# Concentration of Dissolved Pb (Pb passing through a 0.2um Acropak capsule filter) from the US GEOTRACES Arctic Expedition (GN01, HLY1502) from August to October 2015

**Website**: https://www.bco-dmo.org/dataset/764309
**Data Type**: Cruise Results
**Version**: 1
**Version Date**: 2020-11-16

## Project
» U.S. Arctic GEOTRACES Study (GN01) (U.S. GEOTRACES Arctic)
» Collaborative Research: GEOTRACES Arctic section: Spatial variability of lead concentrations and isotopic compositions in the western Arctic basins (GEOTRACES Arctic Pb)

## Program
» U.S. GEOTRACES (U.S. GEOTRACES)

| Contributors | Affiliation | Role |
|---|---|---|
| Boyle, Edward A. | Massachusetts Institute of Technology (MIT) | Principal Investigator, Contact |
| Zurbrick, Cheryl | Massachusetts Institute of Technology (MIT) | Co-Principal Investigator |
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## Abstract
Concentration of Dissolved Pb (Pb passing through a 0.2um Acropak capsule filter) from the US GEOTRACES Arctic Expedition (GN01, HLY1502) from August to October 2015.

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# Coverage

**Spatial Extent**: **N**:89.995 **E**:32.5438 **S**:60.165 **W**:-179.1349
**Temporal Extent**: 2015-08-12 - 2015-10-03

## Methods & Sampling

For the purpose of intercalibration with the UAF and TAMU labs, we analyzed samples for Pb concentrations from three stations (1, 32 and 57) from this cruise.

Sample storage bottle lids and threads were soaked overnight in 2N reagent grade HCl, then filled with 1N reagent grade HCl to be heated in an oven at 60°C overnight, inverted, heated for a second day, and rinsed 5X with pure distilled water. The bottles were then filled with trace metal clean dilute HCl (~0.01N HCl) and again heated in the oven for one day on either end. Clean sample bottles were emptied, and double-bagged prior to rinsing and filling with sample.

Trace metal-clean seawater samples were collected using the U.S. GEOTRACES sampling system consisting of 24 Teflon-coated GO-FLO bottles that had been pre-rinsed with a 24+ hour treatment of filtered surface seawater at the beginning of the cruise (see Cutter and Bruland, 2012 for more information on the sampling system). At each station, the bottles were deployed open and tripped on ascent at 3 m/min. On deck, the bottles were kept in a trace metal clean sampling van over-pressurized with HEPA-filtered air, except immediately prior to and following deployments, in which cases they were covered on both ends with shower caps to avoid deck contamination.

Samples were analyzed at least 5 months after acidification over 6 analytical sessions by a resin pre-concentration method. This method utilized a modification of the batch isotope-dilution ICP-MS method described in Lee et al. 2011. The modification consists of replacing the NTA Superflow® resin by pre-concentration onto Nobias Chelate PA1 resin (Sohrin et al., 2008). After elution from the resin, $^{204}Pb$ and $^{208}Pb$ are analyzed on a Fisons PQ2+ using a 400uL/min nebulizer. Briefly, samples were poured into 30mL subsample bottles. Then, triplicate 1.5mL polypropylene vials (Nalgene) were rinsed three times with the 30mL subsample. Each sample was pipetted (1.3mL) from the 30mL subsample to the 1.5mL vial. Pipettes were calibrated daily to the desired volume. 25 µl of a $^{204}Pb$ spike were added to each sample, and the pH was raised to ~4.3 using a trace metal clean ammonium acetate buffer, prepared at a pH of between 7.95 and 7.98. ~0.16mg of cleaned Nobias Chelate PA1 beads were added to the mixture, and the vials were placed on a shaker table for 3 days to allow the sample to equilibrate with the resin. After equilibration, the beads were centrifuged and washed 3 times with pure distilled water, using a trace metal clean siphon tip to remove the water wash from the sample vial following centrifugation. After the last wash, 350 µl of a 0.1M solution of trace metal clean $HNO_3$ was added to the resin to elute the metals, and the samples were set to shake on a shaker for 1 – 2 days prior to analysis by ICP-MS.

