

An intercomparison of small- and large-volume techniques for thorium-234 in seawater

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Abstract

In this paper, an intercomparison of methods for the determination of ²³⁴Th in seawater is discussed. Samples were collected either from a shore-based 600 m water source, or from standard bottle casts in deep waters off Hawaii and the Southern Ocean. We compared large-volume techniques, which rely upon Mn cartridges for the collection of dissolved ²³⁴Th and its detection via gamma counting (> 200-l samples), with small volume methods that employed either direct beta counting, or beta counting after radiochemical purification (2–20-l samples). Unique to this study is the presentation of small volume (2 and 5 l) ²³⁴Th methods. This new technique is an adaptation of 20-l methods that are based on the coprecipitation of thorium with Mn oxides followed by direct beta counting of the precipitate. The small volume Mn coprecipitation methods were found to be superior to other methods due to ease of sample collection, processing and low overall analytical uncertainties. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thorium-234 ($t_{1/2} = 24.1$ days) is a naturally occurring, particle-reactive radionuclide that is produced continuously in seawater from its soluble parent, uranium-238 ($t_{1/2} = 4.47 \times 10^9$ years). Given this unique chemistry, ²³⁴Th has become a valuable

tool for tracing scavenging processes over time-scales of days to weeks (Bhat et al., 1969; Matsumoto, 1975; Coale and Bruland, 1985; Buesseler, 1998; Buesseler et al., 1992a). In the past decade, the widest application of ²³⁴Th in marine settings has been related to its use in quantifying the sinking flux of organic carbon and other particle associated elements from the upper ocean (e.g. Buesseler, 1998 and refs. therein). Changes in this sinking particle flux may potentially influence the magnitude of carbon storage in the deep ocean. As a result, the

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processes that control the rate and extent of particle export are of great interest to oceanographers worldwide.

The flux of ^{234}Th is commonly derived from the difference between the production and decay rate of ^{234}Th in seawater. In its simplest formulation, the export flux of ^{234}Th , P , is determined using a steady-state, one-dimensional activity balance equation:

$$P = (^{238}\text{U} - ^{234}\text{Th})\lambda, \quad (1)$$

where λ is the ^{234}Th decay constant (0.0288 day^{-1}) and ^{234}Th and ^{238}U are the activities (disintegrations per minute per kilogram; dpm kg^{-1}) of the Th/U pair. Since ^{234}Th fluxes are calculated from the difference between ^{234}Th and ^{238}U , the precision and accuracy of the flux is determined by how well one can quantify their measured activities in marine systems. Due to its high solubility in seawater, ^{238}U activities have been found to vary by only $\pm 1\%$ when normalized to salinity (Atlantic and Pacific data, $n = 23$ from Chen et al., 1986). In contrast, ^{234}Th activities can vary widely ($^{234}\text{Th} = < 0.2\text{--}2.5 \text{ dpm kg}^{-1}$). Low ^{234}Th activities are typically found in the surface ocean, coastal margins, and during periods of enhanced biological export, i.e. within plankton blooms. Errors or biases in ^{234}Th activity, particularly when the $^{234}\text{Th}/^{238}\text{U}$ activity ratio is close to one, can result in relatively large uncertainties in the calculated ^{234}Th export flux.

In this study, an improved method for the determination of ^{234}Th in seawater is compared to existing techniques used in many laboratories. This new procedure utilizes the lowest seawater-sample volumes of all known ^{234}Th methods to date and requires minimal handling and preparation at sea. The best standard for intercalibration of ^{234}Th techniques is pristine deep-ocean water ($> 500\text{--}1000 \text{ m}$), where the activities of ^{234}Th and ^{238}U are known to be in secular equilibrium ($^{234}\text{Th}/^{238}\text{U} = 1$). It was impractical to conduct our methodology intercomparison at sea given the large volume and time requirements. Hence, the primary intercomparison experiment was conducted over a several week period using 600-m-deep seawater collected and processed at the land-based National Energy Lab of Hawaii. In addition, we employed our small volume 2-l method on a

series of Hawaii Ocean Time-series ALOHA station cruises and a similar 5-l method during an expedition to the Southern Ocean. By using smaller sample volumes for seawater ^{234}Th analysis, we will be able to substantially increase sampling intensity and help reduce errors associated with ^{234}Th -derived export rates.

2. Background

Historically, the determination of ^{234}Th in seawater has involved iron hydroxide ($\text{Fe}(\text{OH})_3$) coprecipitation of ^{234}Th from 20 to 30 l of seawater followed by separation of ^{234}Th from the parent nuclide ^{238}U via ion-exchange chromatography. The ^{234}Th isolate was then electrodeposited on stainless steel discs and quantified by low-level beta counting (Anderson and Fleer, 1982). Coupled with the short half-life of ^{234}Th , this labor-intensive process limited the number of samples that could be collected and processed during any given field program or experiment.

An improved approach for measuring dissolved thorium isotopes in seawater was based on their scavenging onto MnO_2 -impregnated acrylic fibers (Moore and Reid, 1973; Bacon and Anderson, 1982). With this method, however, ^{234}Th was not the isotope of interest; rather ^{234}Th was used as a yield tracer for ^{228}Th and ^{230}Th . It was not until Livingston and Cochran (1987) developed an application of two MnO_2 -coated fibers connected in series that ^{234}Th could also be accurately measured using the above technique. The extraction efficiency of dissolved thorium isotopes from seawater can be characterized by:

$$\text{Efficiency} = 1 - \frac{\text{MnB}}{\text{MnA}}, \quad (2)$$

where MnA and MnB are the decay corrected activities of ^{234}Th on the first and second cartridges, respectively. This approach assumes that A and B cartridges are equally effective at extracting and retaining nuclides from seawater.

