

# Nitrate (NO<sub>3</sub>), ammonium (NH<sub>4</sub>), and oxygen & deuterium isotopic composition from snow collected on the US GEOTRACES Arctic cruise (HLY1502) from August to October 2015

**Website:** <https://www.bco-dmo.org/dataset/753356>

**Data Type:** Cruise Results

**Version:** 1

**Version Date:** 2019-01-22

## Project

- » [U.S. Arctic GEOTRACES Study \(GN01\)](#) (U.S. GEOTRACES Arctic)
- » [Collaborative Research: GEOTRACES Arctic Ocean section-Constraining Nitrogen Cycling in the western Arctic Ocean.](#) (US GEOTRACES Arctic Nitrogen Flux)

## Program

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

Contributors	Affiliation	Role
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<a href="#">Granger, Julie</a>	University of Connecticut (UConn)	Co-Principal Investigator
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## Coverage

**Spatial Extent:** N:89.96 E:3.529 S:82.49 W:176.67

**Temporal Extent:** 2015-08-09 - 2015-10-12

## Dataset Description

This dataset contains nitrate and ammonium concentrations, as well as the complete isotopic composition of nitrate (d15N, d18O, D17O) and ammonium (d15N) and the oxygen & deuterium isotopic composition (d18O, dD) from snow collected during the U.S. GEOTRACES ARCTIC research cruise in 2015.

## Methods & Sampling

Sea ice was collected using a trace metal clean Kovacs T-handle corer to collect 1 m long cores at 6 sea ice stations along the Canada Basin transect. Snow was collected into pre-cleaned HDPE bottles, while seawater was pumped from beneath the sampled sea ice hole into a carboy and filtered into pre-cleaned bottles aboard the Healy. All samples were stored frozen until analyses or further sample prep could take place. Ice cores

were bagged and stored at -20 degrees celsius onboard until cores could be cut and sub-sectioned in a cold room at University of Washington in Seattle prior to shipment back to Brown University.

Concentration analysis of samples was completed using an automated colorimetric system (WestCo SmartChem 200); the pooled standard deviation of control standards run within each sample set run was 0.3 micromoles per Liter (6.2 ppb nitrate); detection limit was 0.09 micromoles per Liter. Based upon nitrate concentration, 20 nmol of N were injected into vials containing denitrifying bacteria to convert nitrate to nitrous oxide for isotopic analysis on a ThermoFisher Delta V isotope ratio mass spectrometer. Analysis for d15N and d18O of nitrate are described in Sigman et al. (Analytical Chemistry; 2001), Casciotti et al. (Analytical Chemistry; 2002), McIlvin and Casciotti (Analytical Chemistry; 2011). Kaiser et al. (Analytical Chemistry; 2007) describes similar methodology for the determination of D17O of nitrate. D17O analyses require 50 nmol of N for complete analysis.

## Data Processing Description

NOTES: Not enough nitrate for D17O analysis. Ammonium concentrations were below detection for stations 43 and 46. Due to low concentrations/no detectable ammonium, no icehole seawater samples were measured for d15N-NH4. Sample 59 had no sample left to conduct NH4 or H2O isotope sample analysis. Of the sample volume available and concentration, only two snow samples were measured for d15N-NH4.

As described in Kaiser et al. (2007), isotopic data is corrected and standardized to international reference materials IAEA-N3, USGS34, and USGS35, which are run 3-9 times with each sample run. For d15N, samples are corrected for isobaric interferences and a blank associated with the bacteria. For d18O, samples are corrected for isobaric interferences, blank, and exchange between sample nitrate and background water that takes place during denitrification to nitrous oxide. The pooled standard deviation for the reference materials are (n=88): 0.2 per mil for d15N and 0.7 per mil for d18O of IAEA-N3; 0.3 per mil for d15N and 0.7 per mil for d18O of USGS34; and 0.7 per mil for d18O of USGS35 (sample d15N is not corrected for d15N of USGS35, this is used as an internal quality check and pooled standard deviation across all runs in 0.2 per mil). 10 samples were run in duplicate or triplicate and the paired pooled standard deviation (n=10) is 0.2 per mil for d15N and 0.4 per mil for d18O. Pooled standard deviation for USGS34 and USGS35 run for D17O is 0.6 and 0.9 per mil each (n=14 and 15, respectively), and replicate samples were 0.9 per mil (n=4).

Due to low sample volume and concentrations, only 3 samples were analyzed for d15N-NH4 using hypobromite oxidation to nitrite coupled with the denitrifier method (Felix et al., 2013; Zhang et al., 2007; Sigman et al., 2001). Briefly, ammonium is oxidized to nitrite with hypobromite, and nitrite is quantitatively converted to nitrous oxide with denitrifying bacteria. For the three samples with sufficient analyte, oxidations were conducted in triplicate. Samples were calibrated using ammonium reference materials USGS25 and IAEA-N2. Precision for d15N-NH4 of reference materials was  $\leq 2.7$  per mil and based on the standard deviation of reference replicates. The d15N-NH4 is then computed from the weighted difference from d15N-NO3.

