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Cycling of high-molecular-weight dissolved organic matter in the Middle Atlantic Bight as revealed by carbon isotopic (^{13}C and ^{14}C) signatures

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Abstract

Carbon isotopes (^{13}C and ^{14}C) and elemental composition (C and N) in two fractions of colloidal organic matter (COM) were measured to study the origin and cycling of dissolved organic matter (DOM) in the Middle Atlantic Bight (MAB). COM_1 (1 kDa–0.2 μm) was 59% of the bulk DOM in surface Chesapeake Bay waters and decreased to 30–35% in waters of the MAB. COM_{10} (10 kDa–0.2 μm), which was the high-molecular-weight (HMW) component of COM_1 , comprised 3–12% of the bulk DOM, with highest concentrations in Chesapeake Bay waters and the lowest in deep waters in the MAB. $\Delta^{14}\text{C}$ values of COM_1 decreased from nearshore (–21 to +12‰) to offshore and from surface (–166 to –85‰) to bottom waters (–400 to –304‰). Although $\Delta^{14}\text{C}$ values of surface-water HMW COM_{10} were generally high (–2 to –7‰), values for bottom-water COM_{10} were much lower (–129 to –709‰). The high $\Delta^{14}\text{C}$ values in the surface water suggest a particulate origin of pelagic COM, consistent with the contemporary $\Delta^{14}\text{C}$ values of particulate organic matter (POM). The very low $\Delta^{14}\text{C}$ values of bottom-water COM_{10} imply that in addition to the pelagic origin, sedimentary organic C may serve as an important source for the benthic colloids in the bottom nepheloid layer. The general flow direction of organic carbon is from POM to HMW and to LMW DOM. Three colloidal end-members were identified in the MAB as well as in the Gulf of Mexico: estuarine colloids with high $\Delta^{14}\text{C}$ values, high C:N ratios, and lower $\delta^{13}\text{C}$ values; offshore surface water colloids with intermediate $\Delta^{14}\text{C}$ values, lower C:N ratios, and higher $\delta^{13}\text{C}$ values; and offshore deep-water colloids with low $\Delta^{14}\text{C}$ values, intermediate C:N ratios, and variable $\delta^{13}\text{C}$ values.

Dissolved organic carbon (DOC) is one of the largest reservoirs of organic C on earth. Understanding the cycling of dissolved organic matter (DOM) in the ocean is complicated by the poor characterization of DOM in terms of molecular size and chemistry and has long been a major challenge for oceanographers (Farrington 1992). The measurements of DOC in seawater along with its size characterization and chemical composition, have received increased attention (e.g. Benner et al. 1992; Guo

et al. 1995b; Santschi et al. 1995). However, the sources and cycling rates of DOM in the ocean are still not well constrained (Hedges 1992). The fact that DOM is heterogeneous in terms of sizes or molecular weights and apparent ^{14}C ages may change the classical view of the cycling of DOM in the ocean.

Carbon isotopes have proven useful tracers of sources and sinks of DOM in the ocean (Williams and Druffel 1987; Druffel and Williams 1992; Santschi et al. 1995). Apparent ^{14}C ages of the whole DOM pool in the ocean range from ~1,000 to 6,000 yr (Williams and Druffel 1987; Bauer et al. 1992). These apparent ^{14}C ages for oceanic DOM are averages for the bulk DOM pool and thus are the result of mixing different DOM fractions with differing molecular weights and varying ^{14}C ages (Mantoura and Woodward 1983; Williams and Druffel 1987; Santschi et al. 1995). Therefore, measurements of $\Delta^{14}\text{C}$ in the whole DOM pool alone are not sufficient to constrain the cycling of oceanic DOM in detail.

Part of the DOC is composed of colloids containing different molecular-weight fractions (Guo et al. 1995b).

Acknowledgments

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For example, up to 45% of DOC has been found in the colloidal fraction (>1 kDa) in seawater (Benner et al. 1992; Guo et al. 1994). Recently, cross-flow ultrafiltration techniques have allowed for extraction of large amounts of high-molecular-weight (HMW) colloidal organic matter (COM) from seawater for molecular size and isotopic and biochemical characterization (e.g. Benner et al. 1992; Bianchi et al. 1995; Santschi et al. 1995). Thus, measurements of isotopic signatures of different molecular-weight COM fractions separated from DOM can be used to explore the diverse origins and reactivities of the COM. Santschi et al. (1995) found that the HMW colloidal fraction between $0.2 \mu\text{m}$ and 10 kDa (COM_{10}) in the upper water column of the Gulf of Mexico contained contemporary $\Delta^{14}\text{C}$ values, while $\Delta^{14}\text{C}$ values in the fraction between $0.2 \mu\text{m}$ and 1 kDa (COM_1) were lower and similar to those of the whole DOM in the ocean. Based on turnover times derived from ^{234}Th , they suggested that HMW COM, even though only a small fraction of DOM, cycles rapidly in the upper water column, whereas the low-molecular-weight (LMW) fraction (<1 kDa) of DOM—the major fraction of DOM in the open ocean (Guo et al. 1995b)—turns over on much longer time scales (Amon and Benner 1994; Santschi et al. 1995).

The Middle Atlantic Bight (MAB) off Cape Hatteras is an extremely dynamic ocean margin area. Important aspects of the hydrographic features of the MAB are the proximity of the Gulf Stream and a variable mixing of several source waters (Pietrafesa et al. 1994). Our principle objective was to better understand the production and cycling of fractions of DOM by characterization of carbon isotopic signatures ($\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$) and organic C and N in fractions of the DOM pool in seawater of the MAB. Comparisons were made between the MAB and the less dynamic ocean margin region of the Gulf of Mexico.

Materials and methods

Sampling—Seawater samples were collected for size fractionation of DOM from the MAB during June–July 1994 onboard the RV *Gyre*. Surface water samples from Chesapeake Bay were also collected during the same cruise. Sampling locations and ancillary parameters are shown in Fig. 1 and Table 1. Surface water was transferred directly by an online peristaltic pump through an acid-rinsed $0.2\text{-}\mu\text{m}$ Nuclepore cartridge into a closed 200-liter reservoir for ultrafiltration and DOC sampling. The first 10–20 liters of prefiltered water were discarded. Deep water was collected by Niskin bottles and then pumped peristaltically into the 200-liter reservoir in each ultrafiltration system. In order to sample seawater from the bottom nepheloid layer (BNL), deep water was collected as close to the bottom as possible, usually 5 m above the sediment on the shelf stations and 25–50 m above the bottom at stations from the steep slope areas. Location and hydrography of samples from Galveston Bay and the Gulf of Mexico presented here have been described elsewhere (Guo 1995; Santschi et al. 1995).

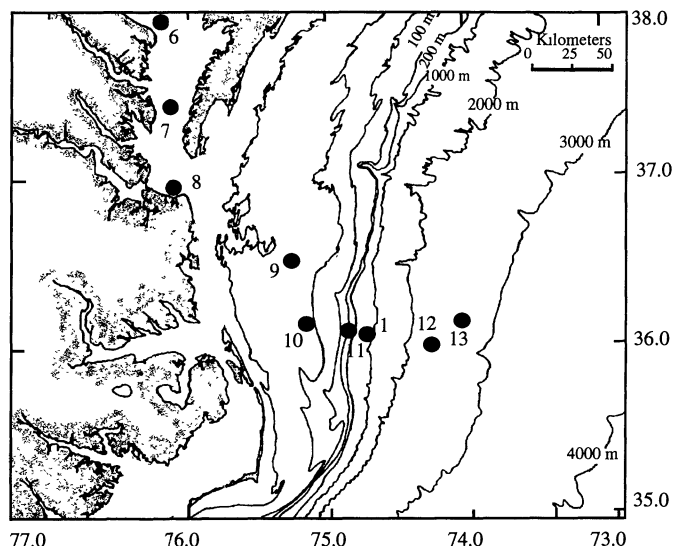


Fig. 1. Map of the Middle Atlantic Bight (MAB) off Cape Hatteras and sampling locations, June–July 1994.

