



# Use of $^{14}\text{C}$ and $^{13}\text{C}$ natural abundances for evaluating riverine, estuarine, and coastal DOC and POC sources and cycling: a review and synthesis

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## Abstract

Though not typically regarded as “biomarkers” in the traditional sense of the word, the radioactive and stable isotopes of carbon ( $^{14}\text{C}$  and  $^{13}\text{C}$ , respectively) can serve as powerful tools for identifying sources and estimating turnover times of organic matter in aquatic systems. Paired  $^{14}\text{C}$  and  $^{13}\text{C}$  measurements of carbon pools can provide an additional degree of specificity for studies of organic matter cycling as a result of: (1) the lower susceptibility of natural isotopes to diagenetic effects that can alter organic biomolecules; (2) the “dual” isotopic nature of the approach; (3) the unique input functions for each isotope; and (4) the greater dynamic range in  $\Delta^{14}\text{C}$  ( $-1000$  to  $\sim +200\%$ ) compared to  $\delta^{13}\text{C}$  ( $\sim -32$  to  $-12\%$ ). Relatively few geochemical studies in rivers, estuaries and the coastal ocean waters have employed  $^{14}\text{C}$  and  $^{13}\text{C}$  analyses of organic matter. In this paper we summarize the available data on  $^{14}\text{C}$  and  $^{13}\text{C}$  measurements in dissolved and particulate organic carbon (DOC and POC, respectively) in these systems. A brief review is presented of current methods for the separation and oxidation of DOC and POC from water samples, for subsequent  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  analyses. We also compile the existing datasets on paired  $^{14}\text{C}$  and  $^{13}\text{C}$  measurements across the riverine to coastal marine continuum in order to elucidate sources, ages, and transformations of organic matter within each system, and during transport from rivers to the coastal ocean. The natural range in the  $\Delta^{14}\text{C}$  values of both DOC and POC across similar system types was 500 and 1000‰, respectively. In general, riverine DOC was enriched in  $^{14}\text{C}$  relative to POC in rivers and estuaries, but the opposite generally held for coastal marine waters. This is indicative of the different sources and transport mechanisms for DOC and POC within and across these three general types of systems. During river and estuarine transport, DOC generally becomes enriched in  $^{13}\text{C}$  and depleted in  $^{14}\text{C}$  due to simultaneous additions from autochthonous production and removals from heterotrophic bacteria and abiotic processes. Bacterial utilization experiments indicate that bacteria preferentially utilize a  $^{14}\text{C}$  enriched (i.e. young) DOC fraction and, therefore, DOC utilization is a partial explanation for the  $^{14}\text{C}$ -depleted riverine and estuarine DOC. It is concluded that through the use of paired  $^{14}\text{C}$  and  $^{13}\text{C}$  measurements in DOC and POC, a more robust interpretation of sources, sinks, and residence times of organic matter may be attained than by using either isotope separately. © 2001 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Rivers and estuaries link the carbon cycle of the continents to the oceans. They transport  $\sim 0.4 \times 10^{15}$  g of organic carbon annually (Meybeck, 1982; Spitzky and

Ittekkot, 1991), a significant amount in the global carbon budget, of which  $\sim 60\%$  is dissolved and 40% is particulate (Spitzky and Ittekkot, 1991). The organic matter exported by rivers represents a major potential source of terrestrial dissolved and particulate organic carbon (DOC and POC, respectively) to the oceans, and can more than account for the apparent steady state flux of  $\sim 0.1 \times 10^{15}$  g C year<sup>-1</sup> for oceanic DOC based on its natural radiocarbon ages of 4–6 kyear (Bauer et al.,

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1992a; Druffel et al., 1992). However, the small quantities of terrestrial plant organic biomarkers found in marine DOC and POC do not support a significant terrestrial component persisting in the oceans (Meyers-Schulte and Hedges, 1986; Hedges et al., 1992, 1997; Opsahl and Benner, 1997). One possible explanation is that terrestrial organic matter is extensively modified and remineralized in rivers, estuaries and the coastal ocean prior to its export to the open ocean. Supporting this idea is the fact that the net CO<sub>2</sub> flux from rivers and estuaries is often equal to or greater than organic matter loadings (Raymond et al., 1997, 2000; Cai and Wang, 1998; Frankignoulle et al., 1998). A second possibility is that a significant quantity of oxidized terrestrial organic matter enters the oceans, but its initial chemical characteristics are significantly altered during transport and it is not measured using biomarker techniques.

The potential importance of coastal systems in global and regional organic carbon budgets is still unclear. One reason is the inherent complexity and variability of rivers, estuaries and the coastal zone, which exhibit tremendous temporal and spatial variation in physical and chemical characteristics (Hobbie, 2000). This variability makes it difficult to constrain carbon budgets by simply measuring concentrations of bulk parameters such as POC and DOC. Stable carbon isotopes ( $\delta^{13}\text{C}$ ) of DOC and POC have been used successfully to increase our understanding of organic matter cycling in estuaries and coastal systems (Peterson et al., 1994; Canuel et al., 1995; Cifuentes and Eldridge, 1998; Coffin and Cifuentes, 1999). However, interpretation of  $\delta^{13}\text{C}$  measurements in these systems can be equivocal due to a significant degree of overlap in the isotopic signatures for the presumed major DOC sources (i.e. terrestrial, estuarine phytoplankton, marsh and marine organic matter). The natural radioisotope of carbon ( $^{14}\text{C}$ ) can provide additional unique information on the sources, ages, and residence times of organic matter and when combined with  $^{13}\text{C}$  can often overcome problems associated with source overlap.

There have been a number of studies that have incorporated  $^{14}\text{C}$  measurements in the oceans (Williams and Druffel, 1987; Druffel et al., 1992; Guo et al., 1996; Bauer and Druffel, 1998; Bauer et al., 1998a, b, and others) and soils (Trumbore et al., 1989; Schiff et al., 1990; Richter et al., 1999; Trumbore, 2000; and others). However, until recently there has been surprisingly little application of  $^{14}\text{C}$  in the organic pools of estuaries and the coastal ocean (Spiker and Rubin, 1975; Hedges et al., 1986; Guo et al., 1996) despite the important role these systems play as sites where considerable amounts of terrestrial organic matter is altered, stored, or remineralized. This paper attempts to review and summarize studies employing natural  $^{13}\text{C}$  and  $^{14}\text{C}$  measurements for organic matter research in rivers, estuaries and the coastal ocean.

## 2. Present methods in organic carbon isotopic studies

### 2.1. Separation of total DOC and POC

A number of different methods have been used with varying degrees of success to separate, extract and analyze for carbon isotopic compositions in aquatic and marine systems. If DOC alone is to be analyzed, then a wide range of filter materials (including glass, alumina, quartz, polycarbonate, polysulfone, polypropylene, etc. –see Hurd and Spencer (1991) for a review of filtration methods and materials) can be used to process the sample, provided they can be cleaned (typically by pre-combustion, or muffling, in the case of inorganic filters, or chemical cleaning, in the case of organic filters) such that no significant blank material is present in the filtrate. Ideally, DOC samples should be processed using filters with a nominal pore size of  $<0.2\ \mu\text{m}$  in order to eliminate bacteria from the filtrate. The presence of bacteria in the filtrate presents two major potential complications: (1) if the sample is not preserved rapidly enough with inorganic poisons (e.g. HgCl<sub>2</sub>) or by freezing, bacterial activity may alter the quantity and quality (e.g. its isotopic and molecular composition) of DOC, and (2) the bacterial biomass itself, and its component biomolecules, which may be significantly different than the ambient DOC, will be included in the operationally defined pool of DOC.

