# Mercury and methylmercury concentrations in aerosols from the US GEOTRACES Arctic cruise (HLY1502, GN01) from August to October 2015

Website: https://www.bco-dmo.org/dataset/779211 Data Type: Cruise Results Version: 1 Version Date: 2021-01-25

#### Project

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

» <u>Collaborative Research: GEOTRACES Arctic Section: Determination of atmospheric wet and dry deposition</u> and air-sea exchange of mercury species from coastal and offshore waters (GEOTRACES Arctic Atmos Hg)

#### Program

» U.S. GEOTRACES (U.S. GEOTRACES)

Contributors	Affiliation	Role
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#### Abstract

The data include measurements of mercury and methylmercury concentrations in aerosols from the GEOTRACES Arctic Ocean cruise in 2015 (HLY1502, GN01).

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# Coverage

**Spatial Extent**: N:89.9447 **E**:176.6365 **S**:56.0743 **W**:-176.7522 **Temporal Extent**: 2015-08-10 - 2019-09-29

# **Dataset Description**

The data include measurements of mercury and methylmercury concentrations in aerosols from the GEOTRACES Arctic Ocean cruise in 2015 (HLY1502, GN01).

# Methods & Sampling

**Methodology:** Details of the methods for the cruise are given in DiMento et al. (2019). Details of the overall method and approach for dissolved gaseous mercury and atmospheric mercury methods are given in Andersson et al. (2008), Mason et al. (2017), Soerensen et al. (2014), and Soerensen et al. (2013). Analytical

methods are detailed in DiMento et al. (2019) with additional information in the papers listed above and in Munson et al. (2014), Morton et al. (2013), and Gichuki & Mason (2014). See "Related Publications" below for complete citations.

**Sampling Procedures:** Fourteen bulk aerosol deployments were made over periods of three to five days using high-volume aerosol samplers following methods in Morton et al. (2013). During each deployment, aerosol samples were collected in triplicate on pre-combusted glass-fiber (GFF) or quartz fiber (QMA) filters. Unused filters were set aside for blank analysis. Sampling duration lasted an average of 31.0 h (11.0 to 80.0 h) with an average volume filtered of 172.5 m3 (60.6 to 451.9 m3). Aerosol filters were stored in acid cleaned polystyrene petri dishes. All samples were kept frozen at -20 degrees C in the dark, and were transported back to the University of Connecticut for analysis.

Methylmercury concentrations were determined following the ascorbic acid-assisted direct ethylation method (Munson et al., 2014) using a Tekran 2700 instrument and autosampler to automate the purging, trapping, and detection via cold vapor atomic fluorescence spectroscopy (CVAFS). Samples were thawed then acidified to 1% (v/v) H2SO4 and left to digest overnight before neutralizing with 8N potassium hydroxide (KOH), buffering with 4M acetate, adding 2.5% (w/v) ascorbic acid and finally 1% (w/v) sodium tetraethyl borate (NaTEB) to ethylate the methylmercury. Total mercury concentrations were determined by dual gold-amalgamation CVAFS utilizing a Tekran 2600 instrument in accordance with U.S. EPA Method 1631. Briefly, waters were digested with bromine monochloride (BrCl) followed by a pre-reduction step with hydroxylamine hydrochloride (NH<sub>2</sub>OH·HCl). Inorganic Hg(II) was then reduced to Hg<sup>0</sup> using stannous chloride (SnCl<sub>2</sub>) prior to automated analysis on the Tekran.

Aerosol filters were digested in acid-cleaned 15-mL centrifuge tubes with 10 mL of 4.57 M trace metal grade HNO3, placed in a covered 60 degrees C water bath for 12 hours (Hammerschmidt and Fitzgerald, 2006). A subsample of this digest was taken for CH3Hg analysis, and the remainder was further digested with BrCl overnight at room temperature.

# **Data Processing Description**

**QA/QC:** Measurements of elemental mercury in surface seawater and in the atmosphere relied on the use of a Tekran air measurement instrument, which has a built-in calibration unit (Hg<sup>o</sup> permeation tube) for calibration, which was done daily. External injections of Hg<sup>o</sup> were also used to check the accuracy of the permeation device. The instruments had a detection limit of <0.2 ng m<sup>-3</sup> for air sampling and <2 fM for water sampling during the cruise (water concentration calculated from the measured value in the equilibrated air). The detection limit for the equilibrator is evaluated based on the sparging of water without water flow. As the DGHg is removed by sparging and not replenished without flow, long-term sparging results in values that reflect the background blank and the variability in this value is used to estimate the detection limit. For the air sampling, the instrument periodically flushes the system with Hg-free air and makes blank measurements. Again, these values and their variability can be used to determine the detection limit for air sampling. Prior studies have compared concentrations measured using the continuous sampler to those with manual methods and verified consistency over a range of seawater temperatures (Andersson et al., 2008; Soerensen et al., 2014). Our data was also compared with measurements by the Hammerschmidt and Lamborg research group made on board for both underway samples and for samples collected from the Go-Flo bottles. Results were comparable.

