



Controls on the variability of organic matter and dissolved inorganic carbon ages in northeast US rivers

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Received 24 November 2003; received in revised form 23 April 2004; accepted 30 June 2004

Abstract

The use of natural ^{14}C in aquatic and marine studies provides unique source, turnover and processing information with respect to local, regional and global carbon budgets. The number of ^{14}C analyses in many aquatic ecosystems is small, however, thus limiting the full potential of ^{14}C as a tool in carbon studies in these systems. This is particularly true for rivers, which form key linkages between terrestrial and oceanic systems. As part of our on-going studies, radiocarbon-based measurements of dissolved and particulate organic carbon (DOC and POC, respectively), as well as dissolved inorganic carbon (DIC), are being conducted in a group of northeast US rivers. The values for bulk $\Delta^{14}\text{C}$ -DOC, and $\Delta^{14}\text{C}$ -POC, $\Delta^{14}\text{C}$ -DIC and their associated $\delta^{13}\text{C}$ ratios are reported for 64 measurements on seven different river systems. While the examined rivers occupy a relatively small geographic area, they individually export both ancient and fully modern post-bomb C to the coastal ocean. The large ranges in $\Delta^{14}\text{C}$ for DOC, POC and DIC point to large spatial and temporal variability in the relative inputs of fossil vs. contemporary C, and the processing of each, in this geographically contiguous set of rivers. Although this represents a fairly well-studied group of rivers with respect to carbon ages, the sample number still precludes an in-depth understanding of specific sources of different aged components to these rivers, or to river systems in general. The collective data permit some preliminary assessments concerning the relative importance of wetlands, ancient uplifted sedimentary marine OM, and within-system modification as important potential controls on riverine carbon ages.

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Keywords: Organic matter; Carbon; ^{14}C age; River; Mid-atlantic bight

1. Introduction

Rivers and estuaries link the terrestrial and ocean carbon (C) cycles and are sites of intense organic

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matter (OM) processing, effectively altering the amounts, isotopic and chemical characteristics, and timing of OM discharged to the coastal ocean (Aller, 1998; Aller et al., 1996; McKee, 2001). This linkage is a critical part of both the oceanic and terrestrial C cycles. Conceptually, rivers have been thought to be responsible for exporting mostly young terrestrial organic matter, originating from contemporary terrestrial primary production, to the oceans. This view initially appeared to be confirmed by a limited number of studies showing that riverine OM contained modern, post-bomb C (Hedges et al., 1986; Spiker and Rubin, 1975), with one recent analysis also arguing for predominantly young riverine carbon export to the coastal oceans (Mortazavi and Chanton, 2004). Since oceanic OM is thousands of years in age (Bauer et al., 2002; Druffel et al., 1992), the great age difference between riverine and seawater OM also appears to support other qualitative arguments (e.g., low lignin concentrations and enriched ^{13}C values; Opsahl and Benner, 1997; Opsahl et al., 1999; Williams and Gordon, 1970) against significant contributions of terrestrial OM to the large old oceanic OM pool. Thus, it follows that young riverine OM (which is assumed in general to be biologically reactive) must be utilized in rivers, ocean margins, or surface ocean waters and the old ^{14}C age of oceanic OM must be entirely due to the aging of marine OM within the ocean basins themselves (Bauer et al., 1992; Druffel et al., 1992).

An alternate and emerging view is that a significant proportion of the export flux of riverine OM to the coastal ocean may consist of highly aged material (Blair et al., 2003; Dickens et al., 2004; Kao and Liu, 1996; Leithold and Blair, 2001; Masiello and Druffel, 2001; Raymond and Bauer, 2001b; Raymond and Bauer, 2001c). These new findings suggest a fundamental shift in conceptual models of riverine OM fluxes with respect to both the terrestrial and oceanic C budgets, yet data are generally inadequate for a thorough assessment of the relative importance of old vs. young carbon export to individual ocean margins or to margins globally.

Although often treated as such, rivers are also not simple conduits transporting terrestrial OM to the ocean. Studies designed to investigate the character of OM exported from rivers, and internal modifica-

tion by autochthonous photosynthesis and microbial heterotrophy, have all demonstrated significant changes in OM composition and quantity during transport (Cifuentes et al., 1988; Hopkinson and Vallino, 1995; Howarth et al., 1996; Kemp et al., 1997; Kirchman and Borch, 2003; Mannino and Harvey, 1999; Moran et al., 1991; Moran et al., 1999; Peterson et al., 1994; Raymond and Bauer, 2001a). Furthermore, studies have shown that the amounts of OM discharged from rivers and estuaries are not simply a function of terrestrial inputs, but are also under internal control (Findlay et al., 1996; Fisher et al., 1998; Newbold et al., 1982; Raymond and Bauer, 2001a; Sanudo-Wilhelmy and Taylor, 1999). Processes contributing to the major transformations and exchanges of organic C in rivers and estuaries include microbial utilization (Coffin et al., 1993; Moran et al., 1999; Raymond and Bauer, 2000; Zweifel, 1999), photochemistry (Amon and Benner, 1996; Mopper et al., 1991; Moran et al., 2000), desorption and adsorption (Hedges and Keil, 1999), and primary and secondary production (Baines and Pace, 1991; Cai, 2003; Cole et al., 1988; Ducklow and Shiah, 1993; Findlay et al., 1991; Hopkinson et al., 1999; Smith and Hollibaugh, 1997).

