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### Permalink

<https://escholarship.org/uc/item/1h38r3cd>

### Journal

Geochimica et Cosmochimica Acta, 59(3)

### ISSN

0016-7037

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### Publication Date

1995-02-01

### DOI

10.1016/0016-7037(94)00378-y

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Peer reviewed



0016-7037(94)00378-5

## LETTER

**Isotopic evidence for the contemporary origin of high-molecular weight organic matter in oceanic environments**PETER H. SANTSCHI,<sup>1</sup> LAODONG GUO,<sup>1</sup> M. BASKARAN,<sup>1</sup> SUSAN TRUMBORE,<sup>2</sup> JOHN SOUTHON,<sup>3</sup>  
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(Received August 15, 1994; accepted in revised form December 1, 1994)

**Abstract**—Previous work has suggested that apparent old <sup>14</sup>C ages for oceanic DOC are the result of mixing of different organic carbon fractions. This report provides direct evidence for a contemporary <sup>14</sup>C age of a high-molecular-weight (HMW) fraction of colloidal organic carbon ( $\geq 10$  kD). Colloidal organic matter, COM<sub>10</sub> (from 10 kDaltons (kD) to 0.2  $\mu$ m), isolated from the upper water column of the Gulf of Mexico and the Middle Atlantic Bight (MAB) region, generally has a contemporary age (i.e., younger than a few decades), while COM<sub>1</sub> (from 1 kD to 0.2  $\mu$ m), is apparently old: 380–4500 y BP. Thus, HMW COM<sub>10</sub> (3–5% of DOC) from the upper water column is derived from living particulate organic matter (POM) and cycles rapidly, while a significant fraction of low-molecular-weight ( $\leq 1$  kD) DOM is likely more refractory, and cycles on much longer time scales. The presence of pigment biomarker compounds in COM<sub>1</sub> from the upper water column points to selected phytoplankton species as one of the sources of COM. Terrestrial carbon as another source of COM is suggested from the inverse correlation between  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values, as well as the increasing  $\delta^{13}\text{C}$  values with increasing salinity. <sup>234</sup>Th-derived turnover times of COM<sub>10</sub> and COM<sub>1</sub> from both the Gulf of Mexico and MAB are consistently short, 1–20 and 3–30 days, respectively. These short residence times support the hypothesis that <sup>14</sup>C ages of colloidal fractions of DOC are the result of COM fractions being a mixture of several endmembers with fast and slow turnover rates.

## INTRODUCTION

Our knowledge of marine carbon cycling is still in its infancy, despite decades of intensive research. As a consequence of advances in DOC analytical chemistry, earlier estimates of the relative size of the DOC reservoir have been confirmed (e.g., Williams and Druffel, 1987; Benner et al., 1992; Sharp, 1993; Guo et al., 1994). In recent years, one of the major challenges in oceanography has been to better understand the role and reactions of components of dissolved organic matter (DOM) (e.g., Farrington, 1992), as well as macromolecular colloidal organic matter (COM) (e.g., Benner et al., 1992; Guo et al., 1994).

One of the most vexing aspects of DOM concerns its low <sup>14</sup>C content and fast turnover times within some of its fractions. Apparent <sup>14</sup>C ages for DOC have been reported to be 1–6  $\times 10^3$  years (Williams and Druffel, 1987; Druffel and Williams, 1990, 1992). In contrast, observations of large horizontal and vertical gradients in DOC (e.g., Guo et al., 1994), rapid microbial carbon uptake and release rates (e.g., Kirchman et al., 1991; Smith et al., 1992; Amon and Benner, 1994) and short COM coagulation times, as determined from <sup>234</sup>Th (Baskaran et al., 1992; Moran and Buesseler, 1992), indicate that major fractions of DOM have turnover times of weeks to months. Measurements of the natural

radiocarbon (Druffel and Williams, 1992, and references therein) suggest that at least a portion of DOM is recycled within the ocean on a  $>10^3$  year time scale, with recycling as a consequence of the removal of old DOM fractions by contemporary particulate organic matter (POM) (Druffel and Williams, 1990). A recent report on the bioreactivity of near-shore COM fractions of the Gulf of Mexico, carried out in batch experiments (Amon and Benner, 1994), revealed that about 50% of COM<sub>1</sub> in near-shore surface waters cycles on short time scales of days to weeks. We provide here constraints on turnover times along transects from near-shore to off-shore stations in the Gulf of Mexico and off Cape Hatteras in the Middle Atlantic Bight (MAB). Furthermore, we show that COM<sub>10</sub> from the upper water column generally contains contemporary  $\Delta^{14}\text{C}$  values, while COM<sub>1</sub> contains less radiocarbon, in amounts similar to that of whole DOM in the ocean (Williams and Druffel, 1987). On the other hand, <sup>14</sup>C values of COM from the more dynamic Cape Hatteras area appear to be older, likely due to the presence of DOM released during resuspension of sediments containing older organic carbon.

## MATERIALS AND METHODS

The term ‘‘colloid’’ is defined by size (i.e., 1 nm to 1  $\mu$ m, Buffle, 1990) that includes macromolecules and microparticles. Ultrafiltra-

tion techniques are used to isolate colloids, and these are calibrated using macromolecules of known molecular weight (and size). However, natural colloidal material includes macromolecules of widely different structures and properties. As a consequence, the molecular weight cut-offs of ultrafilters do not precisely correspond to that particular molecular weight or size.

