# Mercury speciation across the US GEOTRACES North Atlantic Zonal Section from R/V Knorr KN199-04, KN204-01 in the subtropical North Atlantic Ocean from 2010-2011 (U.S. GEOTRACES NAT project)

Website: https://www.bco-dmo.org/dataset/3860

Version: 2

**Version Date**: 2017-04-11

**Project** 

» U.S. GEOTRACES North Atlantic Transect (GA03) (U.S. GEOTRACES NAT)

#### **Program**

» <u>U.S. GEOTRACES</u> (U.S. GEOTRACES)

Contributors	Affiliation	Role
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## Coverage

**Spatial Extent**: N:39.7 E:-9.6601 S:17.3502 W:-69.8

**Temporal Extent**: 2010-10-16 - 2011-12-09

## **Dataset Description**

This dataset includes concentrations of filtered total mercury, elemental mercury, monomethylmercury and dimethylmercury from 11 demi stations (surface to 1000 meters) and 21 full stations (surface to bottom water) across the cruise path.

GT10 depths match GTC bottles. G11 depths are nominal.

## Methods & Sampling

Detailed method descriptions can be found in Hammerschmidt et al. (2011), Lamborg et al. (2012),

Hammerschmidt & Bowman (2012)

Sample collection: Cutter & Bruland, 2012

Sample bottles/cleaning: Hammerschmidt et al., 2012

HgT analysis:

Fitzgerald & Gill (1979), Bloom & Fitzgerald (1988) Tekran Model 2500 CVAFS Mercury Detector

Detection limit: 0.02 pM for a 200-mL sample

Procedural duplicates: 4.8 ± 4.4 relative percent difference

Recovery of known additions:  $99 \pm 5\%$  recovery of Hg2+ addition

Reference material: Recovery of total Hg from BCR-579 =  $10.3 \pm 0.6$  pM (certified range =  $9.5 \pm 2.5$  pM) Hg0 analysis:

Fitzgerald & Gill (1979), Bloom & Fitzgerald (1988)

Tekran Model 2500 CVAFS Detector Detection limit: 0.01 pM for a 2-L sample

Procedural duplicates:  $9.5 \pm 5.8$  relative percent difference

Recovery of known additions: not conducted

MMHq analysis:

Bowman & Hammerschmidt (2011), Tseng et al. (2004), Bloom (1989)

Tekran Model 2500 CVAFS Mercury Detector

Detection limit: 2 - 30 fM (2-L samples)

Procedural duplicates:  $13 \pm 13$  relative percent difference (n = 14)

Recovery of known additions:  $105 \pm 6\%$  recovery of CH3Hg+ addition (n = 3)

DMHg analysis:

Bowman & Hammerschmidt (2011), Tseng et al. (2004)

Tekran Model 2500 CVAFS Mercury Detector

Detection limit: 2 fM (2-L samples)

Procedural duplicates:  $16 \pm 18$  relative percent difference (n = 16)

## **Data Processing Description**

"It DL" indicates that a sample was below the method detection limit

Sample volumes were used to calculate picomolar or femtomolar concentrations of different mercury species.

BCO-DMO added ISO DateTime UTC from the original date and time field provided by PI.

#### Related files and references:

Bloom, N. 1989. Determination of picogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas-chromatography with cold vapor atomic fluorescence detection. Can. J. Fish. Aquat. Sci. 46, 1131-1140.

Bloom, N.S., Fitzgerald, W.F. 1988. Determination of volatile mercury species at the picogram level by low-temperature gas chromatography with cold-vapor atomic fluorescence detection. Anal. Chim Acta 208, 151-161.

Bowman, K.L., Hammerschmidt, C.R. 2011. Extraction of monomethylmercury from seawater for low-femtomolar determination. Limnol. Oceanogr.: Methods 9, 121-128.

Cutter, G.A., Bruland, K.W. 2012. Rapid and noncontaminating sampling system for trace elements in global ocean surveys. Limnol. Oceanogr.: Methods 10, 425-436.

Fitzgerald, W.F., Gill, G.A. 1979. Subnanogram determination of mercury by two-stage gold amalgamation applied to atmospheric analysis. Anal. Chem. 51, 1714-1720.

