Discrete sample measurements of dissolved oxygen, dissolved inorganic carbon, and total alkalinity from US Overturning in the Subpolar North Atlantic Program (OSNAP) cruises in 2020 and 2022 (AR45 and AR69-03)

Website: https://www.bco-dmo.org/dataset/934025
Data Type: Cruise Results
Version: 1
Version Date: 2024-08-30

Project
» Collaborative Research: Gases in the Overturning and Horizontal circulation of the Subpolar North Atlantic Program (GOHSNAP) (GOHSNAP)

Contributors	Affiliation	Role
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Abstract
This dataset contains discrete sample measurements of dissolved oxygen, dissolved inorganic carbon, and total alkalinity collected during cruises in 2020 (AR45) and 2022 (AR69-03) to recover and redeploy Overturning in the Subpolar North Atlantic Program (OSNAP) moorings in the Labrador Sea and western Irminger Sea. Samples in this dataset were collected as part of Gases in the Overturning and Horizontal circulation of the Subpolar North Atlantic Program (GOHSNAP), which has added moored oxygen sensors to the OSNAP mooring array, beginning in 2020. We provide the discrete sample measurements alongside salinity- and oxygen- calibrated Conductivity Temperature Depth (CTD) and oxygen sensor data from the depths where Niskin bottles were closed for sample collection.

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Coverage

Location: Labrador Sea (57.35°N, 50.10°W), Irminger Sea (60.46°N, 38.44°W)
Spatial Extent: **N**:62.62674 **E**:-27.7048 **S**:58.89642 **W**:-51.32417
Temporal Extent: 2020-06-30 - 2022-09-22

Methods & Sampling

These samples were during cruises onboard the R/V Neil Armstrong to recover and redeploy mooring infrastructure of the international Overturning in the Subpolar North Atlantic Program (OSNAP) in 2020 (AR45) and 2022 (AR69-03). The mooring infrastructure maintained on these cruises is located in the eastern Labrador Sea (referred to as the LS line) and western Irminger Sea (referred to as the CF line). Beginning in 2020, the Gases in the Overturning and Horizontal circulation of the Subpolar North Atlantic Program (GOHSNAP) has added moored oxygen sensors to these sections of the OSNAP mooring array. During these cruises, Conductivity Temperature Depth (CTD) casts are conducted to provide data necessary to calibrate the moored sensors (Miller et al., in review), as well as hydrographic data that provide a valuable dataset in and of themselves.

This dataset contains dissolved oxygen, dissolved inorganic carbon (DIC), and total alkalinity (TA) measurements from discrete water samples collected from Niskin bottles on the CTD rosette. Additional context about the cruises and all cruise operations can be found in the cruise reports for AR45 (2020) and AR69-03 (2022). We note that the 2020 cruise was conducted in the context of operational and cruise staffing limitations imposed by the COVID-19 pandemic, which is reflected in the lower number of discrete samples collected and in modifications to the procedure for dissolved oxygen sample analysis.

Data Processing Description

Dissolved Oxygen:

Samples were collected into volume-calibrated flasks and preserved for Winkler dissolved oxygen analysis following standard protocols (Langdon, 2010). For AR69-03, in 2022, all samples were titrated onboard the ship within 24-48 hours of collection using a custom-built Winkler titrator with automated potentiometric end point detection (control software available here: Nicholson et al., 2023). For AR45, in 2020, COVID-19 pandemic restrictions precluded the ability to conduct titrations onboard the ship and samples were instead preserved following the procedures of Zhang et al. 2002 and titrated on land at the end of the cruise.

Precision of the sample collection and analysis procedure is determined by agreement between replicate measurements from the same Niskin bottle. Due to the need to preserve samples for land-based analysis, all samples from AR45 were collected in triplicate. After removal of measurements where outlier data indicated that samples had not been successfully preserved (4 of 63 total samples), median agreement among replicates was 0.15% (0.4 µmol/kg). For AR69-03, all samples were collected either in duplicate or in triplicate and median agreement among replicates was 0.11% (0.3 µmol/kg). In some cases, larger discrepancies among replicates reflect errors in sample collecting and/or preservation; these results are reported for completeness but are flagged as questionable based on outlier analysis conducted in using these samples to calibrate the SBE43 oxygen sensor included in the ship's sensor package (see Related Dataset: Fogaren and Palevsky, 2024).

