GEOTRACES Intercalibration Report

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

- Th_228_SPT_CONC_PUMP::efscqw uBq/kg
- Th_228_LPT_CONC_PUMP::civqb1 uBq/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 Radium intercalibration efforts (that include measurement of dissolved ^{228}Th and its parent ^{228}Ra) are published in Charette et al., 2012. Fifteen labs inter-calibrated for ^{228}Th, 14 of which used Radium Delayed-Coincidence Counters (RaDeCCs), which were the instruments used to produce the data reported here. This intercalibration used dissolved samples only (filtered through a 1-µm polypropylene cartridge filtration system prior to the use of manganese fibers for Ra and Th collection) and the data here are particulate values. There is no published particulate intercalibration for ^{228}Th, however, the particulate method pioneered by Maiti et al. (2014), uses the same instruments (RaDeCCs) and traditional alpha spectrometry for internal laboratory calibration. We followed the guidance set forth in Maiti et al. (2014) for the particulate measurements reported here. The Charette lab has intercalibrated dissolved radium samples from HLY1502 using instruments from the same RaDeCC counting facility at Woods Hole Oceanographic Institution as were used for the ^{228}Th measurements reported here. More details on this cruise-specific intercalibration can be found in that report.

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 and the other Buesseler intercalibration report for ^{234}Th). Size-fractionated particulate ^{228}Th samples were taken at 20 of the 66 stations occupied using high-volume McLane pumps. These are the samples that were used for ^{234}Th measurements as well. 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 for ^{234}Th. The remainder of the 142 mm filter was sealed with tape and stored for counting months later. The average sample volume through the 51 µm pre-filter was 402 L and for the area of the entire QMA was 871 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.

The basic analytical methodology for small particle ^{228}Th (142 mm QMA filters) has been detailed in Maiti et al. (2014). This method was adapted to measure ^{228}Th on large particle Ag filters (25 mm) by Dr. Black and the members of the Buesseler and Charette labs at Woods Hole Oceanographic Institution. Details of the measurement chamber construction and the calibration of the Radium Delayed Coincidence Counters can be found in the appendices of Black (2017). The RaDeCC is an alpha scintillation counter that distinguishes decay events of short-lived radium daughter products based on their contrasting half-lives. This system was pioneered by Giffin et al. (1963) and adapted for radium measurements by Moore and Arnold (1996). The RaDeCC method was chosen here because it is well suited for sequential measurements that involve ^{228}Th as an intermediate (e.g. ^{234}Th,^{228}Th, particulate carbon), as there is no sample loss or chemical interaction. Large particle samples (Ag filters) were used for ^{234}Th beta counting at-sea and in the lab 5-6 months later. They were then demounted, weighed, and placed into a 25-mm chamber for use with the RaDeCC systems. The 142 mm QMA filters were removed from the petri storage dishes and individually counted in larger chambers made for the RaDeCC systems. All particulate samples were counted for an average of 23 hours. After measurement of the 25 mm Ag filters, masses were recorded again to ensure than any mass loss could be monitored (although no significant mass loss was found).

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). Particulate samples flagged with (9) had such low pumping volumes (e.g. 0.1 L) that a ^{228}Th activity was not reportable and in many cases the sample value was indistinguishable from a dipped blank. Particulate samples that had a reportable ^{228}Th value with a pumping volume of ≤20 L were automatically flagged as a bad value (4). Particulate samples that had a reportable ^{228}Th activity 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 generally fit oceanographic trends, but often the precision and accuracy of these measurements were in question because of the lower volumes. The two deepest particulate samples from Station 43, where it is though the pump(s) hit the ocean floor, were flagged as (3). Below detection limit flags (6) are detailed in the next question.

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

For the small particle QMA filters (142 mm), 34 blanks were assessed and for the large particle Ag filters (25 mm), 30 blanks were assessed. Most of these were dipped blanks collected for each particle size using extra filter heads deployed with the McLane pumps, but without a connection to the pumping systems. A few failed pumping effort filters were also counted and assessed (volume < 2 L). Unlike with the shorter-lived ^{234}Th measurements, which are not generally volume- or activity-limited when counted and which are measured multiple times (subtracting out the influence of the filter itself), ^{228}Th particulate sample counts per minute (cpm) often drop to cpm similar to those from dipped blanks. We therefore assess the 'below detection limit' designation (flag 6) with respect to the cpm of the corrected ^{220}Rn (^{228}Th daughter) RaDeCC measurement for samples and blanks.

Blank QMA counts averaged 0.012 cpm ± 0.007 cpm (1 standard deviation) and blank Ag filter counts averaged 0.009 cpm ± 0.004 cpm. Empty chambers produced similar results (e.g. the 25 mm chambers for Ag filters averaged 0.008 cpm ± 0.005 cpm), suggesting sorption of ^{228}Th was not a significant issue. We have blank-corrected all of the measurements reported here to account for the influence of the blank filter cpm on the (usually) single RaDeCC measurements. If the blank-corrected sample cpm (initial cpm – blank average) was within the blank standard deviation of zero cpm, the sample was flagged as (6), non-detect. The resulting sample activities were reported here to show that a sample measurement was made, however, the results are negative and should not be used. If the blank-corrected sample cpm was more than the blank standard deviation from zero cpm, the sample activity was reported as (2) or (3). The (3) flag designation is explained above.

