

EXPORTS NA nuts and TM field data

Website: <https://www.bco-dmo.org/dataset/954941>

Data Type: Cruise Results

Version: 1

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Project

» [Collaborative Research: Diatoms, Food Webs and Carbon Export - Leveraging NASA EXPORTS to Test the Role of Diatom Physiology in the Biological Carbon Pump](#) (Diatoms and carbon export)

Program

» [Export Processes in the Ocean from Remote Sensing](#) (EXPORTS)

Contributors	Affiliation	Role
Buck, Kristen Nicolle	University of South Florida (USF)	Principal Investigator, Contact
Brzezinski, Mark A.	University of California-Santa Barbara (UCSB)	Co-Principal Investigator
Jenkins, Bethany D.	University of Rhode Island (URI)	Co-Principal Investigator
Caprara, Salvatore	University of South Florida (USF)	Scientist
Navarro-Estrada, Delfina	University of South Florida (USF)	Student
Rauch, Shannon	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

Abstract

This dataset includes dissolved trace metal (manganese, iron, cobalt, nickel, copper, cadmium, zinc, lead) and macronutrient (nitrate+nitrite, phosphate, silicic acid, nitrite) concentration data from field samples collected during the EXPORTS North Atlantic campaign at the Porcupine Abyssal Plain-Sustained Observatory (PAP-SO) site on board the RRS Discovery (DY131). These data were primarily collected opportunistically during the course of water collection for incubation experiments (see separate dataset for incubations), and provide field context for the shipboard incubation experiments as well as temporal characterization of a retentive anticyclonic eddy occupied over the course of the cruise. This research focuses on the vertical export of the carbon associated with a major group of phytoplankton, the diatoms in the North Atlantic near the Porcupine Abyssal Plain. The major objective is to understand how diatom community composition and the prevailing nutrient conditions create taxonomic differences in metabolic state that combine to direct diatom taxa to different carbon export pathways. The focus is on diatoms, given their large contribution to global marine primary productivity and carbon export which translates into a significant contribution to the biogeochemical cycling of carbon (C), nitrogen (N), phosphorus (P), iron (Fe) and silicon (Si). It is hypothesized that the type and degree of diatom physiological stress are vital aspects of ecosystem state that drive export. To test this hypothesis, combined investigator expertise in phytoplankton physiology, genomics, and trace element chemistry is used to assess the rates of nutrient use and the genetic composition and response of diatom communities, with measurements of silicon and iron stress to evaluate stress as a predictor of the path of diatom carbon export. The EXPORTS field campaign in the North Atlantic sampled a retentive eddy over nearly a month in May 2021, which coincided with the decline of the North Atlantic Spring Bloom.

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Coverage

Location: Northeast Atlantic Ocean; Porcupine Abyssal Plain-Sustained Observatory (PAP-SO)

Methods & Sampling

Sample Collection:

This work was funded by NSF and conducted in collaboration with the NASA EXPORTS campaign at Porcupine Abyssal Plain-Sustained Observatory (PAP-SO), which sampled the decline of the North Atlantic Spring Bloom (NASB) in May 2021 on board the RRS Discovery (Cruise ID: DY131). All sampling occurred within a retentive eddy named "A2", with a deep anticyclonic structure. Field samples for dissolved (<0.4 or <0.2 micrometer (μm)) trace metals (Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb), and dissolved (<0.4 or <0.2 μm) macronutrients (P, N, Si) from surface and subsurface waters were collected as environmental context for the incubation experiments also conducted as part of this study.

All sampling was performed following trace metal clean procedures. Surface (~2 meters (m)) water was collected using a trace metal clean towfish that was sampled while underway at a speed of 4-6 knots (Mellett and Buck 2020). Surface dissolved trace metal and macronutrient samples were collected from the towfish while filling the 'Long-term' and 'Short-term' experiment incubation bottles, as follows: prior to filling the first set of carboys corresponding to the first replicate of the treatments (three replicates per treatment total), after filling the second set of carboys, after the third set, and after filling all replicate incubation carboys. These samples were filtered inline through a 0.2 μm (Pall Acropak) capsule filter. These samples are labelled "Survey Samples".

