

Does adsorption of dissolved organic carbon and thorium onto membrane filters affect the carbon to thorium ratios, a primary parameter in estimating export carbon flux?



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ABSTRACT

The particulate organic carbon (POC) to ²³⁴Th ratio, or POC/²³⁴Th, is crucial to constrain the ²³⁴Th-derived downward export flux. Marine particles for ²³⁴Th based export studies are typically collected via two sampling modes: filtration of Niskin or GO-FLO bottle water samples and filtration of in situ pumped samples. Large discrepancies have been frequently observed between these bottle and pump filtration methods and attributed to the difference in adsorption of dissolved material. We noted however, that simultaneous measurements of carbon and ²³⁴Th have not been made to evaluate such a putative effect on the POC/²³⁴Th ratio. In this study, we adopted a “two filters in-line” approach method with one stacked on another and we measured both carbon and ²³⁴Th to compare their adsorption behavior in bottle and pump sampling modes. We proposed that the ²³⁴Th and carbon on the second filter (filter-B) might be attributable to direct adsorption from the dissolved phase (including the partial capture from the submicron particles) and/or breakdown of particles initially collected on the first filter (filter-A). The relative importance of these two processes differed between the two filtration modes. For bottle sampling, we observed significantly positive correlation ($R^2 = 0.54$) between the ²³⁴Th recorded on the second filter and dissolved ²³⁴Th activities, suggesting that adsorption was the dominant contributor to the second filter. The overestimation due to adsorption (filter-B/filter-A) is estimated to be $22 \pm 7\%$ for POC and $25 \pm 17\%$ for particulate ²³⁴Th. The effect of adsorption on the POC/²³⁴Th, on the other hand, would be negligible since the adsorption-corrected and -uncorrected POC/²³⁴Th on filter-A were similar. For the large volume pumping mode, the absorbed ²³⁴Th on the filters appeared to reach the saturation state as evidenced by the fact that the amount of particulate ²³⁴Th (dpm cm^{-2}) on filter-B was independent of the filtered sample volume. We justified that the saturation amount should be $>0.21 \text{ dpm cm}^{-2}$ which was the highest unsaturated value from the bottle sample, but $<0.31 \text{ dpm cm}^{-2}$ which was the upper value on filter-B taken from pump samples. The calculated adsorption still dominated for ²³⁴Th on filter-B and particle breakdown might be important in the euphotic zone. The collected POC on filter-B tended to increase with the filtration volume which implied that DOC adsorption remained under-saturated. Similar to bottle filtration, the corrected POC/²³⁴Th was comparable to the uncorrected POC/²³⁴Th on filter-A. We thus conclude that adsorption did not appear to influence the POC/²³⁴Th ratio in either sampling mode. We suggested that the positive offset in POC/²³⁴Th between bottle and pump sampling, if any, cannot be caused by adsorption. Other mechanisms such as zooplankton invasion and/or artificial particle formation need to be examined in order to resolve the discrepancy.

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1. Introduction

Thorium-234 is a naturally occurring radioisotope widely used as a tracer for particle export from the upper ocean (Buesseler et al., 1992; Cochran and Masque, 2003; Waples et al., 2006). In essence, ²³⁴Th is a

short-lived ($t_{1/2} = 24.1 \text{ d}$) particle reactive element that is produced at a constant rate from its conservative and long lived parent, Uranium-238 ($t_{1/2} = 4.5 \times 10^9 \text{ y}$). In the upper ocean where removal of ²³⁴Th to sinking particles is large, there is a ²³⁴Th deficit with respect to ²³⁸U (i.e., total ²³⁴Th $<$ ²³⁸U), which can be used to calculate the ²³⁴Th flux. This ²³⁴Th flux is translated into particulate organic carbon (POC) flux by multiplying the ²³⁴Th flux by the carbon to thorium (POC/²³⁴Th) ratio in sinking particles. Under the condition of steady state and negligible horizontal advectons, estimation of the ²³⁴Th flux

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is achievable and often comparable with those sediment trap-based measurements (e.g. Maiti et al., 2008; Buesseler et al., 2008, 2009). A major assumption in this method lies in our ability to collect a representative sample to constrain the POC/ ^{234}Th ratio associated with sinking particles (Buesseler et al., 2006). Three approaches commonly used to determine POC/ ^{234}Th on particles are sediment traps, in-situ large volume pumps and bottle filtration. Bottle filtration of water samples (typically 8–10 L) onto a 25 mm-diameter, 1.0 μm pore size, micro-quartz (QMA) filter results in POC/ ^{234}Th ratios that are often higher than those from in-situ pumps or sediment traps (Buesseler et al., 2006; Cai et al., 2010; Chen, 2008). For example, Cai et al. (2010) find that bottle POC/ ^{234}Th ratios in Arctic Ocean are up to 30% higher than the pump ratios. In subtropical oceans such as the South China Sea, a similar elevation of ~20% is found in bottle POC/ ^{234}Th (Chen, 2008). One exception was observed in the North Pacific during the VERTIGO project, when POC/ ^{234}Th ratios from the pump were exceptionally high (sometimes > 200 $\mu\text{mol dpm}^{-1}$) due to the use of a small inlet on the filter holder, which was postulated to have caused the capture of zooplankton onto the filters (Buesseler et al., 2009).

The adsorption of dissolved organic carbon (DOC) onto filters and hence overestimation of POC has been proposed as causing elevated POC/ ^{234}Th ratios (Buesseler et al., 2006; Cai et al., 2008). Such a scenario would be more reasonable when sampling open ocean waters where POC concentration is usually very low, at a level of a few $\mu\text{mol C L}^{-1}$. Moran et al. (1999) show that bottle POC can be 2–4 times higher compared to samples collected by pumps in regions where POC concentrations were < 5 $\mu\text{mol C L}^{-1}$. Recent work in the Northeast Pacific also indicates that bottle POC can be > 2 times higher than pump samples (Mackinson et al., 2015). However, thorough examination of such a hypothesis of DOC adsorption is still lacking. In particular, simultaneous measurements of carbon and ^{234}Th , which obviously determine the POC/ Th ratio, have not been made in examining this hypothesis. Some earlier studies in fact suggest that ^{234}Th adsorption onto either QMA or glass fiber filters can also be elevated during bottle filtration owing to its particle reactive nature (Benitez-Nelson et al., 2001; Rutger van der Loeff et al., 2006). Our study therefore considered the adsorption of both DOC and ^{234}Th and compared bottle and pump filtration, aiming to evaluate if such adsorption impacts the estimation of POC/ ^{234}Th ratios, and thus the thorium-derived carbon export fluxes.

2. Methods

2.1. Sample collection

Samples were collected in June 2008 and September 2009 on board R/V *Tangaroa* operated by the National Institute of Water and Atmospheric Research (NIWA) Ltd., New Zealand (NIWA voyage TAN0806) and R/V *Knorr* by Woods Hole Oceanographic Institution, USA. Bottle samples were collected at Station C17 (178.57°E, 44.34°S) located in a high nitrate low Chl *a* sub-Antarctic water region, using 12 L Niskin bottles attached to a CTD rosette sampler. 8 L of seawater was filtered on a 25 mm QMA filter (active area = 3.8 cm^2) for POC and particulate ^{234}Th analysis, and another 4 L was sampled for total ^{234}Th measurements. Pump samples were collected in June 2008 at the Bermuda Atlantic Time-series Study (BATS) site (31.75°N, 64.1°W) which represents an oligotrophic setting. Two different in situ pump systems, a multiple unit large volume filtration system (MULVFS) (Bishop and Wood, 2008) and McLane pumps (McLane Research Laboratories, Inc., USA) were used to collect particulate samples at BATS. For the MULVFS, 3047–14,491 L of seawater was filtered on 293 mm diameter QMA filters (active area = 506 cm^2), while 342–727 L of seawater was filtered on 142 mm diameter filters for the McLane pumps (active area = 133 cm^2). For ^{234}Th and POC analysis, subsamples of 25-mm and 22-mm diameter were taken as punches out of the MULVFS and McLane filters. The effective volumes are listed in Table 1.

