Determination of particulate and dissolved ^{228}Th in seawater using a delayed coincidence counter

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A B S T R A C T

The application of thorium-228 towards understanding particle dynamics in the open ocean is limited because of its low natural abundance in seawater and associated sampling and analytical challenges. Here we describe a fast and nondestructive method for measuring both dissolved and particulate ^{228}Th activities in the open ocean using Radium Delayed-Coincidence Counters (RaDeCC). Particulate and dissolved samples were collected from the upper 1000 m of the Sargasso Sea water column during the US GEOTRACES intercalibration cruise using large volume in situ pumps equipped with Quartz microfiber filters and MnO_2 impregnated cartridges. Samples were directly counted on the RaDeCC system using a custom machined filter sample holder and a commercially available cartridge holder followed by traditional alpha counting. The two methods were found to be in good agreement ($r^2 = 0.95$). We also applied this method to particulate and dissolved samples collected from a US GEOTRACES station near the Cape Verde islands. The particulate and dissolved ^{228}Th distributions were consistent with the expected pattern of upper ocean scavenging and removal of ^{228}Th with activities varying between 0.02 and 0.06 dpm 100 L^{-1} (particulate) and 0.04 and 0.65 dpm 100 L^{-1} (dissolved) over the upper 1000 m of the water column.

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1. Introduction

Within the ocean, particle formation and dissolution play a critical role in the cycling of many natural and anthropogenically produced elements that affect biological production, human health and even Earth's climate. A number of naturally occurring short-lived radioisotopes including ^{234}Th, ^{228}Th, and ^{210}Pb have been used as tracers for understanding particle cycling processes in the marine system. ^{234}Th ($t_{1/2} = 24.1$ days), produced by the radioactive decay of its conservative parent ^{238}U ($t_{1/2} = 4.47 \times 109$ years), has been widely used as a tracer of particle flux in the upper ocean. Unlike its parent, ^{234}Th is highly particle reactive thus the disequilibrium between ^{238}U and ^{234}Th provides an estimate of the net rate of particle export from the upper ocean on time scales of days to weeks (Buesseler et al., 1998).

The application of ^{234}Th–^{238}U disequilibrium to particle dynamics in the mesopelagic or "twilight zone" (~100–1000 m) is limited due to the relatively short half-life of ^{234}Th. This zone forms an important connection between the upper and deep ocean, yet the processes that control material export across the mesopelagic are not well understood

(Buesseler et al., 2008). ^{228}Th ($t_{1/2} = 1.9$ years), which is produced in situ by the decay of its parent ^{228}Ra ($t_{1/2} = 5.8$ years), has shown promise as a tracer of particle and POC fluxes in deeper layers (Luo et al., 1995; Okubo et al., 2007). The disequilibria between this parent–daughter isotope pair can also provide estimates of particle export integrated over longer (months–annual) time scales.

While a recent small volume technique for ^{234}Th measurements (Buesseler et al., 2001; Benitez-Nelson et al., 2001; Pike et al., 2005) has led to higher sample throughput and widespread application of this isotope, methodologies for measuring ^{228}Th in seawater have largely remained unchanged for the past several decades (Cochran et al., 1987, 2000; Baskaran et al., 2009). However ^{228}Th can provide important information on processes such as (i) particle cycling e.g. aggregation/disaggregation (Bacon and Anderson, 1982; Cochran et al., 1995, 2000; Marchal and Lam, 2012), (ii) variability in POC export (Luo et al., 1995; Okubo et al., 2007; Lepore and Moran, 2007; Trimble et al., 2004), and (iii) lateral advection of coastal water masses (Rutgers van der Loeff et al., 2012), when measured in conjunction with other thorium isotopes.

The application of ^{228}Th towards understanding particle dynamics in the open ocean has been hampered by sampling and analytical challenges. The major challenge associated with measuring ^{228}Th in the open ocean is its low activity in seawater (2–3 orders of magnitude

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lower than ^{234}Th), both on particles and in the dissolved phase. This would normally require large volume water samples (~1000 L) followed by time consuming and labor intensive chemical purification procedures required for alpha spectrometry. In this study we describe a rapid, less labor intensive method to non-destructively measure both particulate and dissolved ^{228}Th in marine systems. The method utilizes the RaDeCC system (Moore and Arnold, 1996), which involves alpha scintillation counting of the ^{228}Th granddaughter ^{220}Rn. A combination of laboratory-prepared standards and field samples associated with the US GEOTRACES program was used to verify the technique (http://www.ldeo.columbia.edu/res/pi/geotraces/).

2. Analytical methods

The method utilizes the RaDeCC system, which is being widely used to determine ^{224}Ra and ^{223}Ra in seawater (Moore and Arnold, 1996; Moore, 2008). Briefly, a RaDeCC system consists of a photomultiplier tube (PMT) attached to a large Lucas (alpha scintillation) cell. The samples (usually radium adsorbed to MnO$_2$ coated acrylic fiber) are placed in a holding chamber and helium gas, which carries the Rn daughters (^{220}Rn, ^{219}Rn) is pumped along a closed loop through the scintillation cell and back through the holding chamber. Decay of the Rn and Po daughters in the Lucas cell produces alpha particles that interact with the scintillator to produce light pulses. These signals are amplified by the PMT and processed with a delayed coincidence circuit, which discriminates the decay of the ^{220}Rn and ^{219}Rn daughters. In addition to distinguishing ^{220}Rn and ^{219}Rn, another major advantage of this system is the low background level, which allows counting of samples with low activity. The RaDeCC systems used for this work have an average background of 0.022 cpm after correcting for chance coincidence events in this register.

