

# Nitrate $^{15}\text{N}/^{14}\text{N}$ measurements in two adjacent mesoscale eddies in the North Pacific Subtropical Gyre from water samples collected on R/V Kilo Moana cruise KM1709 in June-July 2017

**Website:** <https://www.bco-dmo.org/dataset/948358>

**Data Type:** Cruise Results

**Version:** 1

**Version Date:** 2025-01-13

## Project

» [CAREER: The biological nitrogen isotope systematics of ammonium consumption and production](#) (Biological Nitrogen Isotope Fractionation)

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## Abstract

Two adjacent mesoscale eddies of opposite polarity were surveyed during the MESO-SCOPE (Microbial Ecology of the Surface Ocean-Simons Collaboration on Ocean Processes and Ecology) expedition in June - July of 2017 aboard R/V Kilo Moana (cruise ID KM1709). The expedition aimed to understand the impact of mesoscale eddies on the ecosystem of the North Pacific Subtropical Gyre. Hydrographic water samples collected during the cruise were measured for nitrate  $^{15}\text{N}/^{14}\text{N}$  isotope ratios using the denitrifier method. These measurements were performed by Mengyang Zhou at the University of Connecticut.

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## Coverage

**Spatial Extent:** N:27.95 E:-157.28 S:24.47 W:-158.72

**Temporal Extent:** 2017-06-29 - 2017-07-01

## Methods & Sampling

Water was collected during the MESO-SCOPE research cruise aboard R/V Kilo Moana (KM1709) during June-July 2017. Upper ocean biogeochemistry was characterized at 11 stations along the transect traversing the cyclonic and anticyclonic eddies, using a rosette mounted with 10-liter (L) Niskin® bottles. Water samples for nutrient and nitrate isotope analyses were collected at ~25-meter (m) intervals from 5 m to 500 m with higher

vertical resolution (~5 m intervals) near the deep chlorophyll maximum (DCM). Samples were frozen at -20 degrees Celsius (°C) after collection pending analysis.

The N isotope ratios of nitrate ( $^{15}\text{N}/^{14}\text{N}$ ) in water samples from stations 4 to 13 were measured with the denitrifier method (Casciotti et al., 2002; Sigman et al., 2001) for concentrations exceeding 0.5 micromoles per liter ( $\mu\text{mol L}^{-1}$ ). Nitrate was converted to nitrous oxide ( $\text{N}_2\text{O}$ ) by cell concentrates of the denitrifying bacterial strain *Pseudomonas chlororaphis* (ATCC 43928, Manassas, VA, USA), which lacks the terminal  $\text{N}_2\text{O}$  reductase. The  $\text{N}_2\text{O}$  gas was extracted and purified using a custom-modified Thermo Fisher Scientific Gas Bench II fronted by dual cold traps and a GC Pal autosampler, and analyzed with a Thermo Delta V Advantage continuous flow gas chromatograph isotope ratio mass spectrometer (Casciotti et al., 2002; McIlvin & Casciotti, 2011). Working solutions were diluted from primary stocks into nutrient-free seawater to concentrations bracketing sample concentrations to account for potential matrix effects (Weigand et al., 2016; Zhou et al., 2021). Individual samples were measured 3 to 9 times to achieve an analytical uncertainty to  $\leq 0.3$  ‰. The oxygen isotope ratios of nitrate ( $\delta^{18}\text{O}\text{NO}_3$ ) were not measured concurrently as we did not secure sufficient sample volumes to estimate these reliably (see Zhou et al., 2021).

## Data Processing Description

The N isotope ratios are expressed in delta ( $\delta$ ) notation in units of per mil (‰) vs. a standard material ( $\text{N}_2$  gas in the air):  $\delta^{15}\text{N}_{\text{sample}} = [(\text{N}_2/\text{N}_2)_{\text{sample}}/(\text{N}_2/\text{N}_2)_{\text{standard}} - 1] \times 1000$ . Nitrate isotopic analyses were calibrated to internationally recognized nitrate reference materials IAEA-NO3 (International Atomic Energy Agency, Vienna, Austria) and USGS-34 (National Institute of Standards and Technology, Gaithersburg, MD, USA), with reported  $\delta^{15}\text{N}$  values of 4.7 ‰ and  $-1.8$  ‰ (vs. air). Individual samples were measured 3 - 9 times to achieve an analytical uncertainty to  $\leq 0.3$  ‰.

## BCO-DMO Processing Description

- Imported original file "Zhou\_etal-BCO-DMO.xlsx" into the BCO-DMO submission.
- Renamed fields to comply with BCO-DMO naming conventions.
- Created ISO-DateTime fields in local (HST) and UTC format.
- Removed the original, separate date and time columns.
- Converted longitude values from positive to negative to indicate the direction is West.
- Saved the final file as "948358\_v1\_nitrate\_15n\_14n\_meso-scope.csv".

