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Temporal and regional variability in sources and cycling of DOC and POC in the northwest Atlantic continental shelf and slope

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Abstract

The $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ distributions in total dissolved and suspended particulate organic carbon (DOC and POC, respectively) and dissolved inorganic carbon (DIC) were measured throughout the Middle Atlantic Bight (MAB) continental shelf and slope in April–May 1994, March 1996, and July–August 1996. The highest $\Delta^{14}\text{C}$ values for both DOC (up to -29%) and POC (up to 78%) were observed in relatively low-salinity shelf waters. The $\Delta^{14}\text{C}$ values for DOC from the shelf and shallow (~ 5 m depth) slope generally increased progressively with proximity to the coast, and along-shelf from northeast to southwest. A significant system-wide increase in $\Delta^{14}\text{C}$ -DOC values occurred between spring and summer 1996, indicating a major flux of young DOC to the MAB over this timeframe. The lowest $\Delta^{14}\text{C}$ -DOC values (as low as -476%) were found in deep (≥ 300 m depth) slope waters, and they were lower than values measured previously at similar depths in the open North Atlantic. A significant inverse relationship was found between $\Delta^{14}\text{C}$ -DOC and $\delta^{13}\text{C}$ -DOC for shelf and shallow slope waters, which we speculate may be due to variable contributions of young, ^{14}C -enriched organic matter of terrestrial and/or riverine origin. The suspended POC of shelf and shallow slope waters was isotopically distinct from DOC, and exhibited little of the characteristic areal variability of DOC concentrations and $\Delta^{14}\text{C}$ across the MAB. In deep slope waters, suspended POC had the greatest ages ever observed for water column POC in any marine system. These ^{14}C -depleted POC values correlated positively and significantly with $\delta^{13}\text{C}$ -POC values, which ranged from -31% to -23% in deep slope waters. A multiple-source dual isotopic mass balance model was applied to the observed $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ distributions to evaluate the potential sources of DOC and POC to shelf and slope waters of the MAB. With the exception of the highly ^{14}C - and ^{13}C -depleted POC from the deep slope, all other DOC and POC values could be constrained by the isotopic signatures of various potential source materials measured for the MAB region. These include varying contributions from potential sources of open ocean, terrestrial and riverine, and bottom nepheloid layer colloidal organic matter, as well as from recent shelf and slope primary production. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Continental shelves and slopes comprise only ~15–20% of the ocean's surface area, yet may account for up to half of the total oceanic primary production and new production (Eppley and Peterson, 1979; Eppley, 1989). These ocean margin systems are also important regions where terrestrial and riverine organic matter is exported and transformed en route to the open ocean (Mantoura and Woodward, 1983; Mulholland and Watts, 1982; Moran et al., 1991; Hedges, 1992; Hedges et al., 1997; Keil et al., 1997; Bauer et al., 2001). Primary production in margins (estimated at $\geq 8 \times 10^{15}$ g C y⁻¹ globally; Valiela, 1995) and inputs of geochemically distinct terrestrial organic matter by rivers ($\sim 0.40 \times 10^{15}$ g C y⁻¹ for the sum of DOC and POC globally; Hedges et al., 1997) make continental shelf and slope systems important and dynamic regions of carbon fixation, flux, and transformation (Wollast, 1998). In addition, margins have been hypothesized to serve as important regions through which the respiration of the ocean's interior may be supplemented (Smith and MacKenzie, 1987; Holland, 1995; del Giorgio et al., 1997; Bauer and Druffel, 1998) via the transport of "surplus" organic matter from continental shelves and slopes into the deep, interior ocean (Walsh, 1988, 1989, 1991; Smith and Hollibaugh, 1993; Bauer and Druffel, 1998; Bauer et al., 2001).

Earlier studies on carbon export from ocean margins focused primarily on particulate organic carbon (POC, typically measured as the organic carbon collected by filtration of seawater through $\sim 0.7\text{-}\mu\text{m}$ glass fiber filters), and mostly evaluated the larger sinking fraction of POC (i.e. that collected in sediment traps). The flux estimates arising from these earlier studies did not include dissolved organic carbon (DOC, or the organic carbon that passes through glass fiber filters), the individual fluxes of which could be quantitatively significant. Concentrations of DOC are typically 1–3 orders of magnitude greater than POC concentrations in most marine (both margin and oceanic) systems (Williams and Druffel, 1987; Druffel et al., 1992, 1996; Bauer et al., 1998). This stands in contrast with riverine (Richey et al.,

1990; Spitzy and Ittekkot, 1991) and estuarine (Fisher et al., 1998) systems, where DOC and suspended POC fluxes can be comparable. Therefore, fluxes of DOC and suspended POC in margins could be comparable to, or greater than, sinking POC fluxes (Bauer and Druffel, 1998; Bianchi et al., 1998; Sherrell et al., 1998) provided the advective and eddy diffusive transports are sufficiently great, particularly in the horizontal dimension (Jenkins, 1977; Hung et al., 1999). The fluxes of DOC and suspended POC vs. sinking POC may be similar in magnitude similar to the differences in horizontal vs. vertical eddy diffusivity (Ledwell et al., 1993).

The physical, geochemical, and biological features of the Middle Atlantic Bight (MAB) region of the northwest Atlantic Ocean have been studied extensively over the past 20 years. The MAB is hydrographically (e.g., Houghton et al., 1994; Shaw et al., 1994; Churchill and Berger, 1998) and geochemically (e.g., Anderson et al., 1994; Guo et al., 1996; Bates and Hansell, 1999) complex in both horizontal and vertical dimensions. Furthermore, the presence of low-salinity, buoyant plume waters on the MAB shelf (Boicourt, 1981; Malone and Ducklow, 1990; Churchill and Berger, 1998; Bates and Hansell, 1999) suggests that there may be significant inputs, transport and turnover of terrestrial, river and estuarine, as well as marine organic matter in shelf and slope waters there (Moran et al., 1991, 1999; Raymond and Bauer, 2000, 2001a,b).

A number of studies have been undertaken recently in the MAB to understand better the distributions and fluxes (Vlahos et al., 1998, 2002; Chen et al., 1996, 2002) and the chemical (Minor and Eglinton, 1999; Aluwihare et al., 2002; Hopkinson et al., 2002) and isotopic (Guo et al., 1996; Mitra et al., 2000; Bauer et al., 2001) characteristics of dissolved and particulate organic matter in shelf and slope waters there. While isotopic natural abundances may have a lower degree of source specificity than organic biomarkers, they may be better "integrators" of organic matter sources and ages, and be less influenced by those diagenetic factors that can alter the abundances and distributions of individual organic compounds. Natural ¹⁴C and ¹³C have been

employed previously to examine organic matter dynamics in the MAB and associated waters (e.g., Guo et al., 1996; Mitra et al., 2000). However, these earlier studies measured exclusively the high molecular weight fraction of DOC (>1 and >10 kD, typically no more than ~ 20 – 30% and ~ 3 – 6% , respectively, of the total DOC), which may or may not be representative of the total DOC pool. These studies were also limited to a small number of selected stations in the southernmost part of the MAB.

Recent work by Bauer et al. (2001) in the MAB shelf and slope, employing a dual carbon isotopic approach using natural ^{14}C and ^{13}C , helped to establish the relative contributions of variably aged allochthonous and autochthonous organic matter to the total DOC and POC pools in spring 1994. The major findings of this study included: (a) a significant inverse relationship between $\Delta^{14}\text{C}$ -DOC and $\delta^{13}\text{C}$ -DOC in all shelf and surface slope waters of the MAB, which was attributed to varying contributions of young, ^{14}C -enriched organic matter of terrestrial and/or riverine origin; (b) the presence of a more highly ^{14}C -depleted DOC source in deep slope waters, which was attributed to relic terrestrial material that had aged in the MAB itself, or was recently discharged to the MAB from rivers and estuaries; and (c) the ^{14}C and ^{13}C signatures of suspended POC were clearly differentiable from DOC, and contained a broad range of both old and young material of terrestrial and marine origin throughout the MAB. The multiple-source isotopic mass balance model (Bauer et al., 2001) showed that shelf and slope DOC was comprised of both an old “marine” fraction (represented by offshore Sargasso Sea material) and either a young “terrestrial/riverine/estuarine” (TRE) component (in shelf and shallow slope waters) or a relic TRE component (in deep, and some shallow slope waters). In contrast, suspended POC from the MAB appeared to originate predominantly from a mixture of recent MAB primary production and old TRE material, similar to that observed in one of the major subestuaries of the Chesapeake Bay. The present study expands upon the earlier work of Bauer et al. (2001) by establishing the temporal (seasonal to inter-annual) and regional (both across and along

the MAB) variability in carbon isotopic signatures and inventories, and potential sources, of total DOC and suspended POC within this major and well-studied ocean margin system. We also include selected parts of the data set presented in Bauer et al. (2001) in order to make the temporal and spatial comparisons complete, and the larger composite data set presented here allows for a stronger, more robust interpretation of the sources and cycling of DOC and POC in the northwest Atlantic ocean margin.

2. Materials and methods

2.1. Study location

A minimum of three stations on each of 3–5 transects across the MAB shelf and slope between Cape Cod and Cape Hatteras were sampled for carbon isotopic characterization of total DOC, suspended POC, and DIC on three separate cruises: (1) April 18–May 1, 1994 on the R/V *Columbus Iselin*; (2) March 1–11, 1996 on the R/V *Endeavor*, and (3) July 28–August 4, 1996 on the R/V *Seward Johnson* (Fig. 1; Table 1). Transects were carried out at a generally perpendicular orientation to the major isobaths, and extended from relatively shallow shelf waters to mesopelagic slope waters. These transects were chosen to provide broad geographic coverage, to evaluate potential differences in regional inputs of organic matter (i.e. from Chesapeake and Delaware Bays and the Hudson River), and to establish the ranges and variability in ^{14}C and ^{13}C signatures for each of the carbon pools throughout the MAB.

On each transect, continental shelf samples were collected from surface (~ 5 m depth) waters and, wherever possible, within ~ 5 m of the seafloor (Table 1). In slope waters, samples were collected from four depths (approximately 5, 300, 750, and 1000 m). Each of the slope stations was at a different lateral distance from the shelf–slope break, and as a result the ~ 1000 m samples were at different heights above the seafloor. Salinities (Table 1) were strongly influenced by the proximity of stations to the major freshwater inputs to the MAB and to the Gulf Stream in the southern

Fig. 1. The MAB, showing transects and stations sampled on the three cruises undertaken for this study. Specific transects and station locations and information for each cruise are given in Table 1. Isobath depths shown are in meters.

MAB. Surface seawater salinities were lowest in inshore and mid-shelf waters, and increased in the offshore slope stations. Surface and shelf water temperatures (Table 1) generally increased from north to south and from onshore to offshore, and a thermocline was often observed in April 1994 and August 1996, even in shallow shelf waters. A full treatment of the hydrographic data obtained during these cruises is presented in Flagg et al. (2002) and a more comprehensive coverage of DOC concentrations made along all eight transects is presented in Vlahos et al. (2002).

