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Terrestrially derived dissolved organic matter in the Chesapeake Bay and the Middle Atlantic Bight

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Abstract—Concentrations of lignin-phenols were analyzed in high molecular weight dissolved organic matter ($0.2\ \mu m > \text{HMW DOM} > 1$ kDa) isolated from surface waters of the Chesapeake Bay (C. Bay), and surface and bottom waters of the Middle Atlantic Bight (MAB). The abundance of lignin-phenols in HMW DOM was higher in the C. Bay ($0.128 \pm 0.06\ \mu g\ L^{-1}$) compared to MAB surface waters ($0.016 \pm 0.004\ \mu g\ L^{-1}$) and MAB bottom waters ($0.005 \pm 0.003\ \mu g\ L^{-1}$). On an organic carbon-normalized basis, lignin-phenol abundances in the HMW DOM (i.e., Λ_6), were significantly higher ($p < 0.05$) in bottom waters compared to sediments at some stations in the MAB. Ratios of syringyl to vanillyl phenols (S/V) in HMW DOM, indicative of angiosperm-derived lignin, ranged from 0.165 to 0.422 in C. Bay, 0.100 to 0.314 in MAB surface waters, and 0.076 to 0.357 in MAB bottom waters. Ratios of vanillic acid to vanillin $(Ad/Al)_V$ in HMW DOM, indicative of lignin decay, ranged from 0.611 to 1.37 in C. Bay, 0.534 to 2.62 in MAB surface waters, and 0.435 to 1.96 in MAB bottom water. Ratios of S/V and $(Ad/Al)_V$ showed no significant differences between each environment, providing no evidence of any compositionally distinct input of terrestrial organic matter into each environment. When considering depth profiles of suspended particulate matter in the MAB, with C:N ratios, and bulk radiocarbon ages and stable carbon isotopic values in HMW DOM isolated from these areas, two scenarios present themselves regarding the sources and transport of terrestrially derived HMW DOM in the MAB. Scenario #1 assumes that a low amount of refractory terrestrial organic matter and old DOC are uniformly distributed in the oceans, both in surface and bottom waters, and that primary production in surface waters increases DOC with low lignin and younger DOC which degrades easily. In this case, many of the trends in age and biomarker composition likely reflect general patterns of Atlantic Ocean surface and bottom water circulation in the area of the MAB. Scenario 2 assumes terrestrial organic matter in bottom waters of the MAB may have originated from weathered shelf and slope sediments in nearshore areas via a combination of mechanisms (e.g., diffusion, recent resuspension events, and/or desorption of DOM from riverine POM buried deep in these sites) and entered bottom waters offshore in the MAB by diffusion along isopycnal surfaces. These results complement recent work which proposes that transport of DOM across continental shelves may be a significant source of "old" organic matter to the deep ocean. *Copyright © 2000 Elsevier Science Ltd*

1. INTRODUCTION

Terrestrial organic matter originating from river runoff and coastal wetlands represents an important source of organic matter to the marine environment (Hedges et al., 1997; Hedges and Cades, 1997). Lateral transport of this terrestrial organic matter across continental margins has been shown to be a significant process in coastal waters (Hedges and Parker, 1976; Jahnke et al., 1990; Prahl et al., 1994; Bianchi et al., 1997), leading to the detection of terrestrial biomarkers in the open ocean (Meyers-Schulte and Hedges, 1986; Opsahl and Benner, 1997). Thus, the quantity, composition, and characterization of the transport pathways of terrestrial organic matter across ocean margins is fundamentally important for conducting mass balances of organic carbon in the oceans.

A significant fraction of particulate transport across continental shelves occurs in the benthic nepheloid layer (BNL) (Biscaye and Eittreim, 1977; Nittrouer and Wright, 1994; Santschi et al., 1999), emphasizing its importance and influence on mass flux across ocean margins. In conjunction with particulate transport across the BNL in continental shelf areas, continental margins have also been suggested to actively transport carbon (particulate and dissolved) along the BNL from nearshore to offshore areas (Anderson et al., 1994; Bauer and Druffel, 1998; Jahnke et al., 1990; Santschi et al., 1999; Guo and Santschi, 2000; Jahnke and Jahnke, 2000).

Dissolved organic matter (DOM) originating allochthonously from rivers and estuaries may be transported to the open ocean via surface water advective and diffusive mixing. Dissolved organic matter may also be introduced in aquatic environments from desorption of particulate organic matter (POM) and sedimentary organic matter (SOM) (Burdige et al., 1992; Thimsen and Keil, 1998; Hedges and Keil, 1999). Despite recent evidence of DOM transport from ocean margins to waters of the open ocean (Bauer and Druffel, 1998), the biochemical composition of DOM in ocean margin areas remains to be characterized.

Recent studies have revealed that bulk DOM in seawater is indeed heterogenous with respect to its size, age, and chemical composition (Williams and Druffel, 1987; Benner et al., 1992; Santschi et al., 1995; Guo et al., 1996; Benner et al., 1997). For example, up to 45% of DOC has been found in the high

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molecular weight dissolved organic matter (1 kDa $<$ HMW DOM $<$ 0.2 μm) fraction of seawater (Benner et al., 1992; Guo et al., 1994). Moreover, Santschi et al. (1995) found that colloidal organic matter (COM) between 0.2 μm and 10 kDa (COM_{10}) in the upper water column of the Gulf of Mexico contained contemporary $\Delta^{14}C$ values, while $\Delta^{14}C$ values in HMW DOM were lower and similar to that of bulk DOC found in the open ocean.

In addition to chemical and isotopic characterization, source-specific biomarkers of natural organic matter, such as lignin, have been shown to be a useful chemical biomarker for quantifying the influx of terrestrial organic matter into aquatic systems (e.g., Hedges and Parker, 1976; Hedges, 1982; Goni et al., 1997). Methoxylated phenols derived from lignin can offer information regarding the amount and source of vascular plant inputs to a system. Lignin oxidation products (LOPs) have been used to quantify the contribution of both dissolved and particulate terrestrial organic matter to rivers, estuaries, and ocean basins (e.g., Wilson et al., 1985; Meyers-Schulte and Hedges, 1986; Bianchi et al., 1997; Opsahl and Benner, 1997; Opsahl and Benner, 1998). However, measurements of source-specific biomarkers in HMW DOM samples in the ocean are still very rare, largely because of the difficulties associated with isolating low concentrations of DOM in seawater.

Our objective in this study was to quantify the role of terrestrially-derived DOM in the Chesapeake Bay and the Middle Atlantic Bight (MAB) (off Cape Hatteras), by examining the distribution of selected LOPs in HMW DOM isolated from these areas. This study represents the first measurements of LOP in the C. Bay and the MAB.

2. MATERIALS AND METHODS

2.1. Study Site

The MAB off Cape Hatteras is one of the most physically dynamic ocean margin areas (i.e., storms and currents) along the eastern U.S. coast. This stretch of the MAB is under the influence of the Gulf Stream as well as several other source waters (Pietrafesa et al., 1994). Surface waters consist of warm waters of the Gulf Stream moving northeastward meeting with the colder Virginia current water, and flowing southward along the shelf of the MAB just off Cape Hatteras, resulting in dynamic mixing patterns. A permanent shelf water/slope water thermohaline front comprises the surface waters of the area, with the inner shelf waters displaying a net southwesterly flow (Biscaye et al., 1994). Bottom waters in this area result from multiple sources including North Atlantic deep water (NADW), Antarctic intermediate and Antarctic bottom water (AAIW and AABW, respectively) (Pickard and Emery, 1990; Santschi et al., 1996).