Nobias Chelate PA1 resin was cleaned with 2 methanol rinses, distilled water rinse followed by leaching with ultrapure 6M HCl for 12-24 hours. This procedure was repeated twice, followed by two one-day leaches with ultrapure 3M $HNO_3$ on a shaker table. The resin was then rinsed six times with distilled water to remove the nitric acid. It was then leached twice with ultrapure 0.1M $HNO_3$ for one day each. The final 0.1N rinse was checked for Pb blank by ICPMS and the resin only used if the blank was acceptably low. The cleaned resin was stored in pure distilled water to prevent resin degradation. If more than 3 days passed between initial cleaning and use, it was re-cleaned for 12 hours with 0.1M $HNO_3$ and then rinsed with pure distilled water until the pH was >4.5 just prior to use.

Nalgene polypropylene (PPCO) vials were cleaned by heated submersion for 2 days at 60°C in 1M reagent grade HCl, followed by a bulk rinse and 4X individual rinse of each vial with pure distilled water. Each vial was then filled with trace metal clean dilute HCl (~0.01M HCl) and heated in the oven at 60°C for one day on either end. Vials were kept filled until just before usage.

On each day of sample analysis, procedure blanks were determined. Replicates (12) of 300µL of an in-house standard reference material seawater (low Pb surface water) were used, where the amount of Pb in the 300µL has been verified as negligible. The procedural blank over the relevant sessions for resin preconcentration method ranged from 2.0 – 6.7pmol/kg, averaging 3.7 ± 1.8 pmol/kg. Within a day, procedure blanks were very reproducible with an average standard deviation of 0.8 pmol/kg, resulting in detection limits (3x this standard deviation) of 2.4pmol/kg. Fifteen replicate analyses of two different large-volume seawater samples (one with ~11pmol/kg, another with ~24pmol/kg, and a third with ~39pmol/kg) indicated that the precision of the analysis is 3% or 1.3 pmol/kg , whichever is larger.

Triplicate analyses of an international reference standards SAFe D2: 26.6 ± 1.7 pmol/kg (consensus value 27.7 ± 1.5) and SAFe S: 46.3 ± 1.9 pmol/kg (consensus value 48.0 ± 2.2). This standard run was linked into our own long-term quality control standards that are run on every analytical day to maintain long-term consistency.

For the most part, the reported numbers are simply as calculated from the isotope dilution equation on the day of the analysis. For one analytical day, however, quality control samples indicated offsets in the blank used to correct the samples, so for this day the blank was estimated as that giving the best agreement of the quality control samples.

The internal U.S. intercalibration between MIT, UAF, and TAMU was good with analyses scattering about a 1:1 line by ± 2 pmol/kg. However, it should be noted that Pb concentrations within the Arctic are as low as 1 pmol/kg, so there is a relatively large relative uncertainty at the lowest concentrations.

There was an external intercalibration on 6 samples from Canadian-collected samples from GN03 with MIT, UBC and UVic data, with comparable agreement as the internal intercalibration just noted. However, comparison of samples independently collected by the U.S. and Canadian groups (along different sections of

the western Arctic) showed some significant differences which may point to spatiotemporal variability.

The MIT Pb measurements were performed by Cheryl Zurbrick.

**Data Processing Description**

Samples were analyzed in triplicate and average values shown in this database were only accepted if reproduced over at least two replicates; otherwise, the data was re-analyzed until a reproducible value was reached.

The standard Ocean Data View flags were used. (Reference all flags at https://www.bodc.ac.uk/data/codes_and_formats/odv_format/):

1: Good Value: Good quality data value that is not part of any identified malfunction and has been verified as consistent with real phenomena during the quality control process.

2: Probably Good Value: Data value that is probably consistent with real phenomena but this is unconfirmed or data value forming part of a malfunction that is considered too small to affect the overall quality of the data object of which it is a part. [Used when only one replicate confirmed the reported value.]

3: Probably Bad Value: Data value recognized as unusual during quality control that forms part of a feature that is probably inconsistent with real phenomena.

4: Bad Value: An obviously erroneous data value.

9: Missing Value: The data value is missing. Any accompanying value will be a "magic number" representing absent data. [All samples collected at the three stations were analyzed].

In this data set, we did not encounter any samples that did not yield acceptably reproducible results upon repeated analysis, so we believe that the data truly represents the concentration of Pb in the sample collection bottle. However, there were a few points that were high based on adjacent samples and for which an obvious hydrographic argument could not be made for the anomaly. These samples may be contaminated, and they are given the quality control flag of 3 (probably bad value).

**BCO-DMO Processing:**
- modified parameter names (removed units; changed "Diss_Pb" to "Pb_D_CONC_BOTTLE");
- formatted time as HHMM;
- reversed lat and lon labels (columns mislabeled);
- added ISO8601 date/time format;
- 2020-11-16: replaced with GEOTRACES DOoR-formatted data.
- 2021-12-29: removed embargo on dataset.