2.2. Sample collection

Pre-cleaned (using methanol, dilute HCl and double distilled water) 12- and 30-l Go-flo bottles were used to collect water for $\delta^{14}\text{C}$ of total DOC, suspended POC, DIC, and for total CO_2 , alkalinity, and salinity. One-liter water samples for DOC analyses were filtered directly from Go-flo bottles through baked (500°C for 4 h) 143-mm diameter Whatman quartz fiber filters (QFF; $0.8\text{-}\mu\text{m}$ nominal pore size) and frozen at -20°C immediately after collection. Suspended POC was

Table 1

Locations, depths and hydrographic information for stations sampled for $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ for the three cruises in the Middle Atlantic Bight in 1994 and 1996. April–May 1994 data from Bauer et al. (2001)

Transect	Station	Station depth (m)	Lat/long	Sampling depth (m)	Salinity	Temp (°C)
<i>April 18–May 1, 1994</i>						
Northern						
2	1–10	42	40°41.80'N/ 72°14.64'W	5 25	31.08 32.57	6.7 3.6
2	1–12	~65	40°19.75'N/ 72°01.97'W	5 50	31.66 33.24	6.1 4.1
2	1–16	1257	39°37.72'N/ 71°37.78'W	5 300 750 1000	33.57 35.29 35.09 35.09	10.2 nd 4.6 4.1
Central						
4	1–40	~18	37°38.13'N/ 75°16.13'W	5	31.42	7.6
4	1–42	23	37°30.31'N/ 74°58.62'W	5 15	29.46 31.91	12.2 9.0
4	1–46	1558	37°11.54'N/ 74°16.91'W	5 300 750 1000	31.29 35.45 35.09 35.31	10.7 9.7 4.8 4.2
Southern						
6	1–62	21	35°39.04'N/ 75°23.83'W	5	32.73	18.8
6	1–58	50	35°38.99'N/ 74°57.18'W	5 40	33.27 35.72	18.8 17.8
6	1–55	~1900	35°39.06'N/ 74°36.78'W	5 300 750 1000	36.16 35.57 35.14 35.09	22.5 10.5 4.8 4.2
<i>March 1–11, 1996</i>						
Northern						
1	2–2	43	40°57.06'N/ 70°20.58'W	5 32	32.544 32.549	2.7 2.7
1	2–4	60	40°37.02'N/ 70°21.06'W	5 52	32.727 32.726	3.7 3.6
2	2–15	1301	39°21.90'N/ 71°37.74'W	3 294 746 994	34.169 35.069 35.006 34.978	8.3 5.8 4.4 4.1
3	2–16	24	39°29.94'N/ 73°58.02'W	5 19	32.306 32.300	2.9 2.9
3	2–18	45	39°13.44'N/ 73°41.70'W	5 37	33.010 33.016	3.8 3.6
3	2–21	76	38°47.64'N/ 73°16.68'W	6 14	33.364 35.293	6.2 6.0
3	2–23	1925	38°29.28'N/ 72°59.70'W	2 279 720 976	35.000 35.294 35.027 34.999	10.9 10.0 4.7 4.3

Table 1 (continued)

Transect	Station	Station depth (m)	Lat/long	Sampling depth (m)	Salinity	Temp (°C)
Central						
4	2–24	23	38°00.12'N/ 74°58.14'W	6 18	32.450 32.554	5.4 5.4
4	2–26	54	37°50.22'N/ 74°33.66'W	3 46	33.405 34.697	6.7 10.0
4	2–28	815	37°49.26'N/ 74°09.42'W	1 231 696	33.621 35.304 35.000	7.4 10.1 4.7
5	2–37	14	36°42.00'N/ 75°52.02'W	4 9	29.405 29.389	4.5 4.5
5	2–33	34	36°42.00'N/ 75°00.54'W	5 15	33.525 33.510	7.6 7.4
5	2–30	1200	36°42.18'N/ 74°34.62'W	7 289 728 975	33.877 35.226 34.980 34.962	9.1 9.4 4.7 4.2
Southern						
6	2–42	23	35°27.42'N/ 75°23.10'W	5 15	31.370 31.441	6.2 7.4
6	2–40	38	35°27.36'N/ 75°02.94'W	5 30	34.457 35.174	11.3 12.0
6	2–38	1200	35°27.18'N/ 74°47.22'W	3 249 690 933	35.299 35.437 35.032 35.013	16.2 11.1 5.0 4.3
<i>July 28–August 4, 1996</i>						
Northern						
1	3–42	40	41°06.73'N/ 70°21.36'W	5 30	31.773 31.666	23.5 23.6
1	3–39	59	40°36.82'N/ 70°21.31'W	5 45	32.059 32.341	23.6 23.8
1	3–35	1200	39°49.77'N/ 70°20.781'W	8 308 770 1021	32.740 35.147 35.000 35.026	20.1 8.0 4.4 4.1
2	3–27	23	41°51.11'N/ 72°20.14'W	5 15	30.179 30.725	18.4 17.6
3	3–26	23	39°29.80'N/ 73°57.74'W	5 15	30.469 31.651	21.4 16.0
3	3–23	54	39°04.81'N/ 73°32.92'W	5 45	30.766 32.405	21.6 5.4
3	3–19	2040	38°28.86'N/ 72°59.59'W	5 299 752	32.876 35.142 34.973	22.3 4.3 3.9

Table 1 (continued)

Transect	Station	Station depth (m)	Lat/long	Sampling depth (m)	Salinity	Temp (°C)
Central						
4	3–18	21	38°00.02'N/ 74°58.05'W	5 15	29.952 31.789	23.4 18.0
4	3–16	55	37°49.89'N/ 74°34.03'W	5 45	30.558 32.515	23.2 22.0
4	3–13	1660	37°35.08'N/ 73°55.79'W	11 299 894 1156	31.554 35.100 35.018 34.973	21.5 nd 4.3 3.9
5	3–6	20	36°42.06'N/ 75°52.11'W	4 9	24.942 31.882	23.2 22.0
5	3–9	24	36°41.88'N/ 75°17.00'W	5 18	31.150 32.302	24.2 12.8
5	3–12	1050	36°41.62'N/ 74°34.92'W	8 305 502 835 1020	32.171 35.157 35.054 35.014 34.988	22.5 8.4 5.4 4.4 4.1
Southern						
6	3–1	20	35°26.94'N/ 75°22.96'W	5 15	30.697 33.426	23.7 20.0
6	3–3	40	35°27.08'N/ 75°03.11'W	4 29	33.337 34.152	25.3 15.8
6	3–5	1767	35°27.84'N/ 74°41.79'W	12 275 777 1046	36.184 35.490 35.032 34.969	28.2 11.4 4.5 4.0

considered to be that fraction collected directly on the QFF filters. The POC sample filters were frozen immediately at -20°C in pre-baked glass jars. The filtered water samples for $\Delta^{14}\text{C}$ of DIC (500 ml), TCO_2 (250 ml) and alkalinity (250 ml) were poisoned with 100 μl of a saturated HgCl_2 solution and stored 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.

2.3. 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 650-ml seawater samples (Bauer et al., 1992a, b, 1998, 2001). Briefly, samples were

acidified to pH 2.5 with phosphoric acid and sparged with ultra-high purity nitrogen gas for 30 min to remove inorganic carbon, saturated with ultra-high purity oxygen gas, and then irradiated with a medium pressure mercury arc UV lamp (Canrad–Hanovia, Newark, NJ) for 2 h. The CO_2 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 CO_2 pressure on the vacuum line. Following quantification, the sample was split approximately 10:1 into two break-seal tubes, 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 exact procedure as for seawater samples. Recoveries

were all $100 \pm 1\%$, and $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of standards were within the analytical measurements of the isotopes, indicating that the method attains accurate concentration and isotopic results, and that there was no significant blank contribution. DOC concentrations were also cross-checked by discrete injection high-temperature catalytic oxidation (HTCO) using aluminosilicate and Pt-impregnated catalysts (Bauer et al., 1993; Williams et al., 1993), and correcting by appropriate system blanks using methods suggested by Hedges et al. (1993), (Sharp et al., 1993), and Peltzer (1994). The UV- and HTCO-derived DOC concentrations agreed to within $2 \mu\text{M}$ of each other in all cases.

2.4. Suspended POC and DIC

The concentrations, $\Delta^{14}\text{C}$, and $\delta^{13}\text{C}$ values of suspended POC were measured from the same sample collections as DOC (see above). The material collected on the quartz fiber filters was acidified overnight with 1% H_3PO_4 to remove carbonates, dried in vacuo, and the POC was oxidized to CO_2 by dry combustion with CuO and Ag metal at 850°C in double 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 $\delta^{13}\text{C}$ values of the sample filters were corrected accordingly. Yields of CO_2 were quantified using an absolute pressure gauge on a vacuum extraction line, and aliquots were taken for $\Delta^{14}\text{C}$ ($\sim 90\%$ of the total) and $\delta^{13}\text{C}$ ($\sim 10\%$ of the total) measurements. Samples for $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ analysis of DIC (250 ml) were acidified using 85% H_3PO_4 . The sample was sparged using ultra-high-purity N_2 gas, the evolved CO_2 was collected cryogenically and purified on a vacuum extraction line, and the sample was split as above for $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ (McNichol et al., 1994).

2.5. Isotopic analyses

The $\Delta^{14}\text{C}$ analyses of the small amounts of carbon ($\sim 50\text{--}500 \mu\text{g C}$) recovered from these procedures were performed by accelerator mass spectrometry (AMS) at the Center for AMS at Lawrence Livermore National Laboratory

(LLNL). The CO_2 derived from all samples was converted to graphite using H_2 over Co 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. Both instruments gave an analytical precision of better than 0.1% .

3. Results

The results of all DOC, POC and DIC concentration, $\Delta^{14}\text{C}$, and $\delta^{13}\text{C}$ analyses are shown in Table 2. The April 1994 data have also been presented and discussed in detail previously by Bauer et al. (2001), but this data set is included here for completeness in our synthesis of the data from all three cruises.

