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Sedimentary sources of old high molecular weight dissolved organic carbon from the ocean margin benthic nepheloid layer

LAODONG GUO* and PETER H. SANTSCHI

Department of Oceanography, Texas A&M University, 5007 Avenue U, Galveston, TX 77551, USA

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Abstract—Average ^{14}C ages of dissolved organic carbon (DOC) in the ocean are 3–6,000 years, and are influenced by old DOC from continental margins. However, sources of DOC from terrestrial, autochthonous, and sedimentary organic carbon seem to be too young to be responsible for the old DOC observed in the ocean. Since colloidal organic carbon (COC, i.e., high molecular weight DOC), which is chemically very similar to that of bulk DOC, can be effectively isolated from seawater using cross-flow ultrafiltration, it can hold clues to sources and pathways of DOC turnover in the ocean. Radiocarbon measurements on COC in the water column and benthic nepheloid layer (BNL) from two continental margin areas (the Middle Atlantic Bight and the Gulf of Mexico) and controlled laboratory experiments were carried out to study sources of old DOC in the ocean margin areas.

Vertical distributions of suspended particulate matter (SPM), particulate organic carbon (POC), nitrogen (PON), and DOC in the water column and bottom waters near the sediment-water interface all demonstrate a well developed benthic nepheloid layer in both ocean margin areas. $\Delta^{14}\text{C}$ values of COC isolated from the BNL (ranging from $-362 \pm 4\%$ to $-456 \pm 3\%$) were distinctly lower than their counterparts in surface waters (with a range of $>0\%$ to $-210 \pm 5\%$). In other words, COC from the BNL was much older than COC from the overlying water column. These results, together with strong concentration gradients of SPM, POC, PON, and DOC, suggest a sedimentary source for organic carbon species and possibly for old COC as well in BNL waters. This is confirmed by the results from controlled laboratory experiments which showed that COC isolated from sediment resuspension had $\Delta^{14}\text{C}$ values between -260% and -352% , which are significantly lower than those of bulk sediment ($-87 \pm 6\%$) or resuspended particles ($-138 \pm 8\%$). The heterogeneity of $\Delta^{14}\text{C}$ signatures in bulk SOC thus points to a preferential release of old organic components from sediment resuspension, which can be the transport mechanism of the old benthic COC observed in ocean margin areas. Old COC from continental margin nepheloid layers may thus be a potential source of old DOC to the deep ocean. Copyright © 1999 Elsevier Science Ltd

1. INTRODUCTION

Dissolved organic carbon (DOC) in seawater is one of the major components in the marine carbon cycle (Hedges, 1992) and is important in the biogeochemistry of many trace elements in the ocean (Coale and Bruland, 1988; Rue and Bruland, 1997). The processes which control the cycling of DOC in the ocean are more complex than previously thought, mainly because DOC is a heterogeneous mixture of organic compounds with varying sources (Meybeck, 1982; Thurman, 1985; Hedges et al., 1997), degradation pathways (Mopper et al., 1986; Miller and Moran, 1997; Azam, 1998), and reactivities (Amon and Benner, 1994; Gu et al., 1995; Santschi et al., 1995; Guo et al., 1996). Recently, it has been demonstrated that a representative fraction of DOC, the colloidal organic carbon (COC) fraction can be collected with a 20–40% efficiency by cross-flow ultrafiltration (Benner et al., 1992; Guo et al., 1994) for chemical characterization. This was an important step, since this COC fraction is similar in composition to that of whole DOC (Benner et al., 1992; Aluwihare et al., 1997; McCarthy et al., 1997).

Continental margin areas, which include shelf and slope areas, are important regions for the cycling of marine organic

carbon (Jahnke et al., 1990; Anderson et al., 1994; Bauer and Druffel, 1998; Santschi et al., 1999). In particular, the ocean margin benthic nepheloid layer (BNL) could be a major conduit through which significant amounts of particulate organic carbon (POC) and DOC species are carried off continental shelves to the open ocean (Anderson et al., 1994; Guo et al., 1996; Bianchi et al., 1997; Mitra et al., 1999; Santschi et al., 1999). However, the role of the BNL overlying ocean margin sediments in the cycling of organic carbon in the ocean is not fully understood. The role of COC has so far largely been overlooked.

Recent studies have suggested that input fluxes of DOC and suspended POC from ocean margins could be more than an order of magnitude greater than those from the surface ocean (Walsh, 1994; Guo et al., 1995; Bauer and Druffel, 1998; Santschi et al., 1999). Furthermore, apparent ^{14}C ages of DOC and POC from continental margin areas are significantly older than those from open oceans (Bauer and Druffel, 1998). However, the main source of this old organic carbon in continental margin waters is not yet identified. One clue comes from the studies of Guo et al. (1996) who showed that a significant fraction of high molecular weight (HMW) DOC from ocean margin BNL areas in the Middle Atlantic Bight (MAB) had old apparent ^{14}C ages. It has therefore been suggested that old DOC from deep water and continental margin BNL areas are largely from sediments (Williams and Druffel, 1987; Hedges,

* Author to whom correspondence should be addressed (guo@tamug.tamu.edu).

Table 1. Sampling locations in the Middle Atlantic Bight (MAB) and the Gulf of Mexico along with concentrations of organic carbon and nitrogen and $\Delta^{14}\text{C}$ (‰), fraction of modern ^{14}C , and apparent ^{14}C ages of colloidal organic matter (COM, 1 kDa to 0.2 μm) collected from the benthic nepheloid layer.