2.2. Filtration technique

In order to evaluate the influence of both DOC and dissolved thorium absorption on the POC/ ^{234}Th ratio, we adopted the similar “two filters in-line” approach used by Turnewitsch et al. (2007). Briefly, two pre-combusted QMA filters were stacked on top of one another during in-line filtration. Seawater was passed first through a 51 μm screen and then through the first filter (filter-A), followed by the filter underneath (filter-B). After filtration, both filter-A and -B were dried in an oven at 50 °C before POC and particulate ^{234}Th analysis. Similarly for pump filtration, filter-A and -B were stacked on top of one another inside the in situ filter holder. The filtration was carried out at ~0.4, 4–8 and 11–54 L min^{-1} for bottle, McLane and MULVFS samples. In order to make a direct comparison of the variability in filtration rates between the three techniques we expressed the filtration rates normalized to active filtration area in Table 1.

2.3. Particulate ^{234}Th and POC measurements

The dried QMA filters were mounted on acid cleaned plastic discs under a layer of Mylar and two layers of aluminum foil, and counted for ^{234}Th using a gas-flow proportional low-level beta counter (Model GM-25-5, RISØ National Laboratory). The samples were re-counted for the backgrounds after 6 months, which were < 0.3 counts per minute (Maiti et al., 2012). After beta counting, all filters were dismounted and analyzed for POC and particulate nitrogen (PN) concentration. Briefly, the inorganic carbon phase was removed through 24 h-fuming with hydrochloric acid, and the samples were then measured using a PE-2400 SERIES II CHNS/O analyzer with an acetanilide standard (C% = 71.09, N% = 10.36). Filter blanks for carbon and nitrogen were < 0.6 $\mu\text{g C}$ and 0.2 $\mu\text{g N}$. The analytical error on carbon and nitrogen was < 5%.

2.4. Total ^{234}Th measurements

Total water column ^{234}Th activities were analyzed using modified MnO_2 co-precipitation technique (Maiti et al., 2012; Cai et al., 2006). The dissolved ^{234}Th activity was calculated by subtracting particulate ^{234}Th activity on filter-A from total ^{234}Th activity.

3. Results

3.1. POC, PN and ^{234}Th on filters-A and -B

The particulate ^{234}Th and POC data from both C17 and BATS are listed in Table 1. For bottle samples, POC concentrations from filter-A in the water column of Station C17 ranged from 0.61 to 3.12 $\mu\text{mol C L}^{-1}$ (Table 1); PN concentrations changed from 0.11 to 0.53 $\mu\text{mol N L}^{-1}$; and particulate ^{234}Th ranged from 0.18 ± 0.01 to 0.47 ± 0.02 dpm L^{-1} . On filter-B, POC, PN and particulate ^{234}Th were much lower, and ranged from 0.21 to 0.45 $\mu\text{mol C L}^{-1}$ for POC; 0.01 to 0.09 $\mu\text{mol N L}^{-1}$ for PN; and 0.04 ± 0.01 to 0.10 ± 0.01 dpm L^{-1} for particulate ^{234}Th . Dissolved ^{234}Th varied from 1.14 ± 0.06 to 2.15 ± 0.08 dpm L^{-1} .

For MULVFS samples, POC and PN concentration from filter-A at the BATS station ranged from 0.15 to 1.42 $\mu\text{mol C L}^{-1}$, and from 0.01 to 0.19 $\mu\text{mol N L}^{-1}$; particulate ^{234}Th from filter-A ranged from 0.12 \pm 0.01 to 0.30 ± 0.02 dpm L^{-1} ; and POC, PN and particulate ^{234}Th from filter-B ranged from 0.02 to 0.25 $\mu\text{mol C L}^{-1}$, 0.004 to 0.04 $\mu\text{mol N L}^{-1}$ and 0.005 ± 0.0003 to 0.04 ± 0.003 dpm L^{-1} . McLane samples were collected from the same sampling site as MULVFS, immediately after recovery of the MULVFS system, which allowed us to compare the difference between the two pumping systems. For the McLane samples, POC, PN and particulate ^{234}Th on filter-A ranged from 0.18 to 1.79 $\mu\text{mol C L}^{-1}$, 0.002 to 0.18 $\mu\text{mol N L}^{-1}$ and 0.15 ± 0.01 to 0.35 ± 0.02 dpm L^{-1} , which were in the same range as the MULVFS samples. For filter-B, POC, PN and particulate ^{234}Th ranged from 0.04 to 0.31 $\mu\text{mol C L}^{-1}$,

Table 1

Particulate ^{234}Th , particulate organic carbon (POC), particulate nitrogen (PN) concentrations on filter-A and -B, dissolved ^{234}Th activities, filtration volume (V) and filtration rate (FR) at Station C17 (178.57°E, 44.34°S) and the Bermuda Atlantic Time-series Study site (31.83°N, 64.17°W), measured in May 2008 and September 2009.

Depth m	Filter-A			Filter-B			Diss. ^{234}Th dpm L ^{-1a}	V L	FR mL cm ⁻² min ^{-1b}
	Part. ^{234}Th dpm L ⁻¹	POC $\mu\text{mol C L}^{-1}$	PN $\mu\text{mol N L}^{-1}$	Part. ^{234}Th dpm L ⁻¹	POC $\mu\text{mol C L}^{-1}$	PN $\mu\text{mol N L}^{-1}$			
<i>Bottle^c</i>									
10	0.47 ± 0.02	3.12	0.53	0.04 ± 0.01	0.45	0.07	1.14 ± 0.06	8	~1.1
20	0.57 ± 0.05	2.43	0.39	0.04 ± 0.01	0.55	0.09	1.23 ± 0.08	8	~1.1
45	0.45 ± 0.02	2.34	0.41	0.06 ± 0.01	0.51	0.07	1.20 ± 0.06	8	~1.1
65	0.25 ± 0.01	1.45	0.23	0.06 ± 0.01	0.28	0.05	1.68 ± 0.07	8	~1.1
100	0.21 ± 0.01	1.36	0.23	0.10 ± 0.01	0.22	0.03	2.10 ± 0.08	8	~1.1
250	0.18 ± 0.01	1.01	0.15	0.08 ± 0.01	0.25	0.01	2.15 ± 0.08	8	~1.1
500	0.22 ± 0.01	1.22	0.20	0.10 ± 0.01	0.27	0.03	1.93 ± 0.08	8	~1.1
750	0.24 ± 0.01	0.61	0.09	0.06 ± 0.01	0.24	0.02	1.94 ± 0.07	8	~1.1
1170	0.36 ± 0.02	1.03	0.11	0.05 ± 0.01	0.21	0.01	1.52 ± 0.07	8	~1.1
<i>MULVFS</i>									
30	0.21 ± 0.01	1.42	0.15	0.04 ± 0.003	0.24	0.02	2.14 ± 0.08	29.5	22.3
55	0.30 ± 0.02	1.38	0.16	0.04 ± 0.003	0.25	0.03	2.15 ± 0.09	32.2	24.3
80	0.25 ± 0.02	1.01	0.19	0.02 ± 0.001	0.15	0.04	2.17 ± 0.09	49.7	37.4
105	0.20 ± 0.01	0.66	0.08	0.02 ± 0.001	0.13	0.02	2.29 ± 0.09	77.1	58.3
155	0.14 ± 0.01	0.33	0.04	0.01 ± 0.001	0.05	0.01	2.41 ± 0.09	101	76.1
205	0.14 ± 0.01	0.28	0.03	0.01 ± 0.001	0.05	0.01	2.46 ± 0.09	102	76.9
255	0.12 ± 0.01	0.26	0.03	0.003 ± 0.0002	0.03	0.01	2.47 ± 0.09	111	84.2
405	0.12 ± 0.01	0.20	0.02	0.003 ± 0.0002	0.05	0.003	2.49 ± 0.09	136	102.6
580	0.13 ± 0.01	0.16	0.02	0.005 ± 0.0003	0.02	0.01	2.50 ± 0.09	140	106.1
780	0.16 ± 0.01	0.16	0.01	0.01 ± 0.001	0.02	0.01	2.49 ± 0.09	123	92.9
880	0.18 ± 0.01	0.15	0.02	0.005 ± 0.0003	0.02	0.004	2.43 ± 0.09	126	94.9
<i>McLane</i>									
30	0.26 ± 0.01	1.67	0.18	0.15 ± 0.01	0.31	0.04	2.09 ± 0.1	10.8	30–45
55	0.35 ± 0.02	1.79	0.18	0.12 ± 0.01	0.16	0.07	2.10 ± 0.1	9.8	30–45
80	0.34 ± 0.01	1.34	0.14	0.08 ± 0.01	0.22	n.a	2.08 ± 0.1	13.3	30–45
105	0.24 ± 0.01	1.33	0.16	0.08 ± 0.01	0.29	0.08	2.25 ± 0.1	12.3	30–45
155	0.21 ± 0.01	0.43	0.06	0.05 ± 0.005	0.14	0.08	2.34 ± 0.1	19.9	30–45
255	0.15 ± 0.01	0.30	0.01	0.04 ± 0.006	0.06	n.a	2.44 ± 0.1	19.3	30–45
405	0.16 ± 0.01	0.24	0.002	0.06 ± 0.006	0.04	n.a	2.45 ± 0.1	19.6	30–45
780	0.22 ± 0.01	0.18	0.02	0.04 ± 0.005	0.08	0.02	2.43 ± 0.1	20.8	30–45

^a Dissolved ^{234}Th was calculated as total ^{234}Th subtracted from particulate ^{234}Th on filter-A.