Similar RaDeCC techniques have been used to determine sedimentary ^{224}Ra–^{228}Th disequilibria as a means to quantify the ^{224}Ra flux across the sediment–water interface in coastal sediments (Cai et al., 2012, 2014). For the present work, we focused on utilizing the RaDeCC system to measure water column dissolved and particulate ^{228}Th to understand particle fluxes in the mesopelagic zone (Maiti et al., 2012). The holding chambers used for counting particles on 142-mm diameter filters were manufactured in-house (Fig. 1A), while the dissolved samples were housed in a commercially available (Cole-Parmer Catalog# T-29650-00; Fig. 1B) water filtration cartridge holder that can accommodate 5 inch MnO$_2$ cartridges (Henderson et al., 2013).

For the initial method development, samples were collected from two water column profiles at BATS (Bermuda Atlantic Time Series station) on the R/V Atlantic Explorer in September 2009. Both dissolved and particulate samples were collected from the upper 1000 m of the water column using battery operated in situ pumps (McLane pumps). Particulate samples were collected on 142-mm diameter micro quartz

filters (Whatman QMA; nominal pore size 1.0 um) while dissolved thorium was scavenged onto MnO$_2$ coated 3 M grooved acrylic cartridges (Henderson et al., 2013) by pumping 800–1000 L water samples per depth at 6 L/min. All samples were stored for a month before being counted, in order to allow time for ^{224}Ra (t$_{1/2}$ = 3.66 days) to achieve secular equilibrium with ^{228}Th. A background measurement is performed before every sample analysis and a running average is used to background correct all field samples. Other corrections include chance coincidence counts and cross-talk between the 220 and 219 channels as described in Moore and Arnold (1996) and Garcia-Solsona et al. (2008).

2.1. Particulate samples

A custom made PVC holding chamber was used to accommodate 142 mm filters for particulate ^{228}Th analysis. The chamber was designed with an inner height of 15.0 mm and diameter of 150 mm (internal volume of 265 cm^3) such that the filter can be laid flat and face up. It has one outlet and three inlets, which are designed to provide even flow of the He carrier gas across the surface of the filter (Fig. 1A).

Since the RaDeCC system measures ^{220}Rn produced by decay of ^{224}Ra, it must be demonstrated that Rn is released consistently from the sample matrix. The emanation of ^{220}Rn from the acrylic MnO$_2$ fiber is a function of the recoil range of ^{220}Rn on the fiber surface and can be modulated by the addition of water to the sample (Sun and Torgersen, 1998). To quantify this effect for marine particles on a depth filter such as the QMA, three samples from the upper 1000 m at Bermuda were completely dried and counted for 1000 min on the RaDeCC system. The filters from 60 m (chlorophyll max), 120 m (within euphotic zone) and 750 m (deep) were chosen to simulate varying particle concentrations. In order to measure the filters in a consistent manner, all the filters were oven dried and stored for a month to allow time for ^{224}Ra (t$_{1/2}$ = 3.4 days) reach secular equilibrium with ^{228}Th. The same filters were recounted after adding 5 mL, 10 mL and 20 mL deionized water to the filter to produce water/sample ratios of 3.7, 7.4 and 11.1 (g/g) respectively. Filters were completely dried between each counting period (Fig. 2). The data indicates that peak counting efficiency occurred with 5 mL water, with significant alpha recoil suppression at 20 mL. All future samples were wetted with 5 mL deionized water (evenly distributed across the filter surface) and counted for 1000–1200 min on RaDeCC. For samples from the North Atlantic Ocean, this produced particulate ^{228}Th data with uncertainties of no greater than ~15% (1 sigma) or lower in the case of upper ocean, particle-rich samples.

2.2. Dissolved samples

Dissolved ^{228}Th samples of varying activities were collected at BATS on MnO$_2$ coated acrylic cartridges via in situ pumps described in
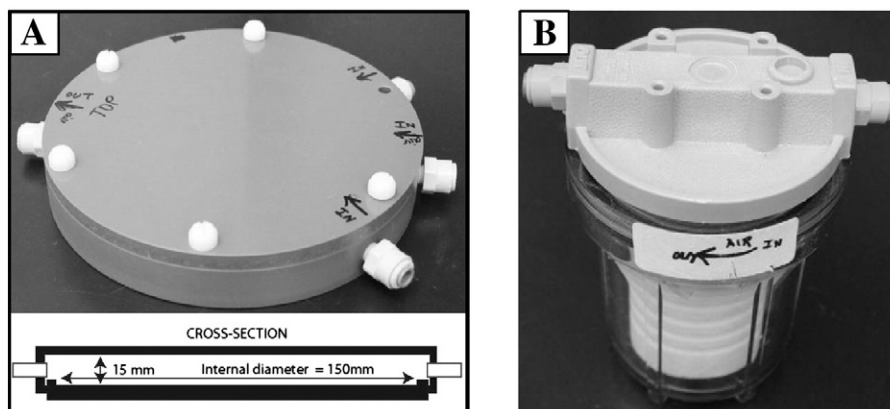

Fig. 1. Holding chambers for particulate (A) and dissolved (B) ^{228}Th samples used with the RaDeCC system.
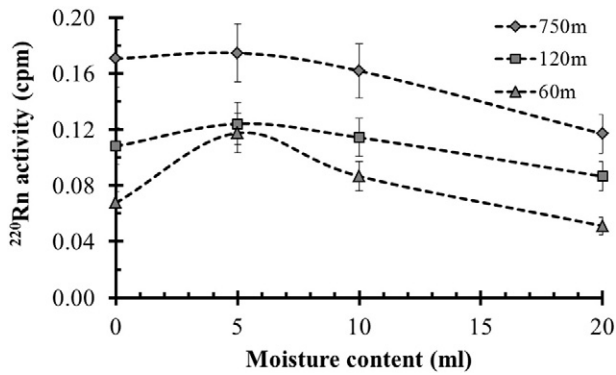
Fig. 2. Effect of water content in 142 mm micro quartz filter on ^{220}Rn counting. Samples were collected during GEOTRACES intercalibration cruise in September, 2009 at BATS.

