# Testing a new small-volume technique for determining $^{234}$Th in seawater

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Thorium-234 is a naturally occurring radionuclide that has been widely studied in ocean sciences. These studies use the disequilibrium between the soluble parent uranium-238 ($T_{1/2} = 4.5 \cdot 10^9$ y), and its particle reactive daughter, $^{234}$Th ($T_{1/2} = 24.1$ d), to quantify the in-situ removal rates of $^{234}$Th on sinking particles. Here, we present additional experiments that test a new 2-l procedure in which $^{234}$Th is co-scavenged with a $MnO_2$ precipitate. Unlike other techniques, this method can be easily applied at-sea with an overall precision and accuracy of ≤5%. Our experiments have sought to elucidate the effects of delaying reagent addition and precipitate filtration, differences in sample bottle types, and issues related to sample backgrounds and $^{234}$Th particulate sampling. Most of these experiments were conducted using water collected on repeated occupations of station ALOHA (22°45.0'N, 158°00.0'W), 100 km North of Oahu, Hawaii.

## Introduction

Thorium-234 is a particle reactive element ($T_{1/2} = 24.1$ d) produced from the decay of its soluble conservative parent, $^{238}$U ($T_{1/2} = 4.5 \cdot 10^9$ y). In essence, it is the balance between production, decay and particulate removal that drives the distribution of $^{234}$Th in the world's oceans. A number of studies have directly linked biological activity and the subsequent export of particulate material to a decrease in upper-ocean $^{234}$Th activity.[1–3] By measuring the ratio of carbon and other elements to $^{234}$Th on sinking particles, researchers have been able to derive sinking particulate carbon export and other elemental fluxes.[4]

Until recently, one of the difficulties with using $^{234}$Th has been either the need for large water volumes and/or extensive chemical purification techniques. A new method has been developed for the measurement of $^{234}$Th in seawater which involves small volumes, little processing, and direct measurement of $^{234}$Th at sea using a low-level beta counter.[5] This work builds upon the methods outlined by BUESSELER et al.[5] and explores issues related to the new procedure. A series of experiments were conducted in order to further examine the importance of delaying reagent addition and/or precipitate filtration, differences in sample bottle types, and prefiltration of $^{234}$Th using various filter media. In addition, we have taken a much closer look at the stability and reproducibility of sample background count rates.

## Experimental

### Study sites

Most of the experiments discussed in detail in this paper rely on samples taken during monthly 5-day Hawaiian Ocean Time-series (HOT) cruises to Station ALOHA (22°45.0'N, 158°00.0'W). At this site, samples were collected throughout the water column to depths of 3,500 m. The 10-year data set of the HOT program has demonstrated relatively low particulate matter export.[6] As such, station ALOHA is ideal for testing the precision and accuracy of the new method in determining particulate export in waters were there is only a small difference in $^{238}$U and $^{234}$Th activities. Additional samples were collected at the National Energy Laboratory of Hawaii (NELHA). Details of this study site can be found in the paper by BUESSELER et al.[5]

### The 2-l technique

The method tested in this study is a modification of the 20-l method developed by RUTGERS VAN DER LOEFF and MOORE[7] for the measurement of $^{234}$Th in seawater. In essence, this technique involves the formation of a $MnO_2$ precipitate, which preferentially scavenges $^{234}$Th and negligible amounts of $^{238}$U. The precipitate is subsequently filtered and measured for $^{234}$Th via the detection of its high-energy beta-emitting daughter, $^{234m}$Pa. Comparisons of the 2-l technique with other methods have been discussed in detail by BUESSELER et al.[5]