Buesseler et al. (1992b) used the two cartridge method to specifically measure $^{234}\text{Th}/^{238}\text{U}$ disequilibria in the upper ocean. Their method eliminated

the need for ion-exchange chemistry, since ^{234}Th adsorbed to the fiber whereas ^{238}U was not retained to any significant extent. After filtering several hundred liters of seawater through MnO_2 -impregnated cartridge pair, the fibers were packed into a reproducible geometry (via ashing at 500°C or crushing the cartridge into a “puck”) and the ^{234}Th activity was determined by gamma counting. The ^{234}Th method developed by Buesseler et al. (1992b) made the ^{234}Th measurement considerably easier to perform, and was adopted by several investigators (Cochran et al., 1995; Bacon et al., 1996; Baskaran et al., 1996; Moran et al., 1997; Charette and Moran, 1999; Santschi et al., 1999). However, there were still several drawbacks, such as: (1) the significant sampling time necessary for the required large volumes, (2) expensive in situ pumps, and (3) the assumption inherent to Eq. (2) that the MnO_2 -impregnated cartridge pair removed ^{234}Th with equal efficiency.

A compromise between the $\text{Fe}(\text{OH})_3$ precipitation method and the MnO_2 -coated fiber technique was recently developed by Rutgers van der Loeff and Moore (1999). The basic premise of the technique was the coprecipitation of ^{234}Th with MnO_2 from 20 l of seawater. Since their approach did not involve a yield tracer, it required recovery of the precipitate with a reproducible high yield, good separation of U and Th, and the minimization or quantification of contributors other than ^{234}Th to the beta count rate. The precipitate was filtered onto a 142-mm-diameter Nuclepore filter that was reproducibly folded and counted directly in a low-level beta counter. Unlike the $\text{Fe}(\text{OH})_3$ method, ^{238}U was not removed with the precipitate and, therefore, no chemistry was required. Though the volume requirements were much less than the MnO_2 cartridge method, they were still significant enough to require a separate hydrocast to obtain a single profile.

Here, an improved method for determining ^{234}Th in seawater based on the procedure developed by Rutgers van der Loeff and Moore (1999) is presented. The major improvement is a reduction in sample volume to as low as 2 l, which enables rapid at sea analysis. The method is validated with a series of laboratory and field studies. The main benefit of this low volume method is increased sample throughput, which enables much higher spatial and

temporal resolution. This is a key requirement in modern particle export studies.

3. Study site and experimental design

The main intercalibration study occurred at the Natural Energy Laboratory of Hawaii (NELHA) located at Keahole Point on the Big Island of Hawaii. At NELHA, deep seawater is transported from a depth of 600 m at a rate of $64 \text{ m}^3 \text{ min}^{-1}$ using a polyethylene pipeline with an inlet located 20 m above the seafloor. This location was ideal because of its on-line seawater supply and chemically stable deep-water signature. Also, compared to at-sea collection of large volumes of deep water, the unlimited supply of seawater at NELHA was a cost-effective solution.

Intercomparison samples were collected directly from three surface outlets and immediately processed using various ^{234}Th methods over a period of 3 weeks. During that time period, deep-water salinity values were constant (34.381 ± 0.033) and dissolved inorganic nutrients, such as nitrate and phosphate, were stable and typical of those found in other deep-water coastal areas ($\text{NO}_3^{2-} = 39.9 \pm 2.3 \text{ } \mu\text{M}$; $\text{PO}_4^{3-} = 3.1 \pm 0.1 \text{ } \mu\text{M}$).

Additional samples were retrieved from Station ALOHA in the North Pacific Gyre ($22^\circ 45.0' \text{N}$, $158^\circ 00.0' \text{W}$) during monthly cruises of the JGOFS Hawaiian Ocean Time-series (HOT) program. Deep-water samples were taken from 3500 m using multiple 12-l Niskin bottles. All samples were immediately collected after deployment and processed using the 2-l ^{234}Th method. Separate salinity samples were also taken from each Niskin and analyzed to calculate ^{238}U activities ($^{238}\text{U} [\text{dpm kg}^{-1}] = 0.06856 \times \text{Salinity}$) and to ensure that the appropriate depths were sampled.

Deep-water calibration of the 5- and 20-l methods was performed on the RV Polarstern expedition ANT XVI/3 to the Southern Ocean (March–May 1999). On several hydrocasts in the area between 46° and 66°S , and between 0° and 20°E , water was collected from 12-l Niskin bottles. For the 5-l method, all 18 analyses from depths $> 250 \text{ m}$ are reported. For the 20-l method, 10 samples were taken by combining

water from two to three bottles from depths ranging from 1000 to 3500 m.

4. Methodological details

4.1. MnO_2 precipitation: 20-l method

The original procedure has been described in detail by Rutgers van der Loeff and Moore (1999). To a weighed 20-l aliquot of seawater, six drops of concentrated ammonia (25 wt.% NH_3) and 250 μl of concentrated (60 g l^{-1}) KMnO_4 solution are added. After rigorous mixing, the sample is spiked with 100 μl of a concentrated MnCl_2 solution (400 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O l}^{-1}$, also used as reagent for oxygen determination with the Winkler method). After mixing, a suspension of MnO_2 is formed. After allowing the MnO_2 particles to nucleate for 8 h, the suspension is filtered over a 142-mm-diameter 1 μm Nuclepore filter. The empty container is shaken vigorously with distilled water to bring remaining adhering MnO_2 particles in suspension and on the filter. The filter is rinsed with distilled water, drained by suction and folded while wet six times to achieve a reproducible 18×18 mm package. The folded filter is held together with a plastic paperclip and allowed to dry before it is wrapped in thin (e.g. 0.01 mm) plastic wrap (polyester or polyethylene), and counted directly in a beta counter. For analysis of unfiltered samples, we use an additional two layers of foil cover to eliminate low energy non- ^{234}Th betas. This foil cover is optional when counting filtered samples.