Samples were collected from the Gulf of Mexico in June 1992 (92G7) and January 1993 (93G1) (Cruise Reports 92G7, 93G1), from Galveston Bay in February 1993 and June 1993, from the Cape Hatteras region of the Middle Atlantic Bight (Cruise Report 93G7). An important difference between the two regions is the occurrence of considerably stronger and better developed nepheloid layers in the MAB, which often reach laterally into open waters, and thus, often occur at intermediate depths.

Two fractions of COM (i.e., COM<sub>1</sub> (1 kD–0.2 μm) and COM<sub>10</sub> (10 kD–0.2 μm)) were isolated and characterized using cross-flow ultrafiltration techniques (Guo et al., 1994). COM<sub>10</sub> is thus contained in COM<sub>1</sub>. Data resulting from the analyses of hydrographic parameters, <sup>14</sup>C, <sup>13</sup>C, DOC, COC<sub>1</sub>, COC<sub>10</sub> and <sup>234</sup>Th are shown in Table 1. <sup>234</sup>Th extraction from large volumes of water (1000–4000 L) onto MnO<sub>2</sub> impregnated fibers and radiochemical assay are described in Baskaran et al. (1992, 1993). Propagated errors (1σ) for the colloidal and total dissolved fractions of <sup>234</sup>Th, <sup>234</sup>Th<sub>c</sub> and <sup>234</sup>Th<sub>d</sub>, as well as for the values of the scavenging rate constant, λ<sub>s</sub>, are generally <10%. The complete <sup>234</sup>Th data set will be published elsewhere (Baskaran et al., 1994; Santschi et al., 1995). Δ<sup>14</sup>C, which was measured by Accelerator Mass Spectrometry (Trumbore, 1994), and δ<sup>13</sup>C analysis (Cifuentes et al., 1988) were made on COM or POM subsets (i.e., 10–30 mg of freeze dried material) of the collected water samples. One sigma errors in Δ<sup>14</sup>C are given explicitly in Table 1. The precision and accuracy of δ<sup>13</sup>C analysis is ±0.1‰, as determined by replicate analysis of standards and samples.

Potentiometric titrations to determine total proton and functional group concentration and pK values were conducted under a nitrogen atmosphere in CO<sub>2</sub>-depleted Nanopure water using custom-designed computer-controlled potentiometric titrator (Redden Rocket; George Redden Enterprises, Menlo Park, CA). Solutions containing the desired amount of COM<sub>1</sub> (~150 mg/L) were titrated with CO<sub>2</sub>-free, standardized NaOH or HCl in a double-walled, closed 50 mL Celstir titration flask, at 25°C. Ionic strength was adjusted with NaClO<sub>4</sub>. Suspension pH was monitored with an Orion pH meter/Ross combination electrode and data were stored on disk.

## Blanks, Recovery, and Calibration experiments

### Ultrafiltration

Surface seawater, or deep water collected from 30 L Niskins, was directly pumped (on line) through an acid rinsed 0.2 μm Nuclepore cartridge and subsequently through a Amicon DC-30 or DC-10 ultrafiltration system with 1 kD spiral-wound cartridges (Amicon, S10N1) or 10 kD hollow fiber cartridges (Amicon, H10P10). COM<sub>1</sub> was extracted from up to 1000 L of seawater using a DC-30 system within 10–12 h and then concentrated to ~2 L using a DC-10 system. COM<sub>10</sub> was separated from ~200 L of seawater within 6–8 h. Colloids were then diafiltered with 20 L Nano-pure water (DOC concentration ≤ 2 μM), frozen on board ship, and subsequently freeze dried. DOC mass balances in ultrafiltration experiments gave satisfactory recoveries (i.e., 100 ± 5%) (Guo et al., 1994). Ultrafiltration system and cartridges were precleaned using cleaning solutions (e.g., NaOH, HCl, EDTA, etc.) and large volumes of Nano-pure water between cleaning solutions, as recommended by the manufacturer. All containers and reservoirs were usually closed to the air, and class 100 clean room vinyl gloves (OAK Technical Inc.) were used during sampling. Total DOC from 20 L Nano-pure water (≤ 2 μM) and cartridges bleeding during diafiltration was about 40–60 μmol C. This was carried out as a worst case using high pressure (~60 psi). However, total COM<sub>1</sub> isolated for diafiltration was ~18,000–40,000 μmol C from 1,000 L seawater with an initial DOC concentrations of 45 μM–100 μM. Total recovered COM<sub>10</sub> was 450–1,000 μmol C from 200 L seawater. Thus, DOC contamination during diafiltration is negligible for both COM<sub>1</sub> and COM<sub>10</sub> fractions.

### DOC analysis

DOC measurements were carried out on a Shimadzu TOC-5000 Analyzer using a high temperature combustion (HTC) method (Guo et al., 1994). DOC concentration in Nano-pure water was ≤ 2 μM. The total blank, including the instrumental blank and water blank was always < 5 μM C. Analytical precision (±1 sigma) of DOC determination is 2%, and accuracy is about the same.

