

# Colloidal organic carbon and $^{234}\text{Th}$ in the Gulf of Maine

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## Abstract

The role of colloids in the biogeochemical cycling of organic carbon and  $^{234}\text{Th}$  was examined in the Gulf of Maine during the summer of 1996 and 1997. The colloidal fraction was separated using a 1 kiloDalton (kDa) cross-flow ultrafiltration (CFF) membrane. The mass balance of CFF was carefully checked in order to evaluate the performance of the CFF system, since this is one of the primary concerns when using CFF methods. For bulk organic carbon (OC), the membrane showed excellent recoveries (94–107%) as long as preconditioning techniques were employed. Although our mass balances for  $^{234}\text{Th}$  were higher than previous efforts (> 55% for most samples), significant losses still occurred. Furthermore, a large percentage of the “lost”  $^{234}\text{Th}$  was irrecoverable even after the CFF membranes were cleaned with weak acid and base rinses.

The colloidal organic C (COC) represented 16–25% of the organic carbon pool, and was correlated with the Chl *a* fluorescence maximum. The profile of colloidal  $^{234}\text{Th}$ , 7–36% of the total  $^{234}\text{Th}$ , followed a similar pattern. The difference between the mass balances for  $^{234}\text{Th}$  and OC suggests that  $^{234}\text{Th}$  may follow only a fraction of COC within the water column. This fraction appears to be the more reactive component of the COC pool. Given the higher and more consistent  $^{234}\text{Th}$  recoveries found using our CFF techniques, we were able to constrain the turnover rate of COC to between 3 and 30 days. Turnover rates of dissolved and particulate OC varied from 14 to 41 and 19 to 68 days, respectively. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Colloidal organic carbon;  $^{234}\text{Th}$ ; Gulf of Maine

## 1. Introduction

The biogeochemical cycling of organic carbon (OC) on continental shelves is an important part of

the global C cycle (Mantoura et al., 1991; Walsh, 1991). Although small in area, the highly productive coastal regions of the world's oceans play a disproportionate role in OC export and burial. Yet, these coastal regimes remain poorly understood. One of the major gaps in current knowledge is the role of marine organic colloids. Colloids are typically defined as that material within the 1 nm to 1  $\mu\text{m}$  size class (Kepkay, 1994). It is becoming increasingly clear that a significant fraction of high molecular

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weight dissolved organic C (DOC) is within this size range (Carlson et al., 1985; Benner et al., 1992, 1997; Amon and Benner, 1994; Dai, 1995; Guo et al., 1994, 1995; Buesseler et al., 1996; Guo and Santschi, 1997; Skoog and Benner, 1997). Colloidal material has been shown to be extensively involved in the biological cycle of OC, and colloidal organic C (COC) may represent one of the most reactive fractions of OC within the upper ocean (Wells et al., 1991; Santschi et al., 1995). Furthermore, colloids may be an important mechanism for the stabilization and/or removal of potentially biologically important trace metals, such as iron (e.g. Wells et al., 1991). Hence, it is essential that we understand the processes that govern the spatial and temporal distribution of these particles in the marine realm.

Thorium isotopes, notably  $^{234}\text{Th}$ , have proven useful in tracing the cycling of COC in marine systems (Moran and Buesseler, 1992, 1993; Niven et al., 1995; Santschi et al., 1995; Guo and Santschi, 1997; Guo et al., 1997). While  $^{234}\text{Th}$  has been widely used as a tracer of particle dynamics,  $^{234}\text{Th}$  studies of colloidal processes have been both limited and controversial (Moran and Buesseler, 1992, 1993; Niven et al., 1995; Santschi et al., 1995; Huh and Prahl, 1995; Greenamoyer and Moran, 1997; Guo and Santschi, 1997; Guo et al., 1997). Colloidal  $^{234}\text{Th}$  represents 0.04–78% of the dissolved  $^{234}\text{Th}$  found in seawater (Guo and Santschi, 1997). It should be noted, however, that many of these earlier studies used 10 kDa cross-flow ultrafiltration (CFF) membranes (Moran and Buesseler, 1992, 1993; Niven et al., 1995), rather than the 1 kDa CFF membranes currently used to separate colloids from the truly dissolved fraction. Recent CFF studies have improved our understanding of CFF (Buesseler et al., 1996; Guo and Santschi, 1996; Benner et al., 1997; Dai et al., 1998), such that we are now able to apply CFF techniques in the investigation of colloidal particle dynamics with greater confidence.

The Gulf of Maine (GoM) is a semi-enclosed coastal sea located on the Northwest Atlantic shelf. Although intensive studies have been conducted in this area during the last three decades, our current understanding of the biogeochemical cycling of C remains limited (Chen et al., 1996; Pilskaln et al., 1996; Townsend, 1996). Due to the potentially significant role that colloidal material plays in the cy-

cling of C and associated trace elements, we have sought to elucidate the size distribution of organic C and  $^{234}\text{Th}$  within this coastal regime. Our results suggest that colloidal  $^{234}\text{Th}$  is a significant fraction of dissolved  $^{234}\text{Th}$  and traces a reactive fraction of colloidal material that has a turnover time of less than 30 days. Thus, our findings have implications for models that seek to elucidate the cycling of colloidal organic material and the bioavailability of associated trace elements throughout the oceanic realm.

## 2. Methods

### 2.1. Study area

The GoM is situated along the northeastern coast of the United States and southwestern Nova Scotia. Water circulation within this area is complex. Within Wilkinson Basin, surface waters generally flow in a cyclonic pattern and are separated from the southwesterly flowing coastal current and the more nutrient rich slope waters which enter Jordan Basin, NE of Wilkinson Basin (Fig. 1). High nutrient Atlantic slope waters enter the deeper waters of the GoM through the Northeast channel (Brooks, 1991). Wilkinson Basin (Station 7) was chosen as the primary study site as it is characterized by insignificant horizontal water transport.

### 2.2. Sampling

Seawater samples were collected in the GoM on two cruises; aboard the *R/V Diane G.* in July 1996 and aboard the *R/V Cape Hatteras* in July 1997. The study area is shown in Fig. 1. The 1996 cruise covered two transects for OC measurements, while the 1997 cruise measured both OC and  $^{234}\text{Th}$  and focused on the center of Wilkinson Basin (Station 7). Samples were collected using 30 l Niskin bottles, pumped directly via Teflon tubing through acid-cleaned polycarbonate Nuclepore™ filters (142 mm diameter; 1.0  $\mu\text{m}$  pore size), and into the CFF system.