4.2. MnO_2 precipitation: 5-l and 2-l method

The 20-l method described above was adapted to even smaller volumes in order to simplify sample collection and processing. These small volume methods allowed us to abandon the filter-folding procedure, which must be done in a reproducible manner in order to achieve constant counting efficiencies. These procedures are based upon the same principles, i.e. the direct detection of beta activity on a MnO_2 precipitate using a low background beta counter. For the 5-l method, we reduced the sample size to 5 l and modified the 20-l procedures to use 5% of the KMnO_4 reagents and a reduction in the

time before filtration to 1 h. These changes reduced wall-effects and the extraction efficiency, determined through repeated extraction, remained over 99%. The precipitate was collected on a 25-mm-diameter Whatman Multigrade GMF filter with a 1 μm nominal pore size, which was dried and beta-counted.

The 2-l method used 10% of the reagents used for the 20-l samples, and the sample was collected using a glass volumetric flask. After formation of the MnO_2 precipitate, it was filtered onto a single 25-mm-diameter silver mesh filter with an effective pore size of 1.2 μm (Poretics). We have used these silver filters in the past for the collection of particulate C and Th. Unlike standard glass fiber filters, which have detectable natural radioactivity within the filter material, the silver filter matrix has a negligible beta-counting blank. These filters are also easily prepared for beta counting and can be subsampled after counting for many stable or radioactive elements. Note that these reductions in sample volume are possible due to the relatively high ^{234}Th activity in open-ocean seawater combined with a high detection efficiency. For example, in typical open-ocean seawater, a 2-l sample with a ^{234}Th activity approaching that of ^{238}U (2.0–2.5 dpm kg^{-1}), will have a total precipitate activity of 4–5 dpm at collection. Given an overall detection efficiency of 38% for the high energy beta emission of $^{234\text{m}}\text{Pa}$ in this geometry (Ag filter covered by one piece of mylar and two pieces of foil; see Section 4.7), we expect a count rate of 1.5–1.9 counts per minute (cpm). This is an order of magnitude higher than the beta detector background (Table 1).

4.3. Fe precipitation

Until recently, the most common method for measuring ^{234}Th involved the coprecipitation of ^{234}Th with $\text{Fe}(\text{OH})_3$ from 10 to 20 l of seawater. The Fe precipitation method is similar to that described by Anderson and Fleer (1982). Deep water from NELHA was collected into several cubitainers and acidified to $\text{pH} < 1$ with concentrated HCl. Then, the ^{230}Th yield tracer was added along with 5 ml of 50 mg l^{-1} FeCl_2 solution. After > 5 h of equilibration, concentrated NH_4OH was added to adjust the sample to $\text{pH} \sim 9$ and an $\text{Fe}(\text{OH})_3$ precipitate allowed to form. The precipitate was allowed to settle for a period of

Table 1
Comparison of average counting and background characteristics

Method	Process	Sample size (kg)	Counting technique	Average gross (cpm) ^a	Average background (cpm) ^b	Average counting time (h) ^c
20 l	Mn ppt	20	direct beta	15	1.05	2–6
5 l	Mn ppt	5–7	direct beta	8	1.42	8–12
2 l	Mn ppt	2	direct beta	2	0.40	12–24
Fe ppt	Fe ppt	20	direct beta	7	0.23	4–12
Fe ppt	Fe ppt	20	chemistry-beta	12	0.20	2–6
Mn cart	Mn cart.	550	gamma	1.8	0.02	12–24
Particles	Nuclepore	20	direct beta	1.8	0.48	12–24
Particles	Nuclepore	20	chemistry beta	1.5	0.20	12–24

These averages are for NELHA waters.

^aGross count rates would vary with different detector configurations, source water activities, decay time between collection and counting, etc.

^bBackground count rates include detector background plus other non-²³⁴Th activities. Note that the 5-l background is highest due to the glass fiber filter used for mounting (see text).

^cAverage counting time is shown here for comparative purposes only. With a gross count rate of 2 and 12 cpm, the 1 σ counting error would be 2.6% after 12 and 2 h, respectively.

12 h before being filtered onto a 142-mm, 1- μ m pore-size Nuclepore filter. The filter was dried, carefully folded and mounted for direct low-level beta counting (identical to 20-l method). After direct counting, samples were purified using ion exchange chromatography, electroplated onto stainless steel planchettes, and recounted.

4.4. Mn cartridges

Large-volume samples (250–750 l) were collected using the MnO₂-coated cartridges described by Buesseler et al., 1992b and Hartman and Buesseler, 1994. Deep water from NELHA was filtered sequentially through a 142 mm diameter, 1.2 μ m pore-size microquartz fiber filter (QMA) followed by a pair of 8-cm-long MnO₂-cartridges to determine ²³⁴Th scavenging efficiency (Eq. (2)). Particulate ²³⁴Th collected by the QMA was analyzed by direct beta counting (Buesseler et al., 1998). Dissolved ²³⁴Th was quantified by crushing the MnO₂ cartridges into reproducible puck geometries and counted on a planar-style germanium detector (Buesseler et al., 1995).

4.5. Radiation detectors

All of the samples measured for ²³⁴Th in this study were analyzed either by beta- or gamma-count-

ing methods. Though beta counting is not isotope specific, it is useful for ²³⁴Th determination because of the high efficiency of detection of its immediate daughter ^{234m}Pa ($E_{\max} \sim 2000$ keV). In this study, a five sample, gas-flow proportional beta counter manufactured by RISØ National Laboratories (Roskilde, Denmark) was used. This unit is PC controlled, and incorporates a single anti-coincidence (AC) shield positioned above the five, 25-mm-diameter sample windows. The entire unit is surrounded by approximately 8 cm of lead bricks and background count rates range from 0.15 to 0.23 cpm. Efficiencies for high energy betas on stainless steel planchettes average 40% and vary by < 2% among detectors. We have transported this counter to and from a wide variety of ships and labs, and find the detectors to be robust and reliable, with undetectable changes in efficiency and background.