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# Data Files

| File |
|------|
| **Pb_Dissolved.csv**(Comma Separated Values (.csv), 8.83 KB)<br>MD5:d59ae77600b76f9639f60d6cc8ac3208 |
| Primary data file for dataset ID 764309 |

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# Related Publications

Cutter, G. A., & Bruland, K. W. (2012). Rapid and noncontaminating sampling system for trace elements in global ocean surveys. Limnology and Oceanography: Methods, 10(6), 425–436. doi:10.4319/lom.2012.10.425 *Methods*

Lee, J.-M., Boyle, E. A., Echegoyen-Sanz, Y., Fitzsimmons, J. N., Zhang, R., & Kayser, R. A. (2011). Analysis of trace metals (Cu, Cd, Pb, and Fe) in seawater using single batch nitrilotriacetate resin extraction and isotope dilution inductively coupled plasma mass spectrometry. Analytica Chimica Acta, 686(1-2), 93–101. doi:10.1016/j.aca.2010.11.052
*Methods*

Planquette, H., & Sherrell, R. M. (2012). Sampling for particulate trace element determination using water sampling bottles: methodology and comparison to in situ pumps. Limnology and Oceanography: Methods, 10(5), 367–388. doi:10.4319/lom.2012.10.367
*General*

Sohrin, Y., Urushihara, S., Nakatsuka, S., Kono, T., Higo, E., Minami, T., … Umetani, S. (2008). Multielemental Determination of GEOTRACES Key Trace Metals in Seawater by ICPMS after Preconcentration Using an Ethylenediaminetriacetic Acid Chelating Resin. Analytical Chemistry, 80(16), 6267–6273. doi:10.1021/ac800500f
*Methods*

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## Parameters

| Parameter | Description | Units |
|---|---|---|
| cruise | Cruise identifier | unitless |
| EXPOCODE | Cruise EXPOCODE | unitless |
| SECT_ID | GEOTRACES cruise identifier | unitless |
| GEOTRC_SAMPNO | GEOTRACES sample number | unitless |
| GEOTRC_EVENTNO | Event number | unitless |
| station | Station number | unitless |
| CTDPRS | CTD pressure | decibars |
| Depth | Sample depth | meters |
| Pb_D_CONC_BOTTLE_vnin6z | Concentration of Pb passing through a 0.2um Acropak capsule filter | picomoles per kilogram (pmol/kg) |
| Flag_Pb_D_CONC_BOTTLE__vnin6z | Quality flag for Pb_D_CONC_BOTTLE_vnin6z | unitless |
| N_Pb_D_CONC_BOTTLE_vnin6z | Number of replicate samples for Pb_D_CONC_BOTTLE_vnin6z | unitless |

| | | |
|---|---|---|
| SD_Pb_D_CONC_BOTTLE_vnin6z | Standard deviation of Pb_D_CONC_BOTTLE_vnin6z | picomoles per kilogram (pmol/kg) |
| Pb_D_CONC_BOAT_PUMP_yyaotn | Concentration of Pb passing through a 0.2um Acropak capsule filter | picomoles per kilogram (pmol/kg) |
| Flag_Pb_D_CONC_BOTTLE_yyaotn | Quality flag for Pb_D_CONC_BOAT_PUMP_yyaotn | unitless |
| N_Pb_D_CONC_BOAT_PUMP_yyaotn | Number of replicate samples for Pb_D_CONC_BOAT_PUMP_yyaotn | unitless |
| SD_Pb_D_CONC_BOAT_PUMP_yyaotn | Standard deviation of Pb_D_CONC_BOAT_PUMP_yyaotn | picomoles per kilogram (pmol/kg) |
| CASTNO | Cast number | unitless |
| SAMPNO | Sequential sample number within a cast | unitless |
| BTLNBR | Bottle number | unitless |
| BTLNBR_FLAG_W | Bottle quality flag | unitless |
| Date | Sampling date; format: YYYY-MM-DD | unitless |
| Time | Sampling time; format: hhmm | unitless |
| LATITUDE | Latitude; positive values = North | decimal degrees |
| LONGITUDE | Longitude; positive values = East | decimal degrees |
| BOTTOMDEPTH | Bottom depth of cast | meters |
| ISO_DateTime_UTC | Date and time of sampling (UTC) formatted to ISO8601 standard: YYYY-MM-DDThh:mmZ | unitless |