### Δ<sup>14</sup>C blank determinations

Δ<sup>14</sup>C blanks were as follows: 1 kD cartridge material had -999.5‰, 10 kD cartridge material had -356.6‰, NaOH extract of fossil wood, passed through 1kD ultrafiltration cartridge, had -990‰. An extensive rinsing of the ultrafiltration cartridges using 2 L of Nanopure water for prolonged periods of time resulted in -463.4‰ for the isolated COC<sub>1</sub>. In addition, using the same sampling techniques and equipment (CTD-Rosette and 30L Niskins) on the same boat (R/V *Gyre*), we also sampled seawater for DIC-<sup>14</sup>C measurements for W.S. Broecker, LDEO. Surface water Δ<sup>14</sup>C values were 86.1 to 100.4‰, while water at 1000 m water depth had -101.7‰, which are typical values for the North Atlantic Ocean (e.g., Broecker and Peng, 1982). Thus, <sup>14</sup>C contamination during sampling and processing was negligible.

### <sup>234</sup>Th analysis of colloids

Updated ultrafiltration procedures are described in Guo et al. (1994), including cartridge cleaning with NaOH. We believe that the higher <sup>234</sup>Th concentrations and *f<sub>c/d</sub>* values published earlier (Baskaran et al., 1992) could have been due to higher recoveries caused by COM not removed by the old cleaning procedures, and due to the use of different types of prefilters.

## RESULTS AND DISCUSSION

### <sup>14</sup>C Evidence for Differential Ages of COM

<sup>14</sup>C apparent ages of COM<sub>1</sub> and COM<sub>10</sub> from the Gulf of Mexico are plotted against distance from shore and water depth in Fig. 1a and b, respectively. Contemporary organic carbon (see note in Fig. 1 caption) is present in the HMW fraction of colloidal material (COM<sub>10</sub>), and also in COM<sub>1</sub> from near-shore environments. The presence of contemporary fractions of DOM in freshwater endmembers has been previously observed by Hedges et al. (1986) for the Amazon River. Our results indicate that Gulf of Mexico colloids have 113–57% modern <sup>14</sup>C (i.e., apparent ages of ≤ 40 to 4.5 × 10<sup>3</sup> years BP, or Δ<sup>14</sup>C of 126 to -432‰; note that 100% = pre-bomb = pre-1950, and 114% = 1992 value). While Druffel et al. (1992) suggested from a mass balance approach to Δ<sup>14</sup>C of DOC data that a fraction of the DOC pool could be composed of young material, these are the first direct <sup>14</sup>C measurements of a contemporary age of a fraction of the DOM reservoir in oceanic environments. Even though these determinations were carried out in shelf and slope waters of the Gulf of Mexico and Cape Hatteras region of MAB, DOC concentrations of 45–100 μM in these study areas (Table 1) are typical of more oligotrophic oceanic environments (e.g., Williams and Druffel, 1987; Tupas et al., 1994). The concentration of HMW colloids of contemporary origin, as well as the percent of contemporary <sup>14</sup>C in COM<sub>1</sub>, generally decreases from near-shore to off-shore, and from surface to bottomwaters (Fig. 1). In addition, COM<sub>10</sub> from surface waters, even though only a small fraction of DOM (i.e., 3–5%), is consistently contemporary down to 355 m water depth in the Gulf of Mexico. As a matter of fact, the sample from 355m had only slightly more <sup>14</sup>C than DIC at the same depth. This

Table 1. Carbon isotopes (<sup>14</sup>C, <sup>13</sup>C), <sup>234</sup>Th (*f<sub>c/d</sub>*,  $\lambda_a$ ), and organic carbon data\* (- means not determined, c = contaminated)