Henderson et al. (2013). The cartridges were rinsed with 500 mL of deionized water and allowed to drip dry for 6 h. Once installed in their filter-holder, they were air dried with compressed air until the disappearance of large water droplets from the outlet, which corresponds to a moisture content of approximately 30% of the cartridge weight (Henderson et al., 2013). The cartridges were then directly counted inside the above mentioned cartridge holders connected to the RaDeCC system for 240–360 min, which resulted in 1 sigma counting errors of less than 10%. Ingrowth corrections were applied to ^{228}Th measurements based on ^{228}Ra activities measured via gamma spectroscopy.

Once the activity on the MnO$_2$ cartridge is known, determination of dissolved ^{228}Th activity and its parent ^{228}Ra in the water column involves additional corrections for the efficiency of Th and Ra uptake under in situ conditions by the MnO$_2$ cartridges. Thus the application of this method requires independent small volume samples for ^{234}Th and ^{226}Ra determination collected at the same depths as the in situ pumps. The activities of ^{234}Th and ^{226}Ra determined from these samples are compared with the same radionuclides on the individual cartridges. The ratio between the two determines the extraction efficiencies of Th and Ra, which is used to correct for the in-situ collection efficiency of dissolved ^{228}Th and ^{228}Ra on a single cartridge.

Immediately after the initial sample counting on the RaDeCC system, the cartridges are ashed at 820 °C and then counted via gamma spectroscopy for ^{234}Th and ^{226}Ra. The corresponding dissolved ^{234}Th activity was determined by collecting a 4 L water sample and subsequent beta counting (Pike et al., 2005). Similarly ^{226}Ra activity was determined by collecting a ~20 L water sampling and passing it through MnO$_2$ fiber (Moore and Arnold, 1996) at <1 L/min. The fibers were ashed and counted via gamma spectroscopy using the ^{214}Pb (295 keV and 352 keV) and ^{214}Bi (609 keV) peaks. For open-ocean ^{226}Ra activities, better precision (3–5%) on 20 L samples can be achieved by the ^{222}Rn emanation technique (Lucas et al., 1990). Alternatively, ^{226}Ra can be determined at high precision via ICP-MS using ~250 mL sample volumes

(Foster et al., 2004) or via ^{222}Rn ingrowth utilizing the RaDeCC system with very long counting periods (Geibert et al., 2013). This latter method presents an inexpensive alternative, however lower precision (~10%), long counting times and a large sample volume requirement (>100 L) make this method less than ideal for open ocean measurements.

Henderson et al. (2013) reported that the scavenging efficiency for Ra isotopes on MnO$_2$ impregnated cartridges at flow rates of ~6 L/min was on average 54% (n = 121 samples). For the same GEOTRACES dataset reported in Henderson et al. (2013), the average Th scavenging efficiency was 51 ± 6%. Scavenging uptake kinetics and sample bypass of poorly sealed cartridges are two factors that can lower the scavenging efficiency of Ra and Th on the cartridges.

2.3. Calibration of RaDeCC system for particulate and dissolved samples

2.3.1. Particulate ^{228}Th

To compare results obtained by RaDeCC with conventional alpha spectrometry, a set of 15 filters collected at BATS with a range of ^{228}Th activities were digested and analyzed via isotope dilution alpha counting, following their initial RaDeCC measurements. First, a known amount of ^{230}Th spike was added to each filter for estimating sample recoveries and the filters were leached with 8 N HNO$_3$ and 10% H$_2$O$_2$. Samples were purified using ion exchange chemistry (BIORAD AGX) following methods outlined by Pike et al. (2005). Thorium was extracted from the final elution using a solution of 0.25 M TTA (Thenoyltrifluoroacetone) in benzene, evaporated on a stainless steel planchette (Li et al., 1980), and counted on a calibrated silicon surface barrier alpha spectroscopy system. If the two techniques are measuring ^{228}Th in the same phase, the slope of a linear regression between sample counts per minute (cpm) on the RaDeCC system and the corresponding activity in dpm determined via alpha spectroscopy will provide a measure of the apparent RaDeCC detector efficiency for filters counted in this sample geometry (Fig. 3). For two RaDeCC systems, the results indicate a detector efficiency of 0.23 ± 0.02 and 0.27 ± 0.03. While the 3% difference between detectors is typical for different RaDeCC systems, the overall efficiency is much lower than that expected for RaDeCC determination of ^{228}Th bound to MnO$_2$ fiber.

To determine the efficiency for the filter geometry directly in the RaDeCC system, we spiked a filter collected at 1200 m (14.00°N, 99.00°E) during GEOTRACES East Pacific zonal transect that had an estimated POC concentration of 0.137 μM and an initial ^{228}Th activity of 0.006 dpm 100 L^{-1} with the ^{232}Th standard solution. The filter was spiked in a series of 4 additions ranging from 0.15 to 6.65 dpm and was prepared for analysis in the same manner as samples and analyzed on two of our RaDeCC detectors after each spike addition. After correcting for the filter blank, the average efficiencies for the two detectors were 0.34 ± 0.03 and 0.36 ± 0.04 respectively. However, we reanalyzed the filter standard approximately one month after preparation and found a 15–28% decrease of the initial efficiency. This is in
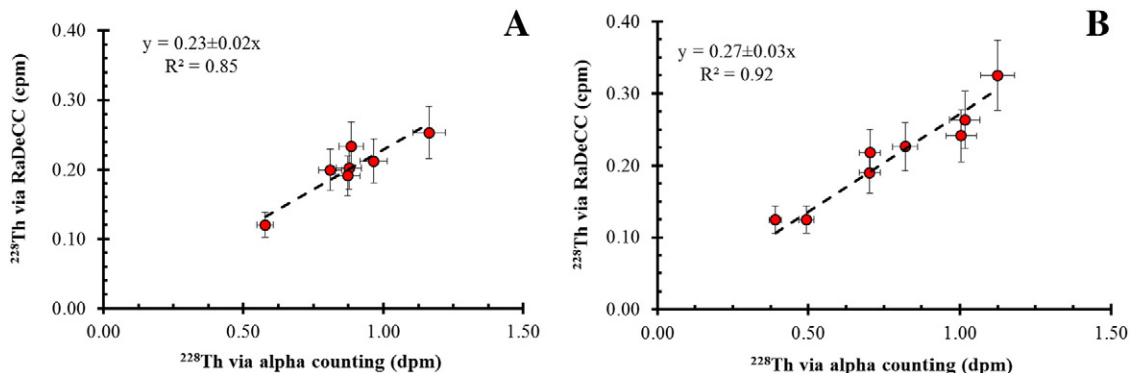