The continental slope off Cape Hatteras has been shown to be a major "depocenter" for sediment and carbon of the MAB (Anderson et al., 1994; DeMaster et al., 1994). Storm-induced currents are the dominant process in resuspending sediments over the inner and middle shelf, as opposed to internal waves and the Gulf Stream in shelf-break and slope sediments (Madsen et al., 1993; Churchill et al., 1994). High rates of biological mixing (bioturbation) by macrofauna in these sediments are also likely to enhance resuspension and inputs of SOM into the BNL (Blair et al., 1994; DeMaster et al., 1994; Blair et al., 1996; Levin et al., 1997). The most likely mechanism whereby shelf-derived particulate materials are laterally transported across the MAB is through the BNL (Churchill et al., 1988; Churchill et al., 1994; Walsh, 1994; DeMaster et al., 1994; Santschi et al., 1999). Thus, the highly dynamic water mixing and lateral transport occurring in the MAB may also significantly influence the cycling of DOM to offshore oceanic waters.

2.2. Sampling

Water and sediment samples were collected in the Chesapeake Bay and the MAB across the continental margin of Cape Hatteras (Fig. 1) onboard the R/V *Gyre* from June 28–July 12, 1994. Sample collection, isolation methods, and most ancillary water column measurements are explained elsewhere (Guo et al., 1996; Guo and Santschi, 1997). Station depths ranged from 25 m nearshore to 2600 m offshore. Surface water samples for isolation of HMW DOM were transferred into 200 L reservoirs directly by pumping through an acid rinsed 0.2 μm Nuclepore cartridge for ultrafiltration and DOC sampling. Deep water samples were filtered in a similar manner but drawn from 30 L Niskin bottles mounted on a General Oceanics 12-place rosette multisampler and triggered electronically at known depth intervals. Surface sediments (0–1 cm) were obtained using a Hampton box corer (25 cm × 25 cm × 40 cm). Subcores were taken from a box corer using PVC pipe corers, sectioned into 1 cm intervals, and examined for percent organic carbon and nitrogen and lignin-phenols.

High molecular weight DOM was isolated from low molecular weight DOM using cross-flow filtration techniques. Filtered seawater samples ($<$0.2 μm) were pumped and ultrafiltered through a spiral-wound cartridge (Amicon, S10N1) using Amicon DC-30 and DC-10 systems (Guo et al., 1995). Immediately after ultrafiltration, HMW DOM samples were diafiltered with Nanopure water to remove sea-salts, frozen, and freeze-dried (lyophilized). In this study, LOPs were used as biomarkers to examine the transport of terrestrially derived DOM across C. Bay and continental shelf in the MAB.

2.3. Extraction and Analysis of Lignin-Phenols

Lignin-phenols were extracted according to the method of Hedges and Ertel (1982). Lyophilized samples of HMW DOM and sediments were each placed in Monel minibombs with 7 mL of 2 N NaOH, 1 g CuO, 50 mg of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in a N_2(g)-filled glove box. The reaction product from each sample was spiked with 100 μl of ethyl-vanillin (1 mg mL^{-1} in 0.1 N NaOH) as an internal standard, then acidified to a pH = 1 prior to extraction with ethyl ether (freshly distilled) over an aqueous solution of nanopure water and $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. Organic extracts were filtered over anhydrous Na_2SO_4 and then concentrated to a thin film in glass vials. Samples were stored at -20°C prior to being derivatized and injected on a gas chromatograph.

Lignin oxidation products in the residual extract were analyzed as trimethylsilyl derivatives (BSTFA reagent, Regis Chemical Co.) by adding 50 μL of a pyridine:BSTFA (1:1-v:v) solution. Lignin-phenols were analyzed using a Hewlett Packard 6890 Series Gas Chromatograph/Mass Spectrometric Detector (GC/MS) in the selective ion monitoring mode with a 30 m × 0.25 mm i.d. × 1 μm film thickness DB-5MS capillary column (J&W Scientific). The GC/MS conditions for sample analysis were as follows: injector and detector temperatures, 300°C; split injection (1/50) with 1.5 $cm^3\ min^{-1}$ of ultrahigh purity He as the carrier gas; initial column temperature 100°C increased to 270°C at 4°C min^{-1} followed by a 16 min isothermal hold. Gas chromatograph response was generally linear over a range of concentrations for each LOP in a mixed LOP standard. Thus, a one-point calibration curve using a specific concentration of the mixed LOP standard was used on a daily basis to confirm retention times, mass spectra, and response factors for each target LOP. Based on GC-MS daily response over one week, analytical precision for individual LOP monomers in the mixed response factor standard ranged from a minimum of 1% for VAL to a maximum of 24% for CAD. Thus, all samples were injected over the course of 3 days to minimize any potential artifact due to changes in GC response for specific phenolic monomers such as CAD.

Lignin-phenol concentrations are presented using the lambda indices that have been typically used to estimate the relative contribution of lignin-phenols to total organic carbon in sediments or HMW DOM, and also on the basis of water volume. Lambda (Λ_6) is defined as the total weight in milligrams of the sum of vanillyl and syringyl phenols normalized to 100 mg of organic carbon (Hedges and Parker, 1976; Hedges and Mann, 1979). Organic carbon normalized lignin-phenol abundances (i.e., Λ_6) are the most appropriate units to compare lignin-phenol abundances between differing sample matrices such as HMW DOM and sediments. However, as terrestrially derived DOC comprises