^b Filtration rate was expressed as filtration rates normalized to active filtration areas which were respectively 3.8, 506 and 133 cm² for bottle, MULVFS and McLane systems.

^c Bottle data for filter-A has been published in Zhou et al. (2012).

0.02 to 0.08 $\mu\text{mol N L}^{-1}$ and 0.04 ± 0.006 to 0.15 ± 0.01 dpm L⁻¹. Interestingly, the concentrations of POC and PN from filter-B in McLane samples were comparable with those from MULVFS samples, but not for particulate ^{234}Th which were higher. The percentage carbon and thorium on filter-B with respect to filter-A was 18–58% and 8.7–42% for McLane samples and 2.5–19% and 11–25% for MULVFS samples.

The profiles of POC and particulate ^{234}Th from filter-A and -B are also shown in Fig. 1. For bottle samples at station C17 (Fig. 1a and d), POC and particulate ^{234}Th concentrations from filter-A in the upper ocean were elevated, i.e., 2.34–3.12 $\mu\text{mol C L}^{-1}$ for POC, and 0.45–0.57 dpm L⁻¹ for particulate ^{234}Th . Their concentrations started to decline below ~50 m, and stabilized at 100 m. From 100 to 750 m, little variation was found for POC and particulate ^{234}Th on filter-A, e.g. 0.61–1.36 $\mu\text{mol C L}^{-1}$ for POC, and 0.18–0.24 dpm L⁻¹ for particulate ^{234}Th . In the bottom water (1170 m), both POC and particulate ^{234}Th were slightly higher compared to the mid-water, i.e., 1.03 $\mu\text{mol C L}^{-1}$ for POC and 0.36 dpm L⁻¹ for particulate ^{234}Th . The profiles of POC and particulate ^{234}Th on filter-B, however, showed a different pattern. The profile of POC on filter-B more or less reflected that on the filter-A, but interestingly for particulate ^{234}Th on filter-B, its profile showed an opposite trend with respect to filter-A, i.e. ^{234}Th concentration went down in filter-B when the corresponding concentrations went up in filter-A. In the upper mixed layer, the POC concentration on filter-B (0.45–0.55 $\mu\text{mol C L}^{-1}$) was about twice that in the mid-water (0.22–0.28 $\mu\text{mol C L}^{-1}$). In contrast, particulate ^{234}Th on filter-B (0.04–0.06 dpm L⁻¹) was half that found in the mid-water (0.08–0.1 dpm L⁻¹). This distribution pattern of particulate ^{234}Th on filter-B was similar to that of dissolved ^{234}Th .

At the BATS station, profiles of POC and particulate ^{234}Th from filter-A collected via MULVFS and McLane a shared similar distribution

pattern as the bottle samples (Fig. 1b, c, e and f). They were high in the upper ocean, decreased gradually with depth and then increased again in the deep ocean. POC and particulate ^{234}Th were 1.0–1.7 $\mu\text{mol C L}^{-1}$ and 0.2–0.35 dpm L⁻¹ in the upper 100 m, and 0.15–0.7 $\mu\text{mol C L}^{-1}$ and 0.1–0.2 dpm L⁻¹ below. For filter-B, POC and ^{234}Th profiles from McLane and MULVFS resembled those from filter-A, in contrast to the bottle samples.

The two stations may have a very different particle characterization. The lower dissolved ^{234}Th (as listed in Table 1) at C17 might indicate a higher particle export compared to the oligotrophic BATS station. The global DOC distribution also showed that BATS station might be characterized with higher DOC concentration (Hansell et al., 2009). Therefore, higher dissolved constituent (DOC and dissolved ^{234}Th) was found in BATS while the particulate loads should be higher at C17. The difference of the particle concentrations between the two stations are induced both by different methodologies and oceanographic settings.

3.2. POC/ ^{234}Th ratios on filter-A and filter-B

The profiles of POC/ ^{234}Th ratios on filter-A and filter-B from bottle, MULVFS and McLane samples are shown in Fig. 2. For bottle samples, the POC/ ^{234}Th ratio on filter-A varied from 2.5 ± 0.3 $\mu\text{mol dpm}^{-1}$ to 6.6 ± 0.3 $\mu\text{mol dpm}^{-1}$, while a larger range was observed on filter-B, from 2.2 ± 0.2 $\mu\text{mol dpm}^{-1}$ to 13.8 ± 3.4 $\mu\text{mol dpm}^{-1}$. The vertical profiles for filter-A and filter-B were also different. For filter-A, the POC/ ^{234}Th ratio was relatively higher in the upper 500 m (4–6 $\mu\text{mol dpm}^{-1}$) and <3 $\mu\text{mol dpm}^{-1}$ below 500 m. For filter-B, the POC/ ^{234}Th ratio was higher at the surface (>10 $\mu\text{mol dpm}^{-1}$) and then decreased to 2.2 $\mu\text{mol dpm}^{-1}$ at 100 m. Below 100 m, it varied between 2 and 4 $\mu\text{mol dpm}^{-1}$. The POC/ ^{234}Th ratio on filter-B was found to