Study area	Location	Sampling date	Water depth (m)	Sampling depth (mab)	SPM (mg l^{-1})	DOC (μM)	COC (fraction)	POC (μM)	OC (%) of COM	TN (‰) of COM	$\Delta^{14}\text{C}$ (‰)	Fraction of modern ^{14}C	Apparent ^{14}C age
MAB	74°55'W 35°50'N	July 1996	75	74	0.43	76	—	9.0	1.1	—	-211 ± 5	0.793	1870 ± 50
			75	1.5	0.95	51	0.38	6.4	0.87	—	-366 ± 4	0.637	3620 ± 60
			75	0.5	1.15	51	0.27	6.0	0.57	—	-456 ± 3	0.547	4850 ± 50
			75	0.2	2.68	52	0.30	14	2.2	—	-399 ± 4	0.604	4050 ± 60
Gulf of Mexico	89°50'W 28°45'N	August 1997	68	66	1.6	88	0.42	23	34.2	2.53	18 ± 5	1.02	>Modern
			68	3	3.5	59	—	11	27.4	1.91	-191 ± 4	0.814	1650 ± 40
			68	1.5	6.7	—	—	16	17.4	1.43	-242 ± 4	0.763	2180 ± 50
			68	0.5	9.8	58	—	20	5.2	1.18	-303 ± 4	0.701	2850 ± 50
			68	0.2	15.2	62	—	35	15.6	1.45	-189 ± 4	0.816	1630 ± 40

SPM = suspended particulate matter; DOC = dissolved organic carbon, COC = colloidal organic carbon, POC = particulate organic carbon, COM = colloidal organic matter, OC = organic carbon; TN = total nitrogen.

1992; Guo et al., 1996). However, sedimentary organic carbon (SOC) and pore water DOC have younger ^{14}C ages (Anderson et al., 1994; Bauer et al., 1995) than DOC from deep waters (Williams and Druffel, 1987; Bauer et al., 1992). This seems inconsistent with the hypothesis of a sedimentary source for DOC. Other major sources of DOC and POC to the ocean are terrestrial inputs and autochthonous primary production in the surface ocean (Meybeck, 1982; Hedges et al., 1997), which have apparent ^{14}C ages which are either contemporary or relatively young (e.g., Meybeck, 1982; Hedges et al., 1986; Druffel and Williams, 1990; Santschi et al., 1995). Thus, DOC derived directly from these latter sources are too young to be credible sources for the old DOC in the ocean margin.

In order to study the sources of old colloidal organic carbon in the BNL, seawater samples were collected using a free vehicle very close to the sediments at 0.2–1.5 m above bottom in two ocean margin areas, the Middle Atlantic Bight and the Gulf of Mexico. Radiocarbon abundance was measured on the high molecular weight (HMW) fraction of DOC. Furthermore, controlled laboratory experiments were carried out to simulate sediment resuspension in the BNL and to examine the heterogeneity of bulk sedimentary organic carbon (SOC) and the role of the BNL in marine carbon cycling. We provide evidence that the apparent contradiction between old benthic COC and relatively young SOC can be resolved by the fact that bulk SOC is isotopically and compositionally heterogeneous and that older macromolecular COC is preferentially released during sediment resuspension.

2. EXPERIMENTAL

2.1. Study Areas and Sample Collection

Seawater samples were collected from both water column and the BNL in two ocean margin areas of the MAB and the Gulf of Mexico, GOM (Table 1). The presence of wind-driven and geostrophic boundary currents, the proximity to terrestrial inputs, elevated primary production due to higher nutrient inputs from land and atmosphere are all characteristics of continental shelves, which are, of course, also found at our sampling sites (e.g., Biscaye et al., 1994; Houghton et al., 1994). Even though there is variability associated with these characteristics on a diurnal, daily, or seasonal time scale, the processes operating at these sites makes them typical and relevant for continental shelves as a

whole, and extrapolations from our measurements to other continental shelves should be permissible.

Samples from the water column were collected using a traditional CTD-Rosette. Benthic samples were collected close to the sea floor at 0.2, 0.5, and 1.5 m above the bottom (mab) using a free vehicle or benthic lander (Boland, 1997) equipped with three go-flo bottles. The benthic lander sampler is designed to hold horizontally 3 to 4 go-flo bottles (20 liter capacity each) and to collect seawater samples from 3 to 4 depths, i.e., 0.2, 0.5, 1.0, and 1.5 m above the bottom (Boland, 1997). Such close interval sampling near the sediment-water interface would not have been possible using traditional CTD operations. Sediments for laboratory experiments were collected at a MAB station using a box core sampler. Sampling locations and their hydrographic features are listed in Table 1.

Aliquots of seawater samples were quantified for concentrations of nutrients (N & P), DOC, suspended particulate matter (SPM), particulate organic carbon (POC) and total particulate nitrogen (PON). Then, the remaining water samples were used for ultrafiltration to extract colloidal organic matter for chemical and isotopic characterization (Guo and Santschi, 1996).

Seawater samples were first filtered through a 0.2 μm Nuclepore filter cartridge and then ultrafiltered using 1 kDa cross-flow ultrafiltration cartridges (Amicon S10N1) to isolate colloidal organic matter (Guo and Santschi, 1996). For processing benthic water samples, a single 1 kDa cartridge was equipped with a Teflon diaphragm pump and a Teflon reservoir. Ultrafiltration was carried out in a close system connected with Teflon tubing. Concentrated colloidal organic materials were further desalted through diafiltration using 20 liters of Nanopure water and subsequently freeze dried for organic carbon and radiocarbon measurements.

2.2. Sediment Resuspension Experiments

A schematic diagram describing the sediment resuspension experiments is shown in Fig. 1. Briefly, surface sediment collected during the DOE 96A cruise (July 1996 aboard R/V Seward Johnson) was first dispersed into pre-ultrafiltered seawater, collected from the same MAB station, which contained mostly <1 kDa DOC. Appropriate amounts of surface sediments (stored frozen) were added to 2–20 liters of pre-ultrafiltered seawater to result in a SPM concentration of about 0.1–2 g/l when fully homogenized. The well dispersed (hand shaken only) samples were allowed to sit overnight, which gave rise to the settling down of most particles with size >1 –2 μm . The supernatant was then filtered through a 0.2 μm glass fiber prefilter and the filtrate was further ultrafiltered to collect COM (1 kDa–0.2 μm) resulting from sediment resuspension.

Conditions in this resuspension experiment may not be exactly the same as those in the field, such as shear forces and sediment concen-

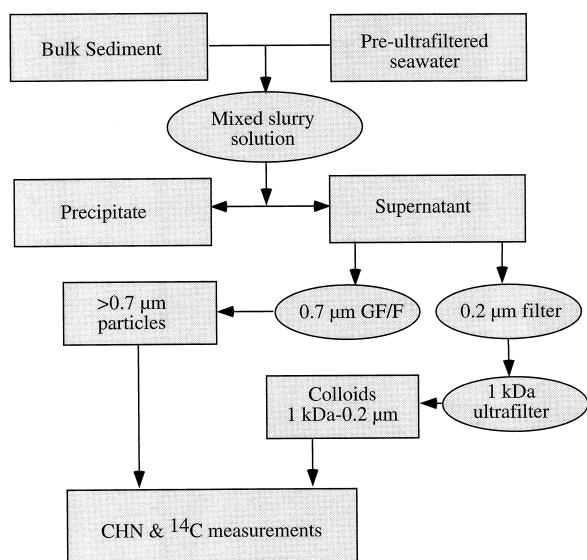


Fig. 1. A schematic diagram of the sediment resuspension experiments

trations in the BNL. However, results from this resuspension experiment will allow us to better understand the physical and chemical processes operating in the BNL.