Ultrafiltration—Colloids are microparticles and macromolecules in the size range from 1 nm to $1 \mu\text{m}$ (Buffle and Leppard 1995). In our study, two fractions of COM were operationally defined: COM_1 as the fraction with sizes or molecular weights between 1 kDa and $0.2 \mu\text{m}$, and COM_{10} as the fraction between 10 kDa and $0.2 \mu\text{m}$. Thus, COM_{10} is a subfraction of COM_1 .

Cross-flow ultrafiltration techniques were used to extract COM from seawater (Benner 1991; Guo and Santschi 1996). Detailed procedures, including information on carbon and ^{14}C blanks and ultrafilter calibration, are given by Guo (1995) and Santschi et al. (1995). Two types of ultrafilter cartridges were used to extract COM samples. One is a spiral-wound cartridge (Amicon, S10N1) with 1-kDa cutoff and the other a hollow-fiber cartridge (Amicon, H10P10) with 10-kDa cutoff. Ultrafiltration systems used were an Amicon DC-30, an Amicon DC-10, and a homemade ultrafiltration system (Guo 1995). To extract enough COM from open-ocean waters for chemical and isotopic characterization, COM_1 was usually extracted from up to 1,000 liters of seawater using the DC-30 system with nine 1-kDa cartridges. Each DC-30 ultrafiltration yielded ~ 20 liters of retentate and was completed in 10–12 h. The retentate was then further concentrated to 2–4 liters with the DC-10 system within ~ 1 h. COM_{10} was separated from ~ 200 liters of seawater in 6–8 h. For the Chesapeake Bay stations, only 20–40 liters of seawater were ultrafiltered for COM_1 and COM_{10} fractions because COM concentrations were relatively high.

Before sampling, the ultrafiltration system and ultrafilter cartridges were cleaned with Micro detergent, NaOH, HCl, and large volumes of low carbon Nano-pure water between cleaning solutions (Guo and Santschi 1996). During cleaning, DOC from the permeate was monitored to ensure the cleanliness of the cartridges and ultrafiltration system. Furthermore, all cartridges were routinely calibrated with macromolecules of known molecular

Table 1. Sampling locations and ancillary parameters at stations in the MAB (June–July 1994). SPM—suspended particulate matter.

Sta.	Location	Water depth (m)	Sampling depth (m)	Salinity	Temp. (°C)	SPM ($\mu\text{g liter}^{-1}$)
02	39°06'N, 76°20'W	6.5	1	5.0	27.5	14,675
04	38°40'N, 76°25'W	30	1	9.1	27.0	8,413
05	38°22'N, 76°20'W	21	1	10.4	26.9	5,840
06	37°55'N, 76°10'W	18	1	15.0	26.0	3,893
07	37°24'N, 76°05'W	15	1	18.2	25.5	5,220
08	36°55'N, 76°05'W	20	1	25.0	25.0	6,060
09	36°30'N, 75°14'W	25	1	35.28	23.6	136
10	36°08'N, 75°10'W	30	2	35.59	22.9	848
10	36°08'N, 75°10'W	30	25	35.83	14.9	563
11	36°06'N, 74°50'W	100	2	36.27	26.5	295
11	36°06'N, 74°50'W	100	90	35.65	13.0	72
01	36°04'N, 74°44'W	800	2	36.29	26.2	345
01	36°04'N, 74°44'W	800	750	34.98	4.5	120
12	36°00'N, 74°15'W	2,350	2	36.08	25.3	185
12	36°00'N, 74°15'W	2,350	2,300	34.95	3.2	111
13	36°09'N, 74°03'W	2,650	2	36.01	27.2	167
13	36°09'N, 74°03'W	2,650	250	35.33	10.4	43
13	36°09'N, 74°03'W	2,650	2,600	34.93	2.8	53

weights to check the integrities of cartridges before cruises (Guo 1995). Briefly, we used vitamin B₁₂ (MW, 1.3 kDa) for 1-kDa cartridges and cytochrome-C (12 kDa) for 10-kDa cartridges (Guo and Santschi 1996). Losses of the macromolecules (e.g. B₁₂) to the cartridges during calibration experiments were minimal (<5%). DOC mass

balances in the calibration experiments and all ultrafiltration experiments gave satisfactory recoveries ($100 \pm 5\%$) (Guo et al. 1994; Guo and Santschi 1996). Cartridges were also cleaned between samples with NaOH, HCl, and large volumes of Nano-pure water. Then, a small volume of prefiltered seawater (4–5 liters for the DC-10 system and 40–50 liters for the DC-30 system) was used to condition the cartridges before ultrafiltration.

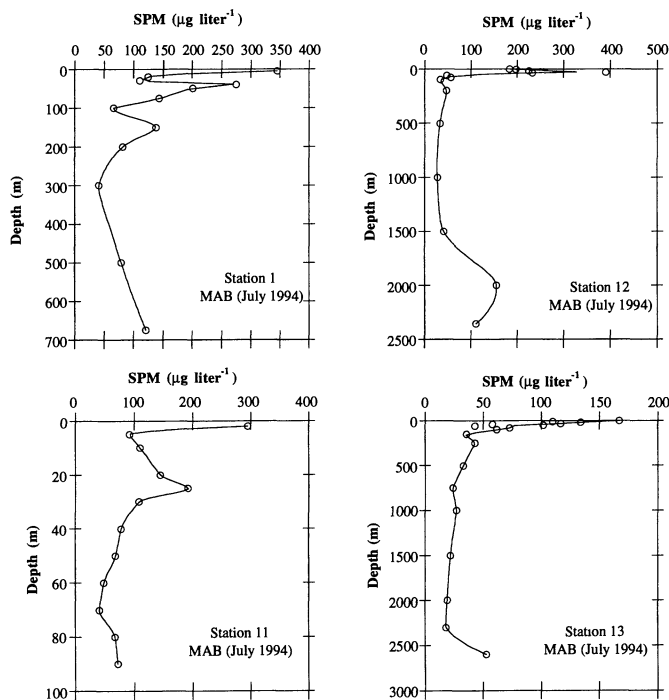


Fig. 2. Profiles of suspended particulate matter (SPM) concentrations at stations in the MAB.

Diafiltration experiments—After ultrafiltration, COM was diafiltered immediately with 20 liters of Nano-pure water to remove sea salts, frozen on-board ship, and subsequently freeze-dried in the laboratory (Guo 1995). Total blank DOC from the diafiltration process, including 20-liter Nano-pure water and cartridges, was $\sim 40\text{--}60 \mu\text{mol C}$ (Guo 1995). The total amount of COC₁ (colloidal organic matter) isolated for diafiltration from 1,000 liters of seawater was $\sim 18,000\text{--}40,000 \mu\text{mol C}$ with an initial DOC concentration of $45\text{--}100 \mu\text{M}$. Total recovered COC₁₀ for diafiltration was $450\text{--}1,000 \mu\text{mol C}$ from 200 liters of seawater. Thus, DOC contamination during diafiltration is negligible for both COC₁ and COC₁₀ fractions.

Measurements of organic carbon concentrations and isotopes—Concentrations of suspended particulate matter (SPM) were measured by filtering seawater through preweighed Nuclepore filters (Guo et al. 1995a). Profiles of SPM at stations in the MAB (Fig. 2) demonstrate elevated concentrations near bottom waters, indicative of sediment resuspension or lateral transport and thus support the existence of a pronounced BNL in this dynamic ocean margin area.