A high-purity germanium detector is used for the analyses of the Mn cartridges. Gamma spectroscopy offers the advantage of isotope specific analysis. Therefore, chemical separations are not necessary for this technique. However, the most useful ²³⁴Th peak (63.3 keV) has a gamma branching ratio of only ~ 4%. This 4% branching ratio combined with a generally low absolute gamma detection efficiency (5–6% for ²³⁴Th at 63 keV counted directly as a Mn cartridge “puck”) results in the requirement of a

vastly greater sample volume than that necessary for beta analysis. The gamma detector we used has an active area of 2000 mm² (Canberra™, LEGe style with U-shape 15-l dewar) and is surrounded by 8 cm of low background lead. A sample holder positions the Mn cartridges, which have been crushed into a reproducible 4 cm tall puck geometry, directly over the detector window (Buesseler et al., 1995). The average background count rate in the 63 keV window is < 0.02 cpm above the baseline. This detector has been used both at sea and in the lab. A summary of the counting characteristics of the different collection and measurement methods used in this study are provided in Table 1.

4.6. Sample counting and data processing

Radiometric methods remain the most sensitive techniques for the detection of ²³⁴Th in seawater. Whether gamma, beta or scintillation based techniques are used, many researchers report the error on any given ²³⁴Th analysis as the one sigma (1σ) uncertainty associated with counting statistics. These random errors are easy to quantify, and essentially propagate as the reciprocal of the square root of the number of total counts detected (Stevenson, 1965). In this regard, large-sample volumes, immediate counting after collection, and longer counting intervals result in the highest net count rates and, hence, the lowest associated counting errors. On the other hand, it is often quite difficult to separate and quantify errors associated with other variables, including detector calibration, background-counting errors, and other sample processing uncertainties (such as sample weights, tracer dilutions, etc.). Such factors will lead to sample biases or unknown variability beyond the errors associated with counting statistics alone. Here, we rely primarily on either the variability between sample replicates or the standard deviation, as an estimate of the overall uncertainty of the methods tested. This variability is expected to be larger than the error due to counting statistics alone, and must be considered in the interpretation of any observational data.

In addition to quantifying the counting and experimental errors, the exact treatment of the raw data and whether single samples are counted more than once will have a further impact on overall uncertain-

ties. When we began using direct beta-counting methods for the detection of ²³⁴Th on both filters and various adsorbers, we advocated counting each sample four to six times over a period of 25–50 days in order to follow the decay of ²³⁴Th (Buesseler et al., 1998). In essence, a two-component curve-fitting technique is used that finds the best fit of gross-counting data to an exponential curve with a decay rate of 24.1 days. Each time point is further weighted by the individual counting uncertainty (SigmaPLOT™; Fig. 1). We call this data processing procedure the “multi-count” method. In addition to the activity of ²³⁴Th at time zero (i.e. at sample collection), the background count rate is calculated. This background activity is due to the detector plus any other supported non-²³⁴Th high-energy beta emitters not removed during sample processing (see Section 5.3).

In the analysis of the NELHA data below, results using the curve-fitting process are compared to a simplified approach where only a first count within 1–5 days of collection, and a final count after > 144 days (> 6 half-lives for ²³⁴Th) are used (the “single/final” method). Any final beta activity that is detected is due to either the detector itself, or

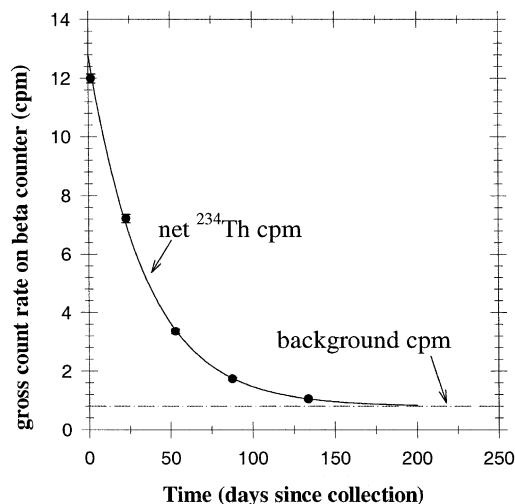


Fig. 1. Plot of ²³⁴Th activity vs. time for a sample from NELHA analyzed via the 20-l method. Exponential curve is best fit to ²³⁴Th data assuming activity detected is from two sources, namely ²³⁴Th itself (with a 24.1 day half-life) and background activity from the detector itself and other non-²³⁴Th beta emitters in the sample.

supported natural radionuclides found in the sample. It should be noted that a correction for a constant background implies that there are no large ingrowth corrections needed for non- ^{234}Th beta emitters carried by the precipitate.

4.7. Detector calibration

The beta counters were calibrated using a ^{238}U solution standard that was spiked onto filters containing Mn precipitate using the same mounting procedures as our samples. In addition, these detectors can be calibrated by comparison of the direct beta-counting methods with predicted deep-water activities at HOT, assuming secular equilibrium between ^{234}Th and ^{238}U . For the gamma counters, detector efficiency for ^{234}Th was determined by cross-calibration of ashed cartridges on a well-type germanium detector and by beta counting of selected samples that underwent chemical-purification and electrodeposition on a standard stainless steel planchette. The correspondence between ^{234}Th determined on the 2- and 20-l Mn precipitates, large-volume Mn cartridge samples, and $\text{Fe}(\text{OH})_3$ precipitate methods at NELHA attests to the internal consistency of our standards and the assumption that ^{234}Th in HOT deep waters is indeed in secular equilibrium with ^{238}U .

