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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A B S T R A C T
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 (R² = 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 ± 7% for POC and 25 ± 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 dpm cm⁻² which was the highest unsaturated value from the bottle sample, but ~0.31 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 ephaptic 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; Cochrane and Masque, 2003; Waples et al., 2006). In essence, 234Th is a short-lived (t₁/₂ = 24.1 d) particle reactive element that is produced at a constant rate from its conservative and long lived parent, Uranium-238 (t₁/₂ = 4.5 × 10⁹ 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 advections, 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/234Th ratio associated with sinking particles (Buesseler et al., 2006). Three approaches commonly used to determine POC/234Th 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/234Th 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/234Th 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/234Th (Chen, 2008). One exception was observed in the North Pacific during the VERTIGO project, when POC/234Th ratios from the pump were exceptionally high (sometimes > 200 µmol 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/234Th 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 µmol 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 µmol L −1. Recent work in the Northeast Pacific also indicates that bottle POC can be 2–4 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 234Th, which obviously determine the POC/234Th ratio, have not been made in examining this hypothesis. Some earlier studies in fact suggest that 234Th 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 234Th and compared bottle and pump filtration, aiming to evaluate if such adsorption impacts the estimation of POC/234Th 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 25 mm QMA filter (active area = 3.8 cm2) for POC and particulate 234Th analysis, and another 4 L was sampled for total 234Th 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 cm²), while 342–727 L of seawater was filtered on 142 mm diameter filters for the McLane pumps (active area = 133 cm²). For 234Th 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/234Th ratio, we adopted the similar “two filters in-line” approach used by Turnewitzsch et al. (2007). Briefly, two pre-combed 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 234Th 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 234Th 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 234Th 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 µg C and 0.2 µg N. The analytical error on carbon and nitrogen was ~5%.

2.4. Total 234Th measurements

Total water column 234Th activities were analyzed using modified MnO2 co-precipitation technique (Maiti et al., 2012; Cai et al., 2006). The dissolved 234Th activity was calculated by subtracting particulate 234Th activity on filter-A from total 234Th activity.

3. Results

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

The particulate 234Th 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 µmol C L −1 (Table 1); PN concentrations changed from 0.11 to 0.53 µmol N L −1; and particulate 234Th ranged from 0.18 ± 0.01 to 0.47 ± 0.02 dpm L −1. On filter-B, POC, PN and particulate 234Th were much lower, and ranged from 0.21 to 0.45 µmol C L −1 for POC; 0.01 to 0.09 µmol N L −1 for PN; and 0.04 ± 0.01 to 0.10 ± 0.01 dpm L −1 for particulate 234Th. Dissolved 234Th 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 µmol C L −1, and from 0.01 to 0.19 µmol N L −1; particulate 234Th from filter-A ranged from 0.12 ± 0.01 to 0.30 ± 0.02 dpm L −1; and, POC, PN and particulate 234Th from filter-B ranged from 0.02 to 0.25 µmol C L −1, 0.004 to 0.04 µmol 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 234Th on filter-A ranged from 0.18 to 1.79 µmol C L −1, 0.002 to 0.18 µmol 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 234Th ranged from 0.04 to 0.31 µmol C L −1.
Particulate 234Th, particulate organic carbon (POC), particulate nitrogen (PN) concentrations on filter-A and -B, dissolved 234Th 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.

The percentage carbon and thorium samples were comparable with those from MULVFS samples, but not for A collected via MULVFS and McLane, a shared similar distribution an opposite trend with respect to

were slightly higher compared to the mid-water, i.e., 1.03 ± 0.02 to 0.08 dpm L⁻¹, 0.28 to 0.06 dpm L⁻¹, and 0.18 to 0.01 dpm L⁻¹, respectively. From 100 to 750 m, little variations were found for particulate 234Th 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 234Th) 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 234Th ratios on filter-A and filter-B

The profiles of POC 234Th ratios on filter-A and filter-B from bottle, MULVFS and McLane samples are shown in Fig. 2. For bottle samples, the POC 234Th ratio on filter-A varied from 2.5 ± 0.3 dpm mol⁻¹ to 6.6 ± 0.3 dpm mol⁻¹, while a larger range was observed on filter-B, from 2.2 ± 0.2 dpm mol⁻¹ to 13.8 ± 3.4 dpm mol⁻¹. The vertical profiles for filter-A and filter-B were also different. For filter-A, the POC/234Th ratio was relatively higher in the upper 500 m (4–6 dpm mol⁻¹) and <3 dpm mol⁻¹ below 500 m. For filter-B, the POC/234Th ratio was higher at the surface (>10 dpm mol⁻¹) and then decreased to 2.2 ± 0.5 dpm mol⁻¹ at 100 m. Below 100 m, it varied between 2 and 4 dpm mol⁻¹. The POC/234Th ratio on filter-B was found to
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/234Th on filter-A from both sampling devices were similar to the pumps, that is high (~6 μmol dpm⁻¹) at the surface and low (~1 μmol dpm⁻¹) at depths below 600 m. Interestingly, POC/234Th ratios on filter-B showed very different depth distributions. The MULVFS POC/234Th ratios on filter-B were higher than those on filter-A at all depths with the highest value (16.7 μmol dpm⁻¹) at 400 m. The McLane POC/234Th 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 C/234Th ratio in the dissolved phase should be much higher compared to particulate ones. DOC concentration in the open ocean normally range from 70–80 μmol C L⁻¹ in the surface to about 40 μmol C L⁻¹ in the deep ocean (Dai et al., 2009), and dissolved 234Th varies from 1.0 to