DOC and COC concentrations were measured on a Shimadzu TOC-5000 analyzer with a Pt-Al catalyst using

Table 2. $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$, and C:N atomic ratios in colloidal fractions in the MAB (June–July 1994). $\Delta^{14}\text{C}$ values were corrected with measured $\delta^{13}\text{C}$ values for carbon isotopic fractionation. When sample $\delta^{13}\text{C}$ values were not available, the average $\delta^{13}\text{C}$ value was used. One-sigma errors are given here for $\delta^{13}\text{C}$, $\Delta^{14}\text{C}$, fraction of modern, and apparent ^{14}C ages; 5,568 yr of ^{14}C half-life was used for age calculations. (Not measured: —)

Sta.	Sampling depth (m)	DOC (μM)	COC size (kDa)	COC:DOC (%)	C:N	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	% of modern ^{14}C (%)	Apparent ^{14}C age (B.P.)
02	1	193	1	65	22	-24.9±0.04	-10±7	99±1	83±54
04	1	205	1	65	22	-26.6±0.14	-8±6	99±1	68±45
05	1	211	1	61	21	-30.8±0.53	12±7	101±1	>modern
06	1	215	1	52	22	-30.1±0.21	17±7	102±1	>modern
07	1	122	1	62	20	-26.8±0.07	3±6	100±1	>modern
08	1	118	1	57	19	-27.8±0.41	-19±6	98±1	156±53
09	1	119	1	53	23	-22.9±0.02	-182±5	82±1	1617±45
10	2	98	1	34	13	-22.1±0.02	-89±5	91±1	751±47
10	25	90	1	31	24	-20.2±0.56	-308±5	69±0.4	2962±52
11	2	88	1	42	16	-26.9±0.11	-117±6	88±1	998±52
11	90	74	1	35	15	-23.6±0.16	-336±4	66±0.4	3288±52
01	2	86	1	35	—	-22.7±0.10	-169±5	83±1	1489±52
01	750	48	1	30	—	-22.0±0.15	-403±4	60±0.4	4143±54
12	2	85	1	34	12	-21.8±0.01	-123±7	88±1	1057±64
12	2,300	49	1	29	14	-24.4±0.29	-392±4	61±0.4	3998±53
13	2	82	1	34	11	-28.2±0.07	-110±6	89±1	935±51
13	250	54	1	29	—	-26.8±0.38	-399±4	60±0.4	4091±56
13	2,600	48	1	28	21	-20.7±0.03	-376±5	62±1	3796±65
02	1	193	10	10	15	-24.4±0.33	-65±6	94±1	541±51
04	1	205	10	10	13	—	-167±8	84±1	1420±90
05	1	211	10	16	13	-23.2±0.14	5±10	101±1	>modern
06	1	215	10	13	14	-24.9±0.13	-89±6	92±1	710±60
07	1	122	10	13	13	—	-84±9	92±1	660±80
08	1	118	10	11	—	—	—	—	—
09	1	119	10	12	24	—	—	—	—
10	2	98	10	11	17	-22.7±0.05	-6±6	99±1	49±51
10	25	90	10	4	15	-22.9±0.07	-132±5	87±1	1135±42
01	2	86	10	5	17	-27.6±1.2	-160±5	84±1	1403±51
01	750	47	10	4	17	-27.6±0.04	-442±5	56±1	4690±66
12	2	85	10	5	17	-23.0±0.01	-9±6	99±1	71±53
12	2,300	49	10	3	36	-28.3±0.03	-558±5	44±1	6555±91
13	2	82	10	6	17	-25.4±0.08	-8±5	99±1	64±40
13	250	54	10	5	25	-25.9±0.06	-611±3	39±0.3	7595±58
13	2,600	48	10	3	—	-23.9±1.5	-709±5	29±1	9931±141

a high temperature combustion method (Guo et al. 1994). DOC concentrations in Nano-pure water were $\leq 2 \mu\text{M}$. The total blank, including the instrumental blank and water blank, was always $\leq 5 \mu\text{M C}$ (Guo 1995). Analytical precision (± 1 sigma) of the DOC determination was $< 2\%$.

$\Delta^{14}\text{C}$ values of subsamples of COM_1 and COM_{10} were measured by accelerator mass spectrometry (Trumbore 1993). One-sigma errors in $\Delta^{14}\text{C}$ values are given explicitly in Table 2. $\delta^{13}\text{C}$ of COM_1 and COM_{10} was measured by isotope ratio mass spectrometry (Cifuentes et al. 1988). The precision and accuracy of $\delta^{13}\text{C}$ analysis was $\pm 0.1\%$ as determined by replicate analysis of standards and samples.

Organic C and N concentrations of COM_1 and COM_{10} were measured on an elemental analyzer (Carlo Erba Strumentazione NA 1500 Series 1). Acetanilide (71.09% C and 10.36% N) was used as a standard. Precision was always $< 5\%$ for both C and N (Guo 1995).

Results and discussion

Size distribution of DOM—DOM was size-fractionated into two colloidal fractions, COM_1 and COM_{10} . Concentrations of total DOC decreased from $\sim 200 \mu\text{M}$ in the estuarine waters in Chesapeake Bay to $80\text{--}90 \mu\text{M}$ in surface waters in the MAB to $\sim 48 \mu\text{M}$ in deep waters (Table 2). Both concentration and percentage ($[\text{COC}]/[\text{DOC}] = F_{\text{COC}}$) of the HMW COC fractions in the bulk DOC pool decreased from Chesapeake Bay to shelf seawater to slope waters (Fig. 3) and decreased vertically from surface to bottom waters. Conversely, the percentage of LMW DOC fraction (i.e. $< 1 \text{ kDa}$) increased from nearshore to offshore and from surface to deep waters. These results indicate that HMW fractions of DOM are of higher reactivities and that they are removed or utilized on their way to the deep ocean, consistent with the recent evidence of fast microbial degradation (Amon and Benner 1994).

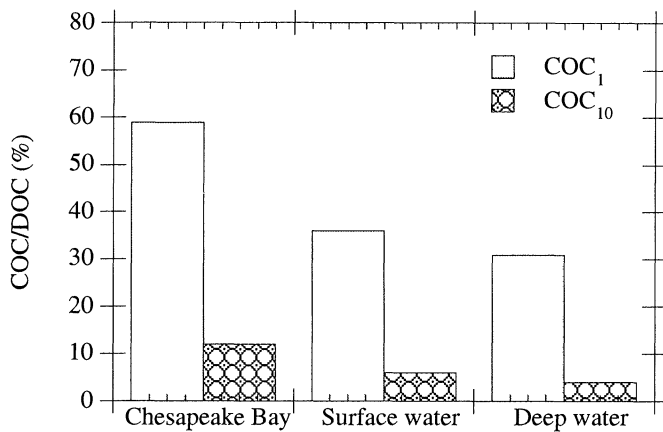


Fig. 3. Distribution of COM₁ and COM₁₀ fractions in estuarine waters of Chesapeake Bay and seawater off Cape Hatteras in the MAB (June–July 1994).

and contemporary origin (Santschi et al. 1995) of HMW DOM fractions in seawater. On average, HMW COM₁₀ comprised 11–16% of the bulk DOC in estuarine waters of Chesapeake Bay, ~6% in surface waters, and 3–5% in deep waters of the slope areas (Fig. 3). For the larger colloidal fraction, COM₁ made up ~59% of the DOC in Chesapeake Bay, ~35% of that in surface waters, and decreased to ~30% of that in deep waters of the MAB (Fig. 3). The distribution and dynamic features of DOC and COM in the study area are presented elsewhere (Guo et al. 1995b).

