



How accurate are ^{234}Th measurements in seawater based on the MnO_2 -impregnated cartridge technique?

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[1] In the past decade, a MnO_2 -impregnated cartridge technique has been widely used to extract ^{234}Th from seawater. One of the inherent assumptions associated with this technique is that all Th species in the dissolved phase are subject to extraction by the MnO_2 cartridges. In this study, an intercalibration between the cartridge technique and a small-volume MnO_2 coprecipitation technique was carried out to test this assumption. We demonstrated that the collection efficiency for ^{234}Th could be substantially overestimated by the MnO_2 cartridge technique. This may be the result of organic complexation of a significant portion of ^{234}Th in seawater, causing this fraction of Th to pass through the MnO_2 cartridges. The overestimate in collection efficiency may explain the deep-water ^{234}Th deficit observed in some oceanographic settings (e.g., the Gulf of Mexico, the Middle Atlantic Bight, and the Gulf of Maine). Sensitivity tests show that using the cartridge technique can yield ^{234}Th -based particulate organic carbon export rates that are overestimated by factors of up to 10. Furthermore, the frequent observed disagreements between Th fluxes recorded by shallow sediment traps and estimated using the cartridge method may be ascribed, at least partially, to this methodological issue.

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1. Introduction

[2] The naturally occurring radionuclide ^{234}Th is a particle-reactive element with a half-life of 24.1 d. In oceanic waters, ^{234}Th is continuously produced at a nearly constant rate by the alpha-decay of its parent nuclide, ^{238}U . Because of its strong affinity with particles, ^{234}Th is generally in deficit with respect to ^{238}U in the upper ocean. Such disequilibrium has been widely used to quantify the sinking flux of organic carbon [e.g., Bacon *et al.*, 1996; Buesseler *et al.*, 2004; Cai *et al.*, 2002; Cochran *et al.*, 1995a; Moran *et al.*, 1997] and other particle-reactive elements/compounds [e.g., Buesseler *et*

al., 2001a; Gustafsson *et al.*, 1997] from the upper ocean.

[3] The early determinations of ^{234}Th in seawater involved the collection of 20–30 L of seawater, followed by iron hydroxide coprecipitation and immediate separation of ^{234}Th from ^{238}U via ion-exchange chemistry. Finally, the Th was electroplated onto a stainless disc and counted sequentially on a beta counter and an alpha spectrometer [e.g., Anderson and Fleer, 1982; Bhat *et al.*, 1969]. This laborious process greatly limits the number of samples that can be processed during a given cruise.

[4] An alternative approach for determining ^{234}Th in seawater is based on MnO_2 -impregnated cartridges. This technique was developed by *Livingston and Cochran* [1987] and was first applied to the measurement of ^{234}Th in seawater by *Buesseler et al.* [1992b]. The technique involves stripping Th from seawater by pumping a sample through two MnO_2 -impregnated cartridges in series. Thorium-234 activities on cartridges are quantified by using gamma spectroscopy. The collection efficiency for dissolved ^{234}Th (hereafter referred to as theoretical collection efficiency) is calculated from the pair of MnO_2 cartridges by the equation

$$E = 1 - B/A, \quad (1)$$

where A and B are the decay-corrected activities of ^{234}Th on the first (A) and second (B) cartridges, respectively [*Livingston and Cochran*, 1987]. This approach eliminates the need for ion-exchange chemistry, since ^{234}Th adsorbs to the MnO_2 -impregnated cartridges whereas ^{238}U is not retained to any significant extent [e.g., *Benitez-Nelson et al.*, 2001]. A further advantage of the MnO_2 -impregnated cartridge technique is the ability to obtain ^{234}Th data at sea by gamma spectrometry of compressed or ashed cartridges. As such, this method was adopted by many researchers and extensively used to collect ^{234}Th from a wide range of oceanographic settings, especially during the JGOFS era [e.g., *Buesseler*, 1998, and references therein].

[5] Since this method does not use a yield tracer, the accuracy of obtained ^{234}Th activities depends essentially upon how well equation (1) can be applied. The assumptions inherent to equation (1) are (1) all Th species in the dissolved phase are subject to extraction by the MnO_2 cartridges and (2) cartridges A and B are equally effective at extracting and retaining Th from seawater. However, in the original paper by *Livingston and Cochran* [1987], neither assumption was verified. In this study, the applicability of this method is assessed through an intercalibration with a newly developed small-volume MnO_2 coprecipitation technique. The latter was developed by *Buesseler et al.* [2001b] and *Benitez-Nelson et al.* [2001] on the basis of a 20-L MnO_2 coprecipitation technique by *Rutgers van der Loeff and Moore* [1999]. With the aid of a yield tracer, the accuracy of ^{234}Th activities based on this technique has been further improved [*Pike et al.*,

2005; *Cai et al.*, 2006; *Rodriguez y Baena et al.*, 2006].