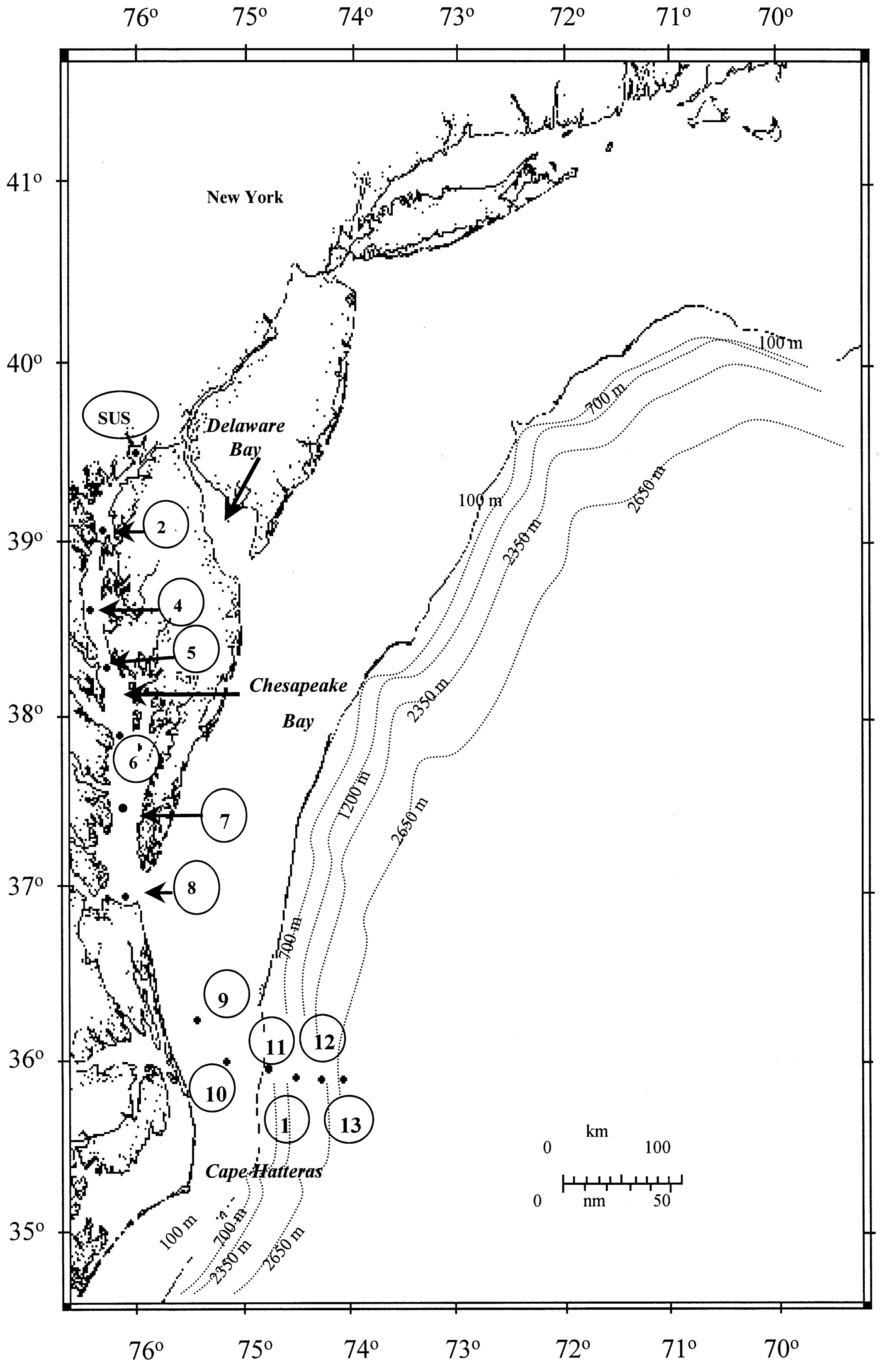

Fig. 1. Map of Chesapeake Bay and Middle Atlantic Bight (MAB) and sampling locations. Station SUS (Susquehanna River) was not sampled but has been included as a geographical reference from which our transect began.

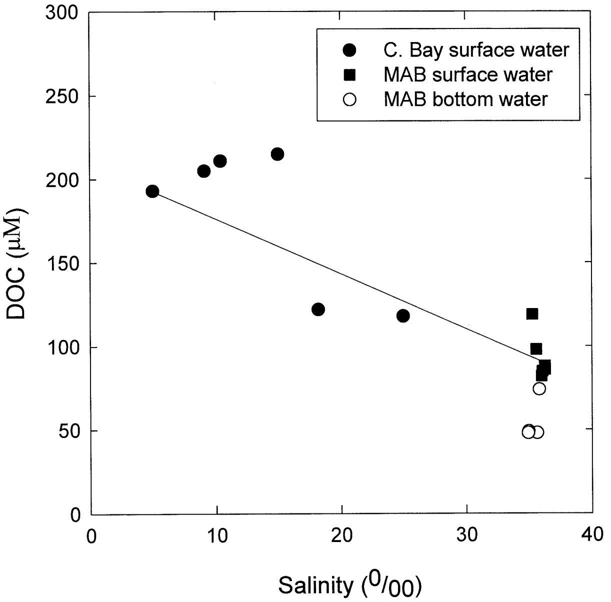

Fig. 2. Bulk dissolved organic carbon concentrations (Guo et al., 1996) versus salinity within C. Bay and MAB waters.

trace amounts of bulk DOC, normalizing to the total concentration of bulk carbon in the HMW DOM pool can be misleading. Thus, lignin-phenol abundances were also expressed in units of μg L^{-1}. *Para*-hydroxy phenols were not included in our discussion as they can be produced by nonlignin constituents (Wilson et al., 1985). The cinnamyl phenols were detectable in sediment samples but were not detectable in any of our HMW DOM samples. This latter observation is congruent with the fact that cinnamyl phenols (oxidation products of herbaceous tissue) are generally more susceptible to degradation and are also subject to analytical artifacts (Benner, private communication) and hence, more difficult to quantify (Haddad et al., 1992).

2.4. Total Organic Carbon and Nitrogen Concentrations and Carbon Isotopes

Organic carbon and nitrogen were measured on an elemental analyzer (Carlo Erba Strumentazione NA 1500 Series 1. In order to remove inorganic carbon from each sample, all sediments were placed in a desiccator with a beaker of 15 ml of concentrated HCl. The fumes in the desiccator decomposed the $CaCO_3$ present in the samples; replicate aliquots of $CaCO_3$ were used to test the efficiency of this method. Acetanilide (71.09% C and 10.36% N) was used as a standard. Precision was always <5% for both C and N (Guo et al., 1996). Details related to analytical measurements of carbon isotopes (δ^{13}C and Δ^{14}C) are described elsewhere (i.e., Santschi et al., 1995; Guo et al., 1996; Guo and Santschi, 1997) and were used to examine the relationship between these bulk source and age parameters and the LOP biomarkers.

2.5. Statistical Analyses

All statistical analyses were conducted with Statgraphics or Sigmaplot. Analysis of variance and paired or nonpaired *t*-tests were conducted on all data and comparisons between variables were considered to be significant at the 95% confidence level ($p < 0.05$). When duplicate samples were not available, analytical precision of GC response for each LOP was used to estimate its standard error. All standard errors were propogated to estimate standard error associated with calculated terms (e.g., Λ_6, C/N).

