater and lateral and atmospheric inputs of DOC to estuaries can be quite considerable (Kelly and Moran, 2002), enhancing the non-point input of DOC and other solutes.

5.02.5.2 Conservative versus Nonconservative DOC Distributions in Different Estuaries

While all three types of DOC behavior (conservative, non-conservative inputs, and nonconservative removal) have been observed in different estuarine systems (Table 5), it is not surprising that the exact mechanisms leading to this behavior in a given system are not well established due to the potentially complex nature of both inputs and sinks of DOC in estuaries. It is generally believed that conservative DOC behavior is a result of (1) riverine DOC being nonreactive, (2) estuarine residence times being relatively short in relation to DOC reactivity, and (3) estuarine sources of DOC being relatively small (see, e.g., Mantoura and Woodward, 1983; Callahan et al., 2004; Middelburg and Herman, 2007). For example, in the Ob and Yenisei estuaries of Arctic Russia, the highly refractory nature of

Table 5 DOC concentrations and mixing behavior in selected estuaries

Estuary	DOC (μM)	Mixing behavior	References
<i>North America</i>			
Merrimack River estuary (Massachusetts)	~250–600	Conservative	Peterson et al. (1994)
Parker River Estuary (Massachusetts)	503–1001	Nonconservative source	Peterson et al. (1994), Raymond and Hopkinson (2003)
Delaware Bay (Delaware)	144–253	Nonconservative source	Sharp et al., (2009), Bauer (in prep.)
Chesapeake Bay (Virginia)	157–374	Nonconservative source in spring–summer Conservative in fall	Fisher et al. (1998)
York River Estuary (Virginia)	254–713	Nonconservative source	Raymond and Bauer (2001b)
Fourleague Bay (Louisiana)	~350–700	Nonconservative source	Peterson et al. (1994)
Corpus Christi Bay (Texas)	560–630	Nonconservative sink	Benoit et al. (1994)
Galveston Bay (Texas)	420–480	Nonconservative source	Guo and Santschi (1997a, 1997b)
Mississippi plume (Gulf of Mexico)	65–440	Nonconservative source in summer Conservative in winter–spring	Benner and Opsahl (2001), Wang et al. (2004)
Columbia River Estuary (Oregon-Washington)	140–180	Nonconservative source	Klinkhammer et al. (2000)
San Francisco Bay (California)	52–155	Nonconservative source	Sobczak et al. (2002)
<i>Europe</i>			
Ems–Dollart (the Netherlands)	33–1300	Conservative	Lanne (1980, 1982), Cadee (1982)
	~250–640	Nonconservative source	Middelburg and Herman (2007)
Rhine (the Netherlands)	108–375	Conservative	Eisma et al. (1982)
Scheldt (the Netherlands)	~180–470	Nonconservative sink	Middelburg and Herman (2007)
Elbe (Germany)	~180–390	Conservative	Ittekkot et al. (1982), Lanne (1984), Middelburg and Herman (2007)
Weser (Germany)	142–492	Conservative	Ittekkot et al. (1982), Lane (1984)
Po River Estuary (Italy)	~125–260	Conservative	Pettine et al. (1998)
Loire (France)	~120–310	Nonconservative source	Middelburg and Herman (2007)
Gironde (France)	~100–160	Nonconservative source	Middelburg and Herman (2007)
Severn (United Kingdom)	258–650	Conservative	Mantoura and Herman (2007)
Thames (United Kingdom)	~50–180	Conservative	Middelburg and Herman (2007)
<i>South America</i>			
Amazon plume	68–327	Conservative	Bauer et al. (unpublished data)
<i>Africa</i>			
Zaire River Estuary (Zaire)	mean: 708	Nonconservative source	Cadee (1984)
Betsiboka (Madagascar)	~50–130	Nonconservative source	Ralison et al. (2008)
<i>Asia</i>			
Huanghe (China)	266–708	NA	Zhang et al. (1992)
Yangtze/Changjiang (China)	166–283	Nonconservative source	Yang et al. (2007)

NA, Not applicable.

permafrost DOC inputs combined with the rapid and selective removal of freshwater labile algal components during transport to the river mouth is believed to result in the observed conservative DOC behavior (Figure 15(a)) (Köhler et al., 2003; Amon and Meon, 2004a, 2004b). Conservative behavior of DOC has also been observed in mangrove estuaries of southwest Florida (USA; Jaffé et al., 2004) due to relatively nonreactive mangrove-derived DOC at low and mesohaline salinities. Phytoplankton inputs of DOC were found to be more reactive leading to nonconservative behavior, while at higher salinities, DOC inputs from estuarine phytoplankton led to nonconservative inputs (Jaffé et al., 2004). Temperate estuaries have also been observed to have conservative DOC distributions, and this type of behavior may be more prevalent in river-dominated estuaries (e.g., Goni et al., 2003) where impacts due to removal processes may be minimized.

Net DOC inputs have been observed in a number of estuaries where there are high rates of DOC input by different

autochthonous primary producer groups (e.g., mangroves, salt marshes, and shallow mudflats; Raymond and Bauer, 2001a, 2001b; Raymond and Hopkinson, 2003; Gardner et al., 2005; Bauer et al., in preparation). For example, in the Delaware Bay, the second largest estuarine system in the US, DOC distributions exhibit evidence of significant inputs (Figure 15(b)) that may result from a combination of significant fringing salt marshes and extensive shallow muddy sediment deposits (i.e., leading to large signal to noise for sediment DOC effluxes). Inputs from SGD to estuaries have also been invoked to help explain nonconservative inputs (Swarzenski et al., 2006; Santos et al., 2008). In addition, experimental work has also shown that sedimentary DOC and POC that are loosely bound to mineral surfaces can be released during resuspension events (Komada and Reimers, 2001). Thus, in many shallow estuarine systems where resuspension is common, this may represent another physicochemical mechanism moderating relatively constant inputs of OM to the water column.

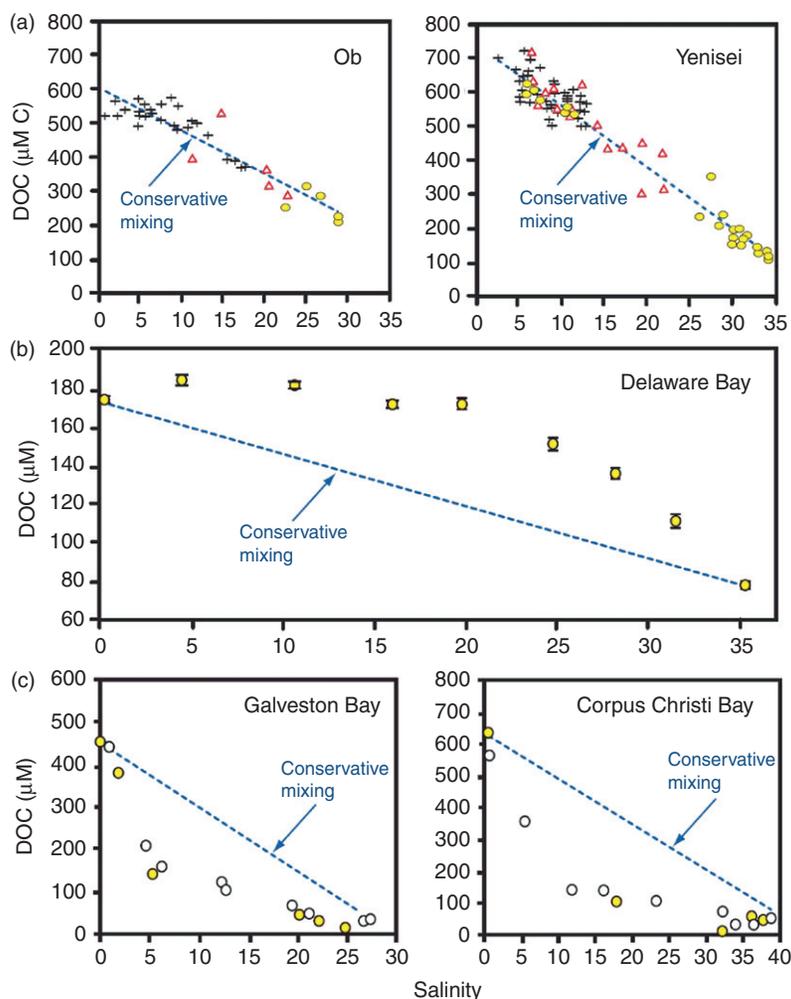


Figure 15 Examples of (a) conservative distributions, (b) nonconservative inputs, and (c) nonconservative removal of DOC in different estuaries (see text for details). (a, c) Modified from Benoit, G., Oktaymarshall, S.D., Cantu, A., Hood, E.M., Coleman, C.H., Corapcioglu, M.O., Santschi, P.H., 1994. Partitioning of Cu, Pb, Ag, Zn, Fe, Al and Mn between filter-retained particles, colloids, and solution in six Texas estuaries. *Marine Chemistry* 45, 307–336; and Bianchi, T.S., 2007. *Biogeochemistry of Estuaries*. Oxford University Press, Oxford, 702 pp. (b) From Bauer et al. (in preparation).

A number of Gulf of Mexico estuaries illustrate the third type of DOC behavior, that is, nonconservative losses (Figure 15(c)). DOC concentrations in the lower-salinity regions are due to riverine inputs of DOC. Seasonal variability of phytoplankton blooms can, at times, change the distribution of DOC in estuaries, whereby higher concentrations of DOC co-occur with the blooms in the lower estuarine region due to lower light attenuation rates. The lower-salinity regions of these estuaries may be important sinks for DOC; within the estuarine turbidity maximum (ETM) where different fractions of DOC (e.g., HMW humics) may be removed due to coagulation, flocculation, and other processes (see Chapter 5.03 for additional details). Some of the earliest work on DOC focused the role of iron and other metals on the initial steps of flocculation (especially of the riverine hydrophobic humic component) across an estuarine salinity gradient. Much of this humic material was composed of humic acids (Eckert and Sholkovitz, 1976; Sholkovitz, 1976; Sholkovitz et al., 1978; Fox, 1983, 1984). Other work showed that changes in tidal/mixing energy and total suspended load, within the turbidity maximum or from resuspension events, had significant effects on

flocculation and deflocculation processes (Biggs et al., 1983; Eisma and Li, 1993). In the Dollart Estuary (The Netherlands), it was concluded that large flocs were formed during short durations of high suspended matter and that deflocculation of these large flocs occurred while settling or at the sediment-water interface (Eisma and Li, 1993). In very large river-estuarine complexes such as the Mississippi, owing to the extended residence and mixing times of river and coastal seawater, both inputs and losses of DOC have been observed in different parts of the system, and attributed to variable contributions from autochthonous primary production, microbial utilization, photochemistry, and flocculation (Wang et al., 2004).

Spectral absorption and other optical techniques for measuring the chromophoric component of estuarine DOC (thought to be largely due to terrestrial aromatic compounds contained in substances such as lignin; Laane, 1981, 1982) have also been used to assess DOC sources and behavior in estuaries (Laane, 1981; Rochelle-Newall and Fisher, 2002; Gardner et al., 2005; Guo et al., 2007; Spencer et al., 2007). While early studies (Laane, 1981) reported a significant component of fluorescence by the LMW (<500 Da) portion of DOC

in estuaries (Ems–Dollart), the fluorescence characteristics of CDOM have also been found to correspond to the absorbance and abundance of colloidal organic material in at least certain estuaries (Flöge and Wells, 2007). This suggests that HMW or even submicron particles often included in operationally defined DOC may be responsible for a disproportionate part of its photoreactive character. Using UV–visible, fixed-wavelength fluorescence, and synchronous fluorescence, terrestrial DOC in a subtropical mangrove-dominated estuary was found to exhibit conservative behavior; however, at the same time, the bulk DOC was found to switch disproportionately from strongly terrestrial to strongly marine character at higher salinities ($\rightarrow 30$), suggesting that there may be a strong sink for the terrestrial component and a correspondingly strong source for the marine component at the marine end of the mixing continuum (Jaffé et al., 2004).

HMW and LMW components of the bulk DOC pool may exhibit significant differences from one another in estuaries. HMW DOC may derive from humified soil materials, fresh litter from terrestrial runoff, or even relatively reactive algal sources (both benthic and pelagic) in the estuary. HMW DOC from pore waters to estuarine waters has also been shown to be important in coastal bottom waters along shelf regions in the Mid-Atlantic Bight (MAB; Mitra et al., 2000). This does not support the open ocean size–reactivity model proposed by Amon and Benner (1996a), which, simply stated, predicts that the older fraction of HMW DOC will reside in the lower-MW classes, typically at deeper water depths. However, the size–reactivity model is generally observed in oceanic waters because of the selective removal of labile younger C as POC produced in the euphotic zone sinks through the water column, accumulating the older smaller MW DOC at depth (Amon and Benner, 1996a; Guo et al., 1996).

5.02.6 Isotopic Distributions of DOC in Estuaries

Although DOC concentrations alone provide insights into the magnitude of DOC input or loss in estuaries, they provide limited information on the fate of different components of DOC. For this, we must rely on isotopic and/or biomarker approaches that lend different degrees of specificity on the characteristics of the components being added to, removed from, or being transported conservatively through estuaries. Similar to DOC concentrations, predicted conservative distributions of the natural-abundance isotopes of DOC, namely, $\delta^{13}\text{C}$ -DOC and $\Delta^{14}\text{C}$ -DOC, may be used to examine the conservative versus nonconservative behavior of isotopically unique components of DOC on the basis of predicted versus observed isotopic distributions. This is a potentially powerful approach in estuaries because the diversity of DOC sources having unique $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signatures, coupled with strong gradients of DOC concentration, allows for sensitive detection of changes during mixing.

The predicted isotopic distribution (I_{mix} , as $\delta^{13}\text{C}$ or $\Delta^{14}\text{C}$) of DOC or any C-containing solute at a given salinity is a function of both the isotopic signature and the DOC concentration, and is described as (Spiker, 1980; Raymond and Bauer, 2001b)

$$I_{\text{mix}} = \frac{(f I_r \text{DOC}_r + (1-f) I_m \text{DOC}_m)}{\text{DOC}_{\text{mix}}} \quad [1]$$

where DOC is the total concentration, I is the isotopic composition of the riverine (r) and high-salinity/marine (m) end members, the riverine fraction, f , is calculated from salinity, and DOC_{mix} is the amount of DOC expected due to conservative mixing of the freshwater and marine end members. Because $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ are defined as isotopic ratios (i.e., $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$), the predicted distributions are curvilinear, compared to linear predicted distributions for concentration versus salinity distributions alone (see Section 5.02.5.2). Relatively few studies to date have characterized the $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signatures of estuarine DOC thoroughly enough to derive robust data sets of observed versus predicted conservative behavior of $\delta^{13}\text{C}$ -DOC and $\Delta^{14}\text{C}$ -DOC.

5.02.6.1 $\delta^{13}\text{C}$ Signatures of Estuarine DOC

A number of detailed $\delta^{13}\text{C}$ -DOC distributions have been measured in North American estuaries. One of the first comprehensive applications of estuarine $\delta^{13}\text{C}$ -DOC transects to examine estuarine DOC sources and sinks was by Peterson et al. (1994) and this approach was subsequently refined by Cifuentes and Eldridge (1998). These workers correctly surmised that $\delta^{13}\text{C}$ -DOC versus salinity distributions were often independent from DOC concentration versus salinity distributions, and provided independent information on DOC sources and sinks within an estuary. As general examples, both the Parker (Massachusetts) and York (Virginia) estuaries, observed $\delta^{13}\text{C}$ -DOC distributions were significantly elevated compared to their predicted $\delta^{13}\text{C}$ -DOC distributions (Figures 16(a) and 16(b)) (Raymond and Bauer, 2001b; Raymond and Hopkinson, 2003). In the absence of any other information, the interpretation of such data is that (1) $\delta^{13}\text{C}$ -enriched DOC (i.e., marine or estuarine DOC) is being added to the estuary, (2) $\delta^{13}\text{C}$ -depleted DOC (i.e., terrestrial or riverine DOC) is being removed from the estuary, or (3) some combination of (1) and (2) is occurring. These types of distributions for $\delta^{13}\text{C}$ -DOC (Figures 16(a) and 16(b)) in estuaries as a function of salinity will always be observed provided the riverine end member is both higher in DOC concentration and lower in $\delta^{13}\text{C}$ compared to its marine counterpart (i.e., lower DOC and elevated $\delta^{13}\text{C}$). These $\delta^{13}\text{C}$ -DOC plots do not, however, tell us anything about DOC concentration distributions in an estuary, which is independent of the $\delta^{13}\text{C}$ -DOC distributions. For example, in the York, there is a net nonconservative input of DOC, whereas, in the Parker, there is a net removal. The $\delta^{13}\text{C}$ -DOC and DOC concentration information when taken together leads to greater confidence in the assessments that the York Estuary has net inputs of $\delta^{13}\text{C}$ -enriched DOC, whereas the Parker estuary has net removal of $\delta^{13}\text{C}$ -depleted DOC (Raymond and Bauer, 2001b; Raymond and Hopkinson, 2003). Similar findings to bulk $\delta^{13}\text{C}$ -DOC measurements have also been found for the $\delta^{13}\text{C}$ of the HMW component of estuarine DOC (-26.1‰ to -20.9‰ in the Chesapeake Bay and Galveston Bay, USA; Guo and Santschi, 1997b; Guo et al., 2003), indicating a shift away from terrestrial to marine OM during estuarine mixing. $\delta^{13}\text{C}$ -DOC distributions have also been used in large river–estuary systems such as the Mississippi to deduce variable inputs of isotopically unique terrestrial, autochthonous, and marine DOC in different parts of the system (Wang et al., 2004).

Relatively few studies have examined detailed $\delta^{13}\text{C}$ distributions of different DOC compound groups in estuarine waters

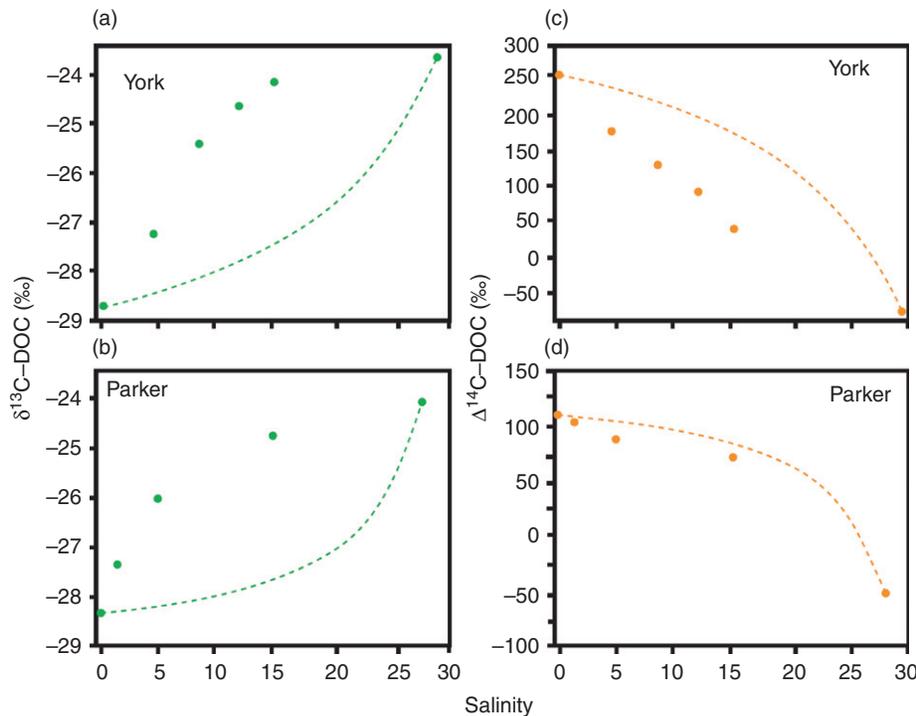


Figure 16 Examples of observed (filled dots) vs. predicted (dashed lines) distributions of $\delta^{13}\text{C}$ -DOC (a, b) and $\Delta^{14}\text{C}$ -DOC (c, d) in the York and Parker River estuaries. Both estuaries contain ^{13}C -enriched and ^{14}C -depleted DOC relative to the distributions predicted by conservative mixing between river and coastal ocean end members (see text for additional detail). Modified from (York River Estuary) Raymond, P.A., Bauer, J.E., 2001b. DOC cycling in a temperate estuary: a mass balance approach using natural ^{14}C and ^{13}C . *Limnology and Oceanography* 46, 655–667; and (Parker River Estuary) Raymond, P. A., Hopkinson, C.S., Jr., 2003. Ecosystem modulation of dissolved carbon age in a temperate marsh-dominated estuary. *Ecosystems* 6, 694–705.