2. Methods

2.1. Sample Collection

[6] The intercalibration was conducted at a station ($20^{\circ}06.42'\text{N}$, $115^{\circ}47.81'\text{E}$) in the oligotrophic northern South China Sea in February 2004. Water depth at this location is ~ 1500 m. Inorganic nitrogen and phosphorus in the mixed layer are usually below detection limits of conventional analytical methods [e.g., *Gong et al.*, 1992]. At this location, DOC concentration decreases from $75 \mu\text{M}$ in surface waters to $\sim 40 \mu\text{M}$ at 900 m (*M. Dai et al.*, unpublished data, 2005).

[7] A large volume (300–500 L) of seawater was sampled at 10, 60, 100, 150, 200, 250, 300, 400, and 500 m with an in situ pump (McLane Lab) equipped with 142 mm diameter filtration holders. Seawater was pumped sequentially through a $53 \mu\text{m}$ Nitex screen, a $10 \mu\text{m}$ Nitex screen, a $0.7 \mu\text{m}$ GF/F filter and two 5-inch MnO_2 -impregnated cartridges (hereafter referred to as Mn-A and Mn-B). The pump flow rates were $4\text{--}7 \text{ L min}^{-1}$. The MnO_2 cartridges were prepared by soaking polypropylene cartridge filters (pore size $\sim 5 \mu\text{m}$) in hot ($>95^{\circ}\text{C}$) 0.5 M potassium permanganate solution for > 6 h until a thick layer of MnO_2 crystal was uniformly adhered. Our experiment shows that $>7\text{--}8 \text{ g}$ of MnO_2 crystal was adhered to each cartridge in this cartridge preparation process, which suggests that each cartridge pair (Mn-A + Mn-B) contained $>15 \text{ g}$ of MnO_2 . Within 3–5 hours of the in situ pumping, small-volume samples for bottle ^{234}Th analyses were collected at the same depths using Go-Flo bottles attached on a CTD rosette sampler. A volume of 4 L of seawater was used to determine total ^{234}Th activities. For the measurement of bottle particulate ^{234}Th , 8 L of seawater was filtered using a 25 mm diameter, $1 \mu\text{m}$ pore size quartz fiber filter (QMA, Whatman). To achieve a higher resolution for total ^{234}Th distribution in the upper 100 m, extra 4-L samples were collected at 1, 30 and 50 m.

2.2. Thorium-234 Analyses

[8] Analysis for total ^{234}Th in 4-L samples was based on the small volume MnO_2 coprecipitation (MnO_2 ppt hereafter) technique following the procedure described by *Buesseler et al.* [2001b] and *Cai et al.* [2006]. Briefly, within 1 h of collection,

unfiltered 4-L samples were acidified to $\text{pH} \approx 2$ with 6 ml of concentrated HNO_3 . Approximately 10 dpm of ^{230}Th were added as a yield tracer. The samples were mixed thoroughly and allowed to equilibrate for >12 h. Upon equilibration, pH was adjusted to 8.0–8.15 with concentrated NH_4OH . Then, 0.25 ml of KMnO_4 solution (3.0 g L^{-1}) and 0.25 ml of MnCl_2 solution ($8.0 \text{ g MnCl}_2 \cdot 4\text{H}_2\text{O L}^{-1}$) were added to form a suspension of MnO_2 . After the samples were heated in a water bath ($>80^\circ\text{C}$) for 2 h and allowed to cool, the suspension was filtered onto a 25 mm diameter, $1 \mu\text{m}$ pore size quartz fiber filter (QMA, Whatman). It has been demonstrated that the heating step dramatically reduces the filtration time for MnO_2 precipitates [Cai *et al.*, 2006]. Finally, the filtered MnO_2 precipitates were dried and mounted under one layer of Mylar film and two layers of aluminum foil for beta counting.

[9] Particles collected on the 53 and $10 \mu\text{m}$ pore size Nitex screens were resuspended by ultrasonication in filtered seawater and recollected on 25-mm $1.0 \mu\text{m}$ QMA filters. The QMA filters were dried overnight at 60°C and prepared for beta counting with Mylar and aluminum covers identical to those used for total ^{234}Th samples. The 142-mm GF/F filters were dried overnight, and two 25-mm subsamples were cut and prepared as replicates for beta counting. Samples for the analysis of bottle particulate ^{234}Th were also dried and prepared for beta counting. Analyses of particulate and total ^{234}Th activities were performed at sea with gas-flow proportional beta counters (Risø GM-5-25) following the methods described by Buesseler *et al.* [2001b].

[10] The MnO_2 -impregnated cartridges were brought back to our land-based laboratory, where they were transferred to 5-L glass beakers. Approximately 10 dpm of ^{230}Th , >2 L of 2 M HNO_3 and 60 ml of 30% H_2O_2 were added to each cartridge. The cartridges were boiled in the solution on a hot plate until they became completely white. After the cartridges were allowed to cool and removed from the leachate, another 2 L of 2 M HNO_3 and 1 L of deionized water were pumped sequentially through them using a cartridge holder. To test the efficiency of our leaching process, we ashed cartridges that had been leached in a parallel experiment. Our results showed that >99% of Th ($99.6 \pm 0.1\%$, $n = 7$) on the intact cartridges was leached out.

