

Dissolved lead data collected from the R/V Pourquoi pas (GEOVIDE) in the North Atlantic, Labrador Sea (section GA01) during 2014

Website: <https://www.bco-dmo.org/dataset/651880>

Data Type: Cruise Results

Version: 1

Version Date: 2017-10-03

Project

» [Filling Gaps in the Atlantic and Pacific Pb and Pb Isotope Spatial and Temporal Evolution \(GA01\)](#)
(GEOVIDE_Pb)

Program

» [U.S. GEOTRACES](#) (U.S. GEOTRACES)

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Abstract

Dissolved lead data collected from the R/V Pourquoi pas (GEOVIDE) in the North Atlantic, Labrador Sea (section GA01) during 2014

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Coverage

Spatial Extent: N:59.79927 E:-10.036 S:40.33325 W:-51.09588

Temporal Extent: 2014 - 2014

Dataset Description

These data describe dissolved lead passing through a 0.2um filter (SARTOBRAN 300, Sartorius) or a 0.45um filter (Pall Gelman Supor, polystersulfone) and analyzed by ICP-MS.

Methods & Sampling

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 degrees Celsius 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.

As stated in the cruise report, trace metal clean seawater samples were collected using the French GEOTRACES clean rosette (General Oceanics Inc. Model 1018 Intelligent Rosette), equipped with twenty-two new 12L GO-FLO bottles (two bottles were leaking and were never deployed during the cruise). The 22 new GO-FLO bottles were initially cleaned in LEMAR laboratory following the GEOTRACES procedures (Cutter and Bruland, 2012). The rosette was deployed on a 6mm Kevlar cable with a dedicated custom designed clean winch. Immediately after recovery, GO-FLO bottles were individually covered at each end with plastic bags to minimize contamination. They were then transferred into a clean container (class-100) for sampling. On each trace metal cast, nutrient and/or salinity samples were taken to check potential leakage of the Go-Flo bottles. Prior to filtration, GO-FLO bottles were mixed manually three times. GO-FLO bottles were pressurized to less than 8 psi with 0.2-um filtered N₂ (Air Liquide). For Stations 1, 11, 15, 17, 19, 21, 25, 26, 29, 32 GO-FLO spigots were fitted with an acid-cleaned piece of Bev-a-Line tubing that fed into a 0.2 um capsule filters (SARTOBRAN 300, Sartorius). For all other stations (13, 34, 36, 38, 40, 42, 44, 49, 60, 64, 68, 69, 71, 77) seawater was filtered directly through paired filters (Pall Gelman Supor 0.45um polystersulfone, and Millipore mixed ester cellulose MF 5 um) mounted in Swinnex polypropylene filter holders, following the Planquette and Sherrell (2012) method. Filters were cleaned following the protocol described in Planquette and Sherrell (2012) and kept in acid-cleaned 1L LDPE bottles (Nalgene) filled with ultrapure water (Milli-Q, 18.2 megaohm/cm) until use. Subsamples were taken into acid-cleaned (see above) Nalgene HDPE bottles after a triple rinse with the sample. All samples were acidified back in the Boyle laboratory at 2mL per liter seawater (pH 2) with trace metal clean 6N HCl.

On this cruise, only the particulate samples were assigned GEOTRACES numbers. In this dataset, the dissolved Pb samples collected at the same depth (sometimes on a different cast) as the particulate samples have been assigned identifiers as "SAMPNO" which corresponds to the particulate GEOTRACES number. In cases where there were no corresponding particulate samples, a number was generated as "PI_SAMPNO".

Upon examining the data, we observed that the sample taken from rosette position 1 (usually the near-bottom sample) was always higher in [Pb] than the sample taken immediately above that, and that the excess decreased as the cruise proceeded. The Pb isotope ratio of these samples were higher than the comparison bottles as well. A similar situation was seen for the sample taken from rosette positions 5, 20 and 21 when compared to the depth-interpolated [Pb] from the samples immediately above and below. Also, at two stations where our near-bottom sample was taken from rosette position 2, there was no [Pb] excess over the samples immediately above. We believe that this evidence points to sampler-induced contamination that was being slowly washed out during the cruise, but never completely. So we have flagged all of these analyses with a "3" indicating that we do not believe that these samples should be trusted as reflecting the true ocean [Pb].