(see, e.g., Wang et al., 2004; Loh et al., 2006). In a comprehensive study of four US estuaries, Wang et al. (2004) observed that $\delta^{13}\text{C}$ values of bulk HMW DOC varied from -22.1‰ to -30.1‰ , and these values differed considerably among the different estuaries. The $\delta^{13}\text{C}$ values of the total carbohydrate component of HMW DOC was enriched (-18.5‰ to -22.8‰) relative to total hydrolysable amino acids (-20.0‰ to -29.6‰) and total lipid (-25.7‰ to -30.7‰) components. These distributions are generally consistent with the values of starting biochemical classes (i.e., carbohydrates, proteins, and lipids) extracted directly from phytoplankton and other aquatic primary producers (Killops and Killops, 2005). In general, the $\delta^{13}\text{C}$ values of the acid-insoluble organic component of HMW were depleted (-23.0‰ to -34.4‰), suggesting the possibility that this material arises in some way from the more lipophilic component of estuarine DOC, or that the two have a common precursor.

5.02.6.2 $\Delta^{14}\text{C}$ Signatures of Estuarine DOC

Similar to $\delta^{13}\text{C}$ -DOC, detailed $\Delta^{14}\text{C}$ -DOC distributions in estuaries are relatively rare and tend to focus on North American systems. Using the same example of the York and Parker River estuaries (Figures 16(c) and 16(d)), $\Delta^{14}\text{C}$ -DOC distributions in both estuaries indicate (1) loss of $\Delta^{14}\text{C}$ -enriched riverine DOC, (2) input of $\Delta^{14}\text{C}$ -depleted autochthonous DOC, or (3) some combination of the two. $\Delta^{14}\text{C}$ offers several major advantages over the use of $\delta^{13}\text{C}$ alone. First, $\Delta^{14}\text{C}$ has a far greater dynamic

range (-1000‰ to $+200\text{‰}$ at the Earth's surface) and, hence, sensitivity than $\delta^{13}\text{C}$ (range of at most -32‰ to -14‰ for OC pools of estuarine interest). Second, $\Delta^{14}\text{C}$ measurements provide both source and age information on a given OC pool. Also similar to $\delta^{13}\text{C}$ -DOC and DOC concentration information, the $\Delta^{14}\text{C}$ -DOC and DOC concentration information together for these two estuaries allows for greater confidence in assessing net inputs of $\Delta^{14}\text{C}$ -depleted DOC for the York Estuary, whereas the Parker Estuary has a net removal of $\Delta^{14}\text{C}$ -enriched DOC (Raymond and Bauer, 2001b; Raymond and Hopkinson, 2003).

Historically, $\Delta^{14}\text{C}$ -DOC measurements of total bulk DOC in saline waters have been difficult to carry out (see Section 5.02.3.2.1), and, therefore, different workers have relied on a variety of extraction techniques to measure $\Delta^{14}\text{C}$ on selected fractions of DOC (Table 6), which, as we shall see, may not be representative of the bulk DOC, but nonetheless may yield important insights on the sources and cycling of different fractions. Radiocarbon values of two size fractions of HMW DOC reveal that the larger size fraction ($>10\text{ kDa}$) was enriched in ^{14}C and more contemporary in age than the smaller fraction ($>1\text{ kDa}$) in surface waters of the MAB and Gulf of Mexico, suggesting that higher MW and colloidal DOC may be derived from fibrillar-like polysaccharide structural components of plants and algae (Santschi et al., 1995; Santschi et al., 1998). However, in deeper waters, the age pattern was reversed (i.e., the $>10\text{-kDa}$ fraction was older than the $>1\text{-kDa}$ fraction), with both being higher in abundance at the lower-salinity regions of Chesapeake Bay and

Table 6 $\Delta^{14}\text{C}$ values for DOC components extracted from selected river–estuarine systems.

River–estuary system	Component	Isolation method	$\Delta^{14}\text{C}(\text{‰})$	Reference
Amazon River system (Brazil) ($S=0$)	Total DOC – river mouth	UV oxidation	28	Raymond and Bauer (2001c)
	HMW DOC – Upriver	>1-kDa ultrafiltration	182	Mayorga et al. (2005)
	Humic acids – upriver	XAD-8	141–180	Hedges et al. (1986a)
	Tulvic acids – upriver	XAD-8	290–344	Hedges et al. (1986a)
Amazon Plume Estuary (Brazil) ($S=0.4$ – 27)	Total DOC	UV oxidation	–153 to 28	Bauer et al. (unpubl. data)
	Humic acids	XAD-8	51	Bauer et al. (unpubl. data)
	Fulvic acids	XAD-8	–78 to 141	Bauer et al. (unpubl. data)
	Hydrophilic acids	XAD-4	–133 to 140	Bauer et al. (unpubl. data)
Susquehanna River– Chesapeake Bay (Maryland and Virginia, USA) ($S=0$)	Total DOC	UV oxidation	–81	Loh et al. (2006)
	HMW DOC	>1-kDa ultrafiltration	4–180	Loh et al. (2006)
	Lipids	Total lipid extract	–487	Loh et al. (2006)
	Proteins	Total hydrolyzable amino acids	16	Loh et al. (2006)
	Carbohydrates	Total hydrolyzable sugars	–167 to –91	Loh et al. (2006)
Chesapeake Bay ($S=22$ – 24)	Total DOC	UV oxidation	–77 to –29	Loh et al. (2006)
	HMW DOC	>1-kDa ultrafiltration	37–41	Loh et al. (2006)
	Lipids	Total lipid extract	–575	Loh et al. (2006)
	Proteins	Total hydrolyzable amino acids	25–39	Loh et al. (2006)
	Carbohydrates	Total hydrolyzable sugars	3–17	Loh et al. (2006)
Boston Harbor (Massachusetts, USA) ($S=26$ – 38)	HMW DOC	>1-kDa Ultrafiltration	–168 to –67	Wang et al. (2006)
	Lipids	Total lipid extract	–880 to –299	Wang et al. (2006)
	Proteins	Total hydrolyzable amino acids	–43 to –19	Wang et al. (2006)
	Carbohydrates	Total hydrolyzable sugars	–73 to –20	Wang et al. (2006)
San Diego Bay (California, USA) ($S=34$)	HMW DOC	>1-kDa Ultrafiltration	–205 to –177	Wang et al. (2006)
	Lipids	Total lipid extract	–872 to –774	Wang et al. (2006)
	Proteins	Total hydrolyzable amino acids	–74 to –32	Wang et al. (2006)
	Carbohydrates	Total hydrolyzable sugars	–32 to –23	Wang et al. (2006)
San Francisco Bay (California, USA) ($S=29$)	HMW DOC	>1-kDa Ultrafiltration	–100	Wang et al. (2006)
	Lipids	Total lipid extract	–965	Wang et al. (2006)
	Proteins	Total hydrolyzable amino acids	–25	Wang et al. (2006)
	Carbohydrates	Total hydrolyzable sugars	–73	Wang et al. (2006)

Galveston Bay estuaries (USA) (Guo et al., 1996; Guo and Santschi, 1997a). These differences were attributed to inputs of older HMW DOC (i.e., more geopolymerized) from pore waters in resuspended sediments.

Other studies, while relatively few in number, have analyzed different MW and biochemical components of DOC and found that there appears to be a size–age relationship, where the age of LMW components < bulk DOC < HMW components < POC in both oceanic and coastal/estuarine settings (Guo and Santschi, 1997b; Aluwihare et al., 2002; Loh et al., 2004, 2006; Guo et al., 2009). The findings from these studies suggest that there is a general inverse relationship between the size of OC and its ^{14}C -based age, and that – nonintuitively – the smallest forms of OC (i.e., LMW) are more refractory than larger forms (e.g., HMW and POC).

Similar to $\Delta^{14}\text{C}$ measurements of different MW components of DOC, $\Delta^{14}\text{C}$ measurements of compound classes and individual compounds are relatively few in number, owing largely to the difficulty in extracting the large sample volumes often necessary for these measurements. Those studies that have been undertaken in river–estuarine systems (Table 6) suggest that there are pronounced differences between different biochemical compound classes (as well as between different MW components and bulk DOC), where, in general, carbohydrates and proteinaceous materials are reflective of

young, contemporary, and possible reactive components, whereas lipophilic materials are far more highly aged (Aluwihare et al., 2002; Loh et al., 2004, 2006; Repeta and Aluwihare, 2006; Wang et al., 2006). This may be a result of hydrophobic lipid materials being more highly sorbed and hence protected from degradation for longer periods of time in different environments, and we cannot exclude the possibility that at least some fraction of the lipid component is petroleum derived, either naturally (e.g., petroleum seeps) or anthropogenically (e.g., fossil fuel inputs) (Loh et al., 2004). Thus far, compound-specific $\Delta^{14}\text{C}$ measurements on DOC from marine settings have been limited to individual carbohydrates, including the monosaccharides glucose, galactose, mannose, xylose, rhamnose, fucose, and arabinose. In surface waters, all of these compounds had modern, bomb-enriched $\Delta^{14}\text{C}$ signatures (47–67‰) that were similar to the HMW DOC, but significantly higher than bulk DOC $\Delta^{14}\text{C}$ signatures (Aluwihare et al., 2002; Repeta and Aluwihare, 2006). In deeper waters, monosaccharides were depleted in $\Delta^{14}\text{C}$ (–155‰ to –123‰), but were still elevated over both the HMW and bulk DOC $\Delta^{14}\text{C}$ signatures (Aluwihare et al., 2002; Repeta and Aluwihare, 2006). It is only a matter of time before compound-specific ^{14}C measurements on other compounds isolated from DOC are forthcoming, lending new insights into the sources and ages of DOC in natural waters.

5.02.6.3 Multiple Isotope Mass Balances for Constraining Estuarine DOC Sources and Sinks

Isotopic mass balances are frequently used to help establish the sources of carbon and other elements to a given organic or inorganic pool. The same can be done for DOC, and a number of studies have convincingly shown the expected changes in $\delta^{13}\text{C}$ -DOC across river to seawater salinities (e.g., Peterson et al., 1994; Mannino and Harvey, 1999; Van Heemst et al., 2000b). While $\delta^{13}\text{C}$ signatures of estuarine DOC have been used to model the mixing of terrestrial and marine end members, as well as additional inputs from uniquely estuarine sources and removal by estuarine sinks (see, e.g., Coffin et al., 1994; Peterson et al., 1994; Hullar et al., 1996; Cifuentes and Eldridge, 1998), multiple isotopes, when used in tandem with one another, provide more accurate constraints on the magnitudes of different sources (and in the case of ^{14}C , ages) of OM contributing to a given pool of DOC (Fry and Sherr, 1984; Kwak and Zedler, 1997; Raymond and Bauer, 2001a; Bauer, 2002; McNichol and Aluwihare, 2007; Alling et al., 2008). Estuaries lend themselves well to the use of a dual isotopic mass-balance approach as using $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signatures together, in conjunction with bulk DOC concentration, one can determine contributions from the three major unknowns: the river/terrestrial end member, the marine end member, and estuarine autochthonous material. The generalized equation for using two isotopes to estimate contributions from three unknown sources of DOC is:

$$I_{\text{mix}} = f_1 I_1 + f_2 I_2 + f_3 I_3 \quad [2]$$

where I is the measured isotopic composition ($\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$) of DOC in the estuarine mixture sample (mix) and for each of the three potential sources. The value f is the relative contribution of each of the three potential sources to the total DOC in the estuarine mixture sample, and $f_1 + f_2 + f_3 = 1.0$. The contribution of f_3 is equal to $(1 - f_1 - f_2)$ and eqn [2] becomes:

$$I_{\text{mix}} = f_1 I_1 + f_2 I_2 + (1 - f_1 - f_2) I_3 \quad [3]$$

Since there are two unknowns (f_1 and f_2) in eqn [3], the equation is solved simultaneously using $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$.

The use of such an approach has allowed multiple isotopic mass-balance calculations (Raymond and Bauer 2001a, 2001b; Raymond and Hopkinson, 2003) using a three end-member (i.e., freshwater + terrestrial, marine, and autochthonous estuarine material) isotopic mixing model using both $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ concomitantly. Raymond and Bauer (2001b) estimated that 20–38% of the DOC at the mouth of the York River Estuary, Virginia, USA ($S \sim 18$) was of riverine (terrestrial + freshwater) origin, while 38–56% was added internally, depending on the isotopic values assigned to the autochthonous DOC end member. Measurements of $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ of DOC and DIC and marsh OM indicate that the internal sources originated from estuarine phytoplankton and marshes. In the York, conservative mixing predicts that ~65% of the DOC at the mouth of the York should be of riverine origin; therefore, the isotopic mixing model indicates a significant loss (27–45%) of riverine DOC during estuarine mixing. Raymond and Bauer (2000) further reported that estuarine bacteria utilized only ~10% of York River Estuary DOC, thus indicating that a second DOC sink (flocculation, particle sorption, etc.) must be present in order to account for the large losses predicted by the isotopic mixing model.

5.02.7 DOC Compound and Compound Class Distributions

The chemical analysis of dissolved organic compounds in saline (i.e., estuarine and marine) waters has historically been challenging primarily due to the interference of salts. The two primary means of characterization include direct aqueous-phase analysis and isolation of DOC from salts (see Section 5.02.3.2.4) with subsequent solid-phase analysis of the lyophilized material (see Benner (2002) for review). The latter essentially amounts to analysis of a particulate organic form of the material, using most of the same techniques described in Chapter 5.03. The most serious limitation of various DOC extraction and isolation methods, however, is that the complete DOC pool is generally not isolated (i.e., typically the hydrophilic or LMW components are lost), leading to potential bias in the quantitative and qualitative characterization of samples (see, e.g., Gustafsson et al., 1996). However, prior to the development and application of such isolation techniques, characterization of estuarine and marine DOC was limited to aqueous-phase analyses that relied on spectrophotometric, colorimetric, and similar methods of functional group characterization such as those contained in monosaccharides and polysaccharides (see, e.g., Burney and Sieburth, 1977; Mopper, 1977; Sieburth et al., 1977; Burney et al., 1981; Johnson et al., 1981; Senior and Chevolut, 1991), large-volume seawater extractions with immiscible organic solvents for concentration of and subsequent gas chromatographic analysis of lipophilic materials (Ehrhardt and Burns, 1999), or derivatization and higher-performance liquid chromatographic techniques for quantification of individual compounds such as free and hydrolyzable amino acids (see, e.g., Lindroth and Mopper, 1979; Jørgensen et al., 1980; Mopper and Dawson, 1986). For a review of these and other early methods of seawater dissolved OM analysis, the reader is referred to Dawson and Liebezeit (1981) and Grasshoff et al. (1999).

Most of our recent insights over the past two decades on the composition of estuarine DOC rely on some sort of extraction of the material by hydrophobic resins, UF, and other methods of isolation and/or concentration. Although detailed chemical characterization of different estuarine DOC fractions have been carried out in an increasing number of studies recently, the number is still relatively small compared to those characterizing water-column particulate and sedimentary OM (see Chapter 5.03). It should also be noted that in studies in which riverine, estuarine, and marine DOC and POC have been evaluated, that a much greater proportion of particulate forms is generally characterized by known biochemical classes than dissolved forms, leading to the general conclusion that dissolved materials are generally more reworked and refractory than particulate materials, which appear to bear a stronger relationship to the starting plant and animal materials (Wakeham, 1997; Benner, 2002; Benner, 2003). Benner (2003) summarized the major chemical characteristics and dominance of different structural moieties of river and surface ocean DOC as collected by both XAD-2 and UF and determined by NMR, and showed that in both environments (1) methylene and methyl groups (C–C) comprised a similar proportion (~25–44%) of the DOC, (2) aromatic (C=C) components were significantly higher in river (16–35%) than in seawater (5–19%), (3) carboxyl and ester (O–C=O) and amide (N–C=O) components were roughly

similar in river and surface ocean waters (13–22%), and (4) more polar groups such as alcohols (C–O) and ethers (O–C–O) were higher in seawater (19–54%) versus river water (12–29%). Aldehydes and ketones (C=O) comprised the smallest fractions (3–6%) in both environments (Benner, 2003). For other recent reviews of the general structural and biochemical characteristics of the compound classes in estuarine DOC discussed in the following sections of this chapter, the reader is referred to Bianchi (2007) and Libes (2009).

Detailed characterization of estuarine DOC has also been established using direct temperature-resolved mass spectrometry (DT-MS) and wet chemical techniques coupled with discriminant analysis and canonical correlation analysis. In the Delaware River and Bay Estuary, OM size class was found to be the major source of molecular-level variability, with POC being enriched in proteins, nucleic acids, fatty acids, chlorophyll, and sterols, and DOC being enriched in amino sugars, furfural, and alkylphenol components (Minor et al., 2001). Using DT-MS analysis, which focuses on sugar components, these same workers found HMW riverine DOC to be enriched in deoxy sugars and methyl sugars compared to estuarine and coastal samples. Similarly, reverse-phase liquid chromatography/mass spectrometry (LC/MS) has also been recently used as a molecular fingerprinting technique for tracing terrigenous DOC and its photochemical alteration in Brazil coastal waters (Dittmar et al., 2007), showing that the molecular characteristics of estuarine DOC strongly resembled coastal DOC following photo-alteration. The molecular patterns of coastal DOC also did not show significant contributions of terrigenous DOC.

Other recent advances in detailed DOC characterization have been achieved through advanced analytical techniques capable of providing detailed molecular fingerprinting. Application of ultra-high-resolution mass spectrometric and spectroscopic methods has allowed for an unprecedented level of detail on the molecular composition of DOC, leading to new insights as to its sources and transformations. For example, electrospray ionization coupled to Fourier transform ion cyclotron resonance mass spectrometry (ESI-FTICR-MS) has been employed to characterize DOC at the molecular level during river–estuarine transport in the lower Chesapeake Bay system (Sleighter and Hatcher, 2008). The resolving power of this technique (>500 000) and mass accuracy of FTICR-MS allow for the resolution of the thousands of individual elemental components in a single sample. The sensitivity of FTICR-MS further allows for direct analysis of low-salinity samples without the need for preconcentration techniques such as C-18 extraction or UF. However, interference by salts in mesohaline and seawater samples requires their removal (e.g., by C-18 SPE, UF, or RO/ED). Along a transect in Chesapeake Bay, ESI-FTICR-MS demonstrated significant differences in DOC molecular composition, with DOC becoming progressively enriched in aliphatic components and depleted in oxygen-rich molecules from inshore to offshore (Sleighter and Hatcher, 2008). Application of ESI-FTICR-MS to DOC molecular analysis from a Brazilian mangrove-dominated tropical estuary showed that the lower MWs observed in estuarine DOC were due primarily to loss of HMW components, possibly due to photo-oxidation, and highly unsaturated and/or aromatic components observed in pore-water DOC (Tremblay et al., 2007).