5. Results

5.1. Uranium ingrowth correction

Both the $\text{Fe}(\text{OH})_3$ and MnO_2 precipitation methods require some type of ^{238}U ingrowth correction. The ingrowth rate of ^{234}Th from ^{238}U is roughly 3% day^{-1} (ingrowth = $^{238}\text{U} \cdot (1 - \exp^{-\lambda t})$; where t is the time between collection and separation). For the $\text{Fe}(\text{OH})_3$ precipitation, it is necessary to make two ingrowth corrections. The first accounts for the amount of ^{234}Th produced prior to filtration of the precipitate. The second correction takes into account the amount of ^{234}Th produced from the fraction of ^{238}U that also coprecipitates with $\text{Fe}(\text{OH})_3$. This residual ^{238}U is not fully removed until purification via ion exchange chromatography. Because the

amount of ^{238}U that coprecipitates with $\text{Fe}(\text{OH})_3$ is potentially variable, a ^{238}U yield tracer needs to be incorporated into the methodology. In contrast, the MnO_2 method does not require acidification. As a result, the U remains strongly bound to its carbonate ligands and is not removed during precipitation. Hence, this approach requires a single ingrowth correction, one that accounts for the amount of ^{234}Th produced from ^{238}U decay prior to the filtration of the MnO_2 precipitate. Knowledge of the time period between sample collection and MnO_2 precipitation enables one to easily make this ingrowth calculation. At NELHA, the mean ingrowth correction was only 0.06 ± 0.01 dpm kg^{-1} , since the samples were processed within 24 h of collection.

5.2. Efficiency of ^{234}Th collection using Mn coprecipitation

The ^{234}Th Mn precipitation collection efficiency and its variability on selected samples at NELHA was evaluated in three ways. The simplest procedure assumed that variations in ^{234}Th recovery will follow the recovery of Mn. We, therefore, tested whether or not samples could be dissolved after counting, and if analysis of stable Mn within the solution could be used to correct for slight variations in the recovery of precipitate during filtration and handling. Unfortunately, variability in Mn recovery among 20-l samples was much larger than our standard deviation for ^{234}Th . It is likely that small variations in the efficiency of Mn precipitate result due to temperature, pH or time that can alter the collection of Mn on the filter. Also, the removal of Mn from the filter using concentrated acid and H_2O_2 is difficult to perform in a quantitative manner.

These Mn recovery experiments were conducted in an attempt to improve the standard 20-l methods by accounting for small variations in ^{234}Th recovery. A more obvious procedure would be to add ^{230}Th yield tracer, though this requires that the sample pH be reduced to < 2 , and significant time be allowed for tracer equilibration (12–24 h). This was attempted at NELHA, but samples processed for ^{230}Th failed using our standard radiochemical purification procedures, possibly due to complications related to the behavior of stable Mn on our ion exchange columns.

The overall precipitation extraction efficiency for ^{234}Th was checked by attempting to analyze for excess ^{234}Th in the filtrate. By combining filtrate from a single series of 20-l experiments into combined 75- and 125-l filtrate samples, we hoped to increase our ability to see the small fraction of excess ^{234}Th that may have passed through the filter. Both filtrate samples showed negligible ^{234}Th over that predicted from ingrowth of ^{234}Th from ^{238}U decay ($^{234}\text{Th} \leq 0.02 \text{ dpm kg}^{-1}$). Using these repeat extraction tests, we have found that the extraction efficiency is greater than 99%. Nonetheless, some precipitate may still adhere to the bottle walls, tubing or filter holder. This loss has been estimated to be $< 2\%$ by rinsing all equipment with a solution of $3\% \text{ H}_2\text{O}_2$ and 1 M HCl and measuring Mn in the leach with atomic absorption. Since the 2-, 5- and 20-l methods are calibrated against deep waters, where $^{234}\text{Th}/^{238}\text{U} = 1$, any relative loss of ^{234}Th during processing is corrected for, assuming that these losses are constant.

5.3. Detector and sample background count rates

All radiochemical methods require a correction for activities not associated with ^{234}Th in the sample. Sources of background include the intrinsic detector background and background associated with the sample and processing steps. Detector background is simple to quantify, and modern gamma and beta detectors are designed with passive shielding and AC circuitry to reduce these background count rates to minimum levels. The background needs to be monitored periodically, as changes in cosmic ray intensity and differences in background sources between land and sea can alter the intrinsic background. The background in our five-sample beta counter varies from 0.15 to 0.23 cpm, with the lowest background corresponding to the detectors furthest from the edges of the AC shield.

More difficult to estimate is the background associated with sample processing and non- ^{234}Th beta emitters. For the large-volume samples collected using Mn cartridges and counted using gamma spectroscopy, the detection technique is energy specific and only ^{234}Th on the cartridge is detected. For beta-counting techniques, however, all beta particles with a high enough energy to penetrate our mounting

material and detector window will be counted as sample activity. This includes potential activity associated with the filter media itself. For example, 5-l Mn precipitate was filtered onto glass fiber filters. From repeat sample counts and by counting blank filters, it was found that these types of filters contain an intrinsic background activity that accounts for 90% of the measured 5-l background (Table 1). Fortunately, this type of background can be avoided in the future by using a different filter media.

The issue of non- ^{234}Th beta activity is most serious in sample precipitates counted directly (Mn precipitate methods), since the Mn precipitate can remove other natural U–Th series radionuclides from seawater and no postsampling radiochemical purification is performed. In a typical precipitate from seawater containing $2.5 \text{ dpm kg}^{-1} \text{ }^{234}\text{Th}$ and $0.15 \text{ dpm kg}^{-1} \text{ }^{226}\text{Ra}$, the contribution from radium daughters and of traces of uranium, which may have coprecipitated and contribute to supported ^{234}Th is approximately 4% of the gross beta count rate measured within a week after sampling (or correspondingly higher if $^{234}\text{Th} < 2.5 \text{ dpm kg}^{-1}$). Using a $30 \text{ dpm }^{226}\text{Ra}$ spike, Benitez-Nelson et al. (2000) show that $> 80\%$ of the immediate ^{226}Ra daughter, ^{222}Rn ($t_{1/2} = 3.8 \text{ days}$) is lost from the 2-l Mn precipitate. The uncertainty in this contribution depends primarily on assumption of steady state balance between production and outgassing of ^{222}Rn during the two measurements of the sample: before and after ^{234}Th decay. Time-series measurements of these ^{226}Ra spiked samples point to a small but constant contribution to the background from ^{222}Rn daughters, which produce high energy betas, such as ^{214}Bi ($t_{1/2} = 20 \text{ min}$) and ^{210}Bi ($t_{1/2} = 5.0 \text{ days}$) (Benitez-Nelson et al., 2000).