### 2.3. CFF processing

The configuration of our CFF system has been described in Dai et al. (1998). Briefly, our CFF

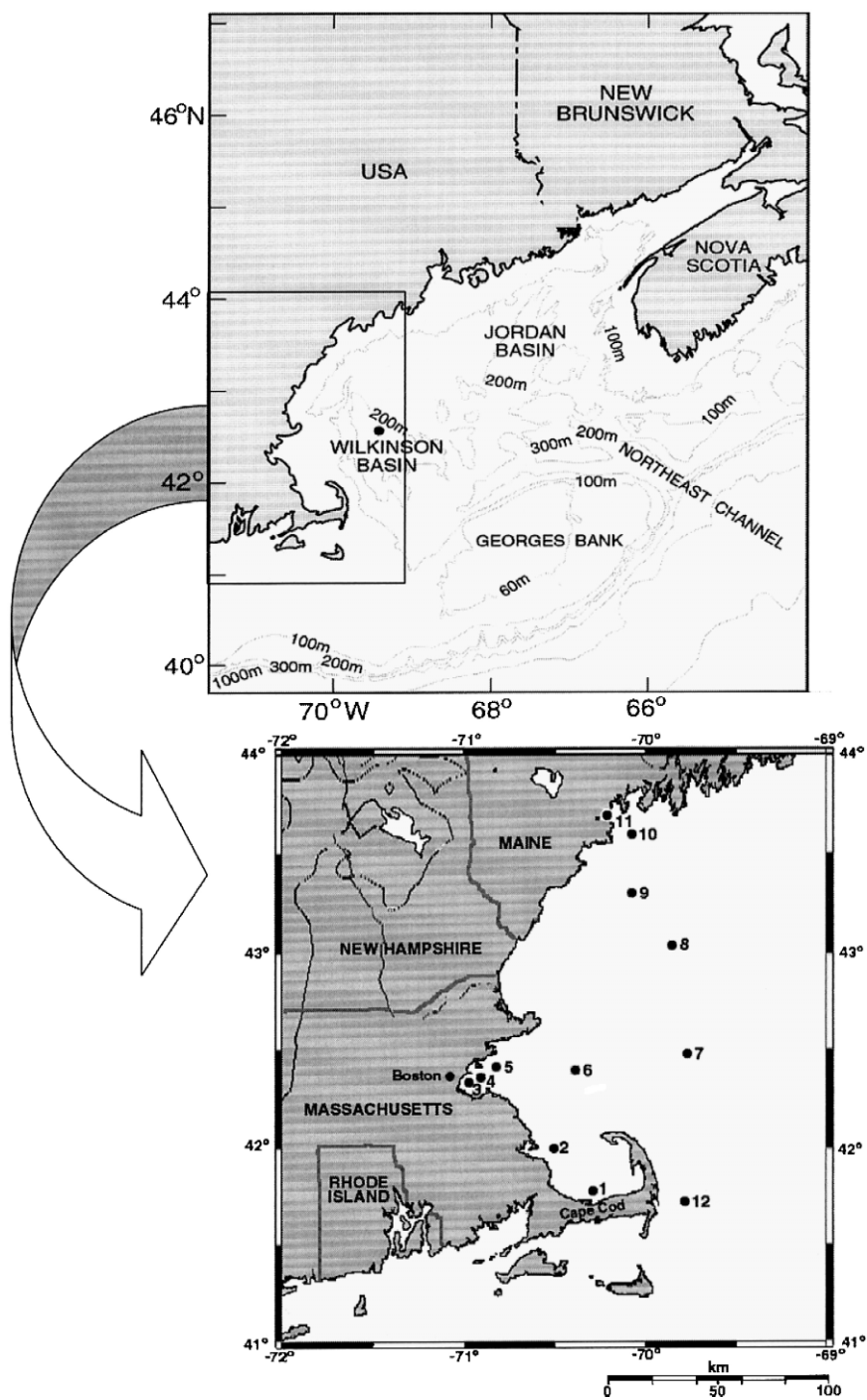


Fig. 1. Map showing the location of the Gulf of Maine and the 1996 and 1997 sampling stations.

system is composed of a Flojet™ polypropylene diaphragm pump, plumbing (mostly of Teflon) and

Millipore Prep/Scale™-TFF PLAC regenerated cellulose CFF membranes. We used three CFF mem-

branes (nominal molecular weight cutoff = 1 kDa) in parallel (surface area  $\sim 2 \text{ m}^2$ ) to increase the ultra-filtration rate to approximately  $150 \text{ ml min}^{-1}$ . Seawater was continuously prefiltered through a  $1 \text{ }\mu\text{m}$  Nuclepore™ filter into a 4 l fluorinated polyethylene bottle. Total volume through the CFF was  $\sim 30\text{--}40$  l. During operation, the membrane pressure was maintained at  $\sim 14\text{--}16$  psi.

Immediately before and after a typical sample run, the CFF system was cleaned by washing with  $> 20$  l Milli-Q water (Q-water) followed by recirculation with 0.01 N NaOH and 0.01 N HCl solutions made in the same Q-water. The system was cleaned with Q-water between acid and base rinses. Following these cleaning steps, the system was conditioned with 4–6 l prefiltered seawater. New CFF membranes were vigorously cleaned and fully calibrated with standard fluorescein-tagged molecules as described previously (Dai et al., 1998). In all test modes, samples were collected at various times or concentration factors (cf) from the permeate and retentate lines for OC analysis. Samples for  $^{234}\text{Th}$  analysis were collected from the integrated permeate and retentate fractions.

#### 2.4. Colloidal concentration

We define the colloidal fraction as that material which passes through a  $1\text{-}\mu\text{m}$  filter and is retained by a 1-kDa CFF membrane. When analyzing data from the sampling mode, the concentration was calculated at the time point when each of the samples was collected. At each sampling point:

$$[\text{colloidal}] = \frac{[\text{retentate}] - [\text{permeate}]}{\text{cf}}$$

$$\text{cf} = \frac{\text{retentate volume} + \text{permeate volume}}{\text{retentate volume}}$$

and

$$[\text{Sum concentration}] = [\text{colloidal}] + [\text{permeate}].$$

The mass balance can then be calculated by comparing the sum with the initial source solution concentration.

#### 2.5. Analysis

Subsamples for OC analysis were collected in either 125 ml pre-combusted glass bottles or 20 ml precombusted glass scintillation vials. Sample caps were acid cleaned and lined with Teflon. Samples were acidified with 50%  $\text{H}_3\text{PO}_4$  to  $\text{pH} \sim 2$  (500  $\mu\text{l}$  for 100 ml sample) immediately upon collection and stored at  $4^\circ\text{C}$  for up to a few weeks or at  $-18^\circ\text{C}$  for longer term storage. OC concentrations in permeate, retentate and prefiltrate fractions were analyzed, in duplicate, with a high temperature catalytic oxidation (HTCO) analyzer (Peltzer and Brewer, 1993). Instrument blanks (usually  $< 10 \text{ }\mu\text{M}$ ) were estimated daily using UV-irradiated Q-water. Calibration standards were also run daily using potassium hydrogen phthalate dissolved in aged seawater. The precision for the OC measurements was  $< 2\%$ . Particulate organic carbon (POC), collected onto precombusted glass fiber filters (Whatman GF/F), was analyzed using a Perkin-Elmer CHN analyzer.

$^{234}\text{Th}$  activity was determined by counting the stronger beta emissions of its daughter  $^{234}\text{Pa}$ , as described in Buesseler et al. (1992) and in Moran and Buesseler (1993). Briefly,  $^{230}\text{Th}$  yield monitors and Fe-carrier were added to each  $^{234}\text{Th}$  sample. After equilibration, samples were concentrated using an  $\text{Fe}(\text{OH})_3$  precipitate and purified via a series of anion exchange columns.  $^{238}\text{U}$  activities were calculated from salinity using the relationship,  $^{238}\text{U} = 0.0797 \cdot \text{Salinity}$  (Chen et al., 1986).  $^{234}\text{Th}$  activities were corrected for ingrowth from  $^{238}\text{U}$  and decay corrected to the mid-point of collection.  $^{234}\text{Th}$  errors were propagated from counting statistics using a non-linear least squares fit of the raw data to the  $^{234}\text{Th}$  decay curve.