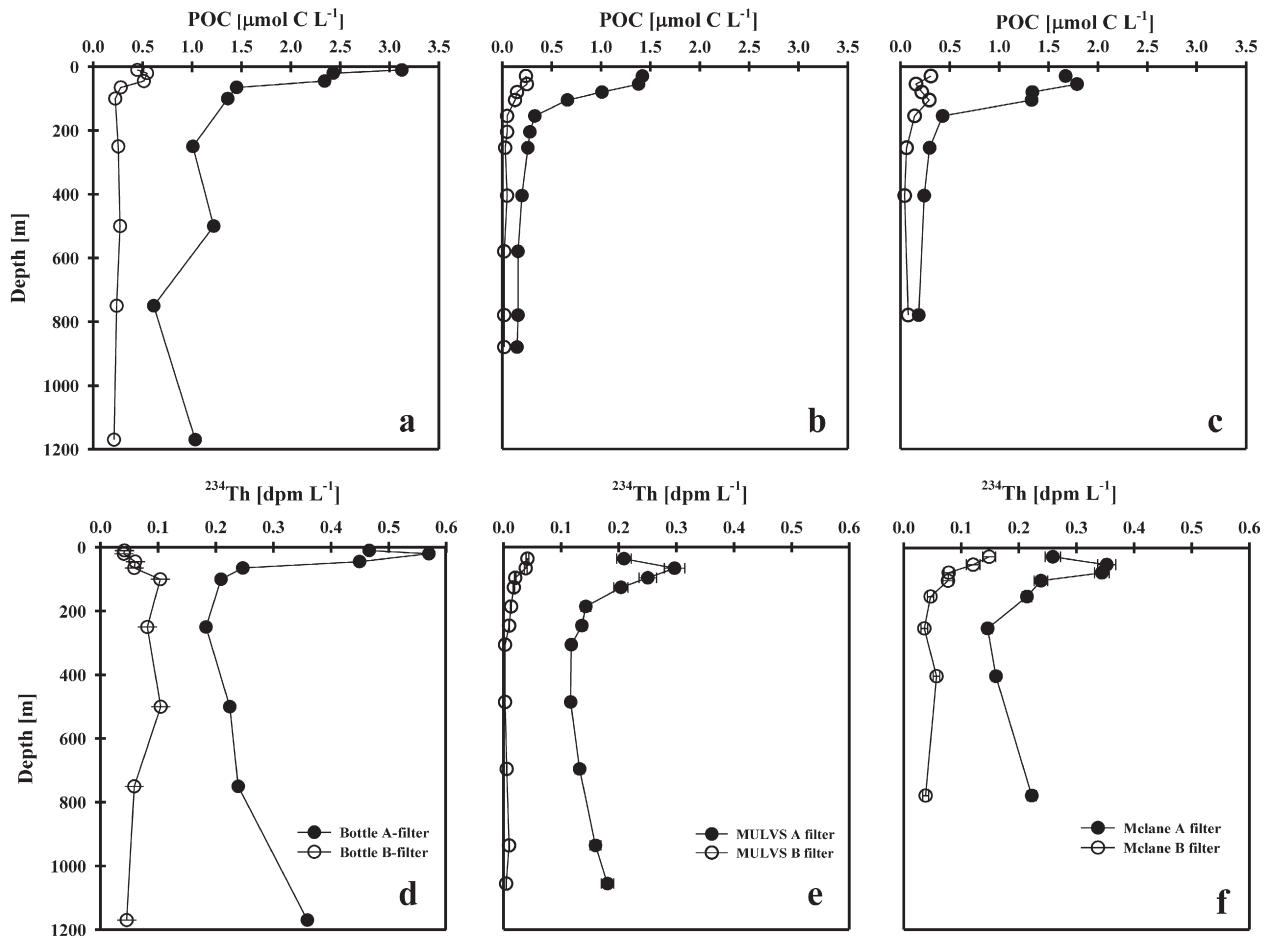


Fig. 1. Profiles of POC and ^{234}Th sampled by bottle (a and d), MULVFS pump (b and e) and McLane pump (c and f) (samples from filter-A and -B are denoted by solid and hollow circles).

be higher than on filter-A at the surface, but this trend switched with filter-A being higher than filter-B between 100 and 500 m. Below 500 m, filter-B was again found to be higher than filter-A.

For McLane and MULVFS samples from the BATS station, the depth distribution of POC/ ^{234}Th on filter-A from both sampling devices were similar to the pumps, that is high ($>6 \mu\text{mol dpm}^{-1}$) at the surface and low ($\sim 1 \mu\text{mol dpm}^{-1}$) at depths below 600 m. Interestingly, POC/ ^{234}Th ratios on filter-B showed very different depth distributions. The MULVFS POC/ ^{234}Th ratios on filter-B were higher than those on

filter-A at all depths with the highest value ($16.7 \mu\text{mol dpm}^{-1}$) at 400 m. The McLane POC/ ^{234}Th ratios on filter-B were lower or similar to that on filter-A for the entire water column with the exception of deeper than 800 m where the ratio was higher on filter-B compared to filter-A.

The $\text{C}/^{234}\text{Th}$ ratio in the dissolved phase should be much higher compared to particulate ones. DOC concentration in the open ocean normally range from $70\text{--}80 \mu\text{mol C L}^{-1}$ in the surface to about $40 \mu\text{mol C L}^{-1}$ in the deep ocean (Dai et al., 2009), and dissolved ^{234}Th varies from 1.0 to

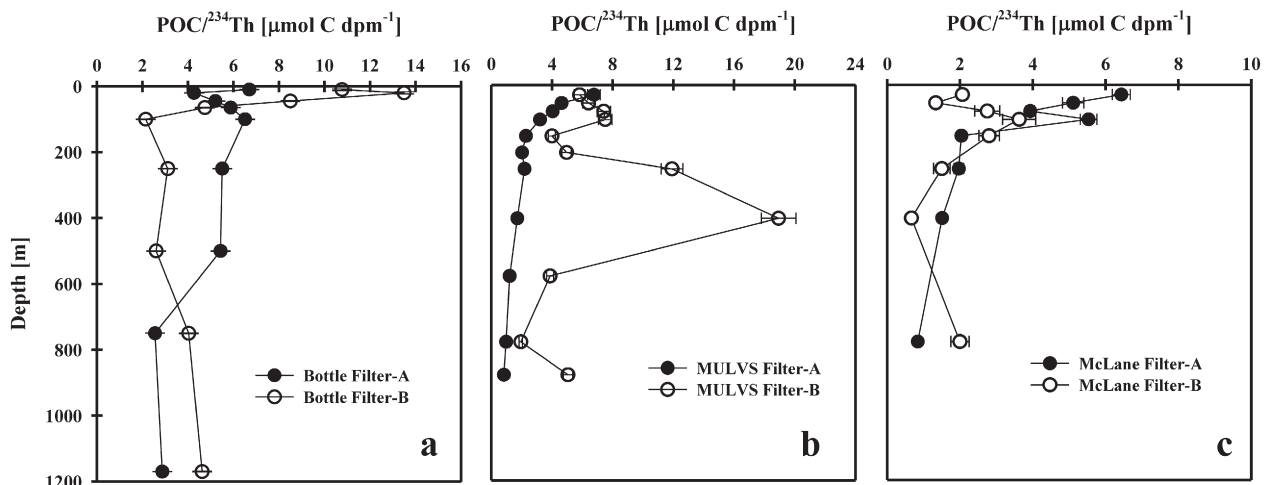


Fig. 2. Profile of POC/ ^{234}Th ratios from filter-A and -B. (a), (b) and (c) are bottle, MULVFS and McLane samples.

2.2 dpm L⁻¹ which means that the dissolved C/²³⁴Th ratio should be on the order of 10–100 μmol C dpm⁻¹.

4. Discussion

4.1. Adsorption of ²³⁴Th and DOC

Two important processes that can explain the presence of particulate ²³⁴Th and POC on filter-B are the particle break-down from filter-A and the adsorption of dissolved material onto both filters. Note that the adsorption process includes the collection of submicron particles whose size is less than the nominal pore size of the filter. Here we assume that the adsorption onto both filters is similar (Liu et al., 2005;

Moran et al., 1999). The mass balance for both carbon and thorium for filter-A and -B can be written as:

$$A = \text{Part.} + \text{Ads.} - \text{loss} \quad (1)$$

$$B = \varepsilon_L \text{loss} + \text{Ads.} \quad (2)$$

where *Part.* is the particulate concentration of ²³⁴Th and POC; *loss* is the particle loss from filter-A which includes >1 μm particles passing through filter-A and <1 μm particles originally broken from >1 μm ones; ε_L is the capture efficiency for the particles lost from filter-A; and *Ads.* the adsorption of dissolved material (<1 μm). Here adsorption means ²³⁴Th and POC collected from <1 μm particles including

