

## GEOTRACES Intercalibration Document Dissolved Pb

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Cruise: HLY1502

### Sampling

The US GEOTRACES carousel was used to collect water samples during HLY1502. Samples were filtered through pre-cleaned, 0.2  $\mu\text{m}$  Pall Acropak Supor filter capsules as described in Cutter et al., 2012. Surface water samples were collected at stations where either ice concentration allowed for an ice station or when there was sufficient open water for the USCGC Healy's small boat to be deployed. In both cases the same pumping system was used to collect the surface water samples. From the small boat the procedure was as follows: Half inch Teflon-lined Tygon tubing was attached to the end of a fiberglass pole such that the tubing extended approximately 3-4 inches beyond the end of the pole. The tubing was filled with Milli-Q water prior to deployment as was attached to a low-density polypropylene magnetically driven centrifugal pump (VWR PN EW-72010-10). A cooler equipped with a sealed battery and 1200 W inverter was modified such that the tubing entered and exited through predrilled holes and the power to the pump could be turned on or off without opening the cooler. Samples were pumped through a 0.2  $\mu\text{m}$  Pall Acropak Supor filter capsules. At each small boat station, at a minimum of approximately 1 km from the ship, the pole would be deployed from the starboard bow while proceeding into the current. At least 5 gallons of water was passed through the tubing and filter prior to rinsing the large carboys used to collect the samples. The 25-liter carboys were rinsed a minimum of three times before being filled and transported back to the ship for subsampling. Subsampling was performed by either the super techs or if unavailable, other experienced personnel. Sampling from the ice was done using the same pumping system-filtration-carboy combination. The on-ice surface samples were collected by first drilling a hole in the ice at the beginning of each ice station using a standard auger 12 inch. Ice was removed from the hole using pre-cleaned low-density polyethylene scoops. A tent (ice fishing, pop-up) was then erected over the hole. The hole was allowed to 'flush' while snow and sea ice samples were collected, usually a minimum of 1.5 to 2 hours. The tubing was lowered to a depth of ~1 meter below the bottom of the ice and the entire pumping system was flushed with ~5-10 gallons of seawater. To prevent pumped rinse water from returning to the sea, 5-gallon plastic buckets were filled in the tent and transported by others outside for disposal. Once rinsed and

filled the carboys were returned to the ship rapidly to prevent freezing and were subsampled by experienced personnel.

### Analytical Methodology

All samples for Pb and Pb isotopes were sent to the Boyle lab at MIT. Samples were acidified with quadruple distilled 6N hydrochloric acid made in the Boyle lab. Rember travelled to MIT to subsample the large volume samples collected for Pb isotope analysis. The subsamples were transferred to 60 ml low density polyethylene Nalgene bottles (3x rinse) that had been cleaned following the procedures detailed in the Sampling and Sample-handling Protocols for GEOTRACES Cruises 'cookbook'. Dissolved Pb was measured at the University of Alaska, Fairbanks using an ThermoFinnigan Element 2 Inductively Coupled Plasma Mass Spectrometer coupled (ICP-MS) to an Elemental Scientific SeaFAST S2 (syringe based system). The online method was similar to that described in Lagerstrom et al., 2013 with the exception that isotope dilution was used to quantify the concentration of dissolved Pb in the sample. Aliquots (15 ml) of sample were spiked with 100  $\mu$ l of  $^{204}\text{Pb}$ -enriched solution ( $\sim 750$  pM) in a 15 ml Teflon test tube, sealed and gently mixed for a minimum of 1 minute before being placed in the autosampler. The ICP-MS was operated in low resolution mode and  $^{202}\text{Hg}$ ,  $^{204}\text{Pb}$  and  $^{208}\text{Pb}$  were determined. The volumes of samples and spikes were assessed using calibrated pipettes. Each 15 ml aliquot was sufficient for two measurements. The reproducibility error within the same test tube was  $<1\%$  and the variability between the same sample measured in two separate test tubes was  $<1.5\%$ . The dissolved Pb blank at UAF was  $\sim 0.52$  pM (spiked Milli-Q water) with a detection limit of  $\sim 0.12$  pM. Repeated runs of US GEOTRACES reference materials (S1, D2, GS) and in-house reference materials suggests a precision of  $<2\%$ .

### Intercalibration:

There were several efforts made to intercalibrate the US Arctic GEOTRACES Pb data. An intercalibration for these low levels of dissolved Pb had not been done prior to these efforts. Table 1 lists intercalibration data for reference waters compiled for water available at the UAF and MIT labs. The UAF lab measured all dissolved Pb samples from the US Arctic GEOTRACES HLY1502 expedition. The MIT lab ran three profiles for intercalibration purposes (Figure 1) as their role was to measure all of the Pb isotope ratios for the cruise. An intercalibration was also conducted with the Jessica Fitzsimmons at TAMU who measured dissolved Pb as an 'extra' measurement from her seaFAST system (Figure 2). In addition, there was an international calibration done with the crossover station data where the US GEOTRACES carousel and Canadian sampling systems were used to collect a set of samples for distribution between the various labs as an actual crossover location was not possible. Not all labs received all samples but the three US labs were able to intercalibrate with a Canadian lab on a set of samples. The participating labs were UAF (Rember), MIT (Boyle), UBC (Orians) and UVic (Jay Cullen).