### 3. Results and discussion

#### 3.1. CFF performance

##### 3.1.1. Blank evaluation

A CFF blank test represents an essential first order check on the performance of the CFF membrane. A low Q-water blank attests to the lack of carryover between sampling. Table 1 shows one

Table 1  
Organic carbon concentrations in Q-water and rinse solutions from the Millipore CFF system

Rinse solution	OC ( $\mu\text{M}$ )		
	Permeate	Retentate	cf
1st Q-H <sub>2</sub> O	7.4	27.2	2
	8.3	36.6	4
NaOH (0.01 N) <sup>a</sup>	5.9	N/A	2
	6.4	17.6	4
HCl (0.01 N) <sup>a</sup>	2.3	6.0	2
	1.2	2.0	4
Last Q-H <sub>2</sub> O	1.8	2.0	2
	0.2	0.8	4

cf = Concentration factor; source Q-H<sub>2</sub>O organic carbon concentration  $\sim 2 \mu\text{M}$ ; the volume of each rinse solution used  $\sim 4 \text{ l}$ .

<sup>a</sup>Rinse the system with Q-H<sub>2</sub>O until pH  $\sim 7$  after the base and acid rinses.

example of the evolution of OC concentration as the CFF system was progressively treated using Q-water, base, and acid solutions after a typical sample run. The source Q-water OC concentration was  $\approx 2\text{--}3 \mu\text{M}$ . Elevated OC concentrations ( $27 \mu\text{M}$  for the retentate and  $7 \mu\text{M}$  for the permeate when  $\text{cf} = 2$ ) in the first Q-water rinse (recirculation for 20–30 min prior to collection) is most likely due to: (1) the release of OC that was retained by the CFF membrane from sorptive processes, and/or (2) sample solution carryover from incomplete draining of the system from the preceding CFF sample. The OC concentration increased in the retentate to  $36 \mu\text{M}$  as CFF cleaning progressed ( $\text{cf} = 4$ ), indicating the continued release of OC. A subsequent base rinse was efficient in lowering the OC blank of the system to levels indistinguishable from the source Q-water ( $\text{OC} = 17$  at  $\text{cf} = 4$ ). We reported a similar experiment for an Amicon™ CFF system in Dai et al. (1998). These results demonstrate that a low bulk OC blank is achievable for CFF systems with configurations similar to ours after careful cleaning.

### 3.1.2. Bulk OC mass balance

Demonstration of proper mass balance is essential to assessing sorptive losses during CFF processing and, thus, quantifying the performance of any CFF membrane. In this study, all of the samples have excellent bulk OC mass balances as long as the CFF system was preconditioned (Table 2). Fig. 2 shows

an example of the OC content that occurred throughout preconditioning and sampling operations using the Millipore™ CFF system. It is clear that significant losses of bulk OC occur during the preconditioning stage. This is most likely due to the fact that equilibrium between the solutes and membranes had not yet been reached. The preconditioning mass balance increased from  $\sim 70\%$  at the beginning to approximately 90% recovery by the end. After this preconditioning stage, the mass balance was essentially 100%. The higher recovery at the first point during the sampling is due to the carryover of OC from the preconditioning step. Hence, this point should be excluded in any calculation of the colloidal abundance, as was also noted in Dai et al. (1998). It is clear from the above results that preconditioning is crucial in ensuring a good mass balance for bulk OC. Therefore, it is essential that one should precondition any CFF system before running marine samples.

### 3.1.3. <sup>234</sup>Th mass balance

In Dai et al. (1998), discouragingly low mass-balances were achieved for the particle-reactive radionuclide <sup>234</sup>Th. It was found that enhanced losses of <sup>234</sup>Th onto the 1 kDa CFF membrane were related to some extent, to the low abundance of organic colloids in the samples processed. In this study, we have confirmed this hypothesis by finding improved mass balances when processing relatively high colloid abundance coastal seawater. Although improved, the loss of <sup>234</sup>Th is still significant, varying from 30–40% for most of the samples processed in this study. The maximum <sup>234</sup>Th loss was on the 200 m sample collected on the July 1997, where COC was the lowest ( $11.7 \mu\text{M}$ , Table 3). In contrast, the highest recovery was found for the sample taken close to the bottom, at 250 m (station depth  $\sim 275 \text{ m}$ ). It is most likely that the bottom colloidal materials originate, in part, from resuspended sedimentary particles that contain refractory organic matter that may be less reactive to the CFF membrane.

In order to identify characteristics of the lost <sup>234</sup>Th, a series of post-sampling rinsing experiments were conducted immediately after each sample run during the July 1997 cruise. This post-sampling rinsing procedure is similar to that used for the blank evaluation experiments described earlier. However,

Table 2  
Organic carbon concentrations in size-fractionated GoM seawater samples

Station	Latitude (N)	Longitude (W)	Depth (m)	Sampling dates	Salinity	cf	TOC ( $\mu\text{M}$ )	DOC ( $\mu\text{M}$ )	Permeate ( $\mu\text{M}$ )	% of total	Retentate ( $\mu\text{M}$ )	COC ( $\mu\text{M}$ )	% of total	Sum ( $\mu\text{M}$ )	Recovery (%)	POC ( $\mu\text{M}$ )	% of total
1	41°47.80'	70°13.50'	5	35251	30.51	25.6	117.31	110.40	88.10	75.10	692.30	23.57	20.09	111.67	101.15	6.91	5.89
2	42°00.11'	70°30.22'	1	35252	31.00		112.30	106.34								5.96	
3	42°20.52'	70°58.59'	6	35255	31.00	8.9	146.71	104.60	80.05	54.56	281.87	22.80	15.54	102.85	98.33	42.11	28.70
4	42°22.00'	70°53.90'	4.3	35255	30.88	9.0	137.01	104.16	82.15	59.96	287.75	22.85	16.68	105.00	100.81	32.85	23.98
5	42°24.90'	70°47.99'	4	35254	30.85	7.5	123.17	104.10	73.80	59.92	289.70	28.62	23.23	102.42	98.38	19.07	15.48
6	42°20.56'	70°23.51'	5	35254	30.74	8.8	113.26	104.80	87.60	77.34	247.10	18.23	16.09	105.83	100.98	8.46	7.47
7	42°28.00'	65°44.00'	5	35252	31.30	12.5	93.30	88.03	70.30	75.35	260.30	15.22	16.32	85.52	97.16	5.27	5.65
7	42°28.00'	65°44.00'	60	35254	32.30	8.1	70.55	67.90	56.85	80.58	152.10	11.81	16.74	68.66	101.12	2.65	3.76
8	43°02.00'	69°53.00'	5	35257	31.52		90.00	90.00								3.79	4.21
9	43°18.00'	70°06.00'	5	35257	30.86		108.60	108.60								12.23	11.26
10	43°37.60'	70°07.87'	5	35256	30.30		128.70	128.70								7.41	5.76
11	43°39.64'	70°14.25'	5	35256	28.90		154.90	154.90								3.79	2.44
12	41°46.50'	69°45.90'	5	35258	30.83		118.47	118.47								9.33	7.88
7	42°29.00'	69°43.70'	1	35620	31.37	10.1	101.45	87.20	73.10	83.83	255.13	18.11	20.77	91.21	104.60	6.88	6.78
7	42°29.00'	69°43.70'	15	35623	31.88	9.7	99.10	90.50	62.00	68.51	281.87	22.74	25.12	84.74	93.63	5.42	5.47
7	42°29.00'	69°43.70'	37	35622	32.31	12.7	82.50	74.60	57.77	77.44	238.13	14.17	18.99	71.94	96.43	10.03	12.15
7	42°29.00'	69°43.70'	65	35622	32.52	9.8	72.93	67.23	50.23	74.71	192.30	14.54	21.63	64.77	96.34	3.94	5.40
7	42°29.00'	69°43.70'	200	35621	34.02	9.2	59.35	58.58	48.13	82.16	155.83	11.71	19.98	59.84	102.14	4.21	7.09
7	42°29.00'	69°43.70'	250	35623	34.09	9.9	57.57	55.57	47.50	85.48	168.13	12.25	22.04	59.75	107.52	5.48	9.51