The data from our 20- and 2-l Mn precipitate samples confirm that our background was due to a combination of both the intrinsic detector background and activity derived from beta emitters collected during precipitation and filtration steps. The measured total background on NELHA samples was on average 0.48 cpm for 20-l particulate samples, 1.05 cpm for 20-l Mn precipitates, and 0.40 cpm for 2-l Mn precipitates (Table 1). The higher background for the 20- vs. 2-l samples supports the conclusion that the background is due to non- ^{234}Th beta emitters removed from seawater by our Mn precipitate. For

the 20-l method, 0.8 cpm must be a result of non- ^{234}Th beta emitters (non- ^{234}Th background = 1.0 cpm total background – 0.2 cpm detector background). This hypothesis was confirmed by testing a series of samples with volumes ranging from 0.25 to 6 l (Benitez-Nelson et al., 2000) and from 2 to 18 l. The non- ^{234}Th component of our background varied as an approximate linear function of the sample volume collected. Using sample recounts at $t > 144$ days after collection, it was possible to quantify individual non- ^{234}Th background count rates in 24 h with a 1σ -counting uncertainty of $\pm 4\%$. This background count rate was stable over time within counting errors.

5.4. Comparison of data processing procedures

Using the 20-l method on one set of samples collected on March 16, 1999 ($n = 10$); the “single/final” counting method and “multi-count” method resulted in net ^{234}Th activities of 1.82 ± 0.12 and 1.81 ± 0.14 dpm kg^{-1} (mean $\pm$ S.D.), respectively. The background count rates determined by the different methods were also indistinguishable (average = 1.12 vs. 1.04 cpm, for final counts at $t > 144$ days vs. background determined by a “multi-count” curve-fit approach). In each set of samples analyzed at NELHA, whether for total, dissolved or particulate ^{234}Th , the “single/final” and “multi-count” methods gave similar results. This provides further support that the total background count rates and detector efficiencies are stable over time. We will, therefore, only discuss ^{234}Th results calculated from the “single/final” method, unless otherwise noted.

6. Discussion

Three different ^{234}Th collection methods were compared (Mn or Fe precipitation and Mn cartridges) on sample sizes ranging from < 2 to > 700 l using direct beta counting of precipitates, direct beta counting of planchettes after radiochemical purification and direct gamma counting of cartridges. All of the methods used here produced mean ^{234}Th activity data that were, within error, identical. There were differences, however, among the methods in precision and reproducibility, as well as large differences in the required sampling and processing effort.

In this section, the strengths and weaknesses of each method are discussed and it is concluded that the MnO_2 precipitation methods offer significant advantages over previous techniques.

A comparison between ^{234}Th data obtained using the different methods at NELHA can be seen in Table 2. There are three sample types: total unfiltered ^{234}Th samples, dissolved ^{234}Th samples (filtrate from either Nuclepore or QMA 1 μm pore-size filters), and particulate ^{234}Th (direct analyses of Nuclepore filters). We found no significant difference in the mean values of all of the samples of a given type (one-way analysis of variance). The only significant difference was between the mean of the 20-l filtrate (1.78 dpm kg^{-1}) and that of the total unfiltered samples (1.94 dpm kg^{-1} ; the difference in mean values exceeds 95% confidence limits using t -test). This difference is attributable to particulate ^{234}Th , as within errors, the total ^{234}Th minus filtrate ^{234}Th equals the particulate ^{234}Th activity (0.21 dpm kg^{-1}).

Some difference in the variability about the mean for ^{234}Th was found between the various tested methods. At NELHA, the smallest sample standard deviation was found for dissolved ^{234}Th using the 2- and 20-l methods ($\pm 5\%$ and 7% , respectively; Table 2). In contrast, the directly-counted $\text{Fe}(\text{OH})_3$ precipitates and the Mn cartridge samples had the highest. On closer inspection of the data, it appears that all of the total ^{234}Th methods have significantly higher variability than the same method used for dissolved ^{234}Th . In addition, there was relatively higher variability in the ^{234}Th particulate samples. These observations suggest that there are variations in the particulate ^{234}Th activities within the NELHA source water and that these variations in particulate ^{234}Th may occur even for samples collected on the same day. One source of this variability may be due to physical breakdown and detachment of biological material growing on the walls of the source water pipes.

In contrast, day-to-day fluctuations in the dissolved ^{234}Th activity appear minimal, as indicated by a lack of obvious variability in the dissolved ^{234}Th activities during the 2-week period when most of the samples were obtained. That ^{234}Th is substantially lower than ^{238}U within the NELHA deep waters indicates that there must be nonradioactive removal of ^{234}Th , i.e. scavenging ($^{234}\text{Th} = 1.78$ dpm kg^{-1}

Table 2
Summary of ^{234}Th activities using different methods

ID	Type	Process	Sample size (kg)	Counting technique ^a	^{234}Th (dpm kg ⁻¹)	Standard deviation (±)	Standard deviation (%)	1 σ counting error (%)	N
<i>NELHA-600 m</i>									
20 l	filtrate	Mn ppt	20	direct beta-up	1.78	0.13	7.3	2.8	17
20 l	filtrate	Mn ppt	20	direct beta-down	1.78	0.12	7.0	2.8	20
2 l	filtrate	Mn ppt	2	direct beta	1.78	0.10	5.3	3.9	8
Fe ppt	filtrate	Fe ppt	20	direct beta	1.65	0.23	13.8	4.9	3
20 l	total	Mn ppt	20	direct beta	1.94	0.19	9.8	2.6	18
2 l	total	Mn ppt	2	direct beta	2.07	0.12	5.6	3.4	4
Mn cart	total	Mn cart	550	gamma	1.99	0.22	10.9	3.5	7
Fe ppt	total	Fe ppt	20	direct beta	2.03	0.31	15.5	3.9	6
Fe ppt	total	Fe ppt	20	Chemistry-beta	1.97	0.10	5.1	4.1	2
Particles	> 1 μm	Nuclepore	20	direct beta	0.21	0.05	21.4	4.8	18
Particles	> 1 μm	Nuclepore	20	Chemistry-beta	0.24	0.02	7.9	4.2	3
<i>HOT-3500 m</i>									
2 l	Total	Mn ppt	2	direct beta	2.37	0.18	7.4	3.0	26
<i>Southern Ocean > 250 m</i>									
20 l	Total	Mn ppt	20	direct beta	2.43	0.08	3.2	1.1	10
5 l	Total	Mn ppt	5	direct beta	2.46	0.08	3.2	1.9	18