Hammerschmidt, C.R., Bowman, K.L. 2012. Vertical methylmercury distribution in the subtropical North Pacific Ocean. Mar. Chem. 132, 77-82.

Hammerschmidt, C.R., Bowman, K.L., Tabatchnick, M.D., Lamborg, C.H. 2011. Storage bottle material and cleaning for determination of total mercury in seawater. Limnol. Oceanogr.: Methods 9, 426-431.

Lamborg, C.H., Hammerschmidt, C.R., Gill, G.A., Mason, R.P., Gichuki, S. 2012. An intercomparison of procedures for the determination of total mercury in seawater and recommendations regarding mercury speciation during GEOTRACES cruises. Limnol. Oceanogr.: Methods, 10, 90-100.

Tseng, C.-M., Hammerschmidt, C.R., Fitzgerald, W.F. 2004. Determination of methylmercury in environmental matrixes by on-line flow injection and atomic fluorescence spectrometry. Anal. Chem. 76, 7131-7136.

#### Additional GEOTRACES Processing:

Version 2017-04-11 replaced version 2013-03-05.

Data version 2013-03-05 was revised with corrected sample\_GEOTRC and station\_GEOTRC values for duplicates of 6963 and 6971:

Changed sample\_GEOTRC 6971 to 6871; station\_GEOTRC 11 to 10

Changed sample GEOTRC 6963 to 6991; station GEOTRC 10 to 11

After the data were submitted to the International Data Management Office, BODC, the office noticed that important identifying information was missing in many datasets. With the agreement of BODC and the US GEOTRACES lead PIs, BCO-DMO added standard US GEOTRACES information, such as the US GEOTRACES event number, to each submitted dataset lacking this information. To accomplish this, BCO-DMO compiled a 'master' dataset composed of the following parameters: station\_GEOTRC, cast\_GEOTRC (bottle and pump data only), event\_GEOTRC, sample\_GEOTRC, sample\_bottle\_GEOTRC (bottle data only), bottle\_GEOTRC (bottle data only), depth\_GEOTRC\_CTD (bottle data only), BTL\_ISO\_DateTime\_UTC (bottle data only), and GeoFish\_id (GeoFish data only). This added information will facilitate subsequent analysis and inter comparison of the datasets.

Bottle parameters in the master file were taken from the GT-C\_Bottle\_GT10, GT-C\_Bottle\_GT11, ODF\_Bottle\_GT10, and ODF\_Bottle\_GT11 datasets. Non-bottle parameters, including those from GeoFish tows, Aerosol sampling, and McLane Pumps, were taken from the Event\_Log\_GT10 and Event\_Log\_GT11 datasets. McLane pump cast numbers missing in event logs were taken from the Particulate Th-234 dataset submitted by Ken Buesseler.

A standardized BCO-DMO method (called "join") was then used to merge the missing parameters to each US GEOTRACES dataset, most often by matching on sample\_GEOTRC or on some unique combination of other parameters.

If the master parameters were included in the original data file and the values did not differ from the master file, the original data columns were retained and the names of the parameters were changed from the PI-submitted names to the standardized master names. If there were differences between the PI-supplied parameter values and those in the master file, both columns were retained. If the original data submission included all of the master parameters, no additional columns were added, but parameter names were modified to match the naming conventions of the master file.

See the dataset parameters documentation for a description of which parameters were supplied by the PI and which were added via the join method.

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## **Data Files**

**Hg\_filt\_joined.csv**(Comma Separated Values (.csv), 95.87 KB)

MD5:1b2bba06a01f5a1bc540ed14cd933d72

Primary data file for dataset ID 3860

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#### **Parameters**

cruise_id	Official cruise identifier e.g. KN199-04 = R/V Knorr cruise number 199-04.	text

egment of a leg of a cruise, where a leg may en into parts: For KN204-01: part A = 11/6/2011	text
Woods Hole to Bermuda) 2011 to 12/11/2011 (Bermuda to Praia, Cabo	
; provided in original data submission.	integer
ng number for US GEOTRACES samples; ranges 078 for KN199-04 and from 6112 to 8148 for upplied values were identical to those in the GEOTRACES master file. Originally submitted as trameter name has been changed to conform to OTRACES naming conventions.	integer
s positive	decimal degrees
is positive	decimal degrees
nple collection	yyyymmdd
	ННММ
n instrument: TMR-trace metal rosette; FISH- d fish	text
	meters
f total mercury	picomoles/liter
uality flag:	integer
f gaseous elemental mercury	picomoles/liter
ntal mercury quality flag:	integer
e I	