TOC—total organic carbon; DOC—total dissolved organic carbon; COC—colloidal organic carbon; POC—particulate organic carbon.

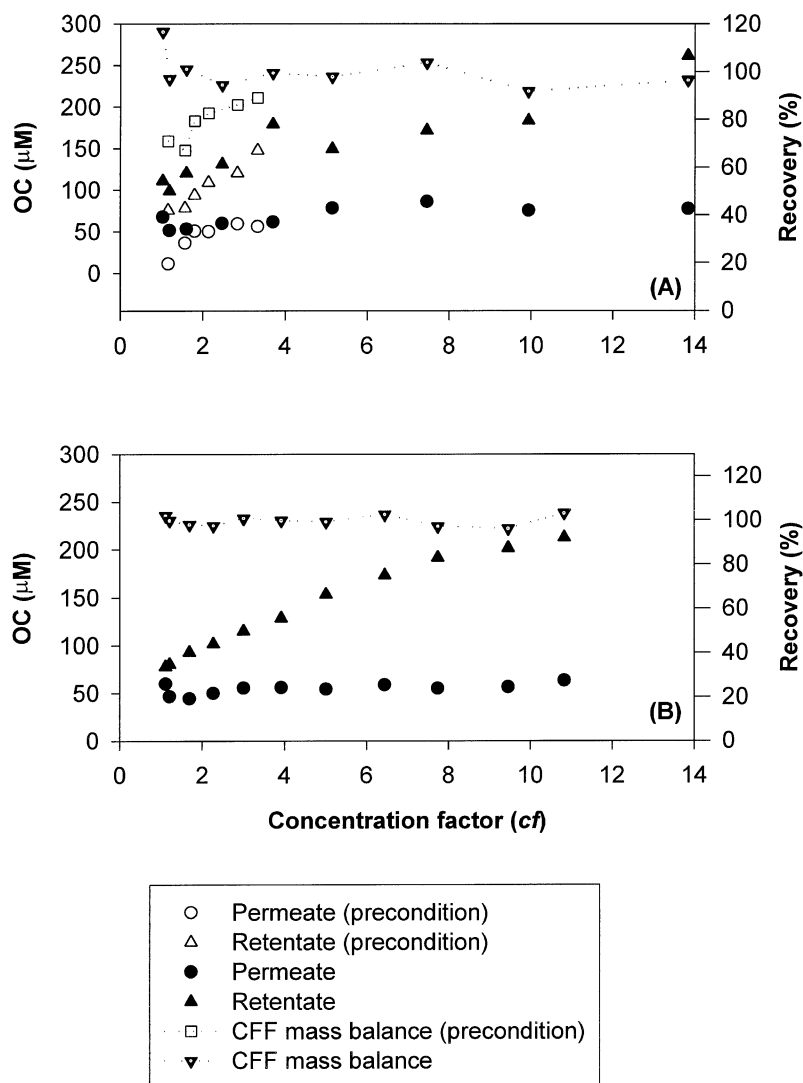


Fig. 2. Time-series results for OC determined in both permeate and retentate lines from the Millipore 1 kDa CFF for surface seawater sampled from Wilkinson Basin (Station 7). “Preconditioning” refers to the sample solution that is passed through the CFF immediately after cleaning. (A) 1996, (B) 1997.

we combined all the rinse solutions prior to  $^{234}\text{Th}$  measurement. The results (Table 3) showed that 10–50% of the “lost”  $^{234}\text{Th}$  can be recovered through acid and base rinsing, with 3–48% recovered in the rinse permeate solution and 0.4–15% recovered in the rinse retentate solution. Assuming the colloidal materials sorbed to the membrane were not destroyed during the acid and base leaching steps, our results suggest that the fraction of  $^{234}\text{Th}$  lost to the membrane through sorption may exist as both low

and high molecular weight material. We should point out, however, that this assumption needs further confirmation through experimentation. We should also mention that we would tend to under-estimate the colloidal fraction by correction if some fraction of the lost colloids were dissolved or decomposed during the rinsing operation. Regardless, the  $^{234}\text{Th}$  lost to the 1 kDa CFF membrane was substantial as greater than 50% of the lost  $^{234}\text{Th}$  was unrecoverable by the rinsing processes described in this study.

Table 3  
<sup>234</sup>Th activity (dpm/kg) in size-fractionated Gulf of Maine sea water samples\*

Depth m	Sampling dates	cf	Permeate		Retenate		Colloidal		Recovery		Total dissolved		Particulate (dpm/kg)	
			dpm/kg	± Error	dpm/kg	± Error	dpm/kg	± Error	R (%)	± Error (%)	dpm/kg	± Error	dpm/kg	± Error
5	06-Jul-96	12.8	0.793	0.207	2.914	0.516	0.166	0.074	74.37	16.22	1.290	0.015	0.362	0.015
1	09-Jul-97	10.1	0.635	0.026	2.297	0.068	0.165	0.007	59.82	3.12	1.337	0.017	0.452	0.017
15	12-Jul-97	9.7	0.695	0.011	2.148	0.046	0.150	0.005	55.78	3.62	1.515	0.018	0.362	0.008
37	11-Jul-97	12.7	0.692**	0.022	2.463	0.072	0.140	0.006	61.66	2.45	1.348	0.012	0.442	0.007
65	11-Jul-97	9.8	0.867	0.011	2.166	0.050	0.133	0.005	66.66	3.79	1.500	0.016	0.594	0.006
200	10-Jul-97	9.2	0.121	0.008	0.452	0.045	0.036	0.005	35.21	2.07	0.445	0.010	1.010	0.008
250	12-Jul-97	9.9	0.172	0.009	0.706	0.034	0.054	0.004	79.89	3.49	0.283	0.010	0.781	0.006
<i>Rinse-corrected</i>														
5	06-Jul-96	12.8	N/A***	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
1	09-Jul-97	10.1	0.699	0.026	2.495	0.068	0.179	0.800	65.62	2.21				
15	12-Jul-97	9.7	0.733	0.011	2.588	0.046	0.192	0.005	61.10	1.08				
37	11-Jul-97	12.7	0.722	0.022	2.869	0.072	0.169	0.006	66.13	1.77				
65	11-Jul-97	9.8	0.917	0.011	2.541	0.050	0.166	0.035	72.20	2.60				
200	10-Jul-97	9.2	0.148	0.008	0.540	0.045	0.043	0.005	42.84	2.38				
250	12-Jul-97	9.9	0.199	0.009	0.768	0.035	0.058	0.004	90.77	4.69				
<i>Recovered from rinsing</i>														
			Total loss dpm/kg	Permeate recovered/ total loss ± Error	%	± % error	Colloidal recovered/ total loss %	± % error	Total recovered from rinsing %	± % error				
1	09-Jul-97	10.1	0.537	0.032	11.95	0.80	4.45	2.27	16.40	2.41				
15	12-Jul-97	9.7	0.670	0.022	5.64	0.32	14.18	1.03	19.82	1.08				
37	11-Jul-97	12.7	1.208	0.025	2.57	0.12	10.40	0.55	12.96	0.56				
65	11-Jul-97	9.8	0.500	0.021	9.96	0.56	14.94	1.52	24.90	1.63				
200	10-Jul-97	9.2	0.288	0.014	9.49	0.71	0.45	1.83	9.94	1.97				
250	12-Jul-97	9.9	0.057	0.014	48.01	11.94	0.48	23.92	48.49	26.74				