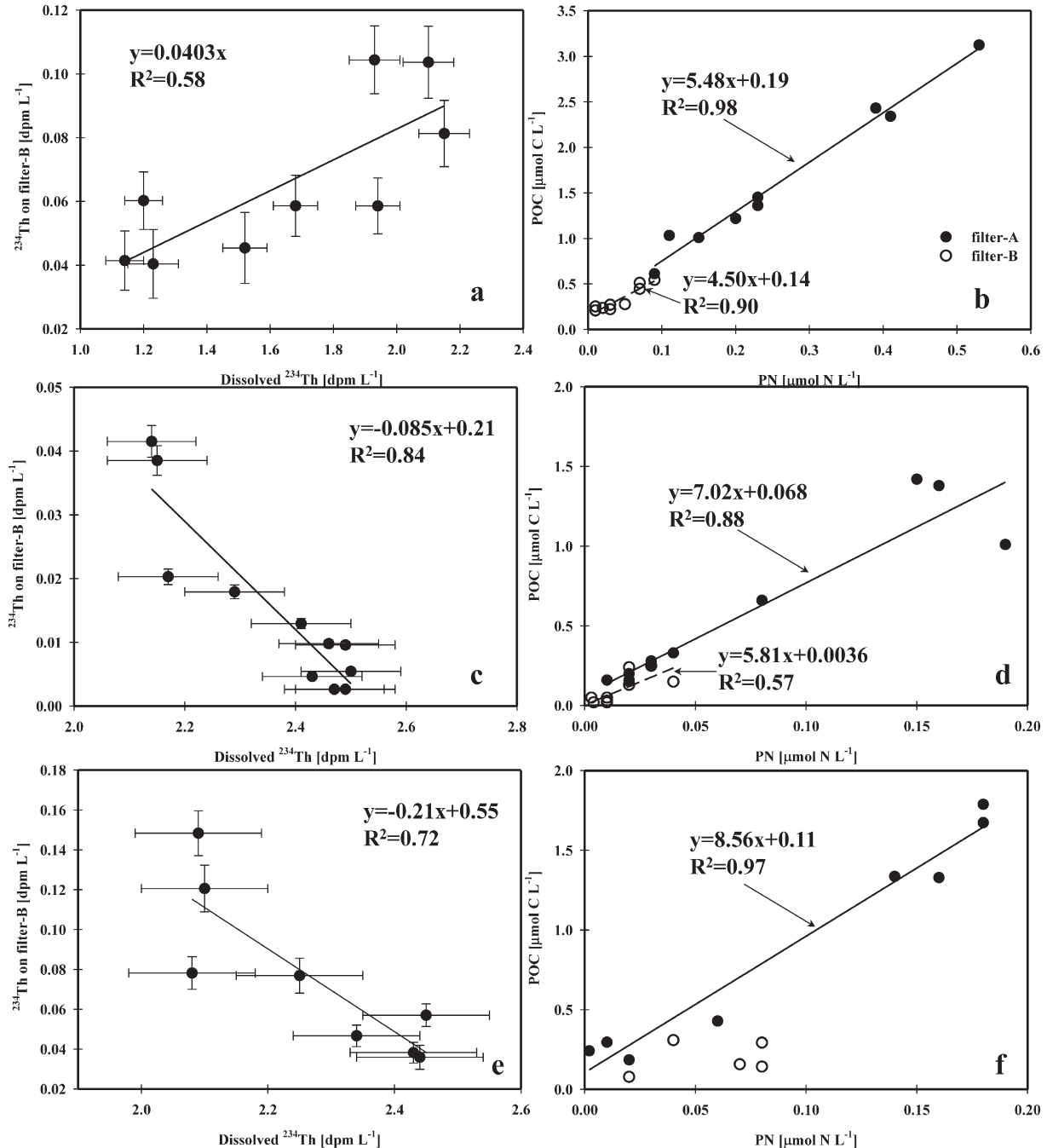


Fig. 3. Correlations between filter-A ²³⁴Th and dissolved ²³⁴Th for bottle (a), MULFVS (c) and McLane (e), and between POC and PN for bottle (b), MULFVS (d) and McLane (f). Note the regression line is not shown for POC vs. PN from filter-B for McLane due to the scarce of the data.

submicron and colloidal particles and adsorption from the truly dissolved phase. However it is important to note that efficiency of particle retention will increase when stacking two depth filters, leading to increased efficiency in collection of particles smaller than nominal size rating of the filter (Bishop and Edmond, 1976). Retention of particles smaller than the nominal size of filters might be different between A and B filter. For this work we have assumed such difference to be negligible and combined such retention under the adsorption term (Turnewitsch et al., 2007). For bottle sampling, the linear correlation between particulate ^{234}Th on filter-B and dissolved ^{234}Th ($R^2 = 0.58$, in Fig. 3a,) indicates that the adsorption of dissolved ^{234}Th might have been the dominant process, since the filtration volumes were 8 L for all samples. Note that the filtration pressure we applied was within 0.2–0.6 atm which should prevent a significant amount of particles from breaking up (Liu et al., 2005). Moreover, there is evidence that the amount that is absorbed on the filter is nitrogen-enriched (Turnewitsch et al., 2007). Indeed, the C/N ratio on filter-B is about 4.5 (Fig. 3b), lower than that on filter-A (5.4, shown in Fig. 3c) consistent with adsorption of dissolved organic matter. The adsorption of ^{234}Th can be estimated using the following equation when it is under-saturated:

$$^{234}\text{Th}_{\text{ads}} = k \cdot ^{234}\text{Th}_{\text{diss}} \quad (3)$$

Here $^{234}\text{Th}_{\text{ads}}$ is the ^{234}Th adsorption concentration; Th_{diss} is the dissolved ^{234}Th concentration; and k is the percentage of dissolved ^{234}Th

absorbed on the filter. We assume that the k value should be similar to the slope of regression line of particulate ^{234}Th on filter-B vs. dissolved ^{234}Th which is 0.0403 (Fig. 3a). ^{234}Th adsorption based on this is calculated and listed in Table 2. For most of the samples, adsorption contributes to 100% of ^{234}Th concentration measured on filter-B.

We can then simplify Eq. (2) by assuming negligible particle loss to:

$$B \approx \text{Ads}. \quad (4)$$

The carbon ratio for bottle samples between filter-A and -B (A:B ratio) ranges from 14 to 39% with an average of $22 \pm 7\%$ ($n = 9$), suggesting the adsorption from DOC is important in the open ocean. The range for ^{234}Th is similar but with a larger variation compared to that of carbon, ranging from 7 to 50%, with an average of $25 \pm 17\%$ ($n = 9$).

For bottle samples, we find that the particulate ^{234}Th from filter-A is negatively associated with that from filter-B, while POC concentration, on the other hand, is positively related (Fig. 4a and b). A possible explanation for this is the fact that dissolved ^{234}Th (thus absorbed ^{234}Th) is usually low in the surface water and high at depth while particulate ^{234}Th in the water column has the opposite distribution. Conversely, the reason that POC concentrations show a positive correlation pattern is due to the fact that DOC and POC are similarly decreasing with depth in the open ocean (e.g. Dai et al., 2009).

For both MULVFS and McLane samplings, particulate ^{234}Th on filter-B and dissolved ^{234}Th are negatively correlated (Fig. 3c and e), while ^{234}Th concentrations on filter-A are found to be positively correlated with those from filter-B (Fig. 4c and e, $R^2 = 0.65$ and 0.35). Such a linear relationship might result for two reasons. First, under conditions of large volume filtration as in the case of in situ pumping with high filtration rates ($>20 \text{ mL cm}^{-2} \text{ min}^{-1}$), particle breakdown might progressively contribute to their concentrations on filter-B. Higher ^{234}Th concentration on filter-A (corresponding to lower dissolved ^{234}Th in Table 1) might then indicate higher particulate ^{234}Th loss to filter-B. Secondly, with filtration of larger volumes, adsorption might be close to and/or reach its saturation state.

Benitez-Nelson et al. (2001) indicated that ^{234}Th adsorption can reach saturation after 300 L of seawater is filtered on a 142 mm diameter filter (9.3 L on a 25 mm diameter filter). Since our filtration volumes for both McLane and MULVFS samplings are all higher than this (Table 1), we believed that the ^{234}Th adsorption might have reached its saturation state in our case. Once the ^{234}Th adsorption is saturated, the apparent concentration of adsorption starts to go down as more seawater continued to be filtered. As shown in Table 1, a higher ^{234}Th concentration on filter-A is usually characteristic of a lower filtration volume (which means higher fraction absorbed) in our case. Therefore, ^{234}Th concentration on filter-A (dissolved ^{234}Th) should have been positively (negatively) correlated with its adsorption concentration for pump samples.

The C/N ratio on filter-B for both pumps is less than that on filter-A (Fig. 3d and f) which is similar to the bottle case, indicating adsorption might be important for pump samples. It is thus hard to tell which process (adsorption or particle loss) contributes more to ^{234}Th on filter-B, since the saturation amount for ^{234}Th on the filter is difficult to measure.

In our bottle case, the highest adsorbed ^{234}Th activity was 0.21 dpm cm^{-2} filter. As both dissolved ^{234}Th activity and the filtration volume are lower at C17 compared to those at BATS, the saturation value at BATS is expected to be higher. We also notice that most of pump ^{234}Th on filter-B lies between 0.20 dpm cm^{-2} and 0.31 dpm cm^{-2} . The high value of 0.31 dpm cm^{-2} is derived from the depth of 55 m where particle ^{234}Th was the highest (0.35 dpm L^{-1}). Particle break down at this depth most likely occurred. Therefore, the saturation value can then be constrained under such justification as $0.21\text{--}0.31 \text{ dpm cm}^{-2}$. The saturation activity of ^{234}Th should depend strongly on the physical properties of the QMA filter (Supplement Fig. S1), e.g. the number of adsorption sites, and to a lesser extent on the concentration of dissolved ^{234}Th , i.e., there are differences in

Table 2
The calculated values for ^{234}Th and POC adsorption from MULVFS and McLane samples.