This paper presents a synthesis and interpretation of the isotopic information and variability observed for DOC, POC and DIC in a regional set of rivers discharging to a common ocean margin, the Middle Atlantic Bight (MAB). The goal of this study is to (i) better constrain the sources, character, and ages of OM exported from the continents to rivers, (ii) evaluate the quantitative and qualitative transformation of this material during its residence time within rivers and estuaries, and (iii) estimate the ultimate signatures of DOC and POC entering the coastal ocean from land via rivers. The findings presented here represent one of the largest ^{14}C datasets for any regional group of rivers globally. In spite of this, the high within- and across-system variations observed for ^{14}C precludes a complete mechanistic description of the controls on riverine carbon ages. In-depth seasonal and transect studies, coupled with studies of small streams exporting OM and C from different landscape end-members will be critical for future progress in this area.

2. Study site and methods

Numerous sites were sampled over a 5-year time period as part of this study. Site descriptions and details of the sampling locations of the Parker River, Hudson mainstem and York River estuary are available elsewhere (Cole and Caraco, 2001; Raymond and Bauer, 2001a; Raymond and Hopkinson, 2003). The Susquehanna sample was collected south of the city of Dauphin (PA), while the Delaware sample was obtained north of Port Jervis (NY). In addition, multiple samples were obtained from small streams in the Hudson River watershed (Fig. 1). All samples were collected from surface waters according to the procedures outlined below.

2.1. Sample collection

Pre-cleaned (10% HCl and Nanopure water) 1 or 2-l polycarbonate bottles were used to collect water for $\Delta^{14}\text{C}$ analysis of total DOC. Samples for DOC analyses were filtered directly from surface water

through pre-combusted (500 °C for 4 h) 47-mm diameter Whatman quartz fiber filters (QFF; 0.8- μm nominal pore size) and frozen at -20 °C immediately after collection. Suspended POC was considered to be that fraction collected directly on the QFF filters. The filtered water samples for $\Delta^{14}\text{C}$ of DIC (500 ml) were poisoned with 100 μl of a saturated HgCl_2 solution and stored in gas-tight glass bottles in the dark at room temperature. All storage bottles and other materials (filters, forceps, etc.) that contacted the samples were pre-combusted at 525 °C for 4 h and stored in baked aluminum foil and air-tight plastic bags prior to use.

2.2. Dissolved organic carbon

Concentrations, $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ of DOC were determined by high-energy UV irradiation (2400 W) of 100 ml samples (Bauer et al., 1992; Raymond and Bauer, 2000). Briefly, samples were acidified to pH 2.5 with phosphoric acid and sparged with ultra-high purity nitrogen gas for 15 min to remove inorganic

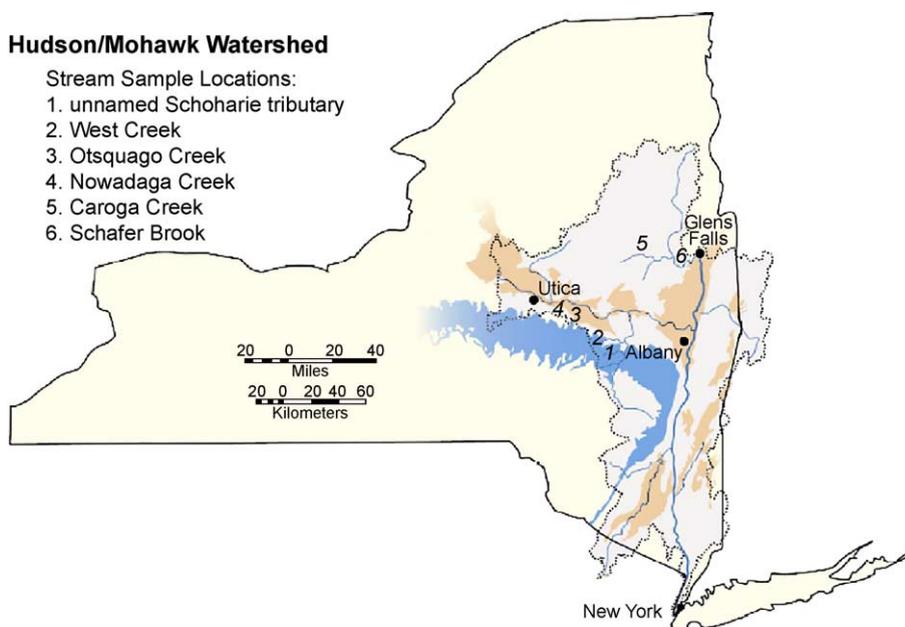


Fig. 1. Map of the Hudson River watershed. Ordovician shales are outlined in orange while Devonian shales are outlined in blue. The six small streams sampled as part of this study are labeled on the figure and depicted as black circles. The Mohawk River is the major tributary of the Hudson branching west just above Albany, while the Upper Hudson River is the secondary tributary of the Hudson, originating in the north and meeting the Mohawk just above Albany. The tidal freshwater Hudson is the region of the Hudson below the confluence of these two major tributaries.

carbon, saturated with ultra-high purity oxygen gas, and irradiated with a medium pressure mercury arc UV lamp (Canrad-Hanovia, Newark, NJ) for 2 h. The CO₂ generated from DOC oxidation was purified and collected on a vacuum extraction line. Concentrations of DOC were determined using a calibrated Baratron absolute pressure gauge (MKS Industries) to measure CO₂ pressure on the vacuum line. Following quantification, the sample was split approximately 10:1 into two break-seal tubes, with the larger portion being used for $\Delta^{14}\text{C}$ analysis and the smaller portion being used for $\delta^{13}\text{C}$ analysis. Recoveries and blanks were assessed periodically by oxidizing dissolved organic standards (oxalic acid, glucose and fulvic acids) using the same procedure as for water samples. Recoveries were all $\pm 1\%$, and $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of standards were within the analytical instrumental error, indicating that the method attains accurate concentration and isotopic results and that there was no significant blank contribution.

