Concentrations of particulate organic matter (POC, PON, POP, PCOD), total oxygen demand, POM ratios, and respiration ratios from samples collected on R/V Atlantic Explorer BATS validation study #58 in the Sargasso Sea in October 2021

Website: https://www.bco-dmo.org/dataset/910948 Data Type: Cruise Results Version: 1 Version Date: 2023-10-10

Project

» <u>Quantifying ocean oxygen-to-carbon demand by chemical analyses and inverse models</u> (oxygen-to-carbon demand)

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Abstract

This dataset includes suspended concentrations of particulate organic carbon (POC), particulate organic nitrogen (PON), particulate organic phosphorus (POP), particulate chemical oxygen demand (PCOD), and total oxygen demand (Sigma_-O2 = PCOD + 2PON) down to a depth of 1000 meters (m) in the Sargasso Sea. This dataset also includes POM ratios (C/N, C/P, & N/P) and respiration ratios (PCOD/POC, Sigma_-O2/C, Sigma_-O2/N, & Sigma_-O2/P) with depth. These measurements were quantified from seawater samples collected aboard the R/V Atlantic Explorer as part of the Bermuda Atlantic Time-series Study Validation cruise #58 (BVal58). BVal58 started at St. George's, Bermuda on 11 October 2021 and the research group disembarked in San Juan, Puerto Rico on 21 October 2021. Euphotic zone samples (5 - 120 m) were collected using a CTD bottle rosette and disphotic zone samples (150 - 1000 m) were collected using large volume pumps. Climate-induced ocean deoxygenation is increasing, but biological components of oxygen loss remain unconstrained. We determined from this dataset that the total respiration quotient, Sigma_-O2/C, and other respiration ratios of POM vary with depth.

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Coverage

Spatial Extent: N:31.667 **E**:-64.168 **S**:19.667 **W**:-65.967 **Temporal Extent**: 2021-10-11 - 2021-10-19

Methods & Sampling

Samples were collected on the& R/V Atlantic Explorer BATS Validation cruise #58 (BVal58) (cruise ID AE2121), which took place from October 11 to 25, 2021, and transited from St. George's, Bermuda to San Juan, Puerto Rico. The research group collecting these data disembarked on October 21, 2021.

Suspended POM Sampling in the Euphotic Zone (Depths of 5 - 120 meters):

Seawater was collected at 5, 40, 80, and 120 meters (m) deep using a CTD rosette fitted with twenty-four 10liter (L) Niskin bottles (OTE). All sampling carboys were rinsed 3 times with collected seawater before filling to 8 L. Particulate Organic Matter (POM) was collected on 25-millimeter (mm) GF/F filters (0.7-micrometer (µm) pore size, Whatman, GE Healthcare) pre-combusted at 500° Celsius (C) for 4 hours. The 6 filters collected at each depth of each station resulted in duplicate samples for the Particulate Organic Carbon and Nitrogen (POC/N), Particulate Organic Phosphorus (POP), and Particulate Chemical Oxygen Demand (PCOD) assays. After filtering 8 L, the filters for the POP assay were rinsed with 5 milliliters (mL) of 0.17 molar (M) NaSO₄ to remove dissolved inorganic phosphorus, and the filters for the PCOD assay were rinsed with 5 mL of deionized water to remove chloride ions. All filters were folded in half after filtration, sealed inside pre-combusted aluminum foil (500°C for 4 hours), and stored at -80°C. Post-assays, we accounted for POM on blank filters by subtracting the average value of 10 dry blanks. The dry blanks were pre-combusted filters that had not been used for filtering.

Suspended POM Sampling in the Disphotic Zone (Depths of 150 - 1000 m):

McLane WTS-LV pumps were lowered to depths of 150, 200, 300, 400, 500, and 1000 m and each directly filtered 557 to 821 L of seawater through a 142 mm diameter pre-combusted GF/F filter (0.7 µm pore size, Whatman, GE Healthcare). After recovering the McLane pumps, the filters were similarly folded in half, sealed with pre-combusted aluminum foil, and stored at -80°C. Post-cruise, we hole-punched the 142 mm diameter filters in 15 places with a carbon-steel 18 mm hole-puncher that had been pre-combusted (500°C for 4 hours). Taking into account the O-ring, each hole punch equaled 3.8% of the total filter area containing POM. One to four chad pairs served as one replicate sample depending on the sensitivity of the assay. Two to four replicate samples were made for each assay. Dry blanks were prepared by hole-punching a pre-combusted, but unused 142 mm GF/F filter.