3.1. Shelf and slope upper water column

3.1.1. Dissolved organic carbon

In general, both DOC and suspended POC concentrations were greatest in shallow shelf and slope ($\sim 5\text{m}$ depth) waters compared to either deeper shelf or deep slope ($\geq 300\text{m}$) waters on all three cruises (Table 2). The $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of DOC in shallow shelf and slope waters are worth noting in several respects (Table 2; Figs. 2A, 3A and 4A). Upper water column values of $\Delta^{14}\text{C}$ -DOC (Figs. 2A, 3A and 4A) spanned a relatively large range (277‰), from a minimum of -306% in the southern MAB in April 1994 (Fig. 2A) to a maximum of -29% near the mouth of Chesapeake Bay in August 1996 (Fig. 4A). The upper value clearly represents the presence of bomb-derived ^{14}C , and as we will show, only those samples with $\Delta^{14}\text{C}$ -DOC values $\geq -150\%$ contain discernible amounts of freshly derived modern material derived from MAB primary production (as reflected by the $\Delta^{14}\text{C}$ -DIC values; Table 2). The large range of 277‰ in $\Delta^{14}\text{C}$ -DOC values indicates that DOC in the upper water column of this system must be comprised of sources having highly disparate $\Delta^{14}\text{C}$ values (see Discussion). Although

Table 2

Concentrations, $\Delta^{14}\text{C}$, and $\delta^{13}\text{C}$ isotopic compositions, and equivalent ages of DOC, POC, and DIC during the three cruises in this study. April–May 1994 data from Bauer et al. (2001)

Transect	Sta no.	Depth (m)	DOC				POC				DIC			
			DOC (μm)	$\Delta^{14}\text{C}$ (‰)	Age (yr BP)	$\delta^{13}\text{C}$ (‰)	POC ($\mu\text{g l}^{-1}$)	$\Delta^{14}\text{C}$ (‰)	Age (yr BP)	$\delta^{13}\text{C}$ (‰)	DIC ($\mu\text{mol kg}^{-1}$)	$\Delta^{14}\text{C}$ (‰)	Age (yr BP)	$\delta^{13}\text{C}$ (‰)
April 18–May 1, 1994														
Northern														
2	1–10	5	102	–186	1653	–22.9	103	15	Mod.	–22.4	1938	56	Mod.	1.4
2	1–10	25	81	–207	1863	–21.9	138	22	Mod.	–23.6	2083	60	Mod.	0.5
2	1–12	5	88	–160	1401	nd	76	25	Mod.	–23.0	1965	60	Mod.	1.0
2	1–12	50	69	–211	1904	–22.2	38	49	Mod.	–21.3	2077	48	Mod.	0.9
2	1–16	5	77	–234	2141	–21.9	148	51	Mod.	–22.4	2030	46	Mod.	1.6
2	1–16	300	46	–433	4558	–21.9	6.7	–57	471	nd	2188	–28	228	0.7
2	1–16	750	47	–418	4348	–21.6	3.6	nd	nd	–23.7	2164	–31	253	1.0
2	1–16	1000	47	–442	4686	–21.7	3.7	nd	nd	nd	2159	–29	236	1.0
Central														
4	1–40	5	99	–92	775	–22.6	190	–16	139	–24.0	1981	nd	nd	nd
4	1–42	5	115	–39	320	–22.7	nd	nd	nd	nd	1880	53	Mod.	1.8
4	1–42	15	89	–76	635	–22.3	143	15	Mod.	–24.3	1973	31	Mod.	1.6
4	1–46	5	91	–107	909	–22.1	131	31	Mod.	–24.5	1981	48	Mod.	0.4
4	1–46	300	53	–403	4144	–21.5	9.4	–73	609	–24.9	2171	–24	195	1.0
4	1–46	750	52	–451	4817	–21.4	3.7	31	Mod.	–23.1	2170	–27	220	1.1
4	1–46	1000	51	–408	4211	–21.3	5.7	–146	1268	–24.1	2175	–42	345	1.1
Southern														
6	1–62	5	112	–98	829	–22.8	186	78	Mod.	–20.4	1937	76	Mod.	0.9
6	1–58	5	111	–145	1258	–22.7	139	66	Mod.	–19.9	2113	44	Mod.	0.9
6	1–58	40	69	–272	2550	–22.0	315	–45	370	–21.4	1929	62	Mod.	1.5
6	1–55	5	83	–306*	2934	–22.4*	45	–44	361	–22.9	2024	79	Mod.	1.5
6	1–55	300	53	–428	4487	–22.3	4	–171	1506	nd	2166	–2	16	0.8
6	1–55	750	50	–438	4629	–22.0	2.7	nd	nd	nd	2165	nd	nd	nd
6	1–55	1000	50	–438	4629	–22.2	3.2	–394	4024	nd	2161	–51	420	nd
March 1–11, 1996														
Northern														
1	2–2	5	84	–172	1513	–23.1	196	30	Mod.	–21.3	2002	nd	nd	nd
1	2–2	32	85	–196	1757	–22.6	296	29	Mod.	–21.3	2005	43	Mod.	1.4
1	2–4	5	78	–214	1932	–22.4	300	31	Mod.	–21.0	2041	43	Mod.	1.2
1	2–4	52	77	–201	1800	–22.5	296	25	Mod.	–21.0	2038	38	Mod.	1.2
2	2–15	3	70	–258	2394	–22.0	94	33	Mod.	–21.5	2040	56	Mod.	1.0
2	2–15	294	49	–400	4105	–21.7	8.0	–662*	8716	–28.0*	2173	–36	299	0.9
2	2–15	746	49	–418	4342	–22.0	3.4	–182	1611	–29.0	2160	–30	243	0.8
2	2–15	994	50	–409	4224	–22.0	4.6	–491	5425	–30.0	2159	–42	344	0.9
3	2–16	5	107	–130	1116	–22.5	336	47	Mod.	–23.6	1977	77	Mod.	17
3	2–16	19	94	–120	1029	–23.0	nd	nd	nd	nd	1974	76	Mod.	1.6
3	2–18	5	89	–164	1443	–22.4	239	42	Mod.	–24.8	2018	60	Mod.	1.4

Table 2 (continued.)

Transect	Sta no.	Depth (m)	DOC				POC				DIC			
			DOC (μM)	$\Delta^{14}\text{C}$ (‰)	Age (yr BP)	$\delta^{13}\text{C}$ (‰)	POC ($\mu\text{g l}^{-1}$)	$\Delta^{14}\text{C}$ (‰)	Age (yr BP)	$\delta^{13}\text{C}$ (‰)	DIC ($\mu\text{mol kg}^{-1}$)	$\Delta^{14}\text{C}$ (‰)	Age (yr BP)	$\delta^{13}\text{C}$ (‰)
3	2–18	37	86	–168	1480	–22.5	274	40	Mod.	–24.8	2013	66	Mod.	1.5
3	2–21	5	70	–200	1793	–22.3	143	46	Mod.	–22.1	2043	53	Mod.	1.2
3	2–21	67	49	–288	2725	–24.1*	52	–13	104	–21.1	2121	52	Mod.	0.9
3	2–23	2	58	–257*	2389	–22.7	46	24	Mod.	–23.8	2090	59	Mod.	1.1
3	2–23	279	42	–388	3949	–21.6	7.6	nd	nd	–23.0	2167	–15	124	0.6
3	2–23	720	47	–418	4350	–22.3	4.3	nd	nd	–23.0	2167	–26	215	0.9
3	2–23	976	47	–401	4120	–22.2	4.3	–430	4518	–30.0	2162	–35	283	1.1
Central														
4	2–24	6	90	–131	1125	–23.2	268	47	Mod.	–23.9	1989	63	Mod.	1.5
4	2–24	18	92	–117	1001	–22.5	336	53	Mod.	–23.8	1996	62	Mod.	1.5
4	2–26	3	63	–209	1884	–22.7	227	47	Mod.	–23.6	2031	55	Mod.	1.0
4	2–26	46	60	–268	2501	–21.8	100	–4	35	–22.2	2099	48	Mod.	0.9
4	2–28	1	67	–206	1853	–23.1	151	33	Mod.	–22.5	2055	49	Mod.	1.1
4	2–28	231	50	–475*	5188	–25.4*	7.7	–243	2231	–28.0	2189	–28	224	0.6
4	2–28	696	42	–420	4378	–22.5	6.6	–386	3923	–28.8	2163	–30	241	0.9
5	2–37	4	126	–77	646	–23.7	296	60	Mod.	–23.1	1892	57	Mod.	0.9
5	2–37	9	96	–50	410	–23.3	nd	nd	nd	nd	1890	59	Mod.	1.3
5	2–33	5	75	–183	1625	–22.7	245	55	Mod.	–24.3	1992	59	Mod.	1.6
5	2–33	15	77	–193	1721	–22.7	328	56	Mod.	–24.1	2018	57	Mod.	1.4
5	2–30	7	73	–189	1687	–22.9	105	25	Mod.	–22.3	2042	53	Mod.	1.2
5	2–30	289	46	–407	4197	–22.0	11	–356	3529	–26.0	2186	–26	208	0.3
5	2–30	728	46	–413	4280	–22.6	6.6	–358	3560	–27.5	2166	–32	261	0.9
5	2–30	975	54	–432	4549	–22.8	7.3	–476	5185	–30.5	2162	–28	224	0.7
Southern														
6	2–42	5	102	–85	709	–23.2	190	39	Mod.	–21.9	1967	73	Mod.	1.1
6	2–42	15	76	–86	722	–23.0	nd	nd	nd	nd	1977	58	Mod.	1.0
6	2–40	5	83	–185	1644	–23.7	177	58	Mod.	–19.6	2024	68	Mod.	0.9
6	2–40	30	59	–188	1674	–22.1	87	35	Mod.	–21.1	2057	62	Mod.	0.8
6	2–38	3	77	nd	nd	–21.8	63	30	Mod.	–21.6	2059	73	Mod.	1.1
6	2–38	249	43	–383	3883	–22.3	14	–259	2405	–27.6	2173	–2	17	0.5
6	2–38	690	47	–401	4120	–22.4	13	–193	1724	–23.6	2173	–46	381	0.7
6	2–38	933	38	–384	3887	–21.4	12	–255	2369	–24.0	2163	–33	269	0.8
July 28–August 4, 1996														
Northern														
1	3–42	5	74	–159	1389	–23.7	27	28	Mod.	–23.5	1948	52	Mod.	1.1
1 ^a	3–42	5	nd	nd	nd	nd	49	35	Mod.	–23.6	nd	nd	nd	nd
1	3–42	30	75	–171	1509	–23.8	178	14	Mod.	–23.3	1945	42	Mod.	1.5
1	3–39	5	69	–172	1521	–23.6	136	31	Mod.	–23.9	1938	38	Mod.	1.8
1	3–39	45	68	–190	1696	–23.7	101	–19	150	–23.2	2003	37	Mod.	1.1
1	3–35	8	70	–187	1661	–23.4	nd	nd	nd	nd	1936	52	Mod.	1.9