$\delta^{13}\text{C}$ values in COM fractions—Values of $\delta^{13}\text{C}$ in COM₁ ranged from -30.8 to -24.9‰ in estuarine waters of Chesapeake Bay and varied from -28.2 to -20.2‰ in the MAB (Fig. 4). In turn, values of $\delta^{13}\text{C}$ in COM₁₀ in the MAB varied from -28.3 to -22.7‰ (Fig. 4A and Table 2). These values have a larger range than measured previously in the COM pool (Sigleo and Macko 1985; Santschi et al. 1995) and in the bulk DOC pool in the ocean (Eadie et al. 1978; Sackett et al. 1979; Druffel et al. 1992).

Although values of $\delta^{13}\text{C}$ in the COM fraction from the Gulf of Mexico changed little (Santschi et al. 1995), $\delta^{13}\text{C}$ values in COM₁ in the MAB regions varied by 8‰, likely due to the physical complexity and variety of carbon sources in the MAB area. The depletion of $\delta^{13}\text{C}$ in estuarine COM₁ compared to that of COM₁ in the MAB implies that carbon sources for COM₁ are distinctly different for estuarine and Cape Hatteras waters. For example, when $\delta^{13}\text{C}$ values of COM₁ are plotted against sigma-*t*, two different COM sources with distinctly different $\delta^{13}\text{C}$ values can be distinguished (Fig. 4B). The variations of $\delta^{13}\text{C}$ values in both COM₁ and COM₁₀ with salinity or sigma-*t* in the MAB (Fig. 4) show no linear distribution, indicating that processes other than mixing are major factors in controlling the distributions of $\delta^{13}\text{C}$ in both COM₁ and COM₁₀ fractions. Furthermore, $\delta^{13}\text{C}$ values in COM₁ increased from surface to bottom waters (Table 2). Lower values of $\delta^{13}\text{C}$ in surface water COM₁

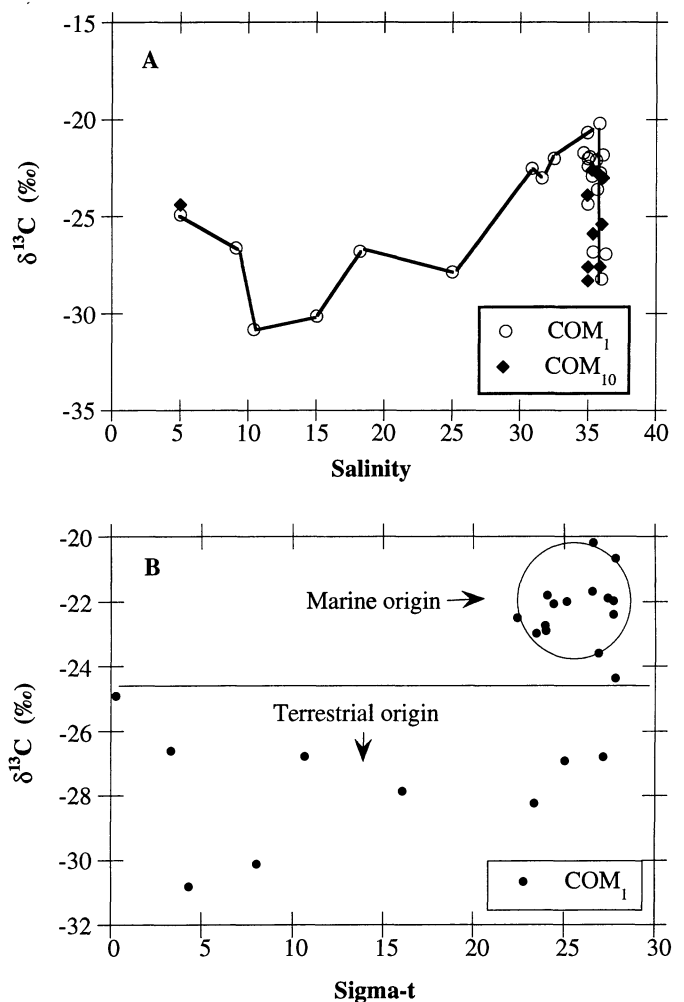


Fig. 4. $\delta^{13}\text{C}$ in COM₁ and COM₁₀ vs. salinity and sigma-*t*.

can be explained by the influence of either terrestrial organic sources or algal products in CO₂-rich condition (Fogel and Cifuentes 1993). Higher values of $\delta^{13}\text{C}$ in bottom water COM₁ imply a marine origin for bottom water COM₁ in the MAB. In contrast to the $\delta^{13}\text{C}$ distribution of COM₁, $\delta^{13}\text{C}$ values in COM₁₀ decreased mostly from surface to bottom waters. The depletion of ^{13}C in bottom-water COM₁₀ in the MAB probably implies a more degraded and fractionated fraction of COM that contains carbon-rich macromolecules with lower $\delta^{13}\text{C}$ values (Benner et al. 1987). Thus, although the bulk of bottom-water colloids seems mostly pelagic in origin, the HMW COM₁₀ fraction could largely originate from sedimentary or degraded organic matter. This finding is consistent with the $\Delta^{14}\text{C}$ results discussed in the following sections.

Elemental (C and N) characterization of COM—Organic C:N atomic ratios of COM₁ and COM₁₀ are listed in Table 2. C:N ratios of COM₁ ranged from 19 to 22 in estuarine waters of Chesapeake Bay, similar to values in bottom-water COM₁ on the shelf. Deep-water C:N ratios of COM₁ changed from 14 to 24, but surface-water

COM₁ values were generally lower and changed less, varying from 11 to 16 (Table 2). Values of C:N in COM₁ are generally higher than those of settling particles (7–10) collected by sediment trap (Walsh and Santschi unpubl. results) or those of POC:PON (6–10) for the MAB (Guo and Santschi unpubl. results).

Due to the preferential decomposition of nitrogen-containing organic matter, C:N ratios have been used to study the early diagenesis of POM in the water column (e.g. Knauer et al. 1979). There are relatively few measurements of C:N in DOM. Sigleo et al. (1983) reported that estuarine colloidal material had C:N ratios ranging from 7 to 37. More recently, values of C:N ratios of COM₁ have been reported to be 15–23 for seawater in the North Pacific Ocean (Benner et al. 1992). Our results are comparable to values previously reported for colloidal materials but significantly lower than the C:N in isolates extracted by the XAD method (Meyers-Schulte and Hedges 1986; Druffel et al. 1992).

C:N in COM₁ decreased with increasing salinity but with no obvious trend when salinity was >35‰ (Fig. 5). If only surface-water data are plotted, C:N decreased from estuarine to nearshore to offshore stations, with no difference between data collected in May 1993 and June–July 1994 in the MAB (Fig. 5). In addition, C:N in COM₁ increased from surface to deep waters (Table 2). Higher C:N ratios of COM₁ in estuarine waters are consistent with lower $\delta^{13}\text{C}$ values and point to a terrestrial origin for estuarine colloids. Moreover, lower C:N ratios of COM₁ in surface waters in the MAB suggest a greater marine contribution, consistent with their higher $\delta^{13}\text{C}$ values. This trend is similar to the horizontal and vertical variations of these values described for the Gulf of Mexico COM₁ (Guo 1995).

Values of C:N in surface-water COM₁₀ ranged from 13 to 17 in the MAB (Table 2). Although C:N ratios of COM₁₀ (13–15) were generally lower than those of COM₁ (19–22) in Chesapeake Bay, values of C:N ratios of surface-water COM₁₀ in the MAB were more comparable to those of COM₁. However, C:N ratios of bottom-water COM₁₀ in the MAB were more variable, reflecting their variability in $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values.

Radiocarbon in the COM₁ fraction— $\Delta^{14}\text{C}$ values of COM₁ in estuarine waters of Chesapeake Bay were generally high, ranging from +17 to –19‰ (Table 2). These values correspond to apparent ¹⁴C ages from contemporary (>100% modern) to ≤156 B.P. In seawater from the shelf and slope areas in the MAB, $\Delta^{14}\text{C}$ values of COM₁ varied from –110 to –182‰ in surface waters and from –308 to –403‰ in bottom waters (Table 2). $\Delta^{14}\text{C}$ values of COM₁ in the MAB were similar to those reported for waters in the Gulf of Mexico (Santschi et al. 1995).