5.02.7.1 Carbohydrates

As a result of their ubiquity as structural and energetic components of terrestrial and aquatic plants (Aspinall, 1983; Parsons et al., 1984), it is not surprising that carbohydrates form a significant fraction of estuarine OM in general. While carbohydrates are often the dominant biochemical component of estuarine DOC, in both polymeric (so-called PCHO) and smaller (e.g., monosaccharides and disaccharides, MCHO and DCHO, respectively) forms, observed percentage contributions are quite large, ranging from undetectable to as much as 90% of the DOC (Table 7; Sigleo and Means, 1990; Zhang et al., 1992; Hedges et al., 1994; Sigleo, 1996; Aluwihare et al., 1997; Sellner and Nealley, 1997; Harvey and Mannino, 1999, 2000, 2001; Aluwihare et al., 2002; Saliot et al., 2002a, 2002b; Gors et al., 2007). When both MCHO and total carbohydrates (TCHO) have been measured simultaneously, PCHO (which is determined as TCHO – MCHO) is nearly always higher than MCHO (Table 7), suggesting that MCHO are more reactive and turned over more rapidly than PCHO. Those studies that have examined spatial variability in the carbohydrate content of estuarine DOC have not identified a universal factor(s) producing predictable longitudinal differences between river and coastal end-members (Figure 17; Mannino and Harvey, 2000; Harvey and Mannino, 2001). However, hydrolysis rates of polymeric carbohydrates in estuaries may be considerable, accounting for nearly the entire daily demand of mono- and disaccharides by heterotrophic bacteria (Kirchman and Borch, 2003; Steen et al., 2008).

Recent detailed work on dissolved polysaccharides has shown high concentrations of acylheteropolysaccharides (APS) in HMW DOC from seemingly unique aquatic systems, including estuaries. This material is believed to be derived ultimately from freshwater and riverine phytoplankton (Aluwihare et al., 2002; Repeta et al., 2002). The relative abundance of seven major neutral sugars (rhamnose, fucose, arabinose, xylose, mannose, glucose, and galactose) in DOC APS is consistent across different environments and believed to indicate that the sources and processes of APS production and fate are similar across these systems (Figure 18).

Although marine and freshwater microalgae are both capable of producing APS (Aluwihare et al., 1997; Repeta et al., 2002), controls on the overall cycling of APS in aquatic systems remains largely unknown. Spectroscopic and molecular data indicate that APS in HMW DOC across divergent systems is very similar (Aluwihare et al., 1997). Multivariate analyses using DT-MS showed that HMW DOC (>1 kDa) from Chesapeake Bay (USA) and Oosterschelde Estuary (Netherlands) was largely composed of amino sugars, deoxysugars, and O-methyl sugars, suggestive of bacterial processing (Minor et al., 2001, 2002). These studies further support the hypothesis that similar lipid composition or signatures found in estuarine DOC (Zou et al., 2004) was ultimately determined by bacterial processing along an estuarine gradient. Such molecular studies also support the idea that estuarine DOC is composed of both labile and refractory components (Raymond and Bauer, 2000, 2001a, 2001b; Van Heemst et al., 2000a; Cauwet, 2002; Bianchi et al., 2004), with much of the labile fraction degraded (i.e., both respiration and significant structural alteration) before being exported to the ocean (see Section 5.02.8). As we shall also see, $\Delta^{14}\text{C}$ analyses of the carbohydrate component of estuarine and marine DOC

Table 7 Relative biochemical composition of DOC from selected river, estuarine, and coastal ocean systems

River–estuary system	Form of DOC	Lignin (% DOC) ^c	Lipids (% DOC) ^c	THAA ^a (% DOC) ^c	TCHO ^b (% DOC) ^c	References
Amazon River (Brazil)	total DOC	~1.2	N/A	N/A	N/A	Ertel et al. (1986), Hedges et al. (1984)
	>1 kDa	N/A	N/A	1.0–1.9	0–2.0	
Mississippi River (USA)	>1 kDa	0.83	N/A	N/A	N/A	Opsahl and Benner (1997)
Chesapeake Bay system (Maryland and Virginia, USA)	>5 kDa	N/A	<1	4–22	20–60	Sigleo et al. (1983), Sigleo and Means (1990)
Delaware Bay Estuary (USA)	1–30 kDa	0.2–0.8	0.1–0.3	1.5–4.2	8–19	Mannino and Harvey (1999), Mannino and Harvey (2000), Harvey and Mannino (2001)
	>30 kDa	0.1–11	0.4–1.6	5–12	30–60	
San Francisco Bay Estuary (California, USA)	Total DOC	N/A	N/A	0.3–7.1	1.8–24.2	Murrell and Hollibaugh (2000)
Ems–Dollart Estuary (the Netherlands)	Total DOC	N/A	3.0–12	2.0–12	10.0–13.0	Laane (1984)
Huanghe River Estuary (China)	Total DOC	N/A	N/A	0.2–6.5	0.6–2.9	Zhang et al. (1992)
Lena River Delta (Russia)	Total DOC	N/A	N/A	<0.5	1.2–2.5	Lara et al. (1998)
Mid-Atlantic Bight (USA)	>1 kDa	N/A	4–16	N/A	73–86	Aluwihare et al. (1997), Aluwihare et al. (2002)
South Atlantic Bight (USA)	Total DOC	<0.15	N/A	N/A	N/A	Moran and Hodson (1994)
Laptev Sea (Russia)	Total DOC	0.02–0.05	N/A	1.2	5–10	Kattner et al. (1999)
Aburatsubo Bay (Japan)	Total DOC	N/A	N/A	0.8	N/A	Tupas and Koike (1990)
Ohtsuchi Bay (Japan)	Total DOC	N/A	N/A	0.9–3.7	N/A	Tupas and Koike (1990)
Baltic Sea coast (Germany)	Total DOC	N/A	N/A	4.9–8.8	13.2–16.9	Gors et al. (2007)
Northern Adriatic coast (Italy)	Total DOC	N/A	N/A	N/A	11.3–25.6	Pettine et al. (2001)

^aTotal hydrolyzable amino acids.^bTotal carbohydrates.^c% of carbon in form of DOC listed.

N/A, Not applicable.

Modified from Harvey, H.R., Mannino, A., 2001. The chemical composition and cycling of particulate and macromolecular dissolved organic matter in temperate estuaries as revealed by molecular organic tracers. *Organic Geochemistry* 32, 527–542; and Gors, S., Rentsch, D., Schiewer, U., 2007. Dissolved organic matter along the eutrophication gradient of the Dar beta-Zingst Bodden Chain, Southern Baltic Sea: I. Chemical characterisation and composition. *Marine Chemistry* 104, 125–142.

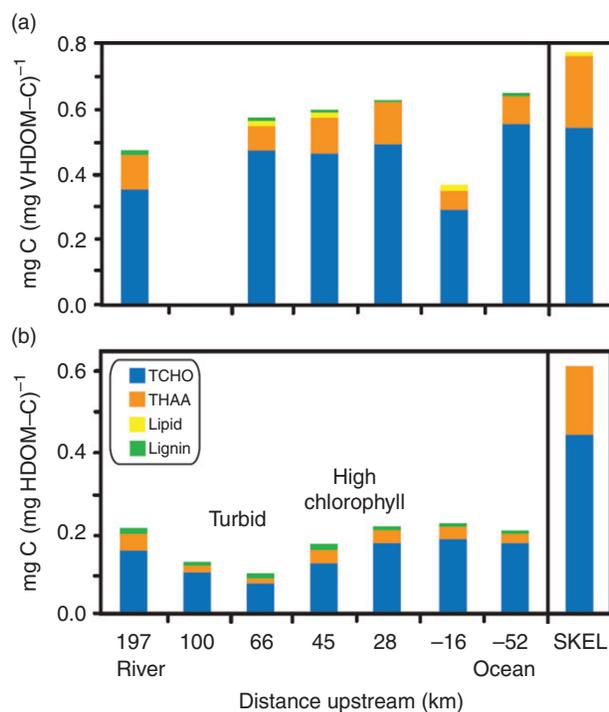


Figure 17 Distribution of polysaccharides and amino acids throughout the Delaware Bay Estuary and in a culture of *Skeletonema costatum* culture (SKEL) in (a) very high MW DOM (VHDOM), defined as material between 30 kDa and 0.2 μ m, and (b) high MW DOM (HDOM), defined as material between 1 and 30 kDa. Modified from Harvey, H.R., Mannino, A., 2001. The chemical composition and cycling of particulate and macromolecular dissolved organic matter in temperate estuaries as revealed by molecular organic tracers. *Organic Geochemistry* 32, 527–542.

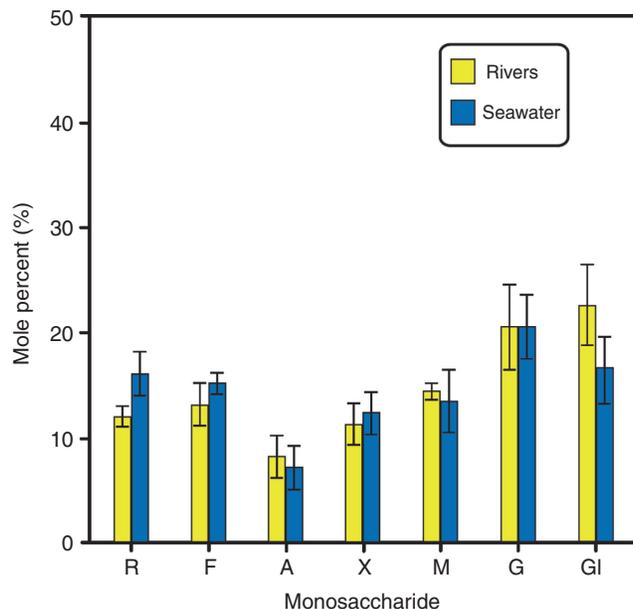


Figure 18 Distributions of rhamnose (R), fucose (F), arabinose (A), xylose (X), mannose (M), galactose (G), and glucose (GI) as mol.% of total sugars in river water and seawater (see text for additional details. Modified from Repeta, D.J., Quan, T.M., Aluwihare, L.I., Accardi, A., 2002. Chemical characterization of high molecular weight dissolved organic matter in fresh and marine waters. *Geochimica et Cosmochimica Acta* 66, 955–962.

indicate that it is dominated by recently produced (i.e., young or modern) material (Aluwihare et al., 2002; Loh et al., 2004, 2006; Wang et al., 2006) that contrasts with the remainder of correspondingly aged DOC and must support a significant fraction of the heterotrophic respiration and production (see Section 5.02.8). Generally high concentrations of estuarine dissolved polysaccharides versus coastal ocean waters, combined with their contribution of similar relative contributions of DOC across these systems and almost universally low estuarine monosaccharide concentrations, have been interpreted as being indicative of extensive degradation of estuarine carbohydrates in general during estuarine transport and mixing (Kirchman and Borch, 2003; Steen et al., 2008).

Earlier studies of marine and estuarine DOC extracted by XAD, UF, and C18 reverse-phase adsorption using ^{13}C -NMR and ^1H -NMR showed that carbohydrate carbon was the dominant form of this DOC (Benner et al., 1992; Hedges et al., 1992). However, more recent studies concentrating greater percentages of total DOC using RO/ED techniques (Koprivnjak et al., 2006; Vetter et al., 2007; Gurtler et al., 2008) have shown using ^{13}C -NMR and ^1H -NMR analyses that there may be less carbohydrate content and proportionately greater alkyl carbon in samples isolated in this manner (Koprivnjak et al., 2009; Figure 19), among other differences. Because most of the earlier methods isolated hydrophobic and/or HMW components, these new findings suggest that significant amounts of DOC are

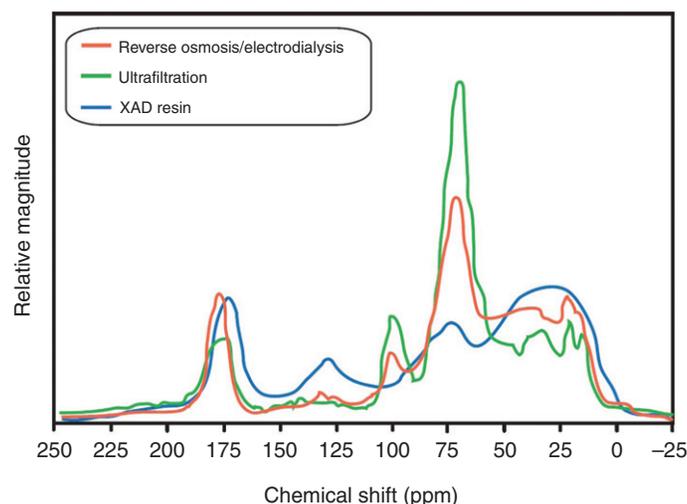


Figure 19 ^{13}C -NMR spectra of seawater DOC isolated using reverse osmosis/electrodialysis, ultrafiltration, and XAD resin (see text for further description). Modified from Koprivnjak, J.F., Pfromm, P.H., Ingall, E., 2009. Chemical and spectroscopic characterization of marine dissolved organic matter isolated using coupled reverse osmosis–electrodialysis. *Geochimica et Cosmochimica Acta* 73, 4215–4231.

dominated by LMW material of a hydrophilic nature, and that it has different biochemical character, and potentially origins and reactivity, compared to the material characterized previously. Therefore, our understanding of the specific biochemical makeup of marine and estuarine DOC continues to evolve as new methods of extraction and isolation are developed and applied.

5.02.7.2 Proteins and Amino Acids

Dissolved proteinaceous materials (also called total hydrolyzable amino acids, or THAA) and their precursor dissolved free amino acids (DFAAs) and combined amino acids (DCAAs) or polypeptides generally comprise the next most abundant form of estuarine DOC after carbohydrates (Table 7). Dissolved amino acids in particular have been measured in marine and estuarine waters since the 1970s because of their ability to be measured directly in the dissolved phase (i.e., without pre-extraction) and the early development of relatively simple HPLC techniques for their quantification (Lindroth and Mopper, 1979; Mopper and Lindroth, 1982; Keil and Kirchman, 1991a, 1993). The DFAAs in estuarine and other marine systems have also received extensive study due to their key role in the control of microheterotrophic activity (Fuhman, 1990; Jørgensen et al., 1993; Kirchman, 2003).

Similar to polymeric carbohydrates (i.e., PCHO) versus LMW sugars (e.g., MCHO), proteinaceous materials in estuarine DOC are almost always dominated by HMW combined forms (i.e., DCAA), with LMW DFAA (Table 7) concentrations being typically significantly lower, presumably owing to the rapid turnover of DFAA by heterotrophic bacteria. While DFAAs generally comprise an insignificant proportion of estuarine and coastal DOC, relatively high percentage contributions of DCAA to the DOC pool have been observed in certain environments (Table 7). Organic-rich estuarine sediments, it should be noted, have also been found to have highly elevated concentrations (tens of micromolar) of soluble proteinaceous materials (i.e., DFAA and DCAA) owing to the high rates of protein degradation, especially in aerobic surface sediments (Burdige and Martens, 1988; Burdige and Martens, 1990). The high calculated fluxes of DFAA across the sediment–water interface of estuaries (Burdige and Martens, 1990) may support much of the total input of these compounds to the overlying water column. Although sediment pore waters have not been examined as extensively for DCAA as for DFAA, studies thus far suggest DCAA concentrations may be significantly higher than DFAA (e.g., Colombo et al., 1998; Lomstein et al., 1998; Pantoja and Lee, 1999), with potentially higher cross-interface fluxes of DCAA versus DFAA as well.

In their comprehensive study of DOC composition in Delaware Bay estuary waters, Mannino and Harvey (2000) and Harvey and Mannino (2001) (Figure 17) observed little change in the distributions of THAA and TCHO as a function of salinity. Such distributions could be due to a variety of factors, including (1) similarities in the river and marine end members, (2) the relative inertness of the polymeric forms of proteins and carbohydrates in estuarine waters during transit, and (3) similar rates of removal and input during mixing and transport. As mentioned previously, this same study also showed that POC much more closely resembles starting planktonic OM, than does DOC of varying MW (Figures 17(a) and 17(b)). Furthermore, the decreasing THAA and TCHO content of HMW (1–30 kDa) DOC

(Figure 17(b)), and its different composition compared to POC and very HMW DOC (>30 kDa; Figure 17(a)) suggest, as has been found in numerous other studies, that the larger and more highly polymerized forms of DOC appear to derive more directly from reactive POC, and that with decreasing size (and increasing time) DOC is increasingly reworked and less reactive, leading to the hypothesis of a size–reactivity continuum (Amon and Benner, 1996a; Benner, 2002; Loh et al., 2004).

There are few studies that have examined the relationship between the ages of estuarine DOC and its biochemical character as a function of estuarine mixing. In the Mississippi River plume (MRP), riverine DOC is young and ^{14}C enriched, arising from a combination of allochthonous soil OM and autochthonous river OM, whereas high-salinity Gulf of Mexico DOC is highly aged (Guo et al., 2009) (Figure 20), resembling open ocean DOC such as has been observed in other estuarine systems (Raymond et al., 2004). In the MRP, the relative age (i.e., ^{14}C content) of DOC is observed to correlate with decreasing OC-normalized THAA and TCHO concentrations, indicating that at least in certain estuaries, young DOC retains its biochemical character to a greater extent than older, more reworked marine material.

5.02.7.3 Lipids

Lipids consist of a diverse array of compounds (dominated by the major classes hydrocarbons, fatty acids, alkanols, and sterols) that can comprise significant portions of bulk OM, and provide unparalleled information as biomarkers on the sources and fates of OM (for review, see Bianchi (2007) and Libes (2009)). The vast majority of studies of estuarine lipid distributions has been conducted in suspended and sinking particulate

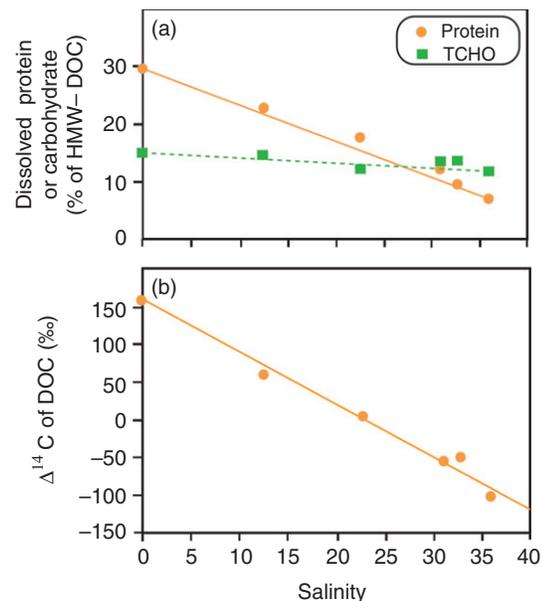


Figure 20 Changes in the (a) dissolved protein and total dissolved carbohydrate (TCHO) content and (b) $\Delta^{14}\text{C}$ signatures of DOC as a function of salinity in the Mississippi River plume. Modified from Guo, L., White, D.M., Xu, C., Santschi, P.M., 2009. Chemical and isotopic composition of high-molecular-weight dissolved organic matter from the Mississippi River plume. *Marine Chemistry* 114, 63–71.

OM and sedimentary OM (see Chapter 5.03), and lipids have been found to be universally much lower than carbohydrates and proteins in both DOC and POC (Harvey and Mannino, 2001). The higher concentrations of OM, combined with the selective partitioning of lipids into particulate phases as a result of their hydrophobic nature, has historically made studies of particulate lipids much more plausible and tractable than for dissolved lipids. Early seawater dissolved lipid studies were challenging, typically requiring large-volume seawater solvent extractions, followed by thin-layer chromatographic cleanup and flame ionization detection (Delmas et al., 1984; Parrish et al., 1988). Nonetheless, studies of lipid distributions in DOC have increased in recent years and have shown not only the expected much lower amounts of total and individual lipid biomarkers in the dissolved pool, but also significantly different distributions in dissolved versus particulate pools, suggesting that the sources and diagenesis of lipophilic materials in dissolved versus particulate pools may be fundamentally different. Here, we briefly review some recent findings for dissolved fatty acids, sterols, and plant pigments in estuaries and coastal waters.