3. RESULTS

3.1. Bulk Dissolved Organic Carbon

Dissolved organic carbon concentrations along the salinity gradient sampled are depicted in Fig. 2. Concentrations of DOC range from 118 μM to 215 μM in the C. Bay, 82 μM to 98 μM in MAB surface waters and 48 μM to 90 μM in MAB bottom waters. Chesapeake Bay DOC levels were significantly higher (*t*-test; $p < 0.001$) than DOC levels in MAB waters. Similarly, MAB surface water DOC concentrations were significantly higher than MAB bottom water DOC concentrations (*t*-test; $p < 0.05$). The trend of higher levels of DOC in oceanic surface waters compared to bottom waters has been noted by other researchers as well (e.g., Williams and Druffel, 1987; Benner et al., 1992; Guo et al., 1996) and attributed to relatively greater amounts of labile marine-derived carbon in surface waters which are rapidly depleted enroute to forming bottom water. The overall trend in DOC versus salinity (Fig. 2) indicates that the mixing behavior of DOC across the C. Bay and MAB was not simply conservative or nonconservative. The headwaters of the Bay appear to be somewhat enriched in DOC relative to the mixing line. Fisher et al. (1998) noted DOC concentrations in the mainstem of C. Bay generally ranged from 100–400 μM from 1990 to 1991, during which time they sampled C. Bay water over the course of several seasons. Furthermore, they noted insignificant differences between surface water and bottom water DOC concentrations and suggest that much of the DOC which fell above the line of conservative mixing in their samples was more likely refractory and slow to be microbially decomposed (Fisher et al., 1998). Based on historical streamflow data for the Susquehanna River (http://www.usgs.gov), the C. Bay was at a period of annual low flow during the time sampled. Thus, intrusion of marine-derived organic matter due to tidal forcing is likely to have been at a maximum at the time of sampling. Taken together with our DOC–salinity plot in Fig. 2, DOC concentrations in excess of the conservative mixing line between a salinity of 4–16 suggest diffusion of DOC-enriched water in the freshwater portions of the C. Bay during the time of sampling.

3.2. HMW DOM and Sediments

Table 1 lists various geochemical parameters of HMW DOM isolated from the C. Bay and the MAB including percent organic carbon, nitrogen, molar C:N ratios, concentrations of LOPs, interclass ratios, and lignin abundance, expressed in units of μg L^{-1} and mg LOP 100 mg OC^{-1} (i.e., Λ_6). Molar C:N ratios in HMW DOM ranged from 19 to 22 in the C. Bay and were significantly higher compared to both surface (11–23) and bottom (14–24) water MAB HMW DOM (ANOVA; $p < 0.05$). Surface water C:N ratios in MAB HMW DOM were significantly lower than MAB bottom water HMW DOM C:N ratios (*t*-test; $p < 0.05$) suggesting that the influence of primary production and marine carbon may be contributing to lower C:N ratios in MAB surface waters compared to bottom waters. Indeed, chlorophyll-*a* in suspended particles in surface waters of the MAB ranged from 0.04 to 0.08 μg L^{-1} compared to 0.002 to 0.03 μg L^{-1} in bottom waters (Bianchi, unpublished).

Lignin-phenol abundances in HMW DOM (Table 1), when

Table 1. Organic carbon (OC) and nitrogen (N) abundances, C:N ratios, and lignin-phenol concentrations, interclass ratios, and yields all based on (mg L-P 100 mg OC^{-1}) unless otherwise noted for (a) Chesapeake Bay high molecular weight dissolved organic matter (HMW DOM), (b) Middle Atlantic Bight (MAB) surface water HMW DOM, and (c) MAB bottom water HMW DOM. "NQ" indicates "not quantified" and implies individual peaks were not able to be resolved to the point of quantification.

Station	Salinity	Depth (m)	OC (%)	N (%)	C:N	VAL	VON	VAD	SAL	SON	S/V	$(Ad/Al)_V$	Λ_6	LOP (μg L^{-1})
(a) Chesapeake Bay HMW DOM														
2	5	1	5.8	0.31	22	0.084	0.050	NQ	0.034	0.023	0.422	NQ	0.19	0.166
4	9.1	1	4.9	0.26	22	0.068	0.057	0.069	0.017	0.015	0.165	1.02	0.225	0.176
5	10.4	1	6.5	0.37	21	0.046	0.032	0.063	0.023	0.023	0.328	1.37	0.187	0.188
6	15.0	1	5.2	0.27	22	0.078	0.045	0.049	0.025	0.019	0.261	0.626	0.216	0.151
7	18.2	1	6.1	0.35	20	0.032	0.025	NQ	NQ	NQ	NQ	NQ	0.057	0.031
8	25	1	6.1	0.36	19	0.041	0.030	0.025	0.012	0.011	0.237	0.611	0.120	0.058
Mean			5.7	0.32	21	0.058	0.039	0.052	0.022	0.018	0.283	0.907	0.166	0.128
(SE)			(0.54)	(0.04)	(1.2)	(0.019)	(0.012)	(0.017)	(0.008)	(0.005)	(0.067)	(0.314)	(0.059)	(0.060)
(b) Middle Atlantic Bight surface water HMW DOM														
9	35.3	1	2.6	0.13	23	0.025	0.015	0.013	0.006	0.004	0.199	0.534	0.064	0.013
10	35.6	2	21.6	2.0	13	0.011	0.006	NQ	0.004	NQ	0.261	NQ	0.021	0.015
11	36.3	2	18.2	1.3	16	0.005	0.003	0.007	0.001	0.001	0.139	1.40	0.017	0.013
01	36.3	2	NQ	NQ	NQ	0.008	0.003	0.017	0.002	0.003	0.314	2.62	0.025	0.015
12	36.1	2	16.4	1.6	12	0.044	0.009	0.010	0.003	0.001	0.131	0.536	0.045	0.025
13	36	2	15.3	1.6	11	0.007	0.008	0.012	0.001	0.001	0.100	1.82	0.029	0.015
Mean			14.8	1.3	15	0.017	0.0073	0.012	0.003	0.002	0.191	1.38	0.033	0.016
(SE)			(6.5)	(0.63)	(4.3)	(0.014)	(0.004)	(0.003)	(0.002)	(0.001)	(0.076)	(0.794)	(0.016)	(0.004)
(c) Middle Atlantic Bight bottom water HMW DOM														
10	35.8	25	2.2	0.11	24	0.030	0.027	0.079	0.006	NQ	0.076	1.96	0.102	0.010
11	35.7	90	2.8	0.22	15	0.038	0.009	NQ	0.0110	NQ	0.242	NQ	0.059	0.004
01	34.9	750	NQ	NQ	NQ	0.044	0.015	0.033	0.008	0.008	0.15	0.877	0.088	0.002
12	34.9	2,300	2.6	0.21	14	0.049	0.019	0.020	0.014	0.007	0.216	0.608	0.095	0.005
13	34.9	2,600	7.1	0.40	21	0.016	0.006	0.007	0.008	0.004	0.357	0.435	0.040	0.005
Mean			3.67	0.23	18.5	0.035	0.015	0.035	0.009	0.006	0.208	0.970	0.077	0.005
(SE)			(2.0)	(0.10)	(4.2)	(0.012)	(0.007)	(0.027)	(0.003)	(0.002)	(0.094)	(0.593)	(0.020)	(0.003)

normalized to amount of carbon or the volume of water sampled, were significantly different in C. Bay compared to MAB surface and bottom waters (ANOVA; $p < 0.05$). Values of Λ_6, were significantly lower in MAB surface waters (0.033 ± 0.016) compared to MAB bottom waters (0.077 ± 0.02) (*t*-test; $p <$ 0.05). Values of Λ_6 were lower than the range of values for Λ_6 in northern Gulf of Mexico HMW DOM (0.42–1.5) (Bianchi et al., 1997) and within HMW DOM isolated from a site in the open Atlantic Ocean (0.021) (Opsahl and Benner, 1997). When considering concentrations of LOPs on a μg L^{-1} basis, the trend in the total abundance of lignin phenols in MAB surface and bottom water HMW DOM, reverses. That is, on a volumetric basis, the concentration of lignin-phenols in MAB surface waters was significantly higher than in bottom waters (*t*-test; $p < 0.05$) (Table 1).

