GEOTRACES Intercalibration Report

Cruise ID*: HLY1502
Submitting investigator*: Ken Buesseler - Woods Hole Oceanographic Institution - kbuesseler@whoi.edu
Parameters to be intercalibrated*:

- Th_234_T_CONC_SUBICE_PUMP::vakpla mBq/kg
- Th_234_T_CONC_PUMP::t8ngm8 uBq/kg
- Th_234_T_CONC_BOTTLE::uap32e mBq/kg
- Th_234_T_CONC_UWAY::eta8ui mBq/kg
- Th_234_SPT_CONC_PUMP::bxe0xx mBq/kg
- Th_234_LPT_CONC_PUMP::qbhjxe 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 intercalibration efforts are published in Maiti et al., 2012. Fifteen labs participated in two cruises that centered on particulate, total and dissolved ^{234}Th intercalibration. Particulate ^{234}Th intercalibration 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 HLY1502 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 the in situ pumps. However, on occasions where pump-associated Niskins did not close prior to recovery, the ODF Rosette was used to obtain deep water for total ^{234}Th. The following sampling methods used on HLY1502 for total and particulate ^{234}Th followed closely those detailed in Black et al., 2018. Where cruise-specific differences exist, they have been noted here.

Total ^{234}Th (Bottle, Pump, Sub-ice Pump, UW):
Total ^{234}Th samples were taken at 31 of the 66 stations occupied on the HLY1502 campaign. Typically, these samples came from single Niskin bottles attached to a wire (i.e. above the McLane pumps) or Niskins in the standard ODF rosette configuration These totals are listed under 'Th_234_T_CONC_BOTTLE. At shallow shelf and near-slope stations (2, 3, 6, 10, 60, 61, 66), total ^{234}Th samples were taken at only 4 to 12 discrete depths, typically using the ODF rosette. The Pacific endmember Station 1 similarly had a single ODF cast for total ^{234}Th with 12 depths. A single sample was also taken at this location from the ship's underway system (0.5 m). At most of the deeper basin stations (14, 19, 26, 30, 32/34, 38, 43, 46, 48, 52, 56, and 57), the full water column was sampled with either 2 casts (1 ODF and 1 Niskin above pumps, 20 depths total) or 3 casts (1 ODF and 2 Niskin above pumps, 28 depths total).

For better resolution within the marginal ice zone and areas with permanent ice cover, total ^{234}Th samples were taken from the ODF rosette and 'Th_234_T_CONC_PUMP' or 'Th_234_T_CONC_SUBICE_PUMP' samples were taken using the ^{7}Be submersible pumping system. In the marginal ice zone on the northern transect (stations 7, 8, 9, 12, 17), additional samples at 1-2 depths were taken using the submersible pumping system (See the ^{7}Be report by Kadko group for more details). On the southbound transect, marginal ice zone samples came from 4 depths at stations 51, 53, 54 using the ODF rosette. For under-ice samples, a hole was made using a gas-powered ice auger and the submersible pump was lowered into the hole. Samples were taken at three discrete depths at ice stations 31 and 33. Note that the beryllium pump samples were not given GEOTRACES numbers and this field in the datasheet has 'NaN'.

At each discrete depth, ~4 L of water was taken from the corresponding Niskin bottle or pump tubing 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):
Size-fractionated particulate ^{234}Th samples were taken at 20 of the 66 stations occupied using high-volume McLane pumps. The filter heads each contained a 51 µm pore size pre-filter followed by either a Supor filter or a pre-combusted and acid-leached QMA filter with a nominal pore size of 1 µm. Filter heads were pumped down 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 (Ag) 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 402 L and for the area of the QMA subsample was 34 L. These volume averages only include samples flagged as (2) or (3), and not (4) or (9). See data flags in the next question for further information.

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

On-ship and at Woods Hole Oceanographic Institution, 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 for more information.

Data Flags:
The data flags used are as suggested at www.geotraces.org/geotraces-quality-flag-policy/. Most values were flagged as 'probably good' (2), per the suggestion on this website. The (1) flag was not used at all. The missing values (9) flag most commonly resulted from a successful deployment of sampling equipment followed by pump failures (i.e. head not connected to the pump or pumps only functioning for a short period and pumping a low volume) or Niskin failures (i.e. non-closure of bottles with messenger deployment).