Subsurface trace metal and macronutrient samples were collected using a trace metal clean rosette (TMC CTD) deployed on synthetic line and outfitted with modified trace metal clean x-Niskin bottles (12-liters (L), OceanTestEquipment, Inc.; Cutter et al. 2017). Samples for dissolved trace metal and macronutrient samples were filtered either inline through a <0.2 μm capsule filter (Pall Acropak) or filtered offline through sequential acid-cleaned polycarbonate track-etch (PCTE) filters (5 μm , 0.4 μm) in a dual stage filtration system (Savillex) on a custom acrylic base. For a subset of profiles, additional unfiltered (total dissolvable, TD) samples were collected and filtered offline after eighteen months of storage and prior to analysis (TD Savillex). All dissolved and total dissolvable trace metal samples were acidified to 0.024 M hydrochloric acid (Optima, Fisher) and stored at room temperature until analyzed at USF. All macronutrient samples were stored frozen (-20 degrees Celsius ($^{\circ}\text{C}$)) until analyzed in the lab at USF. Seven depth profiles were deployed during the cruise, and water from casts #1, #3, and #6 were used to collect seawater for the Grow-Out incubation experiments. All TMC CTD casts occurred between 11 am and 12 pm local ship time.

Analysis of dissolved and total dissolvable trace metals:

Sample analysis for dissolved trace metals was conducted at the University of South Florida (USF) College of Marine Science (CMS), and Florida State University (FSU) National High Magnetic Field Laboratory (MagLab). To prepare for analysis, dissolved trace metal samples were transferred to 30- or 15-milliliter (mL) perfluoroalkoxy (PFA) vials with caps containing a quartz-window to enable UV-oxidization. Samples were UV-oxidized at USF for 90 minutes at ~20 milliwatts per square centimeter (mW cm^{-2}) with an UVO-Cleaner (Jelight; Model No. 5144AX) to liberate organically complexed dissolved Co and Cu (Milne et al. 2010). For cobalt, nickel, and copper, the UV-oxidized and non-UV-oxidized sample results are presented separately.

The automated seaFAST-pico (Elemental Scientific) with a Nobias Chelate-PA1 resin was connected to a High Resolution-Inductively Coupled Plasma-Mass Spectrometer (HR-ICP-MS; Thermo Scientific Element 2 at FSU, Element XR at USF), to preconcentrate and extract trace metals from the seawater samples inline (Lagerström et al. 2013). The reagents and input flow rates for seaFAST were followed from Hollister et al. (2020) and Burns et al. (2023). The elution acid in this study was a solution of 10% HNO_3 (Optima) with 1 ppb Indium as the internal standard. Upon loading the buffered sample ($\text{pH} \sim 6.2 \pm 0.2$; Burns et al. 2023) in the resin column, the column was rinsed with Milli-Q ($\geq 18.2 \text{ M}\Omega \cdot \text{cm}$) to wash out seawater salts, and the chelated trace metals were eluted with the elution acid containing the internal standard. The eluent from seaFAST was then drawn by the ICP-MS and analyzed for the natural abundance of Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb. Samples were analyzed twice, on the Element 2 at FSU, and on the Element XR at USF.

All analytical runs were comprised of seawater samples, instrument-manifold air blanks, quality control (QC) samples, a matrix-matched multielement calibration curve containing all target metals, a matrix-matched molybdenum (Mo) calibration curve, and certified reference materials, including SAFe D2, GEOTRACES GSP, and NASS-7. All seawater calibration curves and reference samples were prepared and treated the same as the seawater samples throughout the analytical runs.

The in-house QC consisted of 2-L aliquots of filtered (<0.2 µm) PAP-SO surface seawater (49.20469 °N, -14.78163 °E) that was collected in bulk on the 2021 EXPORTS cruise and then subsampled and acidified to 0.024 M HCl (Optima) for each QC aliquot. The matrix-matched curves, including the multielement and Mo calibration curves, were made using the same seawater as the QC to match the matrix of the seawater samples. The matrix-matched multielement calibration curve was made by dilution from a set of working stocks containing the target metals. These working stocks were diluted from ICP primary standards of 1000 micrograms per milliliter (µg/mL) in 2% HNO₃ of Mn (SPEX CertiPrep), Fe, Co, Ni, Cu, Cd (ULTRA Scientific), Zn and Pb (RICCA) diluted with 5% HNO₃ (Optima, Fisher) elution acid matrix. The Mo ICP primary standard consisted of 1000 µg/mL Mo in H₂O (SPEX CertiPrep), from which a Mo working stock was made by dilution with 5% HNO₃ (Optima, Fisher).