Ratios of syringyl to vanillyl phenols (S/V), which have been used to assess the relative contribution of lignin-phenols derived from angiosperm tissue versus gymnosperm tissues (Hedges and Mann, 1979) were 0.283 ± 0.067 in the C. Bay and 0.191 ± 0.076 in MAB surface water HMW DOM and 0.208 ± 0.094 in MAB bottom water HMW DOM, with no significant differences in S/V between the C. Bay or MAB waters (*t*-test; $p > 0.05$) (Table 1). In general, these values are slightly lower than the average S/V ratios in DOM for major rivers such as the Amazon (0.35) and Mississippi (1.1) (Meyers-Schulte and Hedges, 1986; Bianchi et al., 1997) but similar to the range (~0.1–0.3) reported by (Opsahl and Benner, 1997) for HMW DOM isolated from their sites in the Atlantic. Ratios of vanillic acid to vanillin $(Ad/Al)_v$ ranged from 0.611 to 1.37 in the C. Bay and 0.534 to 2.62 in MAB surface water and 0.435 to 1.96 in MAB bottom water HMW DOM, with no

Table 2. Lignin-phenol concentrations, interclass ratios, and yields in MAB surface sediments (mg L-P 100 mg OC^{-1}). Individual lignin oxidation products are presented. "NQ" indicates "not quantified" and implies individual peaks were not able to be resolved to the point of quantification.

Stn	OC (%)	N (%)	C:N	VAL	VON	VAD	SAL	SON	SAD	S/V	CAD	FAD	C/V	Λ_6	$(Ad/Al)_V$
10	0.04	0.008	5	0.016	0.006	0.010	0.006	0.004	0.007	0.392	0.031	0.008	1.096	0.046	0.666
1	2.6	0.348	7.5	0.043	0.028	0.048	0.016	0.023	0.020	0.491	0.027	0.003	0.241	0.178	1.118
12	1.09	0.155	7.0	0.026	0.012	0.014	0.013	0.009	0.003	0.446	NQ	NQ	NQ	0.075	0.523
13	0.755	0.115	6.6	0.026	0.016	0.038	0.01	0.011	0.008	0.372	NQ	NQ	NQ	0.109	1.453
Mean	1.12	0.156	6.6	0.027	0.016	0.027	0.011	0.012	0.009	0.425	0.029	0.006	0.669	0.102	0.94
(SE)	(0.93)	(0.123)	(0.93)	(0.009)	(0.008)	(0.016)	(0.004)	(0.007)	(0.006)	(0.046)	(0.002)	(0.003)	(0.427)	(0.049)	(0.368)

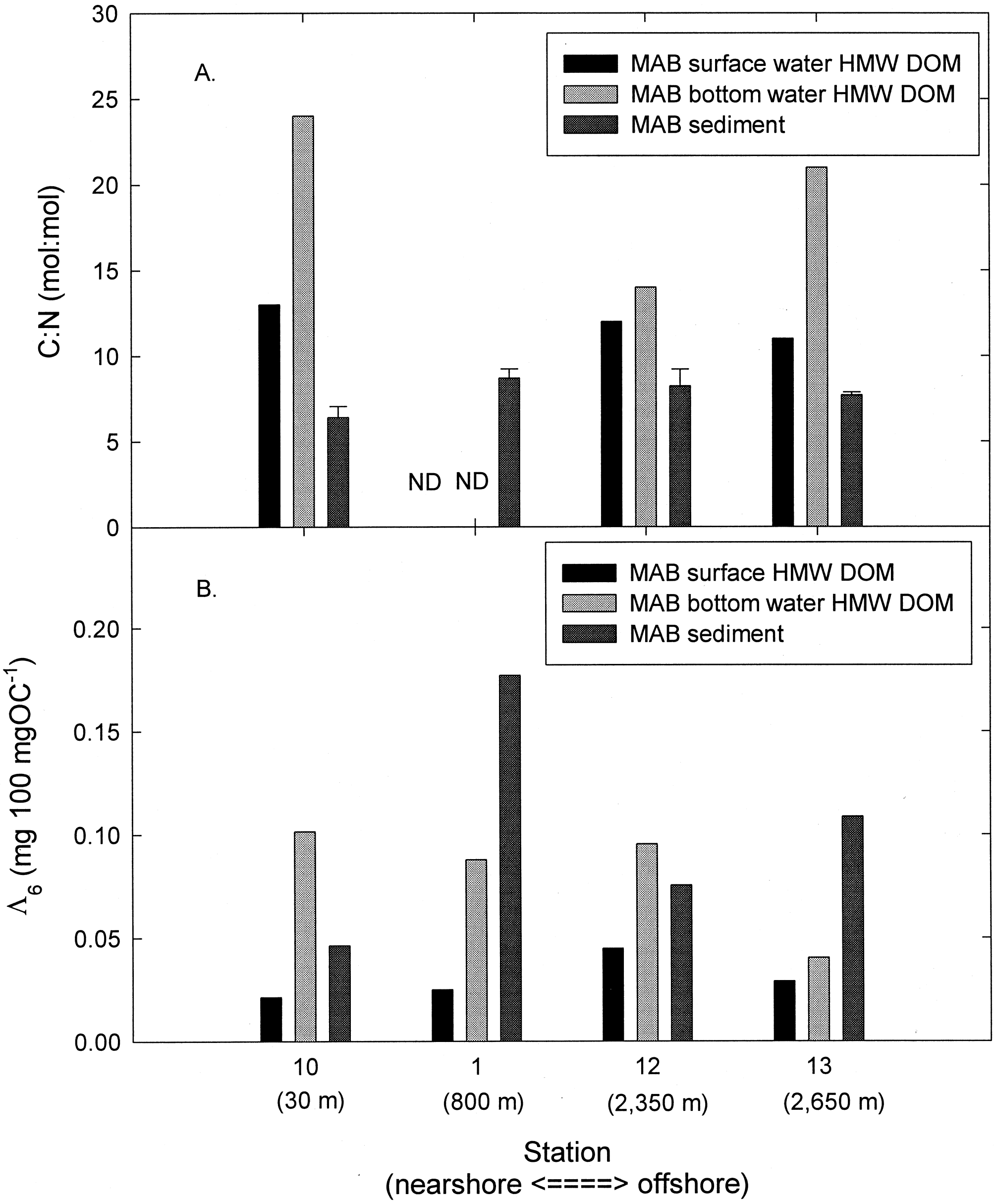

Fig. 3. (A) C:N ratio and (B) lignin-phenol yields (Λ_6) in MAB surface and bottom water HMW DOM and MAB sediments.

significant differences in $(Ad/Al)_v$ between each environment (ANOVA; $p > 0.05$).

Values of Λ_6 in surface sediment samples collected from the MAB are listed in Table 2, with Λ_6 ranging from 0.046 to 0.178. Although values of Λ_6 in bottom water HMW DOM were sometimes higher than in sediments directly below each site at each respective MAB station (Fig. 3), average sedimentary Λ_6 in the MAB was not significantly different from MAB bottom water HMW DOM (*t*-test; $p > 0.05$).

