## Supplementary discrete sample measurements of dissolved oxygen, dissolved inorganic carbon, and total alkalinity from Ocean Observatories Initiative (OOI) cruises to the Irminger Sea Array 2018-2019

Website: https://www.bco-dmo.org/dataset/904722 Data Type: Cruise Results Version: 1 Version Date: 2023-07-19

#### Project

» <u>Collaborative Research: The Annual Cycle of the Biological Carbon Pump in the Subpolar North Atlantic</u> (OOI Irminger BCP)

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 yearly Ocean Observatories Initiative (OOI) turn-around cruises to maintain the Irminger Sea Array (60.46°N, 38.44°W). Samples in this dataset were collected as part of an ancillary research project that joined the OOI turn-around cruises in June 2018 and August 2019 as part of ongoing efforts to enable OOI biogeochemical sensor data to be used to address scientific questions about ocean carbon cycling and the biological carbon pump. Discrete sample data collected and analyzed by this research team complement data collected by the OOI program as part of routine turn-around cruise activities. We provide the supplementary measurements made by our team alongside salinity- and oxygen- calibrated Conductivity Temperature Depth (CTD) and oxygen sensor data from the depths where Niskin bottles were closed for sample collection and additional discrete oxygen measurements made by the OOI team.

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## Coverage

**Spatial Extent**: N:62.7715 **E**:-28.6567 **S**:59.7123 **W**:-39.8835 **Temporal Extent**: 2018-06-06 - 2019-08-15

## **Dataset Description**

The Ocean Observatories Initiative (OOI) is a long-term NSF-funded program that deploys autonomous sensors on both moored and mobile platforms at multiple locations, including the Global Irminger Sea Array (60.46°N, 38.44°W) (Trowbridge et al., 2019). The OOI program conducts yearly turn-around cruises to the Irminger Sea Array to recover and redeploy moorings and gliders deployed year-round at this site. During these cruises the OOI program routinely conducts Conductivity Temperature Depth (CTD) casts and collects water samples from Niskin bottles on the CTD rosette for discrete sample analysis. These turn-around cruise data are critical for validation and calibration of the data from sensors deployed year-round and also provide a valuable dataset in and of themselves (Palevsky et al., 2023).

For this project, our team participated in two of the yearly turn-around cruises to the OOI Irminger Sea Array (AR30-03, 4-24 June, 2018 and AR35-05, 2-25 August, 2019) and collected supplementary additional samples from CTD casts to further support efforts to improve the capacity to produce high-quality data products from OOI's biogeochemical sensors to enable analysis of scientific questions about the ocean's biological carbon pump and other carbon cycling processes (Palevsky and Nicholson, 2018; Palevsky et al., 2023).

These supplemental data provided here were collected in coordination with data collected by the OOI program. The complete collection of shipboard data and cruise documentation from these cruises is available from an OOI managed document storage system called Alfresco (see related publications), following the path: OOI > Global Irminger Sea Array > Cruise Data > {Cruise ID}. For more information on OOI data access options and recommendations for use of cruise data to calibrate OOI biogeochemical sensors, see the OOI Biogeochemical Sensor Data Best Practices and User Guide (Palevsky et al., 2023).

Full cruise data from the OOI Irminger Sea cruises for which discrete sample data are presented here can be accessed via the Rolling Deck to Repository (R2R, see deployments) and OOI's Alfresco data management server (see related publications):

- Irminger Sea 5 cruise, June 2018, AR30-03. Alfresco path: Global Irminger Sea Array > Cruise Data > Irminger\_Sea-05\_AR30-03\_2018-06-05
- Irminger Sea 6 cruise, August 2019, AR35-05. Alfresco path: Global Irminger Sea Array > Cruise Data > Irminger\_Sea-06\_AR35-05\_2019-08-02

The McRaven 2022 datasets (see related datasets) provide salinity-calibrated Conductivity Temperature Depth (CTD) data from the OOI Irminger Sea cruises for which discrete sample data are presented here.

#### Methods & Sampling

#### Dissolved Oxygen:

Samples were collected and preserved for Winkler dissolved oxygen analysis following standard protocols (Langdon, 2010). Supplementary samples collected for this project were collected in duplicate into volumecalibrated flasks and 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: Nicholson et al., 2023).