2.3. Sample Characterization

Concentrations of suspended particulate matter were quantified by gravity filtration using $0.4\ \mu\text{m}$ Nuclepore filters. Concentrations of nutrients (N and P) were measured using an autoanalyzer by the Marine Operation group of the Oceanography Department at Texas A&M University. Particulate organic carbon (POC) and total nitrogen (PON) concentrations were quantified on a CHNS/O elemental analyzer (PE 2400 Series II CHNS/O Analyzer). Cystine (29.99% of C; 11.67% of N) was used as a standard and precision was about 1% for C and 2% for N (Guo and Santschi, 1997a). Concentrations of DOC were measured on a TOC Analyzer (Shimadzu TOC-5000) using a high temperature combustion method (Guo et al., 1994). Radiocarbon $\Delta^{14}\text{C}$ was measured for isolated COM samples by accelerator mass spectrometry (Santschi et al., 1995; Guo et al., 1996).

3. RESULTS AND DISCUSSION

3.1. Benthic Nepheloid Layer Characteristics (SPM, POC, PON, & DOC)

Vertical distributions of nutrients (N and P), DOC, suspended particulate matter (SPM), POC, and PON concentrations in the water column all demonstrate the occurrence of a well developed benthic nepheloid layer at both Gulf of Mexico and MAB continental shelf stations (Fig. 2). These vertical distributions in the water column show elevated concentrations of SPM, POC and DOC that are consistent with our previous observations in the same study areas for SPM and POC (Santschi et al., 1999) and for DOC (Guo et al., 1995). Detailed profiles of SPM, POC, PON, and DOC concentrations in the BNL are shown in Figure 3. Indeed, concentrations of SPM, POC, and PON at 0.2, 1.0, and 1.5 mab all show a strong vertical increase towards the sediment-water interface in the BNL at both Gulf of Mexico and MAB stations (Fig. 3).

Concentrations of DOC in the BNL also show a slight concentration gradient but it is not as strong as for particulate species.

Vertical and lateral processes operating in the BNL complicate a straightforward interpretation of the vertical profiles of SPM, POC and DOC in terms of vertical fluxes. The variability of individual data points is larger than the analytical error. Nonetheless, concentration increases towards the bottom are oftentimes dramatic, especially for SPM and POC. These strong concentration increases in SPM, POC, PON, and DOC towards the bottom, as are evident from Figure 3, suggest that sediments underneath or in lateral proximity of the site can act as strong sources for organic carbon and nitrogen species in ocean margin areas. It is therefore likely that benthic boundary layer processes can be important for the production and transport (or fluxes) of organic carbon from ocean margin areas to the open ocean (Santschi et al., 1999).

3.2. Radiocarbon Characterization

Recent evidence suggests ocean margins as potential sources of radiocarbon depleted organic matter to the ocean (Guo et al., 1996; Bauer and Druffel, 1998). However, sources of OC to ocean margin waters contain either contemporary OC from riverine inputs (Meybeck, 1982; Hedges et al., 1986) or freshly photosynthesized young OC from the upper water column (Druffel and Williams, 1990; Santschi et al., 1995). In addition, radiocarbon depleted DOC in the ocean margin waters could not be derived from sediment pore water DOC, because the relatively young pore water DOC (Bauer et al., 1995) would result in even younger deep ocean DOC.

Our measurements show that the $\Delta^{14}\text{C}$ values of COC isolated from the BNL were distinctly lower than their counterparts in the overlying water at both MAB and GOM stations (Table 1, Fig. 4). These results are consistent with our previous observations in bottom waters of the MAB using a traditional CTD rosette sampler (Guo et al., 1996). In the MAB station, the benthic COC collected within 1.5 mab in the BNL had $\Delta^{14}\text{C}$ values ranging from $-362 \pm 4\text{‰}$ to $-456 \pm 3\text{‰}$, whereas the surface water COC had a $\Delta^{14}\text{C}$ value of $-210 \pm 5\text{‰}$. In the GOM station, the surface water COC contained contemporary or postbomb organic material with a $\Delta^{14}\text{C}$ value of $18 \pm 5\text{‰}$. In contrast, $\Delta^{14}\text{C}$ values of benthic water COC from the GOM ranged from $-190 \pm 4\text{‰}$ to $-303 \pm 4\text{‰}$ (Table 1 and Fig. 4). In addition, COC from the BNL in both the MAB and the GOM was generally more nitrogen-depleted (higher C/N ratio, ranging from 14 to 20) than both suspended particles and surface sediments (lower C/N ratio, varying from 6 to 10), indicating that COC from the BNL contained more diagenetically altered material (Guo and Santschi, 1997a;b). These observations point to a chronologically older and diagenetically more refractory COC in the BNL in ocean margin waters. Thus, old COC in the BNL could be a potential source for some of the old DOC observed in the deep ocean (Bauer and Druffel, 1998).