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## Data Files

File
<b>948358_v1_nitrate_15n_14n_meso-scope.csv</b> (Comma Separated Values (.csv), 2.33 KB) MD5:aa3b1c0b715c61ba6059a6625fef04c4
Primary data file for dataset ID 948358, version 1

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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*

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*

Weigand, M. A., Foriel, J., Barnett, B., Oleynik, S., & Sigman, D. M. (2016). Updates to instrumentation and protocols for isotopic analysis of nitrate by the denitrifier method. *Rapid Communications in Mass Spectrometry*, 30(12), 1365–1383. doi:[10.1002/rcm.7570](https://doi.org/10.1002/rcm.7570)  
*Methods*

Zhou, M., Granger, J., & Chang, B. X. (2021). Influence of sample volume on nitrate N and O isotope ratio analyses with the denitrifier method. *Rapid Communications in Mass Spectrometry*, 36(4). Portico. <https://doi.org/10.1002/rcm.9224>  
*Methods*

Zhou, M., Granger, J., Rocha, C. B., Siedlecki, S. A., Barone, B., & White, A. E. (2024). Nitrogen biogeochemistry of adjacent mesoscale eddies in the North Pacific Subtropical Gyre. <https://doi.org/10.22541/essoar.171352187.73438952/v1>  
*Results*

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## Parameters

Parameter	Description	Units
ISO_DateTime_Local_HST	Date and time of sample collection in the local time zone (HST); in ISO 8601 format	unitless
ISO_DateTime_UTC	Date and time (UTC) of sample collection; in ISO 8601 format	unitless
Latitude	Latitude of sample collection	decimal degrees
Longitude	Longitude of sample collection; negative values = West	decimal degrees
Station	Station number	unitless
Depth	Sample depth	meters (m)
Mean_d15NNO3	Mean of the $\delta^{15}\text{NNO}_3$ measurements for each sample	‰ vs. air
Stdev_d15NNO3	Standard deviation of the $\delta^{15}\text{NNO}_3$ measurements for each sample	‰ vs. air

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## Instruments

<b>Dataset-specific Instrument Name</b>	GC Pal autosampler
<b>Generic Instrument Name</b>	Laboratory Autosampler
<b>Dataset-specific Description</b>	a custom-modified Thermo Fisher Scientific Gas Bench II fronted by dual cold traps and a GC Pal autosampler, and analyzed with a Thermo Delta V Advantage continuous flow gas chromatograph isotope ratio mass spectrometer
<b>Generic Instrument Description</b>	Laboratory apparatus that automatically introduces one or more samples with a predetermined volume or mass into an analytical instrument.

<b>Dataset-specific Instrument Name</b>	10 L Niskins
<b>Generic Instrument Name</b>	Niskin bottle
<b>Generic Instrument Description</b>	A Niskin bottle (a next generation water sampler based on the Nansen bottle) is a cylindrical, non-metallic water collection device with stoppers at both ends. The bottles can be attached individually on a hydrowire or deployed in 12, 24, or 36 bottle Rosette systems mounted on a frame and combined with a CTD. Niskin bottles are used to collect discrete water samples for a range of measurements including pigments, nutrients, plankton, etc.

<b>Dataset-specific Instrument Name</b>	Thermo Delta V Advantage continuous flow gas chromatograph isotope ratio mass spectrometer
<b>Generic Instrument Name</b>	Thermo Fisher Scientific DELTA V Advantage isotope ratio mass spectrometer
<b>Dataset-specific Description</b>	a custom-modified Thermo Fisher Scientific Gas Bench II fronted by dual cold traps and a GC Pal autosampler, and analyzed with a Thermo Delta V Advantage continuous flow gas chromatograph isotope ratio mass spectrometer
<b>Generic Instrument Description</b>	The Thermo Scientific DELTA V Advantage is an isotope ratio mass spectrometer designed to measure isotopic, elemental, and molecular ratios of organic and inorganic compounds. The DELTA V Advantage is the standard model of the DELTA V series of isotope ratio mass spectrometers, which can be upgraded to the DELTA V Plus. The DELTA V Advantage can be operated in Continuous Flow or Dual Inlet mode. The standard collector configuration is the Universal Triple Collector. H2 collectors with online hydrogen capability are optional. The DELTA V Advantage is controlled by an automated, integrated Isodat software suite. A magnet, whose pole faces determine the free flight space for the ions, eliminates the traditional flight tube. The magnet is designed for fast mass switching which is further supported by a fast jump control between consecutive measurements of multiple gases within one run. The sample gas is introduced at ground potential, eliminating the need for insulation of the flow path, ensuring 100 percent transfer into the ion source. The amplifiers register ion beams up to 50 V. The DELTA V Advantage has a sensitivity of 1200 molecules per ion (M/I) in Dual Inlet mode and 1500 M/I in Continuous Flow mode. It has a system stability of < 10 ppm and an effective magnetic detection radius of 191 nm. It has a mass range of 1 - 80 Dalton at 3 kV.