Precision of the sample collection and analysis procedure is determined by agreement between replicate measurements from the same Niskin bottle. Median agreement of replicates across both cruises was 0.12% (0.4  $\mu$ mol/kg).

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 Fujifilm WAKO chemicals. Lab-prepared potassium iodate standards, measured routinely throughout both cruises to verify titration accuracy and stability, were verified and adjusted by measurements against the WAKO standard.

Dissolved oxygen discrete measurements collected and analyzed by the OOI program as part of their routine operations are labeled as Oxygen1. The supplementary dissolved oxygen discrete measurements collected for this project are labeled as Oxygen2 and Oxygen3. Intercomparison across samples collected from the same Niskin bottles by the two groups yielded an offset of  $0.5\pm1.5 \ \mu mol/kg$  for AR30-03 (June 2018) and  $0.4\pm0.6 \ \mu mol/kg$  for AR35-05 (August 2019).

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  $\mu$ L in 250 mL bottles, 200  $\mu$ L 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 (>SD) 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 = 5). 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 0.8  $\mu$ mol/kg. Mean analytical precision for all TA samples in this dataset is 2.9  $\mu$ mol/kg. Individual samples are flagged as questionable (QC flag = 3) if the analytical precision is >8 umol/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  $\mu$ mol/kg.

#### **Data Processing Description**

For details on the processing of the calibrated CTD and oxygen sensor data, see Fogaren and Palevsky, 2023 (see Related Datasets below).

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.

- 1 = not evaluated
- 2 = acceptable (fits model)
- 3 = questionable (model-determined outlier)
- 9 = missing value

Flags are applied individually to all oxygen measurements, both from the OOI program measurements and from supplementary measurements completed for this project.

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

During the August 2019 cruise (AR35-05), failure of the pylon on the CTD rosette precluded the ability to automatically trip Niskin bottles for the majority of the cruise, until a replacement pylon was able to be delivered to the ship. No bottle sample measurements for this cruise are reported prior to cast 10, which was the first cast after the replacement pylon was installed. During AR35-05, there was also an un-resolved issue with the primary CTD and SBE43 sensor oxygen measurements on the CTD rosette. Due to these issues, an Aanderaa oxygen sensor was added to the CTD rosette. Oxygen sensor data from this cruise are calibrated data produced by the Aanderaa oxygen sensor (AAOXY; for more detailed information, see documentation provided with Fogaren and Palevsky, 2023 dataset). All data from this sensor are flagged as questionable (QC flag = 3), since Aanderaa optodes are not typically used on CTD sensor packages because they have a slower response time than the SBE43 and even after lag correction cannot fully resolve steep gradients at the pace that the CTD rosette is raised/lowered.

#### **BCO-DMO Processing Description**

\* Merged files into 1 datafile

\* Added lat/lon/date

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#### **Data Files**

File	
904722_v1_palevsky.csv	Comma Separated Values (.csv), 31.11 KB) MD5:ac60074831acdb461ab46f4791ab5a1d
Primary data file for dataset 90472	22.

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#### Supplemental Files

File		
AR30-03.zip	(ZIP Archive (ZIP), 6.86 KB) MD5:97e7f9c77882fee664bf3c4ae77ee77c	
Individual bottle files for cruise AR30-01. Supplemental data for dataset 904722.		
AR35-05.zip	(ZIP Archive (ZIP), 2.42 KB) MD5:d50416f2ab536d6e3a63755e729214d4	
Individual bottle files for cruise AR35-05. Supplemental data for dataset 904722.		