Station	Latitude/ Longitude	Sampling Depth (m)#	Temp. (°C)	Salinity	DOC ( $\mu$ M)	COC ( $\mu$ M)	Size (kD)	$\Delta^{14}$ C (‰)	Fraction of modern <sup>14</sup> C (%)	<sup>14</sup> C age (y BP)	$\delta^{13}$ C(‰) ( $\pm 0.05$ ‰) in COM <sub>1</sub>	<i>f<sub>c/d</sub></i> ( <sup>234</sup> Th <sub>c/d</sub> / <sup>234</sup> Th <sub>d</sub> )	$\lambda_a$ (d <sup>-1</sup> )
92G7-St.1	28°45.2'N 94°59.9'W	2	29.0	30.566	131	69	1	-46.4±6.7	95.4±0.7	382±56	-23.5	0.20	-
92G7-St.5	26°40.0'N 94°59.9'W	2	29.7	35.960	83	42	1	-188.4±7.8	81.2±0.8	1677±77	-23.0	0.11	0.018
92G7-St.5	26°40.0'N 94°59.9'W	1450 (50)	4.3	34.968	50	20	1	-431.6±11.9	56.8±1.2	4538±168	-22.5	0.18	0.0078
92G7-St.6	27°43.7'N 95°00.0'W	2	30.0	35.639	88	37	1	-125.4±6.3	87.5±0.6	1076±58	-22.1	-	0.015
GB-01	29°50.0'N 94°42.0'W	1	12	0	576	404	1	126.3±7.1	112.6±0.7	>Modern	-24.7	-	-
GB-09	29°20.0'N 94°40.0'W	1	12	23.0	214	134	1	56.5±9.4	105.7±0.9	>Modern	-23.9	-	-
93G1-St.1	28°44.8'N 94°43.7'W	2	19.0	35.032	86	36	1	-137.6±6.9	86.2±0.7	1190±64	-22.0	0.58	0.038
93G1-St.3	27°54.6'N 95°00.4'W	2	22.4	35.679	84	31	1	-174.4±6.4	82.6±0.6	1540±62	-22.4	0.48	0.038
93G1-St.3	27°54.6'N 95°00.4'W	100 (10)	20.8	36.281	71	24	1	-273.8±8.7	72.6±0.9	2570±96	-21.5	-	-
93G1-St.4	27°30.0'N 95°50.9'W	2	23.4	35.908	82	29	1	-119.5±6.1	88.1±0.6	1022±55	-21.85	-	0.038
93G1-St.4	27°30.0'N 95°50.9'W	355 (50)	9.5	35.159	47	-	1	-327.6±7.1	67.2±0.7	3189±85	-22.0	0.15	0.014
93G1-St.5	26°40.1'N 95°00.2'W	2	23.8	36.406	70	28	1	-177.0±5.9	82.3±0.6	1565±57	-21.6	0.28	0.0084
93G1-St.5	26°40.1'N 95°00.2'W	225	18.1	36.436		23	1	-264.6±6.4	73.5±0.6	2469±70	-21.05	0.21	0.0092
93G1-St.5	26°40.1'N 95°00.2'W	1600 (50)	4.3	34.975	45	14	1	-394.9±8.8	60.5±0.9	4036±116	-21.1	0.12	0.0155
93G1-St.1	28°44.8'N 94°43.7'W	2	19.0	35.032	86	4.5	10	89.7±7.5	109.0±0.8	>Modern	-	0.09	0.038
93G1-St.3	27°54.6'N 95°00.4'W	2	22.4	35.679	84	3.0	10	71.2±8.9	107.1±0.9	>Modern	-	0.06	0.038
93G1-St.4	27°30.0'N 95°50.9'W	2	23.4	35.908	82	3.1	10	47.7±8.1	104.8±0.8	>Modern	-	0.02	0.038
93G1-St.4	27°30.0'N 95°50.9'W	355 (50)	9.5	35.159	47	1.8	10	40.2±6.5	104.0±0.7	>Modern	-21.2	0.03	0.014
93G1-St.5	26°40.1'N 95°00.2'W	2	23.8	36.406	70	2.6	10	77.9±7.5	107.8±0.8	>Modern	-	0.035	0.0084
93G1-St.5	26°40.1'N 95°00.2'W	1450 (50)	4.3	34.975	45	1.3	10	-84.7±13.5	91.5±1.4	711±118	-	0.029	0.0155
93G7-St.1	36°04.8'N 74°43.9'W	5	16.6	31.029	85	41	1	-136.1±4.9	86.4±0.5	1176±45	-23.0	0.50	0.086
93G7-St.1	36°05.3'N 74°43.8'W	100 (10)	12.4	35.215	64	31	1	c	c	c	-23.2	0.43	0.029
93G7-St.1	36°04.7'N 74°43.6'W	800 (50)	4.5	34.968	47	20	1	-427.4±3.3	57.3±0.3	4480±46	-22.4	0.26	0.020
93G7-St.2	36°03.1'N 74°46.1'W	2	16.0	30.848	90	40	1	-100.8±5.9	89.9±0.6	854±53	-22.5	0.64	0.087
93G7-St.2	36°03.1'N 74°46.1'W	350 (50)	7.3	35.087	49	20	1	-370.6±4.3	62.9±0.4	3719±55	-21.9	0.27	0.034
93G7-St.10	36°03.5'N 74°49.9'W	90 (10)	0.7	34.650	71	33	1	-204.1±5.4	79.6±0.5	1834±54	-21.7	0.24	0.024
93G7-St.16	36°05.1'N 75°21.4'W	20 (5)	9.0	32.514	90	44	1	-116.1±5.8	88.4±0.6	992±53	-22.0	0.45	0.096
93G7-St.1	36°04.8'N 74°43.9'W	5	16.6	31.029	85	5	10	-66.4±5.9	93.4±0.6	552±51	-	0.09	0.086
93G7-St.24	35°24.4'N 74°54.2'W	2	23.0	34.682	102	8.2	10	-52.9±6.4	94.7±0.6	437±54	-	0.13	-

\* ) <sup>14</sup>C:  $t_{1/2}$  = 5568 yr. was used for age calculation; 100% = prebomb (1950); 114% = 1992 value; <sup>14</sup>C values were corrected for fractionation using measured  $\delta^{13}$ C values, or -22.0‰ when none were available.

<sup>234</sup>Th:  $f_{c/d}$  = percentage of colloidal <sup>234</sup>Th of the total dissolved <sup>234</sup>Th concentration.

$\lambda_a$  = scavenging rate constant.

#) numbers in brackets indicate depth (m) above bottom for deepest sample.

