# Nutrient and nitrate isotope data from the southern Benguela upwelling system from February to August 2017

Website: https://www.bco-dmo.org/dataset/811839 Data Type: Cruise Results Version: 1 Version Date: 2020-05-19

#### Project

» <u>Investigation of mechanisms leading to seasonal hypoxia in the Southern Benguela Upwelling System</u> (SBUS Hypoxia)

Contributors	Affiliation	Role
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#### Abstract

Analysed Particulate Organic Matter data, Nutrient data and Nitrate isotope data from the 2017 Integrated Ecosystem Programme: Southern Benguela (IEP:SB) cruises conducted in February, May, and August 2017. The IEP:SB is a multi-disciplinary, multi-institutional platform to undertake relevant science in the Southern Benguela; also functioning as a platform for collaboration and learning. Nitrate+nitrite concentrations were measured on a Lachat QuickChem flow injection analysis platform in a configuration with a detection limit of 0.1  $\mu$ M, while phosphate and nitrite concentrations were measured using standard benchtop techniques on a Thermo Scientific Genesis 30 Visible spectrophotometer in a configuration with a detection limit of 0.05  $\mu$ M. The N and O isotope ratios of the N2O gas were analysed using a Delta V Advantage continuous flow isotope ratio mass spectrometer interfaced with an online N2O extraction and purification system.

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# Coverage

Spatial Extent: N:-29.3817 E:18.28933333 S:-34.5593 W:14.1348 Temporal Extent: 2017-02 - 2017-08

# **Dataset Description**

CTD data:

The temperature and conductivity probes are calibrated annually by the manufacturer while the oxygen sensor was calibrated against discrete seawater samples analyzed for dissolved oxygen concentrations by Winkler titration (Carpenter 1965; Grasshoff et al. 1983).

Nutrients:

Duplicate samples were measured for nitrate+nitrite on different days, and the standard deviation for

duplicates was <0.5  $\mu$ M, with a lower standard deviation for lower concentration samples Duplicate samples for phosphate and nitrite were measured in duplicate on different days of analysis, yielding a standard deviation for duplicates of ≤0.1  $\mu$ M.

Nitrate isotopes:

The N and O isotope ratios of nitrate were measured in triplicate in separate batch analyses and standard deviations for both  $\delta$ 15N and  $\delta$ 18O were <0.3‰. Certified nitrate isotope ratio reference materials in nutrient-free seawater were measured in all batch analyses. These included IAEA-NO3-, with  $\delta$ 15N of 4.7 ± 0.2‰ vs. N2 air (Gonfiantini et al. 1995) and and  $\delta$ 18O of 25.6 ± 0.4‰ vs. VSMOW (Böhlke et al. 2003), and USGS-34, with  $\delta$ 15N of -1.8 ± 0.1‰ vs. N2 air and  $\delta$ 18O of -27.9 ± 0.3‰ vs. VSMOW (Böhlke et al. 2003). Nitrate isotstandards in individual runs were diluted in nutrient-free seawater to concentrations similar to those of the samples to account for potential matrix effects on the  $\delta$ 18O measurements (Weigand et al. 2016). Reproducibility was monitored by analysis of an internal seawater nitrate standard from the deep North Atlantic.

#### Methods & Sampling

The methods on how the samples were collected and processed for the attached dataset can be found in the methodology section of Flynn et al. (2019).

Hydrographic measurements were made using a conductivity-temperature-depth (CTD) profiler fitted with a temperature, salinity and oxygen sensor.

Nitrate+nitrite concentrations were measured following published auto-analysis protocols (Diamond 1994; Grasshoff 1976), and nitrite and phosphate concentrations were determined using benchtop colourimetric methods (Strickland and Parsons 1968; Bendschneider and Robinson 1952; Parsons et al. 1984).

Nitrate N and O isotope ratios were measured using the "denitrifier method" (Sigman et al. 2001; Casciotti et al. 2002; McIlvin and Casciotti 2011).

Seawater samples were collected at discrete depths from the surface to the seafloor using a tethered rosette holding twelve 6-L Niskin bottles. At each CTD station, nutrient and nitrate isotope samples were collected filtered (0.22  $\mu$ m PES membrane syringe filter) throughout the water column in 60 mL HDPE bottles. Each bottle was rinsed three times prior to being filled, and then immediately frozen at -20°C pending analysis. All nutrient samples were analysed within a year from collection, and nitrate isotopes within 18 months of collection.

#### **Data Processing Description**

BCO-DMO Processing Notes:

- added conventional header with dataset name, PI name, version date
- modified parameter names to conform with BCO-DMO naming conventions
- converted positive latitude values for SHGML005 in May 2017 to negative values as they were incorrect.

- removed extra data row at bottom of Aug sheet.