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In this study, 2-l samples were collected during several days at NELHA in March 1999, and during a series of HOT cruises that occurred from Spring 1999 to Winter 2000. Briefly, unfiltered water samples were collected and the reagents ($KMnO_4$ and $MnCl_2$) were added to form the Mn precipitate. The reagents used here are 1/10th of the concentration used in the original 20-l technique of Rutgers van der Loeff and Moore.[7] The precipitate was allowed to form for 8–16 hours and then filtered onto a 25 mm diameter, 1.2 μm pore sized silver mesh filter. Silver filters have much lower beta backgrounds than other traditional filter media. The silver mesh filters were allowed to air dry for several hours, and then prepared for low-level beta-counting. The extraction efficiency and recovery of the 2-l method is discussed in detail in Buesseler et al.[5]

All mounted samples were counted on a 5 sample, gas-flow proportional low-level beta counter produced by Risø National Laboratories (Roskilde, Denmark). The unit is controlled though an external computer and utilizes an anti-coincidence (AC) shield above the 25 mm diameter sample windows. The entire unit is surrounded by approximately 8 cm of lead. In this manner, background count rates are reduced to extremely low levels, ranging from 0.15 to 0.23 counts·min$^{-1}$ depending on the detector distance from the AC shield. Counting efficiencies for $^{234m}$Pa on stainless steel planchettes covered with Mylar and foil are approximately 40% and vary by less than 2% between detectors. The Risø counter has been easily transported between land based and at-sea labs without any detectable changes in efficiency or background count rates.

## Results and discussion

### Time and bottle type dependence

During at-sea sample collection, there are often time periods when the number of samples collected will exceed that which can be immediately processed. As such, we conducted experiments to evaluate the effect of delays in adding reagents and/or filtration of the Mn precipitate on the measured $^{234}$Th activities. Samples were collected from a depth of 3,500 m at Station ALOHA during HOT cruises Hot 109 (November 1999) and Hot 110 (December 1999). At these depths, $^{234}$Th is assumed to be in secular equilibrium with $^{238}$U ($^{234}$Th/$^{238}$U activity ratio $= 1$) and any deviation from unity would indicate that there are issues that must be considered when sampling. In the first experiment, 2-l samples were collected and the reagents were immediately added. The Mn precipitate was then allowed to settle for 72 hours prior to filtration. There was no statistical difference between the expected and measured $^{234}$Th activities.

In the second experiment, 2-l samples were collected and allowed to stand in the sample bottle for 6–72 hours prior to reagent addition. Once the reagents were added, all samples were filtered within 10–16 hours. At time periods greater than 6 hours, significant bottle adsorption of $^{234}$Th occurred (as high as 25%) and resulted in much lower reproducibility. A similar effect was found when seawater was allowed to remain in the Niskin bottles prior to sampling. These phenomena have been recognized to occur in the past (Turnevich, personal communication). We also tested several different sample bottle types, i.e., polycarbonate versus polyethylene, but found no relationship with decreased $^{234}$Th activities. To avoid potential adsorption issues in the future, care must be taken to ensure that reagents are added within the first hour of collection. Any minor adsorption that does occur in that time period should affect deep-water calibration samples to the same extent.

### Background corrections

In order to ensure accurate quantification of sample background count rates, samples were counted for greater than 6, $^{234}$Th half-lives (144 days) after initial collection. The average background count rate for all $^{234}$Th samples collected using the 2-l method is 0.41± 0.07 counts·min$^{-1}$. This is higher than the 0.15 to 0.23 counts·min$^{-1}$ measured by the instrument alone. Since beta-counters are not isotope specific, all beta-emissions that reach the detector are counted. The 2-l technique does not have extensive purification methods to remove all other beta-emitting radionuclides, hence, the most likely source of the increased background is due to non-$^{234}$Th beta activity in the Mn precipitate itself. While Mn coprecipitation does not carry significant amounts of $^{238}$U (less than 0.5%), it does scavenge other beta emitters, such as radium and its radioactive decay products. In seawater, the average concentration of $^{226}$Ra is approximately 0.3 disintegrations·min$^{-1}$ (dpm)·kg$^{-1}$, although concentrations can vary depending on the regime.[8]