2.3. Suspended POC and DIC

Concentrations, $\Delta^{14}\text{C}$, and $\delta^{13}\text{C}$ signatures of suspended POC were measured from the same sample collections as DOC. The material collected on the quartz fiber filters was acidified overnight with 1% H₃PO₄ to remove carbonates, dried in vacuo, and the POC was oxidized to CO₂ by dry combustion with CuO and Ag metal at 850 °C in 9 mm quartz tubes (Sofer, 1980; Druffel et al., 1992). Filter blanks and backgrounds were measured on separate pre-baked filters, and the $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ ratios of the samples filters were corrected accordingly. Yields of CO₂ were quantified using an absolute pressure gauge on a vacuum extraction line, and aliquots were taken for $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ measurements. Samples for $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ analysis of DIC (250 ml) were acidified using 85% H₃PO₄. The sample was sparged using ultra-high-purity N₂ gas, the evolved CO₂ was collected cryogenically and purified on a vacuum extraction line, and the sample was split as above for $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$.

2.4. Isotopic analyses

The $\Delta^{14}\text{C}$ analyses of the carbon recovered from these procedures were performed by accelerator mass

spectrometry (AMS) at the Center for AMS at Lawrence Livermore National Laboratory (LLNL) or the National Ocean Sciences AMS at Woods Hole Oceanographic Institution. The CO₂ derived from all samples was converted to graphite using H₂ gas and cobalt catalyst (Vogel et al., 1987). Total measurement uncertainties for $\Delta^{14}\text{C}$ analyses of these samples were typically $\pm 5\text{--}10\%$. The $\delta^{13}\text{C}$ measurements of DOC were made using a Finnegan Delta S isotope ratio mass spectrometer, while those for suspended POC and DIC were made using a Micromass 602E unit, or for Hudson headwater streams, a Finnegan Delta S+. All instruments gave an analytical precision of better than 0.1‰.

3. Results

3.1. Variability in $\Delta^{14}\text{C}$ signatures of DOC and POC within and among rivers exporting to the MAB

Dissolved organic carbon concentrations ranged from 113 to 753 μM and averaged $403 \pm 245 \mu\text{M}$ across the river systems studied (Table 1). The York and Parker Rivers consistently displayed elevated, bomb-enriched, young $\Delta^{14}\text{C}$ -DOC signatures (Table 1) compared to the other systems. In contrast, the Hudson (i.e., the tidal freshwater Hudson site) ranged from near-modern present-day atmospheric (October 1998) $\Delta^{14}\text{C}$ values, to highly depleted values (Table 1). The single values obtained for the Susquehanna and Delaware also indicate the presence of ^{14}C -depleted DOC (Table 1). For the York, Parker and Hudson, all of which were sampled on at least three separate occasions, the ranges of $\Delta^{14}\text{C}$ -DOC values within each system were 98‰, 114‰, and 80‰, respectively. Averaging all rivers from this study yields a $\Delta^{14}\text{C}$ -DOC of $-29 \pm 175\%$, while the average flow-weighted $\Delta^{14}\text{C}$ -DOC signature (i.e., a discharge weighted average) is -128% .

Particulate organic carbon concentrations ranged from 13 to 106 μM and averaged $53 \pm 38 \mu\text{M}$ across systems (Table 1) providing a DOC:POC ratio of 8, which is well above the global average of ~ 2 (Meybeck, 1982). With the exception of the Delaware, which was only sampled once, each system had at least one pre-bomb or near-pre-bomb $\Delta^{14}\text{C}$ -POC value (Table 1). The most depleted $\Delta^{14}\text{C}$ -POC value

Table 1
Concentrations and isotopic values of the major forms of carbon in northeast US rivers

System	DOC			POC			DIC		
	μM	$\Delta^{14}\text{C}$	$\delta^{13}\text{C}$	μM	$\Delta^{14}\text{C}$	$\delta^{13}\text{C}$	μM	$\Delta^{14}\text{C}$	$\delta^{13}\text{C}$
<i>Susquehanna</i>									
4/00	113	-236	-27.1	20	-61	-25.6	315	nd	-8.5
<i>Hudson</i>									
7/98	313	-158	-25.5	118	-447	nd	642	-63	-7.6
10/98	343	13	-27.0	43	-425	nd	340	-69	-11.2
4/00	448	-137	-27.0	43	-156	-26.8	456	-6	-8.1
7/00	568	-73	-27.2	14	-101	-28.9	632	-11	-11.1
<i>Delaware</i>									
4/00	242	-114	-27.1	44	6.0	-25.6	223	43	-7.0
<i>York</i>									
7/96	701	216	-28.8	70	24	nd	458	164	-14.6
11/96	443	208	-27.9	30	-38	-28.2	454	110	-7.5
3/97	390	257	-28.0	nd	nd	nd	nd	nd	nd
6/97	435	159	-28.0	218	-190	-30.0	nd	nd	nd
<i>Parker</i>									
6/98	986	111	-28.4	142	-94	-30.0	nd	nd	nd
10/98	503	97	-29.0	36	-190	-33.7	928	75	-15.5
7/00	1001	-3.5	-29.0	104	-46	-31.5	957	53	-11.8
9/00	746	99	-30.3	47	47	-32.9	945	89	-14.0
4/00	531	104	-28.5	18	-160	-30.9	480	93	-13.8

* all isotopic values are per mil, nd=no data.

(-447‰) was from the Hudson. Averaging all rivers gives a $\Delta^{14}\text{C}$ -POC of $-99\pm 108\%$, while the average flow-weighted $\Delta^{14}\text{C}$ -POC signature was -67% for these rivers.