1	3-35	308	43	-414	4296	-21.9	7.3	-148	1289	-26.4	2145	-44	358	0.8
1	3-35	770	41	-398	4070	-23.4	5.9	-285	2697	-30.2	2119	-26	212	0.9
	3-35	1021	451	-395	4036	-23.1	12	-254	2358	-28.6	n/a	-20	161	0.9
2	3-27	5	91	-132	1139	-23.7	62	25	Mod.	-22.4	1897	47	Mod.	1.5
2	3-27	15	90	-130	1120	-23.5	87	9	Mod.	-21.9	1903	46	Mod.	1.3
3	3-26	5	120	-80	666	-23.1	70	8	Mod.	-22.4	1897	53	Mod.	1.4
3	3-26	15	94	-116	989	-23.5	106	37	Mod.	-22.6	2071	42	Mod.	0.0
3	3-23	5	121	-89	744	-22.5	62	15	Mod.	-24.0	1909	61	Mod.	1.5
3	3-23	45	73	-194	1733	-23.6	66	17	Mod.	-23.2	2085	49	Mod.	0.6
3	3-19	5	72	-173	1523	-23.0	28	36	Mod.	-22.1	1966	55	Mod.	1.9
3	3-19	299	36	-427	4476	-23.6	5.9	-267	2500	-25.6	2192	-49	404	0.6
3	3-19	752	44	-357	3546	-23.7	nd	nd	nd	nd	2141	-11	90	0.8
Central														
4	3-18	5	119	-69	577	-23.5	124	49	Mod.	-20.4	1846	57	Mod.	1.8
4	3-18	15	93	-109	928	-23.0	60	8	Mod.	-22.4	2006	48	Mod.	1.1
4	3-16	5	116	-76	633	-23.1	106	34	Mod.	-22.0	1884	61	Mod.	1.8
4	3-16	45	70	-194	1729	-23.3	95	-9	70	-23.8	2077	34	Mod.	0.7
4	3-13	11	92	-151	1312	-22.2	65	-17	141	-24.1	1929	57	Mod.	2.0
4	3-13	299	41	-404	4153	-21.9	12	-312	3002	-30.4	2182	-33	273	0.7
4	3-13	894	39	-389	3955	-22.3	5.0	-348	3441	-28.8	2189	-28	226	0.7
4	3-13	1156	41	-395	4035	-23.0	5.4	-419	4355	-31.6	2162	-21	170	0.9
5	3-6	4	156	-29	235	-23.7	151	18	Mod.	-20.6	1734	59	Mod.	0.6
5	3-6	9	99	-144	1252	-23.4	138	46	Mod.	-19.6	2051	45	Mod.	0.6
5	3-9	5	97	-113	959	-23.4	112	41	Mod.	-22.2	1951	52	Mod.	0.9
5	3-9	18	88	-141	1220	-23.2	194	38	Mod.	-21.4	2010	47	Mod.	1.5
5	3-12	8	88	nd	nd	-23.4	31	-1	7	-23.4	1947	53	Mod.	1.9
5	3-12	305	41	-416	4316	-22.6	8.2	-258	2397	-27.1	2189	-32	260	0.5
5	3-12	502	39	-401	4116	-22.7	6.8	-147	1275	-26.9	2176	-37	306	0.8
5	3-12	835	41	-408*	420-9	-20.9*	7.0	-180	1592	-27.2	2165	-33	272	0.8
5	3-12	1020	41	-391	3984	-22.6	8.7	-352	3479	-28.7	2159	-32	259	0.9
Southern														
6	3-1	5	90	-138	1196	-23.4	118	35	Mod.	-22.4	nd	59	Mod.	1.0
6	3-	15	78	-194	1733	-23.1	122	0	2	-22.0	1976	71	Mod.	1.0
6	3-	4	77	-165	1445	-22.9	61	-16	127	-24.2	2034	64	Mod.	1.4
6	3-	29	70	-197	1760	-22.7	129	10	Mod.	-21.5	2045	58	Mod.	1.2
6	3-	12	68	-nd	nd	-22.9	35	-68	568	-24.5	2023	80	Mod.	1.2
6	3-	275	38	-413	4274	-23.2	9.4	-615*	7672	nd	2205	5	Mod.	0.6
6	3-	777	40	-420	4379	-23.3	8.7	-206	1848	-26.9	2183	-31	252	0.8
		1046	40	-408	4207	-23.4	4.3	-276	2593	-29.2	2163	-20	163	0.9

^a Replicate sample.

Mod.—modern in age.

nd—not determined.

*—value may not appear in all panels of Figs. 9A–D and 10A–C due to its departure from the $\delta^{14}\text{C}$ and $\delta^{13}\text{C}$ ranges used in figures.

Fig. 2. Upper water column distributions of (A) $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ of DOC and (B) $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ of suspended POC in April–May 1994. Sequence of values for each station is: left value— $\Delta^{14}\text{C}$; right value— $\delta^{13}\text{C}$. nd—not determined.

Fig. 3. Upper water column distributions of (A) $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ of DOC and (B) $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ of suspended POC in March 1996. Sequence of values for each station is: left value— $\Delta^{14}\text{C}$; right value— $\delta^{13}\text{C}$. nd—not determined.

the regional variation in $\Delta^{14}\text{C}$ -DOC values can be seen at all three sampling times, it is most apparent during March and August 1996 (Figs. 3A and 4A, respectively) when the sampling densities were

higher than April 1994 (Fig. 2A). With the single exception of the -306‰ value noted above, the $\Delta^{14}\text{C}$ -DOC values were lowest in shallow waters of the northernmost slope station, and increased

Fig. 4. Upper water column distributions of (A) $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ of DOC and (B) $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ of suspended POC in July and August 1996. Sequence of values for each station is: left value— $\Delta^{14}\text{C}$; right value— $\delta^{13}\text{C}$. nd—not determined.

inshore as well as along-shelf toward the southern MAB at all three sampling times. This coincides with an apparent accumulation both inshore and

along-shelf of “excess” DOC produced in shelf waters as well as discharged to the MAB from the dominant rivers and estuaries (Bauer et al., 2001; Vlahos et al., 2002; Chen et al., 2002). The $\delta^{13}\text{C}$ values of upper water column DOC exhibited a range of only 1.9‰ (−23.7‰ to −21.8‰), and did not show evidence of the same consistent qualitative and quantitative changes as concentrations and $\Delta^{14}\text{C}$ of DOC throughout the MAB.

In addition to the marked cross- and along-shelf patterns in DOC concentrations, and $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values, temporal changes in these parameters in MAB shelf and slope surface waters were noted for specific stations and transects, and indeed for the entire MAB, between the three cruises. As before, these temporal comparisons are most apparent for the two 1996 cruises. Comparing first the April 1994 and March 1996 transects, we see that surface DOC concentrations did not differ typically by more than $\sim 5\text{--}10\ \mu\text{M}$ between these two cruises (Table 2). The $\Delta^{14}\text{C}$ -DOC values from the northern and southern transects were also similar between 1994 and 1996 (Figs. 2A and 3A), but values for the entire central MAB transect were significantly lower in March 1996 than in April 1994. However, the most dramatic temporal shift occurred in $\Delta^{14}\text{C}$ -DOC between March and August 1996 (Figs. 3A and 4A), where, with only one exception (transect 6 inshore station), shelf and slope surface values throughout the entire MAB increased from 20‰ to 133‰ at any given station. While this increase in $\Delta^{14}\text{C}$ corresponded to a general increase in DOC concentration (e.g., transects 4, 5 and 6; Table 2) and decrease in shelf mixed-layer salinity ($\sim 1\text{--}2$ salinity units; Table 1), this was not universally the case, as can be seen by the lower DOC concentrations in the northern two transects in August 1996 (Table 2). The $\delta^{13}\text{C}$ -DOC values were also on average more depleted during the two 1996 cruises compared to the 1994 cruise (Figs. 2A, 3A and 4A). Thus, these large-scale shifts in $\Delta^{14}\text{C}$ -DOC between March and August 1996 may be a result of (a) temporal changes in the relative inputs and $\Delta^{14}\text{C}$ of DOC sources, including both shelf primary production and riverine discharge, (b) preferential utilization of young or old DOC in different parts of the MAB at different times of the year, or (c) some combination of (a)

and (b). In the Discussion, we will attempt to constrain the relative roles of these different potential processes affecting DOC in shallow shelf and slope waters.

3.2. Suspended POC

Concentrations of suspended POC in shallow shelf and slope waters ranged over an order of magnitude (compared to a factor of ~ 2 – 3 for DOC), from 27 to 336 $\mu\text{g C l}^{-1}$ (Table 2), and were higher overall in March 1996 than at the other two sampling times. In contrast to DOC, POC showed evidence for the presence of bomb ^{14}C in all samples from the upper shelf and slope water column (Figs. 2B, 3B and 4B). $\Delta^{14}\text{C}$ -POC values ranged over 146‰, from -68 ‰ to 78‰, and were thus much less variable than $\Delta^{14}\text{C}$ -DOC values (see above). Shallow shelf suspended POC was generally slightly lower by up to ~ 20 ‰ in $\Delta^{14}\text{C}$ than surface DIC (Table 2). This indicates that this POC was not comprised of completely modern material derived from shelf primary production, but must contain varying amounts of somewhat older material as well. Shallow slope $\Delta^{14}\text{C}$ -POC values were often significantly lower than shallow shelf values from the same transects (Figs. 2B, 3B and 4B); these slope $\Delta^{14}\text{C}$ -POC values were frequently offset from the corresponding $\Delta^{14}\text{C}$ -DIC values to a much greater extent (up to 148‰; Table 2) than shelf $\Delta^{14}\text{C}$ -POC vs. $\Delta^{14}\text{C}$ -DIC offsets (Table 2). This suggests an even greater contribution of older material (i.e. relative to modern primary production) to slope surface waters than to shelf surface waters.

In contrast to $\Delta^{14}\text{C}$ -POC values, the $\delta^{13}\text{C}$ -POC values were much more variable (range of 4.9‰) than $\delta^{13}\text{C}$ -DOC values in MAB shallow shelf and slope waters, ranging from -24.8 ‰ to -19.9 ‰ (Figs. 2B, 3B and 4B). Also in contrast to DOC, there were no consistent or apparent cross- or along-shelf changes in $\Delta^{14}\text{C}$ -POC or $\delta^{13}\text{C}$ -POC in shallow shelf and slope waters (Figs. 2B, 3B and 4B). However, shallow slope waters from the central and southern transects tended to have the lowest $\Delta^{14}\text{C}$ -POC values, and all shallow slope waters had consistently lower POC concentrations than shallow shelf waters (Table 2).

3.3. Deep shelf waters

3.3.1. DOC and suspended POC

At individual sampling times, deeper shelf waters (≥ 5 m depth) often had dramatically lower DOC concentrations and $\Delta^{14}\text{C}$ values than DOC in surface waters, provided that water column stratification was established (Tables 1 and 2). In April 1994, significant vertical salinity and temperature gradients were observed in shelf waters (often separated by no more than 10–20 m), and this coincided with strong vertical gradients in DOC parameters ($\Delta^{14}\text{C}$ -DOC up to 127‰; DOC up to 42 μM ; and $\delta^{13}\text{C}$ -DOC up to 1.0‰). In contrast, during the March 1996 cruise when shelf waters were well-mixed (see also Flagg et al., 2002) vertical gradients for all of these parameters (Table 2) were smaller (maximal gradients were $\Delta^{14}\text{C}$ -DOC: 88‰; DOC: 30 μM ; $\delta^{13}\text{C}$ -DOC: 0.9‰). At the majority of inner and outer shelf stations in March 1996, vertical gradients in DOC parameters were small to non-existent, and many were within measurement errors. In August 1996, there were also minimal gradients in vertical salinity and DOC parameters at shelf stations sampled on northern transects 1 and 2, but stratification was stronger in shelf waters from transect 3 southward, likely owing to freshwater inputs from Chesapeake and Delaware Bays. In the central and southern MAB during August 1996, the maximal vertical gradients in DOC parameters ($\Delta^{14}\text{C}$ -DOC: 115‰; DOC: 57 μM ; $\delta^{13}\text{C}$ -DOC: 1.1‰) more closely resembled conditions in April 1994 than in March 1996. In contrast to DOC, the concentrations, $\Delta^{14}\text{C}$ values, and $\delta^{13}\text{C}$ values for suspended POC did not appear to be influenced in a predictable manner by water column depth (i.e. shallow vs. deep) or stratification (Tables 1 and 2). The ranges in values for all three parameters in deep shelf waters were similar to and were essentially not differentiable from shallow shelf waters (Table 2).