Fig. 3. Measurements of particulate ^{228}Th on two different RaDeCC systems compared to alpha spectrometry results.

contrast to ^{232}Th–^{228}Ra–^{228}Th standards prepared on Mn-fibers (Moore, 2008; Scholten et al., 2010) and standards prepared by depositing MnO_2 or coastal sediments onto glass fiber filters (Cai et al., 2012; Moore and Cai, 2013). None of these techniques showed a decrease in activity with time. Because the spike is in an acid solution, a small amount of acid is being added to the filter as a part of the spike solution. During drying the strength of the acid in contact with material on the filter increased. It is likely that this acid caused some of the particles on the filter to dissolve, neutralizing the acid. Subsequent additions of MilliQ to the filter may then have caused this material to precipitate, and capture some of the spiked Th. Radon produced by the decay of the captured Th would not be able to reach the detector when the filter was run again, thus lowering the apparent efficiency. To test this hypothesis, 2 mL of 3 M HNO_3 was added to the filter standard that had shown a decrease in activity. The filter was dampened with 4 mL MilliQ, and the damp filter was allowed to sit for 48 h before adding 3 mL of MilliQ to bring the moisture content back to the appropriate level. The efficiencies measured after this addition of acid were found to be similar to the initial values, suggesting that precipitation of Th did cause the decrease in efficiency and that the original measurements reflect the true efficiencies of the systems.

The alpha spec results indicate apparent detector efficiencies of 0.23 and 0.27, which are significantly lower than directly measured efficiencies. It is likely that the RaDeCC system measures surface-bound ^{224}Ra (^{228}Th) on particles, but does not detect activity confined in the crystal lattice (Cai et al., 2012). In contrast, ^{228}Th activity based on alpha spectroscopy will represent all ^{228}Th present in the particles. Particle loading on the filters and chamber geometry are two other factors that may affect the counting efficiencies. We found no significant differences in counting efficiencies between shallow (high loading) and deep water (low loading) particulate samples collected at BATS. Cai et al. (2012) measured no changes in counting efficiency up to a particle loading of 25 g, orders of magnitude greater than the loadings we are measuring.

2.3.2. Dissolved ^{228}Th

For the calibration of the RaDeCC efficiencies for the MnO_2 cartridges, the absolute activity (dpm) per sample is needed. After the initial RaDeCC counting was completed, the cartridges were ashed at 820 °C followed by acid leaching using 8 N HNO_3 and wet chemistry separation (Buesseler et al., 1992). Briefly a known amount of ^{230}Th spike was added to each sample for estimating sample recoveries and the same chemical purification and alpha counting method for the particulate samples outlined above was followed. The counting efficiencies for the cartridge samples were found to be 0.35 ± 0.03 and 0.45 ± 0.05 for the two detectors utilized to run dissolved samples (Fig. 4). In addition to these two detectors, five additional samples were run using two additional detectors for a total of 15 cross-calibration measurements.
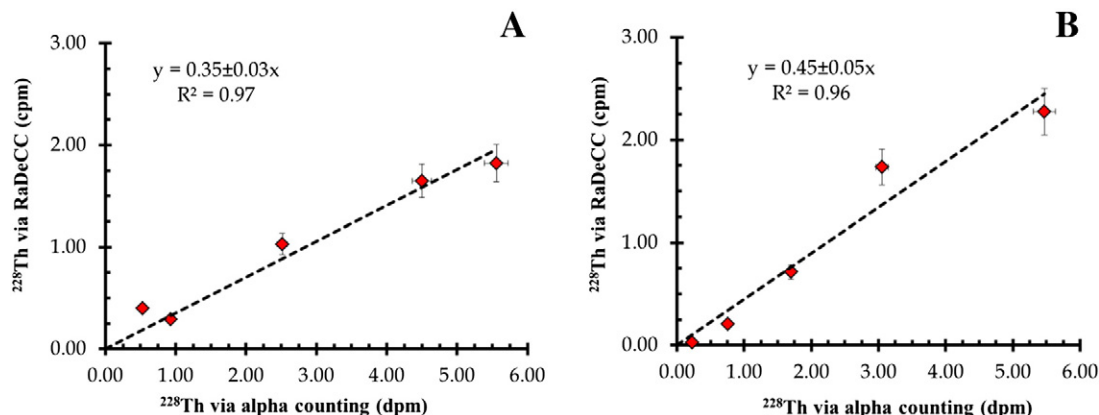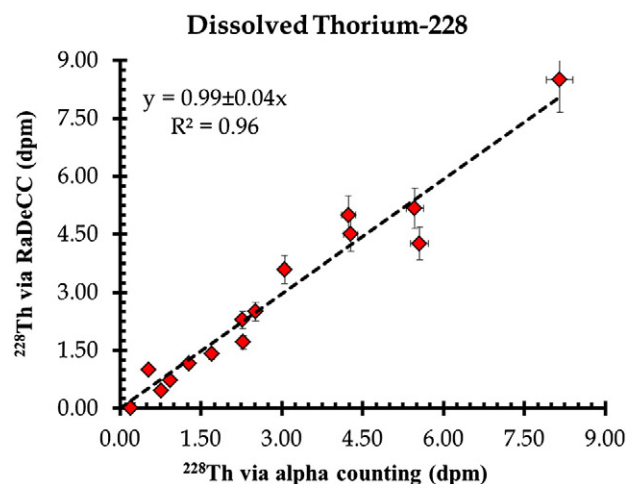

Fig. 5. Dissolved ^{228}Th activity measured using the new methodology versus traditional alpha spectroscopy measurement.