Variations of $\Delta^{14}\text{C}$ in COM₁ with seawater salinity are shown in Fig. 6. Although salinity ranged from ~5 to 25 within Chesapeake Bay, $\Delta^{14}\text{C}$ of COM₁ changed little, with nonsystematic variations from –19 to +17‰ (Fig. 6A). However, $\Delta^{14}\text{C}$ values of COM₁ in seawater of the

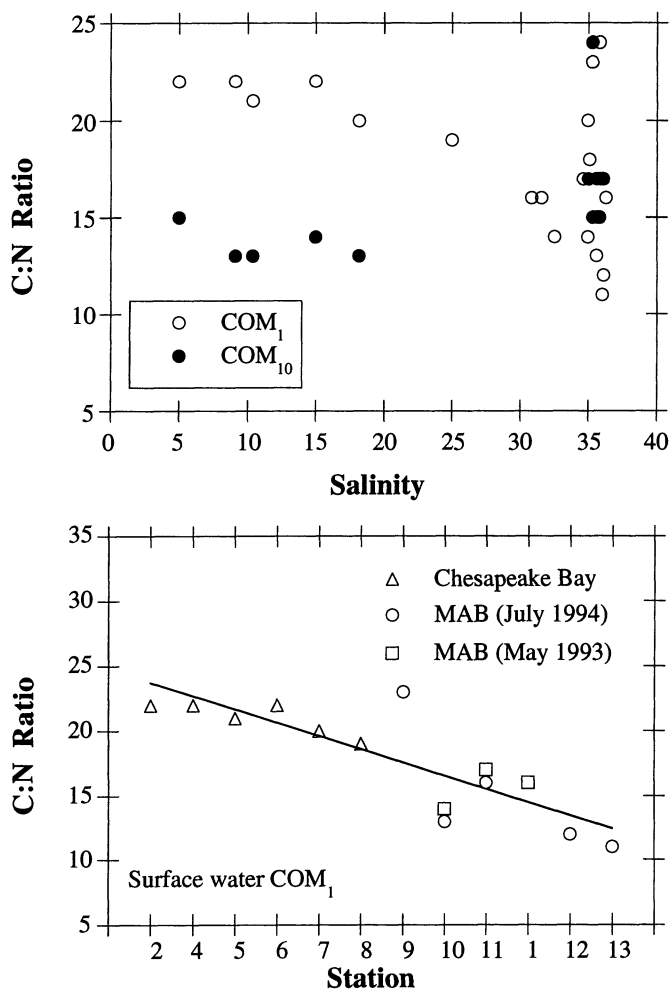


Fig. 5. Organic C:N ratios in COM₁ and COM₁₀ vs. salinity and station numbers for surface-water COM₁ in the nearshore to offshore direction.

MAB varied from –110 to –403‰ within a salinity range from 31 to 36 and showed no significant difference in the $\Delta^{14}\text{C}$ values of COM₁ between 1993 and 1994 (Fig. 6A). When sigma-*t* was used as a mixing index, $\Delta^{14}\text{C}$ values of COM₁ decreased monotonically but nonlinearly with increasing sigma-*t* (Fig. 6B). The complex relationship between $\Delta^{14}\text{C}$ and salinity (or sigma-*t*) indicates that water mixing is not the only factor affecting the distribution of $\Delta^{14}\text{C}$ of COM₁ in the MAB. Superimposed on water mixing is a combination of different source functions (e.g. terrestrial colloids, pelagic colloids originating from biogenic particles in the upper water column, and benthic colloids arising from degraded or fractionated organic matter and sedimentary organic matter in the BNL). The strength of the different source functions is likely the dominating factor affecting the $\Delta^{14}\text{C}$ values of COM₁ in seawater of the MAB (see discussion for $\delta^{13}\text{C}$ and C:N ratios).

The $\Delta^{14}\text{C}$ values of COM generally decreased from nearshore to offshore stations (Fig. 7). Beyond a water depth of >800 m, both surface-water and bottom-water COM₁ $\Delta^{14}\text{C}$ values show a slight increase toward the open

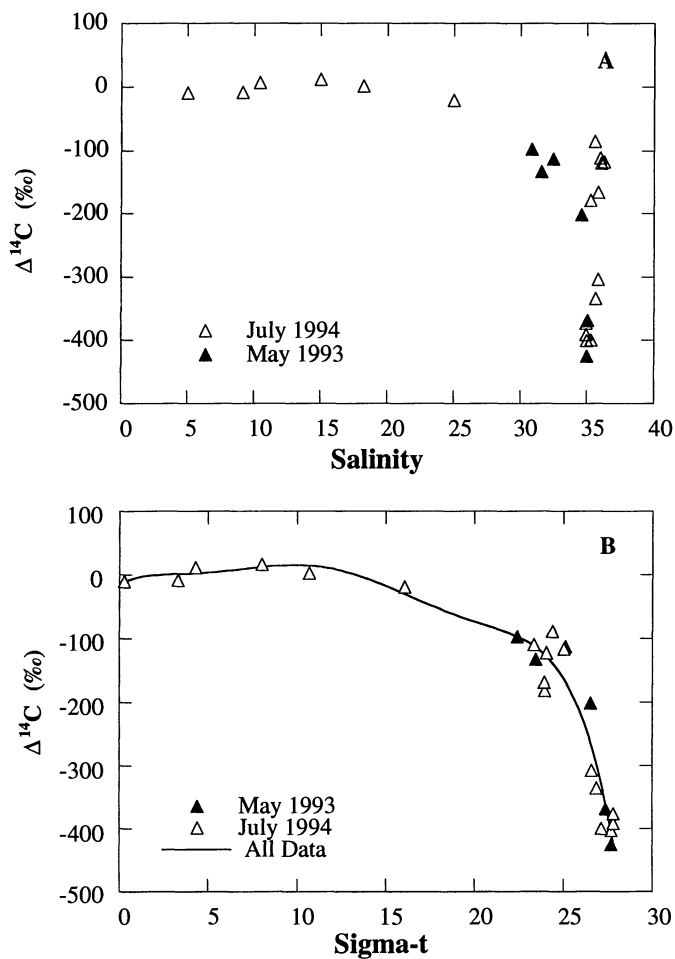


Fig. 6. $\Delta^{14}\text{C}$ values of COM_1 vs. salinity and sigma- t . Data include those of May 1993 (Santschi et al. 1995) and July 1994.

Atlantic (Fig. 7). This trend likely reflects the coupling between terrestrial inputs, in situ production, and sedimentary organic matter inputs in the MAB. High $\Delta^{14}\text{C}$ values in estuarine waters are consistent with their terrestrial origin. For example, $\Delta^{14}\text{C}$ values of DOC in surface freshwaters were previously reported to be close to contemporary atmospheric values (Schiff et al. 1990). In addition, Trumbore (1993) concluded that a large fraction of soil organic matter from temperate regions has a residence time of <50 yr, resulting in a contemporary radiocarbon age due to bomb radiocarbon contamination since the 1950s. The decrease of $\Delta^{14}\text{C}$ values of COM_1 from the coastal station to station 1 perhaps reflects the increase of marine origin coupled with a source effect from sedimentary organic matter by lateral transport in this dynamic ocean margin. In open-ocean stations with water depths >800 m, $\Delta^{14}\text{C}$ values of COM_1 showed a slight increase in surface waters from station 12 to 13 (Fig. 7). It is likely that higher values of $\Delta^{14}\text{C}$ in COM_1 at stations 12 and 13 were due to a greater influence of pelagic colloids from open-ocean waters at these stations and to a lesser influence of alongshore currents carrying particles from shelf nepheloid layers into shelf and slope waters.