## Instruments

| Dataset-specific Instrument Name | Teflon-coated GO-FLO bottles |
|---|---|
| Generic Instrument Name | GO-FLO Teflon Trace Metal Bottle |
| Dataset-specific Description | Trace metal-clean seawater samples were collected using the U.S. GEOTRACES sampling system consisting of 24 Teflon-coated GO-FLO bottles that had been pre-rinsed with a 24+ hour treatment of filtered surface seawater at the beginning of the cruise. |
| Generic Instrument Description | GO-FLO Teflon-lined Trace Metal free sampling bottles are used for collecting water samples for trace metal, nutrient and pigment analysis. The GO-FLO sampling bottle is designed specifically to avoid sample contamination at the surface, internal spring contamination, loss of sample on deck (internal seals), and exchange of water from different depths. |

| Dataset-specific Instrument Name | Fisons PQ2+ |
|---|---|
| Generic Instrument Name | Inductively Coupled Plasma Mass Spectrometer |
| Dataset-specific Description | After elution from the resin, $^{204}$Pb and $^{208}$Pb are analyzed on a Fisons PQ2+ using a 400uL/min nebulizer. |
| Generic Instrument Description | An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer. |

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## Deployments

### HLY1502

| Website | https://www.bco-dmo.org/deployment/638807 |
|---|---|
| Platform | USCGC Healy |
| Report | https://datadocs.bco-dmo.org/docs/302/geotraces/GEOTRACES_ARCTIC/data_docs/cruise_reports/healy1502.pdf |
| Start Date | 2015-08-09 |
| End Date | 2015-10-12 |
| Description | Arctic transect encompassing Bering and Chukchi Shelves and the Canadian, Makarov and Amundsen sub-basins of the Arctic Ocean. The transect started in the Bering Sea (60°N) and traveled northward across the Bering Shelf, through the Bering Strait and across the Chukchi shelf, then traversing along 170-180°W across the Alpha-Mendeleev and Lomonosov Ridges to the North Pole (Amundsen basin, 90°N), and then back southward along ~150°W to terminate on the Chukchi Shelf (72°N). Additional cruise information is available in the GO-SHIP Cruise Report (PDF) and from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/HLY1502 |

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## Project Information

**U.S. Arctic GEOTRACES Study (GN01) (U.S. GEOTRACES Arctic)**

**Website**: https://www.geotraces.org/

**Coverage**: Arctic Ocean; Sailing from Dutch Harbor to Dutch Harbor (GN01)

*Description from NSF award abstract:*
In pursuit of its goal "to identify processes and quantify fluxes that control the distributions of key trace elements and isotopes in the ocean, and to establish the sensitivity of these distributions to changing environmental conditions", in 2015 the International GEOTRACES Program will embark on several years of research in the Arctic Ocean. In a region where climate warming and general environmental change are occurring at amazing speed, research such as this is important for understanding the current state of Arctic Ocean geochemistry and for developing predictive capability as the regional ecosystem continues to warm and influence global oceanic and climatic conditions. The three investigators funded on this award, will manage a large team of U.S.scientists who will compete through the regular NSF proposal process to contribute their own unique expertise in marine trace metal, isotopic, and carbon cycle geochemistry to the U.S. effort. The three managers will be responsible for arranging and overseeing at-sea technical services such as hydrographic measurements, nutrient analyses, and around-the-clock management of on-deck sampling activites upon which all participants depend, and for organizing all pre- and post-cruise technical support and scientific meetings. The management team will also lead educational outreach activities for the general public in Nome and Barrow, Alaska, to explain the significance of the study to these communities and to learn from residents' insights on observed changes in the marine system. The project itself will provide for the support and training of a number of pre-doctoral students and post-doctoral researchers. Inasmuch as the Arctic Ocean is an epicenter of global climate change, findings of this study are expected to advance present capability to forecast changes in regional and globlal ecosystem and climate system functioning.