The analytical runs usually began by conditioning the inline seaFAST-ICP-MS with a few samples of filtered seawater, followed by several air and MQ blanks, calibration curves including the multielement and Mo curves, certified reference materials (also included in the middle of each analytical run to allow replicate measurements), seawater samples, several QC samples spread throughout the analytical run (every ~15th sample), several additional air blanks, and finalized by air blank samples. Sample trace metal concentrations were determined from calibration curves of the intensity counts against standards of known concentrations and corrected for average air blanks in the sequence as described previously by Hollister et al. (2020) and Burns et al. (2023). All dissolved and total dissolvable trace metal analyses were performed by PhD student Delfina Navarro-Estrada with assistance from senior researcher Salvatore Caprara in the Buck lab at the University of South Florida.

Analysis of dissolved macronutrients:

Macronutrient samples were thawed at room temperature and analyzed following standard colorimetric methods (Parsons et al. 1984; Becker et al. 2020) using a QuAAtro39 AutoAnalyzer (SEAL Analytical) at USF. The analytical runs included seawater samples, calibration curves made in artificial seawater, reagent blanks consisting of the artificial seawater used to make the calibration curves, reference materials including CK, CL, and CO (KANSO TECHNOS), and QC samples, including standards with known concentrations of nitrite and nitrate to check the efficiency of the instrument's cadmium column, and the lowest and middle-high standards of the calibration curve to check and correct for drift. QC samples were added approximately every 12th sample to assess the quality of the analytical run. The range in LODs for macronutrients were 0.006-0.048 micromolar (µM) for nitrate+nitrite, 0.011-0.042 µM for phosphate, 0.016-0.108 µM for silicic acid, and 0.004-0.027 µM for nitrite. Values below these limits of detection in each run are reported as 0 µM with accompanying QC Flag 6. Sample analyses for macronutrients were performed by senior researcher Salvatore Caprara in the Buck lab at the University of South Florida.

Data Processing Description

Data were flagged using the SeaDataNet quality flag scheme following GEOTRACES guidelines. See: <https://www.geotraces.org/geotraces-quality-flag-policy/>. Additional notes specific to the application of these flags to this project are noted in brackets [...].

0: No Quality Control: No quality control procedures have been applied to the data value. This is the initial status for all data values entering the working archive. [Not used].

1: Good Value: Good quality data value that is not part of any identified malfunction and has been verified as consistent with real phenomena during the quality control process. [Used for analyses that included replicates and/or reference samples; see **Table 1** for blank and certified reference material values obtained in this study].

2: Probably Good Value: Data value that is probably consistent with real phenomena, but this is unconfirmed or data value forming part of a malfunction that is considered too small to affect the overall quality of the data object of which it is a part. [Used when no replicate measurements or reference samples were available to check the quality of the data].

3: Probably Bad Value: Data value recognized as unusual during quality control that forms part of a feature that is probably inconsistent with real phenomena. [Not used].

4: Bad Value: An obviously erroneous data value. [Not used].

5: Changed Value: Data value adjusted during quality control. Best practice strongly recommends that the value before the change be preserved in the data or its accompanying metadata. [Not used].

6: Value Below Detection Limit: The level of the measured phenomenon was less than the limit of detection (LOD) for the method employed to measure it. [Values below the LOD are represented by "0"].

7: Value in Excess: The level of the measured phenomenon was too large to be quantified by the technique employed to measure it. The accompanying value is the measurement limit for the technique. [Not used].

8: Interpolated Value: This value has been derived by interpolation from other values in the data object. [Not used].

9: Missing Value: The data value is missing. Any accompanying value will be a magic number representing absent data [When sample was not collected the notation 'na' for 'not applicable' was used; when sample collected but there is no result for this parameter, the notation 'nda' for 'no data available' was used].

A: Value Phenomenon Uncertain: There is uncertainty in the description of the measured phenomenon associated with the value such as chemical species or biological entity. [Not used.]

BCO-DMO Processing Description

currently being processed

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Related Publications

Becker, S., Aoyama, M., Woodward, E. M. S., Bakker, K., Coverly, S., Mahaffey, C., & Tanhua, T. (2020). GO-SHIP Repeat Hydrography Nutrient Manual: The Precise and Accurate Determination of Dissolved Inorganic Nutrients in Seawater, Using Continuous Flow Analysis Methods. *Frontiers in Marine Science*, 7. <https://doi.org/10.3389/fmars.2020.581790>

Methods

Burns, S. M., Bundy, R. M., Abbott, W., Abdala, Z., Sterling, A. R., Chappell, P. D., Jenkins, B. D., & Buck, K. N. (2023). Interactions of bioactive trace metals in shipboard Southern Ocean incubation experiments. *Limnology and Oceanography*, 68(3), 525–543. Portico. <https://doi.org/10.1002/lno.12290>

