

# Dissolved N<sub>2</sub>O concentration and stable isotope/isotopomer composition measurements from R/V Knorr cruise KN192-05 in the South Atlantic subtropical gyre and Benguela upwelling region in 2007 (CoFeMUG project)

**Website:** <https://www.bco-dmo.org/dataset/529599>

**Data Type:** Cruise Results

**Version:** 1

**Version Date:** 2014-09-17

## Project

» [Cobalt, Iron and Micro-organisms from the Upwelling zone to the Gyre \(GAc01\)](#) (CoFeMUG)

## Programs

» [Ocean Carbon and Biogeochemistry](#) (OCB)

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

Contributors	Affiliation	Role
<a href="#">Casciotti, Karen L.</a>	Stanford University	Principal Investigator, Contact
<a href="#">Frame, Caitlin</a>	University of Basel (Universitat Basel)	Co-Principal Investigator
<a href="#">Rauch, Shannon</a>	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

## Abstract

Dissolved N<sub>2</sub>O concentration and stable isotope/isotopomer composition measurements made from samples from acid-cleaned, Teflon-coated X-Niskin sampling bottles on the CoFeMUG cruise (KN192-05).

---

## Table of Contents

- [Coverage](#)
  - [Dataset Description](#)
    - [Methods & Sampling](#)
    - [Data Processing Description](#)
  - [Data Files](#)
  - [Related Publications](#)
  - [Parameters](#)
  - [Instruments](#)
  - [Deployments](#)
  - [Project Information](#)
  - [Program Information](#)
  - [Funding](#)
- 

## Coverage

**Spatial Extent:** N:-12 E:14.5 S:-25 W:-20

**Temporal Extent:** 2007-11-22 - 2007-12-11

---

## Dataset Description

Dissolved N<sub>2</sub>O concentration and stable isotope/isotopomer composition measurements made from samples from acid-cleaned, Teflon-coated X-Niskin sampling bottles on the CoFeMUG cruise (KN192-05).

## Methods & Sampling

Single water samples for N<sub>2</sub>O analyses were collected from acid-cleaned, Teflon-coated X-Niskin sampling

bottles (OceanTest Equipment) of 8-liter capacity deployed on an epoxy-coated rosette (Sea-Bird Electronics) as described in Noble et al. (2012). Immediately after rosette recovery, water samples were collected by twice overfilling 160 ml glass serum bottles (Wheaton prod. no. 223748) from the bottom up using tygon tubing attached to each niskin bottle. A small headspace was introduced into each sample by pipetting 1 ml of sample off the top. The sample was then poisoned with 100 ul of saturated HgCl<sub>2</sub> solution and sealed with gray butyl septa (MicroLiter Analytics prod. no. 20-0025) and aluminum crimps. Poisoned samples were stored for several months in the dark at room temperature before analysis.

Isotopic analyses of N<sub>2</sub>O were made using a Finnigan DELTA PLUS XP IRMS calibrated for isotopomer-specific measurements (see Frame & Casciotti (2010) for details) and referenced against injections of a calibrated N<sub>2</sub>O reference tank (d<sub>15</sub>N<sub>bulk</sub> = 0.31‰, SP = -1.2‰, d<sub>18</sub>O = 40.85‰ as calibrated by S. Toyoda, Toyko Tech) with quality control checks against analyses of tropospheric air samples. Bottles were purged with He and N<sub>2</sub>O was trapped on-line with a custom-built purge and trap system (McIlvin & Casciotti, 2010). The molar amount of N<sub>2</sub>O was determined from each bottle using a constant linear relationship of m/z 44 peak area to molar quantity of N<sub>2</sub>O which is 2.15 Vs per nanomole of N<sub>2</sub>O, then converted to a concentration by dividing the molar amount by the volume of sample extracted (154 ml). The ratios of sample N<sub>2</sub>O to reference gas N<sub>2</sub>O values of m/z 31/30, 45/44, and 46/44 were corrected for a small linear dependence of these values on the sample peak area (see McIlvin and Casciotti 2010), with all ratios corrected to a peak area of 20 Vs. For a 160 ml water sample containing 2.2 nmole of N<sub>2</sub>O (typical of the lowest concentrations in this dataset), the precision of the d<sub>18</sub>O = ±0.25‰, d<sub>15</sub>N<sub>bulk</sub> = ±0.09‰, and SP = ±0.33‰. Additional details about measurement precision are included in McIlvin & Casciotti (2010). Triplicate samples of tropospheric N<sub>2</sub>O from Woods Hole, MA had  $\delta_{15}\text{N}_a = 15.0 \pm 0.1\text{‰}$ ,  $\delta_{15}\text{N}_b = -1.9 \pm 0.1\text{‰}$ ,  $\delta_{18}\text{O} = 44.4 \pm 0.2\text{‰}$ ,  $\delta_{15}\text{N}_{\text{bulk}} = 6.5 \pm 0.1\text{‰}$ , SP =  $16.9 \pm 0.1\text{‰}$ , and m/z 44 peak area =  $15.6 \pm 0.2$  Vs. All cruise data are included here except two measurements with background interference.