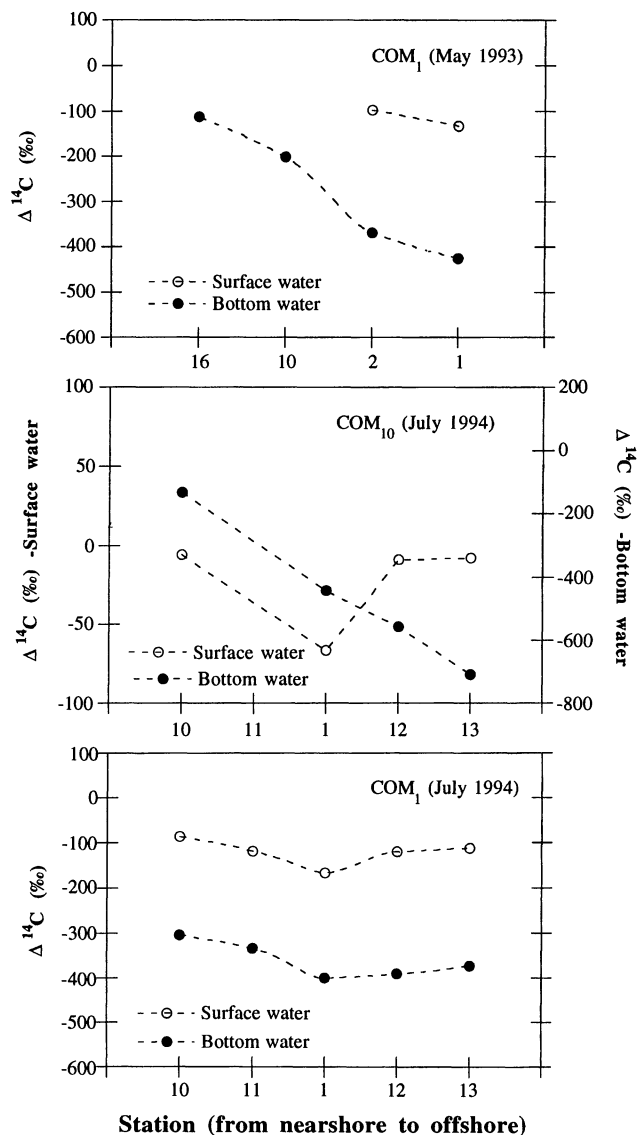


Fig. 7. Plot of $\Delta^{14}\text{C}$ of COM_1 and COM_{10} vs. station numbers in the nearshore to offshore direction.

Radiocarbon in the COM_{10} fraction—Contemporary $\Delta^{14}\text{C}$ values of HMW COM_{10} have been previously reported for waters in the Gulf of Mexico (Santschi et al. 1995). For deep-water COM_{10} in the Gulf of Mexico, the only $\Delta^{14}\text{C}$ value measured was -85‰ , considerably higher than that of COM_1 from the same station (Santschi et al. 1995).

In seawater of the MAB, a substantial fraction of surface-water COC_{10} from both 1993 and 1994 cruises contained contemporary carbon. $\Delta^{14}\text{C}$ values of surface-water COM_{10} were -6 to -9‰ during 1994 (Table 2) and -50 to -66‰ during 1993 (Santschi et al. 1995), considerably younger than those of COM_1 from the same station, a feature similar to the observations in the Gulf of Mexico (Santschi et al. 1995). The only COM_{10} sample from the MAB that had a similar $\Delta^{14}\text{C}$ value as that of COM_1 is from surface water at station 1 (-160‰). This

relatively low $\Delta^{14}\text{C}$ value at station 1 may be related to the complex mixing patterns of water and carbon sources at station 1, which likely contained waters that have been in recent contact with a BNL (see discussion below).

In contrast to surface waters, $\Delta^{14}\text{C}$ values of deep-water COM_{10} in the MAB were consistently low and even much lower than those of COM_1 at the same station (Table 2). Values of $\Delta^{14}\text{C}$ lower than those of COM_1 were also observed for most of COM_{10} from estuarine waters of Chesapeake Bay (Table 2), where turbulent mixing can transport resuspended sedimentary organic matter to the water column. If COM_{10} is largely derived from the surface-water primary production (i.e. pelagic colloids) with a turnover time of ~ 1 month or shorter (Baskaran et al. 1992; Moran and Buesseler 1992; Santschi et al. 1995), deep-water COM_{10} would be expected to have a $\Delta^{14}\text{C}$ value similar to that in surface-water COM_{10} , or higher than that of COM_1 , as was the case in the Gulf of Mexico (Santschi et al. 1995). Instead, extremely old apparent ^{14}C ages of deep-water COM_{10} have been observed in the MAB.

The higher $\Delta^{14}\text{C}$ values of surface-water COM_{10} imply a particulate origin of HMW COM_{10} in the upper water column in the MAB, consistent with the contemporary $\Delta^{14}\text{C}$ values (6–7‰) of particulate organic matter (POM) collected by sediment traps at station 1 in the MAB during the same cruise (Walsh and Santschi unpubl. results). Unlike the plankton origin in the upper water column, low $\Delta^{14}\text{C}$ values of deep-water COM_{10} are a consequence of a different source function for the HMW COM_{10} . Sediment resuspension, which can produce HMW COM in the BNL, is likely the major process responsible for these benthic colloids in this highly dynamic ocean margin area.

Extensive alteration of organic matter on the sea floor changes the chemical composition of the sedimentary organic matter (e.g. Wakeham and Lee 1989). As a result, more labile organic components are oxidized preferentially, leaving more “refractory” components for resuspension from the sediments. For example, POM collected by sediment traps in the MAB contained significant levels of bomb radiocarbon, whereas apparent ^{14}C ages of POM in surface sediments were > 1500 B.P. (Anderson et al. 1994). Using a $\Delta^{14}\text{C}$ and sediment organic C budget in the MAB, Anderson et al. (1994) suggested that up to half of the sedimentary organic C deposited on the slope is refractory. Significant terrestrial particle inputs from sediment resuspension into the whole-water column overlying the slope in the Cape Hatteras area were implied from vertical profiles of particulate ^{232}Th and ^{230}Th (Guo et al. 1995a) and SPM concentrations (Fig. 2). Moreover, processes in the BNL could be important in the production of DOM in seawater in ocean margin areas. For example, benthic fluxes of DOM from sediment pore waters and the disaggregation of sedimentary organic matter during resuspension events could serve as important sources of DOM in the overlying water column (Burdige et al. 1992; Martin and McCorkle 1993). Thus, although contemporary HMW COM_{10} is primarily of recent biogenic origin in the upper water column, old HMW COM_{10} in bottom waters is largely of sedimentary origin. This

finding is further supported by measurements of $\delta^{13}\text{C}$ and organic C:N in the same COM samples.