^aCounting techniques used were either beta or gamma methods. “Direct beta” methods refer to counting folded or single filters without any radiochemical purification, whereas “chemistry-beta” refers to samples counted after purification and electroplating onto stainless steel planchettes. “Direct beta-up” and “direct beta-down” refer to two different configurations used to count the folded 142 mm filters containing Mn precipitate.

vs. $^{238}\text{U} = 2.36 \text{ dpm kg}^{-1}$). During sample collection, visible growth in at least one of the above ground distribution pipes was noted. Either near-bottom scavenging of ^{234}Th near the pipe inlet ($\sim 20 \text{ m}$ above bottom at 600 m), or removal within the pipe due to growth of organisms at the pipe mouth or interior is the likely cause of the $^{234}\text{Th}/^{238}\text{U}$ disequilibrium.

Each NELHA experiment was run in batches of 4–10 samples, all collected within a 24-h period. Some of the individual sets of 2- or 20-l Mn precipitate samples processed by a single individual had overall standard deviations even lower than $\pm 3\%$. For example, the mean and standard deviation on the 2-l filtrate samples is $1.78 \pm 5.3\%$, however, for one of the sample sets ($n = 4$ of 8), the standard deviation is even lower ($\pm 1.5\%$). This suggests that there is user introduced and/or uncontrolled variability in our methods below the 5% certainty level. Note that the sample standard deviation is generally two to three times larger than the counting error for any

given sample type, so the overall error is not limited by counting statistics (Table 2).

A further test of the 2-l method was conducted using 3500-m-deep water collected at station ALOHA during monthly HOT cruises. Five sets of deep-water samples were collected from five separate Niskin bottles from May 1999 to November 1999. Mean deep-water total ^{234}Th activities were 2.37 dpm kg^{-1} with a standard deviation of $\pm 5.8\%$ (^{234}Th predicted from salinity and secular equilibrium with $^{238}\text{U} = 2.38 \text{ dpm kg}^{-1}$). The larger standard deviation in the 2-l method at Station ALOHA than that found at NELHA is most likely due to subtle differences in sample collection and processing. Benitez-Nelson et al. (2000) document in a separate set of experiments at this site that sorptive losses of ^{234}Th can be found if the sample is left for $> 6 \text{ h}$ in the bottle prior to adding reagents. Longer periods between MnO_2 precipitation and filtration, loss of MnO_2 to the walls of the filtration apparatus, and/or changes in beta transmission due to particle loading may have con-

tributed to the variability seen at station ALOHA as well.

Five-liter deep-water samples (> 250 m; $n = 18$) collected from March 26 to May 2, 1999 of the R/V Polarstern expedition had a standard error of 3% and were indistinguishable from the results of the 20-l method (Table 2). Subsequent samples taken near the Polar Front had larger variations, presumably related to deep-water remineralization. Accuracy is estimated at approximately 5% as a result of uncertainties related to the beta contribution from other isotopes.

The “classic” method for ^{234}Th utilizes coprecipitation of ^{234}Th with $\text{Fe}(\text{OH})_3$ from 10- to 20-l seawater samples followed by radiochemical purification and beta counting. Prior studies have shown that this method can produce ^{234}Th activities with counting errors of < 2 –3% and overall mean standard deviations as low as 2–3% (Buesseler et al., 1994). However, the average precision more commonly ranges from 5–10%, similar to that found at NELHA (Table 2). The main advantage of the Fe precipitation method is that ^{234}Th is separated from other interfering beta emitters prior to beta counting. Unfortunately, this is only achievable after extensive purification with ion exchange chromatography, a laborious and hazardous operation, especially if conducted at-sea. This method also necessitates the need to carry calibrated radioactive tracers on board ship in order to begin sample processing. Finally, the Fe precipitate carries significant ^{238}U , as well as ^{234}Th , and not at equal or constant ratios.

Large-volume techniques, based upon the use of in situ pumping systems utilizing Mn cartridges, have been widely used over the past two decades in ocean sciences. The Mn cartridges have the advantage in that they separate ^{234}Th from ^{238}U in-situ, such that ingrowth corrections are negligible (Buesseler et al., 1995). The use of in-situ pumping devices and Mn cartridges was initially developed for the collection of long-lived Th isotopes; ^{232}Th , ^{230}Th , and ^{228}Th . At present, only ^{228}Th requires large-volume samples for radioanalyses (> 100 l), since ^{232}Th and ^{230}Th have sufficiently high atom abundance to allow for detection via modern mass spectrometric techniques (e.g. Moran et al., 1995). As a result, large-volume sampling is now mainly used for the measurement of ^{234}Th and its associated particu-

late phases on size-fractionated samples or for isotopes of other elements such as radium (Rutgers van der Loeff and Moore, 1999). Typically, only 1–10% of total ^{234}Th is associated with the $> 1\ \mu\text{m}$ filters, and 0.1–2% with > 50 – $70\ \mu\text{m}$ filters (Buesseler, 1998; Buesseler et al., 1998). Thus, for the detection of particulate ^{234}Th on rare bigger particles, large-volume sampling will still be needed.

