GEOTRACES Intercalibration Report

Cruise ID*: **TN303**
Submitting investigator*: **Ken Buesseler - Woods Hole Oceanographic Institution - kbuesseler@whoi.edu**
Parameters to be intercalibrated*:

- **Th_234_T_CONC_UWAY::gy2zni mBq/kg**
- **Th_234_T_CONC_BOTTLE::oepuv9 mBq/kg**
- **Th_234_SPT_CONC_PUMP::bm10kg mBq/kg**
- **Th_234_LPT_CONC_PUMP::byeecv mBq/kg**

***Once generated, these headings must not be changed or altered.**

Please fill in as many sections as possible.

1. Did your lab participate in an intercalibration exercise (http://www.geotraces.org/sic/intercalibrate-data/intercalibration-exercices)? If so, please provide a relevant figure or table, describe the results of the intercalibration, identifying your laboratory, and provide a reference for the intercalibration exercise, if published.

Results from the GEOTRACES ^{234}Th inter-calibration efforts are published in Maiti et al., 2012. Fifteen labs participated in two cruises that centered on particulate, total and dissolved ^{234}Th inter-calibration. Particulate ^{234}Th inter-calibration was assessed for small particles collected on QMAs and SUPORs, as well as for large particles collected on 51 μm screen filters. Additional laboratory experiments were performed to understand the effects of filter type, flow rate, particle loading, and other parameters on particulate ^{234}Th activity.

2. Did your sampling method at sea follow the GEOTRACES cookbook (available at: http://www.geotraces.org/cookbook)? Please give a brief description of your sampling methodology (e.g., what bottles were used, what type and size of filters were used, how the samples were treated at sea, etc.).

The sampling methodology followed the GEOTRACES cookbook guidelines outlined in Section IV. Large and small particle particulates were collected using dual-filter head in situ McLane pumping systems (also see Lam datasets from TN303 for additional pumping system details). Generally, shallow total ^{234}Th samples (<1000 m) were collected from Niskins on the ODF Rosette and deep total ^{234}Th samples (>1000 m) were collected from Niskin bottles hung above in situ pumps. The following sampling methods used on TN303 for total and particulate ^{234}Th were originally detailed in (Black et al., 2018) and have been adapted for this document:

Total ^{234}Th (Bottle and Uway):

Total ^{234}Th samples were collected at 35 stations. At super and full stations, 8 to 13 discrete depths were sampled through the upper 400 m. At the remaining stations, 8 to 12 depths were sampled in the upper 400 m. A standard, 12-Niskin rosette was used to collect the total ^{234}Th samples from the upper 400 m and between 4 and 9 of the rosette depths were matched to those of in-situ pumping systems deployed on a subsequent cast to obtain particulate ^{234}Th. At a third of the stations, surface samples for total ^{234}Th were collected from the ship's underway system (~3 m below the surface) and on a few occasions 1 to 2 extra shallow depths were sampled using wire-attached Niskin bottles above in-situ pumps on later casts. Additional total samples were taken to improve the resolution of shallow features. At each depth, ~4 L of water was taken from the corresponding Niskin bottle after rinsing the sample bottle three times. The 4L sample bottles were mass-volume calibrated prior to the cruise and were filled to the marked calibration line.

Particulate ^{234}Th (SPT and LPT):

At super stations, 3 pump casts were performed with 5 to 9 depths in the upper 400 m and approximately 24 discrete particulate ^{234}Th samples for each particle size class were collected through the water column. Pumps were deployed to capture 4 to 6 depths in the upper 400 m on 2 casts at full stations (i.e. 16 discrete depths throughout the full water column) and on 1 cast at shelf stations 2 to 5 and at station 34. (i.e. 5 – 8 discrete depths). The filter heads each contained a 51 µm pore size pre-filter followed by either a Supor filter or a precombusted and acid-leached QMA filter with a nominal pore size of 1 µm. Filter heads were pumped down on-deck and removed from the filter heads in the designated trace metal clean 'bubble' space by the Lam group (see particulate trace metal dataset information from Lam group). The filters were placed in plastic 142 mm petri dishes and brought to the short-lived radionuclide van ('Café Thorium') for processing. The material on the 51 µm pre-filter from the Supor filter head was rinsed onto silver filters using 0.1 µm filtered seawater and dried. The 142 mm QMA filter was oven dried and subsampled with a 25 mm punch. The average sample volume through the 51 µm pre-filter was 404 L and for the area of the QMA subsample was 41 L.