If the POC in a given sample is to be analyzed directly for its isotopic composition, the choice of filter materials is significantly more restricted, and must be limited to inorganic materials that can tolerate high temperatures. Filter materials that fulfill these requirements include glass, quartz, alumina and silver. More recently, tangential-flow ultrafiltration of very large seawater volumes ( $\sim 200\text{--}1100$  liters), using  $0.1\ \mu\text{m}$  polysulfone hollow fiber filter cartridges, has been used to collect and characterize POC, although this method is believed to have large sorptive losses (as high as 60–70%) to the ultrafiltration system (Benner et al., 1997). Typically, glass and quartz are most frequently used for isotopic, as well as other types of, characterization of POC. Pyrex (such as GF/F glass fiber filters) is more suitable for low-temperature ( $\leq \sim 550^\circ\text{C}$ ) sealed tube combustion of glass filters (Sofer, 1980) and flow-through systems in which POC is combusted in a CHN analyzer that is directly interfaced to an isotope ratio mass spectrometer (IRMS) for  $\delta^{13}\text{C}$  analysis (Boutton, 1991). For the more rigorous conditions requiring sealed tube combustion at  $\sim 850\text{--}900^\circ\text{C}$  in which discrete (i.e. non-flow-through) sealed-tube methods are used, quartz filters are more suitable and tolerate these temperatures without melting and compromising the integrity of the sealed quartz tube (Frazer and Crawford, 1963; LeFeuvre and Jones, 1988; Boutton et al., 1983; Druffel et al., 1992, 1996). As a cautionary note, the sorption of DOC to glass

filters (and presumably quartz) has recently been observed to contribute a significant component of “blank” carbon to filters that will be analyzed for POC (Moran et al., 1999), 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.

## 2.2. Sample processing and oxidation of DOC and POC

The processing and oxidation of solid-phase organic materials (including POC) for isotopic analysis has long been established (see references above), and will be discussed only briefly here. For paired or individual  $^{14}\text{C}$  and  $^{13}\text{C}$  analyses, the primary challenge for POC is the collection of adequate amounts of material (minimum of  $\sim 250\text{--}500\ \mu\text{g C}$ ) for natural radiocarbon analysis by AMS (Vogel et al., 1987, 1989; Southon et al., 1991). The general procedure for both  $^{14}\text{C}$  and  $^{13}\text{C}$  analyses is to remove all non-organic carbon (i.e. carbonates, residual aqueous  $\Sigma\text{CO}_2$  that may still be on the filter, etc.), followed by either (a) high temperature oxidation using a CHN analyzer and flow-through analysis for  $^{13}\text{C}$  by IRMS (Boutton, 1991), or (b) sealed tube combustion for  $^{14}\text{C}$ , whereby the  $\text{CO}_2$  produced by the oxidation is then reduced to graphite over cobalt or iron for subsequent analysis by Accelerator Mass Spectrometry, or AMS (Vogel et al., 1987, 1989; McNichol et al., 1994).

For total DOC, sample processing for  $^{14}\text{C}$  and  $^{13}\text{C}$  analysis is considerably more difficult than for POC owing to a variety of factors, including: (a) the choice of method to “extract” the DOC from the aqueous sample; (b) the very small concentrations of DOC, and the very high volumes that consequently must be processed, in certain types of samples (e.g. seawater); and (c) in estuarine and coastal samples, the orders of magnitude greater concentrations of inorganic salts vs. DOC. In riverine and lacustrine environments, the processing of samples for analysis of  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  of DOC can be much simpler than in coastal waters, because of the relatively higher DOC concentrations and low salt contents. For these types of samples, a given volume of DOC-containing water (anywhere from tens of mls to liters) can be dried to remove the water (see, for example, Aravena and Wassenaar, 1993; Murphy and Davis, 1989; Murphy et al., 1989; Schiff et al., 1990, 1997), using methods such as lyophilization and vacuum centrifugation. Although similar methods have also been used in estuarine and marine samples (e.g. Peterson et al., 1994; Fry et al., 1996), the small amount of total DOC relative to total salts makes it more practicable for  $\delta^{13}\text{C}$  than for  $\Delta^{14}\text{C}$  (in which hundreds of  $\mu\text{g}$  of C must be available) analyses.

Ultrafiltration (UF), or cross-flow filtration (CFF), has helped to overcome a number of the difficulties noted above, and has proven to be a very useful tool for

organic geochemical and isotopic studies of DOC (see, e.g. Benner, 1991, 1992, 1997; Guo et al., 1994; Guo and Santschi, 1997; Aluwihare et al., 1997). By using that fraction of the total DOC that has been extracted using UF methods (the so-called ultrafiltered DOC, or UDOC, typically representing no more than 20–30% of marine DOC, but as high as 50–60% of freshwater and estuarine DOC using 1kDalton MWCO filters), the sample may then be de-salted, and dried to produce a solid powder that can be subjected to a number of chemical analyses used for solid-phase material such as POC or sedimentary organic matter (e.g. NMR, CHN, GC-MS, HPLC, sealed tube combustion, etc., see, e.g. Benner, 1991; Benner et al., 1992, 1997; Guo et al., 1994; Guo and Santschi, 1997; Aluwihare et al., 1997; Bianchi et al., 1997; Opsahl and Benner, 1997; McCarthy et al., 1997; Mitra et al., 2000).

Prior to UF, the method of choice for isolating a component (i.e. so-called “humic substances”) of freshwater and marine DOC was the use of cross-linked polystyrene (XAD) resins (e.g. Aiken et al., 1979; Ertel et al., 1986; Hedges et al., 1986; Meyers-Schulte and Hedges, 1986). The issue of the representivity of both the UF and humic fractions of the total DOC have long been questioned, however, without a means of comparing these fractions (which in the case of UF does not account for the low molecular weight DOC; in the case of humics, the more hydrophilic component is under-represented) to the total DOC, this question is still an open one.

Following the processing of a sample for total DOC or a sub-fraction, the sample must be converted to  $\text{CO}_2$  for subsequent isotopic analysis. For “solid-phase DOC” (e.g. UDOC or humic substances), this may be accomplished in the same way as for POC; that is, by flow-through combustion followed by IRMS for  $\delta^{13}\text{C}$  analysis, or by discrete sealed tube combustion for  $\Delta^{14}\text{C}$  analysis by AMS, and/or  $\delta^{13}\text{C}$  analysis by IRMS. The total DOC in a sample may be oxidized using several methods, each of which has its own inherent advantages and disadvantages, including: high energy UV irradiation (Williams and Gordon, 1970; Eadie et al., 1978; Williams and Druffel, 1987; Bauer et al., 1992a); high-temperature ( $\sim 500^\circ\text{C}$ ) sealed tube oxidation of the lyophilized DOC/salt mixture (Peterson et al., 1994; Fry et al., 1996); combined UV-persulfate oxidation (Bauer et al., 1991), and high-temperature flow-through oxidation (Bauer et al., 1992a, b; Clercq et al., 1998). Although none of these methods is simple or routine, factors such as quantitative oxidation and recovery, system blanks, sample sizes relative to blank size, etc. must be considered when deciding on the method to employ for a given sample type. It should be pointed out that the advent of AMS for natural abundance  $^{14}\text{C}$  measurement has dramatically enhanced the ability of organic and carbon isotope geochemists to analyze small (as small as

20–50  $\mu\text{g C}$ ) samples of DOC and other materials. The state-of-the-art presently permits individual chromatographically separated compounds to be analyzed (Eglinton et al., 1996, 1997).

### 3. The role of soils in supplying organic matter to rivers and estuaries

Terrestrial soils store more organic matter in the upper meter (1300–1500 Gt C) than is present in either the atmospheric or living carbon pools (Schlesinger, 1991). Constraining how this large pool of carbon is transported and processed within rivers and estuaries is critical for understanding the linkage between terrestrial and coastal systems. Natural  $^{14}\text{C}$  has been used to estimate the turnover time, or mean residence time, of soil organic matter pools (Trumbore et al., 1989; Trumbore and Druffel, 1995). The utility in using  $^{14}\text{C}$  lies in quantifying the incorporation of bomb-carbon into soils before and after the period of bomb testing (O'Brien, 1986; Richter et al., 1999; Trumbore, 1993).