3.4. Deep slope waters

3.4.1. Dissolved organic carbon

Concentrations of DOC decreased rapidly in deeper slope waters (Table 2) to values that were

only $\sim 5\text{--}10\ \mu\text{M}$ greater than open-ocean values observed from similar mesopelagic depths in the open North Atlantic (Bauer et al., 1992a,b; Hansell and Carlson, 1998). Deep slope $\Delta^{14}\text{C}$ -DOC values decreased from elevated surface values to near-constant values below about 300 m depth, and ranged from -451‰ to -353‰ over all cruises

and depths, with very little temporal (i.e. among the three cruises) or spatial (i.e. among different transects) variability (Figs. 5A–C). The $\delta^{13}\text{C}$ values for deep slope DOC (Figs. 6A–C) also showed a relatively narrow range in values, but values were overall lighter and more variable in August 1996 than during the other two sampling times.

Fig. 5. $\Delta^{14}\text{C}$ values of DOC for all slope stations for (A) April–May 1994, (B) March 1996, and (C) July–August 1996.

Fig. 6. $\delta^{13}\text{C}$ values of DOC for all slope stations for (A) April–May 1994, (B) March 1996, and (C) July–August 1996.

3.4.2. Suspended POC

Perhaps the most striking feature of this data set lies in the isotopic values for suspended POC collected from deep continental slope waters in the MAB (Figs. 7A–C and 8A–C). Concentrations of POC were similar in all deep slope waters and

showed no major differences between the three cruises or between depths (Table 2). However, as previously noted (Bauer and Druffel, 1998; Bauer et al., 2001) these suspended POC concentrations are still several-fold greater than concentrations in open North Atlantic mesopelagic waters. The

Fig. 7. $\Delta^{14}\text{C}$ values of suspended POC for all slope stations for (A) April–May 1994, (B) March 1996, and (C) July–August 1996.

Fig. 8. $\delta^{13}\text{C}$ values of suspended POC for all slope stations for (A) April–May 1994, (B) March 1996, and (C) July–August 1996.

$\Delta^{14}\text{C}$ -POC values decreased most strongly between the surface and ~ 300 m depth (Figs. 7A–C), indicating a rapid and essentially complete loss or dilution of bomb ^{14}C -labeled POC over the top few hundred meters of the water column of the slope. It may be worth noting that the two oldest samples measured in this entire study ($\sim 7,700$ and $8,700$ yr ages; Table 2; Figs. 7B and C) were of suspended POC collected at ~ 300 m depth in slope waters, just below the shelf–slope break. Overall, the ages of suspended POC ranged from modern to ~ 8700 yr, and represent the oldest set of POC profiles ever observed in any ocean environment. The $\delta^{13}\text{C}$ -POC values for deep slope waters were correspondingly among the most depleted ever observed in deep-ocean waters (Figs. 8A–C), and ranged from -31.6‰ to -23.0‰ . As we discuss below, these findings may be evidence of previously unrecognized sources of isotopically unique organic matter to at least certain ocean margins, and possibly the open ocean. Both $\Delta^{14}\text{C}$ -POC and $\delta^{13}\text{C}$ -POC values in deeper slope waters were much more highly variable than values in shelf and shallow slope waters (Figs. 2B, 3B and 4B), and were often observed to decrease to the greatest depth sampled (Figs. 7A–C and 8A–C).

4. Discussion

The extensive assessment of ^{14}C and ^{13}C in total bulk DOC and suspended POC in the MAB in 1994 and 1996 had the following major objectives: (1) to estimate both qualitatively and quantitatively the range in isotopic signatures and ages of potential source terms for DOC and POC in continental shelf and slope waters of a major continental margin system, (2) to evaluate the differences and similarities in sources and cycling of DOC and POC in the MAB, (3) to assess the temporal variability (both intra- and inter-annual) in isotopic compositions, sources, and residence times of DOC and POC, and (4) to understand better the transport and fluxes of organic matter from terrestrial and riverine systems to the continental margin and beyond.

The large-scale regional distributions of ^{14}C and ^{13}C in DOC in surface shelf and slope waters of the MAB (Figs. 2–4; Table 2), and the vertical distributions of ^{14}C and ^{13}C in both DOC and POC in slope waters (Figs. 5–8) indicate that there is a high degree of variability within this system in the isotopic abundances of the two major organic carbon pools. This variability is assumed to result from both short- and long-term temporal as well as regional variations in the relative contributions of isotopically distinct sources of DOC and POC to the MAB shelf and slope, as well as from selective heterotrophic degradation of specific and isotopically distinct components of the bulk DOC and POC pools. In some cases, much of this variability can be attributed to relatively short-term but large-scale temporal (e.g., seasonal or intra-annual) effects, such as the general system-wide increase in $\Delta^{14}\text{C}$ -DOC between March and August 1996 (compare Figs. 3A and 4A). In other cases, the extreme disparity in the isotopic signatures of DOC and POC in shelf waters indicates that major fractions of these two pools are derived from uniquely aged sources.

The predominant flow of shelf water in the MAB is from the northeast toward the southwest, and a significant component of the low-salinity shelf water is believed to derive from an extensive coastal circulation system originating farther north in the Labrador Sea and Scotian Shelf regions (Mountain, 1991; Loder et al., 1998). These source waters may consequently carry their own unique organic isotopic signatures with them. Losses of water and materials from the MAB occur both along its length as well as via eastward offshore transport in the vicinity of Cape Hatteras (Churchill and Berger, 1998; Loder et al., 1998). Both mechanisms may mediate the transfer of materials between the MAB, Gulf Stream, and open North Atlantic (Bates and Hansell, 1999). Finally, the highly dissimilar concentrations and isotopic values of both DOC and POC in shelf vs. slope waters may be a reflection of (a) limited exchange of these two major pools (especially for POC) between shelf and slope waters, (b) uniquely aged sources of DOC and POC to shelf vs. slope waters, and or (c) selective removal of different sources and ages of DOC and POC by biotic and

abiotic processes in shelf vs. slope environments. In the following, we explore some of the spatial and temporal variability in DOC and suspended POC through analyses of various property–property relationships, as well as with respect to several of the dominant hydrographic and biogeochemical features of the MAB. In the previous work of Bauer et al. (2001), in which only the 1994 data set was considered, a quantitative analysis of the contributions of variably aged organic material to the DOC and POC pools was carried out. We also employ this approach here to analyze the data sets from all three cruises, and conclude our discussion of DOC and POC distributions in the northwest Atlantic margin by evaluating the much larger collective data sets of these two pools.

4.1. Isotopic compositions and distributions of DOC and POC

4.1.1. DOC in the MAB

The concentrations of DOC in the MAB measured in shelf and shallow slope waters (49–156 μM ; Table 2) using high-energy UV oxidation are consistent with values reported for the MAB by other investigators. Chen et al. (1996) observed concentrations of 72–85 μM in shallow George's Bank waters, while in March 1996, Vlahos et al. (1998, 2002) found a much broader range of ~ 60 –140 μM throughout the entire MAB. The latter study observed increasing concentrations both onshore and southwestward toward Cape Hatteras. Guo et al. (1996) and Bates and Hansell (1999) also measured relatively high surface concentrations (~ 80 –100 μM) in the southern part of the MAB near Cape Hatteras. Deeper slope waters (~ 300 –1000 m) in the present study had significantly lower concentrations (36–54 μM ; Table 2) than surface waters. Concentrations in deep slope waters varied little with depth, sampling time or location. The concentrations in our slope waters had a somewhat greater range than concentrations reported previously for deep slope waters in various regions of the MAB (47–56 μM ; Chen et al., 1996; Guo et al., 1996; Hopkinson et al., 1997), but this may in part be a result of the greater number of deep slope samples analyzed in the present study.

Mixing relationships between inherently conservative and non-conservative solutes may provide insights into sources and/or sinks in a system. With the exception of the single low-salinity sample near the mouth of Chesapeake Bay in August 1996 ($S = 24.9$, transect 5; Table 1; Fig. 1), the salinity range of samples in this study was relatively narrow ($S = \sim 29.4$ –36.2; Table 1). Indeed, only five samples in the entire study were lower than $S = 30.0$, and all of these were in slope waters of transects 4 and 5, just to the north and south, respectively, of Chesapeake Bay (Table 1; Fig. 1). A strong inverse linear relationship ($y = -11.43x + 454$; $r^2 = 0.731$; $n = 105$) between DOC concentration and salinity was observed for all samples combined (Fig. 9A). The y -intercept for this relationship (454 μM) is nearly identical to the concentrations of DOC observed in various river end-members for subestuaries of the Chesapeake Bay (Raymond and Bauer, 2001a,b). However, two subsets of samples exhibit significant departure from this composite line. The first subset consists of elevated DOC samples located predominantly in the southern MAB (Fig. 9A), and, as noted previously by Bauer et al. (2001), these indicate a source of “surplus” DOC (indicated by “S” in Fig. 9A) of ~ 25 –44 μM , at least at certain times. At least two of the elevated DOC samples are associated with high-salinity water ($S > 36.0$), likely resulting from the intrusion of Gulf Stream water into the southern MAB (Tables 1 and 2; Fig. 9A). The second subset consists of deep slope waters, where it can be seen that the lowest DOC values are clustered beneath the composite mixing line (Fig. 9A). These lower-than-predicted values indicate that either the DOC in slope waters originates from sources other than those dominating the shallower shelf and slope waters, or, assuming mixing between shallow shelf and slope waters and deep slope waters, that there is removal of DOC in slope waters.

With the exception of these two anomalous and non-conservative subsets, DOC throughout the MAB still exhibits at least quasi-conservative behavior across the continuum of relatively low-salinity shelf waters and high-salinity slope and Gulf Stream waters. Conservative behavior has been observed previously for DOC in other studies

Fig. 9. (A) DOC concentration vs. salinity, (B) $\Delta^{14}\text{C}$ -DOC vs. salinity, (C) $\delta^{13}\text{C}$ -DOC vs. salinity, and (D) $\Delta^{14}\text{C}$ -DOC vs. $\delta^{13}\text{C}$ -DOC for all three cruises. Details of linear regressions and correlations are discussed in text. For DOC concentrations vs. salinity (panel A) and $\delta^{13}\text{C}$ -DOC vs. salinity (panel C), the regression lines include all data points. For the $\Delta^{14}\text{C}$ -DOC vs. salinity regression (panel B) and the $\Delta^{14}\text{C}$ -DOC vs. $\delta^{13}\text{C}$ -DOC correlation (panel D), the lines include shelf and shallow slope (5 m depth) waters only, and do not include deep ($\geq 300\text{m}$) slope waters. Between one and three highly anomalous values (indicated by "*" in Table 2) are not plotted in these figures because of their departure from the ranges used for the $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ axes. Points labeled with "S" in panel A indicate elevated DOC concentrations in the southernmost transect during April 1994 and March 1996. Note that the linear relationships plotted in panels B and C are not intended to convey the conservative mixing relationships for $\Delta^{14}\text{C}$ -DOC and $\delta^{13}\text{C}$ -DOC as a function of salinity, which would be slightly concave down and concave up, respectively.

of estuarine (e.g., Mantoura and Woodward, 1983) and shelf–slope (Vlahos et al., 2002) mixing. While lower water temperatures have been observed to limit the rate of DOC degradation in coastal systems (Moran et al., 1999; Raymond and Bauer, 2000), there are no obvious differences between the warmer August 1996 and the colder April 1994 and March 1996 samples (Fig. 9A). The possibility also exists that our sampling and DOC mixing diagrams, in general, are limited in real time and are not truly representative of the full

range of spatial and temporal variability of these dynamic coastal systems.