In addition, we observed high [Pb] in the samples at Station 1 and very scattered Pb isotope ratios. The majority of these concentrations were far in excess of those values observed at nearby Station 11, and also the nearby USGT10-01. Discussion among other cruise participants revealed similarly anomalous data for other trace metals (e.g., Hg species). After discussion at the 2016 GEOVIDE Workshop, we came to the conclusion that this is* evidence of GoFlo bottles not having sufficient time to "clean up" prior to use, and that most or all bottles from Station 1 were contaminated. We flagged all Station 1 data with a "3" indicating that we do not believe these values reflect the true ocean [Pb].

Samples were analyzed at least 1 month after acidification over 36 analytical sessions by a resin pre-concentration method. This method utilized the isotope-dilution ICP-MS method described in Lee *et al.* 2011, which includes pre-concentration on nitrilotriacetate (NTA) resin and analysis 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 ul of a 204Pb spike were added to each sample, and the pH was raised to 5.3 using a trace metal clean ammonium acetate buffer, prepared at a pH of between 7.95 and 7.98. 2400 beads of NTA Superflow resin (Qiagen Inc., Valencia, CA) were added to the mixture, and the vials were set to shake on a shaker for 3 - 6 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, 350ul of a 0.1N solution of trace metal clean HNO₃ 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.

NTA Superflow resin was cleaned by batch rinsing with 0.1N trace metal clean HCl for a few hours, followed by

multiple washes until the pH of the solution was above 4. Resin was stored at 4 degrees Celsius in the dark until use, though it was allowed to equilibrate to room temperature prior to the addition to the sample.

Nalgene polypropylene (PPCO) vials were cleaned by heated submersion for 2 days at 60 degrees Celsius in 1N 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 (0.01N HCl) and heated in the oven at 60 degrees Celsius 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 300uL of an in-house standard reference material seawater (low Pb surface water) were used, where the amount of Pb in the 300uL was verified as negligible. The procedural blank over the relevant sessions for resin preconcentration method ranged from 2.2 – 9.9pmol/kg, averaging 4.6 +/- 1.7pmol/kg. Within a day, procedure blanks were very reproducible with an average standard deviation of 0.7pmol/kg, resulting in detection limits (3x this standard deviation) of 2.1pmol/kg. Replicate analyses of three different large-volume seawater samples (one with 11pmol/kg, another with 24pmol/kg, and a third with 38pmol/kg) indicated that the precision of the analysis is 4% or 1.6pmol/kg, whichever is larger.

Triplicate analyses of an international reference standard gave SAFe D2: 27.2 +/- 1.7 pmol/kg. However, 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 some analytical days, however, quality control samples indicated offsets in the blank used to correct the samples. For the upper 5 depths of Station 29, all depths of Station 40, and the deepest 2 depths of Station 42, the quality control samples indicated our blank was overcorrecting by 3.4pM, and we applied a -3.4pM correction to our Pb concentrations for that day. For the deepest 11 depths of Station 34, the quality control samples indicated our blank was overcorrecting by 10.2pM (due to contamination of the low trace metal seawater stock), and we applied a -10.2 pM correction to our Pb concentrations for that day. With these corrections, the overall internal comparability of the Pb collection should be better than 4%.

The errors associated with these Pb concentration measurements are on average 3.2% of the concentration (0.1 – 4.4pmol/kg). Although there was a formal crossover station (1) that overlaps with USGT10-01 (GA-03), sample quality on the first station of GEOVIDE appears problematical making the comparison unhelpful. However, GEOVIDE station 11 (40.33 degrees North, 12.22 degrees West) is not too far from USGT10-01 (38.325 degrees North, 9.66 degrees West) and makes for a reasonable comparison. It should also be noted that the MIT lab has intercalibrated Pb with other labs on the 2008 IC1 cruise, on the 2011 USGT11 (GA-03) cruise, and on the EPZT (GP-16) cruises, and maintains in-lab quality control standards for long-term data quality evaluation.

Ten percent of the samples were analyzed by Rick Kayser and the remaining ninety percent of the samples were analyzed by Cheryl Zurbrick. There was no significant difference between them for the lowest concentration large-volume seawater reference sample (RK averaged 11.0 +/- 1.6 pmol/kg; CZ averaged 11.6 +/- 1.6 pmol/kg).

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.