Dissolved inorganic carbon concentrations averaged $605\pm 398\ \mu\text{M}$ across all systems (Table 1). With the exception of the Hudson, all rivers were enriched in $\Delta^{14}\text{C}$ -DIC (Table 1). The average $\Delta^{14}\text{C}$ -DIC value was $42\pm 73\%$, with a flow-weighted average signature of -2% . Average $\delta^{13}\text{C}$ values for all systems for DOC, POC and DIC were $-27.6\pm 0.9\%$, $-28.3\pm 2.3\%$, and $-10.0\pm 2.6\%$, respectively, corresponding to flux-weighted $\delta^{13}\text{C}$ values of -27.0% , -26.4% , -9.1% , respectively.

On two occasions, we also sampled the two major tributaries of the tidal Hudson River, the Upper Hudson and Mohawk, which are approximately equal in annual water discharge (Table 2). The Mohawk River is consistently depleted in $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ for all carbon species compared to the Upper Hudson (Table 2). For DOC in April 2000, both the Upper Hudson and Mohawk were $\Delta^{14}\text{C}$ -depleted (-16% and -55% ,

respectively), with the Mohawk being 39% more depleted than the Upper Hudson (Table 2). In July 2000, both major tributaries were ^{14}C -enriched, with the Mohawk ($\Delta^{14}\text{C}=+11\%$) again being more depleted than the Upper Hudson ($\Delta^{14}\text{C}=+35\%$). Data from only a single sampling time is available for POC in these two tributaries, and the Mohawk ($\Delta^{14}\text{C}=-267\%$) was significantly depleted vs. the Upper Hudson ($\Delta^{14}\text{C}=-33\%$). Interestingly, the Mohawk was also more ^{14}C -depleted in DIC than the Upper Hudson, with both sampling dates having a $\Delta^{14}\text{C}$ offset of 47% .

Down-river changes in the isotopic composition of DOC and POC were investigated on three separate occasions in the Hudson River (Table 2). Organic carbon concentrations and isotopic signatures were measured at an upstream station just north ($\sim 5\ \text{km}$) of Albany, NY and a downstream station $\sim 100\ \text{km}$ south of Albany (Fig. 1) to evaluate changes in these parameters during the approximate monthly average transport time between these two stations. The general trend is for all carbon species to become more

Table 2
Concentrations and isotopic values of the major forms of carbon in the Hudson River watershed

	DOC			POC			DIC		
	μM	$\Delta^{14}\text{C}$	$\delta^{13}\text{C}$	μM	$\Delta^{14}\text{C}$	$\delta^{13}\text{C}$	μM	$\Delta^{14}\text{C}$	$\delta^{13}\text{C}$
<i>4/00</i>									
Upper Hudson	448	-16	-27.0	43	-33	-26.8	456	-6	-8.1
Mohawk	439	-55	-27.3	119	-267	-27.1	1307	-53	-9.7
Tidal Hudson -Above Albany	476	-137	-27.0	254	-156	-26.7	1372	-50	-10.0
<i>7/00</i>									
Upper Hudson	530	-35	-27.0	14	-58	-28.9	632	-11	-10.2
Mohawk	456	11	-27.5	19	nd	-31.7	1470	-58	-11.1
Tidal Hudson									
Above Albany	568	-73	-27.2	12	-101	-28.0	756	-58	-11.1
Below Albany	457	-110	-27.0	36	-96	-27.3	1303	-52	-10.5
<i>6/98</i>									
Tidal Hudson									
Above Albany	313	-158	-25.5	118	-447	nd	642	-63	-7.6
Below Albany	342	-40.6	-28.0	116	-98	-28.2	nd	nd	nd
<i>10/98</i>									
Tidal Hudson									
Above Albany	343	14	-27.0	43	-425	nd	nd	-69	-11.2
Below Albany	313	90	-26.9	41	-103	-29.5	nd	nd	nd

* all isotopic values are per mil, nd=no data.

enriched in ^{14}C during transit, indicating the potential for large temporal and/or spatial changes in $\Delta^{14}\text{C}$ values during riverine transport.

3.2. Small stream sampling in the Hudson River watershed

A selected group of small streams within the Hudson River watershed was sampled for carbon contents and isotopic ratios of the POC fraction only. The goal of this sampling was to assess the contributions of old OM from the weathering of ancient sedimentary rocks, one of the original hypotheses put forth by Raymond and Bauer (2001a) in trying to explain the old OM in certain rivers. Preliminary data from six small watersheds in the Upper Hudson and Mohawk valleys indicate that the depleted $\Delta^{14}\text{C}$ -POC values occurred in streams with significant watershed shale outcrops and were ~100‰ lower (Fig. 2) than in watersheds where such outcrops were absent. The lowest values were found in those parts of the system having the highest contribution from agriculture land use (Fig. 2). In addition, $\delta^{13}\text{C}$ -POC values were highest in the four

shale-influenced systems and lowest in the two crystalline rock drainages (Fig. 2).

4. Discussion

The export of organic carbon from watersheds to rivers is the result of a complex set of feedbacks between biological, chemical and geological processes. Assessing the relative importance of different watershed attributes to the ages of different forms of OM exported on a regional basis from land to rivers is key for incorporating these terms into models and budgets of both terrestrial C losses and coastal ocean C inputs. Currently, the type of assessment for the rivers reported here and elsewhere is still incomplete, however a few qualitative features and relationships may now be emerging.

