

# Upper ocean carbon flux determined by the $^{234}\text{Th}$ approach and sediment traps using size-fractionated POC and $^{234}\text{Th}$ data from the Gulf of Mexico

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Size-fractionated particulate  $^{234}\text{Th}$  and particulate organic carbon (POC) fluxes were measured in the Gulf of Mexico during 2000 and 2001 in order to obtain a better estimation of upper ocean organic carbon export out of the euphotic zone within cold core and warm core rings, and to assess the relative merit of sediment trap and POC/ $^{234}\text{Th}$  methods. In 2000, the flux of POC measured by sediment traps at 120 m ranged from 60 to 148 mg C m<sup>-2</sup>d<sup>-1</sup>, while  $^{234}\text{Th}$ -derived POC fluxes in large particles (>53  $\mu\text{m}$ ) varied from 18 to 61 mg C m<sup>-2</sup>d<sup>-1</sup> using the ratio of POC/ $^{234}\text{Th}$  at 120 m, and from 51 to 163 mg C m<sup>-2</sup>d<sup>-1</sup> using an average ratio of POC/ $^{234}\text{Th}$  for the upper 120 m water column. In 2001, the fluxes of POC measured by traps deployed at 120 m water depth ranged from 39 to 48 mg C m<sup>-2</sup>d<sup>-1</sup>, while the  $^{234}\text{Th}$ -derived POC fluxes in large particles (>53  $\mu\text{m}$ ) varied from 7 to 37 mg C m<sup>-2</sup>d<sup>-1</sup> using a ratio of POC/ $^{234}\text{Th}$  at 120 m, and from 37 to 45 mg C m<sup>-2</sup>d<sup>-1</sup> using an average ratio of POC/ $^{234}\text{Th}$  within the 0–120 m interval. The results show that POC fluxes estimated by the  $^{234}\text{Th}$  method using the average ratio of POC/ $^{234}\text{Th}$  within the euphotic zone are similar to those measured by sediment traps. Furthermore, the results demonstrate that the variability in POC export fluxes estimated by the  $^{234}\text{Th}/^{238}\text{U}$  disequilibrium approach is strongly related to the ratio of POC/ $^{234}\text{Th}$  that is taken, and for which we have independent evidence that it may be controlled by the chemical composition of the suspended particles. The results also reveal that using POC/ $^{234}\text{Th}$  ratios in small particles may result in an estimate of the POC export flux that is considerably higher than when using POC/ $^{234}\text{Th}$  ratios in large particles (>53  $\mu\text{m}$ ). The POC flux calculated from ratios in large particles is, however, more comparable to the POC determined directly by sediment traps, but both of these estimates are much lower than that determined by using the POC/ $^{234}\text{Th}$  ratios in sinking particles. Therefore, without reliable flux values to compare with,  $^{234}\text{Th}$ -based and sediment trap approaches are complementary methods for estimating upper ocean POC export, with comparable uncertainties for both of these approaches.

Keywords: POC concentration, POC flux,  $^{234}\text{Th}$ , sediment trap, Gulf of Mexico

## INTRODUCTION

The “biological pump”, i.e., the removal of carbon from the surface ocean *via* removal of biological remains, plays a crucial role in the global cycling of carbon, nutrient and particle reactive elements. Therefore, a self-consistent estimate of fluxes and degradation rates of particulate organic carbon (POC) within the euphotic zone is important for our understanding of the biogeochemical cycling of carbon in the ocean. Sediment traps are often used to measure POC fluxes, despite possible biases by hydrodynamic and swimmer effects (Gardner, 1980; Buesseler, 1991). A knowledge of the extent of  $^{234}\text{Th}$  deficiency relative to  $^{238}\text{U}$  in the euphotic zone, combined with an assessment of the POC/ $^{234}\text{Th}$  ratio in sinking particles, has been the basis for estimating POC fluxes in

different marine environments (e.g., Buesseler *et al.*, 1992, 1995; Cochran *et al.*, 1995; Murray *et al.*, 1996). POC fluxes out of the euphotic zone are therefore determined by the product of the POC/ $^{234}\text{Th}$  ratio in sinking particles and the depth-integrated  $^{234}\text{Th}$  flux (Buesseler, 1998 and references therein). One important assumption in  $^{234}\text{Th}$ -derived POC flux assessments is that the ratio of POC/ $^{234}\text{Th}$  in particles should be relatively constant in time and space. However, recent studies have shown that ratios of POC/ $^{234}\text{Th}$  could vary with water depth, particle size fractions, plankton species, and different hydrographic regimes (e.g., Cochran *et al.*, 1995; Buesseler, 1998; Santschi *et al.*, 1999, 2003; Moran *et al.*, 2003). The ratio of POC/ $^{234}\text{Th}$  is a crucial parameter in marine biogeochemical studies. The mechanisms that control the POC/ $^{234}\text{Th}$  ratio are, however, still unresolved (Bacon *et al.*, 1996; Murray *et al.*, 1996; Buesseler, 1998; Ducklow *et al.*, 2001; Benitez-Nelson *et al.*, 2001; Coppola *et al.*, 2002; Chen *et al.*, 2003; Moran *et al.*, 2003; Santschi *et al.*, 2003).

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In a recent study, Coppola *et al.* (2002) compared POC fluxes measured by  $^{234}\text{Th}$  in suspended particles (without size-fractionation) and sediment traps using 0.6  $\mu\text{m}$  Nuclepore filters in the Barents Sea. Coppola *et al.* (2002) found that POC fluxes might be overestimated if POC/ $^{234}\text{Th}$  ratios in suspended particles are taken, and they concluded that POC flux estimates will be more reliable if the POC/ $^{234}\text{Th}$  ratios in large particles or sediment trap material are used. More recently, Moran *et al.* (2003) analyzed  $^{234}\text{Th}$  and POC data in suspended particles from the Labrador Sea and reported that POC fluxes could vary by a factor of 2–10, both due to natural variability in the POC/ $^{234}\text{Th}$  ratios and the specific procedures used to estimate the Th flux. While these two papers gave encouraging results with respect to estimating POC fluxes, neither Coppola *et al.* (2002) nor Moran *et al.* (2003) measured the POC/ $^{234}\text{Th}$  ratios in both different size-fractionated suspended and sinking particles from sediment traps at the same time. In order to further investigate the relationships between these two methods, we therefore used concurrent data from both sediment traps and size-fractionated particulate  $^{234}\text{Th}$ . Floating sediment traps were deployed at the same time as size-fractionated particulate  $^{234}\text{Th}$  samples were collected *in situ* from contrasting oceanographic settings, Cold Core Rings (CCR) vs. Warm Core Rings (WCR), in the Gulf of Mexico. Our investigation thus allows trap collected POC export fluxes to be compared with POC fluxes from assessments of  $^{234}\text{Th}$  deficiencies combined with POC/ $^{234}\text{Th}$  ratios in large particles ( $>53 \mu\text{m}$ ), small particles, or sediment trap materials.