An excellent example of the application of this method is shown in Fig. 1. In this study Richter et al. (1999) documented the incorporation of bomb carbon into the upper 0.6 m of mineral soil during the eight years following the peak in atmospheric  $^{14}\text{CO}_2$  in the early 1960s. However, after the initial eight years only the 0–7.5 cm soil layer continued to accumulate  $^{14}\text{C}$ -enriched carbon, while the  $^{14}\text{C}$ -content of all other soil layers gradually declined (Fig. 1). A possible mechanism for the loss of this  $^{14}\text{C}$ -enriched organic carbon, aside from decomposition, is export to adjacent streams. Indeed, soil studies indicate that solubilized DOC is younger (i.e.  $^{14}\text{C}$ -enriched) than the soil organic matter

from which it originated (O'Brien et al., 1986; Trumbore et al., 1992), with the DOC of soil pore-waters often being enriched with respect to atmospheric  $^{14}\text{C}$ - $\text{CO}_2$  (Schiff et al., 1997; Trumbore et al., 1989). These results support the hypothesis that terrestrial DOC exported to rivers is generally younger  $^{14}\text{C}$ -enriched material (Hedges et al., 1986).

Despite the incorporation of  $^{14}\text{C}$ -enriched carbon into soils and DOC, they still contain very old organic matter components. In the example used above, at only 35–60 cm below the surface, the  $\Delta^{14}\text{C}$  value of total soil organic matter was  $-80\%$  in 1990, which is  $\sim 300\%$  depleted in  $^{14}\text{C}$  with respect to the surface (Fig. 1). The age of a soil organic matter profile will depend on the amount of time it has taken the soil to develop, the source of parent rock that the soil is derived from, the erosional regime and climate of the watershed, the characteristics of the vegetation at the surface, and the decomposition kinetics of the soils (Bloom, 1991). The range in organic matter ages in just the top meter of soil is from modern to  $> 5000$  years.

### 4. $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ in river studies

A striking general observation for rivers is that the  $\Delta^{14}\text{C}$  signal of POC exported from rivers is significantly depleted with respect to current atmospheric  $\Delta^{14}\text{C}$ - $\text{CO}_2$  levels (Table 1). In fact, in most samples the age of POC is from hundreds to thousands of years. Possible sources of  $^{14}\text{C}$ -depleted POC include old soil horizons (see above), sedimentary fossil (i.e. kerogen) carbon (Kao and Liu, 1996), sorbed petroleum and petroleum byproducts, and sewage sludge (Turekian and Benoit, 1981). Due to the antiquity of these sources (which for

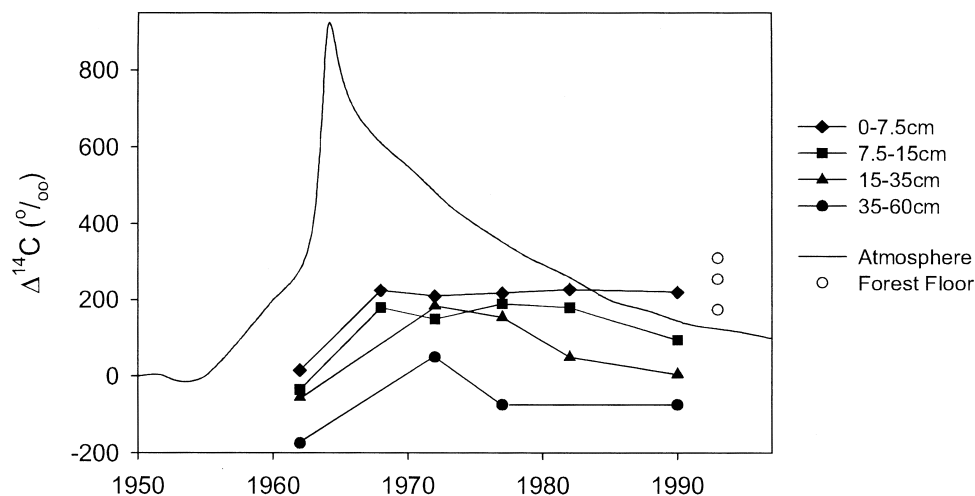


Fig. 1. From Richter et al. (1999). Time trends of  $^{14}\text{C}$  in mineral soils from different soil horizons in the Calhoun forest, South Carolina. The solid line is atmospheric  $\Delta^{14}\text{C}$ - $\text{CO}_2$  from Levin and Kromer (1997).

Table 1

Published values of  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  measurements of DOC and suspended POC in rivers (reported as ranges where available). Values are for total DOC and total POC except where noted

River	$\Delta^{14}\text{C}$ range (‰)	$\delta^{13}\text{C}$ range (‰)	Reference
<b>DOC</b>			
Amazon	28	–28.0	Raymond and Bauer (2001)
Amazon (total humics)	283	n.d.	Hedges et al. (1986)
<b>Chesapeake Bay tributaries</b>			
York (VA)	159 to 257	–28.8 to –27.9	Raymond and Bauer (2001)
Potomac (D.C.)	30 to 364	–29.9 to –32.4	Spiker and Rubin (1975)
Rappahannock (VA)	–83	–31.9	Spiker and Rubin (1975)
Susquehanna (MD)	–81	n.d.	Spiker (1981)
James (VA)	43	–28.0	Spiker and Rubin (1975)
West (MD)	–25 to 170	–24.6 to –29.0	Spiker and Rubin (1975)
Parker (MA)	97 to 109	–28.3 to –29.0	Raymond and Bauer (2001)
Hudson (NY)	–158 to 31	–25.5 to –27.0	Raymond and Bauer (2001)
Sacramento (CA)	–31	n.d.	Spiker (1980)
<b>POC</b>			
York	24 to –190	–28.2 to –30.0	Raymond and Bauer (2001)
Parker	–85 to –190	–30.0 to –33.7	Raymond and Bauer (2001)
Hudson	–426 to –447	n.d.	Raymond and Bauer (2001)
Small Mountainous Rivers of Papua New Guinea	–43 to –285	–22z.3 to –32.6	Raymond (1999)
Lanyang Hsi	75 to –980	n.d.	Kao and Liu (1996)
Amazon	–145	–26.6	Raymond and Bauer (2001)
<b>Amazon</b>			
Fine SPOM	19	n.d.	Hedges et al. (1986)
Course SPOM	227		

kerogen is millions of years old) even a small contribution from these sources will cause the total POC pool to be significantly  $^{14}\text{C}$ -depleted.

Some of the cross-system variation in POC ages between rivers may be due to the dominant form of erosion occurring in the associated watersheds. We would expect rivers draining steep terrains in Table 1 to have weathering-limited denudation regimes (Carson and Kirby, 1972) and have a large potential contribution from relic soils and rocks. Some of the oldest POC ages were recorded for the small mountainous rivers of Papua New Guinea and Taiwan (Table 1), all of which drain mountainous areas (i.e. weathering limited areas). Alternatively, rivers draining flat terrains with thick soils that fall under the transport-limited denudation regime (Carson and Kirby, 1972; Stallard and Edmond, 1983), such as the York may have smaller contributions from relic soils. Varying contributions from relic marine deposits, that are  $\sim 10^8$  years in age (Meybeck, 1993), may also contribute to some of the variation in POC age. The oldest POC ages from the eastern United States were from the Hudson River (Table 1), which has many areas that are underlain by easily erodible Mesozoic shales (Coch and Bokuniewicz 1986).