Depth	Th(ads) ^a dpm L ⁻¹	Th% ^{b,*}	POC (ads) ^c μmol C L ⁻¹	POC% [*]
<i>Bottle</i>				
10	0.046	100	0.45	100
20	0.05	100	0.55	100
45	0.048	81	0.51	100
65	0.068	100	0.28	100
100	0.084	81	0.22	100
250	0.087	100	0.25	100
500	0.078	75	0.27	100
750	0.078	100	0.24	100
1170	0.061	100	0.21	100
<i>MULVFS</i>				
30	0.035–0.052	87–100	0.21–0.24	85–100
55	0.032–0.047	80–100	0.22–0.25	86–100
80	0.021–0.031	100	0.15–0.15	100
105	0.010–0.020	67–99	0.11–0.13	85–99
155	0.010–0.015	100	0.05–0.05	100
205	0.010–0.015	100	0.05–0.05	100
255	0.0093–0.015	100	0.03–0.03	100
405	0.0076–0.014	100	0.05–0.05	100
580	0.0074–0.011	100	0.02–0.02	100
780	0.0084–0.012	84–100	0.019–0.02	92–100
880	0.0082–0.012	100	0.02–0.02	100
<i>McLane</i>				
30	0.074–0.11	49–72	0–0	0
55	0.082–0.12	68–100	0–0.16	0–100
80	0.060–0.089	75–100	0.14–0.22	64–100
105	0.065–0.096	81–100	0.21–0.29	71–100
155	0.040–0.059	80–100	0.12–0.14	86–100
255	0.041–0.061	100	0.063–0.063	100
405	0.041–0.060	68–100	0.011–0.04	28–100
780	0.038–0.057	96–100	0.08–0.08	98–100

^a ^{234}Th adsorption concentration for bottle samples is calculated as 0.0403 multiplied by dissolved ^{234}Th concentration; For pump samples, it is calculated by assuming the adsorption had reached its saturation state and the saturation amount lies between 0.21 and 0.31 dpm cm^{-2} .

^b Th% is the percentage of ^{234}Th adsorption over ^{234}Th on filter-B.

^c POC adsorption concentration for bottle samples is assumed to contribute 100% of carbon on filter-B; For pump samples, it is estimated using the equation $\text{POC}_{\text{ads}} = \frac{\text{POC}_{\text{B}} - a \cdot \text{POC}_{\text{A}}}{1 - a}$, where $a = \frac{\text{Th}_{\text{B}} - \text{Th}_{\text{ads}}}{\text{Th}_{\text{A}} - \text{Th}_{\text{ads}}}$.

* Those numbers calculated as $>100\%$ or $<0\%$ are all forced to 100% and 0% .

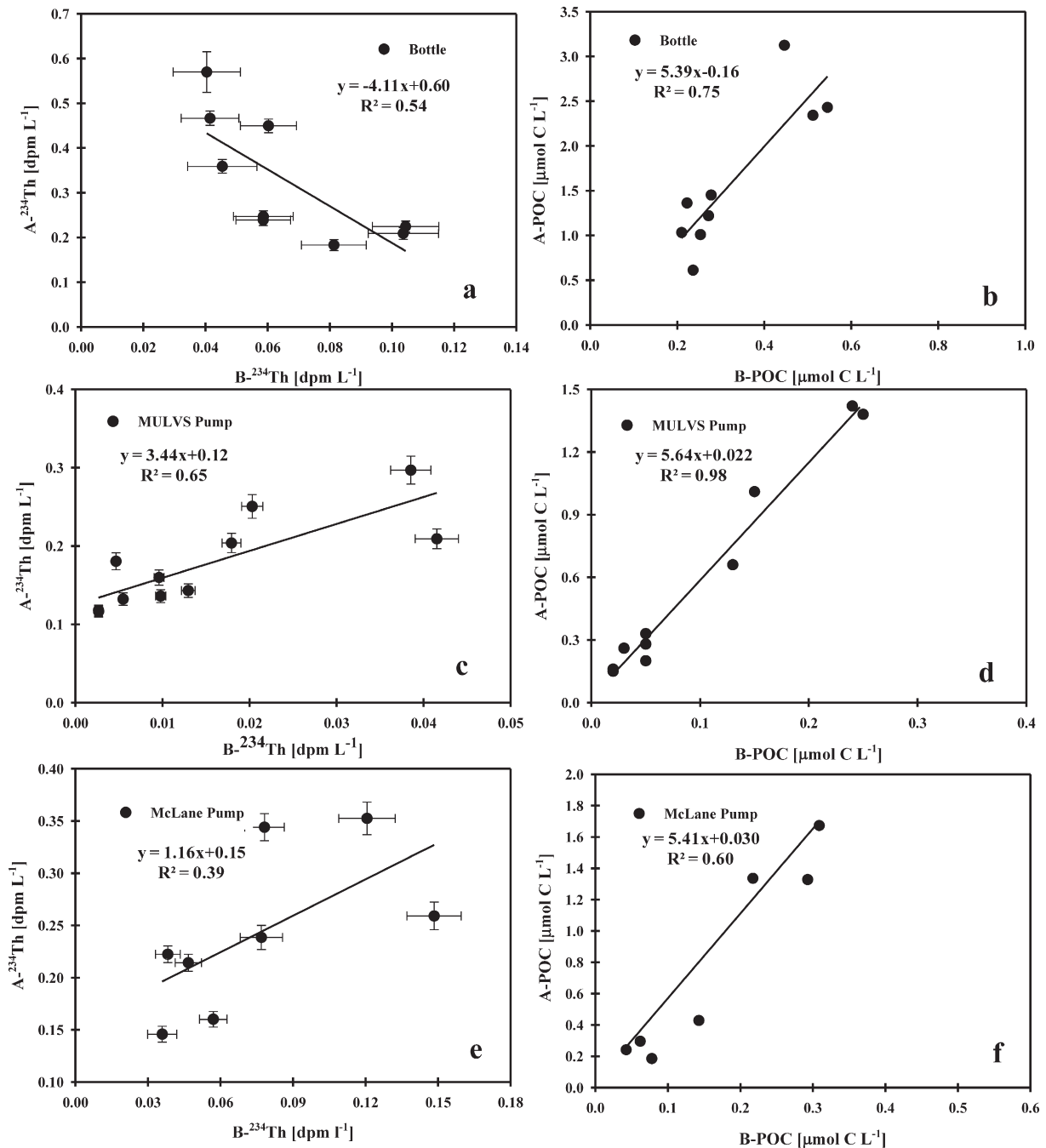


Fig. 4. Correlations between filter-A and filter-B for POC and particulate ^{234}Th : (a) and (d) are for bottle samples, (b) and (e) for MULVFS samples and (c) and (f) for McLane samples.

dissolved ^{234}Th activity in the euphotic zone of the both sites due to export. Based on this assumption, the absorbed ^{234}Th concentration for MULVFS and McLane can be calculated as:

$$Th_{ads} = \frac{A_{Th} \times S}{V} \quad (5)$$

where A_{Th} is the amount of absorbed ^{234}Th ($0.21\text{--}0.31\text{ dpm cm}^{-2}$), V is the filtered volume and S is the effective filtered area. The calculated ^{234}Th adsorption concentrations are listed in Table 2. As can be seen in Table 2, ^{234}Th adsorption still dominates the contribution to filter-B for most of the samples except those from McLane samples in the upper 80 m where particle break down from filter-A

is important. In addition, particle loss can be estimated based on Eq. (2):

$$^{234}\text{Th}_{Loss} = \frac{^{234}\text{Th}_B - ^{234}\text{Th}_{ads}}{\varepsilon_L} \quad (6)$$

Here we assume that ε_L value is 100% and as such the particle loss term is considered to be a lower estimate if our adsorption value is reliable. It seems that the loss of ^{234}Th was more obvious for McLane (low filtration volume) relative to MULVFS samples especially in the upper euphotic zone. This may be caused by the different operation mechanism between MULVFS and McLane. The pressure difference across the filter in McLane pump may increase when filter clogs which might

lead to more particle breakage. It occurs mostly in the upper euphotic zone where particle concentration is higher.