Particulate ^{234}Th samples flagged with (9) had such low pumping volumes (e.g. 0.1 L) that a ^{234}Th value was not reportable and in many cases the sample value was indistinguishable from a dipped blank. Particulate samples that had a reportable ^{234}Th value with a pumping volume of ≤20 L were automatically flagged as a bad value (4). Particulate samples that had a reportable ^{234}Th value with a pumping volume between 20 L and 40 L were evaluated on a sample by sample basis as (3) or (4). Probably bad values (3) corresponded to samples that still fit oceanographic trends and were consistent with the values from depths above and below. Bad values were obviously erroneous (i.e. extremely high or low). There were three particulate samples that had pumping volumes >40 L (i.e. 43.6 L, 50.2 L, and 1050 L), but the data was obviously erroneous and flagged as (4). The two deepest particulate samples from Station 43, where it is though the pump(s) hit the ocean floor, were flagged as (3).

Two total ^{234}Th samples that were flagged with (9) indicate that niskin bottles had not tripped and closed (i.e. no water available for sampling). Four samples that had a yield monitor (^{230}Th added in primary processing step) recovery of less than 40% were flagged as (3), because with these lower yields the results are less reliable. However, we note that the flagged (3) total ^{234}Th results looked oceanographically consistent. There was a failure of the autopipette at station 34 during the dispensing of the yield monitor. As a result, the average recovery for the surrounding stations at the same depth range was used for these 8 samples and the recovery uncertainty (usually 5% or less) was increased to 10%. These data were kept as (2) because the results were oceanographically consistent. With the short-lived nature of ^{234}Th, it is often difficult to evaluate whether something is a 'probably bad' value when there is a slight increase or decrease of total ^{234}Th at a single depth, but there is no issue with the sample processing, yield monitor recovery, or replicate analysis. For instance, at station 38 depth ~1668 m there is a rather low value compared to the surrounding water column (14% difference). We have kept these values as (2) because there is no indication besides this difference that suggests this is anything but a good value. The difference is likely real, and we do not expect that the ^{234}Th profiles will look as smooth as the more conservative parent ^{238}U. Those using this data should note that all abnormal deviations from the surrounding data points were meticulously checked for any possible errors/issues from collection through reporting here. There was once instance at station 43 where a surface value was flagged as (3) because it was almost half the value of the surrounding datapoints. Surface values at the ice-covered stations, like this one, were consistently at equilibrium with parent ^{238}U and the lone decrease at 75 m at this station seemed suspect.

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 and Black et al., 2018). An exact 1 mL aliquot of ^{230}Th (50.39 dpm g^{-1}) was used as the yield monitor and added during initial acidification of the samples. QMAs (25 mm) 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 ODF casts and when the messenger was dropped for deep pumping casts.

To determine ^{234}Th activity deficits, ^{238}U (its parent isotope) activities were calculated using a standard uranium-salinity relationship (Owens et al., 2011). Salinities measured on this campaign ranged from 24.4 to 35.1 and calculated ^{238}U activities from 1.60 dpm L^{-1} to 2.44 dpm L^{-1}. While this salinity range is rather large compared to those found on previous GEOTRACES campaigns in the Pacific and Atlantic, Not et al. (2012) showed that the relationship held for sea ice, sea ice brine, and subsurface water samples from the Arctic ranging in salinity from ~0 to 135. 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 400 m off the seafloor that were not near the coastal shelf. For these sample depths (n= 42) the mean derived ^{238}U activity and standard deviation (s.d.) were 2.431 ± 0.002 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 2 g of a ^{229}Th yield monitor (activity of either 68.87 dpm g^{-1} or 76.27 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 reported values was 88.7% and the median recovery was 92%.

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 Woods Hole Oceanographic Institution. 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.

Thirty-three 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, in counts per minute, 0.33 cpm ± 0.05 (s.d.) and after 5 to 6 months the background count average was 0.29 cpm ± 0.04. The on-ship cpm values were within 1 s.d. of the final cpm values, typical 'empty' detector cpm (see below), and cpm for non-dipped blank filters (i.e. unused QMA filters for total and small particle analysis and unused Ag filters for large particle analysis)

There was a minute difference between the Ag filter blanks when first measured on-ship (0.30 cpm ± 0.04) and after 5 to 6 months (0.25 cpm ± 0.03), however, no correction was made to the data. These blank averages fall about the average for empty detectors (i.e. the detectors are run with no samples inside for a period of 24-48 hours). The average and s.d. of the empty detectors just prior to the running of any samples on this campaign were 0.28 cpm ± 0.04, which is indistinguishable from the initial blank filter measurement average. Furthermore, there has been no evidence of significant addition (e.g. sorption) of ^{234}Th to the blank Ag filters on previous GEOTRACES campaigns and a 'blank' value of 0.05 cpm is only 1% of the average (3.7 cpm) and 2% of the median (2.1 cpm) for the sample Ag filters. Only 10

Ag sample filters had cpm less than 0.5 (potential blank adjustment = 10%). Our uncertainties, which are discussed more in the next section, are set at a minimum of 5% even when propagated counting uncertainties are lower. While we don't think the data supports a significant Ag filter blank, a slight increase in the cpm would be within our assumed uncertainties for almost all of the samples.