As the United States' contribution to the International GEOTRACES Arctic Ocean initiative, this project will be part of an ongoing multi-national effort to further scientific knowledge about trace elements and isotopes in the world ocean. This U.S. expedition will focus on the western Arctic Ocean in the boreal summer of 2015. The scientific team will consist of the management team funded through this award plus a team of scientists from U.S. academic institutions who will have successfully competed for and received NSF funds for specific science projects in time to participate in the final stages of cruise planning. The cruise track segments will include the Bering Strait, Chukchi shelf, and the deep Canada Basin. Several stations will be designated as so-called super stations for intense study of atmospheric aerosols, sea ice, and sediment chemistry as well as water-column processes. In total, the set of coordinated international expeditions will involve the deployment of ice-capable research ships from 6 nations (US, Canada, Germany, Sweden, UK, and Russia) across different parts of the Arctic Ocean, and application of state-of-the-art methods to unravel the complex dynamics of trace metals and isotopes that are important as oceanographic and biogeochemical tracers in the sea.

**Collaborative Research: GEOTRACES Arctic section: Spatial variability of lead concentrations and isotopic compositions in the western Arctic basins (GEOTRACES Arctic Pb)**

**Coverage**: Arctic

*NSF Award Abstract:*
In this project, investigators participating in the 2015 U.S. GEOTRACES Arctic expedition will measure lead concentrations and isotopic compositions in seawater, snow, and aerosol samples collected in the western Arctic Ocean. In common with other national initiatives in the International GEOTRACES Program, the goals of the U.S. Arctic expedition are to identify processes and quantify fluxes that control the distributions of key trace elements and isotopes in the ocean, and to establish the sensitivity of these distributions to changing environmental conditions. Some trace elements are essential to life, others are known biological toxins, and still others are important because they can be used as tracers of a variety of physical, chemical, and biological processes in the sea. Lead is an important substance to measure because it is a toxic trace element, ranked 2nd in the US Agency for Toxic Substances Disease Registry, and can be utilized as a tracer of ocean processes. The study will provide for the training and support of graduate and postdoctoral researchers.

Lead (Pb) is emitted into the atmosphere by high temperature industrial activities and leaded gasoline

consumption and is globally dispersed by the atmosphere. High concentrations of Pb have been observed in Arctic ice cores and aerosols, and there are significant concerns about Pb, mercury, and other toxic trace elements in Arctic ecosystems. However, there remain significant questions about how these toxic trace elements and their isotopes currently exist in the Arctic, as well as how they will change in the future Arctic as a result of retreating summer sea ice and extensive drilling, mining, and industrialization. This proposal is aimed at remedying this deficiency in scientific knowledge by measuring Pb and Pb isotopes from seawater profiles, sea ice/seawater interface, snow and aerosols that will be collected during the U.S. GEOTRACES western Arctic transect. Specifically, researchers will gain knowledge on 1) the penetration of anthropogenic lead into the Arctic Ocean, 2) the primary sources of lead to surface waters, 3) the distributions of lead and their relation to scavenging processes and rates, 4) how the exchange with sinking particles contributes to lead?s distribution, and 5) ocean circulation in the Arctic using lead as a tracer. Results from the study will have important implications for human health by increasing understanding of the distribution and abundance of a toxic trace element.

## Program Information

### U.S. GEOTRACES (U.S. GEOTRACES)

**Website**: http://www.geotraces.org/

**Coverage**: Global

**GEOTRACES** is a SCOR sponsored program; and funding for program infrastructure development is provided by the U.S. National Science Foundation.

GEOTRACES gained momentum following a special symposium, S02: Biogeochemical cycling of trace elements and isotopes in the ocean and applications to constrain contemporary marine processes (GEOSECS II), at a 2003 Goldschmidt meeting convened in Japan. The GEOSECS II acronym referred to the Geochemical Ocean Section Studies To determine full water column distributions of selected trace elements and isotopes, including their concentration, chemical speciation, and physical form, along a sufficient number of sections in each ocean basin to establish the principal relationships between these distributions and with more traditional hydrographic parameters;

* To evaluate the sources, sinks, and internal cycling of these species and thereby characterize more completely the physical, chemical and biological processes regulating their distributions, and the sensitivity of these processes to global change; and

* To understand the processes that control the concentrations of geochemical species used for proxies of the past environment, both in the water column and in the substrates that reflect the water column.

GEOTRACES will be global in scope, consisting of ocean sections complemented by regional process studies. Sections and process studies will combine fieldwork, laboratory experiments and modelling. Beyond realizing the scientific objectives identified above, a natural outcome of this work will be to build a community of marine scientists who understand the processes regulating trace element cycles sufficiently well to exploit this knowledge reliably in future interdisciplinary studies.

Expand "Projects" below for information about and data resulting from individual US GEOTRACES research projects.

## Funding

| Funding Source | Award |
|---|---|
| NSF Division of Ocean Sciences (NSF OCE) | OCE-1459287 |