To evaluate potential contributions of $^{226}$Ra and its daughters to our measured $^{234}$Th activities, we spiked two filters containing a Mn precipitate with 26.5 dpm of $^{226}$Ra. The samples were counted repeatedly for 3 days under an aluminum-coated foil, after which they were removed from the Risø counter. The foil was then sealed (with an electric sealer) to produce a gas tight enclosure and the samples recounted. Using a $^{226}$Ra counting efficiency of 35%, measured $^{226}$Ra activities increased from approximately 9±1% of the expected $^{226}$Ra activity, before being sealed, to greater than 50% thereafter (Fig. 1). This dramatic increase is attributed to the accumulation of $^{222}$Rn and its high-energy daughter, $^{214}$Bi. Our experiment demonstrates that under normal counting conditions, greater than 80% of the $^{222}$Rn is lost.

## $^{222}$Rn ingrowth



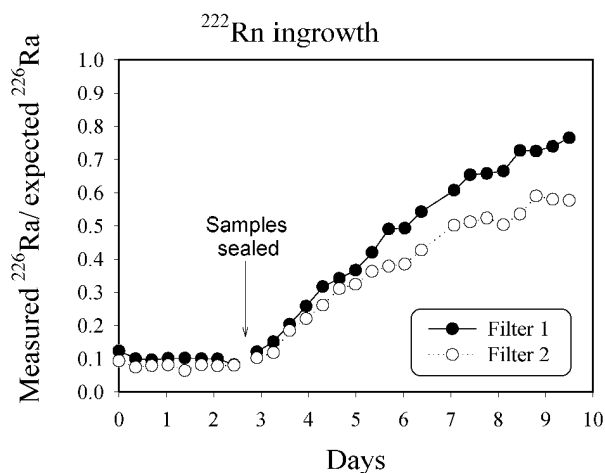*Fig. 1.* Plot of the ratio of measured to expected $^{226}$Ra activity with time. Measured $^{226}$Ra activities were determined assuming a beta-counting efficiency of 35%. Both samples were sealed after 2.5 days
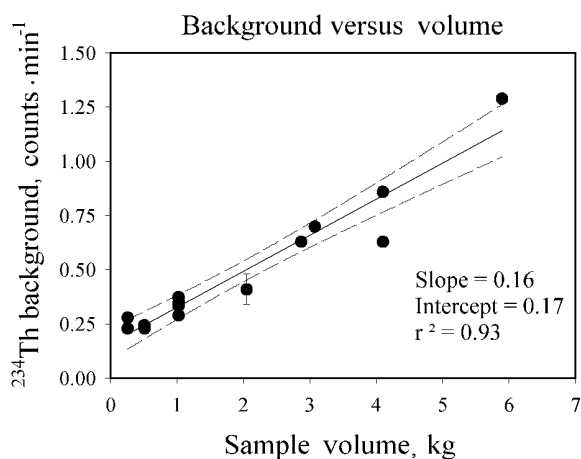
## Background versus volume



*Fig. 2.* Plot of sample background $^{234}$Th activity versus volume. Dashed lines represent the 95% confidence limit

Thus, its daughters have a correspondingly low contribution to our measured $^{234}$Th count rates. This provides additional evidence that it is the residual activity of $^{226}$Ra and its daughters that most likely cause the higher than expected background beta activity. As a result of this additional small background, one must count each sample after >144 days to ensure that the appropriate background correction has been made.

Uncertainty in the actual contribution of $^{226}$Ra depends on the steady state production and outgassing of $^{222}$Rn during the two measurements of the sample: before and after $^{234}$Th decay. To test the background stability, a range of sample sizes were counted and the background count rates determined either from direct counting or from assuming equilibrium in the deep

waters (Fig. 2). The excellent correlation between sample volume and sample count rate ($r^2 = 0.93$) implies that the inherent sample background is stable with time, i.e., any loss of activity due to $^{222}$Rn outgassing between initial and final counting is constant.