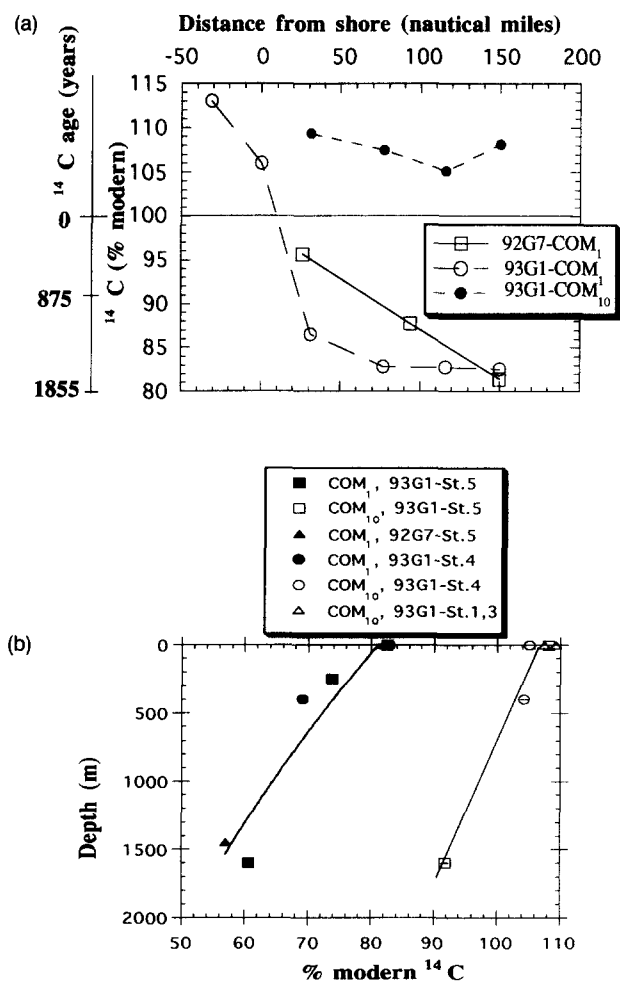


FIG. 1. (a) Variation of apparent  $^{14}\text{C}$  ages of COM<sub>1</sub> and COM<sub>10</sub> in surface water from the Gulf of Mexico, as a function of distance from shore, with the jetties in Galveston as the reference point (100% = pre-bomb value, 115% present-day value of plant matter). (b) Composite profiles of apparent  $^{14}\text{C}$  ages of COM<sub>1</sub> and COM<sub>10</sub> with depth.

observation is consistent with a very short (<5 years) residence time for COM<sub>10</sub>. However, one COM<sub>10</sub> sample from near-bottom waters at 1450 m water depth in the Gulf of Mexico, and two samples from the more dynamic Cape Hatteras region appeared to be somewhat older, likely due to the presence of significant amounts of resuspended sediments in the water. A greater terrestrial influence on particle composition at the Cape Hatteras site was also suggested from a comparison of  $^{232}\text{Th}/^{230}\text{Th}$  data between the two regions (Guo et al., 1995). For example,  $^{230}\text{Th}$  and  $^{232}\text{Th}$  concentrations in suspended matter in surface waters were higher at the Cape Hatteras site by an order of magnitude (e.g., 2 vs. 0.16  $\mu\text{g}$   $^{232}\text{Th}/\text{g}$  suspended matter, respectively). Higher concentrations of these nuclides indicates that suspended matter in these waters contains more soil (or sedimentary) material, likely leaching off some older DOM into the water during resuspension. Organic matter from the surface sediments about 75 km north of our site shows  $^{14}\text{C}$  ages of 1500–2000 years (Anderson et al., 1994).

These young ages of COM<sub>10</sub> and fast microbial degradation of parts of COM<sub>1</sub> (Amon and Benner, 1994), taken together, indicate that the apparent  $^{14}\text{C}$  ages of colloids in both MW groupings are the result of mixing of HMW COM<sub>10</sub> of contemporary origin, with older low molecular weight (LMW) colloidal and dissolved organic carbon species. The possibility and implications of a "mixed" pool of fast- and slow-cycling seawater DOC components were first proposed by Mantoura and Woodward (1983). As an example, if organic matter with 25% contemporary  $^{14}\text{C}$  (i.e., 108.5% modern  $^{14}\text{C}$ , turning over on at least yearly time scales) and 75% old  $^{14}\text{C}$  (i.e., 57% modern  $^{14}\text{C}$ , the lowest observed value in COM<sub>1</sub>, turning over only on a 5,000 year time scale) would have an apparent  $^{14}\text{C}$  age of about 3,000 years. The likelihood that such a large fraction of DOM or COM is turning over on weekly to yearly time scales has been suggested previously from quite disparate observations (e.g., Baskaran et al., 1992; Moran and Buesseler, 1992; Kirchman et al., 1991; Smith et al., 1992; Amon and Benner, 1994).