Rinse-corrected data are also shown using the results from the post CFF rinsing experiment. See text for details.

\*Size fractions: total dissolved, <1 μm; permeate, <1 kDa; colloidal, 1 kDa–1 μm; particulate, >1 μm.

\*\*This permeate concentration is an average of two integrated permeate sample: 0.691 ± 0.019, and 0.693 ± 0.010.

\*\*\*N/A—not available.

It is noteworthy that for the 250-m sample, the rinse recovered portion is close to 50% of the lost  $^{234}\text{Th}$ . As a result, the rinse corrected mass balance for the 250-m sample is 91% vs. < 72% for samples at other depths (Table 3). This again implies that the high molecular weight material at 250 m is mostly refractory in nature and is, hence, more easily recoverable by acid and base rinses. Unfortunately, there is no clear quantitative trend in the lost  $^{234}\text{Th}$  fraction. Thus, correcting our data by including these rinses would be misleading, as it is not clear to which fraction the rinses should be added. Only the measured  $^{234}\text{Th}$  fractionated values are reported.

### 3.2. Size fractionated organic carbon and $^{234}\text{Th}$ distributions

#### 3.2.1. OC

Table 2 and Fig. 3 show the fractionated OC results from this study. Surface DOC concentrations range from 87  $\mu\text{M}$  at Wilkinson Basin to > 120  $\mu\text{M}$

in Casco Bay and Boston Harbor. The lower DOC concentration at Wilkinson Basin is within the upper limits observed on Georges Bank by Chen et al. (1996). The vertical profile of the OC fractions at Station 7 is very similar to that observed at Bermuda (Dai et al., 1998) and in the Pacific and Atlantic Oceans (Benner et al., 1997). Low molecular weight OC declines steadily with depth. DOC follows essentially the same trend with the exception of an excess at 15 m. This excess in OC is also observable in the COC profile, but to a lesser degree. The POC trend is similar to COC, but the maximum in concentration is at 37 m, where the Chl *a* maximum is also located. This suggests that particulate and colloidal material undergo transformations separated in space within the water column.

As previously observed, low molecular weight organic material dominates the OC pool with the remaining 10–24% in the high molecular weight or colloidal fraction (Table 2). COC is generally more abundant than POC, a phenomenon observed in vari-

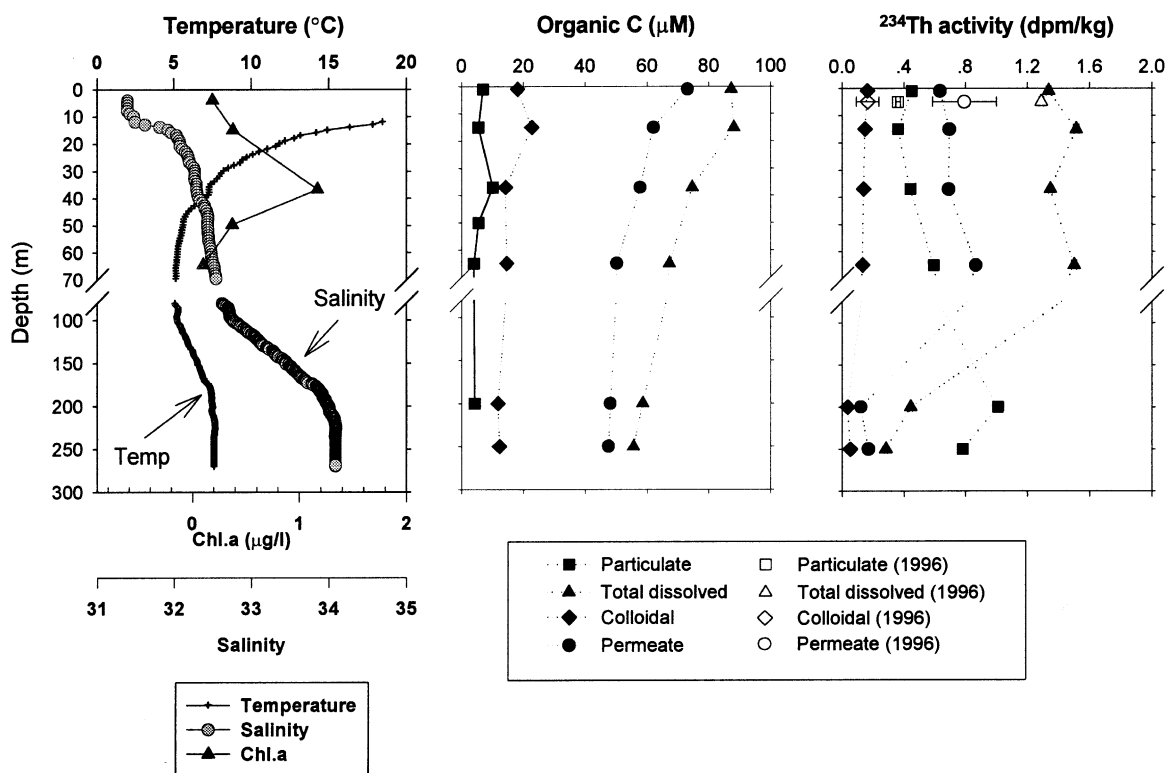


Fig. 3. OC and  $^{234}\text{Th}$  distributions at Wilkinson basin (Station 7, July 1997). Also shown is the CTD profile at Station 7.

ous environmental settings (Dai, 1995), and supports the suggestion that the colloidal fraction represents the largest reservoir of “particulate” OC in the ocean (Kepkay, 1994).

Although measured COC abundance can vary between CFF membranes, depending upon specific protocols employed in CFF processing (Dai et al., 1998), the overall distribution of DOC is similar to that found in other regimes (Benner et al., 1992, 1997; Guo and Santschi, 1996, 1997; Aluwihare et al., 1997; Skoog and Benner, 1997; Dai et al., 1998). The consistency in COC distributions and concentrations also suggests that CFF results are becoming more reproducible when using proper operational protocols.