Particulate Organic Carbon and Nitrogen (POC/N) Assay:

POC/N filters were processed using a JGOFS protocol (Ducklow & Dickson, 1994). Filters for the POC/N assay were dried at 55°C for 24 hours. Filters were then placed in a desiccator with 12 M hydrochloric acid for 24 hours to remove inorganic carbonates. Filters were then re-dried for a minimum of 48 hours at 55°C. After drying, the filters were folded and pelletized into pre-combusted tin capsules (CE Elantech, Lakewood, NJ). Each tin-wrapped sample was analyzed in a FlashEA 1112 Elemental Analyzer using the NC Soils setup (Thermo Scientific, Waltham, MA). Known masses of atropine and acetanilide were used as standards for each run. The minimum detection limits for carbon and nitrogen were 2.4 micrograms (µg) and 3.0 µg respectively.

Particulate Organic Phosphorus (POP) Assay:

We quantified particulate organic phosphorus using an ash-hydrolysis method presented by Lomas et al. (2010). Filters were placed in autoclaved glass vials with 2 mL of 0.017 M MgSO₄, covered with pre-combusted aluminum foil (500°C for 4 hours), and then combusted at 500°C for 2 hours. 5 mL 0.2 M HCl was added and incubated at 80° to 90°C for 30 minutes. After cooling, the solution was poured into a glass centrifuge tube. The glass vial was rinsed with 5 mL of deionized water, which was then poured into the same centrifuge tube. A mixed reagent of 0.0243 M ammonium molybdate tetrahydrate, 5 N sulfuric acid, 0.004 M potassium antimonyl tartrate, and 0.3 M ascorbic acid (2:5:1:2) was added to each tube before being set in the dark for 30 minutes. Tubes were then centrifuged at 4000 rotations per minute (rpm) and quantified at 885 nanometers (nm) with a spectrophotometer using a potassium monobasic phosphate standard (1.0 mM-P). The minimum detection limit was 0.3 µg for phosphorus.

Particulate Chemical Oxygen Demand (PCOD) Assay:

The PCOD assay is a wastewater assay that has been modified by Moreno et al. (2020) to accurately quantify oxygen needed to fully oxidize organic carbon on GF/F filters. Note that because dichromate does not oxidize ammonium, this assay does not quantify oxygen demand for nitrification. Prior to the assay, the filters were dried at 55°C for at least 24 hours. For analysis, filters were added into HACH COD HR+ reagent vials (Product

no. 2415915 containing mercuric sulfate) with 2 mL of milli-Q water. Vials were digested at 150°C for 2 hours, then 92.1 µL of 0.163 M NaCl was added to induce even precipitation of silver chloride. Vials were then inverted twice and centrifuged for 30 minutes at 2500 rpm. The absorbance of each vial was measured at 600 nm using a spectrophotometer. The oxygen demand was quantified using a standard curve made from HACH certified phthalate-based standards. The minimum detection limit was 3.1 µg for oxygen demand.

Calculating Ratios and Σ-O₂:

Elemental ratios (micromolar:micromolar (μ M: μ M)) were quantified using mean concentrations from the same depth and station. We quantified the total oxygen demand for complete remineralization (Σ -O₂) as PCOD plus double PON in units of micromolar.

Data Processing Description

Data were processed using MATLAB R2021b.

Any gaps in sampling are marked as missing entries in the dataset.

BCO-DMO Processing Description

- Imported original file named "BVal58 POM Data Set S1.xlsx" into the BCO-DMO system.

- Renamed parameters/columns to comply with BCO-DMO naming conventions.
- Created ISO 8601 date/time (UTC) column by combining year, month, day, and time fields.
- Removed the original year, month, day, and time columns.
- Saved the final file as "910948 v1 bval58 pom.csv"

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Data Files

File 910948_v1_bval58_pom.csv(Comma Separated Values (.csv), 15.82 KB) MD5:4bef23b338b26b89ec9274b605ca7f16 Primary data file for dataset ID 910948, version 1.