Although they were highly variable, the majority ( $\sim 70\%$ ) of DOC  $\Delta^{14}\text{C}$  values were enriched relative to

POC (Table 1), and are consistent with large contributions from organic matter that was fixed over the last 50 years. The Hudson, Rappahannock, Susquehanna, Sacramento, and West rivers all had DOC that was  $^{14}\text{C}$ -depleted (Table 1), which is consistent with significant contributions of organic matter with ages  $> 50$  years. The Hudson, Susquehanna, and Sacramento drain watersheds that currently have, or historically had, large areas of farm and agricultural land. Agricultural practices commonly bring older horizons to the surface and as a land-use class contribute a proportionally larger fraction of organic matter to rivers (Howarth et al., 1991). Unfortunately there is sparse  $\delta^{13}\text{C}$ -DOC data from these  $^{14}\text{C}$ -depleted rivers, which hinders our ability to accurately elucidate the source of this organic matter. It is also possible that a significant percentage of the DOC found in these particular samples originated from  $^{14}\text{C}$ -depleted organic matter that was sorbed to mineral matrices (Keil et al., 1997; Mayer et al., 1998) and desorbed in the riverine environment. There was no clear trend between  $\Delta^{14}\text{C}$ -DOC and  $\delta^{13}\text{C}$ -DOC across systems, even though the DOC data was dominated by East Coast estuaries. Where data is available for comparison, DOC is always  $^{14}\text{C}$ -enriched compared to POC (Fig. 2). This is due to both a larger contribution from newly produced  $^{14}\text{C}$ -enriched soil and litterfall organic

matter that is continuously leached from soils (Meybeck, 1993) and a potential smaller contribution from the relic sources listed above.

The dominant forms of weathering and transport for DOC vs. POC will also cause them to have different ages within the river basins themselves. DOC export from soils occurs during chemical weathering, a process generally associated with newly produced litterfall and below ground production (Bloom, 1991). In contrast, POC enters streams through mechanical weathering, which may erode deeper/older soil horizons. Once in a river, DOC is transported dissolved in the water, and therefore the residence time of DOC will be equal to the residence time of the water, which for most systems is limited to days-months. In contrast, once in a stream POC transport is controlled by re-suspension/deposition events prior to actual export (Newbold et al., 1982) and the residence time of POC will therefore depend on how long it ages in the streams, rivers, or in the case of the Amazon the associated floodplains (Dunne et al., 1998).

Autochthonous organic matter inputs from riverine primary production within these rivers would enter both the DOC and POC pools and therefore cannot explain the pattern of younger DOC compared to POC. However, varying contributions of autochthonous organic carbon are undoubtedly responsible for some of the across system and within system variation in both  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  for DOC and POC (Peterson et al., 1994). In the York, Hudson, and Parker the dissolved inorganic carbon pool was always significantly (150%)  $^{14}\text{C}$ -enriched with respect to the POC pool (Raymond and

Bauer, unpublished data) and the addition of autochthonously produced organic matter in these rivers would cause the POC pools to become  $^{14}\text{C}$ -enriched. A significant dilution of  $\Delta^{14}\text{C}$ -depleted POC from in situ riverine production may in part be responsible for the anomalous  $^{14}\text{C}$ -enriched values reported for the York and Lanyang Hsi (Table 1).

### 5. Use of natural $^{14}\text{C}$ and $^{13}\text{C}$ in studies of organic matter cycling in rivers and estuaries

Regardless of the specific mechanisms by which DOC and POC are introduced to rivers and estuaries, the fate of terrestrial and autochthonously produced organic matter in rivers is an important component of local and global carbon budgets (Hedges et al., 1997). The fate of dissolved organic carbon in rivers and estuaries is of particular importance because DOC is present in higher concentrations than POC (Spitzzy and Ittekkot, 1991), DOC is readily utilized by estuarine bacteria (Albright, 1983; Amon and Benner, 1996; Coffin and Cifuentes, 1993; Crawford et al., 1974; Findlay et al., 1992; Gardner et al., 1994), and because the global marine DOC pool is one of the largest reactive reservoirs of carbon on earth (Schlesinger, 1991).

$\delta^{13}\text{C}$  has proven to be a very useful tracer for DOC in riverine and estuarine systems (Coffin and Cifuentes, 1993; Peterson, et al., 1994; Cifuentes and Eldridge, 1998). Unfortunately, there is considerable overlap in the  $\delta^{13}\text{C}$  values of several of the major sources of DOC within rivers and estuarine systems. Within a single

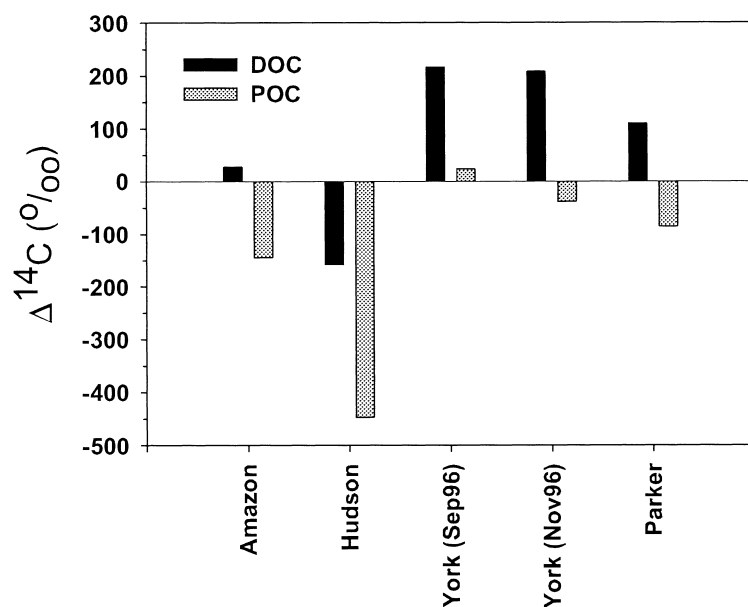


Fig. 2. Riverine sites where  $\Delta^{14}\text{C}$ -DOC and  $\Delta^{14}\text{C}$ -POC were measured concurrently. All values represent a single site. Data from Raymond and Bauer (2001).

system, algal material can have a wide range of  $\delta^{13}\text{C}$  values because  $\delta^{13}\text{C}$ -DIC varies spatially and temporally in rivers and estuaries (Chanton and Lewis, 1999; Fogel et al., 1992; Spiker, 1980). Marshes can also contribute significant quantities of organic matter (Peterson and Howarth, 1987) with  $\delta^{13}\text{C}$  values that range from  $-29$  to  $-12\text{‰}$ , depending on the relative contribution of  $\text{C}_4$  vs.  $\text{C}_3$  plants. The simultaneous use of  $\Delta^{14}\text{C}$ -DOC and  $\delta^{13}\text{C}$ -DOC therefore adds a second dimension to isotopic studies of carbon cycling.

It is becoming increasingly clear in paired riverine and estuarine  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  studies that there can be significant inputs of autochthonous DOC and sinks of terrestrial, riverine and estuarine DOC within these systems. Based on a lack of correlation between DOC concentration and discharge, Findlay et al. (1996) hypothesized that DOC in the Hudson is under internal control. In the Hudson River,  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  showed significant downstream variation (Fig. 3). Based on the spatial variation of  $\Delta^{14}\text{C}$ -DOC (Fig. 3) and  $\Delta^{14}\text{C}$ -DIC, either the removal of upstream DOC and/or the input of autochthonous DOC could contribute to the observed spatial variability. However, in order for satisfy the small net change in DOC concentration at the two end-members both input and removal processes must be occurring simultaneously. Because  $\Delta^{14}\text{C}$  has a much greater dynamic range than  $\delta^{13}\text{C}$ , and less overlap among sources, it may be used with greater precision to constrain the input and removal processes in the Hud-

son. Using a mass balance equation that assigns a range to the possible  $\Delta^{14}\text{C}$  values for the autochthonous DOC ( $A_{14\text{C}}$ ) we can estimate the percentage of DOC turnover necessary to produce the measured changes in  $\Delta^{14}\text{C}$ -DOC from the upstream stations ( $U_{14\text{C}}$ ) to the downstream station ( $D_{14\text{C}}$ ):

$$\% \text{ Turnover} = (D_{14\text{C}} - U_{14\text{C}}) / (-U_{14\text{C}} + A_{14\text{C}}) \quad (1)$$

For  $A_{14\text{C}}$ , we used a range in  $\Delta^{14}\text{C}$  assuming the autochthonous contribution ranged from 100% newly produced emergent and wetland organic matter (i.e.  $\Delta^{14}\text{C} = \sim 90\text{‰}$ ) to 100% phytoplankton ( $\Delta^{14}\text{C} = \sim -40\text{‰}$ , which is equivalent to  $\Delta^{14}\text{C}$ -DIC values in the Hudson for the same transect). Using Eq. (1), we predict large (45–100%) DOC turnover to produce the downstream  $\Delta^{14}\text{C}$  changes, indicating that DOC is indeed under internal control in the Hudson River.