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# **Data Files**

File
iep.csv(Comma Separated Values (.csv), 119.29 KB) MD5:80b2106b6606b3cc211551638df164b6
Primary data file for dataset ID 811839

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# **Related Publications**

Bendschneider, K., and Robinson, R.J. (1952). A new spectrophotometric method for the determination of nitrite in sea water. Technical Report No. 8. University of Washington Methods

Böhlke, J. K., Mroczkowski, S. J., & Coplen, T. B. (2003). Oxygen isotopes in nitrate: new reference materials for 180:170:160 measurements and observations on nitrate-water equilibration. Rapid Communications in Mass Spectrometry, 17(16), 1835–1846, doi:10.1002/rcm.1123 Methods

CARPENTER, J. H. (1965). THE CHESAPEAKE BAY INSTITUTE TECHNIQUE FOR THE WINKLER DISSOLVED OXYGEN METHOD. Limnology and Oceanography, 10(1), 141–143. doi:10.4319/lo.1965.10.1.0141 Methods

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 Methods

Diamond, D. (1994). QuikChem Method 10-114-21-1-B: Silicate by flow injection analysis. Lachat Instruments Methods

Gonfiantini, R., Stichler, W., & Rozanski, K. (1995). Standards and intercomparison materials distributed by the International Atomic Energy Agency for stable isotope measurements (IAEA-TECDOC--825). International Atomic Energy Agency (IAEA) Methods

Grasshoff, K. (1976). Methods of seawater analysis. Verlag Chemie, Weinheim and New York Methods

Grasshoff, K., Kremling, K., and Ehrhardt, M. (1983). Methods of Seawater Analysis. Verlag Chemia, Florida 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 Methods

Parsons, T. R., Maita, Y., & Lalli, C.M. (1984). A manual of chemical and biological methods for seawater analysis. Pergamon Press. doi:10.1016/c2009-0-07774-5 https://doi.org/10.1016/c2009-0-07774-5 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 Methods

Strickland, J.D.H and Parsons, T.R. (1968) A Practical Handbook of Seawater Analysis. Fisheries Research Board of Canada Bulletin 167, 71-75 [as seen in The Quarterly Review of Biology (1969) 44(3), 327-327. doi:10.1086/406210] 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 Methods

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# **Parameters**

Parameter	Description	Units
Cruise	name of the cruise	unitless

Month	Month of observation in text	unitless
Year	year of observation in yyyy format	unitless
Station_ID	identifier for the station	unitless
Monitoring_line	identifier for the mooring line	unitless
Latitude	latitude with negative values indicating South	decimal degrees
Longitude	longitude with positive values indicating West	decimal degrees
Depth	water depth of observation	meters (m)
Temperature	Temperature	degrees Celsius (C)
Salinity	Salinity	psu
Sigma_theta	sigma-theta	kilograms per meter cubed (kg/m3)
NO3_NO2	[NO3-+NO2-]	microMole (uM)
NO3_NO2_Stdev	standard deviation of [NO3-+NO2-]	micr
NO2	NO2-	microMole (uM)
NO2_Stdev	standard deviation of NO2-	microMole (uM)
PO43	PO43-	microMole (uM)
PO43_Stdev	standard deviation of PO43-	microMole (uM)
02	02	microMole (uM)
AOU	Apparent Oxygen Utilization (AOU)	microMole (uM)
N15_NO3	15N_NO3	parts per thousand

N15_stdev	standard deviation of $\delta 15N$	parts per thousand
018_NO3	180_NO3	parts per thousand
O18_stdev	standard deviation of $\delta 180$	parts per thousand

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# Instruments

Dataset- specific Instrument Name	CTD profiler
Generic Instrument Name	CTD - profiler
Dataset- specific Description	Hydrographic measurements were made using a conductivity-temperature-depth (CTD) profiler fitted with a temperature, salinity and oxygen sensor.
Generic Instrument Description	The Conductivity, Temperature, Depth (CTD) unit is an integrated instrument package designed to measure the conductivity, temperature, and pressure (depth) of the water column. The instrument is lowered via cable through the water column. It permits scientists to observe the physical properties in real-time via a conducting cable, which is typically connected to a CTD to a deck unit and computer on a ship. The CTD is often configured with additional optional sensors including fluorometers, transmissometers and/or radiometers. It is often combined with a Rosette of water sampling bottles (e.g. Niskin, GO-FLO) for collecting discrete water samples during the cast. This term applies to profiling CTDs. For fixed CTDs, see <a href="https://www.bco-dmo.org/instrument/869934">https://www.bco-dmo.org/instrument/869934</a> .