MMHg	concentration of monomethylmercury	femtomoles/liter
MMHg_flag	monomethylmercury quality flag: 2) ok 3) questionable 4) bad analysis 5) sample lost 6) mean of replicates	integer
DMHg	concentration of dimethylmercury	femtomoles/liter
DMHg_flag	dimethylmercury quality flag: 2) ok 3) questionable 4) bad analysis 5) sample lost 6) mean of replicates	integer
station_GEOTRC	GEOTRACES station number; ranges from 1 through 12 for KN199-04 and 1 through 24 for KN204-01. Stations 7 and 9 were skipped on KN204-01. Some GeoFish stations are denoted as X_to_Y indicating the tow occurred between stations X and Y. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	dimensionless
depth_GEOTRC_CTD	Observation/sample depth in meters; calculated from CTD pressure. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	meters
event_GEOTRC	Unique identifying number for US GEOTRACES sampling events; ranges from 2001 to 2225 for KN199-04 events and from 3001 to 3282 for KN204-01 events.  Values were added from the intermediate US GEOTRACES master file (see Processing Description).	dimensionless
cast_GEOTRC	Cast identifier numbered consecutively within a station. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	dimensionless
sample_bottle_GEOTRC	Unique identification numbers given to samples taken from bottles; ranges from 1 to 24; often used synonymously with bottle number. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	dimensionless

bottle_GEOTRC	Alphanumeric characters identifying bottle type (e.g. NIS representing Niskin and GF representing GOFLO) and position on a CTD rosette.  Values were added from the intermediate US GEOTRACES master file (see Processing Description).	dimensionless
BTL_ISO_DateTime_UTC	Date and time (UTC) variable recorded at the bottle sampling time in ISO compliant format. Values were added from the intermediate US GEOTRACES master file (see Processing Description).  This standard is based on ISO 8601:2004(E) and takes on the following form: 2009-08-30T14:05:00[.xx]Z (UTC time)	YYYY-MM- DDTHH:MM:SS[.xx] [+/-TZ]
ISO_DateTime_UTC	Cast date/time (UTC) formatted to ISO8601 standard. T indicates start of time string; Z indicates UTC. Calculated from original date and time fields.	YYYY-mm- ddTHH:MM:SS.ssZ

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# Instruments

Dataset- specific Instrument Name	Cold Vapor Atomic Fluorescence Spectrophotometer
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.

Dataset- specific Instrument Name	Underway towed fish
Generic Instrument Name	Pump surface
Instrument	A source of uncontaminated near-surface seawater pumped onto the deck of the research vessel that can be sampled and analyzed. This pumped seawater supply is from an over-the-side pumping system, and is therefore different from the vessel underway seawater system.

Dataset-specific Instrument Name	Trace Metal Bottle
Generic Instrument Name	Trace Metal Bottle
<b>Dataset-specific Description</b>	Trace metal rosette
	Trace metal (TM) clean rosette bottle used for collecting trace metal clean seawater samples.

# **Deployments**

# KN199-04

Website	https://www.bco-dmo.org/deployment/58066	
Platform	R/V Knorr	
Report	http://bcodata.whoi.edu/US_GEOTRACES/AtlanticSection/Cruise_Report_for_Knorr_199_Final_v3.pdf	
Start Date	2010-10-15	
End Date	2010-11-04	
Description	This cruise constitutes the first survey section as part of the U.S. participation in an international program named GEOTRACES. Funding: NSF OCE award 0926423 Science Objectives: To obtain state of the art trace metal and isotope measurements on a suite of samples taken on a midlatitude zonal transect of the North Atlantic. In particular, sampling targeted the oxygen minimum zone extending off the west African coast near Mauritania, the TAG hydrothermal field, and the western boundary current system along Line W. For additional information, please refer to the GEOTRACES program Web site ( <a href="https://www.geotraces.org/">https://www.geotraces.org/</a> ) for overall program objectives and a summary of properties measured. Science Activities include seawater sampling via GoFLO and Niskin carousels, in situ pumping (and filtration), CTDO2 and transmissometer sensors, underway pumped sampling of surface waters, and collection of aerosols and rain. Hydrography, CTD and nutrient measurements were supported by the Ocean Data Facility (J. Swift) at Scripps Institution of Oceanography and funded through NSF Facilities. They provided an additional CTD rosette system along with nephelometer and LADCP. A trace metal clean Go-Flo Rosette and winch were provided by the group at Old Dominion University (G. Cutter) along with a towed underway pumping system. Additional cruise information is available from the Rolling Deck to Repository (R2R): <a href="https://www.rvdata.us/search/cruise/KN199-04">https://www.rvdata.us/search/cruise/KN199-04</a> Other Relevant Links: List of cruise participants: [ PDF ] Cruise track: JPEG image (from Woods Hole Oceanographic Institution, vessel operator) ADCP data are available from the Currents ADCP group at the University of Hawaii: KN199-04 ADCP	