In estuaries, isotopic mixing curves (as a function of salinity) can be used to evaluate carbon dynamics (Spiker, 1980).  $\Delta^{14}\text{C}$  or  $\delta^{13}\text{C}$  mixing curves are produced using both the total DOC concentration and isotopic composition (I) of the riverine (r) and high-salinity/marine (m) end-members. The conservative isotopic value for a sample at a known salinity is then calculated according to the following equation:

$$I_s = \frac{(f I_r \text{DOC}_r + (1-f) I_m \text{DOC}_m)}{\text{DOC}_{\text{mix}}} \quad (2)$$

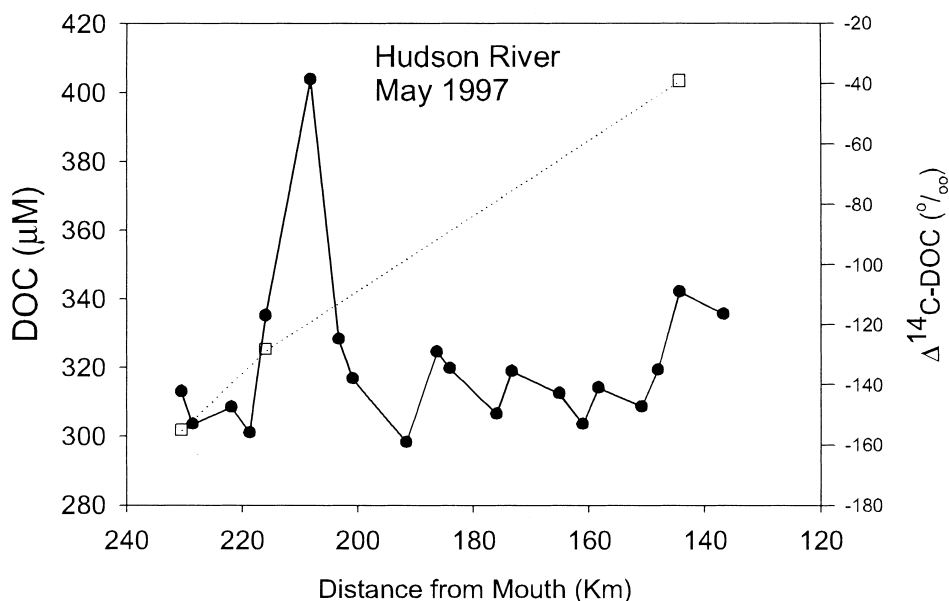


Fig. 3. Measurements of  $\Delta^{14}\text{C}$ -DOC and DOC along a transect in the tidal freshwater Hudson River. Solid circles are DOC concentrations, while open squares are  $\Delta^{14}\text{C}$ -DOC. Trends in  $\delta^{13}\text{C}$ -DOC were  $-25.5$ ,  $-26.8$  and  $-27.2\text{‰}$  for river kilometer 230, 216, and 144, respectively. For the same section of river,  $\Delta^{14}\text{C}$ -DIC and  $\delta^{13}\text{C}$ -DIC ranged from  $-36$  to  $-63\text{‰}$  and  $-5.6$  to  $-7.6\text{‰}$ , respectively (Raymond, Bauer, Cole, and Caraco, unpublished data).

where the riverine fraction,  $f$ , is calculated from salinity, and  $\text{DOC}_{\text{mix}}$  is the amount of DOC expected due to conservative mixing of the freshwater and marine end-members. In the York and Parker River estuaries, isotopic mixing curves indicate non-conservative DOC mixing (Fig. 4). In both estuaries, the  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  mixing curves could be caused by the removal of  $\delta^{13}\text{C}$ -depleted,  $\Delta^{14}\text{C}$ -enriched riverine DOC or the input of  $\delta^{13}\text{C}$ -enriched,  $\Delta^{14}\text{C}$ -depleted autochthonous DOC. In the York, using a three end-member (i.e. freshwater + terrestrial, marine, autochthonous) isotopic mixing model that employed both  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  (Raymond and Bauer, in press) predicted that 20–38% of the DOC at the mouth of the York estuary (salinities of  $\sim 18$ ) was of riverine (terrestrial + freshwater) origin, while 38–56% was added internally, depending on the isotopic values assigned to the autochthonous DOC. Measurements of  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  of DOC and DIC and marsh organic matter indicate that the internal sources originated from estuarine phytoplankton and marshes. In the York conservative mixing predicts that  $\sim 65\%$  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) report that on average estuarine bacteria utilize only  $\sim 10\%$  of York riverine DOC, therefore a second DOC sink is required to meet the large losses predicted by the isotopic mixing model.

In both of the above cases, the riverine DOC losses were not always evident in the mixing curves of DOC concentrations (i.e. vs. salinity) alone. In fact in the York River estuary, DOC measurements indicate the net estuarine input of DOC (Raymond and Bauer, in press). The intense processing of DOC in rivers and estuaries is in direct contrast to the idea that DOC undergoes little change, and mixes conservatively during its transport through estuarine systems (Mantoura and Woodward, 1983).

## 6. Carbon isotopic studies in the coastal ocean

For purposes of the present discussion, the coastal ocean is defined as continental shelf waters from the point of discharge from an estuary or bay to the 200 m isobath. The coastal ocean represents perhaps one of the most challenging environments in which to evaluate the sources of organic matter to the standing stocks of DOC and POC due to the multiple potential input terms (Hedges and Keil, 1999). These include terrestrial and soil organic matter, in situ production within both rivers and estuaries (Valiela, 1995), wet and dry deposition from the continental air masses (Willey et al., 2000), and in situ shelf production (Walsh 1989, 1991). Each of these component inputs may contain DOC and POC of

similar  $\delta^{13}\text{C}$ , yet having very different ages ( $\Delta^{14}\text{C}$ ) as a result of separate reservoir and storage effects within different portions of the individual environments (Trumbore and Druffel, 1995). For example, estuarine sediments may serve as storage and aging reservoirs for both DOC and POC until such time as major discharge events cause much of this sedimentary DOC and POC to be reintroduced to the water column and exported to the coastal ocean (Ruzecki, 1981; Schubel and Pritchard, 1986).

The relatively few studies in which paired  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  measurements of DOC and POC have been made in the coastal ocean are shown in Table 2. For DOC, studies include those in which the total DOC was analyzed, as well as those in which the component UDOC was analyzed. As can be seen, the ranges in  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values are considerable between, as well as within, these different systems. Two major features of these limited data (available for two coastal sites only) are noted. First, the suspended POC is significantly more enriched in  $\Delta^{14}\text{C}$  than DOC (opposite of the river relationship), and second, the POC has a broader range, and is more depleted in  $\delta^{13}\text{C}$  values (with the exception of the single depleted UDOC sample in the southern Mid-Atlantic Bight), than the DOC (Table 2). In the first of these studies (Williams et al., 1992), the  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values for total DOC from the California Continental Borderland shelf (Table 2) closely resemble values observed previously for the open central North Pacific (Williams and Druffel, 1987), suggesting relatively small inputs of non-oceanic DOC and POC to this system. Conversely, the  $^{14}\text{C}$ -enriched POC has relatively low  $\delta^{13}\text{C}$  values. This may be contrasted to the much broader range in both  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values in DOC and POC from coastal systems (e.g. east coast U.S.) where there is a greater range in potential inputs from rivers, estuaries, sediments as well as oceanic waters (Table 2).