## MATERIALS AND METHOD

Seawater, size-fractionated suspended and sinking (*via* sediment traps) particle samples from the Gulf of Mexico were collected aboard the R/V Gyre during July 1–10, 2000 and May 17–25, 2001, along a N-S transect at  $\sim 95^\circ\text{W}$  in the northwest Gulf of Mexico, extending from the coastal area near Galveston to the oligotrophic open Gulf region, and covering a CCR and a WCR, with different tracks and structures each year (Biggs, 1992; Hung *et al.*, 2003a). A CCR contains upwelled nutrient-rich waters with higher primary productivity and higher organic matter fluxes. Conversely, a WCR contains nutrient-depleted waters with lower productivity or biomass, as well as lower organic matter fluxes (Biggs, 1992; Wormuth *et al.*, 2000; Guo *et al.*, 2002a; Santschi *et al.*, 2003). Briefly, suspended particles, defined as the particles retained by filtration, of different sizes (0.5–1, 1–10, 10–53,  $>53 \mu\text{m}$ ) were collected for measurements of  $^{234}\text{Th}$  and POC with an *in situ* filtration system (Guo *et al.*, 2002a; Hung *et al.*, 2003a). In 2000, station 5 ( $27^\circ 30' \text{N}$ ,  $95^\circ 11' \text{W}$ , water depth 985 m), with a surface water temperature of

$28.81^\circ\text{C}$ , was located within a CCR, whereas station 7 ( $26^\circ 00' \text{N}$ ,  $95^\circ 20' \text{W}$ , water depth 1790 m) was a WCR, with a surface water temperature of  $29.40^\circ\text{C}$ . In 2001, the sampling locations also consisted of different hydrographic regimes, with station 4 ( $27^\circ 38' \text{N}$ ,  $94^\circ 59' \text{W}$ , water depth 638 m) inside a CCR, with a surface temperature of  $26.04^\circ\text{C}$ , and station 6 ( $26^\circ 19' \text{N}$ ,  $95^\circ 00' \text{W}$ , water depth 1632 m) within a WCR with a temperature of  $26.50^\circ\text{C}$ .

Sinking particles, defined as the particles collected by sediment traps, were collected with a floating sediment trap array (cylindrical plastic core tubes of 6.8 cm diameter and 1:10 aspect ratio), with a mesh (*ca.* 1 cm  $\times$  1 cm) covering the trap mouth, attached to a surface buoy exposed for 24 h, at depths of 75 and 120 m at stations 5 (CCR), 6, and 7 (WCR) in 2000, as well as at depths of 65, 90, 120 m at stations 4 (CCR) and 6 (WCR) in 2001. Before analysis, swimmers on all filters were carefully removed using forceps. Sinking particles were filtered separately through GF/F filters for the determination of POC and  $^{234}\text{Th}$  concentrations.

Concentrations of  $^{234}\text{Th}$  in dissolved and size-fractionated particles as well as sinking particles were determined with procedures described in Guo *et al.* (2002a). Briefly, large volumes of seawater (up to 1,000–4,000 liters) were collected by either a submersible pump for the upper water column (up to 100 m) or a multiple *in situ* pumping system (MIPS) for deep waters, which have been successfully used in a number of previous studies (Baskaran *et al.*, 1993; Guo *et al.*, 1995; Santschi *et al.*, 1999). Both submersible pump and MIPS were equipped with a series of four filters (polypropylene, Sparkling Clear Industries), with pore sizes of  $53 \mu\text{m}$ ,  $10 \mu\text{m}$ ,  $1 \mu\text{m}$ ,  $0.5 \mu\text{m}$ , followed by two  $\text{MnO}_2$ -impregnated  $0.5 \mu\text{m}$  pore sized filters for the assessment of dissolved activities. The first four consecutive filters were designed to collect  $^{234}\text{Th}$  in size-fractionated suspended particles, while the last two  $\text{MnO}_2$ -impregnated filters were intended to extract the  $<0.5 \mu\text{m}$  dissolved  $^{234}\text{Th}$ . Therefore, the six filters resulted in five different size fractions of  $^{234}\text{Th}$ , including the  $>53 \mu\text{m}$ , 10– $53 \mu\text{m}$ , 1– $10 \mu\text{m}$ , 0.5– $1 \mu\text{m}$ , and  $<0.5 \mu\text{m}$  (Guo *et al.*, 2002a). However,  $^{234}\text{Th}$  concentrations measured in 2001 were from only four fractions, the  $>53 \mu\text{m}$ ,  $10 \mu\text{m}$ ,  $1 \mu\text{m}$ , and  $<1 \mu\text{m}$ .  $^{234}\text{Th}$  in sinking particles was filtered on a GF/F filter and the filter sample was dried for the determination of the  $^{234}\text{Th}$  activity. The gamma emission of  $^{234}\text{Th}$  was determined at 63 keV on a Canberra ultra high purity Germanium well detector (Santschi *et al.*, 1999; Guo *et al.*, 2002a).

POC concentrations from both suspended particles and sinking particles were quantified on a Perkin-Elmer CHNS/O elemental analyzer (Guo and Santschi, 1997). Seawater samples were collected by Niskin bottles in different depths and several liters of subsamples were fil-

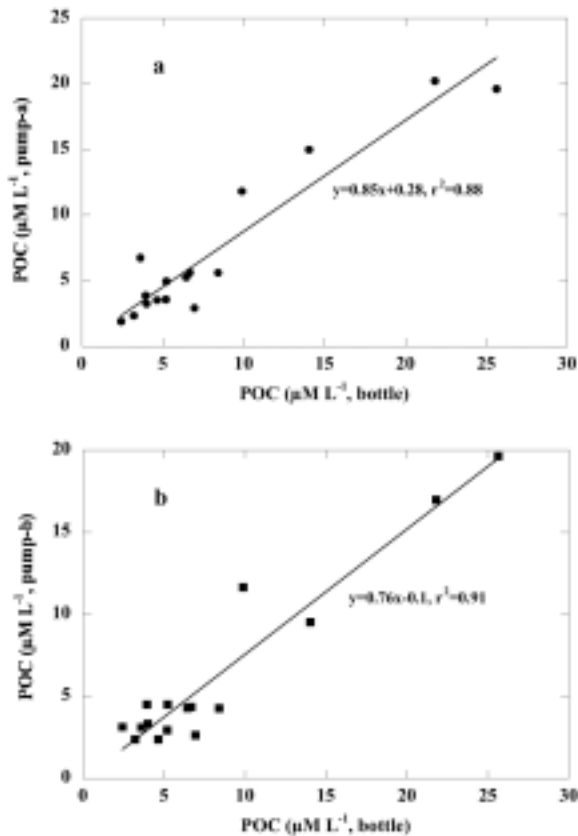


Fig. 1. The relationship between POC collected in 2001 by bottle and in situ pumping (a) POC collected by bottle and in situ pumping into a 20 L container, and subsequent filtration through 0.7  $\mu\text{m}$  GF/F filters (i.e., without size fractionation) (b) POC collected by bottle and in situ pumping, as sum of three fractions, i.e., 1–10, 10–53, >53  $\mu\text{m}$ .

tered through GF/F filters without sized fractionation (called here “bottle POC”). The pump-POC concentrations were measured by two different methods. Seawater was collected by *in situ* pumping on board deck and stored in a big carboy bottle (about 10–20 liter) and then filtered through a GF/F filter (called here “pump POC w/t sized fraction”). The other seawater sample was also collected by *in situ* pumping but filtered through a series of on-line filters, with pore sizes of 53, 10 and 0.7  $\mu\text{m}$ , as described in Guo *et al.* (2002a) and Hung *et al.* (2003b).