## KN204-01

Website	https://www.bco-dmo.org/deployment/58786	
Platform	R/V Knorr	
Report	http://bcodata.whoi.edu/US_GEOTRACES/AtlanticSection/STS_Prelim_GT11_Doc.pdf	
Start Date	2011-11-06	
End Date	2011-12-11	
Description	The US GEOTRACES North Atlantic cruise aboard the R/V Knorr completed the section between Lisbon and Woods Hole that began in October 2010 but was rescheduled for November-December 2011. The R/V Knorr made a brief stop in Bermuda to exchange samples and personnel before continuing across the basin. Scientists disembarked in Praia, Cape Verde, on 11 December. The cruise was identified as KN204-01A (first part before Bermuda) and KN204-01B (after the Bermuda stop). However, the official deployment name for this cruise is KN204-01 and includes both part A and B. Science activities included: ODF 30 liter rosette CTD casts, ODU Trace metal rosette CTD casts, McLane particulate pump casts, underway sampling with towed fish and sampling from the shipboard "uncontaminated" flow-through system. Full depth stations are shown in the accompanying figure (see below). Additional stations to sample for selected trace metals to a depth of 1000 m are not shown. Standard stations are shown in red (as are the ports) and "supper" stations, with extra casts to provide large-volume samples for selected parameters, are shown in green. Station spacing is concentrated along the western margin to evaluate the transport of trace elements and isotopes by western boundary currents. Stations across the gyre will allow scientists to examine trace element supply by Saharan dust, while also contrasting trace element and isotope distributions in the oligotrophic gyre with conditions near biologically productive ocean margins, both in the west, to be sampled now, and within the eastern boundary upwelling system off Mauritania, sampled last year. Funding: The cruise was funded by NSF OCE awards 0926204, 0926433 and 0926659. Additional cruise information is available from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/KN204-01 Other Relevant Links: ADCP data are available from the Currents ADCP group at the University of Hawaii at the links below: KN204-01A (part 1 of 2011 cruise; Woods Hole, MA to Bermuda) KN204-01B (pa	

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## **Project Information**

U.S. GEOTRACES North Atlantic Transect (GA03) (U.S. GEOTRACES NAT)

Website: <a href="https://www.geotraces.org/">https://www.geotraces.org/</a>

**Coverage**: Subtropical western and eastern North Atlantic Ocean (GA03)

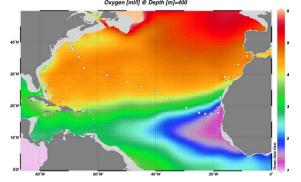
Much of this text appeared in an article published in OCB News, October 2008, by the OCB Project Office.

The first U.S. GEOTRACES Atlantic Section will be specifically centered around a sampling cruise to be carried out in the North Atlantic in 2010. Ed Boyle (MIT) and Bill Jenkins (WHOI) organized a three-day planning workshop that was held September 22-24, 2008 at the Woods Hole Oceanographic Institution. The main goal of the workshop, sponsored by the National Science Foundation and the U.S. GEOTRACES Scientific Steering Committee, was to design the implementation plan for the first U.S. GEOTRACES Atlantic Section. The primary cruise design motivation was to improve knowledge of the sources, sinks and internal cycling of Trace Elements and their Isotopes (TEIs) by studying their distributions along a section in the North Atlantic (Figure 1). The North Atlantic has the full suite of processes that affect TEIs, including strong meridional advection, boundary scavenging and source effects, aeolian deposition, and the salty Mediterranean Outflow. The North Atlantic is particularly important as it lies at the "origin" of the global Meridional Overturning Circulation.