Accuracy of sample measurements depends on standardization of the sodium thiosulfate titrant based on a reference standard. The sodium thiosulfate titrant used on each cruise was determined by standardization with a 0.01N potassium iodate reference solution from Ocean Scientific International Ltd (OSIL). Lab-prepared potassium iodate standards, measured routinely throughout AR69-03 and before, during, and after land-based analysis of the AR45 samples to verify titration accuracy and stability, were verified and adjusted by measurements against the OSIL standard.

Dissolved Inorganic Carbon and Total Alkalinity:

Samples were collected for dissolved inorganic carbon (DIC) and total alkalinity (TA) analysis following standard protocols (Dickson et al., 2007). Samples were collected into either 250 mL or 500 mL borosilicate glass bottles and preserved with saturated mercuric chloride (100 µL in 250 mL bottles, 200 µL in 500 mL bottles) for later analysis.

Samples were analyzed at the Boston College Marine Biogeochemistry Laboratory. DIC was analyzed using an Apollo SciTech AS-C6L DIC Analyzer and TA was analyzed using an Apollo SciTech AS-ALK2 TA Analyzer. Both DIC and TA were measured from each sample bottle. All DIC measurements were made on the day the bottle was opened for analysis, and TA measurements were made within the same week. DIC and TA instruments were calibrated daily and monitored throughout each analysis session by measuring Certified Reference Materials (Andrew Dickson, UCSD).

Analytical replicates were measured for all samples such that after analytical outliers (sigma) were removed, all samples for both DIC and TA retained at least two replicate measurements (median number of replicates for DIC = 3; median number of replicates for TA = 4). Analytical precision was determined for each sample as the standard deviation of analytical replicates. Mean analytical precision for all DIC samples in this dataset is 0.6 µmol/kg. Mean analytical precision for all TA samples in this dataset is 1.8 µmol/kg. Individual samples are flagged as questionable (QC flag = 3) if the analytical precision is >8 µmol/kg. Individual samples for DIC are also flagged as questionable (QC flag = 3) if CRMs run prior and subsequent to the sample in question differ by >8 µmol/kg.

BCO-DMO Processing Description

* Merged data from cruise AR45 and AR69-03 into 1 dataset
* Added cruise id to dataset
* Added ISO date notation to dataset
* Converted missing value flag 9 and missing identifier -999 to blank

Problem Description

Quality flags applied to this dataset follow the recommendations of Jiang et al. 2022:

1 = not evaluated/quality unknown
2 = acceptable
3 = questionable
4 = known bad
6 = median of replicates
9 = Missing value

Quality flags applied to the discrete dissolved oxygen data refer to the fit between the data and the non-linear multiple regression model used to generate the final calibrated dissolved oxygen sensor data based on the fit to the discrete samples. For details on the processing of the calibrated CTD and oxygen sensor data, see Related Dataset: Fogaren and Palevsky, 2024. Flags are applied individually to all oxygen measurements.

For AR69-03, samples with high oxygen concentrations (>316 µmol/kg) resulted in poor model fit between the CTD dissolved oxygen sensor data and the discrete Winkler samples. This may either indicate issues in the CTD dissolved oxygen sensor's sensitivity and fit at these concentrations, or it may indicate a systematic measurement error in the Winkler dissolved oxygen analysis (for instance, due to possible oxygen degassing prior to sample collection and preservation). For all samples from AR69-03 with discrete dissolved oxygen measurements >316 µmol/kg (57 individual Niskin bottles, each sampled in either duplicate or triplicate), samples with poor replicate agreement (>0.5% error) are flagged as a "known bad (analytical error)." Remaining samples with oxygen concentrations >316 µmol/kg and acceptable replicate precision are flagged as "not evaluated", since they were not included in the CTD dissolved oxygen sensor calibration.