## Data Processing Description

### Data Processing:

The following formulas were used to derive SP-N<sub>2</sub>O and d<sub>15</sub>N<sub>bulk</sub> from d<sub>15</sub>N<sub>a</sub> and d<sub>15</sub>N<sub>b</sub>:

SP = d<sub>15</sub>N<sub>a</sub> - d<sub>15</sub>N<sub>b</sub>,

d<sub>15</sub>N<sub>bulk</sub> = (d<sub>15</sub>N<sub>a</sub> + d<sub>15</sub>N<sub>b</sub>)/2

### BCO-DMO Processing Notes:

- Modified original parameter names to conform with BCO-DMO naming conventions;
- Missing values (blank) were replaced with 'nd' to indicate 'no data';
- Calculated lon from original lon\_360 field;
- Added date\_event from the event log based on the ev\_code field.

[ [table of contents](#) | [back to top](#) ]

---

## Data Files

File
<b>nitrous_oxide.csv</b> (Comma Separated Values (.csv), 29.33 KB) MD5:8d94a32e825815879c0410cf7d1f6006
Primary data file for dataset ID 529599

[ [table of contents](#) | [back to top](#) ]

---

## Related Publications

Frame, C. H., & Casciotti, K. L. (2010). Biogeochemical controls and isotopic signatures of nitrous oxide production by a marine ammonia-oxidizing bacterium. *Biogeosciences Discussions*, 7(2), 3019–3059.

doi:[10.5194/bgd-7-3019-2010](https://doi.org/10.5194/bgd-7-3019-2010)

*Methods*

Frame, C. H., Deal, E., Nevison, C. D., & Casciotti, K. L. (2014). N<sub>2</sub>O production in the eastern South Atlantic: Analysis of N<sub>2</sub>O stable isotopic and concentration data. *Global Biogeochemical Cycles*, 28(11), 1262–1278.

doi:10.1002/2013gb004790 <https://doi.org/10.1002/2013GB004790>

## Results

McIlvin, M. R., & Casciotti, K. L. (2010). Fully automated system for stable isotopic analyses of dissolved nitrous oxide at natural abundance levels. *Limnology and Oceanography: Methods*, 8(2), 54-66.

doi:[10.4319/lom.2010.8.54](https://doi.org/10.4319/lom.2010.8.54)

## Methods

Noble, A. E., Lamborg, C. H., Ohnemus, D. C., Lam, P. J., Goepfert, T. J., Measures, C. I., ... Saito, M. A. (2012). Basin-scale inputs of cobalt, iron, and manganese from the Benguela-Angola front to the South Atlantic Ocean. *Limnology and Oceanography*, 57(4), 989-1010. doi:[10.4319/lo.2012.57.4.0989](https://doi.org/10.4319/lo.2012.57.4.0989)

## Methods

[ [table of contents](#) | [back to top](#) ]