5. Report how you monitored the internal consistency of your data (e.g.,

through replicate analyses of samples).

Three internal fiber cartridge standards were measured bi-weekly during the time when the large and small particle filters were measured in the counting facility at Woods Hole Oceanographic Institution. The standards were counted on all detectors and used to monitor any potential changes in detector efficiency.

As a part of the calibration process and method development, 8 large particle ^{228}Th samples were measured at least once on every detector. A few of these samples were measured 3-4 times on a single detector over a few months. These 8 samples were then digested and processed with anion exchange columns to prepare them for traditional alpha spectrometry measurements in the Buesseler lab at Woods Hole Oceanographic. The results from the RaDeCC and traditional counting methods were compared and detector-to-detector consistency (replicability) was assessed.

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

Since this is a new method, there no certified reference materials for particulate ^{228}Th. However, details can be found in the Charette dataset for HLY1502 radium analyses on how samples of ^{228}Ra, the parent of ^{228}Th, have been intercalibrated using the same instrumentation (RaDeCCs).

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.

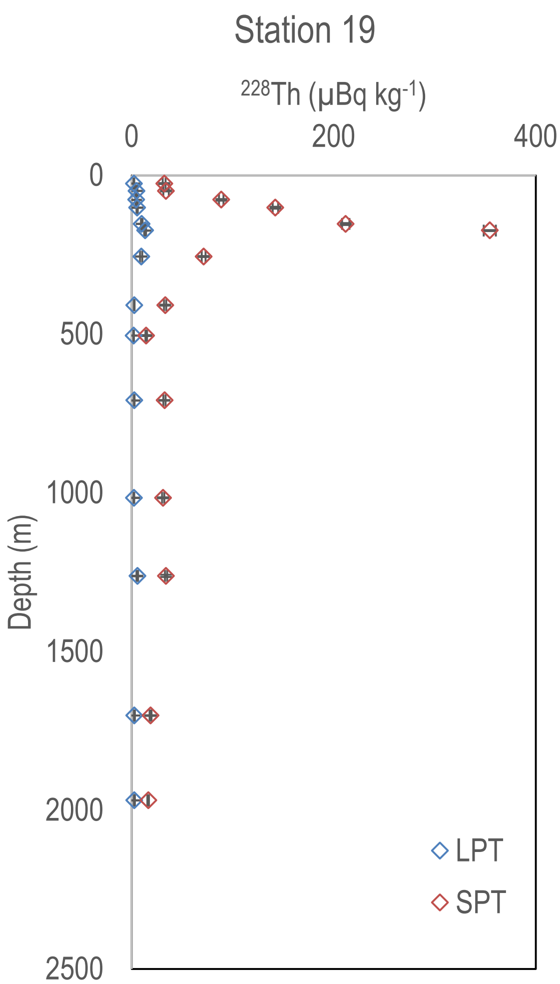
A crossover station was occupied by the PS94 at Station 101 and the HLY1502 at Station 30, however, no labs on the PS94 expedition measured size-fractionated ^{228}Th. However, the size-fractionated particulate data reported here was evaluated within the context of a GEOTRACES pan-Arctic synthesis effort (Rutgers van der Loeff et al., 2018) looking at total and dissolved 228Ra (parent isotope) and ^{228}Th (daughter isotope). The particulate data was determined to be reasonable and consistent with historical measurements of total particulate, dissolved, and total ^{228}Th.

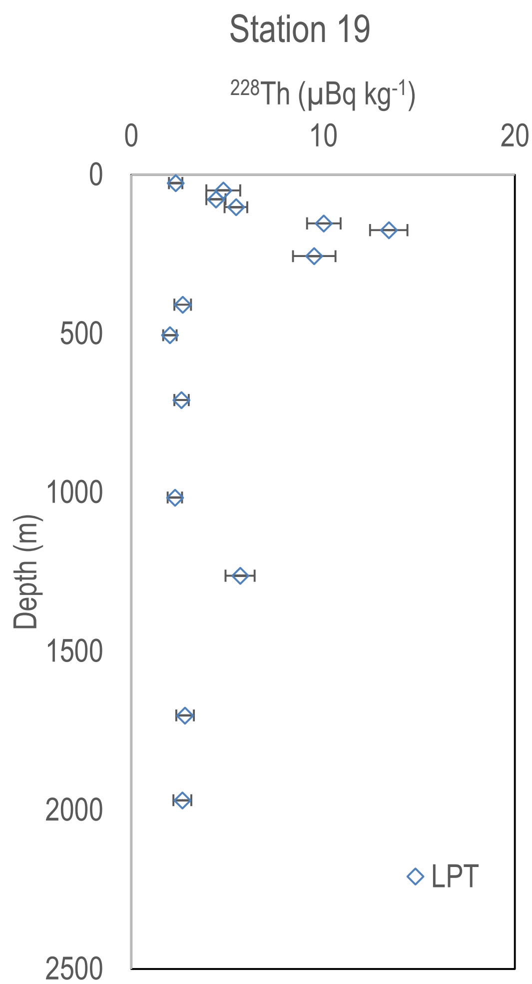
8. If you did not occupy a crossover station, report replicate analyses from a different laboratory, or if there were no replicate analyses (e.g., due to large volumes or short half-lives), explain how your data compare to historical data including results from nearby stations, even though they may not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