6: Value Below Detection Limit: The level of the measured phenomenon was too small to be quantified by the technique employed to measure it. The accompanying value is the detection limit for the technique or zero if that value is unknown.

9: Missing Value: The data value is missing. Any accompanying value will be a magic number representing absent data. [All samples collected were analyzed. Any missing data was not collected.]

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 Notes:

- Column names changed to conform with GEOTRACES conventions
- Originally, data were submitted without GEOTRACES sample numbers. After requesting them from PI, sample numbers were submitted, but they were not GEOTRACES issued. A few of these sample numbers were missing, and so an arbitrary sample number was issued by the PI.
- Two columns were created to accommodate the sample numbers sent by the PI. One was SAMPNO (those not created by PI) and PI_SAMPNO (those created by the PI) in order to distinguish between the two numbers more easily.
- nd was added to blank fields in SAMPNO and PI_SAMPNO

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Data Files

File
dissolved_Pb.csv (Comma Separated Values (.csv), 35.08 KB) MD5:40a96886d858ed5cc24c482d9b54baf6 Primary data file for dataset ID 651880

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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](https://doi.org/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](https://doi.org/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](https://doi.org/10.4319/lom.2012.10.367)
Methods

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Parameters

Parameter	Description	Units
cruise_id	Cruise identification	unitless
SECT_ID	Cruise section identifier	unitless
CASTNO	Cast number	unitless
STNNBR	Station number	unitless
BTLNBR	Bottle number; typically 1-24	unitless
CTDPRS	CTD pressure	decibars
SAMPNO	Sequential sample number within the cast (usually corresponds to the bottle number)	unitless
PI_SAMPNO	PI issued sample number for when a standard SAMPNO was not appropriate.	unitless
Pb_D_CONC_BOTTLE	Pb passing through a 0.2um SARTOBRAN or 0.45 um Supor filter; Sample size was quantified volumetrically at room temperature, then converted to weight units assuming a density of 1.027 g/cc.	picomoles per kilogram
Pb_D_CONC_BOTTLE_SD	Standard deviation of Pb_D_BOTTLE	picomoles per kilogram
NBR_OF_SAMPLES	Number of samples collected	unitless
Pb_D_CONC_BOTTLE_FLAG	Quality flag for parameter Pb_D_CONC_BOTTLE; follows the convention: 1 = good; 3 = questionable; 4 = bad	unitless
BTL_DATE	Date (yyyymmdd) when the bottle was fired according to the bottle file.	unitless
BTL_LAT	Latitude of bottle firing; north is positive.	decimal degrees
BTL_LON	Longitude of bottle firing; east is positive.	decimal degrees

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Instruments

Dataset-specific Instrument Name	12L GO-FLO
Generic Instrument Name	Bottle
Dataset-specific Description	The General Oceanics Inc Model 1018 Intelligent Rosette was equipped with 22 new 12L GO-FLO bottles.
Generic Instrument Description	A container, typically made of glass or plastic and with a narrow neck, used for storing drinks or other liquids.

Dataset-specific Instrument Name	ICP-MS
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Dataset-specific Description	Inductively Coupled Plasma Mass Spectrometer
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

GEOVIDE

Website	https://www.bco-dmo.org/deployment/651998
Platform	R/V Pourquoi pas
Start Date	2014-05-19
End Date	2014-06-25
Description	This is a French GEOTRACES cruise.

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Project Information

Filling Gaps in the Atlantic and Pacific Pb and Pb Isotope Spatial and Temporal Evolution (GA01) (GEOVIDE_Pb)

Website: <http://www.geovide.obs-vlfr.fr/>

Coverage: Subpolar North Atlantic; Labrador Sea; Greenland

Lead is a trace metal that has historically been emitted into the atmosphere through human activities such as coal burning and the use of leaded gasoline followed by deposition into the ocean. Once introduced into the marine environment, lead is dispersed via currents and removed by biota and other sinking particles. This century-scale growth of lead emissions followed by a decline upon the phase-out of leaded gasoline is one of the great global geochemical experiments. In this study, researchers at the Massachusetts Institute of Technology will analyze archived seawater samples to improve our knowledge on the spatial and temporal

variability of lead concentrations and lead isotope ratios. This data will yield new insights into the sources and transport of lead and other metals, document the time-evolving human footprint on the ocean, and assist with validating models.

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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, SO2: 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.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1357224

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