### Particulate $^{234}$Th

In order to separate dissolved and particulate $^{234}$Th and to alleviate difficulties associated with filtration in particle-laden environments (such as that found in the coastal ocean), it will be necessary to prefilter $^{234}$Th samples prior to forming the Mn precipitate. Typically, particulate samples are collected using glass fiber filters (GFFs). A recent study by MORAN et al.,[9] however, has found that GFFs will also adsorb a substantial amount of dissolved organic carbon (DOC). As a result, these types of samples may overestimate the amount of particulate organic carbon (POC) by as much as a factor of 2–4. Given the particle reactivity of $^{234}$Th and recent research that suggests complexation of dissolved $^{234}$Th by DOC,[10,11] we decided to test the effects of small versus large volume seawater samples and differences in filter media on particulate $^{234}$Th activities.

Between 20 and 450 l seawater samples were collected using 142 mm GFFs (nominal pore size ~ 0.7 μm) and Quartz Microfiber (QMA, nominal pore size ~1.0 μm) and Nuclepore filters (nominal pore size ~1.0 μm) (Fig. 3). There were substantial decreases in the particulate $^{234}$Th activity with increasing volume up to ~300 l for both the GFF and QMA filters.

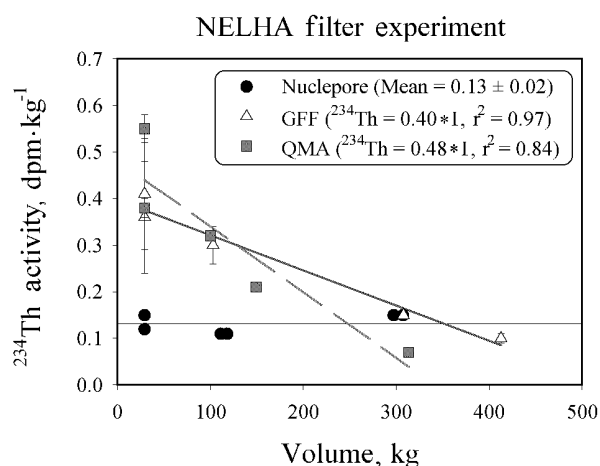## NELHA filter experiment



*Fig. 3.* Plot of particulate $^{234}$Th activities (dpm·kg$^{-1}$) measured on Nuclepore (filled circles) GFF (open triangles) and QMA (filled squares) filters at NELHA. Note that error bars include uncertainties associated with sample volume, counting times, and efficiency. Duplicate samples at ~30 l were collected at two different flow rates. Higher $^{234}$Th activities for the GFF and QMA samples and the lower $^{234}$Th activity for the Nuclepore sample are associated with the lower flow rates of 1 l·min$^{-1}$
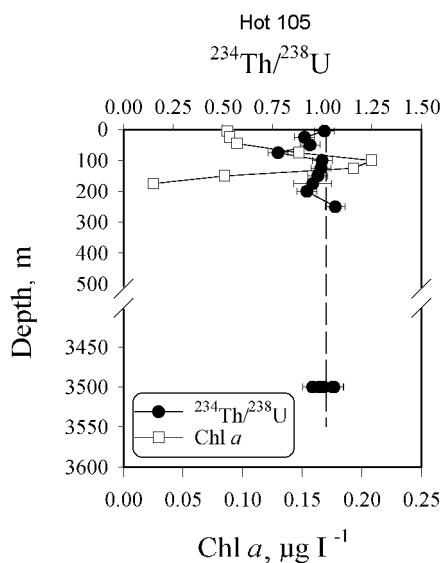
**Hot 105**

$^{234}Th/^{238}U$

*Fig. 4.* Plot of $^{234}Th/^{238}U$ ratio (●) and Chl *a* (□) vs. depth for 2 l samples collected during Hot 105 (May 1999) at Station ALOHA (22°45.0'N, 158°00.0'W) as part of the HOT Program. Surface $^{234}Th/^{238}U$ samples were calibrated to deep water samples (3,500 m) collected on the same cruise. The vertical dashed line represents the $^{234}Th/^{238}U$ ratio expected if at secular equilibrium. Note that the standard deviation of deep-water replicate samples is 6.7%

This is exactly the opposite of what one might expect to occur with filter clogging. In contrast, the Nuclepore filters had constant $^{234}Th$ particulate activities throughout the sample volumes tested. It should be mentioned that all samples were collected within a 2-day period at NELHA and that Nuclepore samples were always collected simultaneously with either a QMA or GFF filter. This suggests that any variability in particle concentrations was minor during our sampling period.