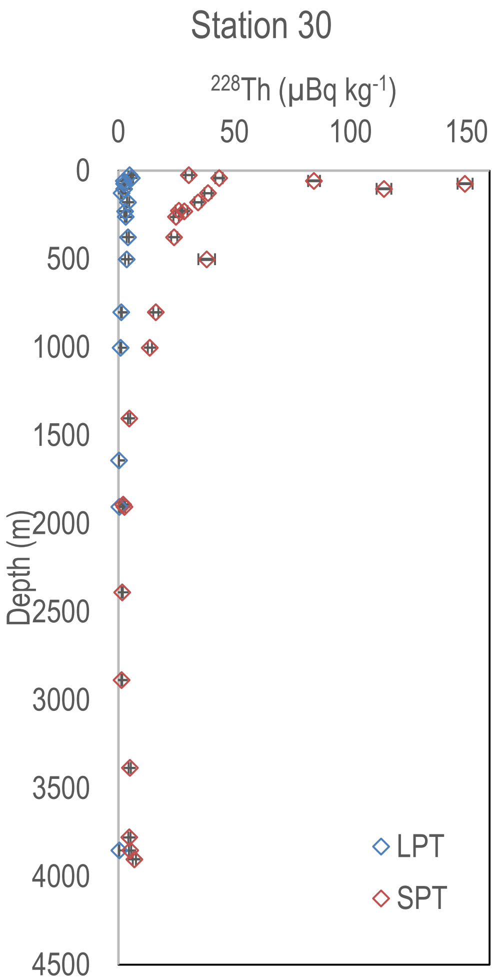
9. If not already included in your responses to the questions above, please provide a representative vertical profile or report the range of values, for the

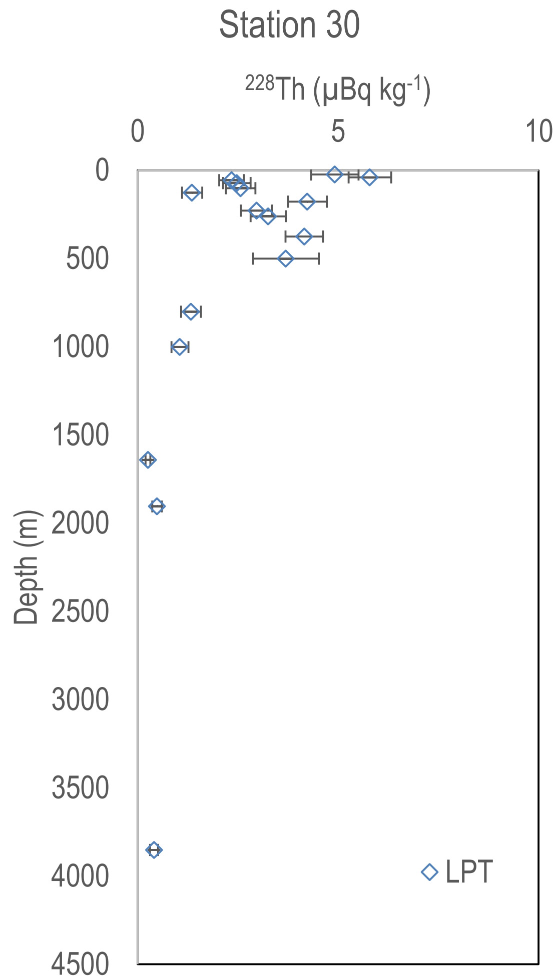
parameter(s) that are addressed in this intercalibration report.

See the representative graphs below for stations 19 and 30. The small particle (SPT) ^{228}Th activities ranged from 1.1 to 461 μBq kg^{-1} and the large particle (LPT) ^{228}Th activities ranged from 0.3 to 20.6 μBq kg^{-1}.









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

References:

Black, E.E., 2017. An investigation of basin-scale controls on upper ocean export and remineralization. MIT-WHOI Joint Program in Oceanography.

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Maiti, K., Charette, M.A., Buesseler, K.O., Zhou, K., Henderso, P., Moore, W.S., Morris, P., Kipp, L., 2014. Determination of particulate and dissolved ^{228}Th in seawater using a delayed coincidence counter. Mar. Chem. 177, 196–202. https://doi.org/10.1016/j.marchem.2014.12.001

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