There was a clear delineation between the DOC of shelf and shallow slope waters and deep slope waters at all three sampling times based on the $\Delta^{14}\text{C}$ -DOC vs. salinity relationship (Fig. 9B). A similar, but slightly less robust, relationship was noted previously by Bauer et al. (2001) using only the April 1994 data set ($n = 13$). Using the composite data set, salinity explained approximately three-quarters of the variance in

$\Delta^{14}\text{C}$ -DOC in shelf and shallow slope waters, with a range (again excluding the single $S = 24.9$ sample) in $\Delta^{14}\text{C}$ -DOC of $>270\text{‰}$ over a concomitant salinity range of only 6.8 ($y = -33.41x + 923$; $r^2 = 0.723$; $n = 64$). It is interesting to note that while the y -intercept of this relationship (923‰) is far greater than the $\Delta^{14}\text{C}$ values observed for riverine DOC end-members of various Chesapeake Bay subestuaries (~ 200 – 250‰ ; Raymond and Bauer, 2001a, b), it is close to the maximum $\Delta^{14}\text{C}$ of atmospheric CO_2 at the height of thermonuclear weapons testing (Levin and Kromer, 1997), and which may at one point have been representative of the riverine DOC. Three of the four lowest salinity shelf water samples ($S = 24.9$ – 29.5) contained detectable bomb ^{14}C ($\Delta^{14}\text{C} = -50$ to -29‰). The 20–133‰ increase in shelf mixed layer $\Delta^{14}\text{C}$ -DOC between March and August 1996 (Figs. 3A and 4A) and the general increase in DOC concentration (Table 2) may be accounted for in large part by the 1–2 unit decrease in salinity (Table 1). Using the relationships in Figs. 9A and B, the lower salinity alone (i.e. greater freshwater and riverine DOC fluxes) predicts an increase in $\Delta^{14}\text{C}$ -DOC between March and August 1996 of approximately 66‰. Below, we calculate this bomb- ^{14}C -enriched DOC to have significant contributions from modern terrestrial/riverine as well as shelf primary production, on the basis of its unique composite $\Delta^{14}\text{C}$ - $\delta^{13}\text{C}$ signature. The present study suggests that the influence of buoyant low-salinity plumes (see reviews by Hickey, 2000; Wright and Nittroter, 1995; Malone and Ducklow, 1990), driven by freshwater discharge from the major eastern US rivers and estuaries, may be manifested by inputs of young, terrestrial and/or coastal organic matter across much of the MAB shelf and surface slope waters.

Deep (~ 300 – 1000 m) slope waters had a considerably narrower range in $\Delta^{14}\text{C}$ -DOC values (-451‰ to -357‰) than shelf and shallow slope waters, over a salinity range of 34.9–35.6 (Fig. 9B). All but six slope samples were lower in $\Delta^{14}\text{C}$ than DOC from mesopelagic depths (~ 300 – 1000 m) in the Sargasso Sea, and as a group the slope values were lower than the average $\Delta^{14}\text{C}$ -DOC value ($-394 \pm 13\text{‰}$, $n = 9$) for abyssal (> 1000 m) Sargasso waters (Bauer et al., 2001). As also noted by

Bauer et al. (2001), this suggests that there may be one or more sources of ^{14}C -depleted DOC to these deeper continental slope waters that is/are older than the DOC found in even the deepest, central-most part of the North Atlantic gyre (Bauer and Druffel, 1998).

The relationships between $\delta^{13}\text{C}$ -DOC and salinity, and between $\delta^{13}\text{C}$ -DOC and $\Delta^{14}\text{C}$ -DOC may provide qualitative information on the potential sources (i.e. terrestrial vs. marine) of both the ^{14}C -enriched and depleted DOC observed in MAB shelf and slope waters (Fig. 9B). Approximately one-third of the total variance in $\delta^{13}\text{C}$ -DOC is explained by salinity when the entire shelf and slope (including deep waters) data set is considered ($y = 0.22x - 29.98$; $r^2 = 0.292$; $n = 104$; Fig. 9C). The y -intercept of this relationship ($\sim -30\text{‰}$) is very close to the riverine DOC end-member for Chesapeake Bay subestuaries (Raymond and Bauer, 2001a, b). Samples from the slope in August 1996 (indicated by the dashed box in Fig. 9C) were significantly lower in $\delta^{13}\text{C}$ -DOC than the other high-salinity samples. As a group (i.e. all shelf and slope waters), the August 1996 samples were shifted to lower overall $\delta^{13}\text{C}$ -DOC values than the April 1994 and March 1996 samples (Fig. 9C), suggesting either an overall input of ^{13}C -depleted DOC, or a loss of ^{13}C -enriched DOC, during this time. The $\delta^{13}\text{C}$ -DOC vs. salinity relationship is thus considerably stronger ($r^2 = 0.482$; $n = 94$) when the August 1996 slope values are excluded.

The anomalous nature of DOC from deep slope waters in general is shown by the relationships between $\Delta^{14}\text{C}$ -DOC and $\delta^{13}\text{C}$ -DOC (Fig. 9D). A highly significant composite relationship (i.e. for all three sampling periods combined) was found for shelf and upper slope waters ($y = -42x - 1125$; $r = 0.378$; $P < 0.01$; $n = 63$), indicating that ^{13}C -depleted material, possibly derived from terrestrial and freshwater sources, contributes a significant fraction of ^{14}C -enriched DOC to MAB shelf and slope waters. However, there was no relationship between $\Delta^{14}\text{C}$ -DOC and $\delta^{13}\text{C}$ -DOC for deep slope waters, suggesting that: (a) there are multiple sources of aged and $\delta^{13}\text{C}$ -variable (nearly 3‰) DOC to slope waters; (b) sources of young (i.e. ^{14}C -enriched) DOC, whether they are enriched or

depleted in $\delta^{13}\text{C}$, have their young component removed preferentially (this has been demonstrated for the degradation of riverine DOC by Raymond and Bauer, 2001b); and (c) shelf and slope waters are completely uncoupled with respect to DOC sources, and each has unique source waters.

4.1.2. Suspended POC in the MAB

The physical and chemical factors affecting the distributions and characteristics of DOC and POC are likely unique for these two major pools of organic matter (Hedges et al., 1986; Hedges and Keil, 1999). While DOC and POC derived directly from unaltered source materials may resemble each other isotopically and even molecularly, a number of processes including sorption, desorption, selective degradation (both biotic and abiotic), photochemical reactivity, etc., may discriminate between and segregate these two major pools in a number of respects in different aquatic systems (Keil et al., 1997; Hedges and Keil, 1999). In those studies (both marine and freshwater) where both $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ of DOC and POC have been examined, large differences have been observed (Hedges et al., 1986; Trumbore et al., 1992; Druffel et al., 1992; Raymond and Bauer, 2001a, b), indicating that DOC and POC can have highly disparate sources and residence times as a result of their physical and chemical properties and biogeochemical processing.

The distributions and $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values for suspended POC (Figs. 10A–C) differed greatly from those for DOC in the MAB. In general, $\Delta^{14}\text{C}$ values of POC from the shelf and upper slope were much more enriched in bomb ^{14}C and spanned a considerably narrower range ($\sim 130\%$) than DOC over the same range of salinities (Fig. 10A). This indicates that the POC from this part of the MAB is derived from significantly younger sources than is DOC. The younger sources of POC may include planktonic biomass produced both autochthonously and imported from other waters, especially from those to the north such as the Scotian Shelf (Wood et al., 1996). High-salinity deep slope waters, on the other hand, had a much greater range of $\Delta^{14}\text{C}$ -POC values ($\sim 475\%$) than shelf and shallow slope

waters (Fig. 10A), and this range was a factor of 4–5 greater than that for $\Delta^{14}\text{C}$ -DOC values ($\sim 100\%$; Fig. 9B) from the same slope waters. It is significant that the $\Delta^{14}\text{C}$ -POC values in deep slope waters cannot be supported entirely by inputs of average sedimentary organic matter in this region, which is enriched in ^{14}C relative to POC (Anderson et al., 1994; DeMaster et al., 2002). The ranges in, and co-variance between, $\Delta^{14}\text{C}$ -DOC and $\Delta^{14}\text{C}$ -POC for shelf and shallow slope waters as well as deep slope waters is more clearly shown in Fig. 11A.

The range of $\delta^{13}\text{C}$ -POC values was relatively much greater (Fig. 10B) than for DOC (Fig. 9C) for all samples and across all salinities (Fig. 11B), and clearly indicates a much more significant contribution to the POC pool than to the DOC pool from isotopically light carbon, throughout the MAB. This is particularly true for deep slope waters, where $\delta^{13}\text{C}$ -POC values ranged from -31.6% to -25.6% (Figs. 10B and 11B). Depleted values such as these have only been noted previously in subarctic ocean waters, where they are controlled by pCO_2 limitation and isotopic fractionation by phytoplankton populations (Rau et al., 1991, 1992). The much lower $\delta^{13}\text{C}$ -POC values in slope waters here indicate that this material is unlikely to be derived directly from shallower waters, but instead must have a unique deep-water source. While fine surficial slope and/or shelf sediments would be likely sources, as we shall see nearly all sediments examined in the MAB have much higher $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values than slope suspended POC, thus requiring a source other than bulk sediment organic matter to the suspended POC pool. The strong positive correlation between $\Delta^{14}\text{C}$ -POC and $\delta^{13}\text{C}$ -POC for all MAB samples (Fig. 10C; $y = 45.3x + 1030$; $r = 0.873$, $P < 0.01$, $n = 91$) indicates that in general, and for the slope especially, suspended POC is older as it attains greater ^{13}C depletion, and is younger concomitant with greater ^{13}C enrichment. This is to be contrasted with DOC, which exhibited no such relationship in slope waters, but did show an inverse relationship between $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ in shelf and shallow slope waters (Fig. 9D). As we show below, it is the co-variance in $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ in both the DOC and POC, and

Fig. 10. (A) $\Delta^{14}\text{C}$ -POC vs. salinity, (B) $\delta^{13}\text{C}$ -POC vs. salinity, and (C) $\Delta^{14}\text{C}$ -POC vs. $\delta^{13}\text{C}$ -POC for all three cruises. Details of linear regressions and correlations are discussed in text. For $\Delta^{14}\text{C}$ -POC vs. salinity regression (panel A) and $\Delta^{14}\text{C}$ -POC vs. $\delta^{13}\text{C}$ -POC correlation (panel C), the lines include all data points. For $\delta^{13}\text{C}$ -POC vs. salinity (panel B), the regression line includes all shelf and shallow slope (5 m depth) waters only, and does not include deep (≥ 300 m) slope waters. One highly anomalous value (indicated by “*” in Table 2) is not plotted in these figures because of its departure from the ranges used for the $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ axes.

the disparity in the $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values between these pools, that enables us to constrain both qualitatively and quantitatively the contributions of potential organic matter sources to these two pools in the MAB using a dual isotope approach.