Charette and Moran (1999) also pointed out that POC/ $^{234}\text{Th}$  might be more biased through differences in POC determinations, i.e., bottle vs. *in situ* pump filtration, rather than due to particulate  $^{234}\text{Th}$  determinations. POC values in suspended particles can be underestimated if one would not correct for the POC that is lost in the second filtration step. Generally, POC samples in intermediate (10–53  $\mu\text{m}$ ) and large (>53  $\mu\text{m}$ ) particles are filtered by Nitex screens and re-filtered through GF/F filters. POC

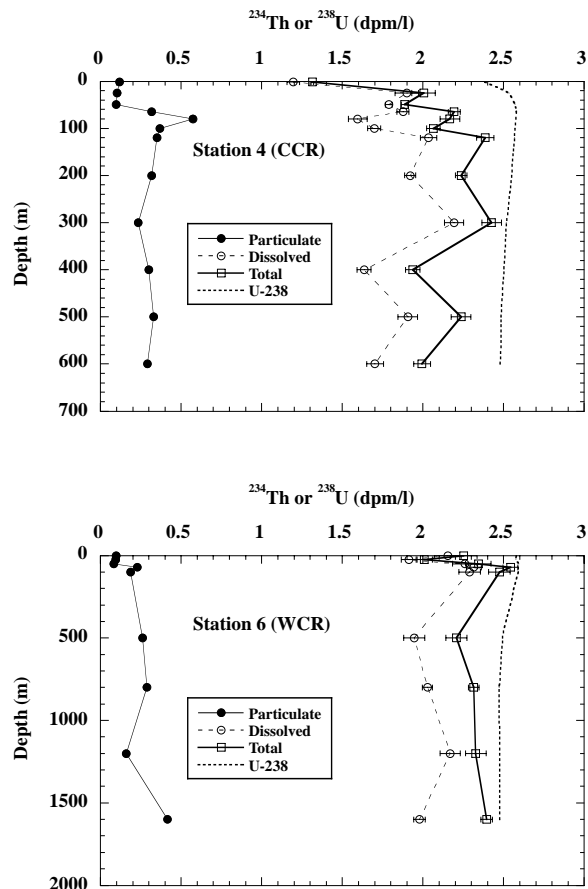


Fig. 2. Vertical distributions of dissolved, particulate and total  $^{234}\text{Th}$  (dpm/l) and  $^{238}\text{U}$  (dpm/l) in the Gulf of Mexico in 2001.

lost in the second filtration step can be as high as  $41 \pm 6\%$  in intermediate particles and  $43 \pm 6\%$  in large particles, respectively. A comparison of our total POC concentrations (>0.7  $\mu\text{m}$ ) obtained from bottle and pump data (Figs. 1a and b) reveals that the slopes of the correlations show only small variations (bottle POC/pump POC = 1.2 to 1.3), suggesting that bottle POC values are 20–30% higher than pump values, possibly due to unaccounted blanks in the bottle POC determinations, or due to the presence of swimmers in bottles. Therefore, pump POC values, which are from larger volumes with smaller biases, are likely more reliable.

## RESULTS AND DISCUSSION

### Disequilibrium of $^{234}\text{Th}$ vs. $^{238}\text{U}$

Results on activity concentrations of dissolved and total particulate  $^{234}\text{Th}$  as well as  $^{238}\text{U}$  ( $^{238}\text{U}$  (dpm/l) =  $0.07081 \times \text{salinity}$ , Ku *et al.*, 1977) in 2001 are listed in Table 1. For data from 2000, they are listed in Guo *et al.* (2002a).

Table 1. Water depth, salinity, and activity concentration (dpm/l) of  $^{238}\text{U}$ , dissolved ( $\text{Th}_d$ ), particulate ( $\text{Th}_p$ ), total  $^{234}\text{Th}$ , and size-fractionated particulate  $^{234}\text{Th}$  ( $\text{Th}_p$ )

Station	Depth (m)	S	$^{238}\text{U}$ (dpm/l)	Total $^{234}\text{Th}$ (dpm/l)	$^{234}\text{Th}/^{238}\text{U}$ ratio	$^{234}\text{Th}_d$ (<1.0 $\mu\text{m}$ )	$^{234}\text{Th}_p$ (>1.0 $\mu\text{m}$ )	$^{234}\text{Th}_p$ (1–10 $\mu\text{m}$ )	$^{234}\text{Th}_p$ (10–53 $\mu\text{m}$ )	$^{234}\text{Th}_p$ (>53 $\mu\text{m}$ )
1	2	35.00	2.48	0.198 ± 0.015	0.08	0.147 ± 0.014	0.051 ± 0.004	0.012 ± 0.002	0.014 ± 0.002	0.025 ± 0.003
2	2	35.00	2.48	0.282 ± 0.006	0.11	0.246 ± 0.006	0.036 ± 0.001	0.012 ± 0.001	0.006 ± 0.003	0.018 ± 0.007
3	2	35.00	2.48	1.225 ± 0.027	0.49	1.105 ± 0.026	0.120 ± 0.004	0.032 ± 0.002	0.031 ± 0.002	0.056 ± 0.002
4 (CCR)	2	33.64	2.38	1.314 ± 0.007	0.55	1.196 ± 0.038	0.118 ± 0.004	0.018 ± 0.001	0.032 ± 0.002	0.068 ± 0.003
4	25	35.81	2.54	2.005 ± 0.073	0.79	1.901 ± 0.073	0.104 ± 0.003	0.027 ± 0.001	0.033 ± 0.002	0.043 ± 0.001
4	50	36.29	2.57	1.886 ± 0.022	0.73	1.787 ± 0.021	0.099 ± 0.003	0.031 ± 0.001	0.031 ± 0.002	0.037 ± 0.002
4	65	36.42	2.58	2.194 ± 0.038	0.85	1.876 ± 0.037	0.318 ± 0.009	0.063 ± 0.003	0.183 ± 0.008	0.073 ± 0.004
4	80	36.39	2.58	2.167 ± 0.060	0.84	1.595 ± 0.058	0.572 ± 0.016	0.035 ± 0.002	0.036 ± 0.002	0.501 ± 0.015
4	100	36.31	2.57	2.064 ± 0.042	0.80	1.697 ± 0.041	0.367 ± 0.010	0.067 ± 0.004	0.070 ± 0.004	0.230 ± 0.008
4	120	36.25	2.57	2.386 ± 0.052	0.93	2.035 ± 0.052	0.351 ± 0.007	0.064 ± 0.003	0.118 ± 0.002	0.169 ± 0.006
4	200	36.00	2.55	2.238 ± 0.036	0.88	1.921 ± 0.035	0.317 ± 0.008	0.067 ± 0.005	0.143 ± 0.005	0.107 ± 0.004
4	300	35.56	2.52	2.426 ± 0.060	0.96	2.193 ± 0.059	0.233 ± 0.006	0.074 ± 0.004	0.086 ± 0.003	0.073 ± 0.004
4	400	35.32	2.50	1.937 ± 0.044	0.77	1.635 ± 0.043	0.302 ± 0.008	0.079 ± 0.003	0.091 ± 0.004	0.132 ± 0.006
4	500	35.08	2.48	2.236 ± 0.061	0.90	1.906 ± 0.060	0.330 ± 0.009	0.175 ± 0.007	0.084 ± 0.003	0.072 ± 0.003
4	600	34.98	2.48	1.994 ± 0.052	0.81	1.703 ± 0.052	0.291 ± 0.008	0.149 ± 0.007	0.073 ± 0.002	0.070 ± 0.003
5	2	35.00	2.48	0.597 ± 0.018	0.24	0.472 ± 0.017	0.125 ± 0.004	0.021 ± 0.001	0.053 ± 0.002	0.051 ± 0.003
6 (WCR)	2	36.42	2.58	2.252 ± 0.083	0.87	2.154 ± 0.083	0.098 ± 0.003	0.038 ± 0.002	0.036 ± 0.002	0.024 ± 0.001
6	25	36.40	2.58	2.008 ± 0.050	0.78	1.914 ± 0.050	0.094 ± 0.003	0.029 ± 0.001	0.049 ± 0.002	0.016 ± 0.001
6	50	36.62	2.59	2.344 ± 0.078	0.90	2.261 ± 0.078	0.083 ± 0.002	0.024 ± 0.008	0.036 ± 0.001	0.024 ± 0.001
6	72	36.60	2.59	2.543 ± 0.047	0.98	2.315 ± 0.046	0.228 ± 0.007	0.038 ± 0.002	0.069 ± 0.002	0.122 ± 0.007
6	100	36.61	2.59	2.475 ± 0.067	0.96	2.289 ± 0.067	0.186 ± 0.007	0.033 ± 0.002	0.056 ± 0.002	0.098 ± 0.006
6	500	35.21	2.49	2.207 ± 0.066	0.89	1.946 ± 0.066	0.261 ± 0.006	0.086 ± 0.004	0.093 ± 0.004	0.082 ± 0.003
6	800	34.92	2.47	2.315 ± 0.032	0.94	2.028 ± 0.031	0.287 ± 0.008	0.060 ± 0.003	0.096 ± 0.005	0.132 ± 0.005
6	1200	34.96	2.48	2.328 ± 0.063	0.94	2.169 ± 0.063	0.159 ± 0.002	0.087 ± 0.002	0.039 ± 0.001	0.033 ± 0.001
6	1600	34.97	2.48	2.395 ± 0.037	0.97	1.979 ± 0.036	0.416 ± 0.010	0.206 ± 0.007	0.078 ± 0.003	0.132 ± 0.006