5.02.7.3.1 Fatty acids

Concentrations of dissolved lipids and fatty acids in estuarine and coastal waters are generally orders of magnitude lower than in the corresponding particulate phase (Leveau et al., 1990; Yunker et al., 1993, 1995; Mannino and Harvey, 1999), on both absolute and OC-normalized bases. The distributions of fatty acids and other lipid groups can be used to qualitatively (and sometimes semiquantitatively) evaluate contributions to the DOC and POC pools of different primary and secondary producers (Laureillard and Salot, 1993; Canuel, 2001; Countway et al., 2007), and even anthropogenic inputs such as sewage (e.g., Quemeneur and Marty, 1992; Thoumelin et al., 1997). These distributions – not unexpectedly – may vary considerably across the terrestrial-

to-marine estuarine gradient (Figures 21(a)–21(c)). Dissolved fatty acids appear to be dominated by saturated compounds, while their particulate counterparts are, at least at times, dominated by mono- and polyunsaturated fatty acids (MUFAs and PUFAs respectively; McCallister et al., 2006a).

However, in contrast to particulate materials, DOC contains little to no measurable amounts of MUFAs and PUFAs (Zou et al., 2004; Loh et al., 2006; McCallister et al., 2006a). These DOC–POC differences in fatty acid distributions have been interpreted as generally indicative of greater contributions of labile, plankton-derived material to POC, while DOC is more highly reworked and refractory. However, depending upon factors such as the magnitude of riverine detrital–mineral inputs, resuspension in the estuarine turbidity zone, etc., DOC may have more contemporary labile character than POC, at least in different regions of certain estuaries such as Chesapeake Bay (Derieux et al., 1998; Loh et al., 2006). Even-numbered fatty acids dominate HMW DOC, with bacteria-derived odd-numbered fatty acids being next in importance (Zou et al., 2004; Loh et al., 2006; McCallister et al. 2006a). Negligible amounts of fatty acids $>C_{20}$ in estuarine HMW DOC have been interpreted as indicating rapid removal of vascular plant-derived materials due to microbial and photochemical oxidation (Mannino and Harvey, 2000; Benner and Opsahl, 2001). However, the greater hydrophobic character of these fatty acids may also result in their preferential partitioning into particulate versus dissolved phases. Not surprisingly, production of fatty acids by estuarine heterotrophic microbial communities was found to depend on the composition of the DOC source (Harvey et al., 2006), suggesting an intimate feedback between the sources, repackaging and release of fatty acids, and other biochemical substrates during estuarine DOC processing.

The absence of PUFAs and low concentrations of MUFAs (both derived from phytoplankton sources) in estuarine HMW

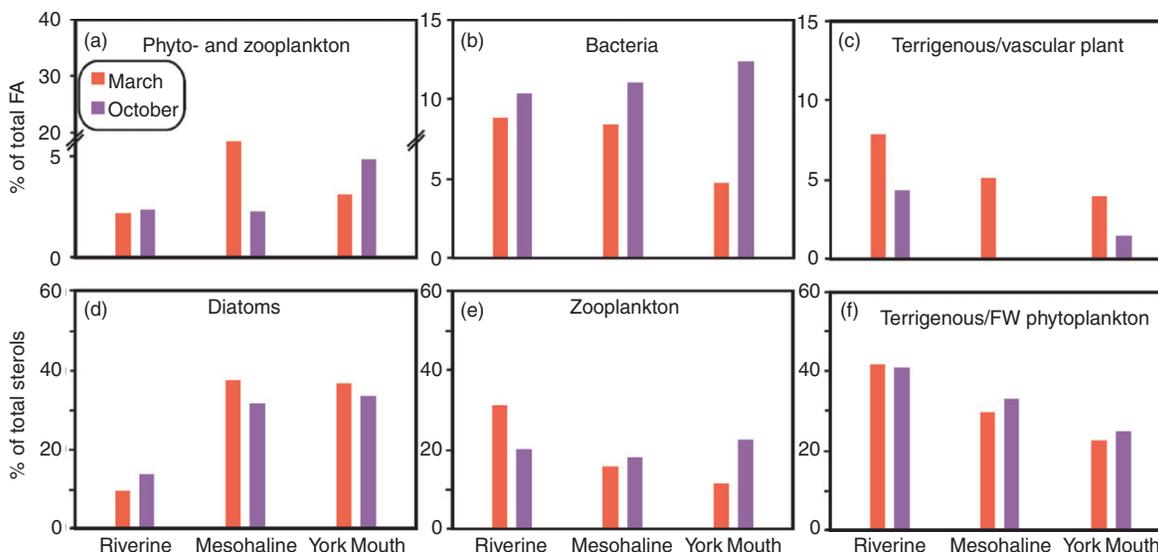


Figure 21 Temporal and spatial variations in fatty acids (FA, as % of total) in high-molecular-weight (HMW) DOM diagnostic for (a) phytoplankton and zooplankton sources, (b) bacterial sources and (c) terrigenous/vascular plant sources and in sterols (as % of total) in HMW DOM diagnostic for (d) diatom sources, (e) zooplankton sources, and (f) terrigenous and freshwater phytoplankton sources in the York River Estuary, Virginia, USA (see text for additional details). Modified from McCallister, S.L., Bauer, J.E., Ducklow, H.W., 2006a. Sources of estuarine dissolved and particulate organic matter: a multi-tracer approach. *Organic Geochemistry* 37, 454–468.

DOC (Zou et al., 2004; Loh et al., 2006; McCallister et al., 2006a) supports other studies which show preferential loss of unsaturated over saturated fatty acids (Gomez-Belinchon et al., 1988; Wakeham and Lee, 1989; Sun and Wakeham, 1994; Harvey and Macko, 1997; Parrish et al., 2000). Thus, it appears that a significant fraction of estuarine HMW DOC is derived from degraded phytodetrital material that has been processed by bacteria in addition to bacterial membrane components. However, lipid composition of POC and the differential lability of lipids are also important in controlling what is processed by bacteria and ultimately partitioned into the DOC pool. Thus, other experimental work has shown rapid decay of unsaturated sterols under oxic conditions, suggesting that chemical structure alone (e.g., unsaturation) may not always be a good predictor of decomposability (Harvey and Macko, 1997). Nevertheless, the remarkable similarity in composition of HMW DOC from different estuarine systems emphasizes the importance of bacterial processing as an important control on the biochemical signature of lipids in HMW DOC (Zou et al., 2004). Finally, it should be noted that physical processes such as solubility and adsorption/desorption are also important in controlling the partitioning of lipophilic and other compounds into HMW DOC and DOC in general.

5.02.7.3.2 Sterols

Similar to fatty acids, sterols may be employed as potentially informative biomarkers to help assess contributions to the DOC and POC pools of different primary producers (e.g., vascular plants and river and estuarine microalgae), secondary producers (e.g., zooplankton and bacteria), and wastewaters, as well as the diagenetic features of biomolecules derived from these sources (Volkman, 1986; Sun and Wakeham, 1998; Canuel and Zimmerman, 1999). While there are a relatively limited number of studies of dissolved sterol distributions in estuarine and coastal DOC, the findings that have been reported are generally consistent with dissolved fatty acid distributions regarding the sources and reactivity of DOC, as well as the apparent uncoupling of DOC and POC sources (Thoumelin et al., 1997; Derieux et al., 1998; Saliot et al., 2002a, 2002b). Also similar to fatty acids, dissolved sterol distributions in estuarine waters may vary considerably across the land–ocean salinity gradient (Figures 21(d)–21(f)). One ubiquitous finding is of the presence of bacteria-derived sterols and sterol degradation products in DOC and HMW DOC in a number of studies, reflecting the importance of bacterial reworking of DOC to a far greater extent than POC (Mannino and Harvey, 1999; Zou et al., 2004; Loh et al., 2006; McCallister et al., 2006a, 2006b). Dissolved fatty acid and sterol distributions support the dominance of terrestrial and vascular plant material in low to mesohaline portions of estuaries, a growing influence of microalgal sources at higher salinities, and significant but more variable contributions from bacteria and zooplankton throughout the estuary (Mannino and Harvey, 1999; Loh et al., 2006; McCallister et al., 2006a). In urbanized and industrialized estuaries, sewage and wastewater inputs may lead to significant enrichments in specific sterols reflective of these sources, and anthropogenic inputs may comprise a significant part of the DOC flux through these systems (Laureillard and Saliot, 1993; Quemeneur and Marty, 1994; Thoumelin et al., 1997).

5.02.7.3.3 Photosynthetic pigments

Similar to other organic components, quantification of photopigment concentrations and distributions in DOC from estuarine and other aquatic environments has not been undertaken to nearly the extent that it has for particulate and sedimentary forms (see, e.g., Bianchi et al., 1997a, 1997b, 1997c, 1998; Dagg et al., 2005; Wysocki et al., 2006). Nonetheless, the detection of pigments and pigment degradation products in DOC using fluorescence and other analytical techniques can be a powerful tool for identifying some of the most contemporary and reactive forms of DOC, as well as constraining important degradation processes, in aquatic environments. Pigments have been isolated and identified in HMW DOC collected from both the Gulf of Mexico and MAB regions of the United States (Bianchi et al., 1995; Santschi et al., 1995), and significant differences in DOC pigment distributions were noted between these two coastal areas. In the Gulf of Mexico (Bianchi et al., 1995), chlorophylls *a* and *b* were detected in HMW DOC, whereas concentrations of the carotenoids zeaxanthin and fucoxanthin in HMW DOC indicated that cyanobacteria, prochlorophytes, and diatoms contributed to the total HMW DOC pool across the continental margin. Low concentrations of pheopigments (except for chlorophyllide) in both POC and HMW DOC suggested that direct exudation from phytoplankton and sloppy feeding by zooplankton were the major mechanisms of release to both pools. As also demonstrated in both the Gulf of Mexico and the MAB, HMW DOC pigment concentrations and distributions reflective of contemporary inputs of reactive autochthonous material may be correlated with a number of other DOC parameters such as radiocarbon age to discern the dominant factors controlling its sources and inputs.

5.02.7.4 Lignin

The abundance and distribution of lignin-derived phenols (LDPs, the analytical form of lignin after it has been chemically oxidized) have been employed in a number of studies for estimating the contributions of terrestrial vascular plant-derived organic materials in estuarine DOC. A corresponding gradient in freshwater and terrestrially derived inputs of lignin in DOC has been documented in riverine/estuarine systems. For example, Benner and Opsahl (2001) found Λ_8 in HMW DOC in the lower Mississippi River and inner plume region that ranged from 0.10 to 2.30 mg/100 mg OC, which is consistent with other HMW DOC measurements in river/coastal margin gradients (Opsahl and Benner, 1997; Opsahl et al., 1999). In the Delaware Bay Estuary, LDP in HMW DOC (1–30 kDa) and very HMW DOC (30 kDa to 0.2 μm) were highest in river water and the ETM (Mannino and Harvey, 2000) where terrigenous and other materials are resuspended and possibly desorbed from particulate to dissolved phases. Using LDP concentrations, these same workers estimated that terrigenous DOC comprised as much as 73% of the HMW DOC in the ETM, but only 12% of HMW DOC at the marine end member of the estuary. As pointed out by Hernes et al. (2007), however, important fractionation processes may occur during the solubilization and sorption of LDP between both soil detrital organic litter and mineral soils, leading to

artificially elevated levels of LDP in river DOC and, thus, potentially overestimating contributions of terrigenous vascular plant materials to river and estuarine DOC. Therefore, the use of LDP in river and estuarine DOC to estimate terrigenous contributions must be done with consideration of this potential bias.

LDPs have also been measured in a number of other unique coastal/estuarine systems, including organic-rich marsh and mangrove systems. In hypoxic Bayou Trepagnier, Louisiana, USA, Engelhaupt and Bianchi (2001) found that HMW DOC contained far lower amounts of LDP than POC or surrounding wetland plants and soils, suggesting that low-oxygen conditions may inhibit the breakdown of the parent organic materials to their dissolved forms (i.e., HMW DOC). Mangrove systems can be significant producers of lignin to estuarine and coastal waters. For example, Dittmar et al. (2001) found that while only about 6% of the area of a fluvial catchment in northern Brazil was covered by mangroves, their contribution to the estuarine DOC (as well as POC) pools generally exceeded by several-fold the terrigenous input from farther inland. These workers also noted that while most of the mangrove-derived POC was removed from the water column, mangrove DOC behaved conservatively during estuarine mixing and transport. In contrast to mangrove systems, oligotrophic wetland systems such as Taylor Slough and Florida Bay (Florida, USA) were found to have much lower LDP levels (0.20–0.39 mg/100 mg UDOC and 0.04–0.07 mg/100 mg UDOC, respectively) than most other coastal/estuarine wetland systems or rivers (Maie et al., 2007), which the authors speculated may be a result of the shallowness of this system (i.e., high overall light penetration) that could enhance photochemical degradation of lignin there. Clearly, the use of reactive and variable (i.e., between systems) biomarkers such as lignin must be assessed for the end members (especially the river source) of each individual system in which LDP concentrations and distributions are being applied, in order to constrain the most accurate river end member for each.

Controls on the abundance of lignin in DOC in estuarine/coastal systems may involve losses from *in situ* microbial breakdown (discussed in greater detail below), flocculation, sorption and desorption processes with resuspended sediments (Guo and Santschi, 2000; Mitra et al., 2000; Harvey and Mannino, 2001), and photochemical alteration and mineralization of lignin molecular structure (Opsahl and Benner, 1998; Benner and Opsahl, 2001). In fact, HMW DOC in bottom waters of the MAB were found to be both relatively highly aged and rich in lignin, and believed to derive from desorption of HMW DOC from sedimentary particles largely derived from Chesapeake Bay and other estuarine systems along the northwest North Atlantic ocean margin (Guo and Santschi, 2000; Mitra et al., 2000). Temporal and spatial variability in the relative importance of such processes can also commonly result in nonconservative behavior of total DOC and lignin in estuaries. These different mechanisms of lignin structural alteration, degradation, and remineralization, as well as other forms of terrestrially derived DOC in estuarine/shelf regions may be, at least in part, responsible for the large deficit in terrigenous DOC observed in the global ocean (Hedges et al., 1997; Opsahl and Benner, 1997).

5.02.7.5 Black Carbon

Another operationally defined class of OM that has received increasing attention in estuarine and coastal DOC and POC studies is BC. BC is defined as the oxidation products (including soot and graphitic and nongraphitic forms) of fossil fuel as well as biomass combustion (Elmquist et al., 2007), as well as naturally produced forms (e.g., kerogens) and it is believed to occur as fine particulate and colloidal forms (Zencak et al., 2007; see Chapter 5.03). Because BC is initially discharged to the atmosphere by combustion processes, its input to estuarine and other aquatic systems must be dominated by atmospheric depositional inputs to estuarine and coastal systems via direct aerosol deposition (e.g., Gustafsson et al., 2009), rainwater, and postdepositional dissolution/desorption to the dissolved phase (Wozniak et al., 2008). Therefore, the presence of BC in DOC is likely to be in its HMW or colloidal forms, rather than LMW forms. An assessment of BC input to the Arctic Ocean from its seven major rivers found that the predominant input mechanism is likely to be from rivers, which integrate over their watersheds, rather than direct atmospheric deposition (Elmquist et al., 2008). This same study also ascertained that BC inputs, at least to the coastal Arctic, are dominated by ancient sedimentary rock forms (~80%), with only about ~20% due to combustion of fossil fuels and biomass. However, the latter are expected to be greater in more highly populated temperate and tropical coastal regions of the world.

Although BC quantification may serve as a proxy for carbonaceous inputs from fossil fuel combustion and biomass burning over the industrial age (Elmquist et al., 2007), its contributions to both POC and DOC fluxes from rivers to estuaries and coastal environments are generally believed to be small quantitatively. Nonetheless, in the only known study of BC in estuarine DOC (HMW form) from surface waters of Delaware and Chesapeake Bay estuaries and the adjacent MAB (USA), BC was found to comprise on average $27 \pm 17\%$ of HMW DOC, which corresponds to ~9% of bulk DOC (Mannino and Harvey, 2004). Greater BC values were found in the heavily urbanized midbay region of the Delaware Estuary with lower amounts in the Delaware River and coastal ocean. The spatial and temporal distributions of BC in HMW DOC throughout the Delaware Bay Estuary during this study (Mannino and Harvey, 2004) suggest that the observed elevated amounts of BC in estuarine surface water may arise from localized sources, possibly from atmospheric deposition or release from resuspended estuarine sediments. Elemental analysis of the BC component of forested stream DOC by ES-FTICR-MS reveals it to have low H:C and to not be metabolized during degradation experiments, compared to degradation of 22–42% of the bulk DOC (Kim et al., 2006), suggesting that BC passes relatively unaltered between land and ocean.

5.02.7.6 Chromophoric DOC

Another component of total DOC that has received considerable attention in recent years in estuaries, and particularly in estuarine and continental shelf waters, is CDOM (see review by Blough and Del Vecchio, 2002). CDOM has

been commonly referred to as Gelbstoff, gilvin, and yellow substance, because of its strong association with humic substances. In fact, CDOM is believed to be primarily composed of humic acids that absorb visible light, UV-A (wavelengths from 315 to 400 nm), and UV-B (wavelengths from 280 to 315 nm) (Blough and Del Vecchio, 2002). Absorption spectra for DOC typically decrease exponentially with increasing wavelength in CDOM samples collected from the Suromoni and Orinoco rivers (Venezuela) in the Amazonian plains (Battin, 1998). The higher absorption values for the Suromoni, a small tributary that drains into the Orinoco, reflect the highly aromatic character of this terrestrially derived CDOM, which is different from the Orinoco that has some autochthonous contributions to the CDOM. The abundance of CDOM in estuarine and coastal waters has been shown to significantly affect biological and optical processes. For example, while CDOM can have beneficial effects on organisms by reducing their exposure to harmful UV-B, it can also reduce photosynthetically active radiation (PAR) to phytoplankton assemblages (Blough and Zepp, 1990; Bidigare et al., 1993; Vodacek et al., 1997; Neale and Kieber, 2000). CDOM also interferes with remote sensing of phytoplankton in estuarine and coastal waters; this has resulted in extensive efforts to improve algorithms that attempt to predict chlorophyll-*a* distribution and phytoplankton biomass from satellite imagery (Carder et al., 1999; Kahru and Mitchell, 2001).

In estuarine systems, CDOM abundance is typically controlled by (1) riverine freshwater inputs of humic substances derived from soil OM in the watershed (Keith et al., 2002; Wang et al., 2004); (2) inputs of CDOM from sediment pore waters during resuspension (Coble, 1996; Burdige et al., 2004); (3) degradation and production of *in situ* algae and vascular plants (Del Castillo et al., 2000); and (4) anthropogenic inputs from the watershed (industrial and agricultural) (Bricaud et al., 1981). Recent work has shown a significantly positive relationship between CDOM absorption and freshwater input in estuaries such as Narragansett Bay (USA), and there was a strong relationship between CDOM absorption and freshwater discharge during mid-spring and summer months (Keith et al., 2002). During late winter and early spring, nutrient inputs from watersheds can result in phytoplankton blooms that dominate CDOM inputs such as have been observed in the Gulf of Maine (USA; Yentsch and Phinney, 1997).

Light absorption by CDOM (principally UV-A and UV-B) can result in loss of its absorption and fluorescence properties (i.e., photobleaching) and the production of reactive intermediates/products. These products can have important implications for (1) speciation of different organic and inorganic substances through the formation of reactive oxygen species (ROS) (e.g., H_2O_2 , O_2^- and OH^-); (2) production of LMW DOC, bacterial substrates, DIC, and trace gases (e.g., CO, CO_2 , and COS); and (3) overall chemical composition of the total DOC pool in estuarine and coastal waters (Wetzel, 1990; Mopper et al., 1991; Wetzel et al., 1995; Bushaw et al., 1996; Moran and Zepp, 1997; Opsahl and Benner, 1998; Del Castillo et al., 1999, 2000; Moran et al., 2000; Engelhaupt et al., 2002; Keith et al., 2002; Moran and Covert, 2003; Yamashita and Tanoue, 2003). Light exposure of DOC collected from the Satilla Estuary (USA) showed that >50% of the original CDOM could be lost through photobleaching over a

period of 51 days (Moran et al., 2000). Moreover, the degree of photobleaching was positively correlated with bacterial uptake of DOC based on bacterial respiration (Moran et al., 2000).