Atomic C:N ratios were significantly higher in bottom water HMW DOM compared to MAB sediments (*t*-test; $p < 0.05$). Specifically, sedimentary C:N ratios in the MAB stations ranged from 5 to 7.5, and were significantly lower (*t*-test; $p < 0.05$) than in HMW DOM from either the C. Bay or MAB surface and bottom waters. Since C:N ratios in surface sediments of the MAB fall within the range of values represented by marine plankton (6–10) (Libes, 1992), the sedimentary environment at the MAB sites reflect the predominance of the marine carbon to the overall sedimentary organic matter in these areas. Ratios of S/V were significantly higher (*t*-test; $p < 0.05$) in surface sediments compared to bottom water HMW DOM while $(Ad/Al)_v$ were not significantly different between bottom water HMW DOM and surface sediments. Furthermore, C/V ratios quantifiable in MAB sediments as CAD and FAD, were detectable in some sediment samples (Table 2). Higher C:N and values of Λ_6 in bottom water HMW DOM relative to sediments directly below and the presence of sedimentary cinnamyl

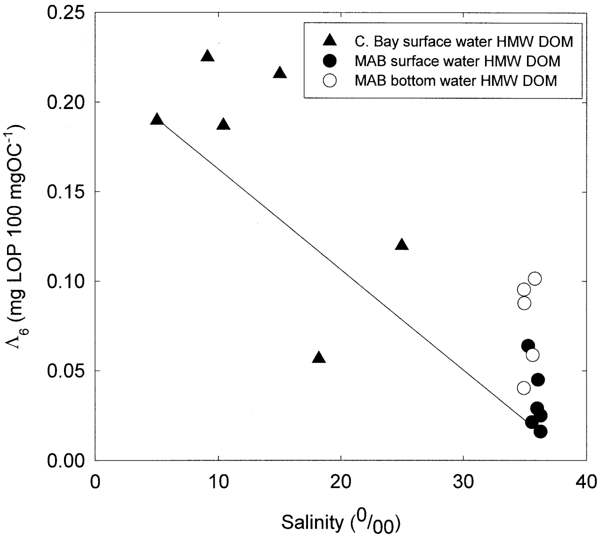

Fig. 4. Lignin-phenol concentrations at all stations versus salinity.

phenols may indicate that bottom water HMW DOM in the BNL of the MAB is enriched in lignin-phenols, diagenetically altered and more refractory than average POC in the surface sediments below.

4. DISCUSSION

4.1. C. Bay HMW DOM

The trend of decreasing Λ_6 when compared to the conservative mixing line in Fig. 4 indicates that the headwaters of the C. Bay may have been enriched in diffusive sources of bulk DOC (Fig. 2) and that this end-member pool of DOC may have been somewhat enriched in terrestrial organic matter. Guo et al. (1996) noted the radiocarbon age in the same HMW DOM which we analyzed for LOPs consisted of mostly modern (>90%) carbon with a terrestrial $\delta\ ^{13}C$ signature throughout the entire C. Bay. Trends in C. Bay HMW DOM S/V and $(Ad/Al)_v$ ratios, coupled with radiocarbon and stable carbon isotopic signatures in the same HMW DOM (Guo et al., 1996) suggest that there were no distinct compositional differences in the type of terrestrially derived HMW DOM along the salinity transect of C. Bay during the time of sampling. Collectively, these results suggest that the enrichment of terrestrially derived HMW DOC observed near the head of C. Bay (Figs. 3 and 4) may have originated from sources other than runoff and advective transport of surface waters. Although we did not sample bottom waters in C. Bay, significantly higher SPM values noted in bottom waters relative to surface waters of mainstem C. Bay in July of 1995 (Canuel and Zimmerman, 1999) support the hypothesis that much of the DOC enrichment in the northernmost stations in the shallower portions of the Bay (i.e., 0–20 m water depth) may have been the result of sediment resuspension events.

Low S/V ratios such as those seen in our HMW DOM samples indicate that much of the terrestrially derived DOM either originated from gymnosperm sources (with lower S/V ratios) or that a significant amount of lignin degradation occurred in the HMW DOM throughout the waters of C. Bay (i.e., syringyl phenols are more labile than vanillyl phenols). The relative abundance of angiosperms and gymnosperms throughout the watershed of C. Bay appears to be similar (Brown and Brown, 1972; Rhoads and Klein, 1993). Furthermore, as mentioned earlier, C. Bay was at its period of annual low flow during the time sampled and hence, it was likely to have been at the annual lowest water level. Opsahl and Benner (1998) and Bianchi et al. (1999) recently indicated that degradation of syringyl phenols as a class of LOPs was closely correlated in natural samples to amounts of UV light. Although the bulk carbon in C. Bay is relatively recent with respect to apparent C^{14} age (Fig. 5A), the generally lower S/V ratios and evenly distributed sources of angiosperms and gymnosperms throughout the watershed of the Bay seem to indicate that the lignin-phenols throughout C. Bay may indeed be fairly degraded.

4.2. HMW DOM and Sediments in the MAB

Surface water HMW DOM in these MAB samples are enriched in LOPs (Table 1) and possesses an apparent ^{14}C age which is significantly younger than bottom water HMW DOM (Fig. 5A) (Guo et al., 1996). Lack of significant differences in S/V and $(Ad/Al)_v$ ratios between surface and bottom water HMW DOM of the MAB argues against distinct sources of terrestrial organic matter into the water column in each environment. Similar stable isotopic signatures of bulk carbon in the surface and bottom waters (Fig. 5B) indicate a ubiquitous presence of weathered bulk marine organic matter throughout both environments as noted by Benner et al. (1997). Two possible scenarios may reconcile the compositional trends in terrestrial biomarker and bulk isotopic signatures seen in surface and bottom water HMW DOM of the MAB.

One may assume that a low amount of refractory terrestrial organic matter and old DOC are uniformly distributed in the oceans, both in surface and bottom waters, and that primary production in surface waters increases DOC with low lignin and significantly “younger” DOC which degrades easily. In this case, many of the trends in apparent ^{14}C age noted by Guo et al. (1996) and biomarker composition observed in this study, may reflect general patterns of ocean circulation. The significantly higher abundance of LOPs in MAB surface waters coupled with the relatively younger apparent ^{14}C age in the bulk carbon of MAB surface water would suggest that relative to bottom water, sources of terrestrial organic matter to surface waters of the MAB are more recent and more concentrated. Surface waters of the MAB are comprised of a heterogenous mixture of both marine and terrestrial as well as labile and refractory POC and DOC (e.g., Guo et al., 1996; Bauer and Druffel, 1998; Minor and Eglinton, 1999). In that context, C:N ratios of surface water HMW DOM in our samples are significantly lower than bottom water HMW DOM. The fact that the C. Bay was at a point of low flow during the time sampled, does not preclude the possibility of estuarine discharge of trace amounts of terrestrial organic matter from the C. Bay or other nearshore rivers and estuaries into surface waters of the MAB. Indeed, a comparison of mean LOP concentrations ($\mu g\ L^{-1}$) to DOC in each environment indicates lignin-phenols comprised approximately 0.006% of the DOC in C. Bay, 0.0014% of the DOC in MAB surface waters, and 0.0007% of the DOC in MAB bottom waters, similar to the 0.004% lignin found in