POC concentrations are also positively correlated between filter-A and filter-B (Fig. 4d and f). If we assumed POC adsorption dominated and there was still under saturation, then the adsorption concentration could be considered to be a function of DOC concentration, i.e. $POC_{ads} = kc$, where k is a constant, and c is the concentration of DOC. Since DOC concentrations are usually higher at the surface compared to at depth, then DOC adsorption should be higher at the surface. However, if we assume that the DOC adsorption has reached saturation, then the adsorption concentration would be a function of filtration volume, i.e. $POC_{ads} = A/V$, where A is the saturated amount of absorbed DOC and V is the filtration volume. In our case, the filtration volume is usually lower at the surface, and thus the absorbed carbon is also higher at the surface. Therefore, with both un-saturated and saturated conditions, the DOC adsorption should be positively correlated with POC on filter-A which is also higher at the surface compared to at depth. Meanwhile, if we assumed particle loss dominated the carbon concentration on filter-B, the loss should have been higher at the surface where higher particle loads are observed, leading to a positive correlation with POC on filter-A. Therefore, although filter-A is positively correlated with filter-B, it is impossible to tell which process (adsorption or particle loss) is more important. Note in the next section, we will verify that adsorption of DOC is unsaturated and contributes more to filter-B compared to particle loss from filter-A.

4.2. Different affinity for adsorption of carbon and thorium

POC/ ^{234}Th ratios on filter-B from MULVFS are higher than those on filter-A and filter-B from McLane in all cases where the volume filtered is higher for MULVFS. If the POC/ ^{234}Th ratios on filter-B are solely due to the particle loss from filter-A, then both filter-A and filter-B should have had similar POC/Th ratios. The fact that the ratios are not similar on the two filters is an indicator that these ratios are also being driven by the differences in adsorption affinity between carbon and thorium. In Fig. 5, the total amounts of carbon and thorium on filter-B are plotted vs. filter volume normalized to active area from both MULVFS and McLane samples. For carbon, the collected POC is low under the low filtered volume but tends to increase as more water is filtered. However, this trend is not as obvious for thorium. The amount of particulate ^{234}Th on filter-B is found to be quite stable with filtration volume which we justify as ^{234}Th being saturated on the filter (except for some samples with large error bars). We hypothesize that the adsorption affinity of thorium is higher than C, thus reaching saturation on the filter sooner than carbon even when smaller volumes of water are filtered. The conceptual curves of ^{234}Th and carbon absorption are shown in Fig. 6a. In this example, more thorium is adsorbed relative to carbon in the McLane pumps which results in lower POC/ ^{234}Th ratios on filter-B (Fig. 2). With the higher volume MULVFS, the POC remains high, which elevates the POC/ ^{234}Th ratios. This is also found to be true for bottle samples.

If carbon and thorium were adsorbed at the same rate, the POC/ ^{234}Th ratio should be similar to the dissolved phase ($10\text{--}100\ \mu\text{mol C dpm}^{-1}$ as mentioned above). Nevertheless, the POC/ ^{234}Th ratio was $2\text{--}14\ \mu\text{mol dpm}^{-1}$ on filter-B indicating that thorium was being adsorbed at a higher rate compared to carbon. The two high POC/ ^{234}Th ratios on filter-B from MULVFS in the mid-depth might be related to analytical caveat. Those high values were driven by the low ^{234}Th concentration on filter-B which is unrealistic in our case.

In order to estimate the adsorption contribution of DOC from the dissolved phase, we assume that the POC/ ^{234}Th ratio for the particles that break-down to filter-B is similar to that for the particles collected on filter-A, and a similar adsorption between A and B, we obtain the following equation:

$$\frac{POC_A - POC_{ads}}{Th_A - Th_{ads}} = \frac{POC_B - POC_{ads}}{Th_B - Th_{ads}} \quad (7)$$

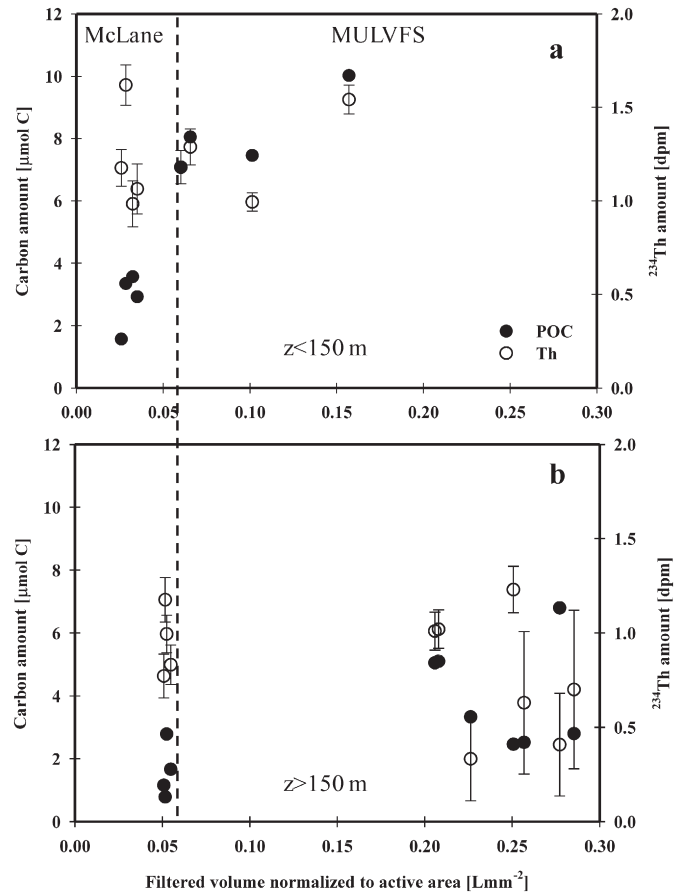


Fig. 5. Carbon and thorium amount collected on filter-B vs. filtered volume (normalized to the active area) for both MULVFS and McLane for the depth < 150 m (a) and > 150 m (b).

Eq. (7) can then be solved as:

$$POC_{ads} = \frac{POC_B - aPOC_A}{1 - a} \quad (8)$$

where $a = \frac{Th_B - Th_{ads}}{Th_A - Th_{ads}}$.

As discussed above, the adsorption from the dissolved phase might have been dominant for ^{234}Th for filter-B with MULVFS, and we also list the Th_{ads} values in Table 2. Next, the POC adsorption concentration is calculated and this is also listed in Table 2. As can be seen, the carbon adsorption from MULVFS and McLane samples is significant except for the McLane surface samples. The low contribution of carbon adsorption for those surface samples might be due to the lower carbon affinity as mentioned above, and also particle break-down is dominated due to the higher pressure differential across the filter for McLane pump.

4.3. POC/ ^{234}Th correction for pump and bottle filtration

For MULVFS and McLane samples, we use the following equation to correct the C/Th ratio:

$$\left(\frac{POC}{^{234}\text{Th}}\right)_{corrected} = \frac{POC_A + POC_B - 2POC_{ads}}{^{234}\text{Th}_A + ^{234}\text{Th}_B - 2Th_{ads}} \quad (9)$$

where POC_A and $^{234}\text{Th}_A$ are the POC and particulate ^{234}Th concentrations on filter-A, and POC_B and $^{234}\text{Th}_B$ are those on filter-B. Although we assume that ^{234}Th saturation activity varies from 0.21 to 0.31 dpm m^{-2} , the corrected POC/ ^{234}Th ratio seems quite stable with the changes of ^{234}Th saturation value, and it is quite comparable with those on filter-A, which implies that these processes played a minor role in impacting