1 = not evaluated
2 = acceptable (fits model)
3 = questionable (model-determined outlier)
4 = known bad (analytical error)
9 = missing value

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Data Files

File	
934025_v1_discretemeasurements.csv	(Comma Separated Values (.csv), 54.69 KB) MD5:ea101e225ebfafe78aeea4d80bda1610
Primary data file for dataset ID 934025, version 1	

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Related Publications

Dnicholson, Barrette, J., & Zoehakai. (2023). *boom-lab/winkler-titrator: v0.1.0-alpha* (v0.1.0-alpha) [Computer software]. Zenodo. https://doi.org/10.5281/ZENODO.8048208 https://doi.org/10.5281/zenodo.8048208
Software

Jiang, L.-Q., Pierrot, D., Wanninkhof, R., Feely, R. A., Tilbrook, B., Alin, S., Barbero, L., Byrne, R. H., Carter, B. R., Dickson, A. G., Gattuso, J.-P., Greeley, D., Hoppema, M., Humphreys, M. P., Karstensen, J., Lange, N., Lauvset, S. K., Lewis, E. R., Olsen, A., ... Xue, L. (2022). Best Practice Data Standards for Discrete Chemical Oceanographic Observations. Frontiers in Marine Science, 8. https://doi.org/10.3389/fmars.2021.705638
Methods

Langdon, C. (2010). *Determination of Dissolved Oxygen in Seaweater By Winkler Titration using Amperometric Technique. In, The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. Version 1,* GO-SHIP. https://doi.org/10.25607/OBP-1350
Methods

Miller, U. K., Fogaren, K., Atamanchuk, D., Johnson, C., Koelling, J., Le Bras, I., Lindeman, M., Nagao, H., Nicholson, D. P., Palevsky, H. I., Park, E., Yoder, M., and Palter, J. B. (in review) Oxygen optodes on oceanographic moorings: recommendations for deployment and in-situ calibration, in review at Frontiers in Marine Sciences.
Methods

Zhang, J.-Z., Berberian, G., & Wanninkhof, R. (2002). Long-term storage of natural water samples for dissolved oxygen determination. Water Research, 36(16), 4165–4168. https://doi.org/10.1016/s0043-1354(02)00093-3 https://doi.org/10.1016/S0043-1354(02)00093-3
Methods

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Related Datasets

IsRelatedTo

Fogaren, K. E., Palevsky, H. I. (2024) **Bottle-calibrated dissolved oxygen (DO) profiles from US Overturning in the Subpolar North Atlantic Program (OSNAP) cruises in 2020 and 2022 (AR45 and AR69-03).** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2024-08-30 doi:10.26008/1912/bco-dmo.933743.1 [view at BCO-DMO]

Rolling Deck To Repository. (2021). *CTD (Conductivity, Temperature, Depth) data collected during research cruise AR45 using a Sea-Bird SBE-911+ instrument system onboard the platform RV Neil Armstrong* (Version 1) [Data set]. Rolling Deck to Repository (R2R) Program. https://doi.org/10.7284/141990

Rolling Deck To Repository. (2023). *CTD (Conductivity, Temperature, Depth) data collected during research cruise AR69-03 using a SeaBird SBE-911+ instrument system onboard the platform RV Neil Armstrong* (Version 1) [Data set]. Rolling Deck to Repository (R2R) Program. https://doi.org/10.7284/153092

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Parameters

Parameter	Description	Units
Cruise_ID	Cruise Identification (AR45 or AR6903)	unitless
Station_ID	Station Identification (equivalent to Cast Number for this cruise)	unitless