3. Briefly outline the analytical methodology used in your laboratory, and provide associated metadata and references, as appropriate.

On-ship and at WHOI, RISØ Laboratory Anti-coincidence Beta Counters were used to quantify total and particulate ^{234}Th. See https://cafethorium.whoi.edu/services/ and https://www.nutech.dtu.dk/english/products-and-services/radiation-instruments/gm_multicounter.

Total ^{234}Th:

^{234}Th was determined by the widely-adopted 4 L method (Buesseler et al., 2001), which has been utilized previously for other GEOTRACES efforts (e.g. Owens et al., 2015). An exact 1 mL aliquot of ^{230}Th (46.34 dpm g^{-1}) was used as the yield monitor and added during initial acidification of the samples. QMAs were used to collect the precipitate from the 4L process and immediately dried. Once dried, they were mounted onto plastic 25 mm discs, covered with a mylar layer and 2 layers of aluminum foil, and immediately beta counted at sea. The filters were counted again 5 to 6 months later to quantify the background radioactivity due to the beta decay of long-lived natural radionuclides that are also precipitated. The mean value of the at-sea counts (decay-corrected to the time of collection) minus the background value for each filter is reported as the ^{234}Th activity (mBq kg^{-1}). Activities for ^{234}Th are generally reported in dpm L^{-1}, but have been converted here using a standard density of 1.025 kg L^{-1} and 1 dpm = 16.667 mBq. Data are decay corrected to the mid-point time between when bottles 1 and 12 were fired for shallow casts, when the messenger was dropped for deep casts, and the time of collection for underway samples.

To determine ^{234}Th activity deficits, ^{238}U (its parent isotope) activities were calculated using a standard uranium-salinity relationship (Owens et al., 2011). The efficiency of the beta detectors was determined by minimizing the ^{234}Th deviation from ^{238}U for samples collected from regions of the water column where ^{234}Th and ^{238}U are expected to be at equilibrium. These included depths below 1000 m and above 500 m off the seafloor that were not near the coastal shelf or the hydrothermal vent. For these samples (n= 93) the mean derived ^{238}U activity and standard deviation were 2.407 ± 0.004 dpm L^{-1}, a value well within observed natural ranges (Owens et al., 2011). The reported ^{234}Th activities were corrected for the chemical recovery efficiency of the ^{234}Th-Mn precipitate method. To determine the percent recovery of the added ^{230}Th tracer, the method detailed in Pike et al. (2005) was followed without the initial ion exchange column chemistry steps. Filters were leached in a nitric acid-hydrogen peroxide solution and 1 g of a ^{229}Th yield monitor (68.87 dpm g^{-1}) was added. Samples were then sonicated for 20 min, allowed to stand covered overnight, diluted, and prepared for analysis by ICP-MS. The mean chemical recovery for all samples was 90.8% with a median value of 91.6%.

Particulate ^{234}Th:

Once the silver filters and the 25 mm QMA subsamples were dried, they were mounted onto plastic 25 mm discs, covered with a mylar layer and 2 layers of aluminum foil, and immediately beta counted at sea. They were counted again 5 to 6 months later at the Buesseler beta counting facility at WHOI. All data were decay corrected back to the mid-pumping times.

4. Report your blank values and detection limits, and explain how these were defined and evaluated.

Forty-one blank particulate samples (dipped blanks) were collected for each particle size using extra filter heads deployed with the McLane pumps, but without a connection to the pumping systems. On ship, blank QMA filters averaged 0.32 cpm ±

0.04 (standard deviation) and after 5 to 6 months the background count average was 0.29 ± 0.04. These values were indistinguishable from each other and from typical 'empty' detector counts. The same was true for the Ag filter blanks which averaged 0.29 cpm ± 0.09 and 0.25 cpm ± 0.03 after 5 to 6 months. The slightly higher standard deviation was due to coastal sample blank that were, on average, higher, but still within the range observed for background counts. Completely blank Ag and QMA filters (i.e. those present in the lab that were not deployed with the McLane pumps as a dipped blank) were also counted. These blanks had slightly lower cpm than the dipped blanks, but were statistically indistinguishable from the dipped blank results.

Limits of detection are not reported because they are not applicable to the ^{234}Th beta counting method. A 'non-detect' for ^{234}Th or a case where there is no ^{234}Th present (initially or after 6 months of decay) will still result in a measurable amount of background radioactivity due to the beta decay of long lived natural radionuclides that are also collected on the pump filters. These background values are utilized and therefore, they are not reported as a non-detection of ^{234}Th.