The utility of paired carbon isotopes in complex environments such as the coastal ocean is that they represent a dual carbon isotope approach, much in the same way that multiple isotopes of different elements have been used to delineate sources of organic matter in estuaries and coastal systems (Fry and Sherr, 1984; Peterson and Howarth, 1987; Michener and Schell, 1994; Kwak and Zedler, 1997). The advantage of using multiple isotopes of the same element is that they may be used to trace more specifically that element (e.g. carbon), rather than generic organic "matter". As an example of this approach for employing  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  simultaneously for assessing carbon sources and inputs to DOC, Fig. 5a illustrates the  $\Delta^{14}\text{C}$  vs.  $\delta^{13}\text{C}$  distributions of DOC for waters of the Mid-Atlantic Bight continental margin (Bauer et al., in press). It can be seen that the  $\Delta^{14}\text{C}$  vs.  $\delta^{13}\text{C}$  distributions of DOC in shelf and slope surface waters lie within the values of the pre-



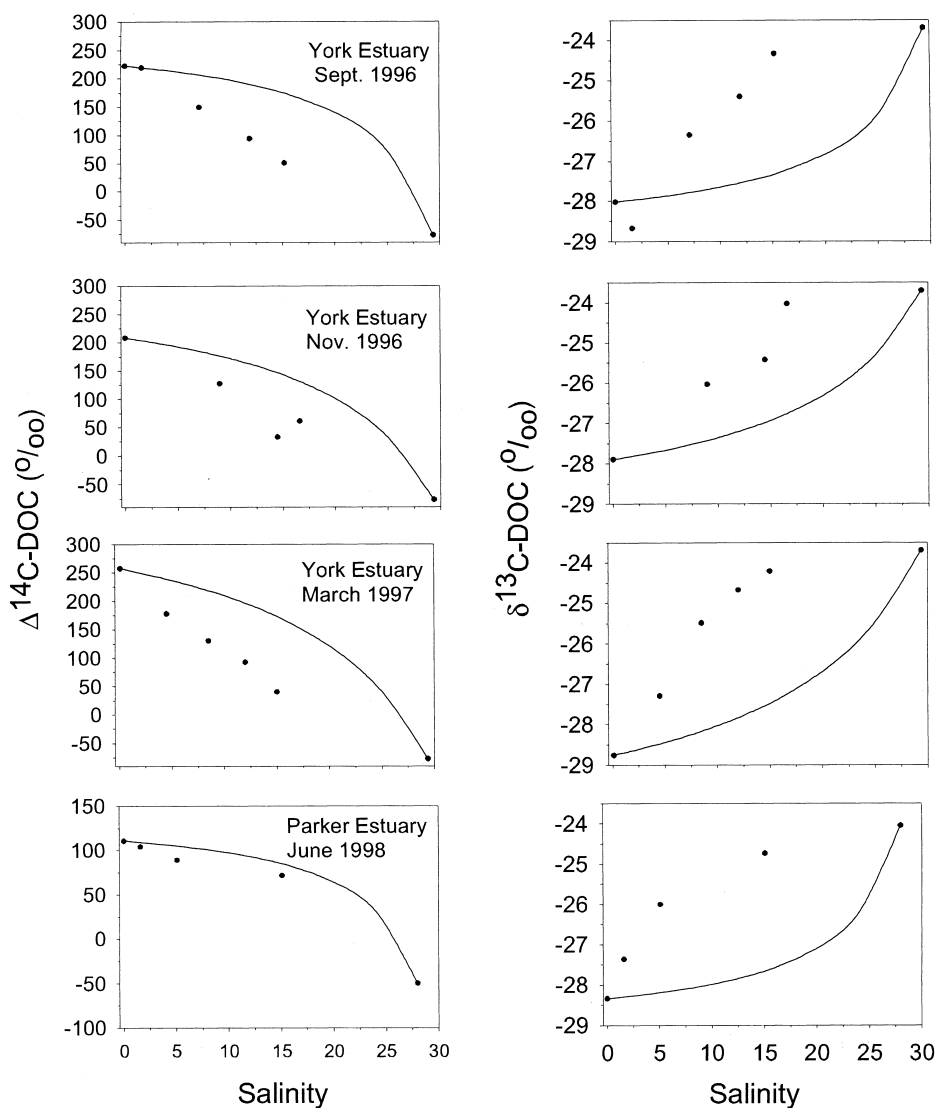


Fig. 4. Measurements of  $\Delta^{14}\text{C-DOC}$  along the salinity gradient in the York (Virginia) and Parker (Massachusetts) estuaries. The solid lines represent the calculated conservative isotopic mixing curves (see text for explanation), while the circles represent measurements. For the York, the seaward end-member is a sample from the Chesapeake Bay mouth (data from Raymond and Bauer (in press), Bauer et al. (in press) and Raymond, Bauer and Hopkinson (unpublished data)).

sumed (and measured) potential sources of DOC to this system. Thus, within the constraints of the available measurements, it is reasonable to a first approximation that shelf DOC is comprised of various admixtures of these potential sources. A similar feature may be observed for POC in the Mid-Atlantic Bight (Fig. 5b), where the  $\Delta^{14}\text{C}$  vs.  $\delta^{13}\text{C}$  distribution also lies within the values for the potential sources of POC to these waters.

In order to evaluate the relative contributions of the different potential sources of DOC and POC to the observed  $\Delta^{14}\text{C}$  vs.  $\delta^{13}\text{C}$  distributions, a two-isotope,

three-source mass balance mixing model (Kwak and Zedler, 1997; Bauer et al., in press) may be applied, of the general form

$$I_{\text{OC}} = f_1 I_{\text{OC}1} + f_2 I_{\text{OC}2} + (1-f_1-f_2) I_{\text{OC}3}$$

where  $I_{\text{OC}}$  is the isotopic composition ( $\Delta^{14}\text{C}$  or  $\delta^{13}\text{C}$ ) for an organic carbon pool (DOC or POC) from the MAB samples for each of the identified potential sources. The value  $f$  is the relative contribution of each of the three potential sources to the organic matter pool

Table 2

Ranges in published values of paired  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  measurements of DOC and suspended POC in the coastal ocean. Values are for total DOC and total POC except where noted

System	$\Delta^{14}\text{C}$ range (‰)	$\delta^{13}\text{C}$ range (‰)	Reference
DOC			
CA Basins, shelf	–197 to –323	–21.9 to –22.2	Williams et al. (1992)
Mid-Atlantic Bight	–39 to –272	–21.9 to –22.9	Bauer et al. (in press)
S. Mid-Atlantic Bight (HMW, > 1kD)	–89 to –336	–20.2 to –26.9	Guo et al. (1996)
Deep MAB (HMW, > 10kD)	–6 to –132	–22.7 to –22.9	Guo et al. (1996)
Gulf of Mexico (HMW, > 1kD)	–46 to –273	–21.5 to –23.5	Santschi et al. (1995)
POC			
CA Basins, shelf	102 to 110	–23.6 to –25.3	Williams et al. (1992)
Mid-Atlantic Bight	78 to –45	–19.9 to –24.3	Bauer et al. (in press)

(DOC or POC) in the MAB samples, and  $f_1 + f_2 + f_3 = 1.0$ . Since there are two unknowns ( $f_1$  and  $f_2$ ) in Eq. (1), the equation must be solved simultaneously using both  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$ . The contribution of the third potential source,  $f_3$ , is equal to  $(1 - f_1 - f_2)$ . In the case of the MAB, the three major (known) sources that can be shown to contribute to the DOC are material derived from offshore (represented by the Sargasso Sea), estuarine material (represented by the York River and Chesapeake Bay) and primary production (Fig. 5a). Calculations utilizing mean  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values from these three sources in the above equation may be used to infer that, while the majority (as much as ~97%) of DOC in Mid-Atlantic Bight shelf waters is comprised of material originating in waters from farther offshore (represented by the values from the Sargasso Sea; Bauer et al., 1992a), there must also be contributions from estuarine/Bay and contemporary primary production, due to the departure of the observed values from the open ocean values (i.e. they are  $^{14}\text{C}$ -enriched and  $^{13}\text{C}$ -depleted compared to the Sargasso values; Fig. 5a). In fact, we find that up to one-third of this DOC may be comprised of terrestrial/riverine organic matter, and as much as ~40% may arise from in situ shelf primary production.