If the old COC in the BNL (in a $<100\ \text{m}$ water column) in both study areas is largely derived from the overlying water column through advective or particle deposition pathways on time scales of decades or less, the apparent ^{14}C ages for the benthic COC in ocean margin areas should be similar to or close to those in the overlying water column, considering that radiocarbon has a mean life of $\sim 8,000$ years. The older benthic

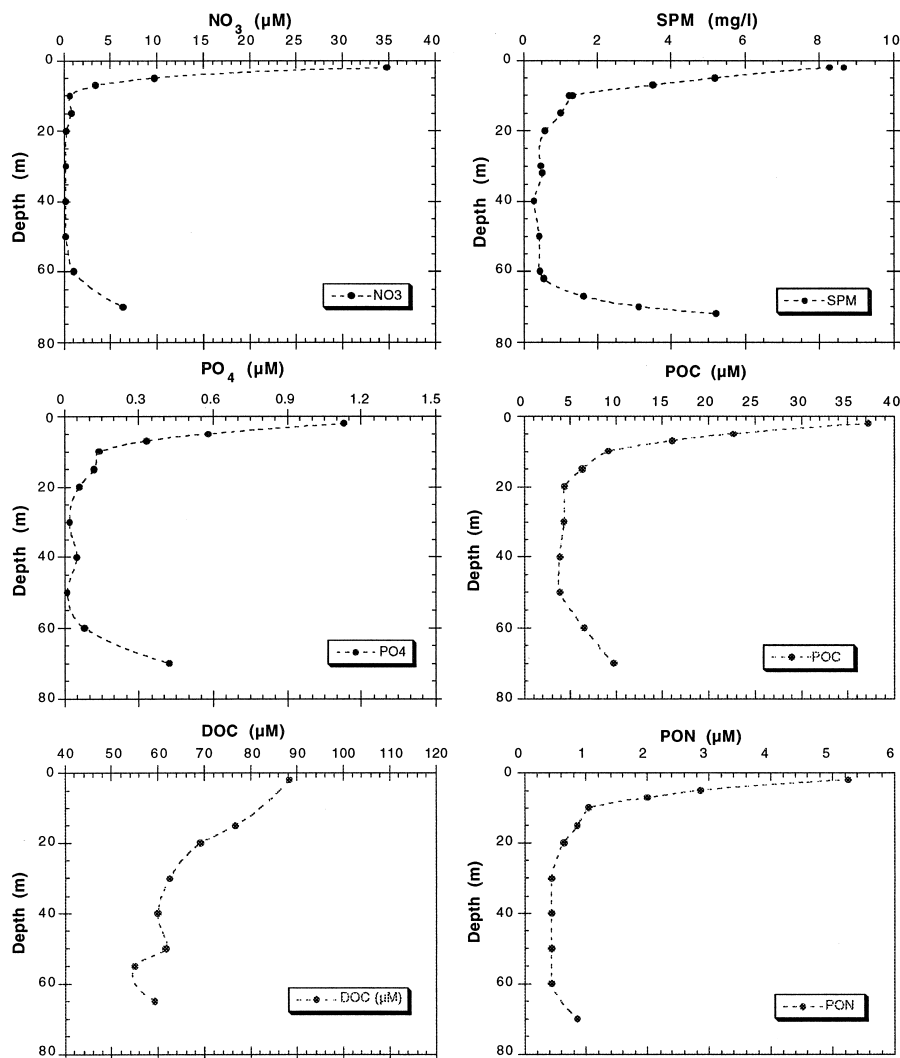


Fig. 2a. Vertical distributions of nutrient (N and P), DOC, SPM, POC, and PON concentrations in the water column at a continental station (28°50N, 89°40W) in the Gulf of Mexico (May 1997). b. Vertical distributions of SPM, POC, and PON concentrations in the water column at a continental station (74°55W; 35°50N) in the Middle Atlantic Bight.

COC cannot be derived from deep ocean either since ocean margin waters contain older DOC and suspended POC than the adjacent central gyres in Atlantic and Pacific (Bauer and Druffel, 1998). These distinctly different radiocarbon signatures between surface water and benthic water COC (Fig. 4) strongly suggest that the source of the older COC in the BNL is largely from bottom sedimentary organic carbon (SOC). However, unlike abyssal marine sediments where the radiocarbon activity of SOC is significantly lower than that of deep water DOC (Williams et al., 1978), $\Delta^{14}\text{C}$ values of SOC ($-87 \pm 6\%$) from surface sediments in the MAB station were significantly higher than the average $\Delta^{14}\text{C}$ value of COC ($-400 \pm 4\%$) from the BNL (Table 2). Both our measurements ($-87 \pm 6\%$, Table 2) and those reported for bulk sediments on the nearby shelf/slope stations (Anderson et al., 1994) reveal higher $\Delta^{14}\text{C}$ values for SOC compared with those of benthic COC in the MAB. These significantly younger apparent ^{14}C ages of bulk SOC appear to contradict a possible

sedimentary source for the older COC observed in the BNL (Fig. 4). Reconciling these seemingly contradictory observations would require that carbon sources for the old benthic COC are largely from older organic components released during sediment resuspension. Our hypothesis is, therefore, that bulk SOC is heterogeneous in terms of chemical composition and isotopic signatures and older macromolecular organic components are preferentially released during sediment resuspension aided by BNL processes in ocean margin areas. This hypothesis can be tested through controlled laboratory experiments as discussed below.

3.3. Heterogeneity of Bulk Organic Matter

A controlled laboratory experiment was conducted to simulate sediment resuspension in the BNL. Both smaller size resuspended POC ($>0.7 \mu\text{m}$) and COC fractions were isolated from a slurry solution and further characterized for their ele-