The steady decrease in particulate $^{234}Th$ activity with increasing volume suggests that the QMA and GFF filters were adsorbing dissolved $^{234}Th$, thereby, artificially elevating particulate $^{234}Th$ activities at lower sample volumes. Further evidence for this phenomenon is found from the flow rates at which the particulate samples were collected. For low sample volumes (25–30 l), each filter was run in duplicate with a flow rate of either 1 or 4–5 l·min$^{-1}$. For both the QMA and GFF filters, significantly higher activities were found at the slower flow rate. It is possible that the difference in activity is due to particle breakdown associated with higher pressures (at the higher flow rates). However, if this were the case, the Nuclepores would exhibit a similar pattern and they do not. Hence, we attribute the $^{234}Th$ activity difference to an increase in water contact time with the GFF (and QMA) filter.

Possible adsorption of dissolved $^{234}Th$ onto QMA filters has been previously suggested by BUESSELER et al.[12] based on particulate $^{234}Th$ samples collected in the Arabian Sea. In general, it was found that surface

small volume (avg. 100 l) particulate samples had average $^{234}Th$ activities that were 50% greater than the large volume (avg. 290 l) samples. Sub-surface differences in particulate $^{234}Th$ activities were even larger: on average 2.7 times higher for the small volume (~49 l) than for the larger (~490 l) volume samples. We, therefore, suggest the use of Nuclepore filters for particulate $^{234}Th$ sampling. It should be mentioned, however, that the Mn precipitate based total $^{234}Th$ measurements will not be affected by the above filtration artifacts.

*Precision and application to marine systems*

The potential of our 2-l technique in elucidating the fine scale structure of upper ocean particulate export can be demonstrated from the $^{234}Th$ depth profile taken during Hot 105 (May 1999) at Station ALOHA (Fig. 4). Disequilibriums in $^{234}Th$ from $^{238}U$ occur in the upper 100 m, just above the chl *a* maximum. This removal is most likely caused by the preferential scavenging of $^{234}Th$ onto biologically derived freshly formed aggregates of sinking particulate matter. Such minute detail in structure would not have been observed with other standard $^{234}Th$ measurement techniques. A further test of the reproducibility of our sampling technique was conducted using three to five deep-water samples (3,500 m) collected from Station ALOHA on each HOT cruise from Hot 104 (April) to Hot 110 (December). Overall $^{234}Th/^{238}U$ activity ratios were 1.00±4%. Within each cruise, the standard error was often as low as 2%.

**Conclusions**

The development of a new 2-l technique to measure total $^{234}Th$ in seawater has the potential to greatly increase our knowledge of $^{234}Th$ derived particulate matter export in the open ocean. In this study, we have further tested this method in regards to sample prefiltration, background activities, and potential issues related to sample collection. Our results suggest that any prefiltration of small volume samples must use either Nuclepore or silver filters to avoid artifacts associated with the collection of dissolved $^{234}Th$. In addition, samples should be collected as soon as possible and reagents added immediately in order to reduce the potential adsorption of $^{234}Th$ onto the container walls. Filtration of the Mn precipitate, however, can be delayed for up to 72 hours, and probably longer. There are no requirements that special sample bottles must be utilized when collecting samples. Finally, our results suggest that all samples must be counted a second time after >144 days have passed in order to ensure high precision and accuracy through an appropriate background correction.

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