## Parameters

Parameter	Description	Units
cruise_id	Official cruise identifier.	dimensionless
sta	Station number.	dimensionless
lat	Latitude; North is positive.	decimal degrees
lon	Longitude; East is positive. Calculated by BCO-DMO from the original PI-provided lon_360 values.	decimal degrees
lon_360	Longitude measured from 0 to 360 degrees.	decimal degrees
press	Pressure.	decibars (db)
ev_code	Event code; type and number of sampling event; matches cruise event log.	dimensionless
event	Event number from the cruise event log.	dimensionless
date_event	Year-month-day of the event; added by BCO-DMO from the cruise event log. in the format YYYYmmdd	unitless
N2O	Dissolved N2O concentration.	nanomoles per liter (nm/L)
d15Nbulk_N2O	d15Nbulk-N2O = average (bulk) isotope ratio (15N/14N) of both nitrogen atoms in N2O. Calculated as $d15N_{bulk-N2O} = (d15N_{a-N2O} + d15N_{b-N2O})/2$ ; referenced to atmospheric N2.	per mil (‰)
SP_N2O	SP-N2O = site preference of 15N in N2O. Calculated as $(d15N_{a-N2O} - d15N_{b-N2O})$ ; the difference between d15Na-N2O and d15Nb-N2O.	per mil (‰)
d18O_N2O	d18O-N2O = isotope ratio (18O/16O) of oxygen in N2O. Calculated as $d18O = (\frac{[18O]_{sample}}{[18O]_{standard}} - 1) \times 1000‰$ ; referenced to VSMOW.	per mil (‰)
d15Na_N2O	d15Na-N2O = isotope ratio (15N/14N) in the internal nitrogen of N2O; $d15N_{a-N2O} = (\frac{[15N]_{a,sample}}{[15N]_{a,standard}} - 1) \times 1000‰$ ; referenced to atmospheric N2 as the standard.	per mil (‰)
d15Nb_N2O	d15Nb-N2O = isotope ratio (15N/14N) in the external nitrogen of N2O; $d15N_{b-N2O} = (\frac{[15N]_{b,sample}}{[15N]_{b,standard}} - 1) \times 1000‰$ ; referenced to atmospheric N2 as the standard.	per mil (‰)

[ [table of contents](#) | [back to top](#) ]

## Instruments

<b>Dataset-specific Instrument Name</b>	Finnigan DELTA PLUS XP IRMS
<b>Generic Instrument Name</b>	Isotope-ratio Mass Spectrometer
<b>Dataset-specific Description</b>	Isotopic analyses of N <sub>2</sub> O were made using a Finnigan DELTA PLUS XP IRMS calibrated for isotopomer-specific measurements; see Frame & Casciotti (2010) for details.
<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>	Teflon-coated X-Niskin sampling bottles (Ocean Test Equipment)
<b>Generic Instrument Name</b>	Trace Metal Bottle
<b>Dataset-specific Description</b>	Single water samples for N <sub>2</sub> O analyses were collected from acid-cleaned, Teflon-coated X-Niskin sampling bottles (OceanTest Equipment) of 8-liter capacity deployed on an epoxy-coated rosette (Sea-Bird Electronics).
<b>Generic Instrument Description</b>	Trace metal (TM) clean rosette bottle used for collecting trace metal clean seawater samples.

[ [table of contents](#) | [back to top](#) ]