It is well understood that many trace metals play important roles in biogeochemical processes and the carbon cycle, yet very little is known about their large-scale distributions and the regional scale processes that affect them. Recent advances in sampling and analytical techniques, along with advances in our understanding of their

roles in enzymatic and catalytic processes in the open ocean provide a natural opportunity to make substantial advances in our understanding of these important elements. Moreover, we are motivated by the prospect of global change and the need to understand the present and future workings of the ocean's biogeochemistry. The GEOTRACES strategy is to measure a broad suite of TEIs to constrain the critical biogeochemical processes that influence their distributions. In addition to these "exotic" substances, more traditional properties, including macronutrients (at micromolar and nanomolar levels), CTD, bio-optical parameters, and carbon system characteristics will be measured. The cruise starts at Line W, a repeat hydrographic section southeast of Cape Cod, extends to Bermuda and subsequently through the North Atlantic oligotrophic subtropical gyre, then transects into the African coast in the northern limb of the coastal upwelling region. From there, the cruise goes northward into the Mediterranean outflow. The station locations shown on the map are for the "fulldepth TEI" stations, and constitute approximately half of the stations to be ultimately occupied.

Figure 1. The proposed 2010 Atlantic GEOTRACES cruise track plotted on dissolved oxygen at 400 m depth. Data from the World Ocean Atlas (Levitus et al., 2005) were plotted using Ocean Data View (courtesy Reiner Schlitzer). [click on the image to view a larger version]

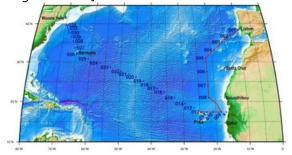


Hydrography, CTD and nutrient measurements will be supported by the Ocean Data Facility (J. Swift) at Scripps Institution of Oceanography and funded through NSF Facilities. They will be providing an additional CTD rosette system along with nephelometer and LADCP. A trace metal clean Go-Flo Rosette and winch will be provided by the group at Old Dominion University (G. Cutter) along with a towed underway pumping system.

The North Atlantic Transect cruise began in 2010 with KN199 leg 4 (station sampling) and leg 5 (underway sampling only) (Figure 2).

## KN199-04 Cruise Report (PDF)

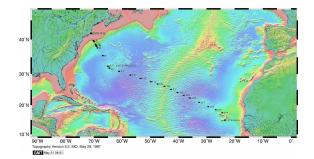
Figure 2. The red line shows the cruise track for the first leg of the US Geotraces North Atlantic Transect on the R/V Knorr in October 2010. The rest of the stations (beginning with 13) will be completed in October-December 2011 on the R/V Knorr (courtesy of Bill Jenkins, Chief Scientist, GNAT first leg). [click on the image to view a larger version]



The section completion effort resumed again in November 2011 with KN204-01A,B (Figure 3).

## KN204-01A,B Cruise Report (PDF)

Figure 3. Station locations occupied on the US Geotraces North Atlantic Transect on the R/V Knorr in November 2011. [click on the image to view a larger version]



Data from the North Atlantic Transect cruises are available under the Datasets heading below, and consensus values for the SAFe and North Atlantic GEOTRACES Reference Seawater Samples are available from the GEOTRACES Program Office: Standards and Reference Materials

**ADCP data** are available from the Currents ADCP group at the University of Hawaii at the links below:

KN199-04 (leg 1 of 2010 cruise; Lisbon to Cape Verde)

KN199-05 (leg 2 of 2010 cruise; Cape Verde to Charleston, NC)

KN204-01A (part 1 of 2011 cruise; Woods Hole, MA to Bermuda)

KN204-01B (part 2 of 2011 cruise; Bermuda to Cape Verde)

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## **Program Information**

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

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

Coverage: Global

**GEOTRACES** is a <u>SCOR</u> 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-0927274
NSF Division of Ocean Sciences (NSF OCE)	OCE-1132515
NSF Division of Ocean Sciences (NSF OCE)	OCE-0928191
NSF Division of Ocean Sciences (NSF OCE)	OCE-1132480

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