### $\delta^{13}\text{C}$ Stable Isotopic Composition of COM

Figure 2a shows that  $\delta^{13}\text{C}$  values of COM<sub>1</sub> covary with salinity and can be explained by the mixing of the following three endmembers: riverine (terrestrial), near-shore (20 m water depth), and off-shore (oceanic). Values for POM also follow the same trend lines as for COM<sub>1</sub> (Fig. 2b), but exhibit more scatter. Within Galveston Bay, the estuary of the Trinity River, and a near-shore station (St.1, 20 m water depth),  $\delta^{13}\text{C}$  values of COM<sub>1</sub> and POM vary little (i.e.,  $\sim 1\text{‰}$ ) compared to the offshore stations, where  $\delta^{13}\text{C}$  varied by about 2‰. Much of the difference is likely due to the large salinity gradient in shelf waters observed in June 1993 (Table 1). This suggests mixing of terrestrial carbon ( $\delta^{13}\text{C}$  of  $-28$  to  $-24\text{‰}$ ), which originates mostly from the Mississippi River (the largest freshwater source to the Gulf), and marine carbon ( $\delta^{13}\text{C}$  of  $-24$  to  $-19\text{‰}$ ) (Eadie and Jeffrey, 1973).

Figure 2b compares  $\delta^{13}\text{C}$ -salinity trend line for COM<sub>1</sub> with that for POM. Due to the small sample size of COM<sub>10</sub>, only one  $\delta^{13}\text{C}$  measurement was made of COM<sub>10</sub>. In this sample from St.4, 355 m water depth, (Table 1), the  $\delta^{13}\text{C}$  value was similar to that in COM<sub>1</sub> (i.e.,  $-21.2\text{‰}$  in COM<sub>10</sub>,  $-22\text{‰}$  in COM<sub>1</sub>).  $\delta^{13}\text{C}$  values of POM scatter more than those of COM<sub>1</sub>, particularly at higher salinities ( $\geq 30$ ); this scatter cannot be explained solely by changes in terrestrial-marine inputs. Lower scatter in the  $\delta^{13}\text{C}$  data of COM<sub>1</sub> compared with POM (a source of COM) might suggest different endmembers, or that COM<sub>1</sub> is a somewhat older carbon pool (i.e., years time scale) in which the short-term variability (i.e., months time scale) of POM has been smoothed out. However, more data are needed for comparison before any firm conclusion can be drawn.

The terrestrial source hypothesis is further corroborated by a significant correlation ( $P \leq 0.01$ ) of  $\delta^{13}\text{C}$  with  $\Delta^{14}\text{C}$  values in COM<sub>1</sub> (Fig. 2c), with no significant difference between the Gulf of Mexico and the Middle Atlantic region. This hypothesis is also supported by an inverse correlation between  $\Delta^{14}\text{C}$  values and C/N ratios in COM<sub>1</sub> (unpublished data, not shown).