Similar to results from 2000, the total  $^{234}\text{Th}$  concentration measured in 2001 was deficient relative to that of  $^{238}\text{U}$  in the upper water column (0–100 m) at both CCR and WCR stations (Fig. 2). The average ratio of  $^{234}\text{Th}/^{238}\text{U}$  within the upper layer in the CCR (0.73) was lower than that in the WCR (0.89). On the other hand, the phytoplankton biomass (expressed as concentrations of chlorophyll *a*) was higher inside the CCR (0.1 to 0.48  $\mu\text{g chl } a \text{ L}^{-1}$ ) than in the WCR (0.05 to 0.25  $\mu\text{g chl } a \text{ L}^{-1}$ , Hung *et al.*, 2003b). As expected, the higher biological activity inside the CCR resulted in higher extent of  $^{234}\text{Th}$  scavenging. A similar trend was also reported for 2000 by Guo *et al.* (2002a). Furthermore, a significant deficiency of total  $^{234}\text{Th}$  relative to  $^{238}\text{U}$  in the bottom water below ~600 m was also observed at the CCR station as well as in the WCR close to 1500 m. The disequilibrium in deep waters is likely caused by strong bottom currents in the Gulf of Mexico (Hamilton and Lugo-Fernandez, 2001). This interpretation is strongly supported by high particulate (1–10  $\mu\text{m}$ )  $^{234}\text{Th}$  activities (0.17 to 0.15 dpm/L) within 500–600 m relative to low particulate  $^{234}\text{Th}$  activity (0.01 to 0.07 dpm/L) in the upper water column at the CCR station in 2001 (Table 1). Moreover, the vertical profiles of suspended particulate matter (SPM) also showed higher values at 400–500 m water depth in the CCR and 1200–1600 m in the WCR, respectively (Fig. 3c). Deep boundary scavenging in the Gulf of Mexico

was also reported by Baskaran *et al.* (1996) and Guo *et al.* (2002a).

Vertical distributions of  $^{234}\text{Th}$  in different size fractions in the CCR (S4) and WCR (S6) are presented in Table 1, Figs. 3a and b. In general, large (>53  $\mu\text{m}$ ) particles had the highest percentage of  $^{234}\text{Th}$ , followed by intermediate (10–53  $\mu\text{m}$ ) particles and then the 1–10  $\mu\text{m}$  fraction. However, in 2000, the highest percentage of  $^{234}\text{Th}$  was observed in the 10–53  $\mu\text{m}$  fraction (Guo *et al.*, 2002a). The difference in  $^{234}\text{Th}$  size distributions between 2000 and 2001 seemed to be affected by the change in major phytoplankton species, and thus, particle sizes and composition. The sorption of thorium, as a particle-reactive element, is strongly dependent on particle characteristics and chemical composition (Guo *et al.*, 2002b; Quigley *et al.*, 2002; Santschi *et al.*, 2003). According to Hung *et al.* (2003b), the main phytoplankton groups in the July 2000 expedition were *prochlorophytes*, *haptophytes* and *cyanobacteria*, while phytoplankton groups in the May 2001 expedition were more diverse, consisting of *prymnesiophytes*, *prasinophytes*, *prochlorophytes*, *pelagophytes* and *dinoflagellates*. In addition, an exceptionally high  $^{234}\text{Th}$  concentration in large (>53  $\mu\text{m}$ ) particles was found within 80–100 m water depth, which coincided with the occurrence of a *prymnesiophyte* maximum, where this species accounted for 65% of total chl *a* concentration (Hung *et al.*, 2003b).

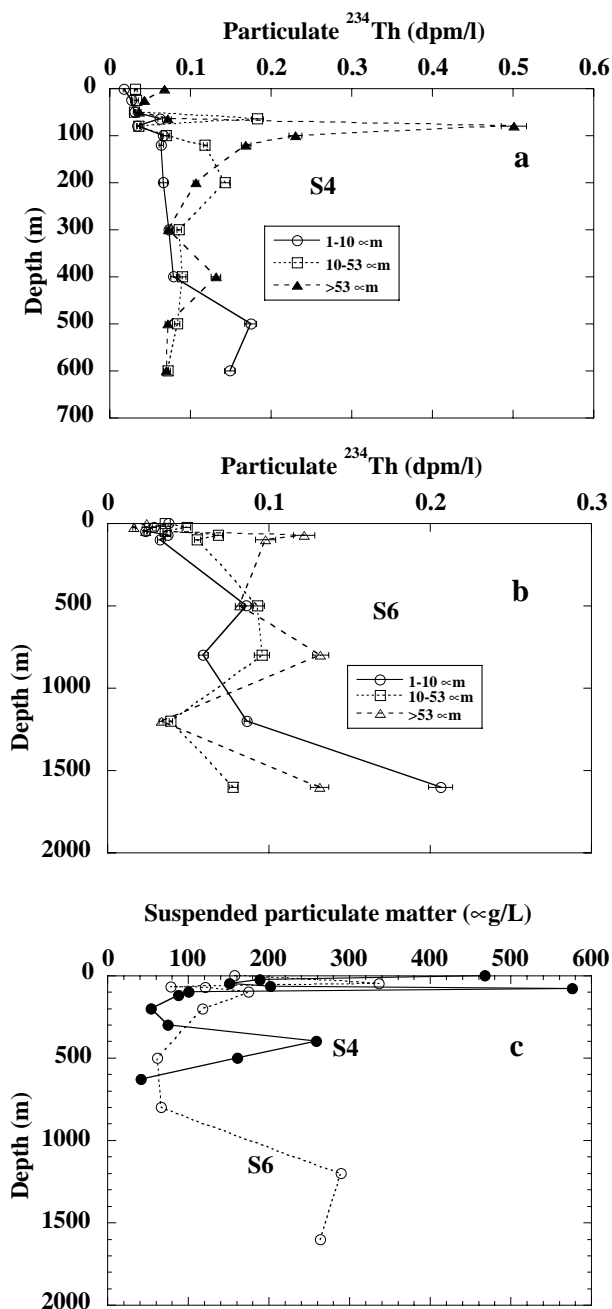


Fig. 3. Vertical profiles of particulate  $^{234}\text{Th}$  in different size fractions (1–10, 10–53, >53  $\mu\text{m}$ ) in the CCR (a, S4) and the WCR (b, S6) as well as suspended particulate matter (c, SPM) in 2001.