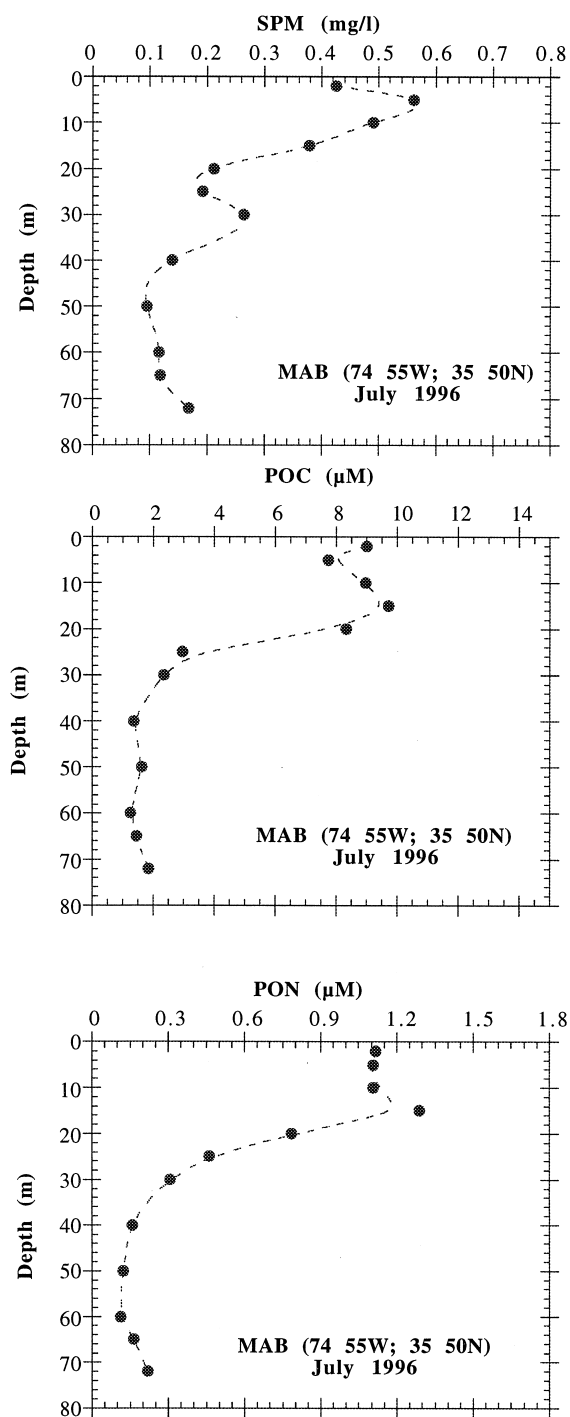


Fig 2. (Continued)

mental composition and radiocarbon signatures to be compared with those of bulk sediments. Organic carbon concentrations in both resuspended POC and the COC isolated from the slurry solution were significantly higher than in bulk sediments (Table 2). In other words, concentrations of OC in size fractionated sediments increased with decreasing sizes, indicating that SOC is heterogeneously distributed, as was previously reported by Keil et al. (1994b).

Furthermore, our replicate results (Table 2 and Fig. 5) showed that COC isolated during sediment resuspension had $\Delta^{14}\text{C}$ values between -260‰ and -352‰ which are significantly lower than those of the bulk sediment ($-87 \pm 6\text{‰}$) and resuspended POC ($-138 \pm 8\text{‰}$). The $\Delta^{14}\text{C}$ values of the SOC pool thus decreased with decreasing sizes and increasing OC content (Fig. 5). While it could be argued that the COC extracted after the suspended sediments settled out could have resulted from the pre-ultrafiltered (<1 kDa) seawater itself, this is highly unlikely. This is because the pool size of the <1 kDa DOC in the pre-ultrafiltered seawater is relatively small. In addition, most of the <1 kDa DOC in the pre-ultrafiltered seawater cannot be isolated by a 1 kDa ultrafilter when diafiltration is used (Guo et al., 1999) and little of this low molecular weight (LMW) DOC would be expected to coagulate into the HMW COC fraction since coagulation of LMW DOC is not very efficient (Stumm and Morgan, 1981; McCave, 1984). Moreover, LMW DOC usually sorbs less onto surfaces compared with those HMW DOC fractions (e.g., Gu et al., 1995 and summarized in Santschi et al., 1997). Therefore, the <1 kDa DOC fraction cannot contribute significantly to the HMW COC fraction. These results, together with recently published studies, indicate that isotopic heterogeneity of sediments occurs not only between individual organic compounds or compound classes (Wang et al., 1996; Eglinton et al., 1997) but also between different size fractions (Fig. 5). It thus strongly supports our hypothesis of old COC released from sediments as a potential source for benthic COC in ocean margin areas.

While $\Delta^{14}\text{C}$ values of COM extracted from sediment resuspension are not exactly the same as those extracted from seawater in the BNL at the same MAB station, sources of COC in the BNL likely integrate over larger areas with varying $\Delta^{14}\text{C}$ values. Lateral transport and exchange processes are thus important in influencing the distribution of COC in ocean margin areas (Bianchi et al., 1997; Santschi et al., 1999).

Organic carbon concentration (%) and molecular composition have been found to be related to particle size or surface area (Keil et al., 1994b; Mayer, 1994; Bergamaschi et al., 1997) and distance from shore (Grant et al., 1987). Chemical heterogeneity of bulk SOC indicates that different organic components may undergo different geochemical pathways during their transport and preservation in marine environments (Wang et al., 1996). The heterogeneity of isotopic and chemical composition in sedimentary organic matter has important implications. For example, it can be expected that the apparent ^{14}C age distributions are strongly affected by sediment hydrodynamic sorting, which could result in fractionation of SOC across ocean margins (Goni et al., 1997) during sediment resuspension and transport. Hydrodynamic sorting of particles would result in finer particles with higher OC contents (Grant et al., 1987; Keil et al., 1994a,b) and lower $\Delta^{14}\text{C}$ values.

3.4. Importance of Marine Benthic Nepheloid Layer Processes

The existence of the bottom nepheloid layer in marine environments and its importance in the transport of particles and thus the organic carbon deposition and preservation have long been recognized (Biscaye and Eitrem, 1977; Jahnke et al., 1990; McCave, 1986; Anderson et al., 1994). One of the