The absolute efficiencies for the RaDeCC systems can also be determined independently using MnO_2 cartridges spiked with a gravimetrically prepared ^{232}Th standard (with Ra and Rn daughters in equilibrium). Briefly two MnO_2 coated acrylic cartridges were placed in filter housings connected in series. The cartridges were primed by passing radium free water through them. Then 1 L of radium free water spiked with 50 dpm of ^{232}Th standard was slowly passed (~10 mL/min) through both the cartridges using a peristaltic pump. The bottle with standard solution was rinsed twice with radium free water (~1 L) and passed through the cartridges. Negligible loss on to tubing walls is assumed. The cartridges were then counted for approximately 2 h on the RaDeCC system following the procedures outlined above until the 1 sigma counting errors were reduced to less than 2%. The first cartridge was treated as the standard while the second cartridge in the series was counted to test for breakthrough of Th standard from the first cartridge. No measurable activity was detected on the second cartridge. The efficiencies were found to be 0.38 ± 0.01 and 0.47 ± 0.01 for the two detectors respectively, which are within the error of those determined via alpha counting (0.35 ± 0.03 and 0.45 ± 0.05 respectively).

These absolute efficiencies for the RaDeCC systems determined independently using ^{232}Th standards were used to calculate the activities of all dissolved samples counted by both the RaDeCC systems and plotted against their corresponding activities measured via traditional alpha spectroscopy. The 1:1 relationship ($r^2 = 0.96$; $p < 4 \times 10^{-13}$) between activities determined via RaDeCC and alpha spectrometry also indicate

Fig. 4. Measurements of dissolved ^{228}Th on two different RaDeCC systems compared to alpha spectrometry results.

that the systems are well calibrated for direct measurement of ^{228}Th activities (Fig. 5).

3. Case study

To illustrate the viability of the method, we present an upper ocean ^{228}Th and ^{228}Ra profile from the US GEOTRACES North Atlantic expedition during October–November 2010 (Fig. 6). The ^{228}Th and ^{228}Ra measurements were carried out following the methodology outlined in Fig. 7 with ^{226}Ra activities determined via the ^{222}Rn emanation technique. The station location was ~200 km south of the Cape Verde Islands in the eastern North Atlantic (17.4°N, 24.5°W). The temperature profile indicated a shallow (~30 m) mixed layer, while dissolved oxygen displayed a broad minimum between 400 and 500 m (Fig. 6A). Particle concentrations as indicated by the transmissometer profile were characterized by a subsurface peak extending just below the mixed layer at 30 m to 60 m (Fig. 6B). Below 60 m, particle concentrations decreased sharply until ~200 m where they reached near baseline values. Conversely, particulate ^{228}Th was low in the upper 100 m (0.026 ± 0.003 dpm 100 L^{-1}), with maximum values of 0.06 ±
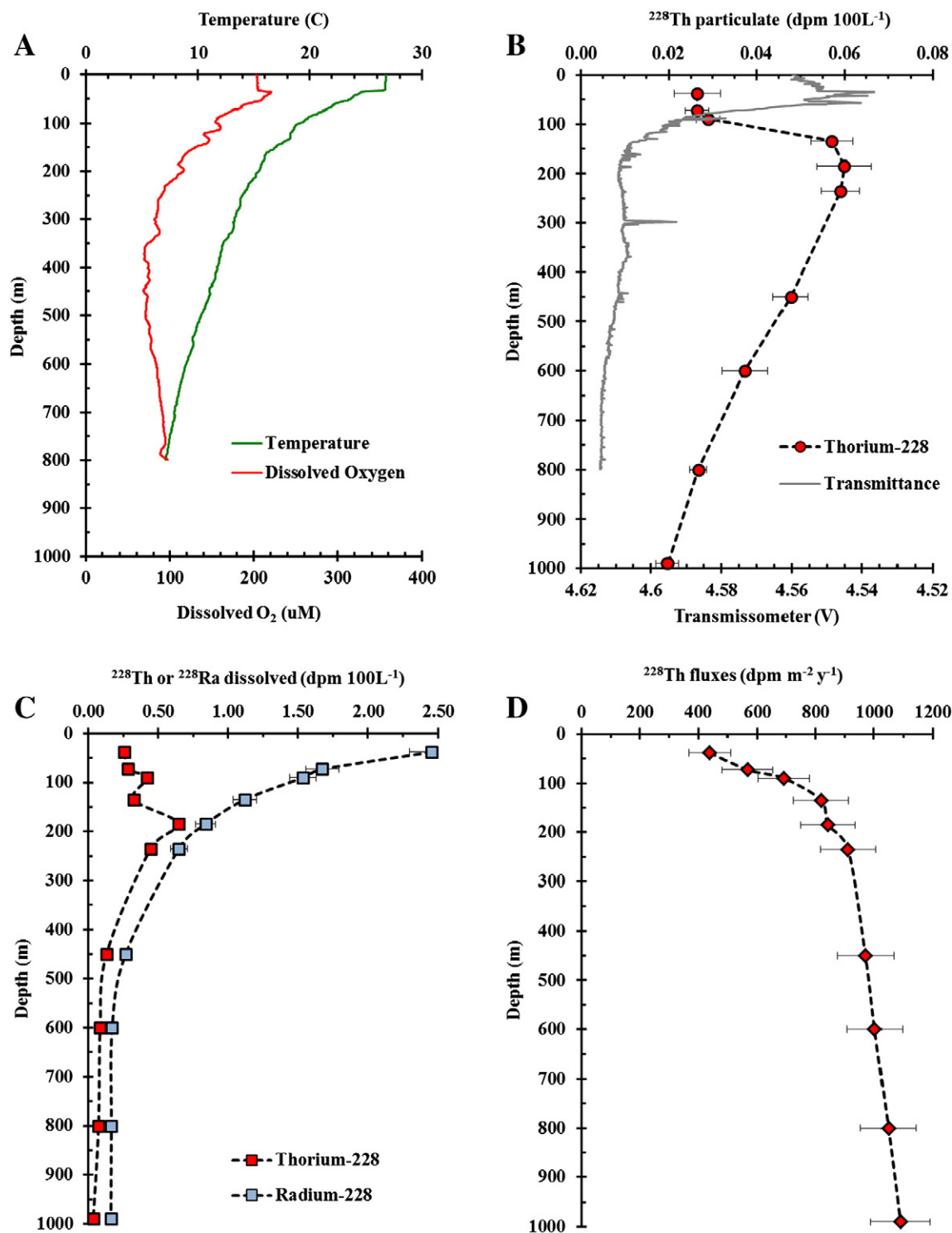