Differences in results between the two cruises can thus be explained by differences in phytoplankton compositions, which may have resulted in different acid polysaccharide-rich Th(IV)-binding ligands in the water column (Santschi *et al.*, 2003). Furthermore, the phytoplankton species size may also be a crucial factor affecting

particulate Th scavenging. Unfortunately, data on the exact sizes of phytoplankton species in our samples are limited. According to Lalli and Parsons (1994), the normal range of phytoplankton sizes in the majority of our samples could have ranged from about 0.2 to 200  $\mu\text{m}$ . Nevertheless, it is interesting to note that *prymnesiophytes*, which have sizes ranging from 2 to 20  $\mu\text{m}$ , accounted for 25 to 65% of the total phytoplankton biomass in the 2001 expedition (Hung *et al.*, 2003b), while the highest concentrations of  $^{234}\text{Th}$  were found in large suspended particles (>53  $\mu\text{m}$ ) rather than in the other particle size fractions (1–10 or 10–53  $\mu\text{m}$ ) within the euphotic zone. One possibility is that *prymnesiophytes* may be responsible for the production of mucilaginous organic matter (Graham and Wilcox, 2000) resulting in larger aggregates, which can coagulate into larger particle sizes and efficiently scavenge  $^{234}\text{Th}$ .

#### Ratios of $\text{POC}/^{234}\text{Th}$ , Th flux and POC flux

The ratios of  $\text{POC}/^{234}\text{Th}$  in different size fractions (1–10, 10–53, >53  $\mu\text{m}$ ) are shown in Fig. 4 for the 2000 and 2001 cruises. The average ratios of  $\text{POC}/^{234}\text{Th}$  in small (1–10  $\mu\text{m}$ ), intermediate (10–53  $\mu\text{m}$ ), and large particles (>53  $\mu\text{m}$ ) in open Gulf waters in 2001 were  $82 \pm 47$ ,  $12 \pm 3$ , and  $2.8 \pm 2.3 \mu\text{mol dpm}^{-1}$ , respectively. Lower ratios of  $\text{POC}/^{234}\text{Th}$  were found in large particles, while higher ratios were observed in small particles, with about two orders of magnitude difference between lowest (1  $\mu\text{mol dpm}^{-1}$ ) and highest (200  $\mu\text{mol dpm}^{-1}$ ) values. The trend of these results is similar to that from the 2000 cruise, showing that  $\text{POC}/^{234}\text{Th}$  ratios increase with decreasing particle size, with an average of 37, 3.6, and 3.1  $\mu\text{mol dpm}^{-1}$  for small, intermediate, and large particles, respectively (Guo *et al.*, 2002a). The ratios of  $\text{POC}/^{234}\text{Th}$  in sinking particles collected in sediment traps at 120 m from both CCR and WCR stations in 2001 were  $5.6 \pm 0.7 \mu\text{mol dpm}^{-1}$ , which is close to the values for intermediate to large particles (Table 2). However, there was an exceptionally high ratio (23.8  $\mu\text{mol dpm}^{-1}$ ) of  $\text{POC}/^{234}\text{Th}$  at station 7 in 2000 cruise, for which we do not have a ready explanation. However, occasional excursions in  $\text{POC}/^{234}\text{Th}$  ratios are also seen in the suspended matter data in 2001. A number of studies have shown that relatively low  $\text{POC}/^{234}\text{Th}$  ratios can be observed in both sediment material ( $\text{POC}/^{234}\text{Th}$  ratios ranging from  $\sim 2$  to 15) and large (>53  $\mu\text{m}$ ) particles ( $\sim 1$  to 8) (Buesseler *et al.*, 1995; Bacon *et al.*, 1996; Murray *et al.*, 1996; Guo *et al.*, 1997, 2002a; Benitez-Nelson *et al.*, 2001; Coppola *et al.*, 2002; Santschi *et al.*, 2003). Our ratios of  $\text{POC}/^{234}\text{Th}$  in both cruises in the Gulf of Mexico are thus in good agreement with previous data.

However, Moran and his colleague reported considerable higher  $\text{POC}/^{234}\text{Th}$  ratios in large particles (>53  $\mu\text{m}$ ), with a large variability, ranging from 5 to 50  $\mu\text{mol}$

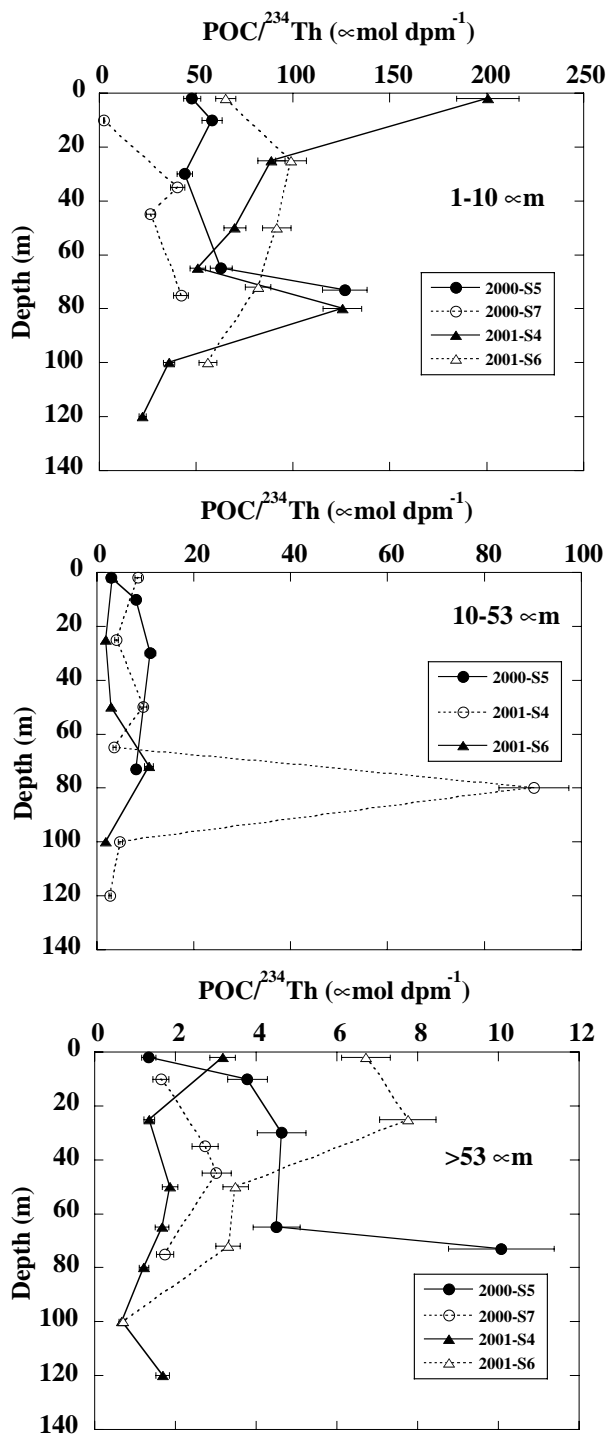


Fig. 4. Ratios of  $\text{POC}/^{234}\text{Th}$  in different size fractions (1–10, 10–53, >53  $\mu\text{m}$ ) in the CCR and WCR in 2000 and 2001.