Fluorescence is another means by which CDOM has been characterized in recent years due to its higher sensitivity and greater applicability to remote sensing than absorbance measurements (Vodacek et al., 1995). Over the past decade, new fluorescence techniques such as three-dimensional excitation emission matrix (3D EEM) spectroscopy have been applied for examining the fluorescence properties of DOC (Coble et al., 1990). Further work indicates that fluorochromes could be divided into the following three major classes: (1) humic like (emission wavelength from 370 to 460 nm); (2) protein like (emission wavelength from 305 to 340 nm); and (3) chlorophyll like (emission wavelength of 660 nm) (Coble et al., 1998). Other work in freshwaters (Wu et al., 2001), estuaries (Mayer et al., 1999), sediment pore waters (Coble, 1996), and on phytoplankton and bacteria indicated that the protein-like fluorochrome was commonly observed. More specifically, the protein-like fluorochrome can be divided into tyrosine-like (emission wavelength of ~300 nm) and tryptophan-like (emission wavelength of ~350 nm) categories (Coble, 1996). Recent work has also shown in Ise Bay Estuary (Japan) that measured concentrations of these aromatic amino acids in relation to these specified fluorescence intensities reflect their being derived from small peptides and not protein molecules (Yamashita and Tanoue, 2003). Other work has recently shown that distinct fluorophores found in the humic-like fraction (in fulvic acids from the International Humic Substances Society (IHHS); Coble, 1996; Mobed et al., 1996) can be used to examine terrestrially/microbially derived aromaticity of DOC (McKnight et al., 2001).

5.02.7.7 Compound-Class and Compound-Specific Isotopic Analyses

Studies of compound-class and compound-specific isotope signatures (i.e., $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$) of estuarine DOC – or DOC from any type of aquatic system for that matter – are relatively few in number (for review of compound-specific isotopic analysis (CSIA) methods, see Hayes et al. (1990) and Evershed et al. (2007)). However, those that have been conducted allow for several important insights as to the sources and ages of the biomolecules comprising estuarine DOC that are not available from measurements of biochemical concentrations and distributions. The $\delta^{13}\text{C}$ of fatty acids has been used to determine sources of HMW DOC in estuaries from four different regions of the United States (e.g., Boston Harbor/Massachusetts Bay, Delaware/Chesapeake Bays, San Diego Bay, and San Francisco Bay) (Zou et al., 2004). This work demonstrated that a fraction of HMW DOC is derived from phytoplankton and bacteria, and that HMW DOC is formed from bacterial membranes and reworking of phytoplankton materials. Finally, isotopic ($\delta^{13}\text{C}$) discrimination between phospholipid fatty acids (PLFA) and smaller labile molecules (e.g., acetate, methane, and methanol) is considerably greater (e.g., >20‰) than that found in comparison to complex substrates (Summons et al., 1994), making such distinctions even more apparent.

Operationally defined HMW DOC compound classes in the Susquehanna River showed that this material was dominated by a molecularly uncharacterized (MUC) fraction, followed by

TCHO, THAA, and total lipid extract (TLE) components (Loh et al., 2006). By contrast, HMW DOC at the mouth of Chesapeake Bay (salinity similar to 22–24) and the North Atlantic was comprised primarily of TCHO, followed by MUC, THAA, and TLE. $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ isotopic signatures of both bulk HWM DOC and its major biochemical classes indicate that Susquehanna DOC is derived in part from old allochthonous terrestrial sources, whereas young marine sources dominate in Chesapeake Bay. In contrast to the other biochemical classes, lipophilic (solvent-extractable) DOC at the river and estuarine sites was very old (equivalent 5000–7000 years BP; Loh et al., 2006), and even older in surface (6000–8000 years BP) and deep (14 000–17 000 years BP) waters of the Atlantic (Loh et al., 2004; Figure 22). One of the major conclusions of this study was that the observed biochemical and lipid biomarker compositions and isotopic signatures of HMW DOC and POC are consistent with previous findings, suggesting that these two major OM pools have dissimilar reactivities and cycling times and derive from comparatively unique source-age materials in river, estuarine, and oceanic waters. In addition, while lipids comprise a relatively small amount of the total DOC, their anomalously old ages raise new questions about natural and anthropogenic sources of aged lipophilic material to coastal and marine DOC pools from both allochthonous terrestrial and riverine sources, and autochthonous marine and estuarine sources.

Similar to the findings for the Chesapeake (Loh et al., 2006), Wang et al. (2004, 2006) found in their study of five US estuaries that TCHO and THAA were the dominant HMW estuarine DOC classes, contributing 33–46% and 13–20% of the OC, whereas TLE material accounted for <2% of the HMW DOC. Estuarine HMW $\delta^{13}\text{C}$ -DOC ranged from -22.1‰ to -30.1‰ among the different estuaries studied as well. Among the compound classes, TCHO was more enriched in $\delta^{13}\text{C}$ (-18.5‰ to -22.8‰) compared with THAA ($\delta^{13}\text{C} = -20.0\text{‰}$ to -29.6‰) and TLE ($\delta^{13}\text{C} = -25.7\text{‰}$ to -30.7‰). The acid-insoluble (MUC) fractions, generally, had depleted $\delta^{13}\text{C}$ values (-23.0‰ to -34.4‰). Similar to the Chesapeake Bay studies (Loh et al., 2006), Wang et al.

(2006) also found the total lipid fraction of HMW DOC in their five estuaries to be the most highly aged DOC component, while the acid-insoluble MUC fraction was only slightly younger but much older than the TCHO and THAA components, which were essentially modern in age. The significant variability in ^{14}C ages among estuarine HMW DOC compound classes (Table 6) suggests that DOC is comprised of at least several sources of highly disparate age, leading to a weighted mean age of the bulk DOC pool by these components, rather than by components originating over a common window of time. In addition, similarities in both $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of the lipid and MUC components of HMW DOC have led to the speculation that MUC is at least in part derived from an aged lipophilic component of DOC, or that lipids and MUC have a common precursor (Loh et al., 2006; Wang et al., 2006). The relative ubiquity of a young or modern component of the carbohydrate component of these operationally defined HMW DOC components, as well as the neutral polysaccharide component of acylpolysaccharide polymers in estuarine and coastal waters (Aluwihare et al., 1997, 2002), further suggests that carbohydrates may be the dominant contemporary component of DOC across a number of environments, and may be turned over rapidly and nearly completely on short timescales in these systems, as well as even in deep ocean waters.

5.02.8 Transformation and Remineralization of DOC in Estuaries and Coastal Waters

River and estuarine transport of both DOC and POC represents a major potential source of terrestrial OC to the oceans, and has been shown to potentially account for the apparent steady-state flux of -0.1×10^{15} g-C yr $^{-1}$ for oceanic DOC based on its natural radiocarbon ages of 4–6 kyr (Bauer et al., 1992; Druffel et al., 1992; Bauer, 2002). However, the possibility of a significant terrestrial component persisting in the oceans is not well documented on the basis of the small quantities of

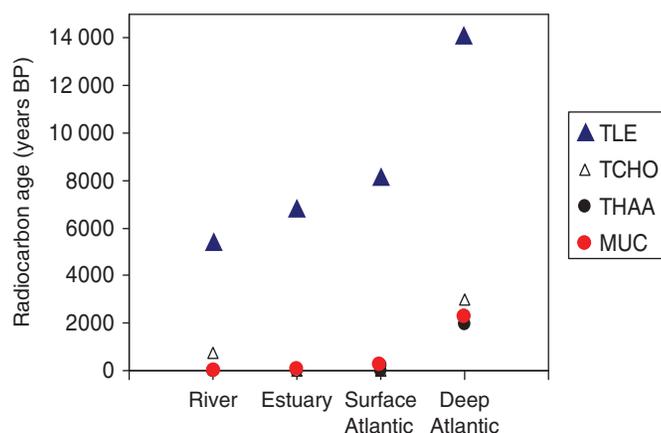


Figure 22 Radiocarbon age distributions of major biochemical compound classes in >1-kDa DOC in Susquehanna River, Chesapeake Bay (estuary) and open North Atlantic surface (~3-m depth) and deep (~1500-m depth) waters. All four classes (TLE, total lipid extract; TCHOs, total carbohydrates; THAA, total hydrolysable amino acids; and MUC, molecularly uncharacterized material) were measured at each site, but may not be visible because of overlap. Modified from Loh, A.N., Bauer, J.E., Canuel, E.A., 2006. Dissolved and particulate organic matter source-age characterization in the upper and lower Chesapeake Bay: a combined isotope and biochemical approach. *Limnology and Oceanography* 51, 1421–1431.

terrestrial plant organic biomarkers generally found in marine DOC (Meyers-Schulte and Hedges, 1986; Hedges et al., 1992, 1997; Opsahl and Benner, 1997). Possible explanations for this include

1. complete destruction (i.e., remineralization to terminal inorganic end products such as CO₂ and CO) of terrestrial OM by bacterial and photochemical degradation in rivers and estuaries – this is supported by observations of very high net CO₂ fluxes from rivers and estuaries (see Chapter 5.04), which can be greater than OM loadings (Raymond et al., 1997; Cai and Wang, 1998; Frankignoulle et al., 1998; Raymond et al., 2000; Cole and Caraco, 2001; Richey et al., 2002);
2. while significant quantities of terrestrial OM enter the oceans, these terrestrial biomarkers are difficult to detect as a result of their significant structural alteration in rivers and estuaries due to microbial, photochemical, and other forms of intermediate degradation; and
3. abiotic interactions between DOC and mineral particles and/or POC in estuaries that cause selective sorption-desorption processes, removing specific DOC constituents from solution and adding others (e.g., due to strong ionic strength changes and ETMs) (see Chapter 5.03).

In particular, estuaries, with their increased residence times, lower turbidity, and unique microbial populations may represent zones of considerable additional transformation and remineralization of river and estuarine-derived DOC, prior to its export to the coastal ocean. We explore each of these three major transformation and remineralization mechanisms and their potential role in modulating estuarine DOC export.

5.02.8.1 Microbial Degradation and Respiration

The Prokaryotes, which constitute the Eubacteria (bacteria) and Archaeobacteria, represent important microbial groups essential in the decomposition of DOC in estuaries. The Archaeobacteria are generally characterized as living in extreme environments such as anaerobic methanogens and halophilic bacteria – both of which are found in estuarine environments, albeit often in specialized environments, such as hypoxic, anoxic, and other extreme conditions. In spite of their functional diversity, much of the recent and current literature still treats them as an undifferentiated black box. Only recently have molecular techniques begun to be employed in a meaningful manner to examine differences in estuarine bacterial communities (see, e.g., Heidelberg et al., 2002) and the specific organic substrates supporting their energetic and biomass demands. Estuarine bacterial communities have been found to express a very high degree of diversity across estuarine temperature and salinity gradients (Valencia et al., 2003). For example, α -proteobacteria (purple bacteria) are generally found at elevated salinities, whereas β -proteobacteria occur closer to sources of river freshwater inputs in estuaries (Yokokawa et al., 2004). The controls on the biomass of these diverse bacterial communities can also vary across different salinities, typically as a function of substrate supply and bacterial mortality (Ducklow et al., 2000; Schultz et al., 2003). For example, Kirchman et al. (2004) found within the Hudson River and Estuary that the composition and activities of the microbial community differed

dramatically in response to DOC collected at different locations, indicating that within such seemingly homogeneous environments significant variability in the sources and cycling of DOC and microbial communities exists. Indeed, tight coupling between heterotrophic bacteria and DOC, including both the impact of DOC and its components on microbial activities and productivity, and the role of bacteria in repackaging DOC, has been the topic of numerous recent studies to better understand the synergistic and inseparable interactions between the two (see, e.g., reviews by Findlay (2003), Foreman and Covert (2003), Findlay and Sinsabaugh (2003b)).

In spite of decades of estuarine studies on the sources and fates of organic materials in estuaries, we still have only a relatively cursory understanding of the processes that control the reactivity of fluvial DOC in the water column and sediments of these systems (Figures 2, 3, and 9). Indeed, while it is routinely noted that most of the carbon burial in continental margins ($\sim 70 \times 10^{12}$ g-Cyr⁻¹) occurs in regions directly impacted by river discharge, including estuaries, deltas, and clinoform systems (Berner, 1982; Hedges, 1992; Hedges and Keil, 1995; de Haas et al., 2002; McKee et al., 2004), this includes only the POC component. Quantitative estimates of the fate of the DOC component in estuaries versus the amounts exported to the coastal and open oceans are much more poorly constrained. Coastal photosynthetic productivity also contributes to sequestration of carbon in these areas, although the recycling of marine OM is believed to be much higher than that of terrigenous OM in coastal systems (e.g., Aller et al., 2004; Gordon and Goni, 2004). While this flux is small relative to discharge or delivery fluxes, it does represent a much longer-timescale removal of carbon. The connection between physical processes and the biogeochemical processing of DOC in these systems is an area of fertile future research.

Our general understanding of river/estuarine OM fluxes suggests that under high-discharge/high-energy periods, elevated amounts of terrigenous OM can be efficiently transported seaward due to factors such as shorter residence times, increased turbidity (i.e., reduced light penetration), etc. Hence, in systems where rivers discharge to narrow, deep shelves and where river discharge is coherent with oceanographic conditions that favor cross-margin export, fluvial colloidal organic carbon (COC) may be efficiently transported to regions with little degradation. By contrast, under low-discharge periods, much of the fluvial DOC may be degraded within estuaries and inner-shelf environments, where it may be efficiently degraded.

The nature of the OM in the system is also centrally important for long-term sediment preservation. A range of reactivities is generally present within the OM in these systems. The conventional wisdom has been that discrete vascular plant debris and freshwater and marine phytoplankton biomass are relatively reactive, while organic material derived from soils and eroded sedimentary rocks is relatively refractory (Prah et al., 1992; Goni et al., 1998; Masiello and Druffel, 2001; Blair et al., 2003; Goni et al., 2005b, 2006). These latter fractions probably account for the majority of the land-derived OC buried in river-dominated margin sediments. Their relative abundance, and the correlation of their mobilization with extreme discharge events, will affect the net carbon burial at any given site (e.g., Blair et al., 2004; Leithold et al., 2005). The complexity of making net flux measurements of different OM pools in

settings where both ocean and river waters have varying influence and where high-frequency tidal and wind fluctuations dominate transport is also responsible for the dearth of data (McKee, 2003). Estimates of net respiration in estuarine settings are also lacking, and there is generally a poor understanding of the relative reactivity of terrestrial OM across the river to coastal ocean continuum.

A considerable amount of research has been conducted over the past two to three decades to better understand the importance of factors such as DOC chemical composition, molecular size, and age in controlling microbial metabolism of DOC (see reviews by Tranvik (1998), Benner (2002, 2003), Findlay (2003), and Kirchman (2003)). The importance of heterotrophic bacteria in DOC cycling was recognized and incorporated into the theory of the microbial loop – which first showed that bacteria are key in controlling the trophic linkages between DOC, POM, and inorganic nutrients in aquatic ecosystems (Figures 13 and 23) (Pomeroy, 1974; Azam et al., 1983). Larger or HMW forms of DOC are generally believed to enter the microbial component via hydrolysis by extracellular enzymes, after which lower-MW products may then be transferred across the outer membrane of bacteria (Kirchman and White, 1999; Arnosti, 2003; Mulholland et al. 2003; Roth and Harvey, 2006; Steen et al., 2008). In the case of model proteinaceous materials, new methods such as ESI-FTICR-MS have been used to follow the progressive hydrolysis and production of lower-MW products during DOC degradation (Roth and Harvey, 2006). Rates of polysaccharide hydrolysis in Chesapeake Bay, for example, were found to potentially account for a significant fraction (>60%) of daily input of monosaccharides to Bay waters (Steen et al., 2008), emphasizing the important and, possibly, limiting role of enzymatic degradation in supporting bacterial populations in estuarine waters, as well as potentially other components of lower and higher food webs dependent upon microbial biomass. These DOC production and uptake processes clearly occur on shorter ecological timescales than those of, for example, humic substances in terrestrial soils. However, they are similar to the timescales of flocculation–deflocculation or sorption–desorption processes in estuaries (i.e., seconds to days).

While it is well established that bacterial utilization of LMW monomers such as amino acids and simple sugars, which can be transported directly from the aquatic medium into bacterial cells, is quite high (see Kirchman (2003) for review), the fates of other LMW intermediate organic products (e.g., small organic acids) formed during macromolecular breakdown remain largely unknown in estuarine waters. In at least certain estuaries, the reactivity of components such as dissolved carbohydrates, as well as changes in reactivity proxies such as DOC fluorescence, can actually be quite low to immeasurable, suggesting that DOC reactivity may be system specific (Van Es and Laane, 1982). In addition, the role and potential bottleneck of extracellular enzymatic hydrolysis of soluble HMW forms of DOC during the initial stages of the degradation and remineralization process, though well recognized (see Arnosti (2003) for review), are in need of far greater study and incorporation into our conceptual and quantitative models of DOC and aquatic OM cycling in general. A large proportion of bacterial production can be supported by DFAA uptake in estuaries (Keil and Kirchman, 1991b; Hoch and Kirchman, 1995).

However, in rivers and estuaries, the input of DOC with a relatively high abundance of aromatic compounds (tannins and lignins) from vascular plant materials in soils and wetlands presumably makes the DOC pool more refractory to microbes (Aitkenhead-Peterson et al., 2003). However, at the same time, higher levels of aromaticity and light absorbance (i.e., color) also make this same DOC potentially more susceptible to photochemical alteration (see below). The interrelationship between small monomeric and large macromolecular molecules in DOC and the roles they play in bacterial metabolism constitute an issue that requires further study in highly dynamic systems, such as estuaries, where allochthonous and autochthonous inputs are significant.

In direct contrast to the earlier studies of the bacterial utilization of specific biochemical compounds mentioned above, a significant body of work has apparently demonstrated that different size classes of DOC are utilized with different efficiencies by the microbial community (see reviews by Tranvik (1998), Benner (2002, 2003), and Findlay (2003)). In fact, the size–reactivity continuum model states that larger size classes of OM are less degraded and more bioavailable than

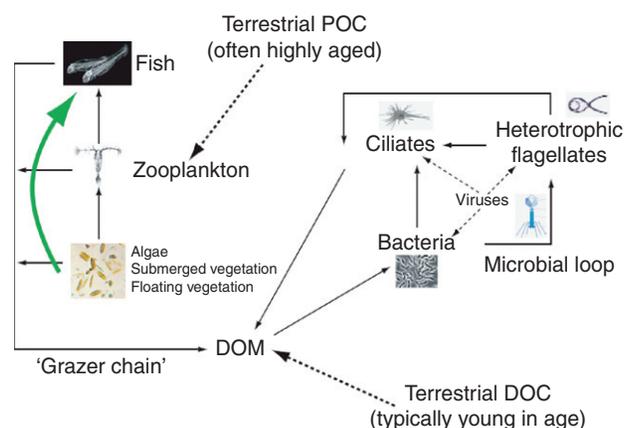


Figure 23 Proposed routes of entry of terrestrial DOC and POC to river and estuarine food webs. Terrestrially derived DOC, which is generally young in age, supports the microbial food web, while terrestrial POC supports the grazer food web (see text for additional description).

smaller size classes that are more refractory as a consequence of extensive processing over time (Amon and Benner, 1996a). However, as pointed out by Sinsabaugh and Foreman (2003), this perspective of size and reactivity may largely depend on the age of DOC inputs to a system as well as the relative importance of trophic versus diagenetic controls on DOC composition. This model also contradicts the earlier biopolymer degradation (BD) and abiotic condensation (AC) models of humic substance formation (Hedges, 1988). Whereby, the BD model states that newly released biopolymers from OM will eventually be broken down into smaller and more reactive products (Hedges, 1988), the AC model conversely states that small molecules can repolymerize outside the cell through condensation reactions over time into larger more refractory macromolecules. It should also be noted that many of the OM reactivity models have been based on soil and sedimentary geochemical perspectives and conceptual models, and, hence, may not be applicable to the unique conditions of river and estuarine aquatic environments. Hence, OM that has aged and become refractory to a significant extent in its initial environment of formation and/or sequestration may be subjected to entirely different biotic and abiotic factors that render even highly aged OM much more reactive in a new system (see, e.g., Keil et al., 1994).