For the POC (Fig. 5b), the results of such calculations using this three-source model (here, represented by York River POC, MAB surface sediments and MAB primary production) are quite different from those for DOC. We find that between half and all of the POC comes from from in situ shelf primary production, up to half is from /riverine/ terrestrial material, and a smaller fraction (up to ~25%) may originate from older, resuspended shelf sediments (Bauer et al., in press). Essentially none of the suspended POC in Mid-Atlantic Bight shelf waters originates from more oceanic sources.

These data emphasize the unique carbon isotopic signatures of DOC and POC in coastal waters and rivers and the variable contributions of different sources and ages of material to each pool. Such interpretations of isotope data would be difficult, if not impossible, using either a single isotope, or multiple isotopes of different elements.

## 7. Sources and ages of DOC utilized by bacteria

A paired  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  approach has also been used in a limited number of studies to evaluate the age and source of DOC that is utilized by heterotrophic bacteria in river and coastal systems. To our knowledge, only three such studies have been undertaken. The first approach has already been discussed above — that is, the use of estuarine mixing curves (i.e. as a function of salinity) can provide information on the age and  $\delta^{13}\text{C}$  signatures of DOC being both removed as well as added to the water column during the transport of river and estuarine waters (Raymond and Bauer, in press).

A second approach is to examine the isotopic compositions of DOC in time series incubation experiments during utilization by bacteria. The loss of DOC (due to bacterial respiration and assimilation), coupled with changes in its isotopic composition during utilization, may be used for simple mass-balance calculations of the isotopic signature of the DOC utilized by bacteria. An example of this is shown in Fig. 6a. It may be seen that in all cases, a  $^{14}\text{C}$ -enriched component of the DOC is being utilized. Furthermore, as more DOC is utilized by bacteria, the shift in  $\Delta^{14}\text{C}$  is greater (Fig. 6b). This relationship is consistent with bacteria utilizing a fraction of DOC that is younger than the remaining DOC throughout the degradation process.

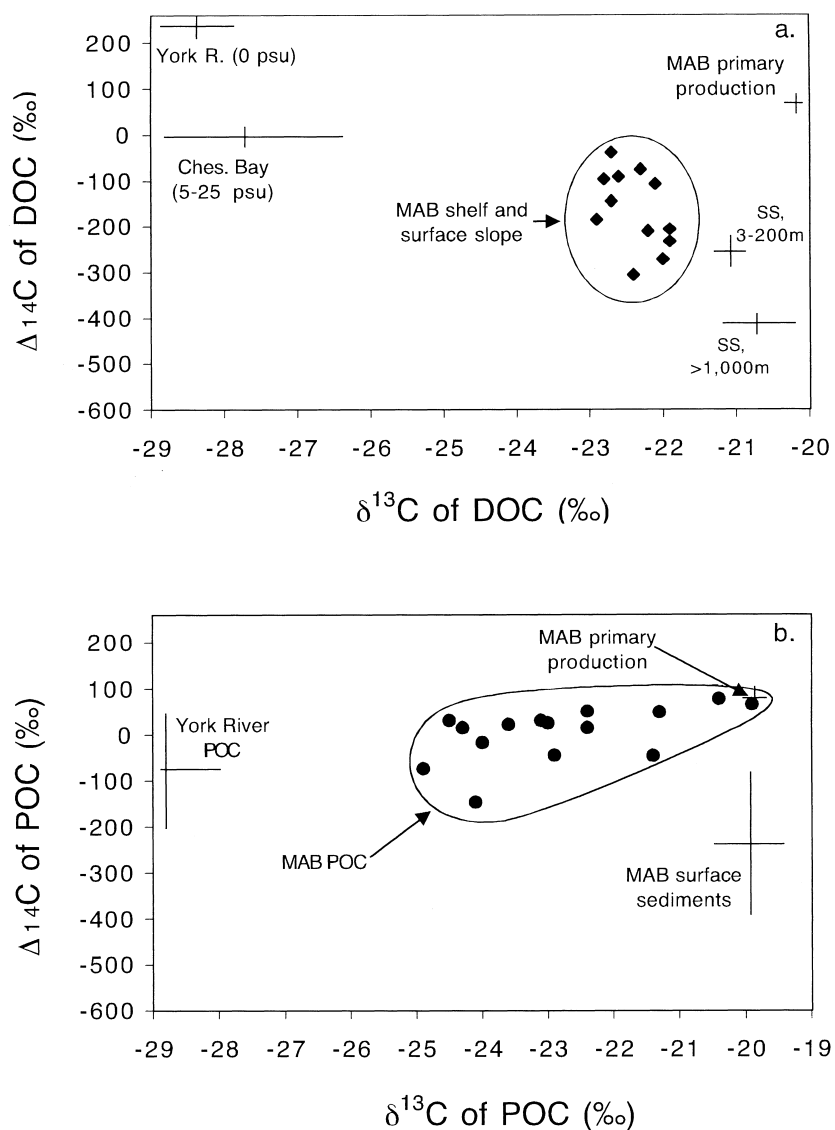


Fig. 5. Paired  $\Delta^{14}\text{C}$  vs.  $\delta^{13}\text{C}$  distributions in coastal waters of the Mid-Atlantic Bight, April 1994, for (a) DOC and (b) suspended POC. Isotope values for potential sources of DOC (panel a) were obtained from the following: York River total DOC — Raymond and Bauer (2001); Chesapeake Bay > 1 kD material — Guo et al. (1996); Sargasso Sea (SS) total DOC — Bauer et al. (1992a, b) and Druffel et al. (1992); MAB primary production — based on  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values for DIC in in shelf surface waters (Bauer et al., in press). Isotope values for potential sources of suspended POC (panel b) were obtained from the following sources: York River suspended POC — Raymond and Bauer (2001); MAB surface sediments — Tanaka et al. (1991) and Anderson et al. (1994); MAB primary production — based on  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values for DIC in in shelf surface waters (Bauer et al., in press). Figure adapted from Bauer et al. (in press).

Finally, a third approach measures the actual isotopic composition of the bacteria themselves. Most commonly, the nucleic acid component of bacteria has been extracted and analyzed (Coffin et al., 1989, 1993). To our knowledge, the bacteria from only a single coastal environment have been measured for paired  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  measurements (Cherrier et al., 1999). The results

(Fig. 7) also indicate that bacteria from this estuary assimilate into their biomass a more  $^{14}\text{C}$ -enriched component ( $\Delta^{14}\text{C} = 120\text{‰}$ ) than the bulk DOC ( $\Delta^{14}\text{C} = 22\text{‰}$ ), which is consistent with the findings of Raymond and Bauer (2001). The mean  $\delta^{13}\text{C}$  signature ( $-20.9\text{‰}$ ) of these same nucleic acids indicates that this  $^{14}\text{C}$ -enriched material has a relatively marine signature,