![Graphs showing depth profiles of POC and 234Th](image)

**Fig. 1.** Profiles of POC and 234Th 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).

**Fig. 2.** Profile of POC/234Th 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/$^{234}$Th ratio should be on the order of 10–100 μmol C dpm$^{-1}$.

4. Discussion

4.1. Adsorption of $^{234}$Th and DOC

Two important processes that can explain the presence of particulate $^{234}$Th 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 $\text{Part.}$ is the particulate concentration of $^{234}$Th and POC; $\text{loss}$ 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; $\varepsilon L$ is the capture efficiency for the particles lost from filter-A; and $\text{Ads}$ the adsorption of dissolved material (<1 μm). Here adsorption means $^{234}$Th and POC collected from <1 μm particles including

Fig. 3. Correlations between filter-A $^{234}$Th and dissolved $^{234}$Th 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 234Th on filter-B and dissolved 234Th (R² = 0.58, in Fig. 3a) indicates that the adsorption of dissolved 234Th 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 234Th can be estimated using the following the equation when it is under-saturated:

$$\frac{234\text{Th}_{ads}}{234\text{Th}_{diss}} = k$$

(3)

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

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

$$B = A + k$$

(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 ± 7% (n = 9), suggesting the adsorption from DOC is important in the open ocean. The range for 234Th is similar but with a larger variation compared to that of carbon, ranging from 7 to 50%, with an average of 25 ± 17% (n = 9).

For bottle samples, we find that the particulate 234Th from filter-A is negatively associated with that from filter-B, while DOC concentration, on the other hand, is positively related (Fig. 4a and b). A possible explanation for this is that dissolved 234Th (thus absorbed 234Th) is usually low in the surface water and high at depth while particulate 234Th in the water column has the opposite distribution. Conversely, the reason that DOC 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 234Th on filter-B and dissolved 234Th are negatively correlated (Fig. 3c and e), while 234Th concentrations on filter-A are found to be positively correlated with those from filter-B (Fig. 4c and e, R² = 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 mL cm⁻² min⁻¹), particle breakdown might progressively contribute to their concentrations on filter-B. Higher 234Th concentration on filter-A (corresponding to lower dissolved 234Th in Table 1) might then indicate higher particulate 234Th loss to filter-B. Secondly, with filtration of larger volumes, adsorption might be close to or reach its saturation state.

Benitez-Nelson et al. (2001) indicated that 234Th 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 234Th adsorption might have reached its saturation state in our case. Once the 234Th 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 234Th concentration on filter-A is usually characteristic of a lower filtration volume (which means higher fraction absorbed) in our case. Therefore, 234Th concentration on filter-A (dissolved 234Th) 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 234Th on filter-B, since the saturation amount for 234Th on the filter is difficult to measure.

In our bottle case, the highest adsorbed 234Th activity was 0.21 dpm cm⁻² filter. As both dissolved 234Th 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 234Th 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 234Th 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 0.21–0.31 dpm cm⁻². The saturation activity of 234Th 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 234Th, i.e., there are differences in

<table>
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* 234Th adsorption concentration for bottle samples is calculated as 0.0403 multiplied by dissolved 234Th 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.
* Th is the percentage of 234Th adsorption over 234Th on filter-B.
* 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 $POC_{ads} = \frac{234\text{Th}_{ads}}{234\text{Th}_{diss}}$, where $\alpha = \frac{234\text{Th}_{ads}}{234\text{Th}_{diss}}$.
* Those numbers calculated as >100% or <0% are all forced to 100% and 0%.
dissolved $^{234}$Th activity in the euphotic zone of both sites due to export. Based on this assumption, the absorbed $^{234}$Th concentration for MULVFS and McLane can be calculated as:

$$Th_{ads} = \frac{A_{Th}}{V} \times S$$

where $A_{Th}$ is the amount of absorbed $^{234}$Th (0.21–0.31 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 breakdown from filter-A is important. In addition, particle loss can be estimated based on Eq. (2):

$$^{234}Th_{loss} = \frac{^{234}Th_{B} - ^{234}Th_{ads}}{\varepsilon_L}$$

Here we assume that $\varepsilon_L$ 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. $\text{POC}_{\text{ads}} = kc$, 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. $\text{POC}_{\text{ads}} = A/V$, 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