The more recent work by Amon and Benner (1996b) also added another component of reactivity to their model, which indicated the HMW DOC fraction of DOC was more bioavailable to bacteria and more photoreactive than LMW DOC. Although this model certainly applies quite well to open ocean systems, where the primary source of POM is phytoplankton, in many cases, it may not be applicable to estuarine and freshwater systems where DOC is commonly derived from rivers (high humic-rich soil inputs), sediment pore waters (see below), and adjacent marsh systems, all of which have high lignocellulosic (particularly lignin) components that result in the HMW DOC fraction being more degraded (refractory) and older (Guo and Santschi, 2000; Mitra et al., 2000; McKnight et al., 2003; Wetzel, 2003). As cautioned by Cottrell and Kirchman (2003), however, it is unlikely that no single phylogenetic group of bacteria dominates the consumption of all forms of DOC, suggesting that the participation of a diverse assemblage of bacteria is essential for the complete degradation of complex DOC in estuarine, coastal, and oceanic waters. These workers also suggest that the role of aerobic heterotrophic bacteria in DOC degradation would be more accurately described by using at least three functional groups of bacteria, instead of the single bacterial compartment currently used in conceptual models of DOC cycling.

Degradation and mineralization of DOC by heterotrophic bacteria in estuaries and other coastal waters are generally assessed in one of two ways. First, changes in the chemical composition of DOC during river and estuarine transport may be used to infer its reactivity and alteration due to degradation (i.e., geochemical approach). This assumes that differences in composition may be assigned entirely to microbial degradation processes, that is, differences due to varying sources and abiotic mechanisms (e.g., photochemical degradation and sorption-desorption processes) are either negligible or can be constrained. In reality, it is often difficult or impossible to separate these different processes in natural waters. Instead, an alternative means of evaluating microbial

degradation, and differentiating it from other processes such as photochemical alteration, is the use of controlled, generally dark, incubation experiments (i.e., experimental approach) where changes in the amounts of bulk DOC, DOC constituents (e.g., different biochemical classes or individual compounds), and/or respiratory reactants and terminal oxidation products such as dissolved O₂ and/or CO₂, are monitored over time. The percentage of reactive or labile DOC in rivers, estuaries, and coastal waters determined in this way is generally relatively low, typically not exceeding 25–30% of the total DOC (see del Giorgio and Davis (2003) for review; also, e.g., Guenther et al., 2008; Lonborg and Sondergaard, 2009). The typical pattern of DOC utilization during experimental batch incubations is one of a decreasing first-order rate of consumption, leading to a nonlinear and ultimately asymptoting decrease in DOC over time. Based on their synthesis and summary of DOC utilization across different systems, del Giorgio and Davis (2003) showed that the reactivity of estuarine DOC as a percentage of the starting concentration was similar to river and marsh DOC utilization (range: 9.3–10.2%), but significantly lower than that for lake (mean: 21.7%) and marine (mean: 26.2%) DOC, suggesting that estuarine DOC reactivity is not simply based on admixtures of its end-member (i.e., river and marine) sources.

While the high turbidity levels and relatively short residence times of rivers generally limit allochthonous OM inputs, estuaries have some of the highest areal rates of primary production among both freshwater and marine environments (Smith and Hollibaugh, 1993). Recent reviews, however, have also concluded that both rivers (Cole and Caraco, 2001) and estuaries (Smith and Hollibaugh, 1993; Heip et al., 1995; Gattuso et al., 1998) are also strongly net heterotrophic systems, and therefore respiration exceeds gross primary production. High rates of bacterial production (Coffin, 1989; Chin-Leo and Benner, 1992; Ducklow and Shiah, 1993) and degrees of CO₂ supersaturation in estuaries (Cai and Wang, 1998; Frankignoulle et al., 1998; Cai et al., 1999; Raymond et al., 2000; Cole and Caraco, 2001) further support the idea that respiration, and, hence, OM degradation and modification, is an important sink for OM in estuaries. The OM subsidizing net heterotrophy in these systems is hypothesized to come predominantly from land (Meyer and Tate, 1983; Hopkinson and Vallino, 1995; Hopkinson et al., 1998).

The number of studies designed to investigate the relative importance of heterotrophic utilization and primary production to OM export in temperate North American river/estuarine systems is small. Yet, all have demonstrated large changes in OM composition and quantity due to internal processing (Howarth et al., 1996a; Kemp et al., 1997; Smith and Hollibaugh, 1997; Cai et al., 1998, 1999; Raymond et al., 2000), and have concluded that the amounts of OM discharged from rivers and estuaries are not simply a function of terrestrial inputs, but also under internal control (Kaplan and Newbold, 1993; Findlay et al., 1996; Fisher et al., 1998; Mannino and Harvey, 1999; Sanudo-Wilhelmy and Taylor, 1999; Webster and Meyer, 1999; Raymond and Bauer, 2000). Processes contributing to the major transformations and exchanges of C in rivers and estuaries include microbial utilization (Coffin et al., 1994; Moran et al., 1999b; Zweifel, 1999), photochemistry (Amon and Benner, 1996b; Opsahl and Benner, 1998; Mopper and Kieber, 2002), air-sea CO₂ exchange (Raymond

et al., 1997; Cai and Wang, 1998; Frankignoulle et al., 1998; Raymond and Bauer, 2000), anaerobic bicarbonate production (Smith and Hollibaugh, 1997; Abril et al., 1999; Raymond and Bauer, 2000), CaCO_3 chemistry (Jarvie et al., 1997), and primary and secondary production (Cole et al., 1988; Kaplan and Bott, 1989; Cole et al., 1991; Findlay et al., 1991; Chin-Leo and Benner, 1992; Howarth et al., 1992; Ducklow and Shiah, 1993; Balsis et al., 1995; Quay et al., 1995; Raymond and Bauer, 2000).

Using a geochemical approach, Mannino and Harvey (2000) suggested that shifts in amino acid composition in the Delaware Bay Estuary could be used to differentiate the extent of degradation for HMW DOC. The lower amino acid and carbohydrate content and higher β -alanine content in HMW DOC suggested that this fraction is more highly degraded compared to either POC or very HMW DOC and provided geochemical evidence in support of the aforementioned size-reactivity continuum hypothesis (Amon and Benner, 1996a). Spatial patterns in organic constituents were also evident with relatively more degraded OM in the turbid mid-Delaware Estuary and the release of relatively fresher DOC from diatoms in the lower estuary. In a related study, Mannino and Harvey (1999) also observed that selective losses of the so-called reactive or labile lipids by the microbial community throughout the Delaware could account for the depletions of unsaturated fatty acids, sterols, and phytol within HMW DOC relative to POC. Similarly, in the Isonzo River Estuary, molecular indicators of DOC degradation such as free fatty acids and monoacylglycerols were significantly lower than in the POC near the river mouth, whereas the contrary was observed at higher salinities (Derieux et al., 1998).

A number of studies also point out the greater abundance of specific bacterial constituents, especially in the lipid fraction, which point to more extensive overall alteration and degradation of the DOC versus POC fractions in estuaries (Derieux et al., 1998; Loh et al., 2006; McCallister et al., 2006a). However, the presence of lipid biomarkers diagnostic of fresh algal material in HMW DOC in the Chesapeake Bay Estuary also suggests its potentially greater reactivity than POC (Loh et al., 2006), which is the opposite of what is observed for

oceanic waters (Loh et al., 2008). The observed biochemical and lipid biomarker compositions and isotopic signatures of HMW DOC in the Chesapeake and other estuaries are also consistent with previous findings of reactivity dissimilar to that of POC, suggesting the two pools in river–estuary–coastal ocean systems arise from sources having dissimilar reactivities.

McCallister et al. (2006a) further found that PUFAs (as percent of total fatty acids, FAs) were a reliable predictor of DOC decomposition in bioassays, thus providing an indicator directly linking DOC reactivity to its composition and indicated a systematic bacterial response to autochthonous DOC sources along the estuarine continuum. These workers further suggested that while algal-derived OM in estuarine DOC may be quantitatively insignificant, it may nevertheless represent a primary source of reactive OM to heterotrophic bacteria in estuarine waters.

Bulk radiocarbon and ^{13}C signatures of both total POC and DOC pools have also proved to be useful in constraining what their sources might be in estuaries (Cherrier et al., 1999; McCallister et al., 2004 and references therein; see also Section 5.02.6). For example, $\Delta^{14}\text{C}$ -DOC is always more ^{14}C enriched compared to $\Delta^{14}\text{C}$ -POC along river-discharging margins and US East Coast estuaries (see Chapter 5.03). As the ^{14}C -enriched DOC is also more depleted in ^{13}C , it appears that these differences are because of greater contribution of ^{14}C -enriched soil and litterfall OM that is leached from soils. Similarly, recent work has shown, using a dual-isotopic tracer approach of isotopic signatures ($\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$) for bacterial nucleic acids collected from different regions and potential C-source materials, that there was good delineation of C sources from aquatic and terrestrial systems in the York River Estuary (Figure 24) (McCallister et al., 2004). In general, the results from these dual-isotopic tracer studies indicate that the broad classification of organic C and the interchangeable use of the terms 'old' and 'refractory' are in many cases not valid. In fact, highly depleted ^{14}C (1000–5000 years old) in the Hudson River Estuary appears to be an important labile source fueling heterotrophy (Cole and Caraco, 2001). Thus, the OM stored for centuries and millennia in soils and rocks can actually become

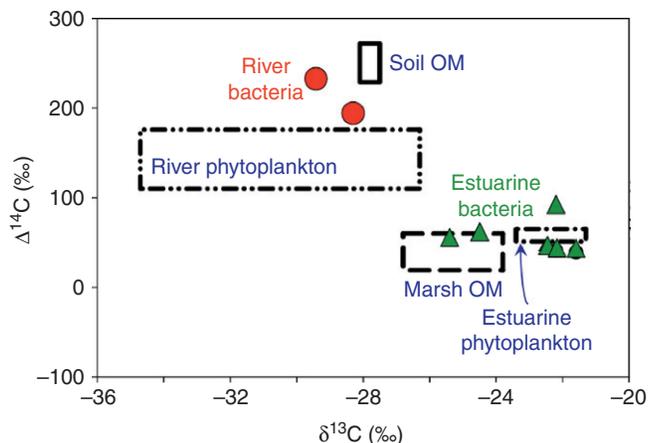


Figure 24 $\Delta^{14}\text{C}$ - $\delta^{13}\text{C}$ plot of the isotopic signatures of potential sources of river and estuarine DOC (boxes) to heterotrophic bacteria in the river (red circles) and estuarine (green triangles) portions of the York River Estuary, Virginia, USA. Modified from McCallister, S.L., Bauer, J.E., Canuel, E.A., 2004. Bioreactivity of estuarine dissolved organic matter: a combined geochemical and microbiological approach. *Limnology and Oceanography* 51, 94–100.

available to aquatic microbes over periods of weeks to months (Petsch et al., 2001), completing a unique linkage between river metabolism and the history of OM preservation in the drainage basin (Cole and Caraco, 2001). $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ natural abundances during estuarine DOC degradation have also been used to demonstrate that the degraded material is not necessarily of the same source and age as the residual, nondegraded material. Instead, in most cases, the bacteria selectively degrade a ^{14}C -enriched younger component, leaving the older, nondegraded component for export to the coastal and open oceans (Raymond and Bauer, 2001c). These types of estuarine modifications of DOC have further implications not only for detecting and quantifying terrestrial and estuarine materials in oceanic waters, but also for closing various loops in estuarine and coastal ocean carbon budgets.

5.02.8.2 Photochemical Degradation and Mineralization

Two major photo-oxidation/degradation pathways of DOC have been identified in aquatic environments: (1) an abiotic pathway involving the direct photochemical production of CO and CO_2 (see next section) and (2) a sequential photochemical/biotic pathway involving the photodegradation of DOC to LMW substrates followed by microbial biomass production and remineralization CO_2 (i.e., respiration). Collectively, these two pathways may account for a global production of 20–50 Gt $\text{CO}_2\text{-Cyr}^{-1}$ (Johannessen, 2000; Mopper and Kieber, 2002; Zafiriou, 2002). Photochemically enhanced respiration appears to be quantitatively more important than substrate incorporation and growth (see Mopper and Kieber (2002) review). This may in part explain the net heterotrophic character of many rivers and estuaries and the high levels of CO_2 supersaturation observed (Smith and MacKenzie, 1987; Smith and Hollibaugh, 1993; Cai and Wang, 1998; Frankignoulle et al., 1998; Raymond et al., 2000; Cole and Caraco, 2001), and may be quantitatively as important as abiotic DIC photoproduction (Zepp et al., 1998; Mopper and Kieber, 2000, 2002).

5.02.8.2.1 Photochemical DOC oxidation, DIC formation, and O_2 consumption

The major identifiable products from the photolytic remineralization of DOC in natural waters are the inorganic species CO and CO_2 (as DIC) (Figure 25). DIC photoproduction has been correlated with initial DOC light absorbance, initial DOC concentration, and photobleaching (Minor et al., 2007), and inversely related to salinity (Minor et al., 2006) in estuarine waters of the Chesapeake Bay system. Together, DIC and CO account for ~70–80 % of the total photoproducts and most of the DOC lost (Mopper et al., 1991; Miller and Zepp, 1995; Stubbins, 2001), with production rates for DIC being ~10–20 times greater than for CO (Mopper et al., 1991; Bates et al., 1995; Miller and Zepp, 1995; Zuo and Jones, 1995; Johannessen, 2000; Stubbins, 2001). The remaining 20–30% of the DOC photoproducts may occur as volatile organic carbon (VOC) and LMW organic acids (Bertilsson and Tranvik, 1998, 2000).

DIC photoproduction appears to be responsible for a major fraction of abiotic O_2 consumption in irradiated surface waters (Laane et al., 1985; Lindell and Rai, 1994). Two main routes for DIC production from DOC have been identified: one via reaction with molecular oxygen and/or reactive oxygen transients (reviewed by Mopper and Kieber (2002)) and the other via O_2 -independent decarboxylation of DOC carboxyl side chains and organic acids. In support of the O_2 -dependent pathway, Lindell and Rai (1994) and Amon and Benner (1996b) found a molar O_2 consumption to CO_2 evolution ratio close to one for lake and river waters, respectively. Other studies suggest that DIC production occurs mainly by O_2 -independent pathways. For example, Kieber et al. (1999, 2001) found that DIC photoproduction in sterile filtered coastal seawater increased by up to ~35% after dissolved O_2 was removed by exhaustive sparging with O_2 -free and CO_2 -free helium. Furthermore, published experimental results are not consistent with the stoichiometric amounts of O_2 required for all purported oxidative processes. For example, about 50–100% of all photochemically consumed O_2 is required for the production of H_2O_2 via dismutation of superoxide (Petasne and Zika, 1987; Blough

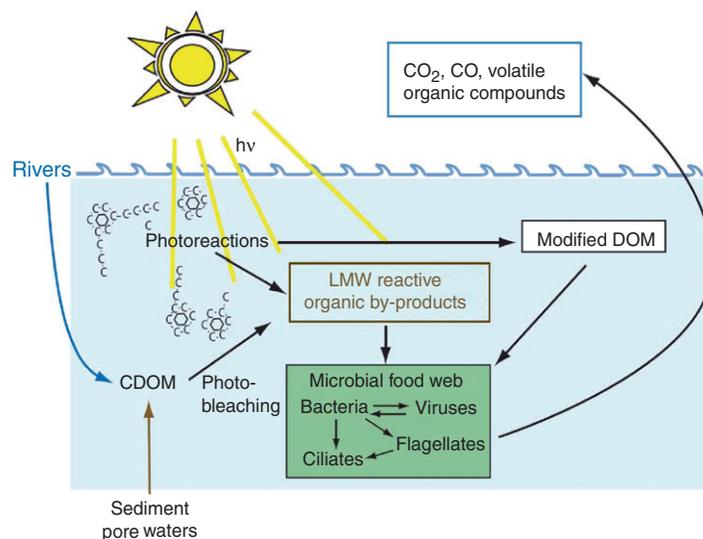


Figure 25 Generalized interactions between sunlight, dissolved organic carbon, and heterotrophic bacteria in estuarine and coastal systems.

and Caron, 1995; Blough and Zepp, 1995, Andrews et al., 2000) and for incorporation into DOC (Blough and Zepp, 1995). This O₂ would, therefore, not be available for DIC formation. Miles and Brezonik (1981), in their lake water study, found a molar ratio of ~1:2 O₂ consumed to CO₂ produced, suggesting that both DIC formation pathways (i.e., O₂ dependent and O₂ independent) may have been active in their samples. The latter studies indicate that at least some of the photochemically formed DIC may be produced by O₂-free pathways, for example, by cleavage of carboxyl groups from DOC (decarboxylation). In fact, IR and NMR spectroscopic studies of fulvic acids have shown that the carboxyl signal associated with aromatic groups is preferentially lost during UV irradiation of aqueous solutions, whereas the aliphatic carboxyl signal increases as residual fulvic acids become more oxidized and less aromatic (Chen et al., 1978; Kulovaara et al., 1996; Schmitt-Kopplin et al., 1998). Thus, the above-mentioned studies support the idea that photochemical DIC production can be independent of photochemical O₂ consumption.

It is evident from the conflicting reports that the major pathways involved in DIC photoproduction, and their relationship to DOC photo-oxidation and O₂ consumption in natural waters, are not yet fully understood. While the evidence supports the existence of both O₂-dependent and O₂-independent pathways, their relative importance is predicted to vary with the geochemical character of the DOC (i.e., terrestrial vs. marine source, age, chemical composition, oxidation state, and photochemical history) and the fluxes of photoproduced oxidative free radicals. In addition, unique aspects of Arctic estuarine and coastal systems such as pervasive sea ice cover reducing UV penetration, may limit terrigenous DOC photomineralization for extended periods of time; however, this could change given different scenarios of more limited sea ice extent and duration under different projections of Arctic Ocean warming (Belanger et al., 2006).

5.02.8.2.2 Photochemically enhanced microbial degradation of estuarine DOC

A number of studies have shown that the alteration of DOC by photochemical reactions can enhance the utilization of the altered DOC over that of nonphotochemically altered DOC (see Mopper and Kieber (2002) and Moran and Covert (2003) for reviews) (Figure 25). For example, early studies of DOC cycling in the Satilla Estuary, Georgia, USA, which is largely (~60%) composed of humic substances derived from soils (Beck et al., 1974), showed that microbial degradation of DOC can be enhanced by photodegradation. Other work has shown that photochemical breakdown of refractory riverine DOC can result in significantly increased bacterial growth and respiration (Smith and Benner, 2005) and enhanced (27–200%) degradation of the photodegraded DOC (McCallister et al., 2006b), with rapid subsequent uptake by microbes (e.g., Amon and Benner, 1996b). However, microbial parameters such as bacterial growth efficiency (BGE) may have more complex relationships to DOC photo-oxidation of HMW starting substrates, including the availability of nutrient elements (McCallister et al., 2006b) and the quality and molecular characteristics of photo-oxidized by-products produced (Kieber et al., 1989; Pullin et al., 2004a). Recent studies employing high-resolution analytical techniques have added

considerable detail to our understanding of the molecular transformations that DOC undergoes during photochemical modification. For example, using DT-MS and ESI-MS, Dalzell et al. (2009) showed large-scale shifts in the MW and chemical composition of photodegraded DOC in river and estuarine waters, such that the degraded material from different sites converged to similar characteristics following degradation. Gonsior et al. (2009), using ESI-FTICR-MS, found that aromatic components of DOC from the Black and Cape Fear River estuaries (North Carolina, USA) were far more reactive photochemically than aliphatic moieties.