$\text{dpm}^{-1}$  in the Atlantic Ocean (Charette and Moran, 1999), 2 to 300  $\mu\text{mol dpm}^{-1}$  in the Gulf of Maine (Charette *et al.*, 2001), and 3.8 to 63  $\mu\text{mol dpm}^{-1}$  in the Labrador Sea (Moran *et al.*, 2003). The discrepancy between data sets

could be related to differences in both sampling procedures of POC and study areas (see also discussion below).

The mechanisms that control the ratios of  $\text{POC}/^{234}\text{Th}$  in suspended and sinking particles are not fully understood. However, several possibilities have been proposed to interpret these observations. 1) Organic carbon can be more easily remineralized than Th(IV) during grazing and bacterial degradation of large aggregates, since Th(IV) appears less sensitive to particle mineralization (Arraes-Mescoff *et al.*, 2001; Coppola *et al.*, 2002), possibly due to more refractory carrier phases or re-adsorption to new phases. 2) Guo *et al.* (2002a) argued that because more  $^{234}\text{Th}$  is found associated with intermediate and large particles than with small particles,  $^{234}\text{Th}$  must be transferred by coagulation from small particles (with large surface area) to intermediate and large particles (with lower surface area) more swiftly than bulk POC. 3) Field measurements suggest that Th(IV) may form strong complexes with transparent exopolymer particles (TEP) or acid polysaccharides produced by bacteria and phytoplankton (e.g., Niven *et al.*, 1997; Guo *et al.*, 2002a; Santschi *et al.*, 2003). 4) Laboratory results show a much stronger Th(IV) binding to polysaccharide-rich exopolymeric material than to inorganic minerals, with the highest affinity of Th(IV) to carbohydrates and acid polysaccharides (Quigley *et al.*, 2002; Guo *et al.*, 2002b). 5) Field results demonstrate that particulate  $^{234}\text{Th}/\text{POC}$  ratios are positively correlated to the content of total acid polysaccharides and uronic acids in both suspended and sinking particles (Santschi *et al.*, 2003). However, the observation that the main direction of organic carbon flow is by degradation from large to small particles (e.g., Santschi *et al.*, 1995; Amon and Benner, 1996; Guo *et al.*, 1996), while Th(IV) is “pumped” up the particle size spectrum from colloids to small to large particles (e.g., Honeyman and Santschi, 1989; Quigley *et al.*, 1996, 2001) is consistent with the overall trend of decreasing  $\text{POC}/^{234}\text{Th}$  ratios with increasing particle size, as observed here and in Guo *et al.* (2002a).

In the following section, the different ratios in different sized particles are used to calculate POC fluxes. The POC flux at a given depth that is derived from  $^{234}\text{Th}$  fluxes and  $(\text{POC}/^{234}\text{Th})_p$  ratio in particles is calculated by Eq. (1):

$$[\text{Flux of POC}] = (\text{POC}/^{234}\text{Th})_p \times [\text{flux of } ^{234}\text{Th}] \quad (1)$$

where  $(\text{POC}/^{234}\text{Th})_p$  is in  $\mu\text{mol dpm}^{-1}$ , and measured in different sized particles collected at a given depth, [flux of  $^{234}\text{Th}$ ] is the integrated flux of  $^{234}\text{Th}$  ( $\text{dpm m}^{-2}\text{day}^{-1}$ ) from the surface down to a given depth, using a trapezoidal integration method to calculate the  $^{234}\text{Th}$  deficiency with respect to  $^{238}\text{U}$ -supported values. Further-

Table 2.  $(POC/^{234}Th)_p$  in different suspended particle fractions and in sinking particles (collected by sediment traps at 120 m), and flux of  $^{234}Th$  ( $dpm/m^2/d$ ), estimated within the euphotic zone (0–120 m) of the Gulf of Mexico

	Ratio 1–10 $\mu m$	Ratio 10–53 $\mu m$	Ratio >53 $\mu m$	Ratio Sinking particles	$^{234}Th$ flux Deficiency	$^{234}Th$ flux Sediment trap
<b>2000</b>						
<b>S5 (CCR)</b>					3148	821
POC/Th (a)	67.6	7.3	4.3			
POC/Th (b)	65.3	6.4	1.6			
POC/Th (c)				9.5		
<b>S6</b>					1016	296
POC/Th (c)				7.7		
<b>S7 (WCR)</b>					1576	287
POC/Th (a)	35.9	n.d.	2.7			
POC/Th (b)	58.5	n.d.	0.9			
POC/Th (c)				23.8		
<b>2001</b>						
<b>S4 (CCR)</b>					1878	651
POC/Th (a)	85.0	17.7	1.7			
POC/Th (b)	22.4	2.7	1.7			
POC/Th (c)				6.2		
<b>S6 (WCR)</b>					845	632
POC/Th (a)	78.9	4.2	4.4			
POC/Th (b)	56.2	1.9	0.7			
POC/Th (c)				5.1		

$POC/^{234}Th$  is given  $\mu mol C dpm^{-1}$ . (a) is the average ratio of  $POC/^{234}Th$  in different sized suspended (1–10  $\mu m$ , 10–53  $\mu m$  and >53  $\mu m$ ) particles from 0 to 120 m. (b) is the ratio of  $POC/^{234}Th$  in different sized suspended particles at 120 m depth. (c) is the ratio of  $POC/^{234}Th$  in sinking particles collected by sediment traps.

more, the fluxes ( $dpm m^{-2}day^{-1}$ ) of different size fractions of particulate  $^{234}Th$ , i.e., 1–10, 10–53 and >53  $\mu m$ , were also estimated by a simple one-dimensional box model (Bacon and Anderson, 1982; Coale and Bruland, 1985; Buesseler *et al.*, 1992; Guo *et al.*, 2002a). This method assumes that only one of these size fractions is representative for the particle assemblage that remove  $^{234}Th$  for the water, in addition, we assumed steady state conditions and neglected advective and diffusive processes. These assumptions are reasonable since inside a WCR or CCR, the 1-D assumption is much more justified than anywhere else, as both are water columns where the euphotic zone had been isolated from the surrounding waters for at least a few months (Biggs, 1992), much longer than the mean life of  $^{234}Th$ . It is thus important to note that steady state only requires that changes are slow compared to the  $^{234}Th$  half-life of 24 days. The particles should be continually formed, removed and/or degraded during the sampling period because the hydrographic regime inside a ring or eddy changes only very slowly over time. Since the POC flux is normally estimated down to 120 m, we used an extrapolation approach to estimate the POC flux down to 120 m when  $^{234}Th$  or POC data in the large particles were not available at a particular depth.