Table 1. Dissolved Pb intercalibration data for reference waters, in pmol/kg-sw.

SAMPLE	UAF	MIT	CONSENSUS
GS	28.3±0.5	-	28.6±1.0
GSC	38.2±0.7	38.9±1.2	-
S1	48.9±1.3	-	48.0±2.2
D2	28.1±0.5	-	27.7±1.5

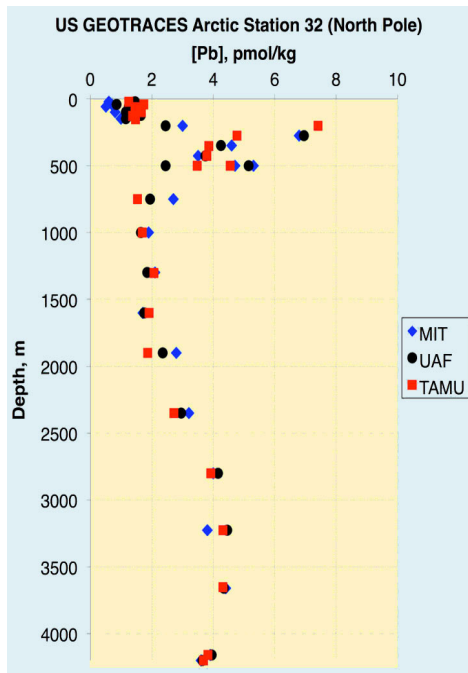


Figure 1. Intercalibration data from the North Pole station (32) determined by the MIT, UAF and TAMU laboratories.

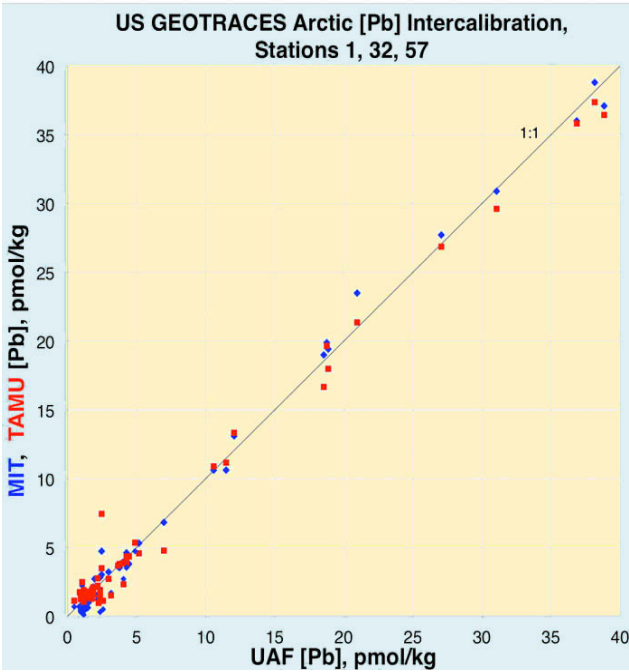


Figure 2. Intercalibration of all three stations measured by the MIT, TAMU and UAF laboratories.

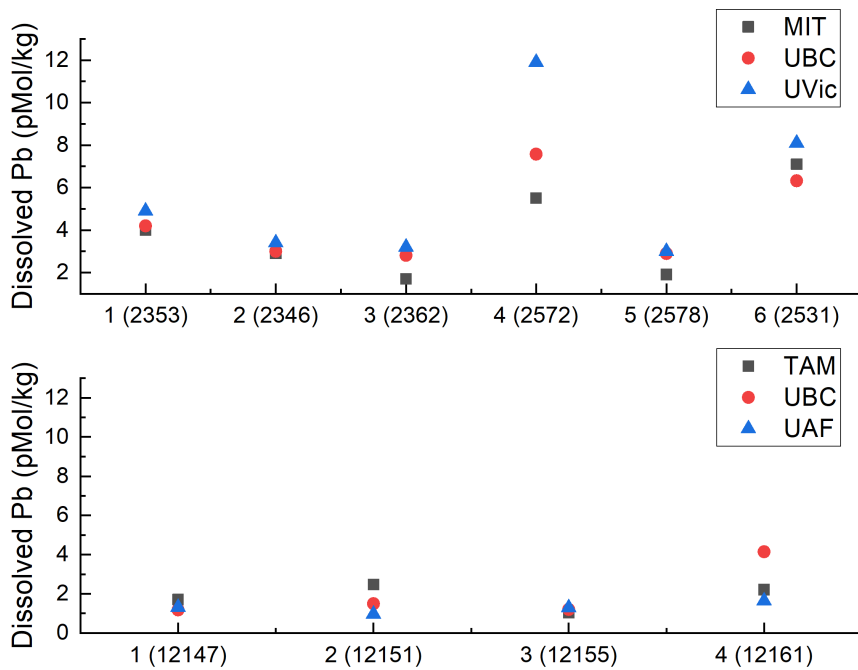


Figure 3. Intercalibration data from the samples collected by the US and Canadian sampling systems and measured by the participating laboratories.