<b>Dataset-specific Instrument Name</b>	Thermo Fisher Scientific Gas Bench II
<b>Generic Instrument Name</b>	Thermo-Fisher Scientific Gas Bench II
<b>Dataset-specific Description</b>	custom-modified Thermo Fisher Scientific Gas Bench II fronted by dual cold traps and a GC Pal autosampler, and analyzed with a Thermo Delta V Advantage continuous flow gas chromatograph isotope ratio mass spectrometer
<b>Generic Instrument Description</b>	An on-line gas preparation and introduction system for isotope ratio mass spectrometry that is designed for high precision isotope and molecular ratio determination of headspace samples, including water equilibration, carbonates and atmospheric gases. The instrument allows for the use of a dual viscous flow inlet system of repetitive measurements of sample and standard gas on a continuous flow isotope ratio mass spectrometer (CF-IRMS) system. The sample volume is the sample vial (instead of a metal bellows), and the reference gas volume is a pressurized gas tank. The instrument consists of a user programmable autosampler, a gas sampling system, a maintenance-free water removal system, a loop injection system, an isothermal gas chromatograph (GC), an active open split interface, a reference gas injection system with three reference ports, and one or two optional LN2 traps for cryofocusing. The gas sampling system includes a two port needle which adds a gentle flow of He into the sample vial, diluting and displacing sample gas. Water is removed from the sample gas through diffusion traps. The loop injector aliquots the sample gas onto the GC column, which separates the molecular species. The reference gas injection system allows accurate referencing of each sample aliquot to isotopic standards. The system can be used with several options including a carbonate reaction kit that allows injection of anhydrous phosphoric acid into sample vials. Note "Finnigan GasBench-II" is the previous brand name of this instrument.

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## Deployments

### KM1709

<b>Website</b>	<a href="https://www.bco-dmo.org/deployment/948369">https://www.bco-dmo.org/deployment/948369</a>
<b>Platform</b>	R/V Kilo Moana
<b>Start Date</b>	2017-06-26
<b>End Date</b>	2017-07-15
<b>Description</b>	Additional information is available from R2R at <a href="https://www.rvdata.us/search/cruise/KM1709">https://www.rvdata.us/search/cruise/KM1709</a> and on the cruise website at <a href="https://scope.soest.hawaii.edu/data/mesoscope/">https://scope.soest.hawaii.edu/data/mesoscope/</a> .

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## Project Information

### CAREER: The biological nitrogen isotope systematics of ammonium consumption and production (Biological Nitrogen Isotope Fractionation)

#### NSF Award Abstract:

The nitrogen (N) cycle in the marine environment is controlled by biological processes. Unfortunately, quantifying these processes and assessing their effect on the N cycle is difficult by direct measurements because of large spatial and temporal differences. Isotopic composition measurements of N provide a means to constrain these processes indirectly; however, there is still a great deal to be understood about isotope

fractionation of recycled nitrogen through biological processes, which has made interpretation of novel nitrogen isotope data difficult. A researcher from the University of Connecticut plans to determine the influence of biological consumption and production on the isotope fractionation in ammonium. By helping to understand the processes surrounding fractionation of recycled ammonium at the organism level, this research will create a basis for which future researchers can better interpret isotope composition data to infer nitrogen cycle dynamics. A graduate student, a postdoctoral fellow, and two or more undergraduate students will be involved in the research. The researcher plans to integrate science with community-engaged learning by developing an undergraduate field and laboratory course that will require the students to present their research to stakeholders in the community. There will be a manual created for this course that will be disseminated in open-access forums for teachers hoping to develop similar courses.

Biological nitrogen isotope fractionation associated with nitrogen recycling remains poorly constrained despite the advent of a variety of new techniques to analyze nitrogen isotopes in recent years. The use of isotopic composition data can be incredibly useful to interpreting nitrogen cycle processes in the ocean that are difficult to measure directly, which makes it crucial to further understand the processes behind fractionation to catch up with the advancement of the datasets available to researchers. This research will characterize the isotope fractionation dynamics of ammonium during biological consumption and production. The researchers will investigate whether the characteristic low concentrations of ammonium in the surface ocean affect isotope fractionation when the ammonium is recycled and whether there is a trophic isotope effect associated with ammonium recycling by protozoan grazers. With this research, there will be a baseline from which researchers can interpret recycled nitrogen dynamics from ammonium isotope datasets. The methods of comparing nitrogen cycling studies will become significantly clearer with such a standard making interpretation uniform by removing significant uncertainties.

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## Funding

Funding Source	Award
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1554474</a>
Simons Foundation (Simons)	<a href="#">329104</a>

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