Performance of the continuous sampler was also verified in the laboratory prior to the cruise by injection and recovery of external standards. Data presented in the table represent the average hourly value for each set of measurements, which were made at 10 minute resolution, and which are only presented for when the ship was underway, and not for times when the ship was on station. Typical variability was 3% and 10% for 1 hr of observations in air and water, respectively; n = 6 for 10-min samples (per hour).

#### **BCO-DMO Processing:**

- modified parameter names to conform with BCO-DMO and GEOTRACES naming conventions;
- split the Sampling\_Dates column into Date\_Start and Date\_End (yyyy-mm-dd);
- filled blanks with "nd" (no data);
- 2021-01-25: renamed fields with the GEOTRACES DOoR barcodes.

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File	
Hg_Aerosol.csv(Comma Separated Values (.csv), 1.94 KB) MD5:339881ea4e0657c7ddf4d2cf895107a5	
Primary data file for dataset ID 779211	

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# **Related Publications**

Andersson, M. E., Gårdfeldt, K., & Wängberg, I. (2008). A description of an automatic continuous equilibrium system for the measurement of dissolved gaseous mercury. Analytical and Bioanalytical Chemistry, 391(6), 2277–2282. doi:<u>10.1007/s00216-008-2127-4</u> *Methods* 

DiMento, B. P., Mason, R. P., Brooks, S., & Moore, C. (2019). The impact of sea ice on the air-sea exchange of mercury in the Arctic Ocean. Deep Sea Research Part I: Oceanographic Research Papers, 144, 28–38. doi:<u>10.1016/j.dsr.2018.12.001</u> *Methods* 

Gichuki, S. W., & Mason, R. P. (2014). Wet and dry deposition of mercury in Bermuda. Atmospheric Environment, 87, 249–257. doi:<u>10.1016/j.atmosenv.2014.01.025</u> *Methods* 

Hammerschmidt, C. R., & Fitzgerald, W. F. (2006). Bioaccumulation and Trophic Transfer of Methylmercury in Long Island Sound. Archives of Environmental Contamination and Toxicology, 51(3), 416–424. doi:<u>10.1007/s00244-005-0265-7</u> *Methods* 

Mason, R. P., Hammerschmidt, C. R., Lamborg, C. H., Bowman, K. L., Swarr, G. J., & Shelley, R. U. (2017). The air-sea exchange of mercury in the low latitude Pacific and Atlantic Oceans. Deep Sea Research Part I: Oceanographic Research Papers, 122, 17–28. doi:<u>10.1016/j.dsr.2017.01.015</u> *Methods* 

Morton, P. L., Landing, W. M., Hsu, S.-C., Milne, A., Aguilar-Islas, A. M., Baker, A. R., ... Zamora, L. M. (2013). Methods for the sampling and analysis of marine aerosols: results from the 2008 GEOTRACES aerosol intercalibration experiment. Limnology and Oceanography: Methods, 11(2), 62–78. doi:<u>10.4319/lom.2013.11.62</u> *Methods* 

Munson, K. M., Babi, D., & Lamborg, C. H. (2014). Determination of monomethylmercury from seawater with ascorbic acid-assisted direct ethylation. Limnology and Oceanography: Methods, 12(1), 1–9. doi:<u>10.4319/lom.2014.12.1</u> *Methods* 

Soerensen, A. L., Mason, R. P., Balcom, P. H., & Sunderland, E. M. (2013). Drivers of Surface Ocean Mercury Concentrations and Air-Sea Exchange in the West Atlantic Ocean. Environmental Science & Technology, 47(14), 7757–7765. doi:<u>10.1021/es401354q</u> *General* 

Soerensen, A. L., Mason, R. P., Balcom, P. H., Jacob, D. J., Zhang, Y., Kuss, J., & Sunderland, E. M. (2014). Elemental Mercury Concentrations and Fluxes in the Tropical Atmosphere and Ocean. Environmental Science & Technology, 48(19), 11312–11319. doi:<u>10.1021/es503109p</u> *Methods* 