[11] All of the leachates were combined and evaporated to ~ 200 ml, transferred to a 250.0 ml flask

and the volume was brought up to 250.0 ml using deionized water. Twenty percent of this solution was removed from the flask and 1.0 mg Fe^{3+} was added. The remaining solution was used for the determination of natural ^{228}Th in seawater. The Th nuclides were coprecipitated with Fe hydroxide by adjusting the pH of the solution to ~ 7.0 with the addition of NH_4OH . Under such pH conditions, Mn^{2+} remained in the supernatant. This step avoided the formation of great amounts of MnO_2 precipitate, which could lead to significant reduction in beta counting efficiency due to the self-absorption effect. The $\text{Fe}(\text{OH})_3$ precipitates were collected on 25-mm $1.0 \mu\text{m}$ pore size QMA filters. The precipitates were dried and prepared for beta counting in a same manner as described above for the total ^{234}Th in seawater.

[12] Each sample was beta-counted 5 times over a period of >150 days in order to follow the decay of ^{234}Th . A two-component fitting technique was applied to find the best fit of gross-counting data to an exponential curve with a half-life of 24.1 days. Each time point was further weighed by the individual counting uncertainty (SigmaPLOT™). The net count rate of ^{234}Th at the midpoint of sample filtration, as well as the background count rate, was estimated. After counting, the precipitates were disassembled and placed in 100 ml Teflon beakers for recovery assessment. Recovery assessment was possible because 10 dpm of ^{228}Th and 2 dpm of ^{229}Th internal standards were added to the MnO_2 and $\text{Fe}(\text{OH})_3$ precipitates respectively prior to radiochemical purification for recovery determination. In the latter case, ^{229}Th was selected over ^{228}Th because there could be a significant amount of natural ^{228}Th in the MnO_2 cartridge samples, given the fact that up to 300–500 L of seawater was processed through each cartridge. The subsequent procedure for the isolation of Th isotopes was according to Cai *et al.* [2006]. Finally, Th was extracted into a 0.25 M TTA/benzene solution, and evaporated onto a stainless steel disc. The discs were counted by alpha spectrometry in ultra ion-planted detectors (Octète™ PC) until the uncertainty of $^{230}\text{Th}/^{228}\text{Th}$ (and/or $^{230}\text{Th}/^{229}\text{Th}$) ratio was lower than 3%. Corrections were applied to ^{234}Th activity calculations on the basis of ^{230}Th recoveries. All data were decay corrected to the time of collection and reported with a propagated uncertainty that includes the standard uncertainty associated with the ^{234}Th fitting curve and 1 sigma counting uncertainty from the recovery measurements. Uranium-238 activities were estimated from salinity measurements using a calibrated CTD and

Table 1. Thorium-234 Activities at the Station in the Northern South China Sea Based on Different Techniques

Depth, m	Particulate ^{234}Th , dpm L^{-1}		Dissolved ^{234}Th , dpm L^{-1}			Total ^{234}Th , dpm L^{-1}		^{238}U dpm L^{-1}
	Pump	Bottle	Mn-A	Mn-B	DTh/Cart. ^a	Cartridge	MnO_2 ppt	
1	—	—	—	—	—	—	—	2.41
10	0.348 ± 0.011	0.292 ± 0.029	0.661 ± 0.015	0.053 ± 0.011	0.718 ± 0.020	1.066 ± 0.023	1.643 ± 0.074	2.41
30	—	—	—	—	—	—	1.773 ± 0.057	2.41
50	—	—	—	—	—	—	1.919 ± 0.088	2.42
60	0.355 ± 0.012	0.422 ± 0.021	0.654 ± 0.015	0.031 ± 0.005	0.686 ± 0.016	1.041 ± 0.020	1.894 ± 0.050	2.42
100	0.290 ± 0.009	0.294 ± 0.027	1.218 ± 0.052	0.177 ± 0.009	1.425 ± 0.063	1.715 ± 0.063	2.429 ± 0.093	2.43
150	0.332 ± 0.005	0.269 ± 0.009	0.927 ± 0.020	0.312 ± 0.015	1.399 ± 0.047	1.731 ± 0.047	2.353 ± 0.068	2.44
200	0.300 ± 0.007	0.338 ± 0.013	1.069 ± 0.021	0.097 ± 0.004	1.176 ± 0.024	1.477 ± 0.025	2.121 ± 0.055	2.43
250	0.330 ± 0.011	0.349 ± 0.013	0.950 ± 0.020	0.502 ± 0.024	2.015 ± 0.124	2.345 ± 0.124	2.446 ± 0.065	2.43
300	0.306 ± 0.004	0.379 ± 0.012	1.345 ± 0.029	0.097 ± 0.003	1.449 ± 0.031	1.756 ± 0.031	2.417 ± 0.078	2.42
400	0.302 ± 0.016	0.312 ± 0.016	0.838 ± 0.039	1.427 ± 0.040	—	—	2.509 ± 0.113	2.42
500	0.314 ± 0.009	0.312 ± 0.016	0.766 ± 0.025	0.359 ± 0.010	1.443 ± 0.072	1.757 ± 0.073	2.383 ± 0.076	2.42

^aBased on the cartridge technique (TCE = 1 - B/A). See text for details.

the relationship of ^{238}U (dpm L^{-1}) = 0.0686 × salinity (‰) × ρ [Chen *et al.*, 1986].