Dataset- specific Instrument Name	Lachat QuickChem flow injection analysis platform
Generic Instrument Name	Flow Injection Analyzer
Dataset- specific Description	Nitrate+nitrite concentrations were measured using a Lachat QuickChem flow injection analysis platform in a configuration with a detection limit of 0.1 $\mu$ M.
Generic Instrument Description	An instrument that performs flow injection analysis. Flow injection analysis (FIA) is an approach to chemical analysis that is accomplished by injecting a plug of sample into a flowing carrier stream. FIA is an automated method in which a sample is injected into a continuous flow of a carrier solution that mixes with other continuously flowing solutions before reaching a detector. Precision is dramatically increased when FIA is used instead of manual injections and as a result very specific FIA systems have been developed for a wide array of analytical techniques.

Dataset- specific Instrument Name	Delta V Advantage continuous flow isotope ratio mass spectrometer	
Generic Instrument Name	Isotope-ratio Mass Spectrometer	
Dataset- specific Description	The N and O isotope ratios of the N2O gas were analysed using a Delta V Advantage continuous flow isotope ratio mass spectrometer interfaced with an online N2O extraction and purification system.	
Generic Instrument Description	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).	

Dataset-specific Instrument Name	Thermo Scientific Genesis 30 Visible spectrophotometer
Generic Instrument Name	Spectrophotometer
Dataset-specific Description	Phosphate and nitrite concentrations were measured using a Thermo Scientific Genesis 30 Visible spectrophotometer in a configuration with a detection limit of 0.05 $\mu$ M.
Generic Instrument Description	An instrument used to measure the relative absorption of electromagnetic radiation of different wavelengths in the near infra-red, visible and ultraviolet wavebands by samples.

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# **Project Information**

# Investigation of mechanisms leading to seasonal hypoxia in the Southern Benguela Upwelling System (SBUS Hypoxia)

Coverage: Southern Benguela Upwelling System

#### NSF Award Abstract:

The Southern Benguela Upwelling System (SBUS) in the eastern Atlantic Ocean ranks among the most fertile region in the world ocean, host to economically important fishing grounds. Unfortunately, waters of the SBUS are subject to events wherein dissolved oxygen is severely depleted, a condition also known as seasonal hypoxia, which have been observed to cause substantial fish kills. To gain a better understanding of the processes triggering severe hypoxic events, the study will combine field observations (analyzing water samples for dissolved nitrate, nitrite, ammonium, soluble reactive phosphorus, and silicic acid, as well as nitrate isotopic ratios to identify the origin and fate of nutrients in upwelling systems) and modeling. This combined approach is a powerful means of identifying the processes that contribute to the development of hypoxia in the SBUS and the mechanisms gleaned from the proposed study are likely to extend beyond the SBUS to other upwelling regions, such as the Northern Benguela, California and Peru Upwelling Systems. For outreach activities, graduate students would create a short film on their research in South Africa. This film, made available on the University of Connecticut and the University of Cape Town websites and YouTube, would serve as a means of communicating the science to broader audiences. Two graduate students would be supported and trained as part of this project. These students would have the opportunity to work with the South African collaborators at the University of Cape Town, Drs. Sarah Fawcett and Jennifer Veitch, involved in the study.

The Southern Benguela Upwelling System (SBUS), off the coasts of South Africa and Namibia, is subject to severe seasonal hypoxia which has been observed to have catastrophic impacts on wildlife, fisheries, and national economies. Researcher from the University of Connecticut posit that the propensity for hypoxic

events in this region is linked to the extent of nutrient trapping on the shelf inshore of the hydrographic fronts. This, in turn, influences the intensity of subsequent blooms, and the consequent oxygen demand when this organic material is ultimately decomposed at the shelf bottom. To confirm the role of nutrient cycling in modulating hypoxic event, the scientists will utilize a combination of observations and quantitative simulations. Analyses of dissolved nutrients and nitrate isotope ratios from water samples collected on quarterly monitoring cruises in the SBUS will be used to assess the role of nutrient cycling in modulating hypoxic events. Concurrently, an idealized circulation model of the SBUS will be initiated to test the hypotheses surrounding inshore nutrient trapping and incident hypoxia. Specifically, the focus will be on the potential roles of wind intensity and periodicity, shelf frontal structure, and the alongshore pressure gradient in modulating the burden of recycled nutrients trapped on the shelf and its association with hypoxia. Finally, the ocean circulation and biogeochemistry of the SBUS will be modeled using a realistic hind-cast model forced with realistic atmospheric, tidal, and ocean boundary conditions to make hind-cast simulations of the 3-D circulation and hydrography throughout the domain. This coupled physical-biogeochemical model would be queried to fully investigate the proposed nutrient trapping mechanism and define its role in modulating the intensity of hypoxia inter-annually and from which a prognostic model can be developed.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

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# Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-1924270</u>

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