A three-component $\Delta^{14}\text{C}$ model—It has been proposed that the apparent ^{14}C ages of DOM are the result of mixing of different organic C components with different ^{14}C ages (Mantoura and Woodward 1983; Williams and Druffel 1987). Although average ^{14}C ages are not linearly related to those in different fractions, $\Delta^{14}\text{C}$ values of different fractions add up linearly because $\delta^{13}\text{C}$ values used to convert $\delta^{14}\text{C}$ to $\Delta^{14}\text{C}$ values change little between DOM fractions. From measurements of $\Delta^{14}\text{C}$ in the bulk DOM pool and different molecular weight fractions, a multicomponent $\Delta^{14}\text{C}$ model for the DOM pool can be established for seawater off Cape Hatteras in the MAB, where $\Delta^{14}\text{C}$ values for DOM are available. Average $\Delta^{14}\text{C}$ values of the bulk DOM in seawater from the MAB were -200‰ for surface water and -430‰ for deep water (Bauer et al. unpubl. results). If we take these $\Delta^{14}\text{C}$ data as representative for the Cape Hatteras area, we can construct a mass balance using three DOM components (COM_{10} , COM_{1-10} , and ultrafiltrate organic matter, UOM) with different percentages, F_{cd} , (F_{10} , F_{1-10} , and F_{UOC}) in the DOM pool and their corresponding $\Delta^{14}\text{C}$ values (Δ_{10} , Δ_{1-10} , Δ_{UOC}):

$$\Delta_{\text{DOC}} = \Delta_{10} \times F_{10} + \Delta_{1-10} \times F_{1-10} + \Delta_{\text{UOC}} \times F_{\text{UOC}}.$$

Δ and F are the $\Delta^{14}\text{C}$ values and percentages of different organic matter fractions, respectively; COM_{10} , COM_{1-10} , and UOM are the organic matter fractions between 10 kDa and $0.2 \mu\text{m}$, 1 and 10 kDa, and < 1 kDa, respectively; $\Delta^{14}\text{C}$ values of COM_{10} and COM_1 are measured (Table 2). Thus, the $\Delta^{14}\text{C}$ values of COM_{1-10} and UOM fractions can be calculated from those of DOM, COM_1 , and COM_{10} . The results from these calculations are shown in Table 3 and Fig. 8.

$\Delta^{14}\text{C}$ values of COM_1 or COM_{1-10} fractions were consistently higher than those in the UOM fraction regardless of station and water depth (Table 3). The large fraction of LMW (< 1 kDa) UOM ($> 60\%$ of the DOM) had lower $\Delta^{14}\text{C}$ values (or older organic C), and the small HMW COM fractions contained higher $\Delta^{14}\text{C}$ values. This is evidence that the bulk DOM is composed of components with variable $\Delta^{14}\text{C}$ values. Thus, DOM is heterogeneous in terms of molecular sizes and turnover times. When we compare $\Delta^{14}\text{C}$ values of selective POM samples collected by sediment traps with those of surface water DOM fractions (COM_{10} , COM_{1-10} , UOM) in the MAB (Table 3), we find that the $\Delta^{14}\text{C}$ values decrease from POM to COM_{10} to COM_{1-10} and then to UOM (Fig. 8). The decrease of $\Delta^{14}\text{C}$ values from POM to the COM and the LMW UOM fraction indicates that the direction of the main flow of organic C is likely from POM to HMW COM and then to LMW DOM in the upper water column. However, this conclusion does not preclude the possibility of flow in the reverse direction of minor and trace components of COM (e.g. through coagulation). All COM fractions generally contained higher $\Delta^{14}\text{C}$ values than the UOM fraction except COM_{10} from bottom waters (Table 3). As pointed out above, resuspension and disaggregation of sedimen-

Table 3. Results of a three-component $\Delta^{14}\text{C}$ (‰) model for oceanic DOM in the MAB. COM_1 , COM_{10} , and COM_{1-10} are the colloidal organic matter (COM) fractions between 1 kDa and 0.2 μm , 10 kDa and 0.2 μm , and 1 and 10 kDa. UOM is the ultrafiltrate organic matter (i.e. <1 kDa) fraction.

Sta.	Depth (m)	COM_{10}		COM_{1-10}		UOM	
		$\Delta^{14}\text{C}$	$F_{c/d}$ *	$\Delta^{14}\text{C}$	$F_{c/d}$	$\Delta^{14}\text{C}$	$F_{c/d}$
10	2	-6 ± 6	11	-128 ± 8	23	-257 ± 8	66
	25	-132 ± 5	4	-334 ± 7	27	-487 ± 7	69
01	2	-160 ± 5	5	-175 ± 7	30	-217 ± 7	65
	750	-427 ± 5	4	-399 ± 6	26	-442 ± 6	70
12	2	-9 ± 6	5	-143 ± 9	29	-240 ± 9	66
	2,300	-558 ± 5	3	-359 ± 6	26	-451 ± 6	71
13	2	-8 ± 5	6	-132 ± 8	28	-246 ± 9	66
	250	-611 ± 3	5	-355 ± 5	24	-443 ± 6	71
	2,600	-709 ± 5	3	-336 ± 7	25	-452 ± 8	72

* $F_{c/d}$ (%) is the percentage of each organic C fraction in the total DOC pool. $F_{c/d}$ and $\Delta^{14}\text{C}$ values of COM_{10} and COM_1 are measured. The $\Delta^{14}\text{C}$ values of COM_{1-10} and UOM fractions can be calculated from those of DOM, COM_1 , and COM_{10} . The $\Delta^{14}\text{C}$ values in unfractionated DOC are taken from Bauer et al. (unpubl. results) for seawater in the MAB (i.e. -200‰ for surface water and -430‰ for deep waters).

tary organic matter or physical and chemical fractionation of COM in the BNL could significantly change this pattern.

The turnover times of COM_{10} and COM_1 derived from ^{234}Th were consistently short and on the order of months (Guo 1995) despite old ^{14}C ages of COM_{10} in the MAB. It seems that the reactivities of DOM in seawater are largely dependent on the predominant phases defined by molecular weight (e.g. Amon and Benner 1994). Short ^{234}Th turnover times and old ^{14}C ages are not incompatible if the source of COM_{10} is resuspended sedimentary organic matter. For example, recent studies show that old (in terms of ^{14}C age) organic matter does not necessarily have to be refractory due to the sorptive preservation of labile organic matter (e.g. Keil et al. 1994) and thus can turn over quickly once it is released from a particulate

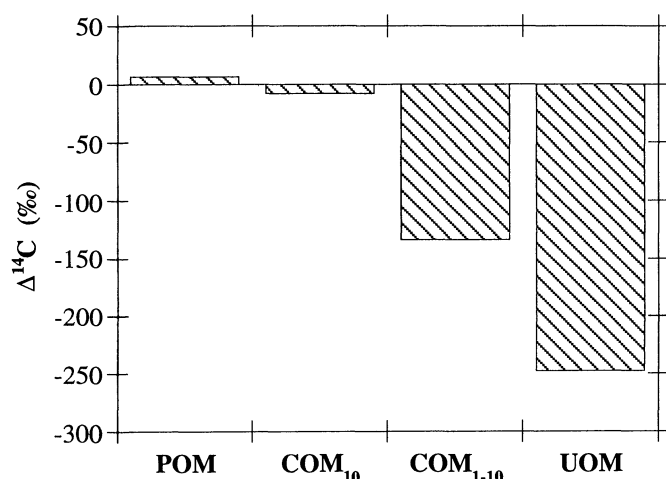


Fig. 8. $\Delta^{14}\text{C}$ values in POM and different DOM fractions (COM_{10} , COM_{1-10} , and UOM) from surface waters in the MAB. $\Delta^{14}\text{C}$ values of selective POM samples collected by sediment traps were provided by Walsh and Santschi (unpubl. results).

surface. The ^{234}Th concentration is a measure of the lifetime of COM in the water column, while the $\Delta^{14}\text{C}$ value is not only an indicator of mean age but also a measure of the source of COM. However, the time scale of ^{14}C half-life ($\sim 5,600$ yr) does not allow for a resolution of less than decadal time scales. A multiple tracers approach can, therefore give rise to a better understanding of the cycling of DOM in the ocean despite the limitations of the individual tracers.