Fig. 6. Water column profiles for hydrography (A), particulate ^{228}Th (B) and dissolved ^{228}Th from a station near Cape Verde in the eastern part of North Atlantic Ocean (17.4°N, 24.5°W).
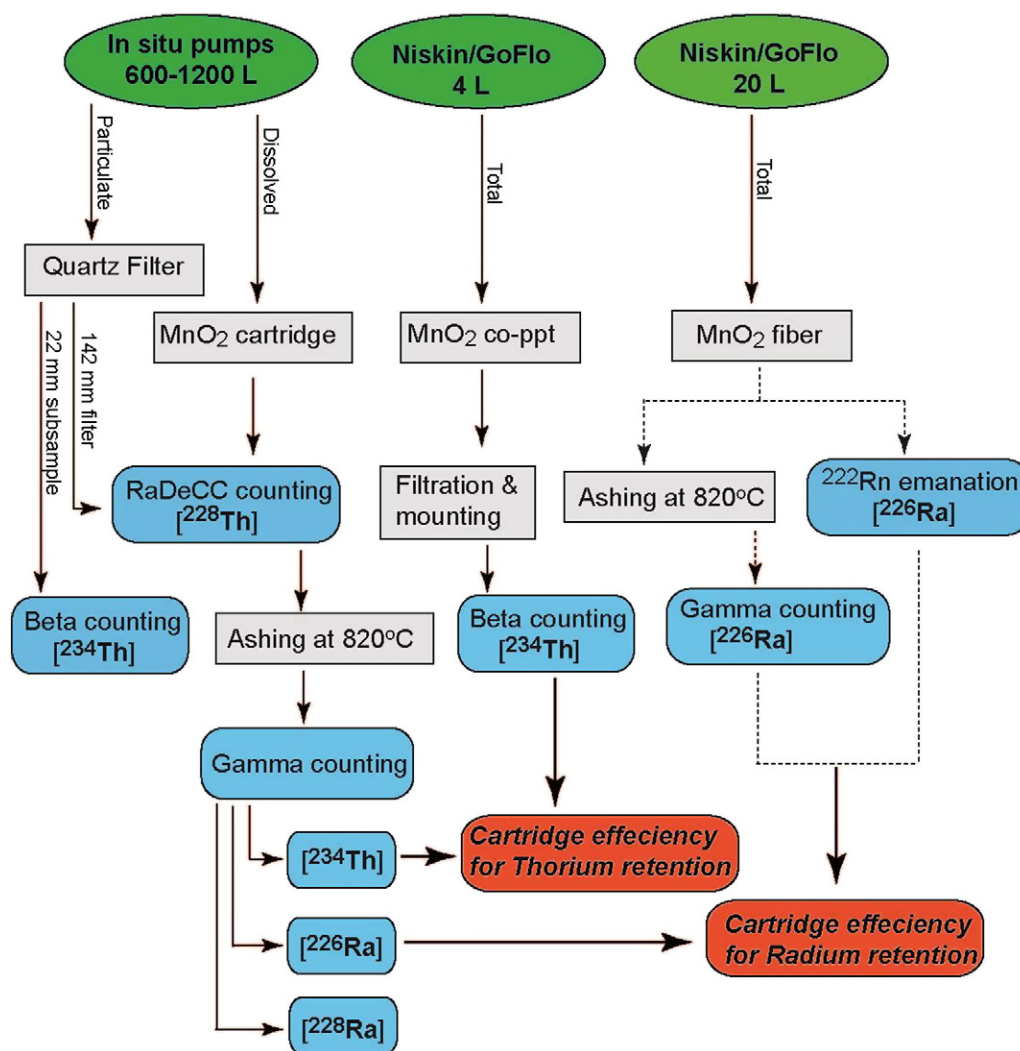
Fig. 7. Flow chart outlining methods for determining ^{228}Ra and ^{228}Th in seawater. Dashed lines represent two alternative methods to measure ^{226}Ra activity in 20 L seawater.

0.006 dpm 100 L^{-1} observed between 135 and 235 m (Fig. 6B). No prior ^{228}Th data is available from this region, however, Cochran et al. (1987) reported particulate ^{228}Th of between 0.09 and 0.29 dpm 100 L^{-1} at the surface to 0.04–0.20 dpm 100 L^{-1} at 800 m in the northwest Atlantic (Cochran et al., 1987).