---

## Deployments

KN192-05

<b>Website</b>	<a href="https://www.bco-dmo.org/deployment/57852">https://www.bco-dmo.org/deployment/57852</a>
<b>Platform</b>	R/V Knorr
<b>Report</b>	<a href="http://bcodata.whoi.edu/CoFeMUG/CruiseReport_KN192-5.pdf">http://bcodata.whoi.edu/CoFeMUG/CruiseReport_KN192-5.pdf</a>
<b>Start Date</b>	2007-11-16
<b>End Date</b>	2007-12-13
<b>Description</b>	<p>The South Atlantic subtropical gyre and Benguela Upwelling region were sampled for chemistry and biological properties relating to the trace metal nutrition and phytoplankton diversity and productivity. Specifically cobalt and iron dissolved seawater concentrations will be measured and related to the abundance of cyanobacteria including nitrogen fixers and eukaryotic phytoplankton. The phytoplankton of the Benguela Upwelling region were also examined to determine if their growth was iron or cobalt limited. A total of 27 station locations were occupied in the study area to collect the water chemistry and biological samples for these analyses (see cruise track). Iron and cobalt analyses will be conducted using inductively coupled plasma mass spectrometry and cathodic stripping voltammetry electrochemical methods. The sample preparation and subsequent analyses are technically demanding, but data generated from the cruise samples are being contributed beginning in mid 2009. The CoFeMUG KN192-5 cruise was supported by NSF OCE award # 0452883 <a href="http://www.nsf.gov/awardsearch/showAward.do?AwardNumber=0452883">http://www.nsf.gov/awardsearch/showAward.do?AwardNumber=0452883</a> A station map showing the 27 sampling locations is available as a PDF file. Original cruise data are available from the NSF R2R data catalog CoFeMUG - South Atlantic 2007 Cruise Participant List 1. Mak Saito (Chief Scientist/WHOI) 2. Abigail Noble (Saito/WHOI) 3. Alysia Cox (Saito/WHOI) 4. Whitney Krey (Delong/Saito/MIT/WHOI) 5. Carl Lamborg (clamborg AT whoi.edu/WHOI) 6. Phoebe Lam (pjlam AT whoi.edu WHOI) 7. Chad Hammerschmidt (chammerschmidt AT whoi.edu, Wright State) 8. Caitlin Frame (cframe AT whoi.edu, WHOI/Casciotti Student) 9. Tyler Goepfert (tgoepfert AT whoi.edu Webb/Saito) 10. Jill Sohm (sohm AT usc.edu) 11. Maria Intermaggio 12. Jack DiTullio (leep AT cofc.edu U. Charleston) 13. Peter Lee (DiTullio U. Charleston) 14. Sarah Riseman (DiTullio U. Charleston) 15. Amanda McLenan (amanda.mclennon AT gmail.com, DiTullio U. Charleston) 16. Mike Seracki (Bigelow) 17. Nicole Poulton (Bigelow) 18. Juan Alba, juanalba AT usp.br (Bigelow) 19. Jane Heywood (Bigelow) 20. Gabrielle Rocap (rocap AT whoi.edu, U. Washington) 21. Emily Nahas (enahas AT u.washington.edu) 22. Michele Wrable (mlw22 AT u.washington.edu) 23. Bob Morris (rmorris AT lifesci.ucsb.edu) 24. Christian Frazar (Chris, U. Washington, Morris lab) 25. Jason Hilton (Zehr, UCSC) 26. Reserved for Angolan Observers 27. Reserved for Angolan Observers Collecting GEOTRACES-compliant samples for: 1. Laura Robinson (Pa Th isotopes) 2. Bob Anderson (Pa Th isotopes - intercalibration) 3. Olivier Rouxel (Se and Fe isotopes) 4. Karen Casciotti (N isotopes) 5. Ben Reynolds (Si and Fe isotopes) 6. Chris Measures (Al) 7. Kristin Buck (FeL)</p>

[ [table of contents](#) | [back to top](#) ]

## Project Information

### Cobalt, Iron and Micro-organisms from the Upwelling zone to the Gyre (GAc01) (CoFeMUG)

**Coverage:** South Atlantic subtropical gyre and Benguela upwelling region

The geochemistries of dissolved cobalt (Co) and iron (Fe) in the oceanic water column share several characteristics such as extremely low concentrations, redox chemistry, low solubility, and utilization as micronutrients by marine microbes. Iron has been the subject of considerable research focus in recent years due to its role in limiting phytoplankton productivity in oceanic and coastal upwelling environments. Cobalt has been much less studied, but recent data show it may be important in influencing primary productivity or phytoplankton community composition in certain geographical areas.