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Related Publications

Ducklow, H. & Dickson, A. (1994). Chapter 2: Shipboard Sampling procedures. JGOFS Protocols (pp. 1-210). *Methods*

Lomas, M. W., Burke, A. L., Lomas, D. A., Bell, D. W., Shen, C., Dyhrman, S. T., & Ammerman, J. W. (2010). Sargasso Sea phosphorus biogeochemistry: an important role for dissolved organic phosphorus (DOP). Biogeosciences, 7(2), 695–710. doi:<u>10.5194/bg-7-695-2010</u> *Methods*

Moreno, A. R., Garcia, C. A., Larkin, A. A., Lee, J. A., Wang, W.-L., Moore, J. K., Primeau, F. W., & Martiny, A. C. (2020). Latitudinal gradient in the respiration quotient and the implications for ocean oxygen availability. Proceedings of the National Academy of Sciences, 117(37), 22866–22872. https://doi.org/<u>10.1073/pnas.2004986117</u> *Methods*

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Parameter	Description	Units
Station	station number where sample was collected	unitless
McLane_Cast	cast number for McLane pump deployments	unitless
ISO_DateTime_UTC	date and time (UTC) of sample collection in ISO 8601 format	unitless
Latitude	latitude; positive values = North	decimal degrees
Longitude	longitude; negative values = West	decimal degrees
Depth_m	depth of sample collection	meters (m)
Volume_L	sample volume	liters (L)
Filter_Num	number for GF/F used	unitless
Duplicate_Filter_Num	number for GF/F used if a duplicate filter was used	unitless
POP1	POP sample replicate #1	nanomolar (nM)
POP2	POP sample replicate #2	nanomolar (nM)
POP3	POP sample replicate #3	nanomolar (nM)
POP4	POP sample replicate #4	nanomolar (nM)
POP5	POP sample replicate #5	nanomolar (nM)
POP6	POP sample replicate #6	nanomolar (nM)
POP_Avg_nM	average of POP sample replicates in nanomolar	nanomolar (nM)
POP_Avg_microM	average of POP sample replicates in micromolar	micromolar (uM)
POC1	POC sample replicate #1	micromolar (uM)
POC2	POC sample replicate #2	micromolar (uM)
POC3	POC sample replicate #3	micromolar (uM)
POC4	POC sample replicate #4	micromolar (uM)
POC_Avg_microM	average of POC sample replicates	micromolar (uM)
PON1	PON sample replicate #1	micromolar (uM)
PON2	PON sample replicate #2	micromolar (uM)
PON3	PON sample replicate #3	micromolar (uM)
PON4	PON sample replicate #4	micromolar (uM)
PON_Avg_mircoM	average of PON sample replicates	micromolar (uM)
PCOD1	PCOD sample replicate #1	micromolar (uM)
PCOD2	PCOD sample replicate #2	micromolar (uM)
PCOD3	PCOD sample replicate #3	micromolar (uM)
PCOD4	PCOD sample replicate #4	micromolar (uM)
PCOD5	PCOD sample replicate #5	micromolar (uM)
PCOD_Avg_microM	average of PCOD sample replicates	micromolar (uM)
C_N	average POC/PON for depth and station	unitless (ratio of uM:uM)
С_Р	average POC/POP for depth and station	unitless (ratio of uM:uM)
N_P	average PON/POP for depth and station	unitless (ratio of uM:uM)
PCOD_POC	average respiration quotient, PCOD/POC, for depth and station	unitless (ratio of uM:uM)

Sigma_02_C	average total respiraiton quotient, (PCOD + 2PON) /POC, for depth and station	unitless (ratio of uM:uM)
Sigma_O2_N	average (PCOD + 2PON)/PON for depth and station	unitless (ratio of uM:uM)
Sigma_O2_P	average (PCOD + 2PON)/POP for depth and station	unitless (ratio of uM:uM)

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Instruments

Dataset- specific Instrument Name	Sea-bird 911 CTD fitted with twenty-four 10 Niskin (OTE) bottles
Generic Instrument Name	CTD Sea-Bird 911
Generic Instrument Description	The Sea-Bird SBE 911 is a type of CTD instrument package. The SBE 911 includes the SBE 9 Underwater Unit and the SBE 11 Deck Unit (for real-time readout using conductive wire) for deployment from a vessel. The combination of the SBE 9 and SBE 11 is called a SBE 911. The SBE 9 uses Sea-Bird's standard modular temperature and conductivity sensors (SBE 3 and SBE 4). The SBE 9 CTD can be configured with auxiliary sensors to measure other parameters including dissolved oxygen, pH, turbidity, fluorescence, light (PAR), light transmission, etc.). More information from Sea-Bird Electronics.

Dataset- specific Instrument Name	Thermo Scientific FlashEA 1112
Generic Instrument Name	Elemental Analyzer
Generic Instrument Description	Instruments that quantify carbon, nitrogen and sometimes other elements by combusting the sample at very high temperature and assaying the resulting gaseous oxides. Usually used for samples including organic material.