The concentration of DOC and COC decreases linearly with salinity in the 1996 horizontal transect data (Fig. 4). Similar distribution patterns have been observed in the Gulf of the Mexico and in the Mid-Atlantic Bight (Guo et al., 1995). The origin of the total OC distribution appears to be predominantly related to physical mixing, a process hypothesized to

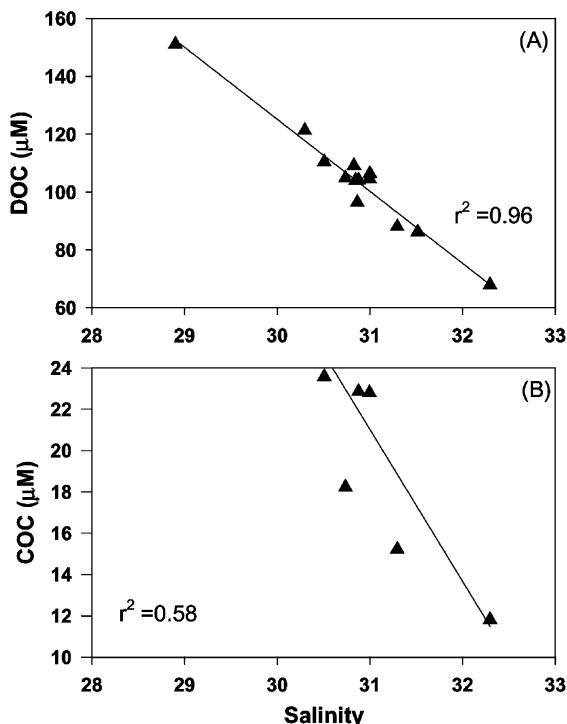


Fig. 4. OC vs. salinity for the 1996 cruise. (A) DOC, (B) COC.

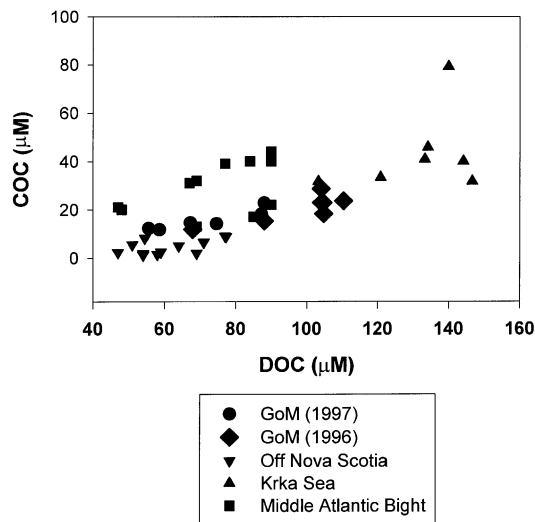


Fig. 5. DOC vs. COC. Data sources: the KrKa Sea, Sempéré and Cauwet (1995); Nova Scotia, Moran and Moore (1989); Mid-Atlantic Bight, Guo et al. (1995).

also control the Pu isotope distribution within the GoM (Dai et al., 2001).

DOC and COC are well correlated (Fig. 5). The correlation appears ubiquitous and has been found in other distinctly different regimes, e.g. in the KrKa Sea (Sempéré and Cauwet, 1995), off Nova Scotia (Moran and Moore, 1989), and in the Mid-Atlantic Bight (Guo et al., 1995). What is interesting is that the slope of the DOC/COC relationship is so similar ( $0.29 \pm 0.07$ ) given that each of these investigators used different types of membranes and operational protocols. The fundamental implication of this correlation is still unclear. However, it may be related to the fact that similar physico-chemical processes control the aggregation and disaggregation of colloidal particles at the low shear rates characteristic of marine environments. The fact that the relationship between COC and DOC is so consistent may provide a means for obtaining seawater COC concentrations from DOC measurements alone. A similar hypothesis has also been discussed by Dai (1995).

### 3.2.2. $^{234}\text{Th}$

Colloidal  $^{234}\text{Th}$  concentrations remain controversial due primarily to the poor mass balances achieved when using 1 kDa CFF membranes. Guo and Santschi (1997) have reviewed the colloidal  $^{234}\text{Th}$  data collected to date, and have pointed out that the method-

ological issues related to  $^{234}\text{Th}$  CFF are the most likely cause of the larger than expected variations in colloidal  $^{234}\text{Th}$  abundance. While sampling protocols and ultrafiltration integrity contributed to the variations, differences in correction techniques have also affected the colloidal  $^{234}\text{Th}$  distribution. For example, Baskaran et al. (1992) and Guo et al. (1997) added the lost fraction that was recovered with rinsing into the colloidal fraction. This correction increased the colloidal  $^{234}\text{Th}$  concentration. In this study, we did not correct our data by adding the rinse solutions.

Colloidal  $^{234}\text{Th}$  represents 8–20% of total dissolved  $^{234}\text{Th}$ , with the majority of total dissolved  $^{234}\text{Th}$  occurring in the low molecular weight size fraction at Wilkinson Basin. The size distribution within the surface waters between the two cruises is identical (Table 3). Note that the two integrated time-series permeate samples at 37 m have indistinguishable  $^{234}\text{Th}$  activities ( $0.691 \pm 0.019$  for cf = 1–8 and  $0.693 \pm 0.010$  for cf = 8–12.7). This suggests that the breakthrough during ultrafiltration found previously for OC and certain trace elements (Logan and Jiang, 1990; Buesseler et al., 1996; Guo and Santschi, 1996; Wen et al., 1996; Dai et al., 1998) may be of less importance for  $^{234}\text{Th}$  when using our Millipore CFF membranes. Particulate  $^{234}\text{Th}$  is a factor of two higher than surface colloidal  $^{234}\text{Th}$  concentrations, and  $> 10$  times higher at depth.

Overall, our  $^{234}\text{Th}$  distribution is in agreement with previous observations, showing a slight maximum in colloidal  $^{234}\text{Th}$  at the depth of maximum Chl *a* (i.e. Huh and Prahl, 1995 using a 10 kDa CFF system). The particulate  $^{234}\text{Th}$  pattern generally increases with depth due to an increase in  $^{234}\text{Th}$  scavenging onto particles. This increase is particularly significant near the bottom as a result of sediment resuspension. Elevated colloidal  $^{234}\text{Th}$  and COC concentrations were also observed near the seafloor.

### 3.3. $^{234}\text{Th}$ derived carbon export and downward diffusion of DOC

July 1997 POC export over the upper 65 m was derived using a simple steady-state model of  $^{234}\text{Th}$  export coupled (e.g. Buesseler, 1998) with a C/ $^{234}\text{Th}$  ratio obtained from water bottle filtration onto GF/Fs. Using this method, we obtained a POC

export flux of  $3.5 \text{ mmol m}^{-2} \text{ day}^{-1}$ ,  $\sim 5\%$  of the annual primary production in GoM ( $66 \text{ mmol m}^{-2} \text{ day}^{-1}$ , O'Reilly and Busch, 1984). This low export of POC is related to the plankton density and community structure in July (Benitez-Nelson, 1998), and the dominant recycling processes within the Wilkinson Basin water column as suggested by time-series sediment trap data (Pilskaln et al., 1996).