Relationship between $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ —The correlation between $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ in COM_1 using all data is weak (Fig. 9). However, when only surface-water data are plotted, a significant linear relationship between $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ values was found for surface water colloids (Fig. 9). The negative relationship between $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ in COM_1 indicates the mixing of terrestrial organic colloids that have low $\delta^{13}\text{C}$ and higher $\Delta^{14}\text{C}$ values with colloids from marine origin that have higher $\delta^{13}\text{C}$ and lower $\Delta^{14}\text{C}$ values. Thus, terrestrial sources are still important for surface-water COM_1 . Our conclusion here is consistent with the recent observations in the Gulf of Mexico (Santschi et al. 1995) and open-ocean water (Meyers-Schulte and Hedges 1986). Bottom-water colloids, on the other hand, had consistently low $\Delta^{14}\text{C}$ values but with a wider range of $\delta^{13}\text{C}$ (see data points below the regression line in the upper graph of Fig. 9) depending on their production and chemical fractionation pathways.

Relationship between $\Delta^{14}\text{C}$ and C:N ratio—There is no linear relationship between $\Delta^{14}\text{C}$ values and C:N ratios in COM_1 in the MAB when all data point are plotted (Fig. 10A). However, three distinctive end-member types can be recognized from Fig. 10, namely estuarine and coastal colloids with higher C:N ratios and $\Delta^{14}\text{C}$ values, offshore surface-water colloids with lower C:N ratios and intermediate $\Delta^{14}\text{C}$ values, and offshore deep-water colloids with intermediate C:N ratios and lower $\Delta^{14}\text{C}$ values,

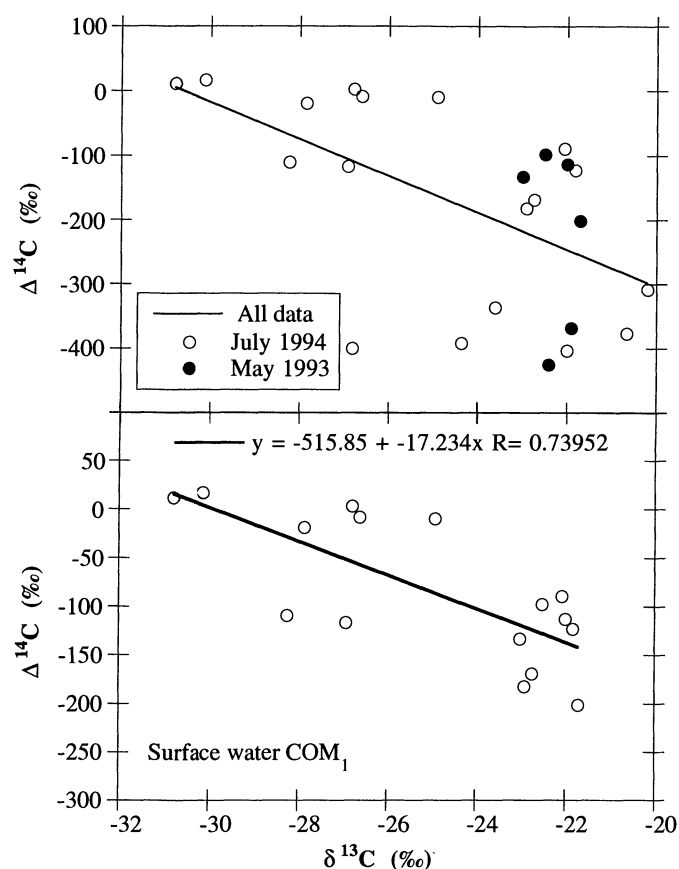


Fig. 9. Relationship between $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ in COM_1 in seawater off Cape Hatteras in the MAB.

although there are a few scattered points outside these data clusters (Fig. 10A).

Higher C:N ratios and $\Delta^{14}\text{C}$ values of the COM_1 from estuarine and coastal areas indicate that colloidal materials there contain younger and more terrestrial organic C, while lower C:N ratios and intermediate $\Delta^{14}\text{C}$ values in the COM_1 from offshore surface water suggest a marine origin for colloids. Furthermore, offshore deep-water colloids have low $\Delta^{14}\text{C}$ values and slightly higher C:N ratios, likely resulting from chemical and isotopic fractionation of organic matter during degradation and the mixing of sources in the BNL (both marine and terrestrial materials at various stages of degradation from lateral mixing processes). The mixing between three colloidal end members in the MAB is further corroborated by the results from the Gulf of Mexico (Fig. 10B), where the pattern is more regular (i.e. linear between end members, Guo 1995). Figure 10B shows a more even mixing picture between estuarine colloids and marine colloids and between surface-water colloids and deep-water colloids in the Gulf of Mexico. These detailed carbon signatures and C:N ratios put significant constraints on the cycling and source functions of fractions of DOM in oceanic environments.

In contrast to the existing picture of the cycling of DOM in the ocean, recent evidence has shown that colloidal or HMW organic C is turning over in the ocean much faster than the bulk DOM. This evidence comes from ^{234}Th (e.g. Moran and Buesseler 1992; Huh and Prahl 1995;

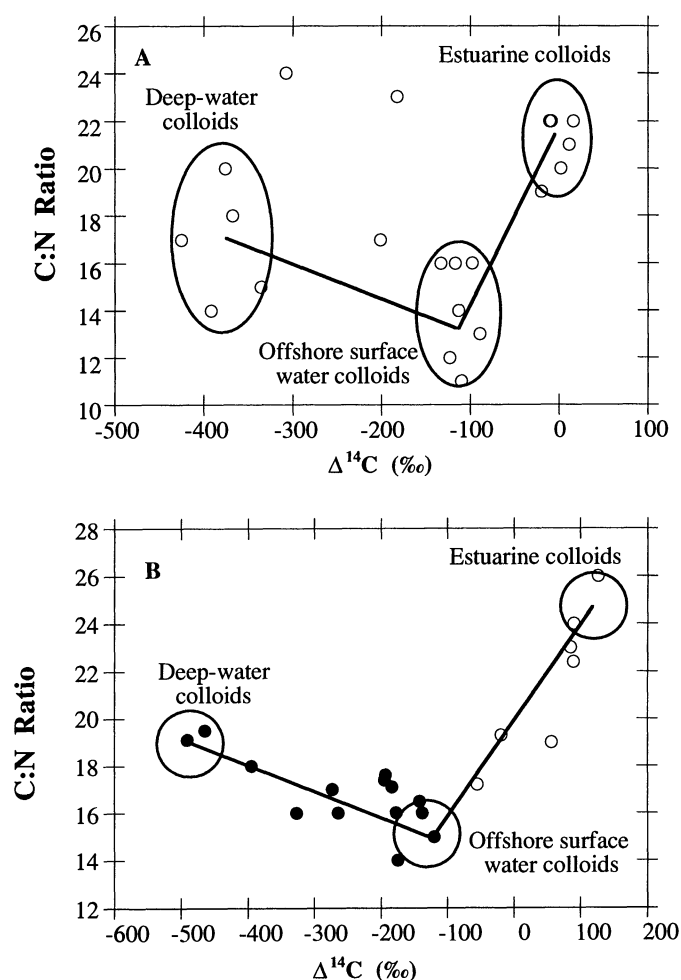


Fig. 10. Relationship between $\Delta^{14}\text{C}$ values and organic C:N atomic ratios of COM in the MAB (A). For comparison purposes, a better example from the Gulf of Mexico (B) showing the three colloid end members is also shown (data from Guo 1995). Three types of COM with distinctly different $\Delta^{14}\text{C}$ values and organic C:N ratios can be distinguished: estuarine and coastal colloids, offshore surface-water colloids, and offshore deep-water colloids.

Santschi et al. 1995), from microbial degradation experiments (e.g. Kirchman et al. 1991; Amon and Benner 1994), and from other biochemical studies (e.g. Benner et al. 1992; Pakulski and Benner 1994). DOM seems to be heterogeneous in terms of molecular sizes and reactivities in the ocean. The cycling of DOM in the ocean is more complex than previously thought and presents further challenges for oceanographers.

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