Niskin_ID	Unique Niskin bottle number from the CTD rosette	unitless
Year_UTC	Calendar Year in UTC	unitless
Month_UTC	Calendar Month in UTC	unitless
Day_UTC	Calendar Day in UTC	unitless
ISO_Date_UTC	ISO notation of date (UTC timezone)	unitless
Latitude	Latitude in decimal degrees North	decimal degrees
Longitude	Longitude in decimal degrees East (negative for western hemisphere)	decimal degrees
CTDPRES	Hydrostatic pressure recorded from CTD at the depth where the sample was taken	dbar
Depth	Depth at which sample was taken	meters
CTDTEMP_ITS90	In situ temperature recorded from CTD on the ITS-90 scale	degrees Celsius
CTDTEMP_flag	Quality control flag; all data processed by McRaven (2022) marked as 2	unitless
CTDSAL_PSS78	Calibrated salinity (Practical Salinity Scale of 1978) calculated from conductivity recorded with CTD	unitless
CTDSAL_flag	Quality control flag; all data processed by McRaven (2022) marked as 2	unitless
CTDOXY	Calibrated dissolved oxygen content from oxygen sensor mounted on the CTD	umol/kg
CTDOXY_flag	Quality control flag; see data documentation with this and Fogaren et al. dataset	unitless
Oxygen1	Dissolved oxygen content measured from discrete-bottle-based Winkler titration by OOI program	umol/kg
Oxygen1_flag	Quality control flag; see data documentation with this dataset	unitless

Oxygen2	Dissolved oxygen content measured from discrete-bottle-based Winkler titration by this project team	umol/kg
Oxygen2_flag	Quality control flag; see data documentation with this dataset	unitless
Oxygen3	Dissolved oxygen content measured from discrete-bottle-based Winkler titration by this project team	umol/kg
Oxygen3_flag	Quality control flag; see data documentation with this dataset	unitless
DIC	Total dissolved inorganic carbon content	umol/kg
DIC_flag	Quality control flag; see data documentation with this dataset	unitless
TA	Total alkalinity content	umol/kg
TA_flag	Quality control flag; see data documentation with this dataset	unitless

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Instruments

Dataset-specific Instrument Name	Apollo SciTech AS-ALK2 TA Analyzer
Generic Instrument Name	Apollo SciTech AS-ALK2 total alkalinity titrator
Generic Instrument Description	An automated acid-base titrator for use in aquatic carbon dioxide parameter analysis. The titrator provides standardisation and sample analysis, using the Gran titration procedure for alkalinity determination of seawater and brackish waters. It is designed for both shipboard and land based laboratory use. The precision of the instrument is 0.1 percent or higher, and sample volumes may range from 10-25 ml. Titration takes approximately 8 minutes per sample, and the repeatability is within plus or minus 1-2 micromoles per kg.

Dataset-specific Instrument Name	Apollo SciTech AS-C6L DIC Analyzer
Generic Instrument Name	Apollo SciTech AS-C6L Dissolved Inorganic Carbon (DIC) analyzer
Generic Instrument Description	An instrument designed for the analysis of dissolved inorganic carbon in samples from various aquatic environments. It comprises of a laser-based CO2 detector (LI-7815), a digital syringe pump, a mass flow controller, CO2 stripping reactor, an electronic cooling system and a computer communication assembly (RS-485, USB). The AS-C6L supersedes the earlier AS-C3 model, which used non-dispersive infra-red CO2 detection (LI-7000, discontinued). The AS-C6L improves on the AS-C3 by incorporating a multi-sampler of one set of standards plus 8 samples, and uses improved Apollo SciTech software. The AS-C6L is suitable for use in either shipboard or land-based laboratories. It maintains a precision of +/-0.1 % for seawater (or +/-2 umol/kg), enables sample volumes ranging from 0.5 - 3.5 ml per analysis, and an analytical rate of approximately 3 minutes.

Dataset-specific Instrument Name	Custom-built Winkler dissolved oxygen titrator
Generic Instrument Name	Winkler Oxygen Titrator
Dataset-specific Description	Custom-built Winkler dissolved oxygen titrator: Documentation and code developed and used for oxygen titrations (Nicholson et al., 2023: https://doi.org/10.5281/zenodo.8048208)
Generic Instrument Description	A Winkler Oxygen Titration system is used for determining concentration of dissolved oxygen in seawater.