$\text{POC}^{234}\text{Th}$ 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 $\text{POC}^{234}\text{Th}$ 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 $^{234}\text{Th}$ on filter-B is found to be quite stable with filtration volume which we justify as $^{234}\text{Th}$ 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 $^{234}\text{Th}$ and carbon adsorption are shown in Fig. 6a. In this example, more thorium is adsorbed relative to carbon in the McLane pumps which results in lower $\text{POC}^{234}\text{Th}$ ratios on filter-B (Fig. 2). With the higher volume MULVFS, the POC remains high, which elevates the $\text{POC}^{234}\text{Th}$ ratios. This is also found to be true for bottle samples. If carbon and thorium were adsorbed at the same rate, the $\text{POC}^{234}\text{Th}$ ratio should be similar to the dissolved phase (10–100 μmol C dpm$^{-1}$ as mentioned above). Nevertheless, the $\text{POC}^{234}\text{Th}$ ratio was 2–14 μmol dpm$^{-1}$ on filter-B indicating that thorium was being absorbed at a higher rate compared to carbon. The two high $\text{POC}^{234}\text{Th}$ ratios on filter-B from MULVFS in the mid-depth was related to analytical caveat. Those high values were driven by the low $^{234}\text{Th}$ 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 $\text{POC}^{234}\text{Th}$ 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:

$$P O C_A - P O C_{a d s} \over T h_A - T h_{a d s} = P O C_B - P O C_{a d s} \over T h_B - T h_{a d s}$$

(7)

Eq. (7) can then be solved as:

$$\text{POC}_{\text{ads}} = {\text{POC}_B - a \text{POC}_A \over 1 - a}$$

(8)

where $a = \text{Th}_A - \text{Th}_{ads} \over \text{Th}_A - \text{Th}_{B}$. As discussed above, the adsorption from the dissolved phase might have been dominant for $^{234}\text{Th}$ for filter-B with MULVFS, and we also list the $\text{Th}_{ads}$ 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. $\text{POC}^{234}\text{Th}$ correction for pump and bottle filtration

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

$$\left( {\text{POC} \over \text{Th}} \right)_{\text{corrected}} = \left( {\text{POC}_A + \text{POC}_B - 2 \text{POC}_{\text{ads}} \over 2 \text{Th}_A + 2 \text{Th}_B - 2 \text{Th}_{\text{ads}}} \right)$$

(9)

where $\text{POC}_A$ and $2\text{Th}_A$ are the POC and particulate $^{234}\text{Th}$ concentrations on filter-A, and $\text{POC}_B$ and $2\text{Th}_B$ are those on filter-B. Although we assume that $^{234}\text{Th}$ saturation activity varies from 0.21 to 0.31 dpm m$^{-2}$, the corrected $\text{POC}^{234}\text{Th}$ ratio seems quite stable with the changes of $^{234}\text{Th}$ saturation value, and it is quite comparable with those on filter-A, which implies that these processes played a minor role in impacting
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\textsuperscript{234}Th ratio in the colloidal phase (>10 kDa) is similar with that in POC (>1 µm), 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/234Th ratios as follows:

\[
\frac{POC}{234Th}_{\text{corrected}} = \frac{POC_A - POC_B}{234Th_A - 234Th_B}
\]

where POC\textsubscript{A} is the POC concentration on filter-A and POC\textsubscript{B} on filter-B, and 234Th\textsubscript{A} and 234Th\textsubscript{B} are the 234Th concentrations on filter-A and -B. The corrected and uncorrected (filter-A) profiles of POC/234Th are shown in Fig. 7a. In the upper (0–65 m) and deep (750–1170 m) ocean, the corrected and uncorrected POC/234Th are similar, with their ratios close to 1. In the mid-water (100–500 m), the corrected POC/234Th 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/234Th 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/234Th ratio should not be compared directly as they are sampled from different oceanographic settings, although POC/234Th 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/234Th 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/234Th ratio. Baena et al. (2007) note that the POC/234Th ratio in zooplankton in the northwest Mediterranean Sea ranges from 120 to 11,600 µmol C dpm\textsuperscript{-1}, which is 1–3 orders of magnitude higher than marine particles. As such, an increase of the POC/234Th 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 µmol C L\textsuperscript{-1}, and that it is possible to induce an increase in the POC/234Th ratio given the high C/234Th ratio in the dissolved phase. However, the mechanism of this coagulation/aggregation is unknown and thus how this process affects POC/234Th is still in question.

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.

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

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

In order to explain the difference between bottle and pump POC\(^{234}\text{Th}\)/\(^{238}\text{Th}\) ratio, both adsorption and particle break-down of DOC and \(^{234}\text{Th}\) 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\(^{234}\text{Th}\)/\(^{238}\text{Th}\) ratios between bottles and pumps. This adsorption was important in determining the POC and particulate \(^{234}\text{Th}\) concentrations from bottle filtration, accounting for 22 ± 7% of POC and 25 ± 17% of particulate \(^{234}\text{Th}\). However, their influence on the POC\(^{234}\text{Th}\)/\(^{238}\text{Th}\) ratio was quite limited. In addition, particle break-down and adsorption did not seem to influence the POC\(^{234}\text{Th}\)/\(^{238}\text{Th}\) 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\(^{234}\text{Th}\)/\(^{238}\text{Th}\) difference between pumps and bottles, and these need to be fully investigated in the future.

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