4.1. Ancient sedimentary OM contributions to rivers

Previous studies in small mountainous rivers have demonstrated the export of ^{14}C -depleted POC and DOC (Kao and Liu, 1996; Leithold and Blair, 2001;

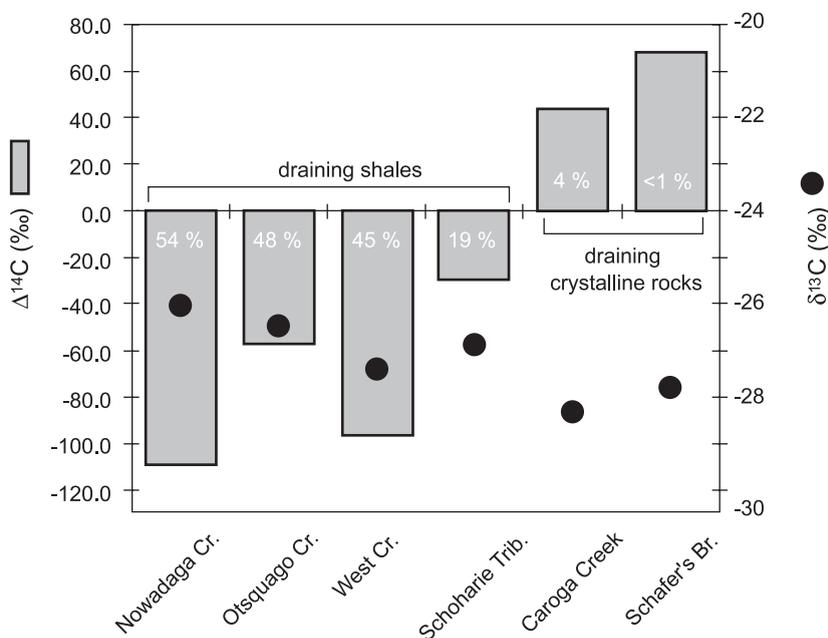


Fig. 2. $\Delta^{14}\text{C}$ -POC and $\delta^{13}\text{C}$ -POC for Hudson watershed small streams sampled in April 2003. Locations of each stream are shown in Fig. 1.

Masiello and Druffel, 2001). Common to these studies is the presence of OM-rich sedimentary rocks underlying the associated watersheds. Because of the episodically high erosion and discharge rates of small mountainous rivers, deep soil formation is inhibited and OM in freshly eroded bedrock can be transported with little if any remineralization, providing an extremely ^{14}C -depleted OC source to river OM pools (Blair et al., 2003).

Among the northeast US rivers (Table 1), two stand out in having particularly depleted $\Delta^{14}\text{C}$ signatures for DOM and POM: the Hudson (and even more conspicuously, its major tributary, the Mohawk) and the Susquehanna. In contrast to the small mountainous rivers, these rivers exhibit more extensive soil development, modest relief, and greater overall discharge that is distributed more evenly on an annual basis than small mountainous systems. In addition, they also exhibit longer residence times of water, dissolved and suspended load, and riverbed sediment. However, similar to the small mountainous rivers exporting highly aged OM, the northeast US rivers also drain watersheds underlain in part by ancient, OM-rich sedimentary rocks in the form of black shales. Several recent

studies have investigated changes in both the abundance and composition of ancient OM during weathering of black shales (Di Giovanni et al., 2002; Petsch et al., 2000; Petsch et al., 2001), using the assumption that lateral transport to streams is a potential sink for a portion of the weathered shale OM. Within our preliminary data set there is no evidence of ^{14}C -depleted river OM in any northeast US river in which the drainage basin is not underlain at least in part by ancient sedimentary rocks (Tables 1 and 2). This suggests a strong potential for an ancient terrestrial sedimentary contribution to these systems.

Our sampling of small watersheds (<250 km²) indicates the potential for significant (~10%) shale contributions to small stream systems (Fig. 2). That is, streams draining small watersheds with shale outcrops contain POC that is ~100‰ depleted relative to watersheds without shale outcrops. It is also notable that the shale watersheds have a greater percentage of their land use areas dedicated to agriculture (Fig. 2), in contrast to the non-shale sites which are almost entirely forested. Furthermore, the shale watershed with the greatest amount of agricultural development (Nowadega) also had the

most ^{14}C -depleted POM (Fig. 2). This is consistent with one of the original hypotheses of Raymond and Bauer (2001a), i.e., that agricultural practices may export older soil profiles to streams. However, in the case of agricultural watersheds with significant shale surficial geology, at least a portion of the OM in the soil profile may be derived from ancient sedimentary shale OM. In such cases, background sedimentary inputs of aged OM from soils may be established which are then supplemented by aged OM inputs from agricultural practices, exporting both aged soil OM and sedimentary OM that otherwise would have been stored and remineralized in soils. In summary, both current agricultural practices and weathering of ancient marine deposits may contribute to the pattern of older POC export from the shale sites in Fig. 2, however, the small size of this preliminary data set does not permit the differentiation of these two mechanisms. An important aspect of future research into this topic should therefore be to document the watershed factors that contribute to the export of ^{14}C -dead shale organic carbon to river systems and to scale the results from small watershed studies to larger watersheds and river systems.

4.2. The role of wetlands in modifying riverine OM age

Freshwater wetlands have long been argued to be one of the primary controls on the amount of DOC exported from watersheds to rivers (Kortelainen, 1993; Mulholland and Kuenzler, 1979; Raymond and Hopkinson, 2003). Recent studies, including the data presented here on the Parker River, also document that the DOC exported from wetlands is generally ^{14}C -enriched material associated with contemporary NPP (Palmer et al., 2001; Raymond and Hopkinson, 2003; Schiff et al., 1998). Thus, it appears that wetland watershed coverage may be a critical determinant of within-system seasonal and across-system spatial variation in DOC input and mean age.