[13] The detection efficiency of our beta counters was estimated using open ocean seawater with salinity >34, which was filtered and acidified upon collection, and stored for >5 months to ensure secular equilibrium between ^{234}Th and ^{238}U . The average counting efficiency for the MnO_2 precipitate covered with one layer of Mylar film and two layers of aluminum foil (with a density of 3.6 mg cm^{-2}) was 0.50 ± 0.01 and varied by <2% among detectors. In this study, the filter loading of the actual particle samples varied in a relatively narrow range of 0.13–1.31 mg. Note that the filter loading was not directly determined, but estimated from POC measurements using a conversion factor of 2.5. This particle loading is similar to the MnO_2 load of the calibration and small compared to the load on the MnO_2 filters. As such, we believe that self-absorption did not significantly interfere during beta counting of the particle samples. Thus the same detection efficiency was applied to the $\text{Fe}(\text{OH})_3$ precipitate samples and the particle samples.

3. Results and Discussion

[14] Thorium-234 activities as estimated using the MnO_2 cartridge technique and the MnO_2 ppt technique are summarized in Table 1. Particulate ^{234}Th activities based on in situ pumping were calculated as the sum of the activities in the size-fractionated samples. As shown in Table 1, there is no significant difference in pump versus. bottle particulate ^{234}Th activities (pump ^{234}Th /bottle ^{234}Th = 0.986 ± 0.062 , $n = 9$). This observation is in contrast to the recent study by Liu *et al.* [2005], which suggested systematic undercollection of POC by in situ pump compared to bottle sampling. Their conclusion is that marine sampling bottles preferentially capture motile zooplankton relative to most current pumping systems. If this were the case, our observation would not contradict that by Liu *et al.* [2005], as previous studies have suggested little ^{234}Th in living zooplankton [e.g., Buesseler *et al.*, 1994].

[15] The theoretical collection efficiency (TCE) for the MnO_2 cartridge (Table 2) is obtained by using equation (1). The derived collection efficiency (DCE) can be calculated from

$$\text{DCE-A} = \text{ThA}/(\text{Th}_T - \text{Th}_P), \quad (2)$$

$$\text{DCE-B} = \text{ThB}/[(\text{Th}_T - \text{Th}_P) - \text{ThA}], \quad (3)$$

Table 2. Derived Collection Efficiency and the Theoretical Collection Efficiency as Well as the Coprecipitation Efficiency for MnO_2 ppt^a

Depth, m	Derived Collection Efficiency				DCE-A/TCE	Coprecipitation Efficiency MnO_2 ppt
	DCE-A	DCE-B	DCE-A&B	TCE 1-B/A		
10	0.515 ± 0.026	0.085 ± 0.019	0.556 ± 0.027	0.920 ± 0.016	0.560	0.912 ± 0.023
60	0.425 ± 0.017	0.035 ± 0.006	0.445 ± 0.017	0.953 ± 0.007	0.446	0.969 ± 0.024
100	0.569 ± 0.035	0.192 ± 0.024	0.652 ± 0.035	0.854 ± 0.010	0.666	0.943 ± 0.021
150	0.459 ± 0.018	0.286 ± 0.023	0.614 ± 0.020	0.663 ± 0.017	0.692	0.854 ± 0.019
200	0.587 ± 0.021	0.130 ± 0.011	0.641 ± 0.022	0.909 ± 0.004	0.646	0.874 ± 0.020
250	0.449 ± 0.017	0.430 ± 0.033	0.686 ± 0.022	0.471 ± 0.027	0.952	0.853 ± 0.020
300	0.637 ± 0.027	0.127 ± 0.014	0.683 ± 0.027	0.928 ± 0.003	0.687	0.810 ± 0.023
400	0.380 ± 0.026	1.042 ± 0.097	1.026 ± 0.046	-0.703 ± 0.092	-0.540	0.865 ± 0.027
500	0.370 ± 0.018	0.276 ± 0.019	0.544 ± 0.020	0.531 ± 0.020	0.697	0.861 ± 0.022

^aDCE, derived collection efficiency; TCE, theoretical collection efficiency. DCE-A&B refers to the derived collection efficiency for the cartridge pairs.

where DCE-A and -B are the derived collection efficiencies for Mn-A and -B; ThA and ThB are ²³⁴Th activities determined in Mn-A and -B; Th_T is the total ²³⁴Th activity based on the MnO_2 ppt technique; and Th_P is the particulate ²³⁴Th activity in seawater based on in situ pumping.