4.2. Constraining sources and inputs of DOC to the MAB

The stable and radiocarbon isotopic compositions of DOC and POC may be used to estimate the contributions of different sources of organic matter to these two pools, provided the isotopic compositions of the potential sources (a) have been identified, (b) are adequately constrained

isotopically and (c) have non-overlapping ranges in both $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ simultaneously. The much greater dynamic range of $\Delta^{14}\text{C}$ values ($\sim -1000\text{‰}$ to $\sim +200\text{‰}$) compared to $\delta^{13}\text{C}$ values (typically $\sim -23\text{‰}$ to -19‰) in naturally occurring reservoirs of exchangeable marine organic matter, may allow natural ^{14}C to be used as a more sensitive source indicator (as well as an age indicator) in these and other systems. As pointed out by Bauer et al. (2001), the relative contributions of different sources of organic matter to a given sample type have been estimated primarily using single isotopes (e.g., $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{34}\text{S}$ or $\Delta^{14}\text{C}$, etc.), and by knowing or assuming the isotopic “end-member” components contributing to the sample. A linear

Fig. 11. Ranges in (A) $\Delta^{14}\text{C}$ -DOC vs. $\Delta^{14}\text{C}$ -POC and (B) $\delta^{13}\text{C}$ -DOC vs. $\delta^{13}\text{C}$ -POC for all three cruises.

mixing model is then applied to establish the relative contributions of the different sources. In simple or well-constrained systems, single isotope linear mixing models are often adequate for establishing first-order estimates of the sources contributing to a sample. However, the number and isotopic variability of autochthonous and allochthonous sources of organic matter in systems such as coastal marine environments can be greater than in many other aquatic environments. In complex systems such as these, the use of multiple natural isotopes may provide a greater degree of discrimination between multiple sources than single isotopes (Williams et al., 1992). The

same principles and mixing equations hold for the application of multiple isotopes of the same element (i.e. $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$) as for multiple stable isotopes of different elements (Fry and Sherr, 1984; Peterson and Howarth, 1987; Michener and Schell, 1994; Kwak and Zedler, 1997). Furthermore, the concurrent use of $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ should provide a greater degree of specificity for organic carbon than multiple isotopes of different elements (e.g., $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) used for studies of more general organic matter sources and cycling.

The $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ ranges for those potential sources of DOC to MAB shelf and slope waters, which have been identified, are shown in Table 3 (means) and plotted in Fig. 12A (means and ranges). These sources include: (a) total freshwater DOC from Chesapeake Bay, as represented by one of its major subestuaries, the York River estuary (Raymond and Bauer, 2001a), (b) the high molecular weight ($>1\text{ kD}$) component of DOC from the mainstream of Chesapeake Bay (Guo et al., 1996), (c) the very high molecular weight ($>10\text{ kD}$) component of MAB near-bottom material from the nepheloid layer (Guo et al., 1996), (d) present-day primary production in MAB surface waters, estimated from the $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of DIC (Table 2), and (e) previous estimates of fully marine values for the surface and deep Sargasso Sea (Bauer et al., 1992a, b; Druffel et al., 1992), taken to be representative of open North Atlantic waters in general. Use of the isotopic values of Chesapeake Bay $>1\text{ kD}$ and deep MAB $>10\text{ kD}$ fractions of DOC (Guo et al., 1996) as terrestrial/riverine end-members is supported by the findings of Mitra et al. (2000), who showed that both of these components contained elevated amounts of lignin-derived phenols originating from terrestrial plants.

Taken as a whole, the DOC samples measured in this study are reasonably assumed to be comprised of one or more of the indicated potential sources, since the measured sample values lie within the field(s) established by one or more of the indicated sources (Fig. 12A). Furthermore, shelf and shallow slope DOC (Fig. 12B) appears to be comprised of different end-member sources than deep slope DOC (Fig. 12C). Bauer et al. (2001), using the more limited 1994 data set,

Table 3

Mean $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of potential sources of DOC and POC to the Mid-Atlantic Bight (see also Figs. 12 and 13). Adapted from Bauer et al. (2001)

Potential source	Mean $\Delta^{14}\text{C}$ (‰)	Mean $\delta^{13}\text{C}$ (‰)	Reference
<i>DOC sources</i>			
York River	200	−28.4	Raymond and Bauer (2001a)
Freshwater DOC			
Chesapeake Bay (5–25 psu)	−1	−27.8	Guo et al. (1996)
HMW (> 1 kD) DOC			
Deep MAB VHMW (> 10 kD) DOC	−580	−26.4	Guo et al. (1996)
MAB primary production ^a	55	−20 ^b	Bauer et al. (2001) and this study
Deep Sargasso DOC	−394	−20.8	Bauer et al. (1992a, b)
Surface Sargasso DOC	−238	−21.2	Druffel et al. (1992)
<i>POC sources</i>			
York River	−68	−29.1	Raymond and Bauer (2001a)
Freshwater POC			
Deep MAB VHMW (> 10 kD) DOC	−580	−26.4	Guo et al. (1996)
MAB primary production ^a	55	−20 ^b	Bauer et al. (2001) and this study
MAB surface sediments	−251	−20.1	Tanaka et al. (1991)
	−151	n.d.	Anderson et al. (1994)
	−121	−21	DeMaster et al. (2002) and Thomas et al. (2002)

^a Based on $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ of surface ocean DIC (Table 2).

^b Assumes fractionation of −19‰ during CO_2 fixation by marine phytoplankton
n.d.—not determined.

speculated that this might be a result of unique sources and ages of DOC to these two major parts of the margin system. It is also possible from Fig. 12A for admixtures of MAB modern primary production and > 10 kD nepheloid material to give $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values similar to those observed in MAB shelf and shallow slope waters. However, two factors argue against this proposed scenario. First, the > 10 kD ^{14}C -depleted material in deeper waters comprises only 3–6% of the total DOC (Guo et al., 1996). Second, the observations of Guo et al. (1996) indicate that in shallow waters of the MAB, the > 10 kD fraction was actually similar in both $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ to values for MAB primary production (Fig. 12A).

For shelf and shallow slope waters, we assume that the predominant DOC inputs to the MAB (shown as Groups 1, 2 and 3 in Fig. 12B) can be described reasonably by varying contributions from (a) surface Sargasso material (which itself is comprised of deep Sargasso material and recent primary production; Bauer et al., 1992a, b; Druffel et al., 1992), (b) Chesapeake Bay material (which must also contain some York River material, so this is not included explicitly), and (c) material derived from contemporary MAB primary production. We note that it is also possible that not all potential sources have been identified and measured for $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$, and that the isotopic variability of potential sources has not been

Fig. 12. (A) Means and ranges in $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of potential sources of DOC to MAB shelf and slope waters (indicated by crosses) and actual observed values (indicated by symbols). Isotope values for potential sources were obtained from the studies summarized in Table 3. (B) The $\Delta^{14}\text{C}$ vs. $\delta^{13}\text{C}$ fields of potential source combinations of DOC to MAB shelf and surface slope waters and (C) MAB deep slope waters. The full $\Delta^{14}\text{C}$ range for the > 10 kD nepheloid layer material in panels B and C (and hence the lines connecting it to the SS, 3–200 m and SS > 1000 m fields) extends below the x-axis. Symbol key: (○) April 1994 data; (■) March 1996 data; (△) August 1996 data. SS—Sargasso Sea. See text and Tables 3 and 4 for details.

assessed adequately. In spite of these limitations, however, the mixing fields (Fig. 12B) indicate that all but four shelf and shallow slope samples (Group 3) can be described by mixtures of these three major sources. The majority of these samples (Group 2) can be described by a simple admixture of DOC resembling that from Chesapeake Bay and the surface Sargasso Sea (Fig. 12B). Group 1 DOC, because it lies within the field described by Chesapeake Bay, surface Sargasso Sea, and MAB primary production, is predicted to consist of three, instead of two, components. Group 3 samples (i.e. from the southern MAB) must have an additional source of older material, which is best represented by the ^{14}C - and ^{13}C -depleted nepheloid layer material (see below). It should be noted that, within the constraints of this approach, DOC in shelf and shallow slope waters cannot be described by a mixture of material derived exclusively from Chesapeake Bay/York River and MAB primary production. A significant contribution to all shelf and shallow slope waters is required from old, offshore oceanic DOC (Fig. 12B).

We follow the approach of Bauer et al. (2001) where a three-source isotopic mixing model similar

to those of Fry and Sherr (1984) and Kwak and Zedler (1997) was employed to estimate the contributions of the various sources to shelf and slope DOC. The generalized mixing equation is

$$X_{\text{DOC-MAB}} = f_1 X_{\text{DOC-}f_1} + f_2 X_{\text{DOC-}f_2} + (1 - f_1 - f_2) X_{\text{DOC-}f_3}, \quad (1)$$

where X is the isotopic composition ($\Delta^{14}\text{C}$ or $\delta^{13}\text{C}$) of DOC 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 total DOC 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 $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$. The contribution of the third potential source, f_3 , is equal to $(1 - f_1 - f_2)$. We note that this model is applicable only when three or fewer sources can be reasonably assumed.

Similar to the findings of Bauer et al. (2001) using the 1994 data set only, the predominant component in all shelf and shallow slope waters is comprised of open-ocean material (i.e. resembling Sargasso surface DOC; Table 4). However, material similar in isotopic composition to Chesapeake

Table 4

Estimates of relative inputs of different potential sources of DOC and POC to the Middle Atlantic Bight, based on results of three-source isotopic mixing models. Adapted from Bauer et al. (2001). See text for details

DOC or POC	Relative contribution (%) of:					
	Ches./York	MAB prim. prod.	Sargasso shallow	Sargasso deep	MAB nepheloid	MAB surf. sediments
DOC						
<i>Shelf and shallow slope</i>						
Group 1 ^a	19–58	8–43	11–52	n.a.	n.a.	n.a.
Group 2 ^a	9–48	0–15	50–97	n.a.	n.a.	n.a.
Group 3 ^a	2–8	n.a.	77–89	n.a.	10–21	n.a.
Deep slope ^b	0–6	n.a.	n.a.	46–100	0–52	n.a.
POC						
<i>Shelf and shallow slope</i>						
Group 1 ^c	0–50	49–100	n.a.	n.a.	n.a.	0–27
<i>Deep slope</i>						
Group 2 ^c	45–54	0–8	n.a.	n.a.	n.a.	48–52
Group 3 ^c	32–94	n.a.	n.a.	n.a.	6–68	0–17

^aAs shown in Fig. 12b.

^bAs shown in Fig. 12c.

^cAs shown in Fig. 13 and described in text.

n.a.—not applicable (end-member not used in mass balance).