Since European colonization, one of the most dramatic land cover changes in the United States has been associated with the loss of wetlands, with the spatial coverage of wetlands in the United States decreasing dramatically during the

past two centuries (Dahl, 1990). The loss has been particularly large in the MAB and Mississippi watersheds, with estimates of wetlands associated with the MAB watershed ranging from approximately 12% of watershed coverage in the 1780s, to <6% in the 1980s (Dahl, 1990). Wetland losses may be predicted to cause a shift in DOC age by reducing the relative contributions of these high-productivity systems as a significant ^{14}C -enriched DOC source to rivers. While a 6% reduction in wetland land cover is a small portion of the total surface area of the the MAB-associated watershed, the loss is compounded because wetlands may contribute up to 5–10-fold more DOC than other land use types (Mulholland and Kuenzler, 1979; Raymond and Hopkinson, 2003). The loss of wetlands from MAB watersheds could be responsible for as much as a 20–30% reduction in the amount of modern DOC exported to the MAB. Furthermore, because most human land uses that replace wetlands (agriculture, urban and suburban) could increase the export of stored and relic OM (Raymond and Bauer 2000), wetland loss may be effectively replacing a relatively large $\Delta^{14}\text{C}$ -enriched OM source with a smaller $\Delta^{14}\text{C}$ -depleted one.

4.3. DIC isotopic signatures and relationships to OM

The northeast US river systems possess a wide range of $\Delta^{14}\text{C}$ -DIC values (Table 1 and 2), from +164‰ in September 1996 in the York sample to –69‰ for the Hudson above Albany in October of 1998. The potential sources of DIC in river waters include atmospheric CO_2 , CO_2 derived from soil respiration and the decay of OM, and the dissolution of carbonate rocks, and isotopically these sources have unique $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signatures. $\delta^{13}\text{C}$ -DIC has previously been used as a tracer of DIC sources and sinks in streams and rivers (Finlay, 2003; Kendall et al., 1992; Quay et al., 1992; Tan and Edmond, 1993). Utilizing $\delta^{13}\text{C}$ in tandem with $\Delta^{14}\text{C}$ provides additional source and age information (Fig. 3).

There are multiple processes that can influence the isotopes of DIC in aquatic systems. Stream inorganic carbon dynamics are linked to the soils in the watershed they drain (Finlay, 2003; Jones and Mulholland, 1998). Soil interstitial water CO_2 con-

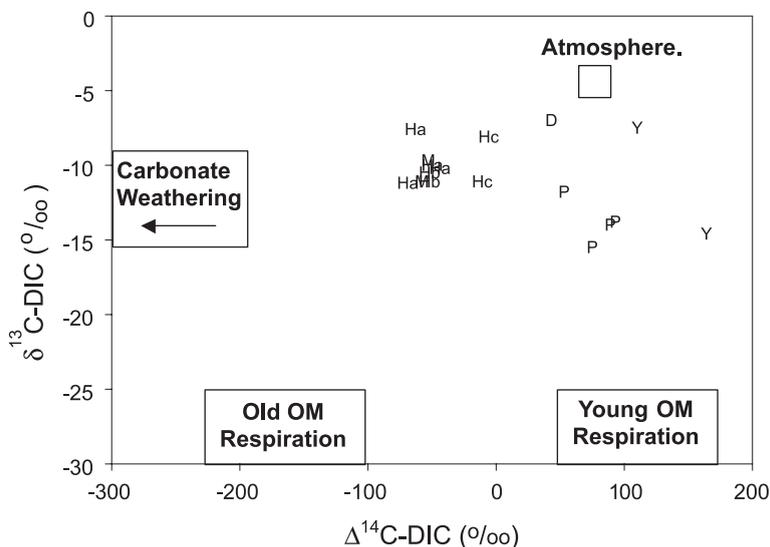


Fig. 3. $\delta^{13}\text{C}$ vs. $\Delta^{14}\text{C}$ for observed DIC signatures and potential DIC sources. The “D” is the Delaware River, the “Ha” symbols are the tidal Hudson River above Albany, the “M” symbols are the Mohawk River, the “P” symbols are the Parker River, the “Hb” symbols are the tidal Hudson River below Albany, the “Hc” symbols are the Upper Hudson River, while “Y” symbols are the York River.

centrations are generally much higher than atmospheric CO_2 and are controlled by soil respiration and atmospheric exchange (Schlesinger and Andrews, 2000). Theoretically, the $\Delta^{14}\text{C}$ signature from soil respiration could have a wide range due to the decomposition of organic carbon pools of varying age. To date, however, studies on the ^{14}C content of respired soil CO_2 indicate that the majority of soil respiration is from OM sources having a $\Delta^{14}\text{C}$ greater than 0‰ (Keller and Bacon, 1998; Torn et al., 2003; Trumbore, 2000; Winston et al., 1997), which is likely due to the large contribution of autotrophic root respiration to soil respiration fluxes (Schlesinger and Andrews, 2000). The $\delta^{13}\text{C}$ of respired soil CO_2 will reflect the $\delta^{13}\text{C}$ of the OM source, which for temperate C_3 dominated systems is $\sim -25\text{‰}$. The DIC of freshwaters in equilibrium with atmospheric CO_2 has modern-day $\Delta^{14}\text{C}$ -DIC values of $\sim 80\text{‰}$ and $\delta^{13}\text{C}$ -DIC values of $\sim -8\text{‰}$ (Mook et al., 1974). During the dissolution of carbonate rocks, approximately equal amounts of carbonate from both rocks (^{14}C -dead, $\delta^{13}\text{C} \sim -0\text{‰}$) and soil CO_2 (variable $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$ of -18 to -29‰) are predicted to contribute to riverine DIC (Stumm and Morgan, 1996). Thus, DIC derived from carbonate rock dissolution will be greatly $\Delta^{14}\text{C}$ -depleted and have a $\delta^{13}\text{C}$ signature intermediate

between these two sources. The weathering of silicates also produces DIC, all of which is derived from soil CO_2 .