Recent studies have shown that the photochemical-biological couple is complicated because photochemical reactions can both form and destroy biological substrates. Photochemical reactions can alter DOC in at least three possible ways: (1) by initiating redox reactions that change (increase) the oxidation state of DOC; (2) by cleaving (photolyzing) chromophoric and nonchromophoric moieties, mainly within humic substances, to create smaller molecules; and (3) by initiating cross-linking reactions (Chen et al., 1978; Kulovaara et al., 1996; Schmitt-Kopplin et al., 1998; Vähätalo et al., 1999; Opsahl and Zepp, 2001). Photochemical cross-linking and humification reactions of labile biomolecules, such as proteins, unsaturated lipids, polysaccharides, fresh algal extracts or exudates, and fresh macrophyte leachates, have been experimentally documented. These reactions are expected to be particularly important in environments containing high concentrations of freshly released algal DOC, as encountered in biologically productive estuarine waters (see review by Mopper and Kieber (2002)). Based on recent field and laboratory studies, it has been hypothesized that the net effect of photochemical reactions on microbial growth (stimulation, inhibition, or neither) depends on the relative proportions of fresh algal-derived DOC versus nonalgal and/or humic DOC in the irradiated sample (Obernosterer et al., 1999; Benner and Ziegler, 2000; Tranvik et al., 2000; Ziegler and Benner, 2000). It is highly likely that the variable effects of photochemistry on DOC bioavailability reported in estuarine studies (summarized in Mopper and Kieber (2002)) result from the relative importance of these three processes (photo-oxidation, photolysis, and cross-linking) during transit through the estuary. For example, near the freshwater end of the estuary, the predominance of photobleaching and photodegradation of terrestrially derived humic substances should result in a significant production of biologically available substrates. Near the mouth of the estuary, the predominance of cross-linking reactions of algal-derived DOC and the intense oxidation of terrestrially derived DOC could create more biologically refractory DOC. Studies of photochemically enhanced DOC degradation provide further support for significant transformation and utilization of terrestrially derived DOC across estuarine gradients that may be critical in understanding the deficiency of terrestrially derived DOC in the global ocean (Meyers-Schulte and Hedges, 1986; Hedges et al., 1997; Opsahl and Benner, 1997; Hedges, 2002).

5.02.8.3 Abiotic Sorption and Desorption Processes

Numerous physical and chemical factors have been found to control DOC sorption in soils even before this material is

exported to streams, rivers, and estuaries, including clay content, mineral surface area, temperature, pH, specific mineral content (including cations and oxides), ionic strength, organic content and character of different soil horizons, and the characteristics of the DOC itself (see, e.g., Hedges and Hare, 1987; Kaiser and Guggenberger, 2000; for review see Aitkenhead-Peterson et al. (2003)). Many of these characteristics (e.g., clay content, surface area, temperature, pH, and ionic strength) have similarly been found to control DOC sorption in river and estuarine waters. Some of the earliest work on this topic focused on the thermodynamic flocculation of DOC in river–estuarine waters of changing ionic strength and pH (Sholkovitz, 1976), with approximately 10% of the total DOC, but the majority of dissolved humic substances being effectively transformed from the dissolved to particulate phase by this mechanism.

Other factors, besides thermodynamic considerations, causing DOC flocculation include river flow, turbidity (Spencer et al., 2007), and, particularly, the relative and absolute amount of clay minerals in the suspended load (Hedges and Keil, 1999; Amarnson and Keil, 2000; Satterberg et al., 2003). The exchange between dissolved and particulate organic phases in estuaries is not, however, exclusively a sorptive system, and significant desorption of OM from POC to DOC has also been observed in different river–estuarine systems (Keil et al., 1997; Komada and Reimers, 2001), and depends on the specific system and characteristics of the OM being affected. These mechanisms of DOC production from and uptake to particulate forms have profound implications for our understanding of the global mass balances of OM transfer between land and the ocean. These implications are relevant in terms of both the quantities and chemical characteristics (see, e.g., Keil et al., 1997; Aufdenkampe et al., 2001; Hwang et al., 2006; Middelburg and Herman, 2007) of material transported from land and rivers to the interior ocean in dissolved form, and organic materials that are more likely to be removed in estuarine and continental margin sediments in particulate form (Sholkovitz, 1976; Hedges et al., 1997; Hedges and Keil, 1999; Verdugo et al., 2004).

In addition to direct abiotic particle–DOC interactions in estuaries, processes that affect the chemical composition of this DOC during river and estuarine transport, such as microbial and photochemical alteration, will similarly affect DOC–POC exchanges. For example, the hydrolysis and remineralization rates of particle-sorbed forms of protein were found to be 10^2 – 10^3 times faster than nonsorbed protein (Taylor, 1995), while other studies have observed lower rates of sorbed protein hydrolysis (Nagata and Kirchman, 1996; Borch and Kirchman, 1999). Such differences may depend on the specific proteins as well as the microbial assemblages involved. Both UV and visible sunlight have recently been found to drive photodissolution of POC to DOC (up to tens of percent of starting POC concentrations; Mayer et al., 2006) in Mississippi River suspended sediments, but this photodissolution was not found to be related to mineral oxyhydroxide content of waters. For DOC, photoirradiation by UV light has been found to generally decrease the abundance of HMW components and concomitantly increase the abundance of LMW components, resulting in decreased sorption of the LMW DOC to mineral surfaces (e.g., the Fe(III) oxyhydroxide mineral goethite; Pullin et al., 2004b). The number, type, and

complexity of interactions between river and estuarine DOC and particles are increasingly recognized as a dominant factor controlling the physical state (i.e., dissolved vs. particulate) of OM transported from land to the oceans via estuaries, and are in need of additional future study.

5.02.9 Implications of DOC Transformations in Rivers and Estuaries

5.02.9.1 Land–Ocean DOC Budgets

Rivers and estuaries receive large subsidies of nutrients and OM from terrestrial systems (Meybeck, 1982; Mantoura and Woodward, 1983; Spitzzy and Ittekkot, 1991; Webster and Meyer, 1999). The inputs of only DOC from rivers alone can account entirely for the turnover of DOC as represented by its mean ^{14}C age in seawater (Williams and Druffel, 1987; Bauer, 2002; Figure 26). However, estuarine systems also have some of the highest areal rates of primary production among both freshwater and marine environments (Smith and Hollibaugh, 1993). Recent reviews, however, have concluded that rivers (Cole and Caraco, 2001) and estuaries (Smith and Hollibaugh 1993; Heip et al., 1995; Gattuso et al., 1998) are strongly net heterotrophic systems, and, therefore, respiration exceeds gross primary production. High estuarine bacterial production rates (Coffin 1989; Chin-Leo and Benner, 1992; Ducklow and Shiah, 1993) and CO_2 supersaturation (Cai and Wang, 1998; Frankignoulle et al., 1998; Cai et al., 1999; Raymond et al., 2000; Cole and Caraco, 2001) support the idea that respiration is an important sink for OM in estuaries. The OM subsidizing net heterotrophy in these systems is hypothesized to come from land (Hopkinson and Vallino, 1995; Hopkinson et al., 1998).

Studies on the internal processing of estuarine OM composition and quantity (Howarth et al., 1996a; Kemp et al. 1997; Smith and Hollibaugh 1997; Cai et al., 1998, 1999; Raymond et al., 2000) conclude that the amounts of OM discharged from rivers and estuaries are not simply a function of terrestrial inputs, but also under internal control (Kaplan and Newbold, 1993; Findlay et al., 1996; Fisher et al., 1998; Mannino and Harvey, 1999; Sanudo-Wilhelmy and Taylor, 1999; Raymond and Bauer, 2000). Processes contributing to the major transformations and exchanges of OM in rivers and estuaries include primary and secondary production, microbial utilization, photochemistry, and physical exchange processes (see Section 5.02.8).

The relative importance of internal processing on the amounts, chemical characteristics, and isotopic signatures of DOC discharged to the coastal ocean has been demonstrated in preliminary studies of two systems: the lower Hudson River and York River Estuary. Inputs to the lower Hudson (i.e., south of Albany, NY) of both DOC and POC are quite old (~2000 and 5000 years BP, respectively), and both pools decrease in mean age downriver (Cole and Caraco, 2001; Raymond and Bauer, 2001a), indicating that there is selective loss of the oldest DOC fractions. This also indicates that terrestrial processes mobilize large amounts of very old DOC into the upper reaches of these systems, and, although apparently resistant to degradation in soils and small watersheds, it is readily bioavailable during mainstem transport. This was further supported by DIC ages in the Hudson that were significantly older than

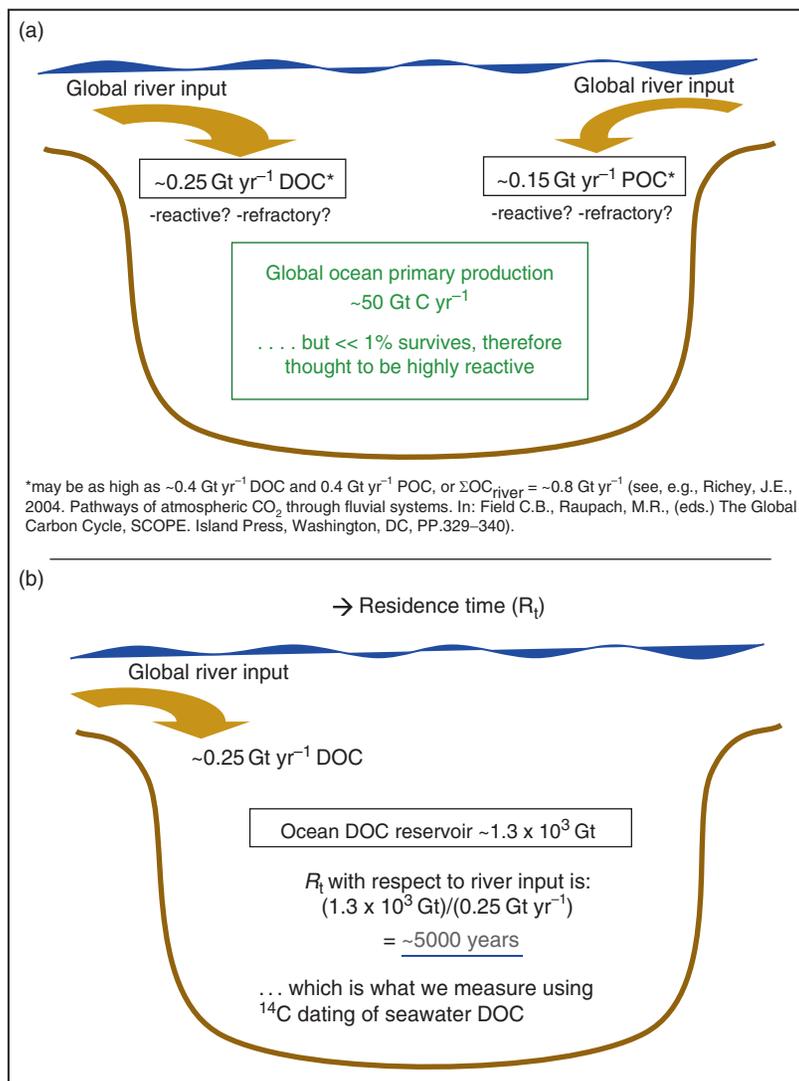


Figure 26 (a) Global inputs of terrestrial DOC and POC relative to marine primary production and (b) residence time calculation of ocean DOC with respect to the global input of riverine DOC (see text for additional explanation).

atmospheric CO₂ upriver, and decreased even further downriver (Cole and Caraco, 2001). In the York (a subestuary of Chesapeake Bay), which is dominated by highly bomb ¹⁴C-enriched DOC (Raymond and Bauer, 2001a, 2001b), non-conservative additions of DOC and DIC concentrations (data not shown) and shifts in isotopic signatures (both $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$, shown for DOC in Figure 16) demand that internal losses of ¹⁴C-enriched terrestrial (i.e., $\delta^{13}\text{C}$ -depleted) DOC be balanced by an internal source(s) of DOC and DIC, representing ~24% and 40% of the annual total fluxes, respectively (Raymond and Bauer, 2001b; Raymond et al., 2000). However, despite its major potential importance to land-ocean OM fluxes, the relative contribution of *in situ* processing of DOC within rivers and estuaries on a regional or global carbon scale has not been evaluated systematically. A major goal of future studies should therefore be to assess the role of internal processing of DOC produced by both autotrophic and heterotrophic processes and its impact on the net export of altered versus unaltered DOC to the coastal ocean.

5.02.9.2 Accounting for Terrestrial, Riverine, and Estuarine DOC Inputs in Coastal Ocean Carbon Models

One of the enigmas in global organic geochemistry is why we detect so little terrestrial OM in the oceans (Hedges, 1992, 1997; Hedges, 2002), and why only minor amounts of unambiguous terrestrial compounds are found in seawater and sediments. One possibility is that the vast majority of terrestrial OM is remineralized to CO₂, whereas OM of planktonic origin is selectively preserved. A second possibility is that global OM fluxes are in error due to unidentified sources and/or sinks (Hedges et al., 1997). Recent work (almost exclusively in sediments) using vascular land plant compounds such as lignin and photosynthetic pigments has shown that while biomarker-derived inputs (which are almost certainly minimal estimates) of contemporary terrestrial OM to coastal systems may be significant (Moran et al., 1991a; Prah et al., 1994; Goni et al., 1998; Bianchi et al., 2002), inputs of ancient terrestrial OM, not discernible by biomarker concentrations

alone, may be even greater (Barrick et al., 1980; Rowland and Maxwell, 1984; Eglinton et al., 1997, 1998, 2002; Leithold and Blair, 2001). Highly altered, ancient terrestrial OM may, therefore, be a significant flux from land (which may contain both ancient terrestrial as well as marine OM; Tissot and Welte, 1978; Killops and Killops, 2005) to the sea (Kao and Liu, 1996; Masiello and Druffel, 2001; Raymond and Bauer, 2001a; Blair et al., 2003) that has gone largely undetected.

The biochemical and isotopic information contained in riverine end-member DOC and (as well as POC – see Chapter 5.03), used to estimate terrestrial contributions to both seawater and marine sedimentary OM reservoirs, may have large uncertainties. Markers specific to vascular land plants (lignin phenols, wax alkanes, and pigments; see, e.g., Simoneit, 1977; Ertel et al., 1986; Hedges et al., 1986a; Peltzer and Gagosian, 1989; Prahll et al., 1994; Opsahl and Benner, 1997), and the $\delta^{13}\text{C}$ ratios in both bulk DOC and POC (Fry and Sherr, 1984; Michener and Schell, 1994; Guo et al., 1996; Fry et al., 1998) and specific organic compounds or classes (Prahll et al., 1992; Goni and Eglinton, 1996; Eglinton et al., 1997) have all been used for this purpose. Individual biomarkers, however, typically represent a very small fraction of the total OM pool, and, therefore, small changes in the ratio of a biomarker to total OM can result in large errors in estimates of OM inputs. Recent comparative studies of DOC and POC in US rivers have demonstrated considerable system-specific variability in parameters. For example, Onstad et al. (2000) reported very large ranges in $\delta^{13}\text{C}$ (–26.4‰ to –18.5‰) of suspended POM in 17 US rivers, the more enriched values of which are indistinguishable from marine values. In 12 of the rivers, these workers found the POM to be lignin poor, and comprised of highly degraded soil OM. Consequently, terrigenous inputs to ocean margins calculated by lignin content or $\delta^{13}\text{C}$ may be significantly underestimated (Onstad et al., 2000). The relative reactivity of DOC to river and estuarine bacteria has also been found to be controlled to a large extent by compositional differences (e.g., lignin content, elemental composition, and aliphatic:aromatic C content) in DOC versus POC (Hopkinson et al., 1998). In addition, Leithold and Blair (2001) found that suspended particles and sediments in the Eel River (California, USA) and shelf (in particular, the clay fraction which is dispersed farthest in the ocean) contained significant (>44%) kerogen-like material from continental rocks, which is fossil in age and has

$\delta^{13}\text{C}$ signatures (from ~–35‰ to –15‰) that overlap with marine and terrestrial OM (Tissot and Welte, 1978; Deines, 1980; Sackett, 1989; Killops and Killops, 2005), as well as river and estuarine OM (Mook and Tan, 1991).

Biomarker studies of seawater DOC have shown that while nearshore inputs of terrestrial OM may be large (Moran et al., 1991a, Bianchi et al., 1997c), the compounds are often highly ephemeral in nature, and even small alterations in their structures due to bacterial and photochemical processes (Amon and Benner, 1996b; Opsahl and Benner, 1998; Benner, 2002; Mopper and Kieber, 2002) can cause a significant and rapid loss of specificity. In this respect, natural carbon isotopes, especially ^{14}C , may offer a more robust alternative tracer for different forms and sources of DOC as well as POC (see Table 8), including both young and ancient terrestrial and marine OM because (1) it more fully integrates the average source composition of a bulk OM pool than specific organic biomarkers – a result of the small degree of isotopic alteration of bulk OM as biochemicals are degraded or respired (see Michener and Schell (1994) for review) and (2) the very large dynamic range of natural ^{14}C (i.e., $\Delta^{14}\text{C}$ values range from 1000‰ for relic OM, to >+200‰ for bomb-enriched OM, compared to a $\delta^{13}\text{C}$ range of at most 15–20‰ across terrestrial to marine sources of OM; see Trumbore and Druffel (1995) and Bauer (2002) for reviews). This considerable dynamic range gives $\Delta^{14}\text{C}$ an intrinsically greater degree of source specificity and sensitivity than $\delta^{13}\text{C}$, which is also not compromised by structural alteration or loss such as with organic biomarkers. A more thorough assessment of DOC and POC source and age distributions and their constituent biomolecules discharged from rivers and estuaries to the coastal ocean is an important first step toward improving our understanding of nonmarine OM in seawater and its impact on estimates of oceanic OM turnover.

In the only study to couple biomarker and ^{14}C information, Mitra et al. (2000) demonstrated that both very old and contemporary aged HMW DOC was enriched in lignin in MAB seawater, suggesting that lignin is not a tracer of exclusively young, recently produced OM. In addition, Bauer et al. (2001, 2002) demonstrated that the relationships between $\Delta^{14}\text{C}$ of both DOC and suspended POC as a function of salinity were significantly stronger than $\delta^{13}\text{C}$ of DOC and POC versus salinity, and explained more of the salinity-based variance (and

Table 8 Advantages and limitations of biomarker vs. carbon isotopic approaches for tracing DOC in river–estuarine systems

Organic biomarkers

Advantages:

- Highly sensitive with respect to marine vs. terrestrial sources
- Highly sensitive with respect to specific plants, animals, bacteria, etc.