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# Parameters

Parameter	Description	Units
Deployment	Aerosol sampler deployment number	unitless
EVENT_ID	GEOTRACES event number	unitless
SAMPLE_ID	GEOTRACES sample number	unitless
Lat_average	Average latitude during deployment	decimal degrees
Hg_Me_A_T_CONC_HIVOL_6xqvwk	High volume sampler/aerosol methylmercury. Values are the average of duplicate filter analyses.	femtomoles per cubic meter (fmol/m3)
Hg_A_T_CONC_HIVOL_o2llrs	high volume sampler/aerosol total mercury. Values are the average of triplicate filter analyses.	femtomoles per cubic meter (fmol/m3)
SD1_Hg_A_T_CONC_HIVOL_o2llrs	Standard deviation of Hg_A_T_CONC_HIVOL	femtomoles per cubic meter (fmol/m3)
Start_Latitude	Latitude at start of deployment; positive values = North	decimal degrees
Start_Longitude	Longitude at start of deployment; positive values = East	decimal degrees
End_Latitude	Latitude at end of deployment; positive values = North	decimal degrees
End_Longitude	Longitude at end of deployment; positive values = East	decimal degrees
Sampling_Dates	Sampling date range (GMT); format: mm/dd-mm/dd	unitless
Date_Start	Start date of deployment (GMT); format: yyyy-mm- dd	unitless
Date_End	End date of deployment (GMT); format: yyyy-mm- dd	unitless
Sample_Group	Sample Group (A or B)	unitless
Run_Time	Run time	hours
Air_Volume	Volume of air sampled	cubic meters (m3)

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# Instruments

Dataset-specific Instrument Name	high-volume aerosol samplers	
Generic Instrument Name	Aerosol Sampler	
Generic Instrument Description	A device that collects a sample of aerosol (dry particles or liquid droplets) from the atmosphere.	
Dataset-specific Instrument Name	Tekran 2600; Tekran 2700	
Generic Instrument Name	Automated Mercury Analysis System	
Dataset-specific Description	ekran 2600 automated sampler for total mercury and Tekran 2700 automated sampler for methylmercury	
Generic Instrument Description	xamples include Tekran Models 2600 and 2700	

Dataset- specific Instrument Name	Tekran 2537B mercury analyzer
Generic Instrument Name	Cold Vapor Atomic Fluorescence Spectrophotometer
Description	A Cold Vapor Atomic Fluorescent Spectrophotometer (CVAFS) is an instrument used for quantitative determination of volatile heavy metals, such as mercury. CVAFS make use of the characteristic of mercury that allows vapor measurement at room temperature. Mercury atoms in an inert carrier gas are excited by a collimated UV light source at a particular wavelength. As the atoms return to their non-excited state they re-radiate their absorbed energy at the same wavelength. The fluorescence may be detected using a photomultiplier tube or UV photodiode.

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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 global 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: Determination of atmospheric wet and dry deposition and air-sea exchange of mercury species from coastal and offshore waters (GEOTRACES Arctic Atmos Hg)

#### NSF Award Abstract:

In this project, a group of investigators participating in the 2015 U.S. GEOTRACES Arctic expedition will measure concentrations of atmospherically-derived mercury in the Arctic Ocean. In common with other multinational 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. Mercury, primarily as methylmercury, is an element that substantially bioaccumulates through aquatic food webs and impacts neurological functions in humans and wildlife, and it is therefore critical to understand the inputs of mercury to the region. Educational activities as part of this study include training and mentoring of undergraduate and graduate students and a postdoctoral researcher. Researchers will also conduct public outreach activities about mercury impacts to local Arctic communities.

In the Arctic Ocean, subsistence local fishermen and several species of Arctic wildlife, such as beluga whales, seals and polar bears, commonly have elevated levels of methylmercury in their system. Atmospheric deposition is the major pathway of mercury input to the marine environment as both wet and dry (aerosol and gaseous ionic mercury) deposition. Therefore, measurements of mercury and a better understanding of its cycling in the Arctic Ocean are critical. This study will provide further understanding of the drivers of mercury speciation in air and surface waters, including snow/ice, melt ponds, and surface seawater and how these concentrations, and other physical and biological factors, impact deposition rates at the air-sea interface. The primary measurements to be made include a baseline of mercury measurements over the open water from the ship, and over sea-ice environments of the Arctic Ocean, which will be compared to simultaneous and historic coastal measurements, as well as model studies. Overall, results will provide the crucial data and information necessary to comprehend the role of human activity and climate change in exacerbating or ameliorating the exposure of humans and wildlife to methylmercury in the Arctic Ocean.

# **Program Information**

**U.S. GEOTRACES (U.S. GEOTRACES)** 

Website: <u>http://www.geotraces.org/</u>

Coverage: Global

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

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.

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# Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-1434998</u>

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