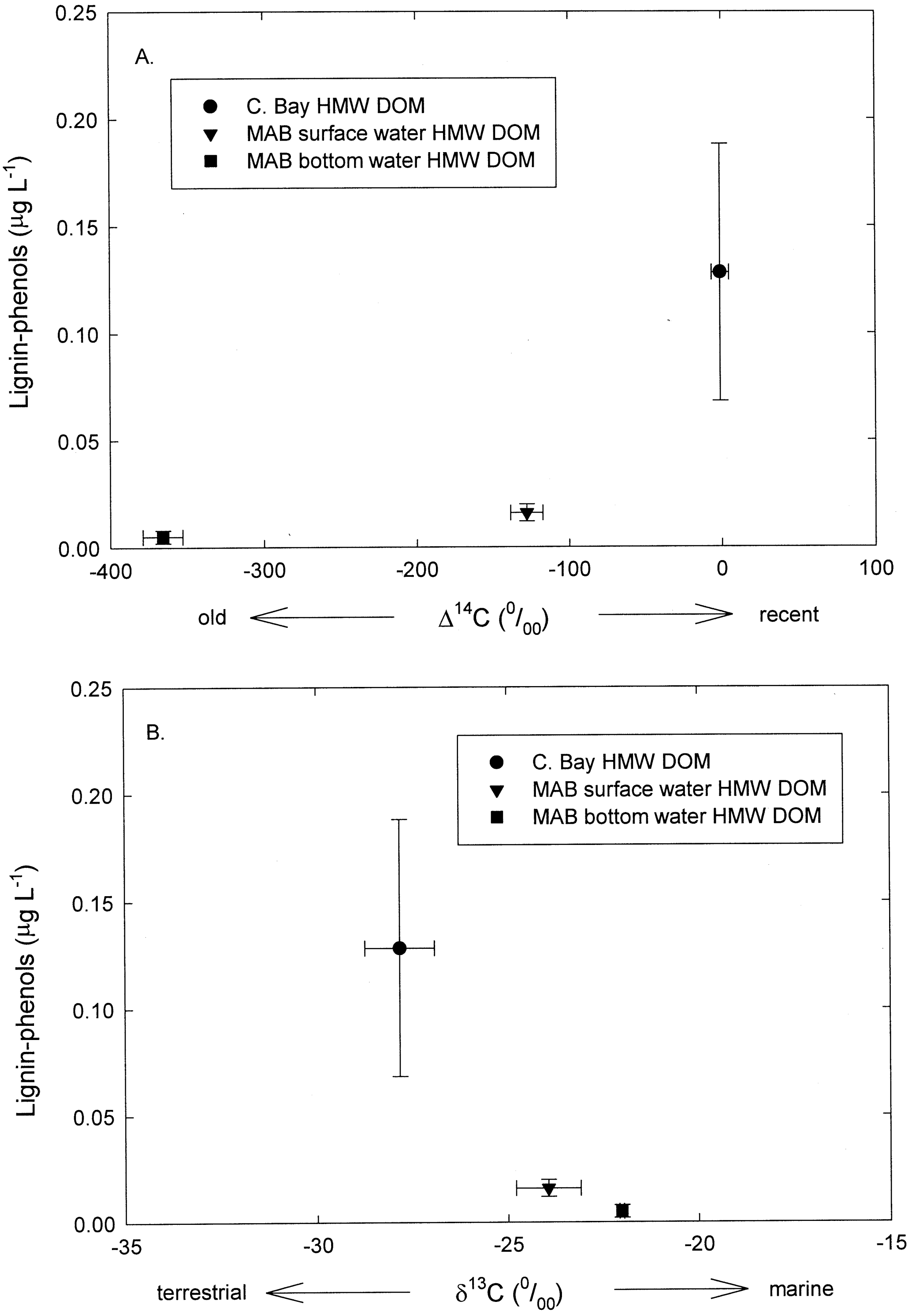

Fig. 5. Lignin-phenol abundance in C. Bay and MAB HMW DOM correlated against (A) Δ^{14}C value and (B) δ^{13}C. Radiocarbon and stable isotopic ratios originally noted in Guo et al. (1996) and Guo and Santschi (1997).

Atlantic Ocean DOC by Opsahl and Benner (1997). Mixing of such trace amounts of coastally derived terrestrial organic matter with enriched amounts of authochthonous marine organic matter would result in the bulk carbon and lignin-phenol profiles seen in MAB surface waters during the time of sampling.

The significantly lignin-depleted offshore and "old" bottom waters of the MAB compared to the higher concentrations of lignin-phenols and higher Δ^{14}C values in surface water HMW DOM, suggests that terrestrial organic matter in bottom waters of the MAB did not originate directly from MAB surface