Decomposition of OM within river systems themselves will also contribute to riverine DIC, and hence will alter DIC isotopic ratios (Raymond et al., 2000). However, there is virtually no information on the relationship between OM reactivity (i.e., respiration and turnover) and age in rivers (Raymond and Bauer, 2001b), and therefore the $\Delta^{14}\text{C}$ -DIC values from river metabolism must also be assumed to have a wide range. The $\delta^{13}\text{C}$ -DIC of within-system OM remineralization will vary and reflect the $\delta^{13}\text{C}$ signature of the riverine OM, which for this study ranged from -25.5‰ to -33‰ (Table 1). It is also important to note that atmospheric exchange (i.e., with soils and water) and primary production will both fractionate for $\delta^{13}\text{C}$, but not $\Delta^{14}\text{C}$, and could thus result in shifts in $\delta^{13}\text{C}$ during riverine transport.

According to Fig. 3, the apparent sources of DIC contributing to the observed DIC isotopes vary significantly across the different northeast US river systems. The most depleted $\Delta^{14}\text{C}$ values are in the Hudson River system, where all stations exhibited at least one $\Delta^{14}\text{C}$ -DIC value lower than 0‰. Of the two main tributaries of the Hudson, the Mohawk ($\Delta^{14}\text{C}$ -

DIC= $-42\pm 15\text{‰}$) was more $\Delta^{14}\text{C}$ depleted in DIC compared to the Upper Hudson ($\Delta^{14}\text{C}\text{-DIC}=\mathbf{+9\pm 36\text{‰}}$). The Mohawk (DIC= $1388\pm 115\ \mu\text{M}$) also had significantly higher DIC concentrations than the Upper Hudson ($544\pm 124\ \mu\text{M}$), presumably a result of a larger contribution of carbonate weathering in the watershed, which may also be responsible for the more ^{14}C -depleted values. The importance of atmospheric CO_2 exchange on DIC isotopes is also evident in Fig. 3 with all points clustering near the atmospheric end-member.

4.4. Convergence of OM and DIC isotopes

Internal river processing may ultimately result in a convergence of DIC and OM isotopes, provided that river OM remineralization is significant relative to other processes. Conceptually, the coupling between riverine OM cycling and the modification of carbon isotopic signatures during riverine transport are illustrated in Fig. 4. A general convergence of DIC and OM $\Delta^{14}\text{C}$ signatures will result from the simultaneous actions of system respiration and primary production (Fig. 4). The efficiency of these two processes in driving isotopic convergence will depend on the relative rates of these metabolic pathways and the residence time of water in the system. Atmospheric exchange does not cause isotopic fractionation of $\Delta^{14}\text{C}$ (Stuiver and Polach, 1977) but does inject

^{14}C -enriched atmospheric CO_2 (Raymond and Hopkinson, 2003) and will therefore drive DIC and newly formed OM (i.e., via primary production) toward ^{14}C -enriched values. The relative importance of atmospheric exchange in altering the $\Delta^{14}\text{C}$ signatures of both DIC and OM will depend on the rate of atmospheric exchange, the total pool size of DIC, and the gradient between atmospheric $\Delta^{14}\text{C}\text{-CO}_2$ and riverine $\Delta^{14}\text{C}\text{-DIC}$, while for OM it will also be dependent on the rate of net POC and DOC production by river autotrophs (Fig. 4).

Watershed inputs of DIC will also be an important determinant of $\Delta^{14}\text{C}\text{-OM}$ values. For watersheds having a significant amount of carbonate weathering, both DIC and OM isotopes will become more ^{14}C -depleted (Fig. 4) over time and space. For silicate-dominated systems the $\Delta^{14}\text{C}\text{-DIC}$ signature originates predominately from soil respiration (which we argue is dominated by ^{14}C -enriched CO_2) with the potential for some contribution from atmospheric CO_2 . Thus, watersheds with little contribution from carbonate weathering should be dominated by more ^{14}C -enriched DIC and OM. The isotopic signal of the watershed OM will also be an important determinant of OM isotopes through the production of DIC from labile OM via heterotrophic respiration. To our knowledge, there are currently no estimates of the $\Delta^{14}\text{C}$ signatures of labile watershed OM. Raymond and Bauer (2001a) reported a ^{14}C -enriched value for total labile DOC in the York

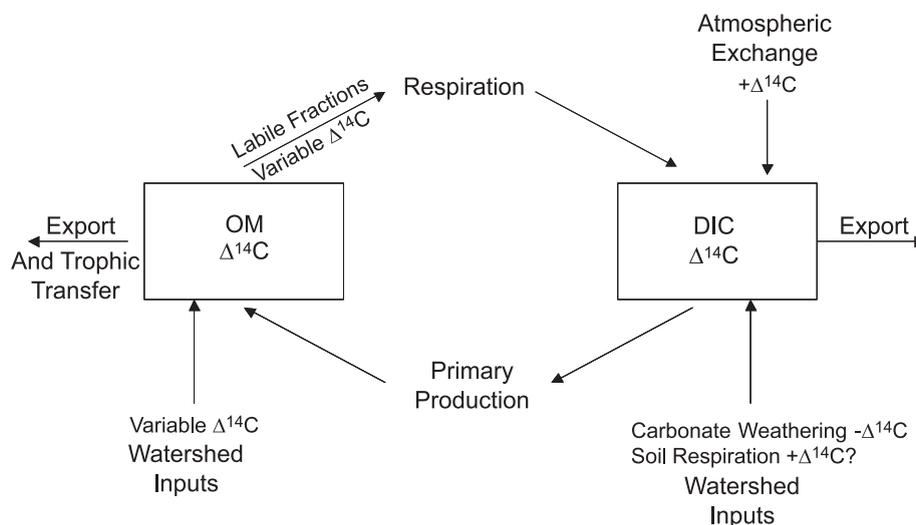


Fig. 4. Conceptual model of potential controls on $\Delta^{14}\text{C}\text{-OM}$ and riverine $\Delta^{14}\text{C}\text{-DIC}$ modification during river transport.