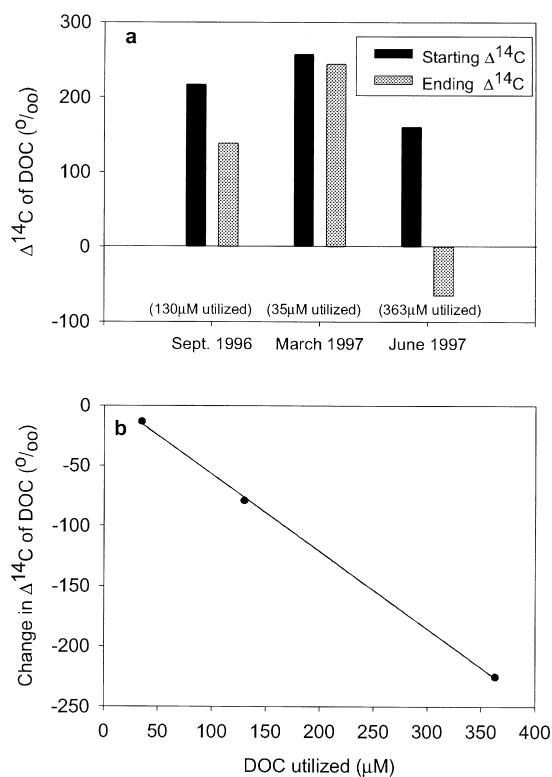


Fig. 6. Results from three  $\Delta^{14}\text{C}$ -DOC utilization experiments performed in the York River (adapted from Raymond and Bauer, 2001). Incubations were performed on filtered (0.7  $\mu\text{m}$ ) York River freshwater, and were carried out in the dark at in situ temperatures (23°, 10°, and 20°C for the September, March, and June experiments, respectively). (a) The concentrations of DOC and  $\Delta^{14}\text{C}$ -DOC values were measured at the beginning and end of each incubation. Values in parentheses indicate the amounts of DOC utilized by bacteria during each long-term incubation. September 1996 and March 1997 incubations both lasted for 60 days, while the June 1997 incubation lasted for 365 days. The smaller DOC and  $\Delta^{14}\text{C}$  changes in the March 1997 incubation were likely due to low (10°C) incubation temperatures. The percentages of DOC used in these incubations were 15, 8, and 63% for the September, March and June, incubations respectively. (b) The change in  $\Delta^{14}\text{C}$  vs. the amount of DOC utilized by bacteria for incubations in Fig. 1a. The strong relationship ( $r^2=0.99$ ,  $P<0.05$ ) indicates that as bacteria utilize greater amounts of DOC, the fraction remaining becomes progressively depleted in  $\Delta^{14}\text{C}$ .

suggesting that estuarine bacteria may rely in some instances on recently produced marine DOC, as opposed to more refractory, terrestrially influenced DOC ( $\delta^{13}\text{C}=-25.7\text{‰}$ ). We also cannot exclude the possibility that these observed nucleic acid  $\delta^{13}\text{C}$  values arise from admixtures of multiple DOC sources found within estuaries, e.g. freshwater algae, terrigenous  $\text{C}_4$  plant material, etc. rather than from marine phytoplankton and terrigenous  $\text{C}_3$  plant material.

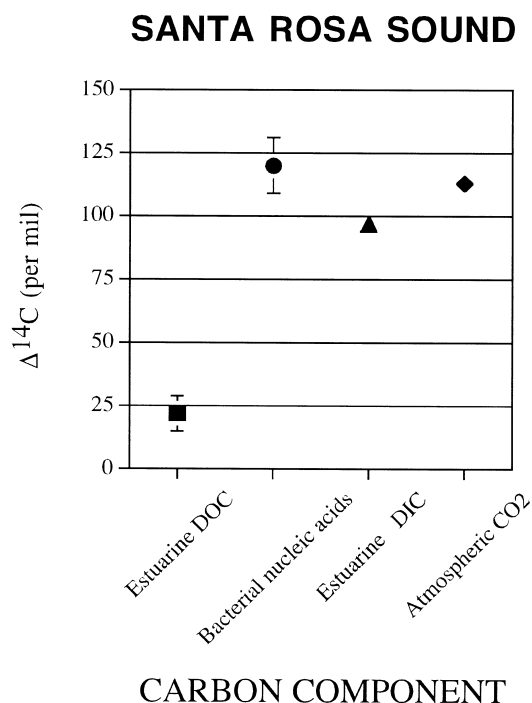


Fig. 7. Mean  $\Delta^{14}\text{C}$  values of bacterial nucleic acids and potential sources of carbon to bacteria in an estuary, Santa Rosa Sound, FL. Contemporary organic matter produced by recent primary production would be expected to have  $\Delta^{14}\text{C}$  values close to bulk DIC (estuarine phytoplankton) or atmospheric  $\text{CO}_2$  (land plants). Figure adapted from Cherrier et al. (1999).

The preferential utilization of young DOC may have important implications for the global carbon budget. However, it is currently unknown if this pattern holds with older DOC pools found in the coastal and open ocean. There is some intriguing indirect evidence that appears to support this possibility. All  $\Delta^{14}\text{C}$ -DOC values from the Mid-Atlantic Bight, and east coast rivers and estuaries are graphed against DOC concentrations in Fig. 8. According to Fig. 8, as DOC concentrations ultimately decline due to removal and mixing with the coastal ocean waters, the  $\Delta^{14}\text{C}$  of DOC becomes correspondingly depleted. However the age/DOC relationship is not linear, which may be explained by the preferential removal of  $^{14}\text{C}$ -enriched young material and the selective preservation of old DOC along the entire DOC continuum.

## 8. Conclusions

The rivers reported above represent systems of varying annual discharge, watershed size, land-use patterns, and surficial geology. Findings demonstrate significant spatial and temporal variation in the  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$

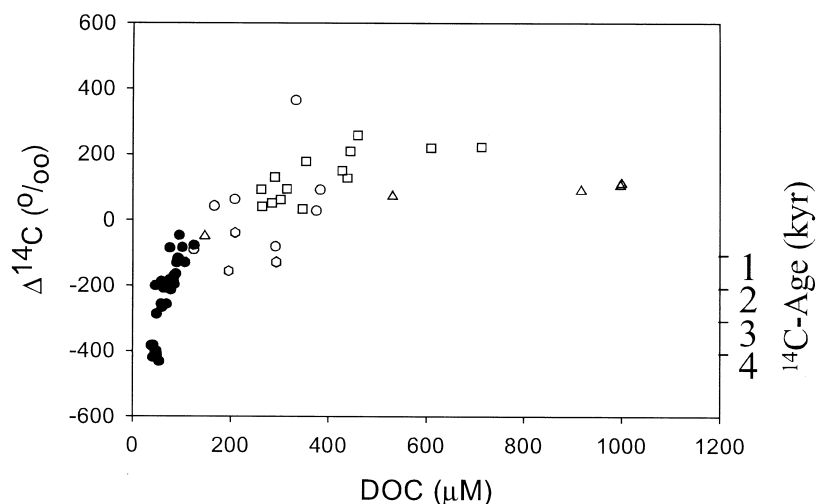


Fig. 8.  $\Delta^{14}\text{C}$ -DOC vs. DOC concentration from riverine, estuarine and coastal samples from the Mid-Atlantic Bight region. The closed circles are from the ocean margin region (Bauer et al., submitted), the open squares are from the York River estuary (Raymond and Bauer, submitted), the open triangles are from the Parker estuary (freshwater samples from Raymond and Bauer, submitted, estuarine samples for Raymond, Bauer and Hopkinson, unpublished data), the open hexagons are from the Hudson River (Raymond and Bauer, submitted), while the open circles are Chesapeake Bay tributaries from Spiker and Rubin (1975).

values of riverine organic matter, yet the database is too small to elucidate the causative factors and parameters controlling the isotopic distributions. In spite of these limitations, results indicate that rivers export a fraction of old,  $^{14}\text{C}$ -depleted DOC and POC to the oceans, which disputes the current paradigms that rivers exclusively export  $^{14}\text{C}$ -enriched organic matter to the oceans (Hedges et al., 1986) and the old age of oceanic DOC can be attributed entirely to aging in the ocean basins themselves (Druffel et al., 1992). Isotopic mixing curves and incubation experiments also suggest that for DOC, riverine and estuarine processes can significantly alter both  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values by preferentially removing the younger pools. As a result only a percentage of riverine/terrestrial organic matter reaches the ocean (we estimate that this percentage may be as high as 30% in the Atlantic). Furthermore, preferential utilization of a young organic matter fraction by bacteria during transport represents a mechanism for delivering material to the oceans that is older than the bulk material found in rivers.

Estuaries and coastal systems have two important functional roles in the global carbon budget. They are sites where large amounts of organic matter are both removed and added by biotic and abiotic pathways, and where the ages of soil and riverine organic matter may be altered significantly. Future studies should concentrate on: (a) understanding the cross-system variation in riverine POC and DOC ages; (b) determining the relative importance of abiotic processes in removing riverine organic matter in estuaries; (c) further assessing the  $^{14}\text{C}$  values of DOC and POC in rivers and coastal systems in order to understand how both natural and

anthropogenic factors may affect the sources and turnover times in regional and global C budgets; and (d) determining if the preferential removal of young organic matter by bacteria is an important process across systems.

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