Limits of detection are not reported because they are not applicable to the ^{234}Th beta counting method and for total ^{234}Th, specifically, there is never an instance where the 4L volume results in a shipboard sample activity that is anywhere close to the limits of the detectors or a 'blank' or unused QMA value. 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 net cpm for total and particulate ^{234}Th samples here was always higher than 0.05 cpm and in almost all cases was well above this value. Only 4 particulate samples had net cpm between 0.06 cpm and 0.2 cpm. See the previous data flag explanation for our sample volume limits (i.e. the pump volume below which the data are likely unreliable and unrepresentative).

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

Five 'low-level' uranium standards, with activities close to those measured for total and particulate samples, and five 'high-level' standards ranging from 238 dpm to 365 dpm were run on the RISØ detectors to confirm correct operation and to determine detector to detector variability. These uranium standards have been used for all GEOTRACES cruises performed by the Buesseler lab. These standards were run at the beginning and end of this cruise, as well as periodically during the cruise when sample demands were lower. Analysis of the lower activity uranium standard data suggested that a minimum 5% detector uncertainty should be used. Since the counting uncertainty for total ^{234}Th samples was always below 5% (square root of the number of counts), the uncertainty on each total ^{234}Th measurement was set at 5%. Some of the particulate ^{234}Th samples with relatively low activities had counting uncertainties above 5% and in these cases the counting uncertainty was used as the final measurement uncertainty.

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. Instances where the replicates were different by more than 10% were individually evaluated (i.e. the raw counting data) and re-counted as needed. The few instances where the 10% difference was noticed occurred where the activities were lowest and the ^{234}Th deficits relative to ^{238}U activities the largest (i.e. over the Arctic shelves). Depths were sometimes occupied twice on different casts at the same station, such as with Station 30 (see crossover evaluation below). The 225 m depth was sampled in this way and the independent replicates (i.e. two separate bottles at two separate times) are well within uncertainties (see blue dots in 3-paneled figure in Question 7). Good agreement and consistency between overlapping depths on subsequent casts at a given station were found.

In addition, to assess 'within bottle' variability and replication, we took 4, 4L samples from a Niskin bottle deployed at 2019 m at station 48. The average value was 38.4 mBq kg^{-1} (2.36 dpm L^{-1}) with a standard deviation of 1.3 (0.08) and RSD of 3.4%. A single salinity sample was taken from this bottle, but we recommend taking 4 in the future for comparison, each one after a 4L sample is taken.

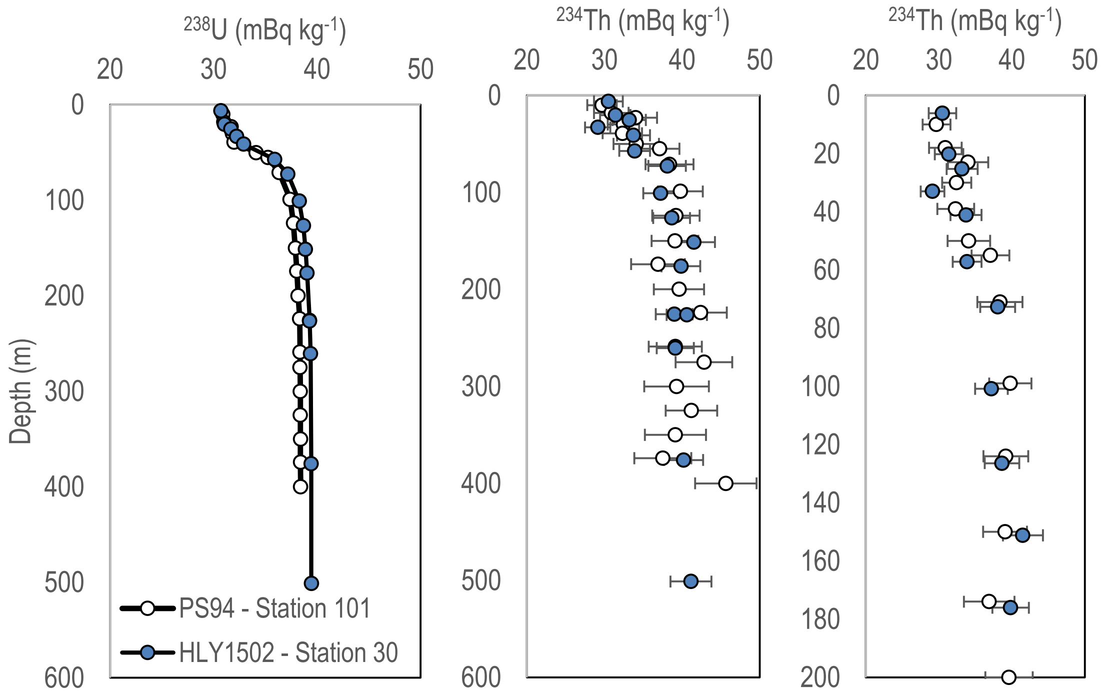
6. Report the external consistency of your data (e.g., results from analyses of certified reference materials and/or consensus materials).