Using our DOC data and vertical eddy diffusivity (K<sub>z</sub>) estimates made during the same cruise with  $^7\text{Be}$  (Benitez-Nelson et al., 2000), we can estimate the downward diffusive flux of DOC as  $0.1 \text{ mmol m}^{-2} \text{ day}^{-1}$  from the upper 65 m of the water column. This downward DOC flux is comparable to that estimated in the Gulf of Mexico ( $0.36 \text{ mmol m}^{-2} \text{ day}^{-1}$ , Guo et al., 1995) and in the Mid-Atlantic Bight ( $0.17\text{--}0.18 \text{ mmol m}^{-2} \text{ day}^{-1}$ , Guo et al., 1995), and represents only  $\sim 3\%$  of the  $^{234}\text{Th}$  derived POC flux over the same depth interval. Benitez-Nelson et al. (2000) have pointed out that abrupt changes in mixed layer depths may overestimate the eddy diffusivity during the spring and early summer. As a result, we may have overestimated the DOC diffusive flux. Hence, our numbers represent an upper limit of the downward DOC flux. This low DOC diffusive flux suggests that POC export dominates the vertical OC transport in the GoM during the summer.

### 3.4. Colloidal $^{234}\text{Th}$ turnover times

Estimates of the residence times of size fractionated  $^{234}\text{Th}$  are made using a box model similar to that of Moran and Buesseler (1992, 1993). In this model, the activity of  $^{234}\text{Th}$  is maintained by the balance between production from  $^{238}\text{U}$ , radioactive decay of  $^{234}\text{Th}$ , and scavenging by colloidal and particulate matter. The model assumes irreversible scavenging of  $^{234}\text{Th}$  and that the advection and diffusion terms are negligible compared with net removal fluxes (Coale and Bruland, 1985; Buesseler et al., 1992; Moran and Buesseler, 1992, 1993).

The differential equations for total  $^{234}\text{Th}$  scavenging model are as follows:

$$\frac{\partial A_{\text{Th}}^{\text{tot}}}{\partial t} = A_{\text{U}} \lambda - A_{\text{Th}}^{\text{tot}} \lambda - P_{\text{Th}}$$

and for  $^{234}\text{Th}$  in each size fraction:

$$\frac{\partial A_{\text{Th}}^{\text{d}}}{\partial t} = A_{\text{U}} \lambda - A_{\text{Th}}^{\text{d}} \lambda - J_{\text{Th}}$$

$$\frac{\partial A_{\text{Th}}^{\text{c}}}{\partial t} = J_{\text{Th}} - A_{\text{Th}}^{\text{c}} \lambda - C_{\text{Th}}$$

$$\frac{\partial A_{\text{Th}}^{\text{p}}}{\partial t} = C_{\text{Th}} - A_{\text{Th}}^{\text{p}} \lambda - P_{\text{Th}}$$

where  $A_{\text{U}}$  is the  $^{238}\text{U}$  activity,  $\lambda$  ( $0.0288 \text{ day}^{-1}$ ) is the decay constant of  $^{234}\text{Th}$ , and  $A_{\text{tot}}$  is the total  $^{234}\text{Th}$  activity.  $J$ ,  $C$  and  $P$  represent the net removal flux from dissolved, colloidal and particulate pools respectively in units of  $\text{dpm l}^{-1} \text{ day}^{-1}$ , or  $\text{dpm m}^{-2} \text{ day}^{-1}$  if the water depth is taken into consideration. At steady state:

$$\frac{\partial \text{Th}^{\text{diss}}}{\partial t} = \frac{\partial \text{Th}^{\text{coll}}}{\partial t} = \frac{\partial \text{Th}^{\text{part}}}{\partial t} = 0.$$

Using the  $^{234}\text{Th}$  data, the residence times for dissolved, colloidal and particulate fractions are estimated to be 17, 3 and 19 days, respectively. We have mentioned that loss of  $^{234}\text{Th}$  during CFF processing is significant. While we did not correct our data for this loss, we can consider the  $^{234}\text{Th}$  size fractionation at two extreme conditions: either the lost  $^{234}\text{Th}$  is in the  $< 1 \text{ kDa}$  size class or it is in the colloidal size class. Table 4 lists the residence times of the various fractions under these two conditions. Depending on where the lost  $^{234}\text{Th}$  is added, colloidal and particulate residence times range from 3 to 30 and 19 to 68 days, respectively.

### 3.5. Comparisons of colloidal residence times and implications for future studies

Our estimates of the colloidal residence time are longer than those reported previously by Moran and Buesseler (1993) for the GoM ( $\sim 0.5$  days), but similar to those for the Atlantic (Moran and Buesseler, 1992). Santschi et al. (1995) and Guo and Santschi (1996) also reported similar  $^{234}\text{Th}$  derived colloidal residence times of 3–30 days for the Gulf of Mexico and Mid-Atlantic Bight.

Although these  $^{234}\text{Th}$  colloidal residence times range on the order of  $< 1$  day to as long as several weeks, they are still several orders of magnitude shorter than  $^{14}\text{C}$ -based ages of COC measured by Santschi et al. (1995) and Guo and Santschi (1997). These  $^{14}\text{C}$ -based investigations found that colloidal material in the  $> 1 \text{ kDa}$  size fraction was composed of a mixture of LMW, refractory compounds ranging in age from 400–4500 years. In contrast, COC in the HMW fraction ( $> 10 \text{ kDa}$ ) was significantly younger ( $\sim 30$  years). Santschi et al. (1995) pointed out that rapid  $^{234}\text{Th}$ - and  $^{14}\text{C}$ -derived turnover times do not necessarily have to agree with contemporary radiocarbon ages. Rather, they suggested that the shorter  $^{234}\text{Th}$ -based ages are due to indiscriminate scavenging of  $^{234}\text{Th}$  onto older, more refractory suspended materials, that are coagulating to form colloidal material. We suggest an alternative explanation: that  $^{234}\text{Th}$  is tracing an even more reactive pool of organic material. A number of studies have provided evidence that both dissolved and particulate matter are composed of a diverse range of compounds. These compounds are bioavailable over a range of

Table 4

Residence times of the different OC fractions in the Gulf of Maine derived from a three-phase  $^{234}\text{Th}$  scavenging model. The two extreme conditions add the  $^{234}\text{Th}$  lost during CFF processing to either the colloidal or truly dissolved fraction. Also shown are the POC export fluxes at 65 m

	Residence times ( $\tau$ , days)			POC export ( $\text{mmol m}^{-2} \text{ day}^{-1}$ )
	Dissolved	Colloidal	Particulate	
Apparent <sup>a</sup>	17	3	19	9.3
Lost $^{234}\text{Th}$ is 100% colloidal	14	30	68	3.5
Lost $^{234}\text{Th}$ is $< 1 \text{ kDa}$	41	7	68	3.5

<sup>a</sup>Without any correction.

timescales and can be as short as days to weeks (Kirchman et al., 1991; Bronk et al., 1994; Amon and Benner, 1994; Benitez-Nelson and Buesseler, 1999). Thus, it is not difficult to extend this short time-scale hypothesis to the colloidal realm, where the operational definition of COC (1 kDa to 1  $\mu$ m) contains everything from bacteria and viruses, to carbohydrates, proteins and lipids (Benner et al., 1992). In fact, a recent study by Amon and Benner (1996) suggests that colloidal organic matter supports a substantial fraction of marine heterotrophic bacterial production.

