Macronutrients and dissolved and particulate trace metals collected from the R/V Atlantic Explorer cruise AE1913 in the Sargasso Sea in June of 2019

Website: https://www.bco-dmo.org/dataset/916429
Data Type: Cruise Results
Version: 1
Version Date: 2023-12-07

Project
» Collaborative Research: Direct Characterization of Adaptive Nutrient Stress Responses in the Sargasso Sea using Protein Biomarkers and a Biogeochemical AUV (Nutrient Stress Responses and AUV Clio)

Contributors	Affiliation	Role
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Abstract
This data includes macronutrients and dissolved and particulate trace metals collected from the AE1913 expedition on the R/V Atlantic Explorer in June 2019. Seawater was collected with a trace metal rosette and filtered through a 0.2 um filter. Filtrate was used for nutrients and dissolved trace metals, and the filter was saved for the particulate metal analysis at select sites. Instruments used were a Alpkem Rapid Flow Analyzer, Technicon AutoAnalyzer II, and iCAP Q inductively coupled plasma mass spectrometer (ICP-MS). The goal of this analysis was to explore the relationship between trace metal/macronutrient availability and microbial metabolism across a section of the North Atlantic Ocean. This data was collected by Mak Saito and Natalie Cohen.

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Coverage

Location: Sargasso Sea, beginning at Bermuda Atlantic Time-series Station (BATS) and ending in the northeast shelf of Woods Hole Oceanographic Institution (WHOI)
Spatial Extent: **N**:39.31658 **E**:-64.1663 **S**:31.666888 **W**:-71.1232
Temporal Extent: 2019-06-16 - 2019-06-27

Dataset Description

See the "Related Datasets" section on this page for other data from coordinated deployments, and the ELOG from cruise AE1913.

Methods & Sampling

Methods are described in a forthcoming manuscript by Cohen et al. Dissolved nitrate+nitrite, nitrite and silicate were measured on an Alpkem Rapid Flow Analyzer, and ammonium and phosphate were measured on a Technicon AutoAnalyzer II at Oregon State University.

For the dissolved metal analysis, filtered seawater was acidified to pH 1.8 using hydrochloric acid, and stored for 6 months at room temperature in the dark. Seawater preconcentration was performed using the seaFAST automated preconcentration system followed by quantification via inductively coupled plasma mass spectrometry. Reagents consisted of a 4M ammonium acetate pH 6.0 buffer prepared using high purity ammonium hydroxide and acetic acid, a 1% nitric acid rinse solution, 10% nitric acid elution acid, and a second internal standard 10% nitric elution acid solution containing 10 ppb indium (115In). Polypropylene conical tubes used with the autosampler were HCl acid-soaked and pH 2-rinsed prior to use. Process blanks consisted of Milli-Q HCl-acidified to pH 2 , and were run alongside samples. A stable isotope cocktail, which consisted of ^{57}Fe, ^{61}Ni, ^{65}Cu, ^{67}Zn and ^{111}Cd, was spiked (50 µL) into each 15 mL sample to account for recovery and matrix effects. Following offline seaFAST preconcentration to 500 µL, the samples were analyzed using an iCAP Q inductively coupled plasma-mass spectrometer (ICP-MS). A six-point external standard curve was used with multi-element and indium (In) standards, diluted to range from 1-10 ppb in 5% nitric acid. Dissolved metal concentrations were determined using isotope dilution. Nitric acid (5%) injection blanks were subtracted from sample metal cps values except for Zn, in which injection blanks were generally higher than process blanks. Accuracy was determined using the 2009 Geotraces surface coastal (GSC) seawater intercalibration standard (n=5): dFe = 1.65 ± 0.19 nM [GSC = 1.56 ± 0.12 nM], dZn = 1.65 ± 0.17 nM [GSC = 1.45 ± 0.10 nM], dCu = 1.38 ± 0.16 nM [GSC = 1.12 ± 0.15 nM], dCd = 0.37 ± 0.03 nM [GSC = 0.37 ± 0.02 nM], dNi = 4.28 ± 0.17 nM [GSC = 4.5 ± 0.21 nM], and dMn = 2.42 ± 0.29 nM [GSC = 2.23 ± 0.08 nM]. The limit of detection was determined by calculating 3x the standard deviation of process blanks dataset-wide: dFe = 0.23 nM (n=14), dZn = 0.35 nM (n=16), dCu = 0.03 nM (n=18), dCd = 0.0103 nM (n=16), dNi = 0.07 nM (n=18), dMn = 0.03 nM (n=18). Blanks that were overtly contaminated with Fe (4 of 18), Zn (2 of 18) or Cd (2 of 18) were not included in the LOD estimation. In the case of Zn, high deep water (>1,000 m) concentrations altered the spiked:stable isotope ratio, and accurate concentrations were not able to be obtained.