Oxygen and hydrogen isotope ratios of water (d18O-H2O vs. VSMOW, dD-H2O vs. VSMOW) were measured using wavelength-scanned cavity-down ring spectroscopy on a Picarro L1102-I liquid analyzer calibrated to international reference standards USGS46, USGS49 and VSMOW. Raw data are corrected for memory and drift effects followed by normalization using a standard calibration (Vaughn and Claymoore, INSTAAR, University of Colorado). Precision for d18O and dD was better than  $\pm 0.1$  and  $\pm 0.4$  per mil, respectively, based upon repeated measures of an internal standard (BW-1).

BCO-DMO Processing:

- modified parameter names (replaced spaces with underscores);
- separated Dates\_of\_collection field into Date\_Start and Date\_End (yyyy-mm-dd).

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## Data Files

**File****Snow\_NO3\_NH4\_H2O.csv**(Comma Separated Values (.csv), 1.66 KB)

MD5:b1593fc660b60c8fbc93e9f515852dd

Primary data file for dataset ID 753356

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## Related Publications

Casciotti, K. L., Sigman, D. M., Hastings, M. G., Böhlke, J. K., & Hilkert, A. (2002). Measurement of the Oxygen Isotopic Composition of Nitrate in Seawater and Freshwater Using the Denitrifier Method. *Analytical Chemistry*, 74(19), 4905–4912. doi:[10.1021/ac020113w](https://doi.org/10.1021/ac020113w)

*Methods*

Felix, J., Elliott, E. M., Gish, T. J., McConnell, L. L., & Shaw, S. L. (2013). Characterizing the isotopic composition of atmospheric ammonia emission sources using passive samplers and a combined oxidation-bacterial denitrifier approach. *Rapid Communications in Mass Spectrometry*, 27(20), 2239–2246. doi:[10.1002/rcm.6679](https://doi.org/10.1002/rcm.6679)

*Methods*

Kaiser, J., Hastings, M. G., Houlton, B. Z., Röckmann, T., & Sigman, D. M. (2007). Triple Oxygen Isotope Analysis of Nitrate Using the Denitrifier Method and Thermal Decomposition of N<sub>2</sub>O. *Analytical Chemistry*, 79(2), 599–607. doi:[10.1021/ac061022s](https://doi.org/10.1021/ac061022s)

*Methods*

McIlvin, M. R., & Casciotti, K. L. (2011). Technical Updates to the Bacterial Method for Nitrate Isotopic Analyses. *Analytical Chemistry*, 83(5), 1850–1856. doi:[10.1021/ac1028984](https://doi.org/10.1021/ac1028984)

*Methods*

Sigman, D. M., Casciotti, K. L., Andreani, M., Barford, C., Galanter, M., & Böhlke, J. K. (2001). A Bacterial Method for the Nitrogen Isotopic Analysis of Nitrate in Seawater and Freshwater. *Analytical Chemistry*, 73(17), 4145–4153. doi:[10.1021/ac010088e](https://doi.org/10.1021/ac010088e)

*Methods*

Vaughn, B., and V. Claymoore. Water isotope correction method. INSTAAR. University of Colorado.

*Methods*

Zhang, L., Altabet, M. A., Wu, T., & Hadas, O. (2007). Sensitive Measurement of NH<sub>4</sub>+<sup>15</sup>N/<sup>14</sup>N (δ<sup>15</sup>NH<sub>4</sub><sup>+</sup>) at Natural Abundance Levels in Fresh and Saltwaters. *Analytical Chemistry*, 79(14), 5297–5303.

doi:[10.1021/ac070106d](https://doi.org/10.1021/ac070106d)*Methods*[\[ table of contents \]](#) | [\[ back to top \]](#)

## Parameters

Parameter	Description	Units
GEOTRC_SAMPNO	Geotraces Arctic Sample ID	unitless
Dates_of_collection	Cruise collection dates in 2015, mm/dd/yy	unitless
Date_Start	Date at start of collection period. Format: yyyy-mm-dd	unitless
Date_End	Date at end of collection period. Format: yyyy-mm-dd	unitless
Latitude	Latitude of collection; positive is North	decimal degrees
Longitude	Longitude of collection; negative is West	decimal degrees
Ice_Station	Collection station number	unitless
Sample_Type	Description of sample type (e.g. snow, sea ice, icehole, ice pond)	unitless
Sampling_Depth_cm	Depth of sampling event at various depths beneath ice	centimeters (cm)
NITRATE_D_CONC_SNOW	Nitrate concentration	micromoles per Liter (umol/L)
NITRATE_15_14_D_DELTA_SNOW	delta 15N of nitrate	permil vs. atmospheric N2
NITRATE_18_16_D_DELTA_SNOW	delta 18O of nitrate	permil vs. VSMOW
NITRATE_17_16_D_DELTA_SNOW	capital delta 17O ( $D_{17O} = d_{17O} - 0.5 * d_{18O}$ ) of nitrate	permil vs. VSMOW
AMMONIUM_D_CONC_SNOW	Ammonium concentration	micromoles per Liter (umol/L)
AMMONIUM_15_14_D_DELTA_SNOW	delta 15N of ammonium	permil vs N2
WATER_18_16_D_DELTA_SNOW	delta 18O of water	permil vs VSMOW
WATER_D_H_D_DELTA_SNOW	delta Deuterium of water	permil vs VSMOW