Direct evidence that  $^{234}\text{Th}$  is tracing a more biologically active pool of COC is limited. However, other indirect evidence is more plentiful. For example, Niven et al. (1995) demonstrated that the fraction of  $^{234}\text{Th}$  within the surface COC pool increased during a spring phytoplankton bloom. They attributed this rise to increasing phytoplankton exudates. In addition, a number of studies have demonstrated that  $^{234}\text{Th}$  traces freshly produced, sinking particulate organic matter (e.g. Buesseler, 1998). When these particles are remineralized, colloidal material is also presumably produced and a number of water column profiles of dissolved  $^{234}\text{Th}$  throughout the world's oceans have shown it to be in 'excess' at depth (e.g. Bacon et al., 1996; Van Der Loeff et al., 1997; Dai et al., 1998).

What is interesting, however, is that there is a relatively wide range in  $^{234}\text{Th}$ -based COC residence times in oceanic environments. We believe that this is most likely due to a combination of environmental and methodological issues. Our minimum estimates of the COC residence time is short (3 days), but still longer than the  $\sim 0.5$  days found previously by Moran and Buesseler (1993) in the GoM area. This may be due in part to the different size cutoffs used between the studies (10 vs. 1 kDa in this study). As stated previously,  $^{14}\text{C}$ -based COC analyses have found a significant increase in age as one moves from higher MW (> 10 kDa) to lower MW colloidal material (> 1 kDa). We believe that our longer calculated COC residence time is evidence that the 1–10 kDa material is slightly more refractory, i.e. composed of fundamentally different OC compounds.

It is also possible, however, that some of the difference between our measured COC residence

times and those measured previously in the GoM and in other regimes, may be attributable to spatial and temporal variability in plankton activity. The GoM is an enclosed basin with a water mass circulation that results in a longer residence time of nutrients within the gyre, longer than that typically found in many coastal regions. Our samples were collected in the center of Wilkinson Basin, the 'oldest' water in the GoM and during a period of low biological productivity and export (July). Evidence from other radioisotope studies indicate that nutrient cycling at that time was low and that the residence times of dissolved nutrients were greater than 2 weeks (Benitez-Nelson and Buesseler, 1999). This implies that the measured COC may have been less bioavailable during this period, and hence, have a longer residence time.

Given the difficulties in mass balancing CFF fractionated  $^{234}\text{Th}$ , we obtain COC residence times that range from 3 to 30 days, depending on where the 'lost'  $^{234}\text{Th}$  is added. We believe that COC residence times are better represented by the shorter turnover times. The longer COC residence times are obtained when all of the 'lost'  $^{234}\text{Th}$  is assumed to be colloidal. However, this is unlikely, since  $^{234}\text{Th}$  that is complexed by colloids is hypothesized to be less reactive. Therefore, it is more likely that most of the 'lost'  $^{234}\text{Th}$  is from the larger, more reactive dissolved pool. It should be noted that in many of the other COC/ $^{234}\text{Th}$  studies to which we are comparing our data (i.e. Santschi et al., 1997, Guo et al., 1997), the  $^{234}\text{Th}$  that was 'lost' in their CFF systems was added to the colloidal phase. Thus, their numbers would tend towards longer COC residence times.

The idea that marine colloids may contain a significant fraction of C that is available for uptake over biologically relevant time scales indicates that colloids can play a major role in primary and export production: both as a source of more labile organic matter, and as an intermediary in the transfer and/or stabilization of trace elements. There have been many lines of evidence that colloidal matter is essential in mediating particle uptake and transport of trace elements in the marine realm (Benoit et al., 1994; Dai et al., 1995; Guentzel et al., 1996; Greenamoyer and Moran, 1997; Wen et al., 1999; Guo et al., 2000; Wells et al., 2000). Colloids are essentially reactive intermediaries in the sorption of trace metals onto

suspended and sinking particulates. Wen et al. (1999) and Wells et al. (2000) found that there was a non-uniform distribution of trace metals within colloidal size fractions and suggested that this was due to specific metal/colloid interactions. While it is feasible that at least some reactive COC and associated trace metals may be transported from the coast over large distances, the rapid turnover of COC suggest that this fraction is minor.

While the transport of COC from the coastal ocean to the open ocean is small, the role of colloids that are produced in the open ocean is potentially significant. We have demonstrated that COC is linearly related to DOC. Recent evidence suggests that DOC concentrations are steadily rising in the oligotrophic regions of the world's oceans as a result of climate mediated changes in plankton community structure (Church et al., 2000). Hence, it is possible that COC may also be rising in these regimes and play an essential role in climate related processes. For example, trace metals may be of larger importance in plankton or bacterial nutrition due to increasing abundances of nitrogen fixing organisms (e.g. Tortell et al., 1999). Colloids may help to stabilize trace metals in the upper ocean that are deposited from the atmosphere and/or upwelled from deep waters below.

#### 4. Summary

Our results have found that COC represents 15–25% of total OC and is similar to that measured in other areas. Both COC and DOC decrease with salinity, suggesting the distribution of OC fractions are controlled primarily by physical mixing processes. The strong relationship between COC and DOC may further provide a new mechanism for estimating the concentration of COC from DOC measurements alone.

Colloids traced by  $^{234}\text{Th}$  have rapid turnover rates that range from 3 to 30 days. Dissolved and particulate  $^{234}\text{Th}$  ages were similar, although slightly older, and ranged from 14 to 41 and 19 to 68 days, respectively. The colloidal ages are significantly less than the HMW organic matter ages derived from  $^{14}\text{C}$  dating. This difference, coupled with those found between  $^{234}\text{Th}$  and OC mass balances, suggests a

large heterogeneity within COC. Given the rapid turnover rates and low COC  $^{234}\text{Th}$  recoveries, it appears that  $^{234}\text{Th}$  traces the more reactive COC fraction. The rapid turnover of reactive COC further implies that the trace elements associated with this pool may be available over biologically significant timescales. Hence, it is necessary to include the colloidal fraction in future modeling efforts of OC in coastal regimes if we are to accurately understand the mechanisms that control OC production and removal in the water column.

This study also confirms our previous research (Dai et al., 1998) that CFF systems can achieve excellent performance in OC fractionation studies as long as proper cleaning and preconditioning techniques are employed. Problems persist, however, when looking at  $^{234}\text{Th}$ , due to poor mass balances. A large percentage of the  $^{234}\text{Th}$  lost during CFF is irrecoverable in weak acid or base rinsing, indicating that the material lost is highly reactive. As a result, in order for  $^{234}\text{Th}$  to be utilized as a quantitative tracer of COC, CFF membranes with better mass balancing needs to be established. In addition, it is essential that a better understanding of the composition of colloidal material and the speciation of complexed colloidal  $^{234}\text{Th}$  and other trace metals be reached if we are to determine the role that colloids play in natural waters. Many radioisotopic studies have focused on either  $^{234}\text{Th}$  or  $^{14}\text{C}$ . We suggest that other radionuclides, spanning a range of reactivities, be further investigated in both natural environments and in tracer studies in order to more closely examine COC composition and residence time differences.

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