Bay DOC and recent MAB primary production can comprise up to 58% and 48% of Groups 1 and 2, respectively, of shelf and shallow slope DOC (Fig. 12B; Table 4). Although neither chlorophyll-*a* nor primary production was measured on these cruises, measurements made in the southern MAB in March and July 1996 showed that while shelf chlorophyll-*a* was lower in March, integrated shelf primary production was greater at this time (Lohrenz et al., 2002). This indicates that the accumulation of ^{14}C -enriched DOC in the shelf and slope mixed-layer observed between March and July 1996 (compare Figs. 3A and 4A) may have resulted directly or indirectly from this increased production (e.g., via phytoplankton exudation, grazing, cellular lysis, etc.), in conjunction with decreases in mixed layer depth (Flagg et al., 2002). Group 3 samples must, in addition to the three potential sources already described, also have a component that is much older in order to account for the observed values. The only material that has been identified that can fulfill the requirement of a simultaneously ^{14}C - and ^{13}C -depleted DOC component is the very high molecular weight DOC ($> 10\text{ kD}$) from the nepheloid layer (Guo et al., 1996). When this source is mass balanced against shallow Sargasso and TRE material, we find that it may comprise up to nearly half of the total DOC, while younger TRE material represents less than 10% of the contribution (Table 4).

For deep slope waters, the isotopic composition of DOC can be described almost exclusively by co-varying fractions of deep Sargasso and $> 10\text{ kD}$ nepheloid layer material (Fig. 12C). Up to about half of the deep slope DOC may be comprised of an old, ^{13}C -depleted high molecular weight component (Table 4). Recent studies (Druffel and Williams, 1990; Sherrell et al., 1998; Bianchi et al., 1998; Bauer and Druffel, 1998; Druffel et al., 1998; Honda et al., 2000) have suggested that lateral inputs of organic matter from both the nepheloid layer and sediments in continental margins may be significant sources of DOC and suspended POC to slope waters and open-ocean waters. The high molecular weight component also has substantial terrestrial $\delta^{13}\text{C}$ character (Guo et al., 1996; Guo and Santschi, 2000), and may represent an aged

component of terrestrial and shelf/slope-derived organic matter that gradually diffuses from sediments to the overlying water column (Bauer et al., 1995; Burdige and Gardner, 1998; Burdige et al., 1999; Alperin et al., 1999). It is also possible that the TRE end-member used here is not fully represented by York River and Chesapeake Bay DOC, but actually has a greater local component in some coastal waters of even older riverine DOC, such as that observed for the Hudson River ($\Delta^{14}\text{C}\text{-DOC} = \sim -158\text{‰}$) by Raymond and Bauer (2001b).

4.3. Constraining sources and inputs of POC to the MAB

The $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ signatures of suspended POC in the MAB indicate that this pool of organic matter has unique origins and input terms from those of DOC (Figs. 2B, 3B, 4B, 7 and 8). While shelf and shallow slope POC was relatively young, its isotopic signatures were nearly always lower than those for DIC sampled at the same time (Table 2), indicating that surface POC, and especially slope POC, contained varying amounts of old, ^{13}C -depleted material from other sources (also seen in Fig. 13). Potential sources to MAB shelf and slope waters of ^{14}C -depleted POC with considerable terrestrial $\delta^{13}\text{C}$ character include shelf and slope sediment resuspension from tidal and wind-driven mixing (Meade et al., 1975; Fischer, 1980; Csanady et al., 1988; Nittrouer and Wright, 1994) or even commercial trawling (Churchill, 1989). The isotopic compositions of bulk sedimentary organic matter (Tanaka et al., 1991; Anderson et al., 1994; DeMaster et al., 2002) and our observed $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of suspended POC (Fig. 13) are not alike, limiting the magnitude of a bulk sedimentary source. However, a single $\Delta^{14}\text{C}$ value reported for lignin phenols extracted from MAB surface slope sediments (2700 m depth; Tanaka et al., 1991) was similar (-327‰) to the value for bulk sediments (-294‰), indicating that relic terrestrial material is indeed present in these sediments, and by inference, may be a component of suspended POC.

Most of the suspended POC in our MAB shelf and shallow slope samples (Figs. 10C and

Fig. 13. Means and ranges in $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ fields of potential sources of suspended POC to MAB shelf and slope waters (indicated by crosses) and actual observed values (indicated by symbols). Isotope values for potential sources were obtained from the studies summarized in Table 3. Symbol key: (○) April 1994 data; (■) March 1996 data; (△) August 1996 data. See text and Tables 3 and 4 for details. The two lowest $\Delta^{14}\text{C}$ -POC and $\delta^{13}\text{C}$ -POC samples do not appear because of their departure from the ranges used for the $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ axes. UC—"unconstrained" samples for which all the potential sources of DOC have not been identified. The highly $\Delta^{14}\text{C}$ -depleted value of -615‰ is not presented in the figure (see also Table 2 caption).

13) is best described by a combination of recent shelf-slope primary production and material similar to that found in the York River estuary (Raymond and Bauer, 2001a). We take the values for the York (Table 3) to be representative of suspended POC discharged from Chesapeake Bay and other Mid-Atlantic river and estuary systems in general (Raymond and Bauer, 2001b). In order to account for the lower $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ in deep slope samples (Figs. 10C and 13), both MAB surface sediments and $>10\text{ kD}$ HMW nepheloid material are required to make significant contributions to the suspended POC pool. Inherent in the use of the $>10\text{ kD}$ HMW material is the assumption that it either sorbs to, or aggregates to form, POC-sized (i.e. $\geq 0.8\text{ }\mu\text{m}$) material. We note that there are several unconstrained samples (indicated by "UC" in Fig. 13) that have a more highly ^{14}C - and ^{13}C -depleted source(s) than those so far identified in the MAB.

We may calculate the relative contributions of MAB primary production, TRE-POC (as represented by the York River values; Table 3), surface sediments, and $>10\text{ kD}$ nepheloid material

to the suspended POC of the MAB (Fig. 13; Table 4) by again using a dual isotope, three-source mixing model. For the first group of POC samples (i.e. shelf and surface slope POC, Group 1), we solve Eq. (1) simultaneously using both $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values, and assume inputs only from MAB primary production, York River POC, and MAB surface sediments. The vast majority of these samples are dominated by simple two-component admixtures of TRE material and MAB primary production (Table 4; Figs. 10C and 13). Although generally of secondary importance to MAB primary production, ^{14}C - and ^{13}C -depleted TRE material can comprise up to $\sim 50\%$ of POC in the shelf and surface slope, as observed previously by Bauer et al. (2001). The second major type of POC is dominated by the deep slope samples (Groups 2 and 3; Fig. 13), and which is characterized by a greater number of potential combinations of sources (Fig. 13) than the shelf and shallow slope samples. Interestingly, it is not necessary for the "constrained" deep slope samples to be described by more than two sources simultaneously, even though contributions from more than two sources cannot be ruled out, and are even likely. Group 2 of the deep slope samples is dominated by admixtures of sedimentary material (approximately half of the total) balanced by TRE (i.e. York River) material (also approximately half of the total). The other deep slope samples (Group 3) are described by admixtures of material similar in isotopic composition to the $>10\text{ kD}$ nepheloid material ($\sim 6\text{--}68\%$) balanced by TRE material (up to $\sim 94\%$), with much smaller contributions from material resembling bulk sediment organic matter (Table 4). While material resembling bulk-sediment organic carbon may not constitute a direct source of organic matter to the DOC pool, selective fractionation of isotopically distinct sedimentary and porewater components (Guo and Santschi, 2000) during resuspension and hydrodynamic sorting (Keil et al., 1994), desorption from particles (Wang and Lee, 1993; Keil et al., 1997), or from porewater diffusion (Bauer et al., 1995) may still help to account for the generally low $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values for DOC and POC observed in the southern MAB and in MAB slope waters.

The final group of samples (indicated by “UC” in Fig. 13) is unconstrained by the known potential sources that have been measured in this system, and hence we cannot estimate the contributions of various potential sources to it. Sources of ^{14}C -depleted POC have been identified previously in the abyssal open ocean (Druffel and Williams, 1990), but this POC did not have the low $\delta^{13}\text{C}$ values of the MAB slope samples. The very low $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of the deep slope POC in the present study suggest contributions from either a highly aged terrestrial component, or possibly from natural hydrocarbon seepage. The latter seems unlikely, insofar as we would have expected to also see this reflected more extensively in the isotopic signatures of deep slope DOC; but this was not observed (Fig. 9D; Table 2). However, some evidence does exist for the potential occurrence of natural hydrocarbon seeps on the MAB slope (Boehm and Requejo, 1986; Dugan and Flemings, 2000). Additionally, elevated concentrations of methane in the MAB water column and sites of formerly living seep and vent communities and organisms in the vicinity of the Baltimore and Wilmington Canyons have been found (M. Scranton, pers. comm.). Assuming that the two primary sources of deep slope DOC (mean $\Delta^{14}\text{C} = -412 \pm 17\text{‰}$; mean $\delta^{13}\text{C} = -22.3 \pm 0.7\text{‰}$) are deep North Atlantic DOC (mean $\Delta^{14}\text{C} = -391 \pm 12\text{‰}$; mean $\delta^{13}\text{C} = -20.8 \pm 0.3\text{‰}$; Bauer et al., 1992a, b; Druffel et al., 1992) and fossil petroleum hydrocarbons (mean $\Delta^{14}\text{C} = -1000\text{‰}$; mean $\delta^{13}\text{C} = -30\text{‰}$), we calculate by simple linear isotopic mass balance that only between 2% (using $\delta^{13}\text{C}$) and 16% (using $\Delta^{14}\text{C}$) of the DOC need arise from natural seepage. A similar calculation for deep slope POC (mean $\Delta^{14}\text{C} = -297 \pm 101\text{‰}$; mean $\delta^{13}\text{C} = -27.2 \pm 2.5\text{‰}$), where the two main assumed sources are surface plankton biomass (mean $\Delta^{14}\text{C} = 55 \pm 10\text{‰}$; mean $\delta^{13}\text{C} = -20.0 \pm 0.5\text{‰}$) and natural hydrocarbons (mean $\Delta^{14}\text{C} = -1000\text{‰}$; mean $\delta^{13}\text{C} = -30\text{‰}$) yields petroleum contributions of between 28% and 67%, using $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ isotopic mass balances, respectively. The higher calculated percentages for POC vs. DOC are not necessarily intuitive, but may occur if petroleum hydrocarbons preferentially sorb to the particulate phase. If present, natural hydrocarbon seepage could

provide a source of ^{14}C -dead, ^{13}C -depleted DOC and POC to parts of the MAB.

If deep slope POC contains an aged terrestrial component, this aging must be occurring in margin (slope and/or shelf) sediments, as the POC discharged from Mid-Atlantic rivers and estuaries has thus far not been found to be as depleted in ^{14}C (Raymond and Bauer, 2001a, b). However, slope failure, seafloor cracking and erosion of submarine canyon walls have been documented for the MAB slope (Robb, 1990; Driscoll et al., 2000; Dugan and Flemings, 2000), and may provide a mechanism for the reintroduction to the slope water column of highly aged, fine-grained terrigenous particles such as those observed here. Evidence for the lateral transport of lithogenically derived particles and associated POC has been shown for a number of shelf/slope systems (Sherrell et al., 1998; Hung et al. 1999), and suggests that seaward inputs of old, terrestrial material may be significant (up to about half of the POC) in these environments. Finally, even in the open ocean, highly ^{14}C - and ^{13}C -depleted DOC (sea surface microlayer; Druffel et al., 1992) and ^{13}C -depleted suspended POC, concurrently enriched in land plant-derived lignin (Benner et al., 1997), have been found, indicating that inputs to the ocean of old, terrestrial organic matter may not be limited to the coastal ocean.

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