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## **Related Publications**

Cruise data. (2022, September 16). Ocean Observatories Initiative. <u>https://oceanobservatories.org/cruise-data/</u> General

Dickson, A.G.; Sabine, C.L. and Christian, J.R. (eds) (2007) Guide to best practices for ocean CO2 measurement. Sidney, British Columbia, North Pacific Marine Science Organization, 191pp. (PICES Special Publication 3; IOCCP Report 8). DOI: https://doi.org/<u>10.25607/OBP-1342</u> *Methods* 

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.8048209 <u>https://doi.org/10.5281/zenodo.8048209</u> *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/<u>10.25607/OBP-1350</u> Methods

Palevsky, H., Clayton, S., Atamanchuk, D., Battisti, R., Batryn, J., Bourbonnais, A., Briggs, E. M., Carvalho, F., Chase, A. P., Eveleth, R., Fatland, R., Fogaren, K. E., Fram, J. P., Hartman, S. E., Le Bras, I., Manning, C. C. M., Needoba, J. A., Neely, M. B., Oliver, H., ... Wingard, C. (2023). *OOI Biogeochemical Sensor Data Best Practices and User Guide. Version* 1.1.1. [GOOS ENDORSED PRACTICE]. Ocean Observatories Initiative, Biogeochemical Sensor Data Working Group. <u>https://doi.org/10.25607/OBP-1865.2</u> *Methods* 

Trowbridge, J., Weller, R., Kelley, D., Dever, E., Plueddemann, A., Barth, J. A., & Kawka, O. (2019). The Ocean Observatories Initiative. Frontiers in Marine Science, 6. https://doi.org/<u>10.3389/fmars.2019.00074</u>

## **Related Datasets**

#### IsRelatedTo

Fogaren, K. E., Palevsky, H. I. (2023) **Bottle-calibrated dissolved oxygen profiles from yearly turnaround cruises for the Ocean Observations Initiative (OOI) Irminger Sea Array 2014 - 2022.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2023-07-19 doi:10.26008/1912/bco-dmo.904721.1 [view at BCO-DMO] Relationship Description: Bottle-calibrated dissolved oxygen (DO) profiles collected from Conductivity Temperature Depth (CTD) casts.

McRaven, L. (2022). Water temperature, salinity, and others taken by CTD and Niskin bottles from the research vessel Neil Armstrong, Irminger Sea 5 cruise AR30-03, in the North Atlantic from 2018-06-06 to 2018-06-22. (NCEI Accession 0252116) [Data set]. NOAA National Centers for Environmental Information. https://doi.org/10.25921/BFSV-YP35 <u>https://doi.org/10.25921/bfsv-yp35</u>

McRaven, L. (2022). Water temperature, salinity, and others taken by CTD and Niskin bottles from the research vessel Neil Armstrong, cruise AR35-05, in the North Atlantic from 08-02-2019 to 08-25-2019 (NCEI Accession 0251721) [Data set]. NOAA National Centers for Environmental Information. https://doi.org/10.25921/61KN-QV10 <a href="https://doi.org/10.25921/61kn-qv10">https://doi.org/10.25921/61kn-qv10</a>

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#### Parameters

Parameter	Description	Units
Cruise	Cruise ID	unitless
Cast	Cast number	unitless
Lat	Sampling location latitude, south is negative	decimal degrees
Lon	Sampling location longitude, west is negative	decimal degrees
Date_UTC	Sampling date in UTC format (yyyy-mm-ddThh:mmZ)	unitless
Niskin_ID	Unique Niskin bottle number from the CTD rosette	unitless
CTDPRES	Hydrostatic pressure recorded from CTD at the depth where the sample was taken	dbar
CTDTEMP_ITS90	In situ temperature recorded from CTD on the ITS-90 scale	degrees C
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
CTDOXYCUR	Oxygen current from the SeaBird SBE43 oxygen sensor on the CTD package, processed with the SBE default hysteresis correction	volts
CTDOXYCUR_flag	Quality control flag; see data documentation with Fogaren and Palevsky, 2023 and Palevsky et al. 2023 datasets.	unitless
CTDOXY	Calibrated dissolved oxygen content from oxygen sensor mounted on the CTD	umol/kg