[16] The theoretical collection efficiency and the derived collection efficiency are listed in Table 2 and shown in Figure 1. Also listed in Table 2 are the derived collection efficiencies for each MnO_2 cartridge pair (DCE-A&B = (ThA + ThB)/(Th_T - Th_P)), and the coprecipitation efficiency for MnO_2 ppt. It is striking to notice how the derived collection efficiency is substantially lower than the theoretical collection efficiency throughout the water column, except at 400 m. As can be seen

from Figure 1, the theoretical collection efficiency varies from 0.471 to 0.953 (mean: 0.779 ± 0.194 , with data at 400 m excluded). In contrast, the derived collection efficiency ranges from 0.37 to 0.637 (0.488 ± 0.094 , 1 SD). Thus ²³⁴Th collection efficiency has been substantially overestimated by the MnO_2 cartridge technique using equation (1). While it remains an open question what caused this overestimation, it must be related to the interaction between ²³⁴Th and the MnO_2 cartridge. We suggest that this may be due to the organic complexation of a significant portion of ²³⁴Th in seawater, rendering it less able to adsorb to the MnO_2 cartridge.

[17] Moreover, there are substantial differences between the derived collection efficiency of Mn-A and Mn-B (Table 2 and Figure 1). The DCE-B

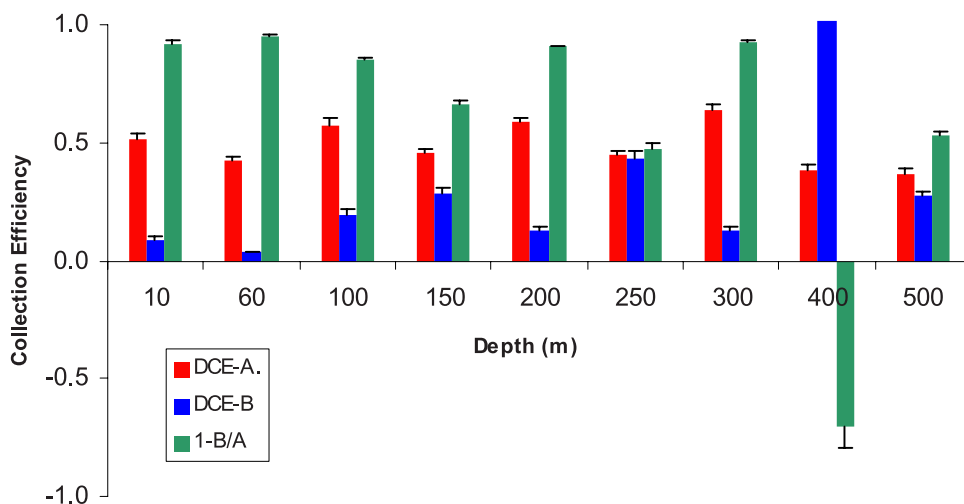


Figure 1. Comparison between the derived collection efficiency (DCE) and the theoretical collection efficiency (TCE). DCE-A and -B represent the derived collection efficiencies for Mn-A and Mn-B. Note that DCE-A and DCE-B were assumed to be identical and equal to TCE in the traditional technique.

Table 3. Summary of Published Collection Efficiency and Sampling Parameters in Applying the MnO_2 Cartridge Technique

Location	Flow Rate, min L^{-1}	Sample Volume, L	Sample Number	Theoretical Collection Efficiency	References
North Atlantic	2–7	4000	12	0.827 ± 0.075	<i>Livingston and Cochran</i> [1987]
North Atlantic	4–8	3450	40	0.87 ± 0.08	<i>Buesseler et al.</i> [1992a]; <i>Cochran et al.</i> [1993]
Equatorial Pacific	3–5	300–600	103	0.79 ± 0.09	<i>Buesseler et al.</i> [1995]
Greenland Shelf	5–16	1000–1600	79	0.80 ± 0.08	<i>Cochran et al.</i> [1995a]
Arctic	NR ^a	NR ^a	28	0.74 ± 0.17	<i>Cochran et al.</i> [1995b]
Equatorial Pacific	1–8.5	1000–2000	72	0.905 ± 0.127	<i>Bacon et al.</i> [1996]
Gulf of Mexico	10–35	1000–4000	36	NR ^a	<i>Baskaran et al.</i> [1996]
Arctic	2–3	200–600	30	0.896 ± 0.073	<i>Moran et al.</i> [1997]
Arabian Sea	5–7	>250	56	0.87 ± 0.07	<i>Buesseler et al.</i> [1998]
NE Pacific	5–7	2500–3500	161	0.82 ± 0.12	<i>Charette et al.</i> [1999]
Atlantic	4.8–13	750–2000	23	0.79 ± 0.083	<i>Charette and Moran</i> [1999]
Middle Atlantic Bight	10–35	2000–4000	64	NR ^a	<i>Santschi et al.</i> [1999]
Beaufort Sea	NR ^a	200–600	24	0.89 ± 0.07	<i>Moran and Smith</i> [2000]
Ross Sea	4–8	100–1000	72	$\frac{1}{4}$ samples <0.50	<i>Cochran et al.</i> [2000]
Gulf of Maine	NR ^a	200–400	66	0.86 ± 0.08	<i>Benitez-Nelson et al.</i> [2000]
Southern Ocean	4–8	300–500	196	0.85	<i>Buesseler et al.</i> [2001a]
Gulf of Maine	5–8	100–1500	149	0.75 ± 0.12	<i>Charette et al.</i> [2001]
Gulf of Mexico	>10	1000–4000	32	0.84 ± 0.07	<i>Guo et al.</i> [2002]
North Water	NR ^a	100–1000	30	0.88 ± 0.07	<i>Amiel et al.</i> [2002]
Labrador Sea	NR ^a	200–1200	12	NR ^a	<i>Moran et al.</i> [2003]
Arctic	10–15	351–1185	27	2 samples <0.65	<i>Baskaran et al.</i> [2003]
Baltic Sea	5–8	500–800	28	0.75 ± 0.12	<i>Gustafsson et al.</i> [2004]
Gulf of Mexico	>10	1000–4000	25	NR ^a	<i>Hung et al.</i> [2004]
Arctic	10–15	300–2000	31	0.776	<i>Trimble and Baskaran</i> [2005]
South China Sea	4–7	300–500	9	0.779 ± 0.194	this study