The  $^{234}Th$  fluxes estimated by the  $^{234}Th$  deficiency with respect to  $^{238}U$ -supported values ranged from 1016 to 3148 in 2000, and 845 to 1878  $dpm m^{-2}d^{-1}$  in 2001 (Table 2). The integrated  $^{234}Th$  fluxes in small, intermediate and large particles in the CCR assessed according to Guo *et al.* (2002a) ranged from 2594 to 3440, 2371 to 3262 and 1832 to 3153  $dpm m^{-2}d^{-1}$ , respectively, in both years, while the predicted  $^{234}Th$  fluxes in the WCR varied from 1245 to 2015, 1075 to 1688, and 851 to 1569  $dpm m^{-2}d^{-1}$ .

The results demonstrate that 1) the calculated  $^{234}Th$  fluxes for different size fractions decreased with increasing particle size, (i.e., (1–10  $\mu m$ ) > (10–53  $\mu m$ ) > (>53  $\mu m$ )); 2) higher biological activity inside the CCR resulted in higher  $^{234}Th$  fluxes; and 3)  $^{234}Th$  fluxes by large particles (>53  $\mu m$ ) are similar to those expected by the  $^{234}Th$  deficiency. The first phenomenon can be explained by coagulation resulting in the transfer of  $^{234}Th$  from smaller to larger particles (Guo *et al.*, 2002a). The second phenomenon indicates that biological activity plays an important role in Th scavenging. Indeed, the phytoplankton biomass in the CCR was higher than that in the WCR during both expeditions, suggesting that the  $^{234}Th$  flux was strongly related to nutrient supply and *in situ*

phytoplankton biomass (Hung *et al.*, 2003b).

The  $^{234}\text{Th}$  fluxes in drifting sediment traps were 2–4 times (excluding one high value at the WCR station in 2000) lower than those estimated in large particles ( $>53\ \mu\text{m}$ ). When  $^{234}\text{Th}$  fluxes collected by sediment traps are compared to expected fluxes calculated from the  $^{234}\text{Th}$ -deficiency, the trapping efficiency of sediment traps was only about 30%, if we assume that all  $^{234}\text{Th}$  produced from  $^{238}\text{U}$  was totally removed by particles. The results thus indicate that  $^{234}\text{Th}$  fluxes might be undercollected by sediment traps. Alternatively, other factors might be responsible, such as  $^{234}\text{Th}$ -binding organic matter leaching out into the dissolved fraction during deployment period. In 2001, the average amount of DOC that leached off the POC during filtration (e.g., the filtrate in the solution after filtration of sinking particles) normalized to POC ranged from 18%, 21%, and 31% of POC at 65 m, 90 m and 120 m, respectively. The result illustrates that a considerable amount (about 23%) of POC was released during the filtration process, amounts for which reported POC concentrations were corrected for. It is also possible that some  $^{234}\text{Th}$  may have been also lost during the filtration of POC, for which the  $^{234}\text{Th}$  concentration could not be corrected for due to detection problems. However, such possible losses likely do not explain a factor of 3 discrepancy. Additionally, natural current and swimmer activity may also have affected the trapping efficiency. Regardless of the exact factor, our results are in good agreement with previous studies, where both approaches had been compared (Buesseler *et al.*, 1995; Buesseler, 1998).

#### Comparison of POC fluxes determined by sediment traps and $^{234}\text{Th}$ fluxes

In 2000, the POC fluxes measured directly by sediment traps at 120 m, ranged from 60 to 148  $\text{mg C m}^{-2}\text{d}^{-1}$ , while  $^{234}\text{Th}$ -derived POC fluxes in large particles ( $>53\ \mu\text{m}$ ) varied from 51 to 163  $\text{mg C m}^{-2}\text{d}^{-1}$ , using the average ratio of  $\text{POC}/^{234}\text{Th}$  within 0–120 m, and from 17 to 60  $\text{mg C m}^{-2}\text{d}^{-1}$  using a single ratio of  $\text{POC}/^{234}\text{Th}$  at 120 m (Table 3). If the POC flux is estimated by using the  $\text{POC}/^{234}\text{Th}$  ratio in sinking particles multiplied by the calculated  $^{234}\text{Th}$  flux from the euphotic zone, one would calculate POC fluxes ranging from 94 to 450  $\text{mg C m}^{-2}\text{d}^{-1}$  (Table 3). In 2001, the fluxes of POC measured by traps deployed at 120 m water depth ranged from 39 to 48  $\text{mg C m}^{-2}\text{d}^{-1}$ , while the  $^{234}\text{Th}$ -derived POC fluxes varied from 38 to 45  $\text{mg C m}^{-2}\text{d}^{-1}$ , using the average ratio of  $\text{POC}/^{234}\text{Th}$  integrated from 0 to 120 m, and from 7 to 38  $\text{mg C m}^{-2}\text{d}^{-1}$  using the  $\text{POC}/^{234}\text{Th}$  ratio at 120 m depth. If the POC flux would be estimated by the product of the  $^{234}\text{Th}$  flux and the  $\text{POC}/^{234}\text{Th}$  ratio in sediment trap material, one would calculate POC fluxes varying from 52 to 140  $\text{mg C m}^{-2}\text{d}^{-1}$  (Table 3). If we would choose  $\text{POC}/$

Table 3. Flux of POC ( $\text{mg C m}^{-2}\text{d}^{-1}$ ) measured directly by sediment traps and estimated by the  $^{234}\text{Th}$ -flux and  $(\text{POC}/^{234}\text{Th})_p$  ratios from large suspended particles ( $>53\ \mu\text{m}$ ) or sinking material from the Gulf of Mexico

	POC Sediment trap	POC <sup>(a)</sup> ( $>53\ \mu\text{m}$ )	POC <sup>(b)</sup> ( $>53\ \mu\text{m}$ )	POC <sup>(c)</sup> (sinking material)
2000				
S5-120 m	148	163	60	359
S6-120 m	65	n.d.	n.d.	94
S7-120 m	60	51	17	450
2001				
S4-120 m	48	38	38	140
S6-120 m	39	45*	7*	52*

<sup>(a)</sup>POC was calculated by the  $^{234}\text{Th}$  deficit times average ratio (0–120 m) of  $\text{POC}/^{234}\text{Th}$  in large particles ( $>53\ \mu\text{m}$ ).

<sup>(b)</sup>POC was calculated by the  $^{234}\text{Th}$  deficit times ratio of  $\text{POC}/^{234}\text{Th}$  in large particles ( $>53\ \mu\text{m}$ ) at 120 m.

<sup>(c)</sup>POC was calculated by the  $^{234}\text{Th}$  deficit times ratio of  $\text{POC}/^{234}\text{Th}$  in sinking particles (collected by sediment traps) at 120 m.

\* $^{234}\text{Th}$  fluxes were integrated down to 120 m, but the  $\text{POC}/^{234}\text{Th}$  ratio was chosen at as the value at 100 m.

$^{234}\text{Th}$  ratios from small and intermediate particles to calculate the POC flux, the POC export fluxes estimated from small (1–10  $\mu\text{m}$ ) and intermediate (10–53  $\mu\text{m}$ ) particles would be much higher, with large variations, ranging from 505 to 2554  $\text{mg C m}^{-2}\text{d}^{-1}$  for small particles, and from 19 to 399  $\text{mg C m}^{-2}\text{d}^{-1}$  for intermediate particles, respectively, for both expeditions. These high values might likely be an overestimate. Similar results have been reported by other investigators (Murray *et al.*, 1996; Coppola *et al.*, 2002) and the results demonstrate that small particles are not a suitable particle fraction to estimate POC export fluxes.