Dissolved ^{228}Ra activities were highest near the surface at ~2.5 dpm 100 L^{-1}, gradually decreasing with depth to 0.16 dpm 100 L^{-1} at 600 m and below (Fig. 6C). There was a deficiency of dissolved ^{228}Th with respect to ^{228}Ra in the upper 200 m with activities ranging from 0.26 ± 0.09 dpm 100 L^{-1} at the surface to 0.074 ± 0.008 at 800 m. The dissolved ^{228}Th/^{228}Ra ratio increases from ≪1 in the euphotic zone to ~1 in the deeper water column indicating that ^{228}Th removed by particles from surface waters may be partially released back to the water column as the particles sink. The dissolved ^{228}Th activity peak of 0.65 ± 0.09 dpm 100 L^{-1} is observed at 185 m reflecting surface scavenging and subsurface regeneration of ^{228}Th and a concurrent increase in particulate ^{228}Th activities around 135–235 m (Fig. 6B). The dissolved ^{228}Ra and ^{228}Th values are similar to those observed by Li et al. (1980) in this region as a part of Geochemical Ocean Section Program (GEOSECS). Similar subsurface peaks in dissolved ^{228}Th have been observed in both Atlantic and Pacific Oceans (Li et al., 1980; Luo et al., 1995).

The ^{228}Ra–^{228}Th disequilibria observed at this station may be used to calculate a ^{228}Th flux of 911 ± 94 dpm m^{-2} y^{-1} at 450 m and 1089 ± 100 dpm m^{-2} y^{-1} at 1000 m, assuming a 1-D steady state model

(Fig. 6D). This is within the range of previously reported ^{228}Th fluxes of 510 ± 300 and 1120 ± 400 dpm m^{-2} y^{-1} at 350 m for two locations nearest to our station (Li et al., 1980).

4. Conclusions

Particle dynamics in the mesopelagic region of the ocean play an important role in the biogeochemical cycling of organic carbon, nutrients and trace metals in the global ocean. Traditionally this region of the ocean has not been well studied using natural radioisotope tracers. The major hurdle towards progress in this regard is expensive, analytically challenging and time consuming procedures associated with the collection and chemical analysis of such samples. In this study we have developed a rapid, nondestructive method for measuring ^{228}Th in both the dissolved and particulate phase based on the delayed coincidence counting system.

The method has been demonstrated to be very precise and rapid. Overall the biggest challenge associated with this method is collection of large volume water using in situ pumps. We recommend at least 600 L for upper ocean and 1200 L for deeper ocean in order to carry out particulate ^{228}Th measurements with an analytical uncertainty of 15% or less. In combination with ^{228}Ra measurements in the water column, future application of ^{228}Ra–^{228}Th will enable researchers to quantify material flux integrated over annual time scales in both the upper ocean and the mesopelagic zone. In areas of low scavenging, this isotope

pair can be used to quantify shelf-basin exchange rates as recently demonstrated for the eastern Arctic Ocean (Rutgers van der Loeff et al., 2012). This method is relatively simple in principle but requires a number of steps to properly calibrate the RaDeCC (especially for the QMA filter geometry) and to quantify scavenging efficiencies for dissolved Ra and Th on MnO_2 cartridges (Fig. 7). The major advantages of this method, once calibration is performed, are the relative ease of measurement, which distinguish ^{228}Th that has been scavenged by surface adsorption.

The need to use one single MnO_2 cartridge to determine cartridge efficiency reduces the effort by 50% compared to traditional cartridge methods, which require analyses of two cartridges connected in series to determine efficiencies (Livingston & Cochran, 1987; Buesseler et al., 1992). The nondestructive nature of this procedure allows particulate samples collected via in situ pumps to be subsequently analyzed for other trace elements and isotopes of interest on the same filters.

Acknowledgments

References

Bacon, M.P., Anderson, R.F., 1982. Distribution of thorium isotopes between dissolved and particulate forms in the deep sea. J. Geophys. Res. Oceans 87 (C3), 2045–2056.

Baskaran, M., Hong, G.-H., et al., 2009. Radionuclide Analysis in Seawater. CRC Press.

Benitez-Nelson, C., Buesseler, K.O., Rutgers van der Loeff, M., Andrews, J., Ball, L., Crossin, G., Charette, M., 2001. Testing a new small-volume technique for determining thorium-234 in seawater. J. Radioanal. Nucl. Chem. 248 (3), 795–799.

Buesseler, K.O., Cochran, J.K., et al., 1992. Determination of thorium isotopes in seawater by nondestructive and radiochemical procedures. Deep Sea Res. Part A 39 (7–8), 1103–1114.

Buesseler, K., Ball, L., et al., 1998. Upper ocean export of particulate organic carbon in the Arabian Sea derived from thorium-234. Deep-Sea Res. II Top. Stud. Oceanogr. 45 (10–11), 2461–2487.

Buesseler, K.O., Ball, L., Andrews, J., Cochran, J.K., Hirschberg, D.J., Bacon, M.P., Fleer, A., Brzezinski, M., 2001. Upper ocean export of particulate organic carbon and biogenic silica in the Southern Ocean along 170°W. Deep-Sea Res. Part II 48, 4275–4297.

Buesseler, K.O., Trull, T.W., et al., 2008. VERTIGO (VERtical Transport In the Global Ocean): a study of particle sources and flux attenuation in the North Pacific. Deep-Sea Res. II Top. Stud. Oceanogr. 55 (14–15), 1522–1539.

Cai, P., Shi, X., Moore, W.S., Dai, M., 2012. Measurement of ^{224}Ra:^{228}Th disequilibrium in coastal sediments using a delayed coincidence counter. Mar. Chem. 138–139, 1–6.