^aNR, not reported.

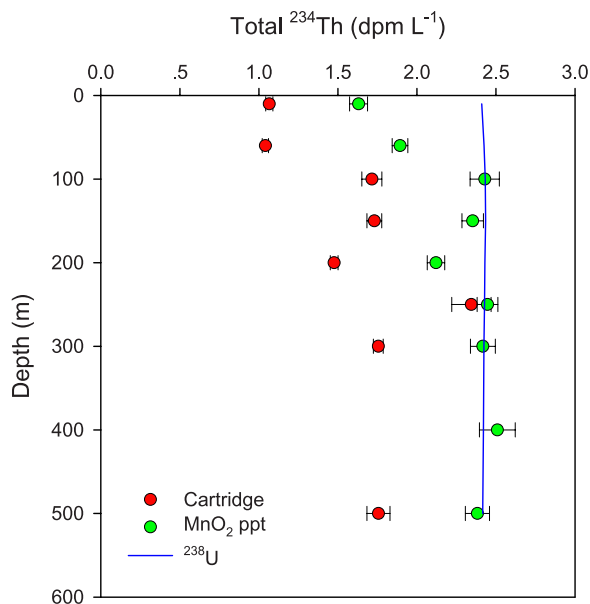


Figure 2. Depth profiles of total ²³⁴Th activities based on the MnO₂ cartridge technique and on the MnO₂ coprecipitation technique. The solid line represents depth distribution of ²³⁸U.

ranges from 0.035 to 0.43 (0.195 ± 0.129 , with data at 400 m excluded), lower than DCE-A by more than a factor of 2. This suggests that Mn-A retains most of the absorbable Th and Mn-B extracts Th to a much less extent. Given the fact that the derived collection efficiencies for the cartridge pairs (DCE-A&B, Table 2 with data at 400 m excluded) is always lower than 0.70, it can be inferred that there is a fraction of dissolved Th not retained by the MnO₂ cartridges. Therefore we may hypothesize that Th occurs in the dissolved phase as different chemical species, e.g., Th^E, Th^H and Th^C. Th^E represents the easily absorbable Th species, and Th^H is less able to be retained by the cartridges. Th^C, which is not collected by the MnO₂ cartridges, may be considered to be colloid-bound. From this study, it appears that under typical sampling conditions, Mn-A is “skimming the cream” by getting most of the Th^E and some of the Th^H. Then, the Mn-B has mostly Th^H to adsorb, leading to a substantially lower derived collection efficiency for Mn-B than for Mn-A.

[18] The different retention of Th on Mn-A and Mn-B is not that surprising. *Rutgers van der Loeff et al.* [2006] found that in coastal settings, the theoretical collection efficiency based on the MnO₂ cartridge technique decreases with increasing total organic carbon loads. These authors ascribed the decrease in collection efficiency to the complexation of a fraction of ²³⁴Th with organic ligands.

Meanwhile, several investigators have observed a decrease in the ²³⁴Th collection efficiency with an increase in flow rate [*Charette and Moran, 1999; Cochran et al., 1995a*], suggesting that adsorption of ²³⁴Th on the MnO₂ cartridge is kinetically limited. Compared to the MnO₂ cartridge technique, the much longer exposure time involved in the MnO₂ ppt technique favors the exchange of ²³⁴Th between organic compounds and MnO₂ sites. Also, the acidification step required when a Th spike is added prior to MnO₂ coprecipitation may enhance the H⁺-triggered displacement of some ²³⁴Th from organic complexes.

[19] Overall, one would expect substantially higher collection efficiency for ²³⁴Th by using the MnO₂ ppt technique because of the longer exposure time and the acidification step. Indeed, as shown in Table 2, the collection efficiency by using the MnO₂ ppt technique varies between 0.81 and 0.969 (0.882 ± 0.05 , 1SD), which is substantially higher than the derived collection efficiency by using the MnO₂ cartridge pair (DCE-A&B = 0.603 ± 0.083 , with data at 400 m excluded). It is noteworthy that even by using the MnO₂ ppt technique, we found a collection efficiency for ²³⁴Th lower than 1, which is in good agreement with *Pike et al.* [2005]. During the Southern Ocean Fe Experiment (SOFeX), these authors derived a mean collection efficiency of 0.913 for ²³⁴Th ($n = 103$; 19 samples with collection efficiency <0.85 were not included) by using the MnO₂ ppt technique coupled with the addition of a yield tracer.