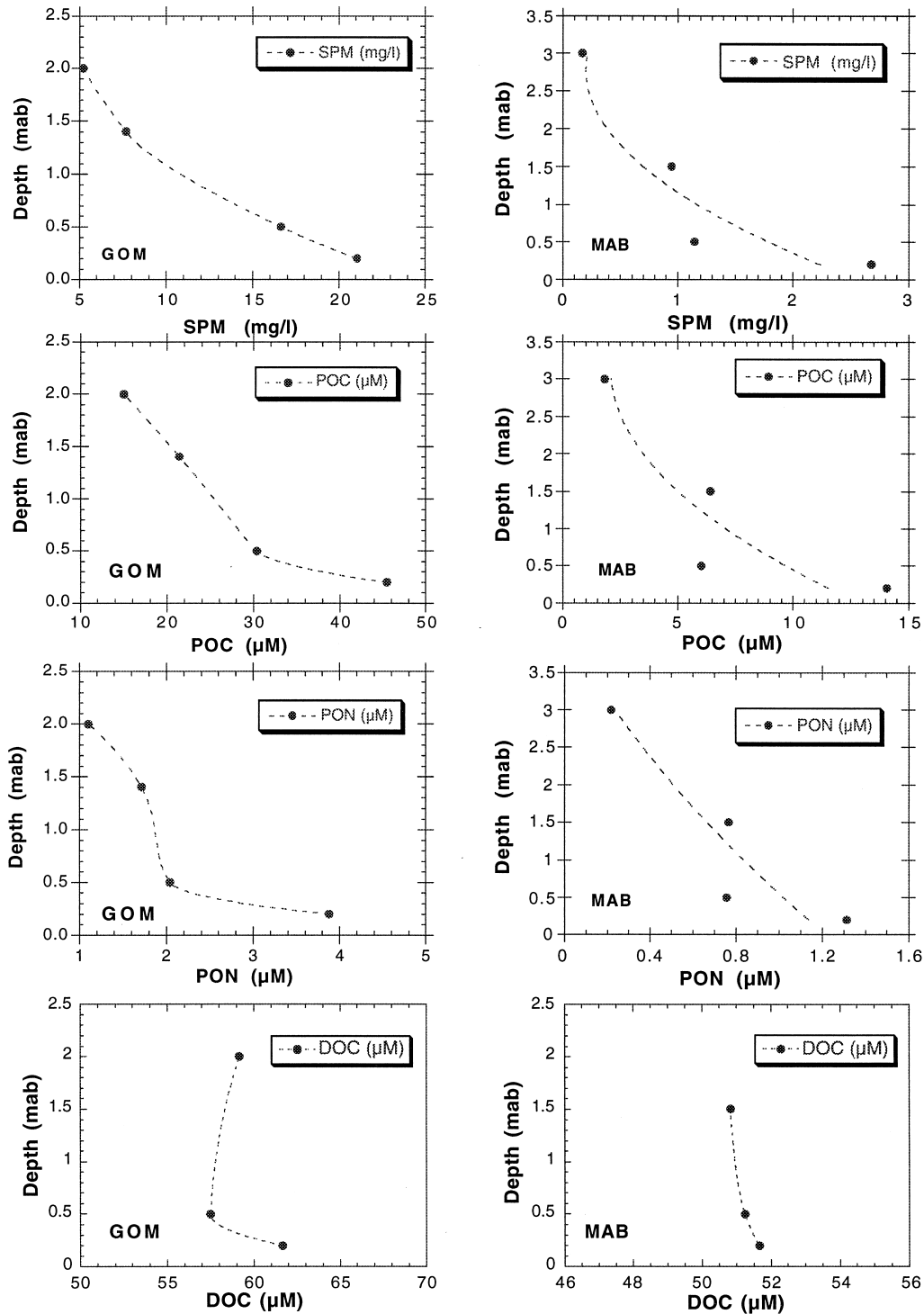


Fig. 3. Characteristics of suspended particulate matter (SPM), POC, PON, and DOC concentrations in the BNL (left panels: Gulf of Mexico station; right panels: Middle Atlantic Bight station).

important features of the BNL is the relatively high concentration of suspended particulate matter resulting from resuspension of bottom sediments (Table 1, and section 3.1). Lateral transport of turbid bottom mixed layers in ocean margin environments can lead to nepheloid layers which are detached from

the bottom. Due to high particle concentrations in the BNL, lateral transport processes can transport large amounts of POC and DOC from continental margin areas to the open ocean (Jahnke et al., 1990; Anderson et al., 1994; Bauer and Druffel, 1998; Mitra et al., 1999; Santschi et al., 1999). However,

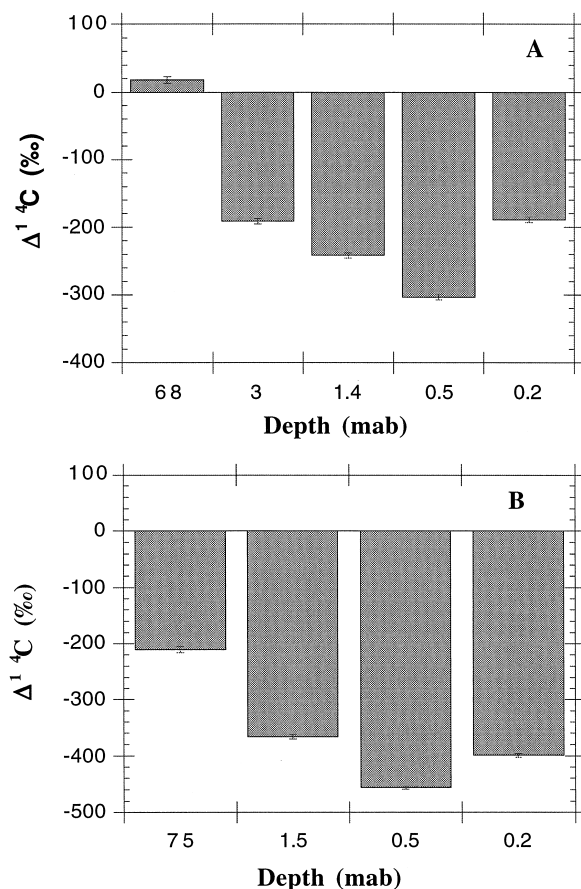


Fig. 4. Distributions of $\Delta^{14}\text{C}$ values in colloidal organic matter (COM) samples from the BNL from continental shelf stations in the Gulf of Mexico (A) and the Middle Atlantic Bight (B). Water depths are in meter above bottom (mab).

previous studies have not examined the flux of macromolecular COC and its relative importance. Our radiocarbon data clearly suggest that one potential source of old DOC is macromolecular COC released preferentially during bottom sediment re-suspension aided by BNL processes (Table 2 and Figs. 4 & 5). However, for COC to be important as a source of old DOC in the deep ocean, it would have to be degraded or disaggregated subsequently to LMW DOC. These results thus reveal, for the first time, a series of coupled physical and geochemical processes and pathways for old COC delivery from the ocean margin areas to the deep ocean.