For the particulate metal analysis, whole 142 mm filters were extracted using an acid leachable digestion and quantified with ICP-MS. Process blanks were prepared in the laboratory and consisted of acid-cleaned Supor filters that were soaked for 1 week in oligotrophic seawater to condition with salt and remove residual metals introduced from high purity cleaning acids. Plastic forceps were used to place thawed filters into acid-cleaned polypropylene tubes containing 8mL of 5% nitric acid containing 1 ppb In. Filters were digested at 140°C for 3-4 hours, until less than ~4 mL was remaining. Filters were removed and the remainder of the solution was allowed to evaporate in the heat block until completely dry. Two mL of fresh 5% nitric acid was added to the precipitates. Tubes were vortexed, and 900 µL replicates of each sample were pipetted into an 81-well acid-rinsed plate alongside SPEX + In diluted standards. Metal quantification was performed using the iCAP Q ICP-MS. Particulate metal concentrations were calculated following Cox et al. 2014.

Data Processing Description

Dissolved metal concentrations below the limit of detection were removed from the final dataset.

For dissolved metals, flags were used following the Geotraces policy: https://www.geotraces.org/geotraces-quality-flag-policy/:

1 = good value

3 = probably bad value (for Zn, in samples with suspected 66Zn/67Zn (stable:spike) ratio too high)

4 = bad value (for Zn, in samples with suspected 66Zn/67Zn (stable:spike) ratio too high)

6 = below detection limit

For macronutrients:

empty= no data value or removed due to oceanographically inconsistent profiles and potential thawing during sample transport.

Only select sites/depths were analyzed for particulate metals, the rest are blank.

BCO-DMO Processing Description

BCO-DMO Data Manager Processing Notes:
* File "metals_bcodmo.csv" was imported into the BCO-DMO data system.
** Missing data values are displayed differently based on the file format you download. They are blank in csv files, "NaN" in MatLab files, etc.
* * Column names adjusted to conform to BCO-DMO naming conventions designed to support broad re-use by a variety of research tools and scripting languages. [Only numbers, letters, and underscores. Can not start with a number]
* Timestamps added to the data table for deployment and recovery times obtained from the ELOG GPS times for these events (see Related Datasets section for ELOG). The times in the elog are UTC time. timestamp columns were added by joining on key "station" in metals_bcodmo.csv and second file supplied by the submitter stations_metals.csv which contained the station and timestamps.
* Format of timestamps converted to ISO 8601 format for timestamp with timezone.

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Related Publications

Cohen, N.R., Krinos, A.I., Kell, R.M., Chmiel, R. J., Moran, D.M., McIlvin, M.R., Lopez, P.Z., Barth, A., Stone, J., Alanis, B.A., Chan, E.W., Breier, J.A., Jakuba, M.V., Johnson, R., Alexander, H., Saito, M.A. (2023) Microeukaryote metabolism across the western North Atlantic Ocean revealed through autonomous underwater profiling. Submitted to Nature Communications.
Results

Cox, A. D., Noble, A. E., & Saito, M. A. (2014). Cadmium enriched stable isotope uptake and addition experiments with natural phytoplankton assemblages in the Costa Rica Upwelling Dome. Marine Chemistry, 166, 70–81. https://doi.org/<u>10.1016/j.marchem.2014.09.009</u>
Methods

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Related Datasets

IsRelatedTo

Saito, M. A., Cohen, N. (2023) **CTD profiles from R/V Atlantic Explorer cruise AE1913 in the Sargasso Sea in June of 2019.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2023-12-07 http://lod.bco-dmo.org/id/dataset/916411 [<u>view at BCO-DMO</u>]
Relationship Description: Data from coordinated deployments during the same cruise.

Saito, M. A., Cohen, N. (2024) **Amended Rolling Deck to Repository (R2R) event log (ELOG) taken on the R/V Atlantic Explorer cruise AE1913 in the Sargasso Sea in June of 2019.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2024-05-03 http://lod.bco-dmo.org/id/dataset/926526 [<u>view at BCO-DMO</u>]
Relationship Description: Data from coordinated deployments during the same cruise.

Saito, M. A., Cohen, N., Johnson, R. J. (2024) **Pigment concentration data from AUV Clio dives conducted during R/V Atlantic Explorer cruise AE1913 in the Sargasso Sea in June of 2019.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2024-05-03 http://lod.bco-dmo.org/id/dataset/926546 [<u>view at BCO-DMO</u>]
Relationship Description: Data from coordinated deployments during the same cruise.