The data flags used are as suggested at www.geotraces.org/geotraces-quality-flag-policy/. Most values were flagged as 'probably good' (2). A few missing values were noted (9).

5. Report how you monitored the internal consistency of your data (e.g., through replicate analyses of samples).

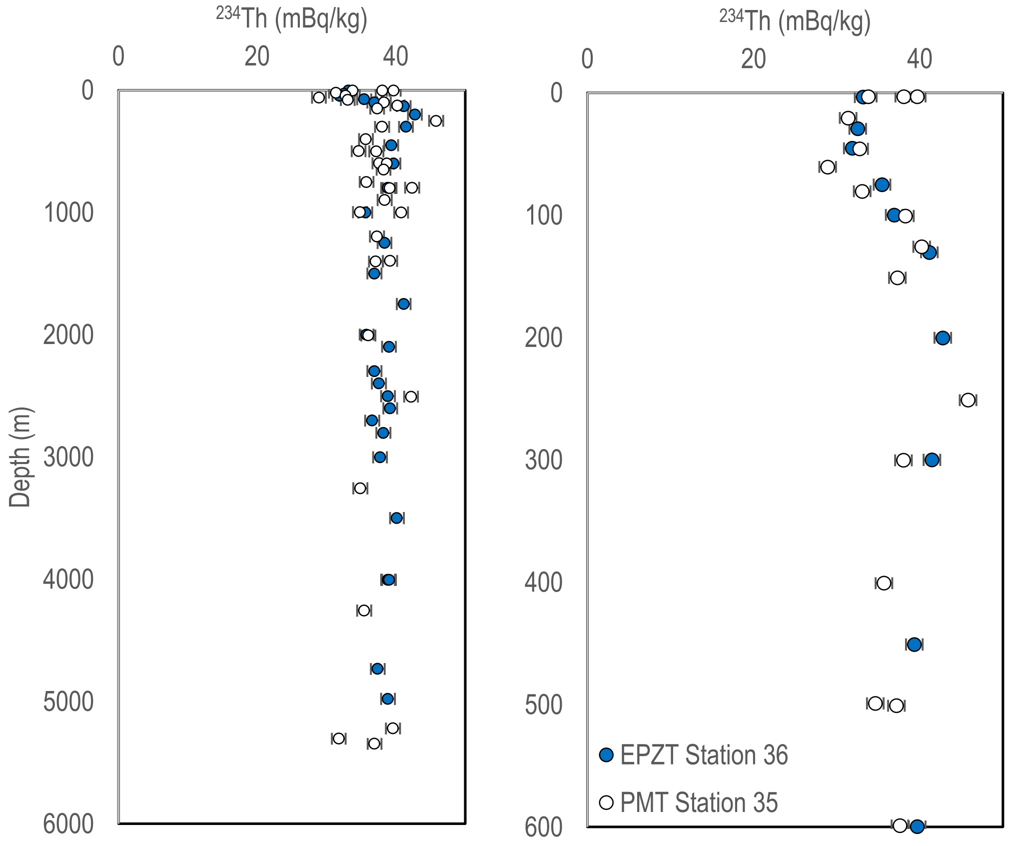
At the start and conclusion of the cruise, five high activity (238 cpm to 365 cpm) ^{238}U standards and background counts (empty detectors) were measured to confirm correct operation of the RISØ detectors and to determine detector to detector variability. These uranium standards have been used for all GEOTRACES cruise performed by the Buesseler lab. The reported uncertainty on each ^{234}Th measurement represents the propagated counting uncertainty and detector to detector normalization. Counting uncertainty is generally the largest source of uncertainty so whenever possible samples were counted until errors were below 5%. For the low-volume (i.e. 4L) total ^{234}Th samples, all filters were beta counted twice for a minimum of 12 h at sea. As long as the calculated gross counts per minute from these 2 measurements were within 10%, they were averaged for the at-sea ^{234}Th value.

6. Report the external consistency of your data (e.g., results from analyses of certified reference materials and/or consensus materials).

Reference materials are not typically used for short-lived radioisotopes, like ^{234}Th. The intercalibration efforts (see Maiti et al., 2012) and the internal consistency steps discussed in question 5 were carried out to understand the natural sample variability and potential lab-to-lab variability. All analyses and quality control checks take the results presented in Maiti et al. into consideration.