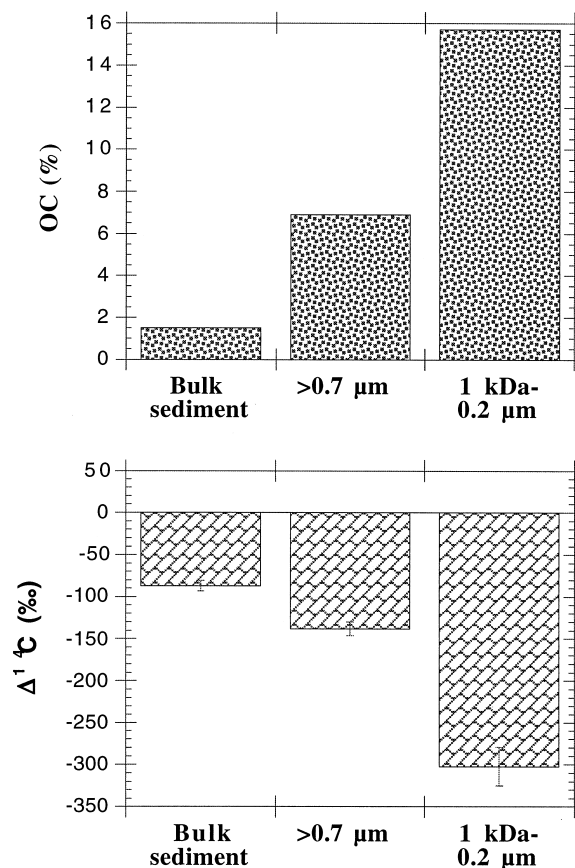


Fig. 5. Results from controlled laboratory experiments showing the heterogeneity of $\Delta^{14}\text{C}$ values (‰) and organic carbon (OC) concentrations in size fractionated surface sediments from the Middle Atlantic Bight station.

Near bottom lateral transport of COC from ocean margin areas to the open ocean may have a seasonal signal or may be episodic in nature (Anderson et al., 1994; Bianchi et al., 1997; Santschi et al., 1999), but is likely a reoccurring and semi-continuous process. Our laboratory experiments show that, after sediment resuspension, concentrations of both SPM and POC decrease rapidly after stirring is interrupted. However, the DOC concentration increases from $<40 \mu\text{M}$ before sediment suspension to $\sim 130 \mu\text{M}$ after sediment suspension and then remains fairly constant (Fig. 6). This indicates that, while POC can settle out quickly after sediment resuspension stops, DOC released from sediments during resuspension can indeed make

Table 2. Values of $\Delta^{14}\text{C}$ (‰) in size fractionated surface sediments (including bulk sediments, re-suspended particulate organic matter (POM), and re-suspended colloidal organic matter, COM) from the Middle Atlantic Bight station.

Sample type	Size	OC (%)	$\Delta^{14}\text{C}$ (‰)	Fraction of modern ^{14}C	Apparent ^{14}C age
Bulk Sediment	Bulk	1.5	-87 ± 6	0.918	690 ± 60
Re-susp. POM	$>0.7 \mu\text{m}$	6.9	-138 ± 8	0.804	1150 ± 80
Re-susp. COM	1–200 nm	15.7	-272 ± 6	0.732	2510 ± 70
Re-susp. COM	1–200 nm	—	-353 ± 18	0.652	3440 ± 240
Re-susp. COM	1–200 nm	—	-260 ± 9	0.744	2370 ± 110
Re-susp. COM	1–200 nm	—	-321 ± 10	0.683	3060 ± 120

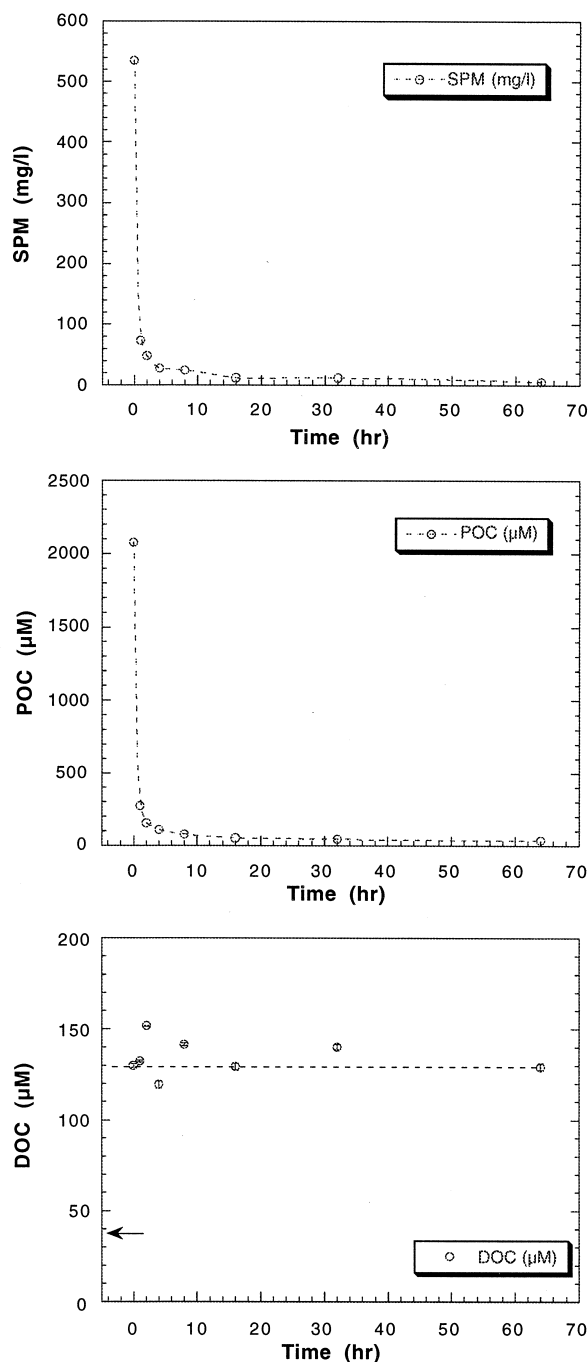


Fig. 6. Results from the sediment resuspension experiment using pre-ultrafiltered seawater containing <1 kDa DOC (<40 μM). The concentrations of both SPM and POC decreased rapidly after sediment suspension ceased while DOC concentrations remained constant.

a lasting contribution to the DOC concentration in the overlying waters and could then be available for further transport in the BNL. However, this increase in DOC concentration of 90 μM resulted from resuspending sediments at an overall concentration of 1–2 g/l. Therefore, the resulting increase in DOC concentrations in the BNL areas would depend on the amounts of sediments which initially get resuspended, but would not

necessarily be easily detectable due to rapid lateral diffusion and advective processes (Figs. 2a and 3).