[20] Both this study and that by *Pike et al.* [2005] have shown that ~10% of total ²³⁴Th was “missing” during the sample processing. As it has been demonstrated that physical losses of the MnO₂ ppt due to bottle-wall adherence and filter breakthrough can only account for <2–3% of the total ²³⁴Th in seawater [*Buesseler et al., 2001b*], we deduce that even in open ocean conditions, up to >7–10% of dissolved ²³⁴Th, i.e., Th^C, is not subject to collection by MnO₂ precipitates. This is supported by previous studies on colloidal ²³⁴Th, which was shown to account for ~10% of total ²³⁴Th in open ocean water [e.g., *Baskaran et al., 2003; Huh and Prahl, 1995*]. In coastal sea settings, this fraction could be even higher [e.g., *Dai and Benitez-Nelson, 2001*]. *Quigley et al.* [2001] further demonstrated that the Th-COM (colloidal organic matter) complex is tightly bound, and even EDTA is unable to displace the ²³⁴Th from its association with COM. Thus it is conceivable that a larger portion of ²³⁴Th would pass through the

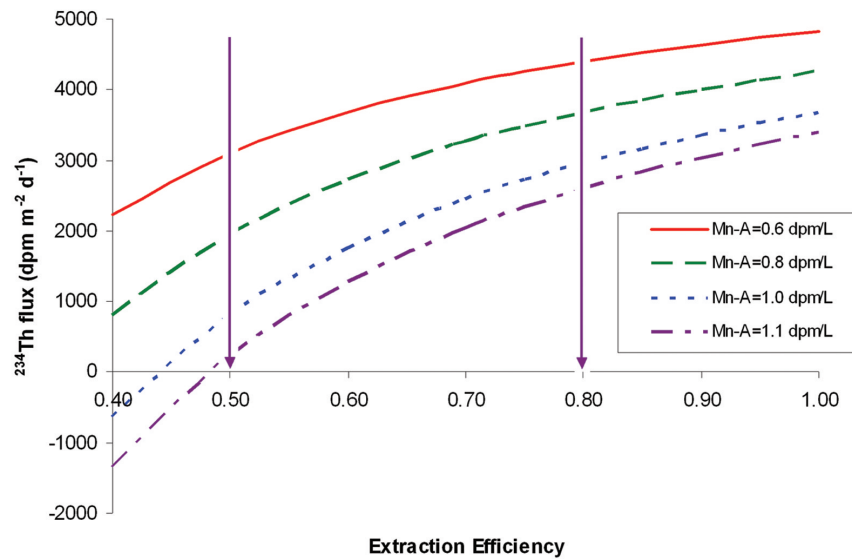


Figure 3. Sensitivity of the collection efficiency (for MnO_2 cartridges) in the calculation of ^{234}Th flux at 100 m. Calculations refer to theoretical ^{234}Th activities of 0.6, 0.8, 1.0, and 1.1 dpm L^{-1} .

MnO_2 -impregnated cartridge pair, given the much shorter exposure time for the exchange of ^{234}Th .

[21] Table 3 summarizes the theoretical collection efficiency, as well as some relevant sample processing information in previous studies. It is noticeable that our procedure for cartridge preparation and sample processing, as well as sampling regime are typical for the application of the MnO_2 cartridge technique. Moreover, the theoretical collection efficiency in this study is similar to those derived by other researchers. The reason for the apparently negative collection efficiency (i.e., $\text{Th}_B > \text{Th}_A$) at 400 m (Table 2) is unclear. However, it is not unusual to observe a negative collection efficiency. Similar scenario has also been observed in previous studies (e.g., K. O. Buesseler, personal communication, 2005), and could be attributable to water bypassing a poorly sealed Mn-A.

[22] To demonstrate how this overestimate in collection efficiency may affect our interpretation of $^{234}\text{Th}/^{238}\text{U}$ disequilibrium in the water column, the depth profiles of total ^{234}Th activities based on the two techniques are compared (Figure 2). For the depth profile based on the MnO_2 ppt technique, ^{234}Th activities are lower than equilibrium in the upper 100 m, indicating that significant particulate export is occurring. Below 100 m, a secular equilibrium is reached between ^{234}Th and ^{238}U except at 200 m. This structure is in good agreement with relatively modest particle scavenging below the euphotic zone. The reason for ^{234}Th deficit at 200 m is unclear. One possible explanation is the

subduction of ^{234}Th -deficit surface water into this depth. Alternatively, it could be due to the repackaging of small, nonsinking particles into large, fast-sinking particles at this depth.

[23] In contrast, the depth profile based on the MnO_2 cartridge technique shows ^{234}Th deficit relative to ^{238}U throughout the 0–500 m water column. Similar structure has been observed in the Gulf of Mexico and in the Middle Atlantic Bight [e.g., Baskaran *et al.*, 1996; Hung *et al.*, 2004; Santschi *et al.*, 1999], and was ascribed to benthic nepheloid layer exchange processes over the continental slope.