Although the POC flux estimated by  $^{234}\text{Th}$  and sediment traps can have large variations (Moran *et al.*, 2003), and the optimal approach for estimating POC export fluxes from the euphotic zone are still being debated (Buesseler, 1991), estimating the POC export flux from sediment trap data still remains an important approach. In our study, the POC flux was also estimated by drifting sediment traps, which were seldom assessed in the Gulf of Mexico. As discussed above, sediment traps might underestimate POC fluxes due to particle degradation during the collecting period (24 hrs) and undertrapping due to effects of currents or swimmer activity. While POC loss was corrected (about 20% of POC lost), an unknown amount of  $^{234}\text{Th}$  could have been lost during the same time that was not corrected. Regardless, our POC flux data estimated by sediment traps fall within the range of previously reported POC fluxes for oligotrophic oceanic areas (Murray *et al.*, 1996; Hernes *et al.*, 2001; Bidigare *et al.*, 2003). Thus, the POC flux, estimated by sediment

traps as a reference, can be compared to  $^{234}\text{Th}$ -derived fluxes, i.e., by the product of [ $^{234}\text{Th}$  flux] and the average  $\text{POC}/^{234}\text{Th}$  in large particles ( $>53\ \mu\text{m}$ ) from the euphotic zone at 120 m (Table 3). The results demonstrate that the POC fluxes estimated by an average ratio within the euphotic zone multiplied by the  $^{234}\text{Th}$  flux are close to the POC flux measured by sediment traps, with an average value for the flux ratio of  $0.97 \pm 0.19$  (Fig. 5). While these comparable results cannot be taken as a sign for the accuracy of the flux estimates, they do indicate that taking an average ratio of  $\text{POC}/^{234}\text{Th}$  within the euphotic zone might be a suitable approach for estimating POC fluxes in the future. Conversely, ratios of POC flux estimates relying on  $\text{POC}/^{234}\text{Th}$  ratios from a given depth or from sediment trap material, to the POC flux measured by sediment traps, range from 0.2 to 0.8 (average  $0.42 \pm 0.26$ ), and from 1.3 to 7.5 (average  $3.5 \pm 2.7$ ), respectively. These results show that POC fluxes estimated by both approaches ( $\text{POC}/^{234}\text{Th}$  ratios at a certain depth or from sinking particles) seem to be significantly lower or higher than the POC flux measured by drifting sediment traps, assuming the sediment trap POC flux can be used as a reference value.

Recently, Moran *et al.* (2003) reported that the POC flux estimated by the  $^{234}\text{Th}$  approach can vary over an order of magnitude, depending on methods for assessing it. As mentioned before, the ratios of  $\text{POC}/^{234}\text{Th}$  in large particles ( $>53\ \mu\text{m}$ ) reported by Moran and his colleagues (Charette and Moran, 1999; Charette *et al.*, 2001; Moran *et al.*, 2003), are much higher than other values reported in the literature (Buesseler *et al.*, 1995; Buesseler, 1998; Bacon *et al.*, 1996; Murray *et al.*, 1996; Benitez-Nelson *et al.*, 2001; Guo *et al.*, 2002a; Coppola *et al.*, 2002; Bidigare *et al.*, 2003). The high ratios of  $\text{POC}/^{234}\text{Th}$  in large particles ( $>53\ \mu\text{m}$ ) reported by Moran, Charette and coworkers appear to result from high POC concentration values for large particles (e.g.,  $>53\ \mu\text{m}$ ,  $0.1$  to  $2\ \mu\text{M-C}$  vs.  $0.05$  to  $0.4\ \mu\text{M-C}$  by other investigators). Charette and Moran (1999) also pointed out that the difference in  $\text{POC}/^{234}\text{Th}$  might be associated with sampling techniques used for assessing POC (i.e., bottle vs. *in situ* pump filtration) rather than to particulate  $^{234}\text{Th}$ . Besides differences in sampling techniques and sample treatments, the discrepancy of POC concentrations among these different investigations is likely due to differences in sampling locations and seasons. This is confirmed by the study of Gardner *et al.* (2003), who analyzed POC data from the literature. These authors reported that POC ( $>0.7\ \mu\text{m}$ ) measured by filtration from bottles or by *in situ* filtration with pumps can vary by factors as large as 200 (bottle POC/pump POC) between sampling methods in cold, high-latitude, water, while it would only vary by a factor of 1.2 to 5 in temperate waters. Gardner *et al.* (2003) listed several possible reasons for interpreting the distinction

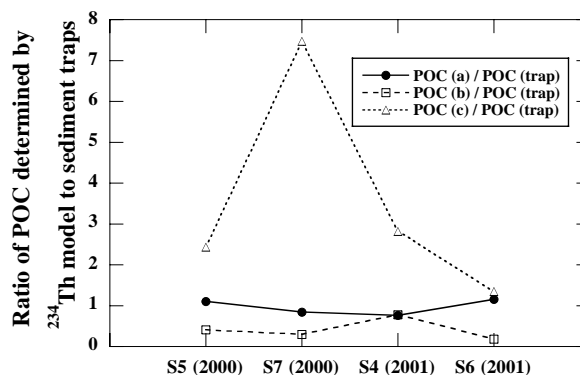


Fig. 5. Ratio of POC export flux determined by the  $^{234}\text{Th}$  approach to that determined by sediment traps. (a) is the average ratio of  $\text{POC}/^{234}\text{Th}$  in different sized ( $1\text{--}10\ \mu\text{m}$ ,  $10\text{--}53\ \mu\text{m}$  and  $>53\ \mu\text{m}$ ) suspended particles from 0 to 120 m. (b) is the ratio of  $\text{POC}/^{234}\text{Th}$  in different sized suspended particles at 120 m. (c) is the ratio of  $\text{POC}/^{234}\text{Th}$  in sinking particles collected by sediment traps.  $\text{POC}(\text{trap})$  is the POC flux directly measured by sediment traps.

between the two sampling methods and they concluded that the one to two orders of magnitude differences of POC in high latitude, cold-water regimes cannot be readily explained by sampling biases, and would need further investigations.

## CONCLUSIONS

Taking POC export flux from sediment trap data as a reference, and comparing them to those measured by the  $^{234}\text{Th}$  method, it can be concluded that 1) the POC fluxes estimated from small and intermediate sized particles by the integral  $^{234}\text{Th}$  approach are much higher than POC flux measured by sediment traps; 2) although the data in this study are only from an oligotrophic regime, there is a good consistency between the POC flux measured by sediment traps and by the integrated  $^{234}\text{Th}$  flux multiplied by the average ratio of  $\text{POC}/^{234}\text{Th}$  in large ( $>53\ \mu\text{m}$ ) particles from the euphotic zone, more temporal and seasonal investigations using a similar approach are needed to confirm this; 3) the variability in POC export fluxes estimated by the  $^{234}\text{Th}$ -based approach is strongly related to the ratio of  $\text{POC}/^{234}\text{Th}$  in different sized particles, for which we have independent evidence that it may be controlled by the content of exopolymeric acid polysaccharides. More field experiments are needed to further explore the  $\text{POC}/\text{Th}$  ratio in suspended and sinking particles, as well as its dependency on physical, biological and chemical factors.

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