The mechanisms through which older COC are released preferentially from sediments to the BNL water column likely act continuously in a fashion where

- 1) younger or fresher organic materials are deposited on the sea floor from sinking POC;
- 2) during temporary storage in shelf sediments, organic carbon fractions are selectively oxidized during sediment diagenesis which makes them more hydrophilic and thus lowers the sorptive forces to SOC;
- 3) during sediment resuspension, those now older and more hydrophilic organic components are preferentially released to the water column while other more hydrophobic components remain adsorbed on the surfaces of sediment particles (Gu et al., 1995).

An alternative scenario would be that younger OC components desorbed from sediments are degraded at a rate that is much faster than those of older components (Keil et al., 1994a) and allowing the older OC to be accumulated and transported to the deep ocean. However, the results of our laboratory experiment do not support this latter scenario (Fig. 5) because of the short time scale.

3.5. Implications for Organic Carbon Transport and DOC Residence Time

In ocean margin areas, $\sim 85\%$ and 40% of the bulk SOC on the slope and the shelf, respectively, is resuspendable (Grant et al., 1987) while up to 50% of sorbed OC in slope sediments can be desorbed (Keil et al., 1994a). Jahnke et al. (1990) estimated that more than half of the OC input to the sea floor is through lateral transport processes. Similarly, Anderson et al. (1994) showed that $\sim 80\%$ of SOC in the ~ 1000 m isobath region is derived from resuspended POC.

Lateral transport flux of resuspended POC in the MAB was estimated to be about 53 $\text{mg-C/m}^2/\text{day}$ (e.g., Anderson et al., 1994). From our measurements of POC and COC in the BNL in the MAB area, concentrations of POC in the BNL ranged from 6 to 14 μM while COC concentrations varied from ~ 14 to 20 μM (Table 1). If we take our measured COC/POC concentration ratio of ~ 2 in the BNL as a representative one in ocean margins and $\sim 15\%$ of the world ocean area as ocean margins, then the input of old COC off continental shelves and slopes to the open ocean could be of the order of $13\text{--}14 \times 10^{14}$ g-C/yr, which is equal in magnitude to the downward DOC flux from the upper ocean (e.g., Carlson et al., 1994; Peltzer et al., 1996). Thus, fluxes of COC to the deep ocean through sediment resuspension in ocean margin areas may make up a significant component in the cycling of DOC in the ocean.

One of the major components of marine COC is polysaccharides (Benner et al., 1992; Santschi et al., 1998). Therefore, a $\Delta^{14}\text{C}$ mass balance of polysaccharides was used here as an example to estimate the contribution of lateral transport. Our $\Delta^{14}\text{C}$ measurements on polysaccharides extracted from the bulk COC samples collected from deep waters of the MAB and the Gulf of Mexico (Santschi et al., 1998) show that the polysaccharide component is at least 700–800 yr younger than the bulk COC. However, $\Delta^{14}\text{C}$ values of the deep water poly-

saccharide enriched fraction are still low, e.g., $-321 \pm 6\%$ in the MAB and $-340 \pm 5\%$ in the Gulf of Mexico. Since surface water polysaccharides and HMW COC contain mostly contemporary OC (Santschi et al., 1995, 1998; Guo et al., 1996) and carbohydrates in sediments also have significantly higher $\Delta^{14}\text{C}$ values than the bulk SOC (Wang et al., 1996; 1998), it will be difficult to reconstruct the observed radiocarbon results in the deep water without lateral transport of old polysaccharides and other COC fractions. For example, deep water polysaccharides with a $\Delta^{14}\text{C}$ value of $-321 \pm 6\%$ to $-340 \pm 5\%$ (Santschi et al., 1998) require a much older polysaccharide component to compensate for any modern surface water polysaccharides settling rapidly on marine snow. Thus, the $\Delta^{14}\text{C}$ mass balance of the deep water COC component also requires a substantial lateral flux of old COC to the ocean.

If the deep ocean DOC is 6000 years old (Williams and Druffel, 1987) and the newly produced COC in the margins is about 4000 years old (see Table 1 for the MAB station), and taking the radiocarbon ages at face value, then the overall residence time of the old COC fraction in the water column will be ~ 2000 years, considering that the old DOC from continental margin areas is a major source for the deep ocean. Using $\Delta^{14}\text{C}$ values of DOC from the MAB continental slope as an example, apparent ^{14}C ages of DOC in deeper waters of the western North Atlantic are at least 500–1,000 years younger than those in the Sargasso Sea (Bauer and Druffel, 1998). Since the old DOC in the continental margin contributes significantly to the DOC in open ocean (i.e., with a flux which is over an order of magnitude greater than that from the upper water column), the real turnover time of old DOC in ocean waters must then be significantly shorter than the time scale derived from the overall apparent ^{14}C ages. Therefore, apparent ^{14}C ages of DOC are not the same as the turnover time of DOC if the ages of its carbon sources are not considered. This may help explain some discrepancies in the carbon cycling of DOC in the ocean.

4. CONCLUSIONS

The observed well developed BNL in two ocean margin areas and strong concentration gradients of SPM, POC, PON, and DOC towards the sediment-water interface indicate that sediments are a potential source for organic carbon species in the BNL. Therefore, significant amounts of organic carbon species could be transported from continental shelf/slope areas to the open ocean through lateral processes. Lateral fluxes could be of equal or higher magnitude than the amounts of COC which are vertically delivered to the deep ocean.

At both ocean margin stations with a water depth of ~ 70 m, colloidal organic carbon (COC), which comprises ~ 25 – 40% of the bulk DOC, extracted from seawater in the BNL has $\Delta^{14}\text{C}$ values which are much lower than those in the overlying waters. For the MAB station, the average $\Delta^{14}\text{C}$ value is -407% for BNL COC vs. -211% for surface water COC. For the Gulf of Mexico station, these values are -245% vs. $+18\%$. Significantly older COC in the BNL points to a potentially old COC source from the bottom sediments to the deep ocean.

Laboratory experiments revealed that the $\Delta^{14}\text{C}$ value of sedimentary organic carbon decreased with decreasing size while the OC content increased with decreasing size of OC

fractions. Older COC in the BNL than the bulk sediments requires that older OC be preferentially released from sediments if the old carbon sources are from sediments. Preferential release of old COC was documented by the results from the laboratory experiments. The heterogeneity of isotopic signatures in SOC thus reconciles these seemingly contradictory results between old benthic COC and relatively young SOC.

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