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## Instruments

<b>Dataset-specific Instrument Name</b>	WestCo SmartChem 200 discrete chemistry analyzer
<b>Generic Instrument Name</b>	Discrete Analyzer
<b>Generic Instrument Description</b>	Discrete analyzers utilize discrete reaction wells to mix and develop the colorimetric reaction, allowing for a wide variety of assays to be performed from one sample. These instruments are ideal for drinking water, wastewater, soil testing, environmental and university or research applications where multiple assays and high throughput are required.

<b>Dataset-specific Instrument Name</b>	ThermoFisher Delta V isotope ratio mass spectrometer
<b>Generic Instrument Name</b>	Isotope-ratio Mass Spectrometer
<b>Generic Instrument Description</b>	The Isotope-ratio Mass Spectrometer is a particular type of mass spectrometer used to measure the relative abundance of isotopes in a given sample (e.g. VG Prism II Isotope Ratio Mass-Spectrometer).

<b>Dataset-specific Instrument Name</b>	Picarro L1102-I Liquid Analyzer
<b>Generic Instrument Name</b>	Picarro L1102-i Isotopic Water Liquid Analyzer
<b>Generic Instrument Description</b>	A portable analyzer designed for laboratories or field based isotope analysis. It uses Cavity Ring-Down Spectroscopy (CRDS) to measure the spectral signature of the molecule of interest. The instrument includes a closed-loop temperature and pressure control. The L1102-i can be used for analysis of liquid water only. It has a typical precision of 0.1 per mil for d18O and 0.5 per mil for dD.

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## Deployments

### HLY1502

<b>Website</b>	<a href="https://www.bco-dmo.org/deployment/638807">https://www.bco-dmo.org/deployment/638807</a>
<b>Platform</b>	USCGC Healy
<b>Report</b>	<a href="https://datadocs.bco-dmo.org/docs/302/geotraces/GEOTRACES_ARCTIC/data_docs/cruise_reports/healy1502.pdf">https://datadocs.bco-dmo.org/docs/302/geotraces/GEOTRACES_ARCTIC/data_docs/cruise_reports/healy1502.pdf</a>
<b>Start Date</b>	2015-08-09
<b>End Date</b>	2015-10-12
<b>Description</b>	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): <a href="https://www.rvdata.us/search/cruise/HLY1502">https://www.rvdata.us/search/cruise/HLY1502</a>

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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 activities 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 Ocean section-Constraining Nitrogen Cycling in the western Arctic Ocean. (US GEOTRACES Arctic Nitrogen Flux)**

**Coverage:** Chukchi shelf and western Arctic Ocean basins

In this project, a group of investigators from the University of Connecticut, the University of Massachusetts-Dartmouth, and Brown University will participate in the 2015 U.S. GEOTRACES Arctic expedition to determine the biogeochemistry of nitrogen in the region. 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. Nitrogen is one of the two major nutrients required universally by plankton in the ocean, and this study in the Arctic Ocean will increase our understanding of the ocean's ecology, productivity, and carbon cycle. This study will also provide training for graduate and undergraduate students, and results will be shared through public outreach events.

The state of knowledge of Arctic nitrogen (N) biogeochemistry remains cursory as compared to that in other ocean basins despite the fact that understanding Arctic Ocean nitrogen cycling is central to understanding its global biogeochemistry. For one, benthic nitrogen loss on Arctic continental shelves may represent a globally significant sink of oceanic fixed nitrogen. Second, benthic nitrogen loss on the Arctic continental shelf and slope reduces the ratio of nitrate to phosphate substantially below the mean requirements of phytoplankton nitrogen, consequently limiting primary production at the ice-free surface of the western Arctic Ocean. In light

of the rapid changes in Arctic climatology, the characterization of its biogeochemistry and establishment of a baseline from which to monitor future changes is critical. Researchers will use the stable N isotope ( $^{15}\text{N}/^{14}\text{N}$ ) ratio in nitrate, nitrite, ammonium, and nitrogen gas determined for a suite of dissolved, particulate, atmospheric, snow, and sea-ice samples to better constrain the spatial and temporal variability of biological nitrogen transformations in the Arctic. Results from this study will provide a first order understanding of the contribution of water masses to the regional nitrogen budget, identify regional nitrogen sources and sinks, and diagnose important biological nitrogen transformations that occur on the Chukchi shelf, and in the central basins.

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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
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1435002</a>
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1433989</a>

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