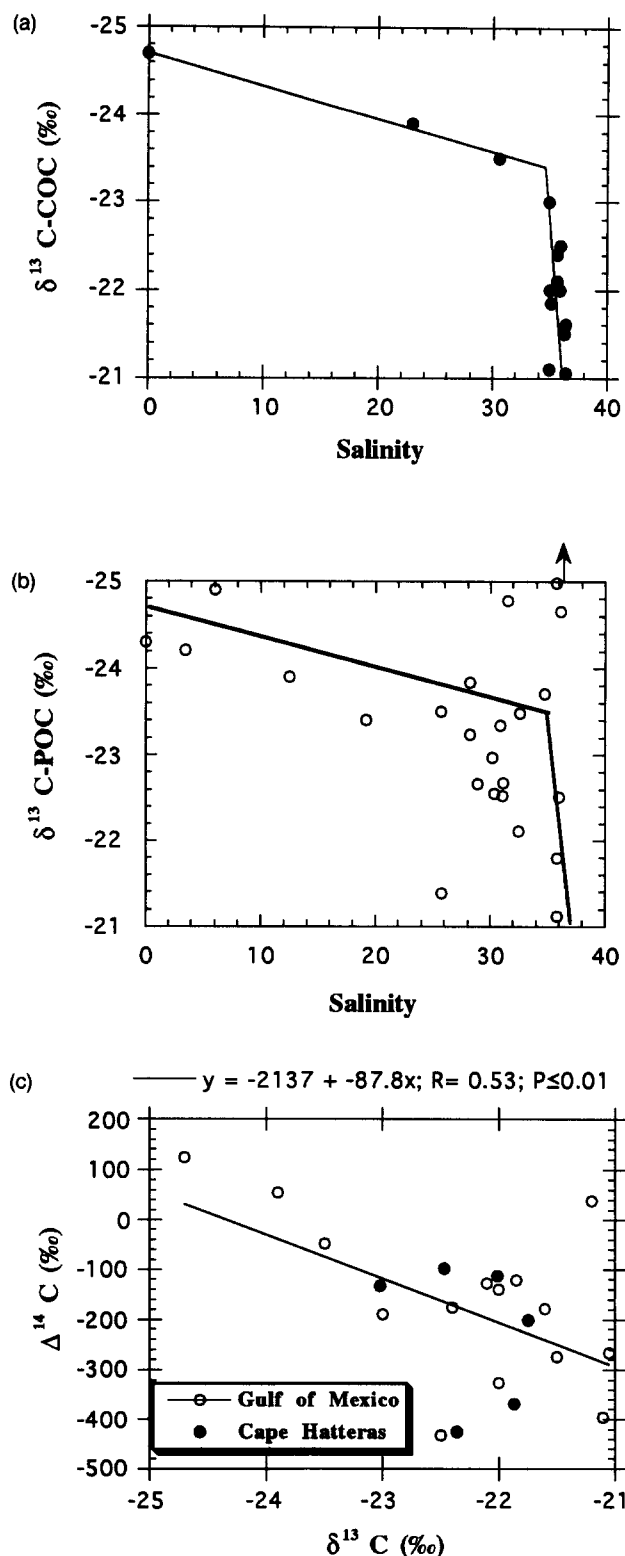


FIG. 2.  $\delta^{13}\text{C}$  in (a)  $\text{COM}_1$  and (b) POM in surface waters (collected separately in July 1990 and May 1992) from the Gulf of Mexico, as a function of salinity. The solid lines in (b) are shown for comparison purposes only. The arrow signifies additional data (not shown) originating from a third endmember, the Mississippi River. (c) The significant correlation ( $P \leq 0.01$ ) of  $\Delta^{14}\text{C}$  with  $\delta^{13}\text{C}$  values in  $\text{COM}_1$  suggests a more terrestrial source for  $\text{COM}_1$  with increasing radio-carbon content, independent of location.

### Data from Pigments Indicating Possible Sources of $\text{COM}_1$

Analyses of  $\text{COM}_1$  and POM indicate that some pigment biomarkers (e.g., Chlorophyll a, fucoxanthin, zeaxanthin) are also found in  $\text{COM}_1$ , but at low concentrations ( $\leq 1\%$ , Bianchi et al., 1994). Since pigments (chlorophylls and carotenoids) have molecular weights of less than 1 kD, and are highly photosensitive (Nelson, 1993) in the upper water column, their presence in  $\text{COM}_1$  is surprising and suggest that they are present in the form of protective micelles (Buffle, 1990). The predominance of the carotenoids fucoxanthin (a marker for diatoms) and zeaxanthin (a marker for cyanobacteria) suggests that these classes of phytoplankton represented the dominant forms of POC and may also be the most likely sources of  $\text{COM}_1$  in the northwestern Gulf of Mexico. Phaeopigment concentrations in  $\text{COM}_1$  are consistently low: concentrations of phaeophorbide are 0.02, phaeophytins 0.01, and chlorophyllides 0.02–0.05  $\mu\text{g}/\text{mg}$  COC. Pigment degradation during ultrafiltration, as described in Bianchi et al. (1994), makes these concentrations lower limits; however, their low concentration ratios to chlorophyll a, fucoxanthin and zeaxanthin concentrations would have changed little. Their relative absence in  $\text{COM}_1$  thus suggests that the majority of pigments found in  $\text{COM}_1$  is likely derived from direct exudation products and/or from sloppy feeding by zooplankton (Bianchi et al., 1994).

### $^{234}\text{Th}$ -Derived Colloid Residence Times (Turnover Rates) and Surface Properties of Colloidal Matter

It was shown by Honeyman and Santschi (1989) that Th(IV) can be used as a ‘‘coagulumeter’’, i.e., for the *in-situ* measurement of rates of colloid-particle interaction. When colloidal material is transferred through the submicron particle size spectrum via various coagulation mechanisms, Th(IV) complexed with functional groups in COM (B. D. Honeyman, unpubl. data) is also transferred through the colloid pools. The net effect of coagulation and particle regeneration processes is the transfer of thorium from the dissolved phase to large, settling particles (‘‘colloidal pumping,’’ Honeyman and Santschi, 1989).

The relationship between the thorium scavenging rate constant,  $\lambda_s$ , and the coagulation/sedimentation rate constant  $\lambda_c$  can be simplified as

$$\lambda_s = f_{c/d} \lambda_c, \quad (1)$$

where

$$f_{c/d} = \frac{[^{234}\text{Th}_c]}{[^{234}\text{Th}_d]} \quad (2)$$

and

$$\lambda_s = \lambda_{\text{Th}} \frac{[^{238}\text{U}_d]}{[^{234}\text{Th}_d]} - 1. \quad (3)$$

The coagulation/sedimentation rate constant,  $\lambda_c$ , is a function of Brownian and shear coagulation kernels and particle concentration.  $[^{238}\text{U}_d]$  and  $[^{234}\text{Th}_d]$  are dissolved  $^{238}\text{U}$  and  $^{234}\text{Th}$  activity concentrations (dpm/L).  $[^{234}\text{Th}_c]$  is the  $^{234}\text{Th}$  activity concentration in the  $\text{COM}_1$  or  $\text{COM}_{10}$  fractions, and  $\lambda_{\text{Th}}$  is the  $^{234}\text{Th}$  decay constant ( $0.029 \text{ d}^{-1}$ ).

Average colloid turnover times (i.e., residence times),  $\tau_c$ , can be obtained directly from Eqn. 1 or from a plot of  $\lambda_s$  as a function of  $f_{c/d}$ . The result of the  $^{234}\text{Th}$  data in the  $\text{COM}_1$  and  $\text{COM}_{10}$  fractions are consistent with average  $\tau_c$  values of 3–30 days and 1–20 days, respectively (Fig. 3). While there are differences between data sets and size fractions, the calculated colloid turnover times are consistently short. Since  $\text{COM}_{10}$  is a sub-fraction of  $\text{COM}_1$ , the difference in apparent turnover times of the two size fractions are a consequence of the difference in average pool sizes. True turnover times with respect to coagulation and aggregation of COM could be longer if  $^{234}\text{Th}$  is not only reacting serially (i.e., as assumed here, uptake mainly by colloids which coagulate with larger particles) but also undergoing parallel reactions (e.g., direct interaction with larger particles). If  $^{234}\text{Th}$  only traces a minor fraction of colloids, i.e., those which coagulate directly with larger particles, “true” coagulation times would be longer by the ratio of total colloids to coagulating colloids. Primary evidence for predominantly serial reactions comes from controlled laboratory experiments using thorium tracers (e.g., Nyffeler et al., 1984; Honeyman and Santschi, 1989; Niven, 1989), which show that slow uptake of Th(IV) (ascribed to coagulation) amounts to 50% or more of the total uptake of ionic Th(IV) onto suspended matter, regardless of the colloids to particle mass ratio.