For total ^{234}Th measurements, Mn cartridges have significant disadvantages over discrete small volume sampling. In addition to the extra effort, wire time, and costs associated with in situ pumping, the total ^{234}Th activity is derived from three ^{234}Th activity measurements, i.e. a prefilter activity and the activity of dissolved ^{234}Th derived from two Mn cartridges placed in sequence (Eq. (2)). Fluctuations in the collection efficiency of ^{234}Th on cartridge pairs is common in most field programs, due to differences in volume, flow rate, cartridge preparation and possibly temperature. Collection efficiencies can vary by as much as 10–30% between temporally adjacent cartridge pairs. As a result, uncertainties in total ^{234}Th activities, which should include errors associated with the cartridge collection efficiency, are typically > 10 –15%. One positive attribute of large-volume sampling is that ^{234}Th can be detected via

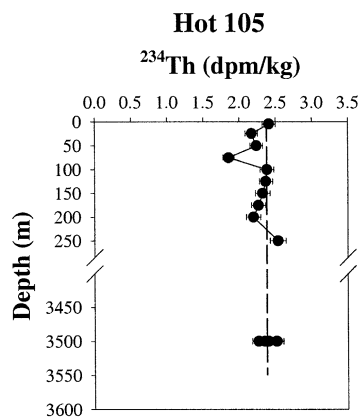


Fig. 2. Plot of ^{234}Th activity vs. depth for samples collected during HOT 105 (May 1999) at Station ALOHA ($22^{\circ}45.0'\text{N}$, $158^{\circ}00.0'\text{W}$) as part of the Hawaiian Ocean Time-series Program. All samples were collected using the 2-l method. Surface samples were calibrated to deep-water samples (3500 m) collected on the same cruise. The vertical dashed line represents the ^{234}Th activity expected if at secular equilibrium. Note that the standard deviation of deep-water replicate samples is 5.8%.

less sensitive, but isotope specific gamma-counting methods. Hence, no chemical purification steps are needed, but physical reduction in the cartridge size, using crushing or ashing techniques, is still recommended.

The potential of our 2-l method in elucidating upper ocean-particulate export is shown from a ^{234}Th depth profile taken during HOT 105 (May 1999) at Station ALOHA (Fig. 2). Activities are lower than equilibrium in the upper 150 m, indicating that significant particulate export is occurring. It cannot be over stressed that such fine scale structure would have been difficult to observe with other ^{234}Th measurement techniques.

7. Conclusions

We conclude from this study that the accuracy and precision of the simple Mn precipitation methods equals or exceeds that of the other techniques. The obvious advantages are the smaller sample volume requirements and minimal sample processing required prior to beta counting. Since many ^{234}Th applications are primarily concerned with the calculation of surface fluxes, it is of the utmost importance to accurately and precisely determine the relative difference between total ^{234}Th and ^{238}U activities (Eq. (1)). We have shown that a single analysis for ^{234}Th using the 20-, 5- or 2-l methods provides a robust and simple procedure for determining total ^{234}Th activities in the open ocean. Since the $^{234}\text{Th}/^{238}\text{U}$ activity ratio is unity in deep water, the calibration against this “standard” demonstrates that proper corrections for background, detector calibration, sampling and experimental error have been made. This method was developed for both unfiltered and filtered samples, though in particle laden waters, prefiltration and separate analyses of filter and filtrate will improve reproducibility. At-sea, beta counting is possible and highly recommended for cruises of longer duration than 1 week (due to the short half-life of ^{234}Th). Using a single five-sample beta-counting instrument with 12 h counting intervals, up to 10 samples can be analyzed per 24 h period at sea.

For the application of ^{234}Th as a tracer of particulate organic carbon (POC) flux, both total ^{234}Th

activities and the $\text{POC}/^{234}\text{Th}$ ratio on particles at depth are necessary ($\text{POC flux} = ^{234}\text{Th flux} \cdot [\text{POC}/^{234}\text{Th}]$ on sinking particles; reviewed in Buesseler, 1998). This new small volume procedure opens up the possibility for obtaining multiple profiles of total ^{234}Th both spatially and temporally, thus enabling a more accurately defined field distribution of the ^{234}Th flux (Eq. (1)). For the determination of $\text{POC}/^{234}\text{Th}$ ratios on sinking particles, size-fractionated filtration is commonly used, with the assumption that larger particles (nominal diameter > 50–70 μm) are a better representation of sinking particles in the ocean (as opposed to material caught on standard 1 μm pore-size filters). For such work, large-volume samples will still be needed given the low POC and ^{234}Th abundancies in these size fractions (< 1–5% of total). In most cases, the $\text{POC}/^{234}\text{Th}$ ratio on particles is only required from the depth at which one is interested in calculating upper-ocean export (typically 100–150 m). Existing studies suggest that this ratio at depth is less variable than the total ^{234}Th activity field; hence, less frequent in-situ large-volume filtration would be necessary. Alternatives to large-volume filtration include the direct collection of sinking particles using upper ocean-sediment traps. However, biases in sample composition and flux are possible with current trap designs. Recent advances in neutrally buoyant sediment traps (Buesseler et al., 2000) may eliminate many of these potential biases. Ultimately, the combination of numerous small volume ^{234}Th samples collected using a standard CTD Rosette system and selected sampling for the $\text{POC}/^{234}\text{Th}$ ratio will be particularly appealing for applications of ^{234}Th as an upper ocean-particle flux proxy.

This study demonstrates that sample reproducibility of $\pm 3\text{--}7\%$ is obtainable if care is used for most ^{234}Th methods, and that during single experiments, standard deviations as low as 3% can be achieved. At these higher levels of precision, the main source of error is unlikely to be counting uncertainty and these counting errors can be minimized by using the larger 20-l volume method and/or longer counting times on smaller samples. Experimental error will be much harder to control and will be related to a combination of factors including: detector performance; background stability; changing beta transmission due to variability in particle loading and type;

efficiency of collection of the MnO_2 precipitate; volumetric or gravimetric errors; and possible losses of ^{234}Th to the sample bottle and container walls. Due to uncontrolled variability in these experimental errors, calibration of this procedure via the analyses of ^{234}Th in deep waters cannot be overemphasized. We are optimistic that some combination of the Mn technique, with a reproducible sampling and processing protocol, will lead to continued improvements in this method.

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