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Parameters

Parameter	Description	Units
Station	Station number	unitless
Latitude	Latitude	decimal degrees
Longitude	longitude	decimal degrees
depth	Depth of seawater collected using the trace metal clean rosette	meters (m)
DateTime_deploy	Trace Metal Rosette deployment event timestamp with timezeone (ISO 8601 format)	unitless
DateTime_recover	Trace Metal Rosette recovery event timestamp with timezeone (ISO 8601 format)	unitless
dFe	dissolved iron	nanomolar (nM)
dFeFlag	quality control key value (see Data Processing section)	unitless
dZn	dissolved zinc	nanomolar (nM)
dZnFlag	quality control key value (see Data Processing section)	unitless
dCd	dissolved cadmium	nanomolar (nM)
dCdFlag	quality control key value (see Data Processing section)	unitless
dNi	dissolved nickel	nanomolar (nM)
dNiFlag	quality control key value (see Data Processing section)	unitless
dCu	dissolved copper	nanomolar (nM)
dCuFlag	quality control key value (see Data Processing section)	unitless
dMn	dissolved manganese	nanomolar (nM)
dMnFlag	quality control key value (see Data Processing section)	unitless
PO4	dissolved phosphate	micromolar (uM)
NO2_NO3	dissolved nirate and nitrite	micromolar (uM)
Si	dissolved silicate	micromolar (uM)
NO2	dissolved nitrite	micromolar (uM)
NH4	dissolved ammonium	micromolar (uM)
pMn	particulate manganese	picomolar (pM)
pFe	particulate iron	picomolar (pM)
pNi	particulate nickel	picomolar (pM)
pCu	particulate copper	picomolar (pM)

pZn	particulate zinc	picomolar (pM)
pCd	particulate cadmium	picomolar (pM)

Instruments

Dataset-specific Instrument Name	Alpkem Rapid Flow Analyzer
Generic Instrument Name	Continuous Flow Analyzer
Generic Instrument Description	A sample is injected into a flowing carrier solution passing rapidly through small-bore tubing.

Dataset-specific Instrument Name	iCAP Q inductively coupled plasma-mass spectrometer (Thermo-Fisher Scientific)
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Generic Instrument Description	An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer.

Dataset-specific Instrument Name	X-Niskin bottles
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.

Dataset-specific Instrument Name	seaFAST preconcentration system (Elemental Scientific)
Generic Instrument Name	SeaFAST Automated Preconcentration System
Generic Instrument Description	The seaFAST is an automated sample introduction system for analysis of seawater and other high matrix samples for analyses by ICPMS (Inductively Coupled Plasma Mass Spectrometry).

Dataset-specific Instrument Name	Technicon AutoAnalyzer II
Generic Instrument Name	Technicon AutoAnalyzer II
Generic Instrument Description	A rapid flow analyzer that may be used to measure nutrient concentrations in seawater. It is a continuous segmented flow instrument consisting of a sampler, peristaltic pump, analytical cartridge, heating bath, and colorimeter. See more information about this instrument from the manufacturer.

Deployments

AE1913

Website	https://www.bco-dmo.org/deployment/916412
Platform	R/V Atlantic Explorer
Start Date	2019-06-16
End Date	2019-06-28
Description	coordinated deployments: McLane pumps, AUV Clio, CTD, trace metal rosette

Project Information

Collaborative Research: Direct Characterization of Adaptive Nutrient Stress Responses in the Sargasso Sea using Protein Biomarkers and a Biogeochemical AUV (Nutrient Stress Responses and AUV Clio)

Coverage: Bermuda Atlantic Time Series

NSF Award Abstract:

Microscopic communities in the ocean can be surprisingly diverse. This diversity makes it difficult to study the individual organisms and reactions that control specific reactions controlling nutrient cycles. Past studies confirm that iron and nitrogen are vital elements for biological growth. There is increasing evidence, however, that other chemicals such as silica, zinc, cobalt, and vitamin B12 may be just as important. This project will provide an unprecedented view of community distributions using new molecular methods to isolate and link active proteins to specific chemical cycles during the very first research deployment of a brand-new autonomous underwater vehicle (AUV). The AUV will collect samples in programed patterns by pumping water directly into its filtering mechanism and then return the samples to the ship for analysis. The Bermuda Atlantic Time-series Study (BATS) station, which provides abundant supporting data, is the site for this innovative investigation into the microbial ecology and chemistry of the open oceans. Additionally, data will be widely distributed to other scientists through the Ocean Protein Portal website being developed by the Woods Hole Oceanographic Institute (WHOI) and the Biological and Chemical Oceanography Data Management Office. Data will also contribute a new teaching module in the Marine Bioinorganic Chemistry course at WHOI.

This first scientific deployment of the newly engineered and constructed biogeochemical AUV, Clio, will generate a novel dataset to examine marine microbial biogeochemical cycles in the Northwestern Atlantic oligotrophic ocean in unprecedented detail and at high vertical resolution. First the project proposes to understand if the microbial community reflects the varying chemical composition and cyanobacterial species through nutrient

response adaptations. Additionally, the research will determine if iron stress in the low light Prochlorococcus ecotyope found in the deep chlorophyll maximum is a persistent feature influenced by seasonal dust fluxes. The highly resolved vertical data from the in situ pumping capabilities of Clio are fundamental to a rigorous examination of these biogeochemical questions. This highly transformative dataset will greatly advance understanding of the nutrient and trace element cycling of this region and will be the first field validation of the potentially revolutionary capability these new approaches represent for the study of marine microbial biogeochemistry.

Funding