The use of Th(IV) species as a colloid tracer depends on significant complexation of thorium with colloid functional groups. The fact that the  $[\text{}^{234}\text{Th}_c]/[\text{}^{234}\text{Th}_d]$  ratios ( $f_{c/d}$ ) are broadly similar to the COM/DOM ratios for different size fractions (not shown) strongly suggests that all size fractions are relatively uniformly complexed by  $^{234}\text{Th}$ . The overwhelming majority of  $\text{COM}_1$  functional groups are organic in nature, as indicated by our unpublished results of high carbon content in  $\text{COM}_1$  and <1000 ppm for the sum of all inorganic elements, as determined by ICP-MS of more than twelve samples from the Texas shelf and slope waters and Galveston Bay. Potentiometric titration of Gulf of Mexico colloidal matter (Rosow, 1994) indicates that  $\text{COM}_1$  has 1.4 meq/g of proton-reactive sites, which is intermediate between that of humic and fulvic acids (10–16 meq/g) and of polysaccharides (0.3–0.8 meq/g) (Buffle, 1990). Such data implies that  $\text{COM}_1$  is moderately hydrophilic. If approximately 14% of identifiable groups in COM are carboxylic acid groups (free and esterified) (Benner et al., 1992), then a significant fraction (ca. 20%) of the carboxylic acid groups are in the free form and, presumably, available to complex thorium. This is significant because carboxylic and dicarboxylic acids are among the strongest Th-binding organic ligands (Martel and Smith, 1992) known.

The  $^{234}\text{Th}$  data suggest that a fraction of COM is removed rapidly by coagulation/sedimentation. Biochemical evidence, however, suggests that about 50% of COM can be rapidly removed by microbial degradation (e.g., Amon and Benner, 1994). While both mechanisms can undoubtedly occur simultaneously, their relative importance is still unclear. Furthermore, rapid  $^{234}\text{Th}$ -derived turnover times do not necessarily have to coincide with contemporary radiocarbon ages, as  $^{234}\text{Th}$  could also bind to older, and likely more hydrophilic, COM. The geochemical significance of our preliminary  $^{14}\text{C}$  and  $^{234}\text{Th}$  data from individual size fractions of the dissolved

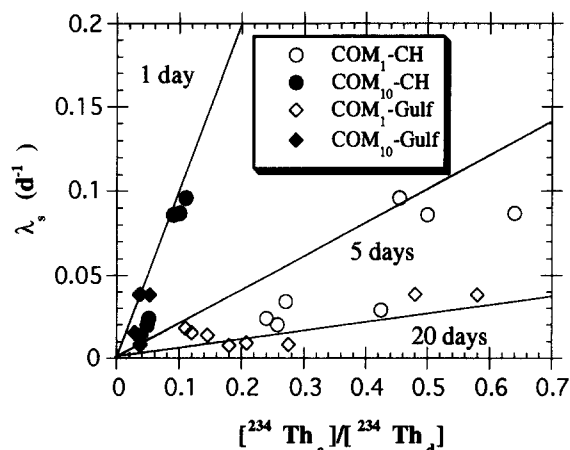


FIG. 3. Rate constants for colloids turnover,  $\lambda_c$ , can be calculated from the slope of the scavenging rate constant,  $\lambda_s$ , plotted as a function of  $f_{c/d}$ . The colloids turnover time,  $\tau_c$ , is 3–30 days for  $\text{COM}_1$ , and 1–20 days for  $\text{COM}_{10}$ . Gulf = Gulf of Mexico, CH = Cape Hatteras data.

organic carbon pool lies therefore in suggesting rapid turnover times of HMW size fractions ( $\text{COM}_{10}$ ) in the upper water column. Furthermore,  $\Delta^{14}\text{C}$  correlations with  $\delta^{13}\text{C}$  and salinity indicate a dominant terrestrial origin of major portions of  $\text{COM}_1$ , while the pigment data point to marine phytoplankton as an important contributor to the COM pool.

*Acknowledgments*—We thank the crew and officers of the R/V Gyre, Kent Warnken, Shauna Asbill, Patty Gomez, and Roberta Corvalho, Liang-Saw Wen, Matt Quigley, and Sarah Oktay for their assistance in sample collection. Diego Lopez-Veneroni kindly provided the unpublished  $^{13}\text{C}$  data of POM. This research is based in part upon work supported by the US National Science Foundation (Grant OCE-9012103), the Department of Energy (Grant DE-FG05-92ER61421), and the Texas Institute of Oceanography.

*Editorial handling:* J. D. Macdougall

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