CTDOXY_flag	Quality control flag; see data documentation with Fogaren and Palevsky, 2023 and Palevsky et al. 2023 datasets.	unitless
AAOXYCUR	Raw oxygen current from the Aanderaa oxygen optode added to the CTD package	volts
AAOXYCUR_flag	Quality control flag; see data documentation with Fogaren and Palevsky, 2023 and Palevsky et al. 2023 datasets.	unitless
ΑΑΟΧΥ	Calibrated dissolved oxygen content from oxygen optode added to the CTD package	umol/kg
AAOXY_flag	Quality control flag; see data documentation with Fogaren and Palevsky, 2023 and Palevsky et al. 2023 datasets.	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 Palevsky et al. 2023 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 Palevsky et al. 2023 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 Palevsky et al. 2023 dataset.	unitless
DIC	Total dissolved inorganic carbon content	umol/kg
DIC_flag	Quality control flag;see data documentation Palevsky et al. 2023 dataset.	unitless
ТА	Total alkalinity content	umol/kg
TA_flag	Quality control flag; see data documentation with Palevsky et al. 2023 dataset.	unitless
file_name	File name of separate file	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	Inorganic Carbon Analyzer
Generic Instrument Description	Instruments measuring carbonate in sediments and inorganic carbon (including DIC) in the water column.

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 for this project (Nicholson et al., 2023: <u>https://doi.org/10.5281/zenodo.8048208</u> )
Generic Instrument Description	A Winkler Oxygen Titration system is used for determining concentration of dissolved oxygen in seawater.

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#### Deployments

#### AR30-03

Website	https://www.bco-dmo.org/deployment/904745
Platform	R/V Neil Armstrong
Start Date	2018-06-05
End Date	2018-06-24

#### AR35-05

Website	https://www.bco-dmo.org/deployment/904747
Platform	R/V Neil Armstrong
Start Date	2019-08-02
End Date	2019-08-24

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#### **Project Information**

# Collaborative Research: The Annual Cycle of the Biological Carbon Pump in the Subpolar North Atlantic (OOI Irminger BCP)

#### Coverage: Irminger Sea

#### NSF abstract:

Ocean biology plays an important role in the Earth's carbon cycle. While most of the organic material produced by phytoplankton in the sunlit surface waters of the oceans is eaten and recycled in the surface waters, a small amount sinks to the deep ocean in what is called the "biological carbon pump." The biological pump is particularly hard to study in high latitude regions, which can be difficult to get to and challenging to work in. It is also particularly important to understand the biological pump in these parts of the ocean, where much of the world's deep ocean waters are formed. The export of carbon to deep waters can be estimated by carefully measuring the amount of excess oxygen left behind in surface waters. Oxygen in seawater can be measured very precisely using sensors deployed on moorings, floats, and gliders. These sensors can be deployed for years at a time, but their measurements must be carefully calibrated. In this project, investigators would use carefully calibrated oxygen sensors on gliders to, in turn, calibrate the oxygen sensors on a set of moorings in the high latitude North Atlantic Ocean, to study the biological carbon pump over a period of two years. The project would train several undergraduate students and a graduate student, and result in the development of educational laboratory materials that incorporate glider and mooring data from the project.

The goal of this proposal is to observationally constrain the annual magnitude and seasonal timing of the biological carbon pump (determined as annual net community production; ANCP) and its influence on air-sea carbon dioxide flux by using biogeochemical sensor measurements from the Ocean Observatories Initiative (OOI) Irminger Sea Array. However, existing OOI oxygen sensor calibration suffers from both pre- and postdeployment drift, currently precluding the ability to calculate ANCP by oxygen mass balance. The investigators therefore propose to improve the accuracy and utility of OOI Irminger Sea oxygen measurements by deploying two gliders configured for air calibration of their oxygen sensors when surfacing between profiles. These aircalibrated gliders will be used to intercalibrate all 12 existing oxygen sensors on the Irminger Sea Array and produce a calibrated oxygen product incorporating data from all sensors, which will ensure sufficient accuracy to calculate ANCP. Both the annual magnitude and seasonal timing of ANCP, including upper ocean biological productivity and thermocline respiration, will be determined using an oxygen mass balance approach within a data- constrained 1D physical model. A suite of 1D model simulations including the inorganic carbon system. gas exchange, and ANCP determined from oxygen mass balance will be used, together with OOI carbon dioxide measurements, to diagnose influences of physical and biological drivers of air-sea carbon dioxide flux, improving both guantitative and mechanistic understanding of how the biological pump influences the carbon cycle.

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-1946072</u>
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-1756613</u>
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-1755574</u>

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