[24] Since $^{234}\text{Th}/^{238}\text{U}$ disequilibrium is commonly used to quantify the particulate organic carbon (POC) export rate from the upper ocean, we performed a sensitivity analysis of the calculated ^{234}Th flux (and hence POC export rate) based on the difference between the theoretical collection efficiency and the derived collection efficiency for ^{234}Th (Figure 3). The basis of our analysis is as follows. First, a typical ^{238}U activity of 2.48 dpm L^{-1} and a particulate ^{234}Th activity of 0.20 dpm L^{-1} are assigned to the upper 0–100 m water column. The ^{234}Th flux at 100 m can then be calculated on the basis of the equation

$$F = \lambda[U - (\text{Th}_d + \text{Th}_p)] \times 100 = 2876 \times (2.28 - \text{Th}_A/E), \quad (4)$$

where F is ^{234}Th flux ($\text{dpm m}^{-2} \text{d}^{-1}$); λ is the decay constant of ^{234}Th (0.02876 d^{-1}); Th_d , Th_p

are the dissolved and particulate ^{234}Th activities, respectively; ThA is the ^{234}Th activity measured on the Mn-A; and E is the collection efficiency applied to Mn-A. Second, the curved lines in Figure 3 represent various decay-corrected ^{234}Th activities measured on Mn-A. For a given collection efficiency on the x axis, the ^{234}Th flux can be calculated by locating the intersection with the appropriate ThA activity. For example, taking an efficiency of 0.50 and a ThA activity of 0.8 dpm L^{-1} , the ^{234}Th flux would be $1956 \text{ dpm m}^{-2} \text{ d}^{-1}$. Taking the same initial activity of ^{234}Th and an overestimate in the collection efficiency by 0.30, the ^{234}Th flux would be $3681 \text{ dpm m}^{-2} \text{ d}^{-1}$. Meanwhile, for an initial ThA activity of 1.1 dpm L^{-1} , a same overestimate in the collection efficiency, i.e., 0.50 versus 0.80, would lead to an overestimate in ^{234}Th flux, and hence ^{234}Th -based POC export rate by as much as an order of magnitude (i.e., 230 versus $2602 \text{ dpm m}^{-2} \text{ d}^{-1}$). If the cartridge technique used by *Santschi et al.* [1999] had suffered from a similar overestimate in collection efficiencies, this sensitivity analysis would explain the discrepancy between ^{234}Th fluxes expected from the ^{234}Th deficit in the water column and from the sediment trap deployed in the Middle Atlantic Bight, where the water column deficit below 200 m amounted to $8300\text{--}13,000 \text{ dpm m}^{-2} \text{ d}^{-1}$, while in the sediment trap at 800 m, on average, only $1000\text{--}3000 \text{ dpm m}^{-2} \text{ d}^{-1}$ were collected [*Santschi et al.*, 1999]. Similarly, it is possible that the under-collection of ^{234}Th by shallow sediment trap as observed in some studies [e.g., *Gustafsson et al.*, 2004; *Hung et al.*, 2004] can be ascribed, at least partially, to this collection efficiency issue.

[25] Many researchers used deep water to calibrate their gamma detectors [e.g., *Buesseler et al.*, 1992b; *Moran et al.*, 1997]. This would serve to constrain the combined collection efficiency and detector efficiency by comparing net count rates to ^{234}Th activity concentration in deep water, which is assumed to be in equilibrium with ^{238}U [*Coale and Bruland*, 1987]. In the absence of accurate knowledge of cartridge or precipitation efficiency, this standardization is critically important, and some examples of deep-water ^{234}Th deficiency may be the result of not employing this approach. The inherent assumption behind this calibration for MnO_2 cartridges, however, is that the collection efficiencies in surface and deep water samples are similar. As the DOC concentration, the nutrient level and the temperature in deep water are, in general, dramatically different from surface water,

this standardization could introduce significant error to the ^{234}Th activities. Indeed, as shown in Table 2, the average ratio of the derived collection efficiency to the theoretical collection efficiency is 0.668 ± 0.143 (1 SD). In this case, if one used deep water for calibration, the error associated with the derived ^{234}Th activities should be no better than $\pm 20\%$ ($0.143/0.668 = 0.21$). To understand the behavior of ^{234}Th on the MnO_2 cartridges, future studies on the in situ speciation of Th isotopes in seawater are needed. At present, it is recommendable to adopt the small volume MnO_2 coprecipitation technique for the determination of total ^{234}Th in seawater, given that it has offered advantages over the MnO_2 cartridge technique [*Buesseler et al.*, 2001b]. In particular, we recommend the small volume MnO_2 ppt technique with the addition of a yield monitor, since all losses of ^{234}Th due to colloidal complexation and physical loss of MnO_2 ppt can be corrected by Th recoveries [*Cai et al.*, 2006; *Pike et al.*, 2005; *Rodriguez y Baena et al.*, 2006]. However, it should be pointed out that the MnO_2 ppt technique has a major disadvantage of its inability for the determination of particulate ^{234}Th in seawater. Selection of different Th sampling techniques in order to suit different research objectives has been recommended by *Rutgers van der Loeff et al.* [2006].

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