7. If you occupied a crossover station, include a plot and a table that show relevant data and their level of agreement, and explain any significant discrepancies (e.g., where discrepancies may reflect differences in the depth of isopycnal surfaces between occupations). If possible, please also include a profile of Temperature & Salinity.

The data in the graphs and tables below are from TN303 station 36 (this cruise 12/16/2013) and RR1815 station 35 (11/16/2018) from the crossover station at ~10.5 °S, 152 °E. We would not necessarily expect that the ^{234}Th activities from these two sampling events would agree, even at a similar location and at the same time of year, due to the nature of short-lived isotopes and their response to local variations in particle dynamics and changes in surface communities. However, the activities from the crossover station agree quite well, especially in the upper 600 m (right panel), where it is of most use for assessing the export of particulate species. The deeper water column values (left panel) are also relatively consistent between the two sampling events, which reflects the major source of ^{234}Th in this part of the ocean, its parent isotope ^{238}U (~conservative behavior).



2013	Depth_M	Th_234_T_CONC_BOTTLE	1SD_Th_234_T_CONC_BOTTLE
	3.5	33.2	1.0
	29.4	32.5	1.0
	45.3	31.9	1.0
	75.1	35.4	1.0
	99.8	36.9	1.0
	130.4	41.1	1.1
	200.2	42.8	2.1
	299.9	41.5	1.1
	450.8	39.3	1.1
	599.6	39.7	1.1
	800.3	38.9	1.1
	1000.9	35.6	1.0
	1249.6	38.4	1.1
	1499.6	36.9	1.1
	1749.6	41.1	1.3
	1999.1	35.8	1.1
	2099.1	39.0	2.0
	2297.6	36.9	1.0
	2399.1	37.6	1.0
	2502.4	38.9	1.1
	2602.4	39.2	2.0
	2702.9	36.6	1.0
	2802.9	38.2	1.0
	3002.4	37.7	1.0
	3499.9	40.2	1.1
	4005.4	38.9	1.1
	4005.4	39.0	1.1
	4733.6	37.4	1.0
	4978.1	38.9	1.1
	5083.6	40.3	1.1

2018	Depth_M	Th_234_T_CONC_BOTTLE	1SD_Th_234_T_CONC_BOTTLE
	3.0	33.8	1.1
	3.0	38.1	1.0
	3.0	39.7	1.0
	20.6	31.4	0.7
	45.7	32.8	0.9
	60.5	28.9	0.8
	80.4	33.1	0.7
	100.7	38.3	0.9
	125.7	40.2	0.7
	151.2	37.3	0.9
	251.1	45.8	0.9
	300.3	38.0	0.9
	400.7	35.7	0.7
	498.9	34.6	0.9
	500.9	37.2	0.9
	598.7	37.6	0.9
	600.8	38.7	0.9
	650.9	38.2	0.9
	750.6	35.8	0.7
	798.3	42.4	1.0
	800.4	39.1	0.9
	898.6	38.4	0.8
	997.9	34.8	0.9
	1000.2	40.8	0.9
	1197.4	37.3	1.0
	1397.0	39.2	1.0
	1402.2	37.1	0.9
	2006.2	36.0	0.8
	2507.2	42.2	0.9
	3256.2	34.9	0.9
	4256.2	35.4	0.9
	5220.3	39.6	0.8
	5304.4	31.8	0.8
	5345.9	36.9	0.9

8. If you did not occupy a crossover station, report replicate analyses from a different laboratory, or if there were no replicate analyses (e.g., due to large volumes or short half-lives), explain how your data compare to historical data including results from nearby stations, even though they may not be true crossover stations.

9. If not already included in your responses to the questions above, please provide a representative vertical profile or report the range of values, for the parameter(s) that are addressed in this intercalibration report.

Total ^{234}Th activities range from 8.5 mBq kg^{-1} to 48.0 mBq kg^{-1}, with the lowest activities being found in the productive surface ocean. Small particle and large particle ^{234}Th activities range from 0.8 mBq kg^{-1} to 26.8 mBq kg^{-1} and from 0.03 mBq kg^{-1} to 6.1 mBq kg^{-1}, respectively.

Once completed, please upload the report here:
https://geotraces-portal.sedoo.fr/pi/

References:

Black, E.E., Buesseler, K.O., Pike, S.M., Lam, P.J., 2018. ^{234}Th as a tracer of particulate export and remineralization in the southeastern tropical Pacific. Mar. Chem. 201, 35–50. https://doi.org/10.1016/j.marchem.2017.06.009

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