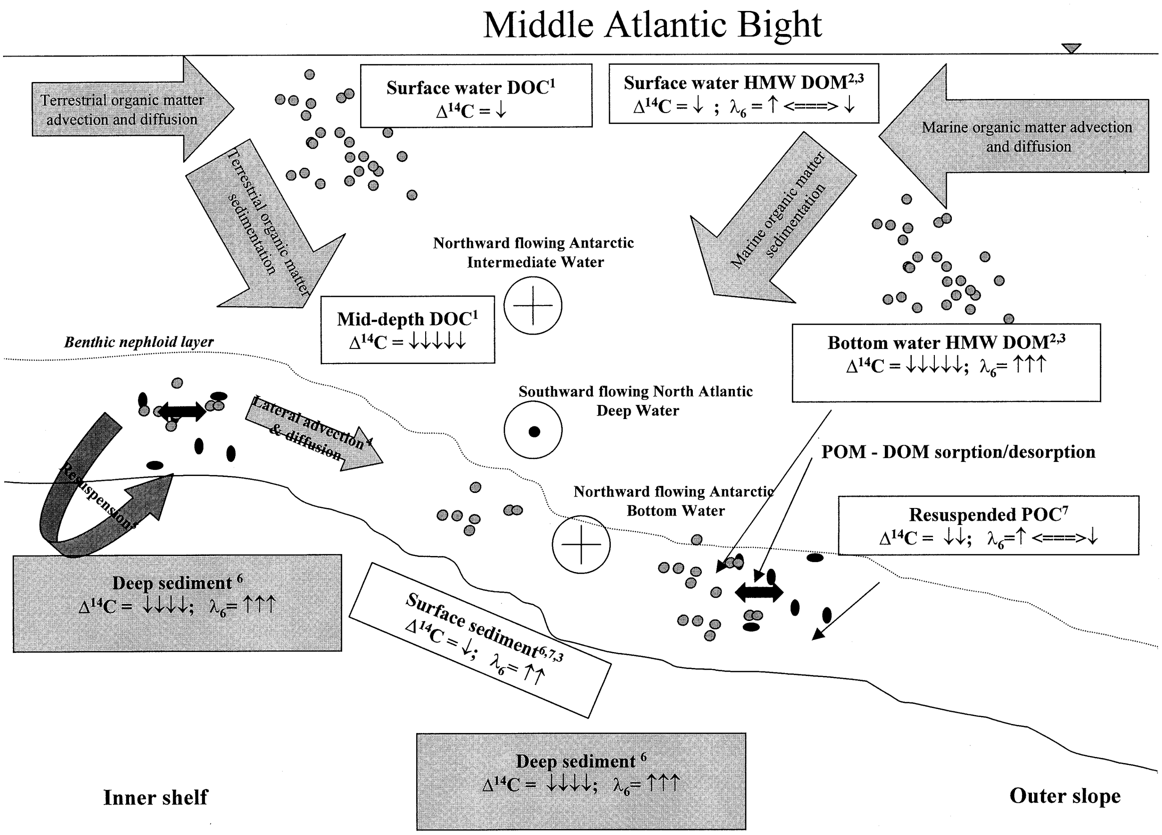

Fig. 6. Conceptual model (not to scale) reconciling the observed trends in our data with processes known to occur in the MAB. Reference 1, Bauer and Druffel, 1998; Ref. 2, Guo et al., 1996; Ref. 3, this study; Ref. 4, Falkowski et al., 1994; Jahnke and Jahnke, in press; Ref. 5, Churchill et al., 1994; Ref. 6, Anderson et al., 1994; Ref. 7, Guo and Santschi, 2000.

waters. The MAB serves as a confluence of several parcels of water (Biscaye et al., 1994) including old northward flowing AAIW (Tanaka et al., 1990) and AABW and southward flowing NADW (Pickard and Emery, 1990). We are not aware of any existing measurements of terrestrial biomarkers in any of these water masses and thus, are unable to constrain the sources of lignin-phenols in our bottom water HMW DOM samples which may have originated directly from these parcels of water. Considering the ice masses comprising the Greenland Ice Sheet and Antarctic subcontinent, the sources of NADW, AAIW, and AABW are not likely to be enriched in lignin-phenols at their point-of-origin. Furthermore, it is unlikely that lower salinity estuarine and coastal surface waters are advectively downwelled into continental shelf bottom waters. Thus, it seems more likely that terrestrial organic matter originating in the North Atlantic coastline must somehow diffuse into bottom waters during their transport through areas such as the MAB.

Concentrations of suspended particulate matter (SPM) were consistently elevated in bottom waters above the seabed at all stations in the MAB at the time of sampling (Guo et al., 1996; Santschi et al., 1999). Elevated SPM concentrations in the bottom waters indicate the presence of a well-developed benthic nephloid layer in the MAB, which may affect the transport of DOM in this ocean margin area (Guo and Santschi, 2000). When considering the SPM profiles and the relatively old apparent ^{14}C age of bulk carbon in the water column at the MAB sites (Guo et al., 1996), an alternative scenario can be used to explain the lignin-phenol distributions in HMW DOM isolated from bottom waters of the MAB. Benthic nepheloid layers in the western Atlantic Ocean margin areas have been suggested to be significant conduits of organic matter (Bauer and Druffel, 1998; Guo and Santschi, 2000; Jahnke and Jahnke, 2000). Furthermore, research using biomarkers has shown that POM can be injected into the water column and can traverse large distances along the BNL. For example, one recent study (Bianchi et al., 1998) demonstrated that pyrophaeophorbide-*a* (a degradation product of chl-*a*) was present in the water column at mesopelagic depths of an abyssal site in the Pacific Ocean. This was interpreted to be the result of lateral transport from the continental slope rather than local vertical resuspension into the BNL. To that end, terrestrial organic matter in bottom waters of the MAB may have originated from cross-shelf transport of weathered shelf and slope sediments in near-shore areas via a combination of mechanisms (e.g., diffusion, recent resuspension events, and/or desorption of DOM from riverine POM buried deep in these sites).

Disaggregation of sedimentary organic matter during resuspension events coupled to isotopic fractionation could also serve as an important source of HMW DOM to the bottom waters of these dynamic ocean margin areas (Guo and Santschi, 1997; 2000). Guo and Santschi (2000) showed that mean $\Delta^{14}C$ in HMW DOM (-302 ± 43‰) isolated during sediment resuspension experiments was significantly lower than that of bulk sediment (−87 ± 6‰) or resuspended POC (−138 ± 43‰). Isotopic (and possibly compositional) heterogeneity in SOM could lead to these differences between HMW DOM, SPM, and SOM as a result of hydrodynamic sorting during resuspension events in the MAB. Although we did not directly analyze lignin-phenols in this desorbed material, such selective desorption would likely result in large differences in biomarker signatures between benthic HMW DOM and SOM in an environment as dynamic as the MAB. Given these recent findings by Guo and Santschi (2000) and the dynamic equilibrium between sorption/desorption processes involving organic matter-mineral surfaces in aquatic environments (Hedges and Keil, 1999), it is reasonable to assume that the heterogenous composition of sediment aggregates can result in older and likely more oxidized and hydrophilic pools of terrestrial organic matter being desorbed more readily into bottom waters with each repeated resuspension event.

We have invoked two principal mechanisms reconciling the potential sources of terrestrial organic matter and old carbon in bottom waters of the MAB with potential sources of terrestrial organic matter and newer carbon in surface waters of the MAB. The conceptual model shown in Fig. 6 attempts to reconcile some of the observed trends in our data with that of other investigators who have assessed age and potential sources of bulk carbon in the MAB. As shown in our conceptual model, we speculate that old HMW DOM and terrestrial organic matter in bottom waters of the MAB may arise from multiple sources such as bottom water transport *and* desorption of weathered shelf and slope sediments. Delineating the actual contribution of each of these mechanisms of introducing terrestrial organic matter to bottom water HMW DOM remains a difficult problem. Unique state-of-the-art analytical techniques such as compound-specific isotopic measurements (Eglinton et al., 1996) to measure the apparent ^{14}C age and isotopic fractionation of carbon in lignin-phenol molecules isolated from each environment may offer sufficient information to actually identify the potential source(s) of extremely old DOC to the open ocean.

5. SUMMARY

Coastal sediments may represent an important source of DOC to the deep ocean. Recent evidence suggests that dynamic ocean margins such as the MAB may serve as a significant contributor of sediment-derived DOC to the deep ocean, and that the MAB margin areas serve as a thoroughfare for advectively transported POC into the waters affected by the Gulf Stream. The MAB off Cape Hatteras, North Carolina, serves as a dynamic mixing zone for several converging water masses in the surface and bottom waters. Old pools of HMW DOM enriched in lignin-phenols may form (1) from sources originating in deep water masses such as the NADW or AAIW or (2) in nearshore bottom waters of the MAB from sediments which are old and enriched in terrestrial organic matter but which remain deposited well below the sediment/water interface. These older pools of desorbed organic carbon might then be transported via the BNL. Given these assertions, transport of terrestrially derived HMW DOM modulated by BNL processes including hydrodynamic fractionation during resuspension and deposition is quite likely. Thus, organic matter originating from a pool of recently desorbed carbon would not only be relatively "old" but also enriched in refractory terrestrial organic material. Seaward transport of this material from continental margins may then represent a significant source of this refractory organic matter to the deep ocean.

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