Dataset- specific Instrument Name	McLane Large Volume - Water Transfer System (WTS-LV) pumps
Generic Instrument Name	McLane Large Volume Pumping System WTS-LV
Generic Instrument Description	The WTS-LV is a Water Transfer System (WTS) Large Volume (LV) pumping instrument designed and manufactured by McLane Research Labs (Falmouth, MA, USA). It is a large-volume, single-event sampler that collects suspended and dissolved particulate samples in situ. Ambient water is drawn through a modular filter holder onto a 142-millimeter (mm) membrane without passing through the pump. The standard two-tier filter holder provides prefiltering and size fractioning. Collection targets include chlorophyll maximum, particulate trace metals, and phytoplankton. It features different flow rates and filter porosity to support a range of specimen collection. Sampling can be programmed to start at a scheduled time or begin with a countdown delay. It also features a dynamic pump speed algorithm that adjusts flow to protect the sample as material accumulates on the filter. Several pump options range from 0.5 to 30 liters per minute, with a max volume of 2,500 to 36,000 liters depending on the pump and battery pack used. The standard model is depth rated to 5,500 meters, with a deeper 7,000-meter option available. The operating temperature is -4 to 35 degrees Celsius. The WTS-LV is available in four different configurations: Standard, Upright, Bore Hole, and Dual Filter Sampler. The high-capacity upright WTS-LV model provides three times the battery life of the standard model. The Bore-Hole WTS-LV is designed to fit through a narrow opening such as a 30-centimeter borehole. The dual filter WTS-LV features two vertical intake 142 mm filter holders to allow simultaneous filtering using two different porosities.

Dataset- specific Instrument Name	10 L Niskin bottles (OTE)
Generic Instrument Name	Niskin bottle
Generic Instrument Description	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.

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Deployments

AE2121

Website	https://www.bco-dmo.org/deployment/911024
Platform	R/V Atlantic Explorer
Start Date	2021-10-11
End Date	2021-10-25
Description	R/V Atlantic Explorer BATS Validation cruise #58 (BVal58) Oct 11 to Oct 25, 2021 St. George's, Bermuda to San Juan, Puerto Rico Chief Scientist - Paul Lethaby (BIOS, <u>paul.lethaby@bios.edu</u>) See more cruise information at R2R: <u>https://www.rvdata.us/search/cruise/AE2121</u>

Project Information

Quantifying ocean oxygen-to-carbon demand by chemical analyses and inverse models (oxygen-to-carbon demand)

Coverage: Subtropical North Atlantic (Sargasso Sea) from St. George's, Bermuda to San Juan, Puerto Rico

NSF Award Abstract:

The marine carbon and oxygen cycles are intimately linked through the production and consumption of oxygen during photosynthesis and respiration. The amount of oxygen consumed per mole of respired organic carbon, the respiration quotient, is key for accurately predicting ocean oxygen concentrations and how ocean oxygen levels will respond to climate change. Despite this importance, the respiration quotient has rarely been measured directly. The aim of this research is to estimate the respiration quotient and its variability across ocean regions and depth. This will be done through an integration of direct chemical measurements of particulate organic matter collected from multiple ocean regions and indirectly by using an ocean circulation model to analyze a global database of dissolved oxygen and carbon concentration with a circulation model. In addition to advancing the understanding of the ocean oxygen cycle in the scientific community, this project will provide research training for researchers and students. The project will also improve awareness and understanding in the general public about possible future changes to marine oxygen concentrations.

One of the main uncertainties in predicting current and future oxygen levels is the regulation of the biological respiration demand. The respiration quotient describes the amount of oxygen needed during the consumption of one mole of organic carbon and thus is a key link between the carbon and oxygen cycles. Here, we propose to measure the amount of oxygen consumed per mole of respired organic carbon, the respiration quotient, in particulate organic matter (POM) from the surface and thermocline using a newly developed chemical technique. Thus, we aim to obtain new direct chemical measurements of the respiration quotient across distinct oceanic regimes and depths. Subsequently, we propose to incorporate these observations into a seasonally-resolved inverse model using global hydrographic tracer concentration data. This combined approach will provide the first global-scale estimates (and uncertainties) of the mean and regional variability of the respiration quotient in the POM stock and export flux. Different parameterizations linking the respiration quotient to regions or environmental variables will be applied to test how they impact and replicate global oxygen concentrations and the extent of the oxygen minimum zones.

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-1948842

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