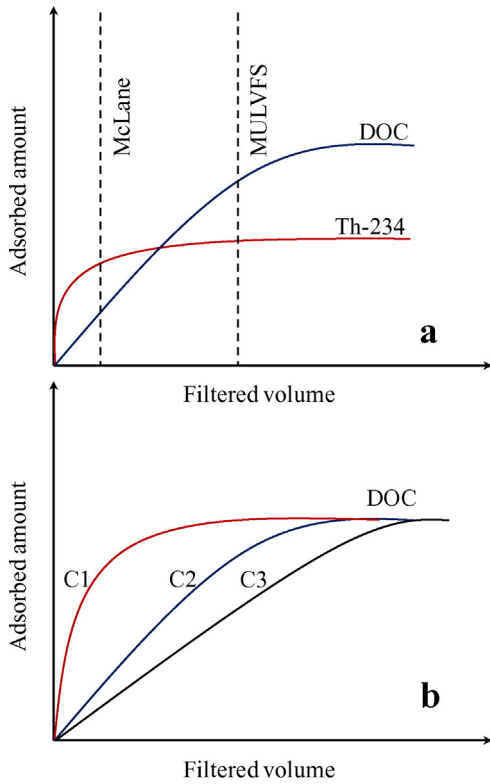


Fig. 6. Conceptual adsorption curves for POC and thorium at specific depth (a). The adsorption rate of thorium was higher relative to carbon, leading to thorium reaching its saturation state earlier during filtration. Since thorium concentration was much lower compared to carbon in the seawater, the saturation concentration on the filter was also expected to be low. Conceptual adsorption curves for carbon at different depths where the absorbable concentrations ($C1 > C2 > C3$) were different (b). According to the Langmuir adsorption model, a higher absorbable concentration enables a higher adsorption rate. Here, “absorbable” implies that some portion of the dissolved organic carbon is refractory and not involved in adsorption.

the “true” $POC/^{234}Th$ ratios (Fig. 7b and c). We are now sure that both particle loss and adsorption do not influence the $POC/^{234}Th$ ratio for large volume samples, and that this is probably due to the volume effect, which results in the concentrations from these two processes being much lower compared to the particulate concentration. Therefore, no correction will be needed for large volume pump samples.

For bottle samples, it is important to understand what fraction of the dissolved phase is adsorbed by the filters, and we expected that a ^{234}Th -

enriched fraction in the dissolved phase is preferentially adsorbed by the filter. This is probably true, as evidenced by Santschi et al. (2006) that the $C/^{234}Th$ ratio in the colloidal phase (>10 kDa) is similar with that in POC ($>1 \mu m$), but lower than that in >1 kDa phase.

Thus, for bottle samples where equal adsorption is assumed for filter-A and -B, we can calculate the $POC/^{234}Th$ ratios as follows:

$$\left(\frac{POC}{^{234}Th}\right)_{corrected} = \frac{POC_A - POC_B}{^{234}Th_A - ^{234}Th_B} \quad (10)$$

where POC_A is the POC concentration on filter-A and POC_B on filter-B, and $^{234}Th_A$ and $^{234}Th_B$ are the ^{234}Th concentrations on filter-A and -B. The corrected and uncorrected (filter-A) profiles of $POC/^{234}Th$ are shown in Fig. 7a. In the upper (0–65 m) and deep (750–1170 m) ocean, the corrected and uncorrected $POC/^{234}Th$ are similar, with their ratios close to 1. In the mid-water (100–500 m), the corrected $POC/^{234}Th$ is even higher compared to the uncorrected one, with ratios of 1.35–1.66, which might be elevated by the fresh organic matter (high C/Th ratio) horizontally transported from the nearby Chatham Rise. Thus, the adsorption effect might not have been large enough to elevate bottle $POC/^{234}Th$ ratios as other workers have reported (Buesseler et al., 2006; Cai et al., 2008). We must mention here that for large particles, which are collected with screens and re-filtered with relatively small volumes of seawater, such adsorption effect will be negligible.

It should be noted that the bottle and pump $POC/^{234}Th$ ratio should not be compared directly as they are sampled from different oceanographic settings, although $POC/^{234}Th$ do not seem to be influenced by the adsorption effect in either location. Nonetheless, the effect of adsorption should be calculated to interpret the elevated $POC/^{234}Th$ levels in bottle filtration observed in others studies (e.g. Cai et al. (2010)). Liu et al. (2005) indicate that bottle filtration can be biased by zooplankton invasion on the filter that will increase carbon concentrations. Such a process would impact the $POC/^{234}Th$ ratio. Baena et al. (2007) note that the $POC/^{234}Th$ ratio in zooplankton in the northwest Mediterranean Sea ranges from 120 to 11,600 $\mu mol C dpm^{-1}$, which is 1–3 orders of magnitude higher than marine particles. As such, an increase of the $POC/^{234}Th$ ratio is expected even with a minor level of zooplankton contamination. In addition, Turnewitsch et al. (2007) indicates that artificial particle formation during bottle filtration can add up to a maximum of 2–3 $\mu mol C L^{-1}$, and that it is possible to induce an increase in the $POC/^{234}Th$ ratio given the high $C/^{234}Th$ ratio in the dissolved phase. However, the mechanism of this coagulation/aggregation is unknown and thus how this process affects $POC/^{234}Th$ is still in question.

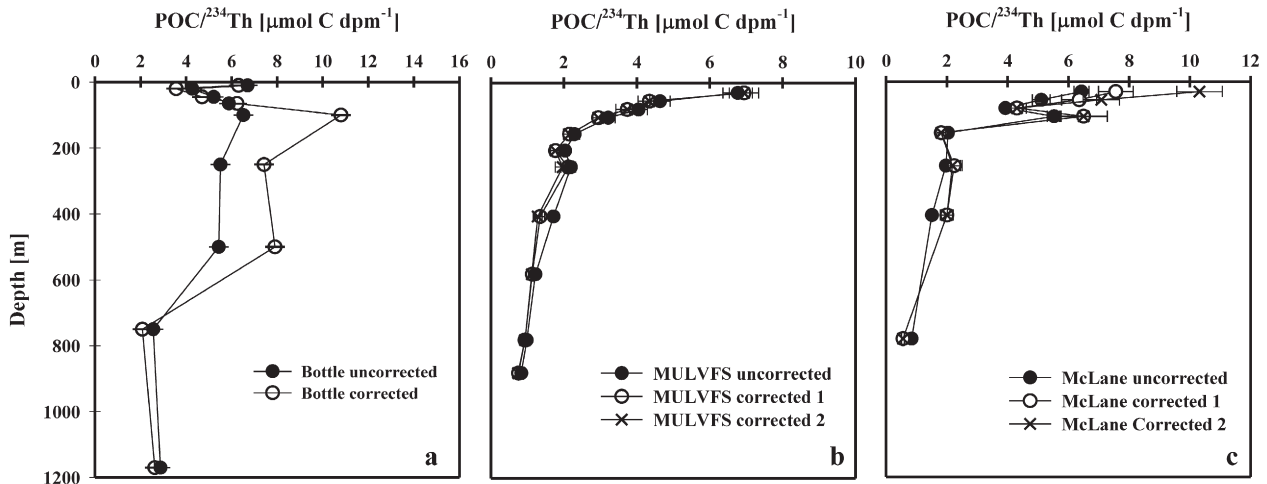


Fig. 7. Profiles of corrected and uncorrected $POC/^{234}Th$ ratios. (a), (b) and (c) are for bottle MULVFS and McLane samples. Note that corrected 1 & 2 means the corrected $POC/^{234}Th$ ratios by assuming a ^{234}Th saturation value of 0.21 $dpm cm^{-2}$ and 0.31 $dpm cm^{-2}$, respectively.

5. Conclusions

In order to explain the difference between bottle and pump POC/²³⁴Th ratio, both adsorption and particle break-down of DOC and ²³⁴Th for bottle and pump filtration was investigated. We observed that the adsorption effect dominates during the bottle filtration, while both particle break-down and adsorption are important for large volume pump filtration. We observed that thorium had a higher absorption rate than carbon by comparing POC/²³⁴Th ratios between bottles and pumps. This adsorption was important in determining the POC and particulate ²³⁴Th concentrations from bottle filtration, accounting for 22 ± 7% of POC and 25 ± 17% of particulate ²³⁴Th. However, their influence on the POC/²³⁴Th ratio was quite limited. In addition, particle break-down and adsorption did not seem to influence the POC/²³⁴Th ratios from the pump samples. Therefore, other factors such as zooplankton invasion and/or artificial particle formation are still needed to account for the POC/²³⁴Th difference between pumps and bottles, and these need to be fully investigated in the future.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.marchem.2016.06.004>.

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