Limitations:

- May be highly susceptible to bacterial, photochemical, etc. degradation/structure modification; lose specificity

Natural isotopes (^{14}C and ^{13}C)

Advantages:

- More integrative than organic biomarkers
- Not as affected by degradation/modification as biomarkers
- ^{14}C has very high dynamic range, and potential sensitivity

Limitations:

- Lower degree of source specificity than organic biomarkers

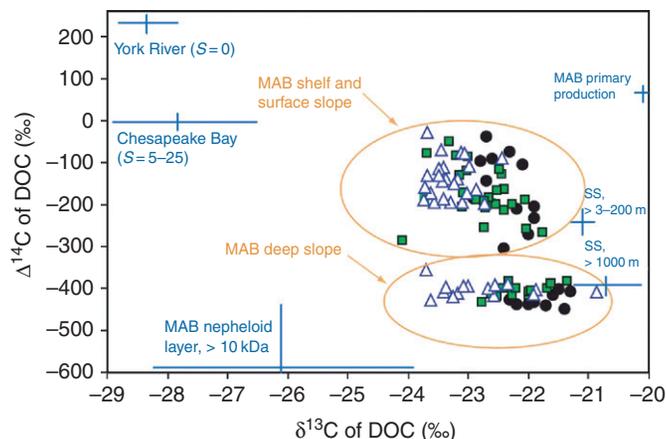


Figure 27 $\Delta^{14}\text{C}-\delta^{13}\text{C}$ plot of potential sources of river–estuarine and marine DOC (ranges shown as crosses) to continental shelf and slope DOC (open triangles, green squares, and black circles) in the Mid-Atlantic Bight (MAB). SS, open ocean values from the Sargasso Sea. Modified from Bauer, J.E., Druffel, E.R.M., Wolgast, D.M., Griffin, S., 2001. Cycling of dissolved and particulate organic radiocarbon in the northwest Atlantic continental margin. *Global Biogeochemical Cycles* 15, 615–636.

hence relative terrestrial vs. marine inputs) than $\delta^{13}\text{C}$. These workers and others (Santschi et al., 1995) further showed that by adequately constraining simultaneously the $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ signatures of potential sources (both marine and terrestrial) of OM in coastal waters (Figure 27), the relative contributions of these sources to the DOC and POC pools in MAB shelf and slope waters could be estimated. In shelf waters, up to half of the DOC was estimated to be derived from young, terrestrial C, whereas, in deeper slope waters, up to half of each pool consisted of very old terrestrial material, with concomitantly and highly depleted ^{13}C values as low as -31‰ , consistent with a relic, kerogen-like source. Therefore, the different major sources (terrestrial, marine, young, and ancient) of OM contributing to a bulk organic pool such as DOC in river, estuarine, and coastal waters may be qualitatively and quantitatively estimated provided they can be (1) adequately constrained in terms of overall isotopic variability and (2) differentiated from one another (i.e., have nonoverlapping ranges). However, as also pointed out by Bauer et al. (2001, 2002), the sensitivity of these estimates is limited most by our present need for information on the riverine/estuarine end members being discharged to the coastal ocean. Clearly, the sources and contributions of terrestrial OM from contemporary OM

production as well as ancient storage reservoirs delivered from land via rivers and estuaries to the coastal ocean are in need of reassessment. In addition, the processes within rivers and estuaries that both remove and add exportable OM, and modify its age structure and bioavailability, must be further evaluated.

5.02.10 Summary and Future Directions in Estuarine and Coastal DOC Studies

A major recent realization by earth, aquatic, and marine scientists is that virtually all systems have been already altered to greater or less extents by both direct and indirect aspects of human activity; that is, our findings of the ecological and biogeochemical function of these systems are increasingly biased away from natural to altered states. River and estuary systems have been extensively and directly altered by human activity, this is only expected to increase as more and more human development activities are focused on coastlines and along rivers (Serageldin, 1995; Postel et al., 1996; Figure 28). For example, in one of the few recent studies attempting to compare impacted and

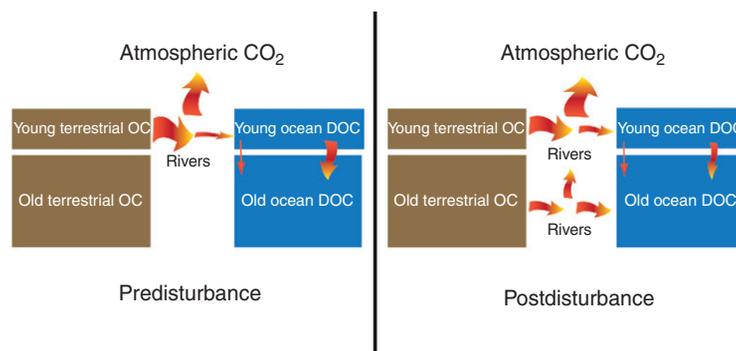


Figure 28 Conceptual models of pre- and postdisturbance DOC and CO_2 fluxes between rivers, estuaries, the atmosphere, and oceans (see text for further description).

nonimpacted systems, Perakis and Hedin (2002) found that small forested streams from the temperate Andes Mountains contained exceedingly low amounts of nitrate, and the nitrogen pools were dominated by dissolved organic nitrogen (DON). By contrast, temperate forested streams from North America were dominated by nitrate from anthropogenic sources, and DON was a trivial part of the total. Similar factors are likely to be found in the DOC and POC pools from impacted and nonimpacted river and estuarine systems globally. However, comparative studies of this nature will likely be increasingly difficult to conduct, due to the waning availability of nonimpacted systems globally.

Human activities can have a variety of effects on watersheds, rivers, and estuaries, sometimes in opposite senses. Deforestation, tillage, hydrological alteration (Barnett et al., 2008), and irrigation-enhanced erosion have increased loads of sediments and particulate carbon to rivers (Ver et al., 1999); widespread construction of dams, however, has resulted in significant retention of carbon and sediments in reservoirs (Meade et al., 1990; Walter and Merritts, 2008). Furthermore, the reduction of river suspended loads by dams around the world has generally resulted in increasing light availability and the potential role of phytoplankton biomass in river and estuarine biogeochemistry (Thorp and Delong 1994; Humborg et al., 1997, 2000; Ittekkot et al., 2000; Sullivan et al., 2001). The combination of increased tillage in the Mississippi watershed with increases in the river's discharge over the last several decades has led to significant increases in the discharge of bicarbonate alkalinity (Raymond and Cole, 2003; Raymond et al. 2008). Inputs of nutrients to river/estuarine systems by industrial, municipal, and agricultural runoff have experienced significant anthropogenically driven increases (Howarth et al., 1996b; Jickells, 1998; Socolow, 1999), potentially leading to net atmospheric CO₂ uptake in river-influenced margins by increasing primary production. Dams may moderate this effect as well: P may be retained in reservoir sediments (Jickells, 1998); Si may be retained by decreased weathering rates (Humborg et al., 2000); and nitrate and Si may be reduced by freshwater diatom blooms in stratified impoundments (Pocklington and Tan, 1987; Humborg et al., 2000; Sullivan et al., 2001). Other human impacts on the geomorphology of the estuary-ocean interface (e.g., dredging, diking, and loss of marshes) may have an effect on sediment transport and carbon burial, and on water residence time and reactions within estuaries.

Long-term monitoring studies of rivers and estuaries are valuable tools for assessing change due to both natural and human factors, but studies of this nature have been relatively rare when it comes to OM and DOC. Nonetheless, those that exist suggest that there has been a long-term decadal increase in the concentrations and fluxes of DOC transported by rivers and estuaries in temperate North America and Europe (Freeman et al., 2001; Worrall et al., 2003; Freeman et al., 2004; Findlay 2005; Skjelkvale et al., 2005; Evans et al., 2006; Roulet and Moore, 2006; e.g., see Figures 29 and 30). Suggested causes for this include increasing global temperatures, changes in watershed hydrology, increasing nitrogen deposition to watersheds,

land-use change, etc., and it is expected that these river and estuarine DOC levels and export fluxes will continue to increase over time. However, others have suggested that these increasing levels of DOC are actually returning to their preindustrial levels (and for which monitoring data is not available) as a result of decreased deposition to soils of sulfate aerosol (e.g., from anthropogenic acid rain and deposition), and from decreasing acidification of soils (Monteith et al., 2007). Decreasing acidification (i.e., higher pH) causes mineral-sorbed DOC to become less stable and to desorb compared to acidified conditions, which tend to stabilize sorbed DOC and reduce its release. These changes in the export of soil-sorbed DOC may also be reflected in changes in CDOM, such as has been recently documented for lakes (Cole, 2009; Karlsson et al., 2009), and which can change fundamental parameters such as light penetration and primary production. Whether these decades-long lower DOC fluxes from rivers and estuaries have had an effect on river-estuarine and coastal communities and metabolic balances is not yet known, nor is it yet known how they may change in the future.

Estuaries are also tremendously sensitive to long-term global climate change. Changes in river discharge in a warming climate are predicted to be particularly large in Arctic regions as snowpack and glacial water retention decrease and precipitation and runoff increase. Arctic regions also contain among the largest reservoirs of soil and peat OM in the world, largely in permafrost soils of West Siberia and North America. Increased atmospheric CO₂ and warmer temperatures, combined with changes in river discharge to estuaries, could have a significant impact on the amounts of terrestrial OM exported to Arctic coastal waters and may provide a positive feedback for global warming through respiration of the mobilized soil-derived DOC and subsequent atmospheric release of DOC-derived CO₂ (Figure 31; Peterson et al., 2002; Frey and Smith, 2005), thus impacting the DOC, alkalinity, and DIC contents of the primary river water supplied to estuaries. Rising sea levels that outpace the growth of estuary mouth sills (or bars) could also subject previously protected estuaries to increased wave-energy regimes, altering the depositional and redox environment on estuary floors.

Dramatic fluctuations in major biogenic nutrient (N, P, and Si) loading alone over the past 50–75 years have undoubtedly led to fluctuations in C and OM fluxes and cycling in rivers and estuaries that may be unprecedented over at least the Holocene, if not longer (Figure 32; Meybeck and Vörösmarty, 2005; see also Section 5.02.9). Thus, the current state of river and estuarine C and DOC (as well as POC) biogeochemical cycles will be difficult, if not impossible, to place in any sort of reasonable historical context owing to the relative lack of both earlier (i.e., pre-anthropogenic) studies and technical sophistication in existing earlier studies. Nonetheless, monitoring studies of rivers and estuaries, not only to document changing hydrological conditions but also to assess changes in soil OM losses and concomitant changes in river and estuarine carbon and OM inputs, are critical for providing baseline information for future studies and assessments of the impacts of these changes in river, estuarine, and coastal ocean biogeochemical cycles, metabolic balances, and ecosystem function.

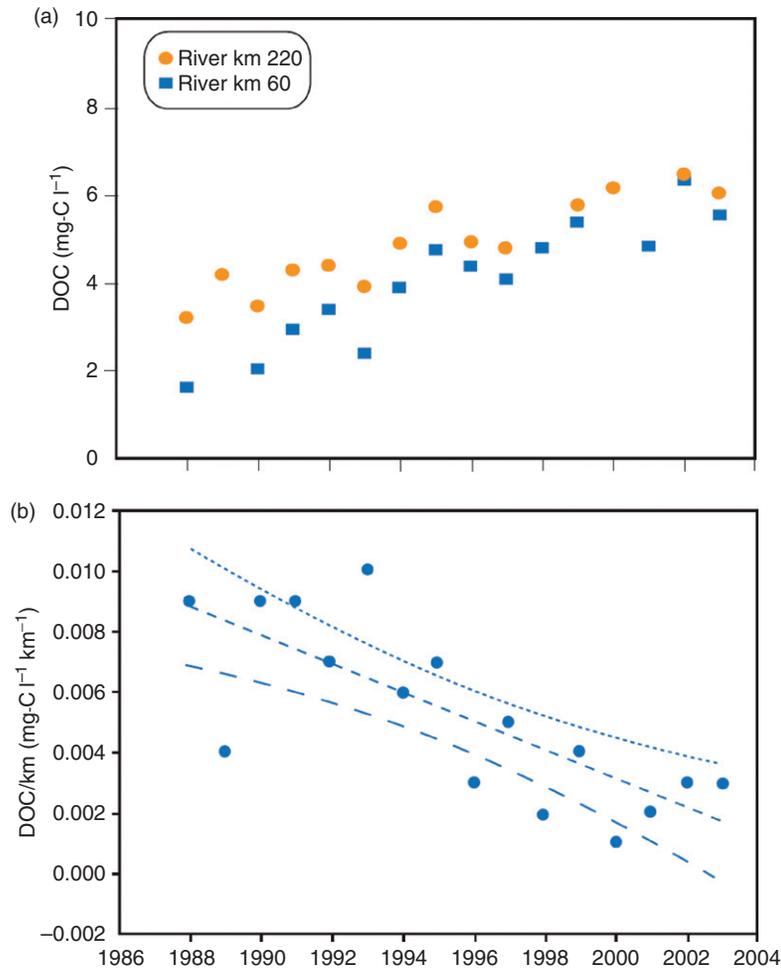


Figure 29 Changes in (a) DOC concentrations and (b) its loss during transport in the Hudson River. The net result of these two factors is a predicted increased in the export flux of DOC from the Hudson. Modified from Findlay, S.E.G., 2005. Increased carbon transport in the Hudson River: unexpected consequence of nitrogen deposition? *Frontiers in Ecology and the Environment* 3, 133–137.

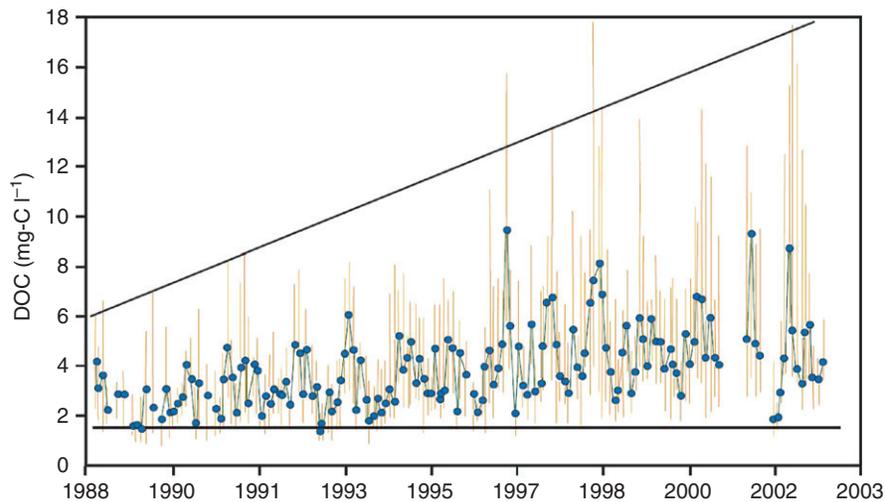


Figure 30 Means (blue dots) and ranges (vertical orange lines) of DOC concentrations in streams from the United Kingdom. Solid horizontal line shows 1988–93 baseline concentrations, and solid diagonal line shows maximum potential increase since 1988. Modified from Evans, C.D., Chapman, P.J., Clark, J.M., Monteith, D.T., Cresser, M.S., 2006. Alternative explanations for rising dissolved organic carbon export from organic soils. *Global Change Biology* 12, 1–10.

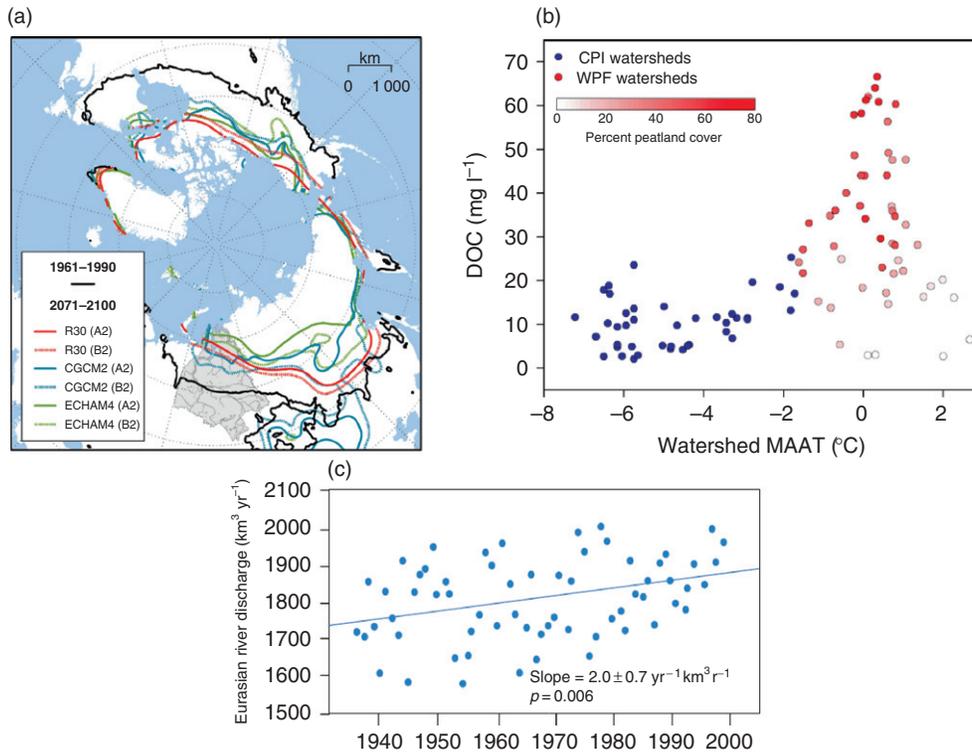


Figure 31 Evidence of increasing mean annual air temperatures and stream water DOC concentrations in Arctic permafrost regions. (a) Observed (1961–1990: black line) and modeled (2071–2100: colored lines) 2 °C mean annual air temperature (MAAT) isotherms in Arctic polar regions. (b) Observed watershed DOC concentrations in West Siberia peatlands as a function of MAAT; CPI, cold permafrost watersheds; WPF, warm permafrost-free watersheds. (c) Observed increases in river discharge from Eurasian watersheds, 1935–2000. Modified from Frey, K., Smith, L., 2005. Amplified carbon release from vast West Siberian peatlands by 2100. *Geophysical Research Letters* 32, L09401. doi:10.1029/2004GL022025; and Peterson, B.J., Holmes, R.M., McClelland, J.W., 2002. Increasing river discharge to the Arctic Ocean. *Science* 298, 2171–2173.

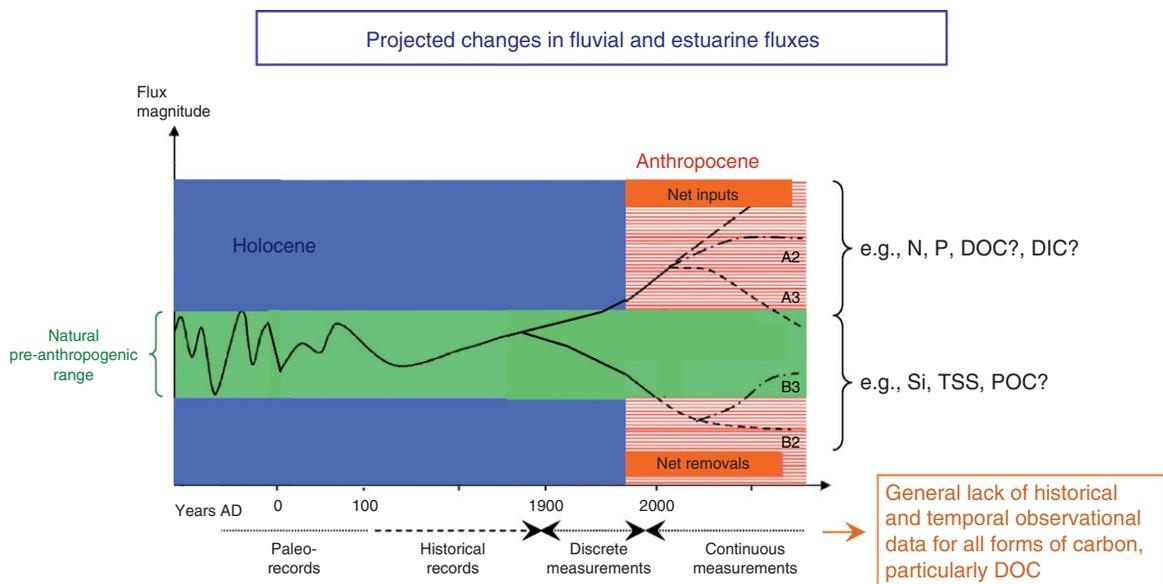


Figure 32 Hypothetical historic and future projected changes in nutrient and associated organic and inorganic carbon fluxes in river and estuarine systems. A2, A3, B2, and B3 represent potential projected changes under different scenarios of changing nutrient input and land use. Modified from Meybeck and Vörösmarty (2005).

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