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.

There were 3 Arctic GEOTRACES campaigns in 2015 with intended crossovers between the Canadian-led efforts, the German-lead efforts, and the HLY1502 campaign. The Canadian ship was not able to reach the intended crossover station, however, total ^{234}Th data from the German-U.S. crossover near the North Pole is shown below. It is important to note that we would not necessarily expect that these two sampling efforts to produce data in exact agreement, even though the stations were occupied at the same time of year and in the same general vicinity. Small differences in total ^{234}Th can easily occur due to the nature of short-lived isotopes and their response to local variations in particle dynamics and changes in surface communities.

There is rather good agreement between the PS94 and HLY1502 efforts in the upper 500 m (center panel), with most activities overlapping between the two efforts at similar depths. For determining carbon export in the upper ocean, the total ^{234}Th is most important in the upper 200 m. The right panel shows the striking similarity between the data from the two cruise efforts from 0 to 200 m. The similarity suggests that the two labs were successful in intercalibrating and producing precise measurements. However, the nature of short-lived isotopes results should be kept in mind when assessing crossover intercalibrations. The activity of parent isotope ^{238}U (~conservative behavior with salinity) is shown in the left panel and data tables have been include below.



Total ^{234}Th Data from HLY1502 Station 30:

Depth	^{238}U mBq kg^{-1}	^{234}Th mBq kg^{-1}	Uncertainty
6.1	30.7	30.5	1.9
20.2	31.1	31.4	2.0
25.3	31.7	33.2	2.1
33.0	32.2	29.1	1.6
41.1	32.9	33.7	2.1
57.2	35.9	33.9	2.0
72.7	37.2	38.1	2.4
100.8	38.3	37.2	2.2
126.4	38.7	38.7	2.4
151.2	38.9	41.5	2.7
176.1	39.0	39.9	2.5
225.5	39.3	39.0	2.4
226.2	39.3	40.6	2.6
260.6	39.4	39.1	2.4
375.9	39.4	40.2	2.5
501.2	39.4	41.1	2.6

Total ^{234}Th data from PS94 Station 101:

Depth	^{238}U mBq kg^{-1}	^{234}Th mBq kg^{-1}	Uncertainty
10.0	30.9	29.7	1.9
18.0	31.0	30.9	2.2
23.0	31.7	34.0	2.7
30.0	31.8	32.5	2.0
39.0	32.0	32.3	2.5
50.0	34.1	34.1	2.9
55.0	35.3	37.1	2.6
71.0	36.3	38.4	3.1
99.0	37.4	39.8	2.9
124.0	37.7	39.2	3.1
150.0	37.9	39.1	3.0
174.0	38.0	36.9	3.5
200.0	38.2	39.6	3.2
224.0	38.3	42.4	3.4
259.0	38.3	39.1	3.4
275.0	38.3	42.8	3.6
300.0	38.4	39.3	4.2
325.0	38.4	41.2	3.3
350.0	38.4	39.1	3.9
374.0	38.4	37.5	3.7
400.0	38.4	45.6	3.9

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 5.8 mBq kg^{-1} (station 3) to 45.9 mBq kg^{-1} (station 19), with the lowest activities being found over the productive shelves. Small particle and large particle ^{234}Th activities range from 0.8 mBq kg^{-1} (station 38) to 14.2 mBq kg^{-1} (station 60) and from 0.03 mBq kg^{-1} to 4.5 mBq kg^{-1}, respectively.

Once completed, please upload the report here:

https://geotraces-portal.sedoo.fr/pi/

References:

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