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Deployments

AR69-03

Website	https://www.bco-dmo.org/deployment/933797
Platform	R/V Neil Armstrong
Report	https://cchdo.ucsd.edu/cruise/33VB20220819
Start Date	2022-08-19
End Date	2022-09-24

AR45

Website	https://www.bco-dmo.org/deployment/933794
Platform	R/V Neil Armstrong
Report	https://doi.org/10.35090/gatech/66767
Start Date	2020-06-23
End Date	2020-08-01

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Project Information

Collaborative Research: Gases in the Overturning and Horizontal circulation of the Subpolar North Atlantic Program (GOHSNAP) (GOHSNAP)

Coverage: Subpolar North Atlantic

NSF Award Abstract:
Every winter, frigid winds blowing eastward from the North American continent cool the surface waters of the Labrador Sea, which is situated between Canada and Greenland. As the ocean cools, oxygen and carbon dioxide are mixed from the atmosphere into a thick layer of water that ultimately spreads southward to fill a large volume of the North Atlantic and beyond. The presence of this water mass prevents the North Atlantic anywhere from becoming completely devoid of oxygen. Vertical mixing in the Labrador Sea also redistributes carbon dioxide into the deep ocean, where it can remain for hundreds of years, preventing it from contributing to the greenhouse effect. Yet, the processes governing the uptake of gases by the ocean are not well understood or quantified. Given that, over the last century, the ocean has become steadily more depleted in oxygen while also absorbing a large fraction of anthropogenic carbon dioxide, observing gas exchange processes is essential for understanding and predicting the evolution of the ocean and climate system. The circulation of the Labrador Sea has been monitored since 2014 with an array of instrumented cables extending from the seafloor to nearly the ocean surface. This project adds gas sensors to this array to investigate the rates and processes governing gas exchange. Through this project, a student and postdoc will be trained in interdisciplinary oceanography with a rich network of international collaborators. Responding to the need to increase public ocean literacy, the project scientists will work with University of Rhode Island's Inner Space Center to broadcast live, interactive science sessions to educators at partner high schools and will follow-up with in-person science cafés at three participating schools.

Given the unique role of the Labrador Sea in providing a pathway for oxygen (O_2) and carbon dioxide (CO_2) to enter the intermediate depths of the ocean, a quantification and mechanistic understanding of the gas uptake and transport in the basin is a leading scientific priority. Oxygenation of Labrador Sea water prevents large-scale hypoxia from developing anywhere in the Atlantic Ocean and anthropogenic CO_2 storage in the basin is the highest in the global ocean. The assumption that, in the Atlantic Ocean, O_2 and CO_2 uptake and their variability are tied to the dynamics of heat loss and the overturning circulation pervades the literature but has never been evaluated on the basis of direct observations. Thus, GOHSNAP (Gases in the Overturning and Horizontal circulation of the Subpolar North Atlantic Program) addresses this gap and the urgent need to better understand interactions between gas uptake, transport, and the overturning circulation. Specifically, this program will provide a continuous 2-year record of the trans-basin, full water column transport of O_2 across the southern boundary of the Labrador Sea, leveraging the mooring infrastructure of the US-lead, international Overturning in the Subpolar North Atlantic Program (OSNAP). The addition of O_2 sensors at various depths on this array, supplemented by observations collected by autonomous platforms will allow for the quantification of O_2 export from the Labrador Sea. The data will further be used to empirically model carbon concentrations and estimate carbon export. Proposed instruments will also measure the mixed layer O_2 and pCO_2 for two winters, from which air-sea gas exchange will be calculated and compared against analogous observations in the convective interior of the Labrador Sea.

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)	OCE-1947829
NSF Division of Ocean Sciences (NSF OCE)	OCE-1947970
NSF Division of Ocean Sciences (NSF OCE)	OCE-1947567

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