River, but this was presumably a mixture of watershed and autochthonous OM.

Some initial evidence for the hypothesized convergence of organic and inorganic C isotopic signatures exists in the DIC and DOC isotope signatures from the present study (Fig. 5). Across the seven systems there is a general positive relationship between DIC and DOC carbon isotopes (Fig. 5). The relationships shown in Fig. 5 are based on a preliminary data set and are decidedly influenced by measurements in only a few systems, yet they are important initial indicators that primary and secondary riverine production may exert strong controls on carbon isotopes. That is, the two major explanations proposed for convergence in the $\Delta^{14}\text{C}$ of both pools are (1) that allochthonous DOC is remineralized to DIC in soils or rivers (i.e., respiration in Fig. 4) and (2) that significant quantities of DOC are produced

from autotrophic DIC uptake (i.e., primary production in Fig. 4). An interesting ramification of the latter is that in systems with ^{14}C -depleted DIC, such as the Mohawk and tidal Hudson, there is the potential for generation of ^{14}C -depleted OM from autochthonous riverine production. If the former explanation is true, and the convergence between DOC and DIC is due to the remineralization of labile DOC, simultaneous remineralization of ^{14}C -depleted DOC is required to produce the trends in the lower left hand portion of Fig. 5B.

Evidence for coupling between net metabolism and DIC and OM isotopic compositions also exists in down-stream trends in Hudson River OM ages (Table 2). On two occasions in 1998, inputs to the tidal freshwater Hudson of both DOC and POC were quite old (~2,000 and 5,000 years B.P., respectively), and both pools *decrease* in mean age downriver (Cole and Caraco, 2001; Raymond and Bauer, 2001a), indicating the potential for selective *loss* of the oldest OM fractions in this system. Downriver ages approach more modern values, yet concentrations do not change appreciably, suggesting that internal controls may simultaneously remove older OM pools and replace them with younger ones originating from autotrophic production on the enriched $\Delta^{14}\text{C}$ -DIC values. Despite this initial evidence, the net effects of within system OM and C modification in the Hudson and other rivers in general cannot be readily assessed at present, despite its likely importance in regional carbon budgets. Future studies should be directed at evaluating the net effects of within system modification on the age of OM and C exported from rivers to the coastal ocean.

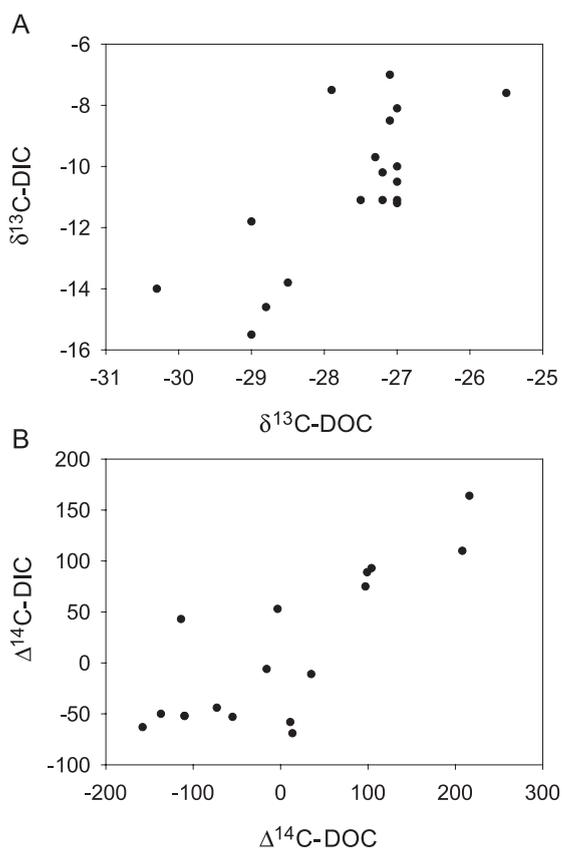


Fig. 5. Relationships between $\delta^{13}\text{C}$ of DIC and DOC (A) and $\Delta^{14}\text{C}$ of DIC and DOC (B) for all data from this study.

5. Conclusions and future directions

- (1) Despite recent arguments to the contrary (Mor-tazavi and Chanton, 2004), the riverine $\Delta^{14}\text{C}$ data indicate export of aged organic carbon to the MAB. Three of the largest rivers exporting to this ocean margin, the Susquehanna, Delaware, and Hudson all demonstrate DOC pools that are significantly ^{14}C -depleted.
- (2) The loss of wetlands may have led to a significant decrease in the export of young DOC to the MAB potentially depleting bulk $\Delta^{14}\text{C}$ -DOC values. There is also preliminary

evidence for the export of ancient marine shale deposits to the Hudson River.

- (3) Currently, temporal and spatial data is inadequate to resolve the controls on the average ages of the two major forms of organic carbon (DOC and POC) exported to the MAB on a regional basis.
- (4) Future work should assess (i) the ages of highly labile, semi-labile and non-labile OM pools in different parts of river, estuarine and coastal ocean systems, (ii) the general relationships between riverine processing and OM age, (iii) the potential production of ^{14}C -depleted OM by primary production in carbonate rich watersheds, and (iv) the effects of land-use change on riverine OM fluxes and character.

Acknowledgements

We would like to thank Chuck Hopkinson at the Plum Island LTER, Micheal Kashgarian and Constanze Weyhenmeyer at Lawrence Livermore National Laboratory Center for AMS ^{14}C facility, and Anne McNichol and John Hayes at the National Ocean Sciences AMS Facility. This work was supported in part by the NSF Chemical Oceanography Program, the NSF DEB Ecosystems Program and the Hudson River Foundation.

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