Cai, P., Shi, X., Moore, W.S., Peng, S., Wang, G.i, Dai, M., 2014. ^{224}Ra:^{228}Th disequilibrium in coastal sediments: implications for solute transfer across the sediment–water interface. Geochim. Cosmochim. Acta 125, 68–84.

Cochran, J.K., Livingston, H.D., et al., 1987. Natural and anthropogenic radionuclide distributions in the northwest Atlantic Ocean. Earth Planet. Sci. Lett. 84 (2–3), 135–152.

Cochran, K.J., Hirschberg, D.J., et al., 1995. Natural and anthropogenic radionuclide distributions in the Nansen Basin, Artic Ocean: scavenging rates and circulation timescales. Deep Sea Res. Part II 42 (6), 1495–1517.

Cochran, J.K., Buesseler, K.O., et al., 2000. Short-lived thorium isotopes (^{234}Th, ^{228}Th) as indicators of POC export and particle cycling in the Ross Sea, Southern Ocean. Deep-Sea Res. II Top. Stud. Oceanogr. 47 (15–16), 3451–3490.

Foster, D.A., Staubwasser, M., Henderson, G.M., 2004. 226Ra and Ba concentrations in the Ross Sea measured with multicollector ICP mass spectrometry. Mar. Chem. 87 (1–2), 59–71.

Garcia-Solsona, E., Garcia-Orellana, J., Masqué, P., Dulaiova, H., 2008. Uncertainties associated with 223Ra and 224Ra measurements in water via a Delayed Coincidence Counter (RaDeCC). Mar. Chem. 109 (3–4), 198–219.

Geibert, W., Rodellas, V., Annett, A., van Beek, P., Garcia-Orellana, J., Hsieh, Y., Masque, P., 2013. ^{226}Ra determination via the rate of ^{222}Rn ingrowth with the Radium Delayed Coincidence Counter (RaDeCC). Limnol. Oceanogr. Methods 11, 594–603.

Henderson, P.B., Morris, P.J., et al., 2013. Methodological advances for measuring low level radium isotopes in seawater. J. Radioanal. Nucl. Chem. 296, 357–362.

Lepore, K., Moran, S.B., 2007. Seasonal changes in thorium scavenging and particle aggregation in the western Arctic Ocean. Deep-Sea Res. I Oceanogr. Res. Pap. 54 (6), 919–938.

Li, Y.-H., Feely, H.W., et al., 1980. ^{228}Ra and ^{228}Th concentrations in GEOSECS Atlantic surface waters. Deep Sea Res. Part A 27 (7), 545–555.

Livingston, H.D., Cochran, J.K., 1987. Determination of transuranic and thorium isotopes in ocean water: in solution and in filterable particles. J. Radioanal. Nucl. Chem. 115, 299–308.

Lucas, H.F., Markun, F., et al., 1990. Methods for measuring radium isotopes: emanometry. Chapter 3-2. The Environmental Behaviour of Radium. Technical Reports Series No. 310 1. I. A. E. Agency, Vienna, pp. 149–172.

Luo, S., Ku, T.-L., et al., 1995. Tracing particle cycling in the upper ocean with ^{230}Th and ^{228}Th: an investigation in the equatorial Pacific along 140 °W. Deep-Sea Res. II Top. Stud. Oceanogr. 42 (2–3), 805–829.

Maiti, K., Buesseler, K.O., Zhou, K., Charette, M.A., 2012. Determination of particulate and dissolved ^{228}Th using delayed coincidence counter. Ocean Sciences Meeting, Feb 2012 (https://www.sgmeet.com/osm2012/viewabstract2.asp?AbstractID=11455).

Marchal, O., Lam, P.J., 2012. What can paired measurements of Th isotope activity and particle concentration tell us about particle cycling in the ocean? Geochim. Cosmochim. Acta 90 (0), 126–148.

Moore, W.S., 2008. Fifteen years experience in measuring ^{224}Ra and ^{223}Ra by delayed-coincidence counting. Mar. Chem. 109 (3–4), 188–197.

Moore, W.S., Arnold, R., 1996. Measurement of ^{223}Ra and ^{224}Ra in coastal waters using a delayed coincidence counter. J. Geophys. Res. Oceans 101 (C1), 1321–1329.

Moore, W.S., Cai, P., 2013. Calibration of RaDeCC systems for ^{223}Ra measurements. Mar. Chem. 156 (130–137), 2013.

Okubo, A., Obata, H., et al., 2007. Particle flux in the twilight zone of the eastern Indian Ocean: a constraint from ^{234}U–^{230}Th and ^{228}Ra–^{228}Th disequilibria. Deep-Sea Res. I Oceanogr. Res. Pap. 54 (10), 1758–1772.

Pike, S.M., Buesseler, K.O., Andrews, J., Savoye, N., 2005. Quantification of 234Th recovery in small volume sea water samples by inductively coupled plasma mass spectrometry. J. Radioana. Nucl. Chem. 263 (2), 355–360.

Rutgers van der Loeff, M., Cai, P., et al., 2012. Shelf-basin exchange times of Arctic surface waters estimated from ^{228}Th/^{228}Ra disequilibrium. J. Geophys. Res. Oceans 117 (C3), C03024.

Scholten, J.C., Pham, M.K., Blinova, O., Charette, M.A., Dulaiova, H., Eriksson, M., 2010. Preparation of Mn-fiber standards for the efficiency calibration of the delayed coincidence counting system (RaDeCC). Mar. Chem. 121 (1–4), 206–214.

Sun, Y., Torgersen, T., 1998. Rapid and precise measurement method for adsorbed ^{224}Ra on sediments. Mar. Chem. 61 (3–4), 163–171.

Trimble, S.M., Baskaran, M., et al., 2004. Scavenging of thorium isotopes in the Canada Basin of the Arctic Ocean. Earth Planet. Sci. Lett. 222 (3–4), 915–932.