The CoFeMUG project predated GEOTRACES, so while it is not formally recognized as a GEOTRACES section, it is considered a GEOTRACES-related project and the CoFeMUG data are GEOTRACES compliant.

State-of-the-art geochemical and molecular biological techniques were used to address biogeochemical questions in the South Atlantic, and focus especially on the two trace metals, cobalt and iron. The 27-day cruise in November and December 2007 to the South Atlantic was designed to study cobalt and iron biogeochemistry and focus on four major hypotheses.

- (1) Large fluxes of labile cobalt are associated with upwelling systems even in Aeolian dominated environments.
- (2) Cobalt and phosphate show correlations in (and only in) surface waters due to micronutrient utilization and rapid remineralization. The slope of the correlation is dependent on the chemical speciation of cobalt.
- (3) The absence of *Trichodesmium* populations in the subtropical and tropical South Atlantic is caused by iron limitation.
- (4) Based on work from the California and Peru Upwelling regimes, primary productivity in the Benguela upwelling regime off of South West Africa may be iron limited or iron-cobalt colimited.

A combination of geochemical and biological/molecular analyses were made across an oligotrophic-upwelling transition to examine how changing metal regimes affect the physiology and growth of the important primary producers *Trichodesmium* and *Synechococcus*.

CoFeMUG project results are published in:

Noble, Abigail E., Carl H. Lamborg, Dan C. Ohnemus, Phoebe J. Lam, Tyler J. Goepfert, Chris I. Measures, Caitlin H. Frame, Karen L. Casciotti, Giacomo R. DiTullio, Joe Jennings, and Mak A. Saito (2012) Basin-scale inputs of cobalt, iron, and manganese from the Benguela-Angola front to the South Atlantic Ocean. *Limnology & Oceanography*. Vol. 57(4), July 2012. pgs 989-1010. doi:10.4319/lo.2012.57.4.0989 ([www.aslo.org/lo/toc/vol\\_57/issue\\_4/0989.pdf](http://www.aslo.org/lo/toc/vol_57/issue_4/0989.pdf))

[ [table of contents](#) | [back to top](#) ]

---

## **Program Information**

### **Ocean Carbon and Biogeochemistry (OCB)**

**Website:** <http://us-ocb.org/>

**Coverage:** Global

The Ocean Carbon and Biogeochemistry (OCB) program focuses on the ocean's role as a component of the global Earth system, bringing together research in geochemistry, ocean physics, and ecology that inform on and advance our understanding of ocean biogeochemistry. The overall program goals are to promote, plan, and coordinate collaborative, multidisciplinary research opportunities within the U.S. research community and with international partners. Important OCB-related activities currently include: the Ocean Carbon and Climate Change (OCCC) and the North American Carbon Program (NACP); U.S. contributions to IMBER, SOLAS, CARBOOCEAN; and numerous U.S. single-investigator and medium-size research projects funded by U.S. federal agencies including NASA, NOAA, and NSF.

The scientific mission of OCB is to study the evolving role of the ocean in the global carbon cycle, in the face of environmental variability and change through studies of marine biogeochemical cycles and associated ecosystems.

The overarching OCB science themes include improved understanding and prediction of: 1) oceanic uptake and release of atmospheric CO<sub>2</sub> and other greenhouse gases and 2) environmental sensitivities of biogeochemical cycles, marine ecosystems, and interactions between the two.

The OCB Research Priorities (updated January 2012) include: ocean acidification; terrestrial/coastal carbon fluxes and exchanges; climate sensitivities of and change in ecosystem structure and associated impacts on biogeochemical cycles; mesopelagic ecological and biogeochemical interactions; benthic-pelagic feedbacks on biogeochemical cycles; ocean carbon uptake and storage; and expanding low-oxygen conditions in the coastal and open oceans.

## 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, 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.

[ [table of contents](#) | [back to top](#) ]

---

## Funding

Funding Source	Award
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-0452883</a>
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1031271</a>
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-0928414</a>
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-0752291</a>

[ [table of contents](#) | [back to top](#) ]