Methods

Cutter, Gregory, Casciotti, Karen, Croot, Peter, Geibert, Walter, Heimbürger, Lars-Eric, Lohan, Maeve, Planquette, Hélène, van de Flierdt, Tina (2017) Sampling and Sample-handling Protocols for GEOTRACES Cruises. Version 3, August 2017. Toulouse, France, GEOTRACES International Project Office, 139pp. & Appendices. DOI: <http://dx.doi.org/10.25607/OBP-2>

Methods

Hollister, A. P., Kerr, M., Malki, K., Muhlbach, E., Robert, M., Tilney, C. L., Hubbard, K.A., & Buck, K. N. (2020). Regeneration of macronutrients and trace metals during phytoplankton decay: An experimental study. *Limnology and Oceanography*. doi:[10.1002/lno.11429](https://doi.org/10.1002/lno.11429)

Methods

Lagerström, M. E., Field, M. P., Séguret, M., Fischer, L., Hann, S., & Sherrell, R. M. (2013). Automated on-line flow-injection ICP-MS determination of trace metals (Mn, Fe, Co, Ni, Cu and Zn) in open ocean seawater: Application to the GEOTRACES program. *Marine Chemistry*, 155, 71–80. doi:[10.1016/j.marchem.2013.06.001](https://doi.org/10.1016/j.marchem.2013.06.001)

Methods

Mellett, T., & Buck, K. N. (2020). Spatial and temporal variability of trace metals (Fe, Cu, Mn, Zn, Co, Ni, Cd, Pb), iron and copper speciation, and electroactive Fe-binding humic substances in surface waters of the eastern Gulf of Mexico. *Marine Chemistry*, 227: 103891. doi:[10.1016/j.marchem.2020.103891](https://doi.org/10.1016/j.marchem.2020.103891)

Methods

Milne, A., Landing, W., Bizimis, M., & Morton, P. (2010). Determination of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in seawater using high resolution magnetic sector inductively coupled mass spectrometry (HR-ICP-MS). *Analytica*

Chimica Acta, 665(2), 200–207. doi:[10.1016/j.aca.2010.03.027](https://doi.org/10.1016/j.aca.2010.03.027)
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

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Parameters

Parameters for this dataset have not yet been identified

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Instruments

Dataset-specific Instrument Name	ThermoScientific Element II
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Dataset-specific Description	ThermoScientific Element II high resolution inductively coupled plasma mass spectrometer was used to measure dissolved metal concentrations.
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	QuAAtro39 AutoAnalyzer (SEAL Analytical)
Generic Instrument Name	Nutrient Autoanalyzer
Dataset-specific Description	QuAAtro39 AutoAnalyzer (SEAL Analytical) was used to measure macronutrient concentrations in seawater samples.
Generic Instrument Description	Nutrient Autoanalyzer is a generic term used when specific type, make and model were not specified. In general, a Nutrient Autoanalyzer is an automated flow-thru system for doing nutrient analysis (nitrate, ammonium, orthophosphate, and silicate) on seawater samples.

Dataset-specific Instrument Name	Elemental Scientific seaFAST-pico system
Generic Instrument Name	SeaFAST Automated Preconcentration System
Dataset-specific Description	Elemental Scientific seaFAST-pico system was used to preconcentrate dissolved trace metals from project samples for the ICPMS analyses.
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	ThermoScientific Element XR
Generic Instrument Name	Thermo Scientific ELEMENT XR high resolution inductively coupled plasma mass spectrometer
Dataset-specific Description	ThermoScientific Element XR high resolution inductively coupled plasma mass spectrometer was used to measure dissolved metal concentrations.
Generic Instrument Description	A high-resolution (HR) inductively coupled plasma (ICP) mass spectrometer (MS) composed of a dual mode secondary electron multiplier (SEM) and a Faraday detector. The ELEMENT XR instrument has a dynamic range of 5×10^7 to 1×10^{12} counts per second (cps), and allows simultaneous measurement of elements at concentrations over 1000 ug/g.

Dataset-specific Instrument Name	Towfish
Generic Instrument Name	towed unmanned submersible
Dataset-specific Description	Towfish: Seawater samples were collected with a custom surface sampling system, "towfish" (Mellett and Buck 2020), comprised of acid cleaned Bev-A-Line-IV tubing and an Almatec Double PTFE Diaphragm Pump.
Generic Instrument Description	A vehicle towed by rigid cable through the water column at fixed or varying depth with no propulsion and no human operator (e.g. Towfish, Scanfish, UOR, SeaSoar).

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Deployments

DY131

Website	https://www.bco-dmo.org/deployment/893299
Platform	RRS Discovery
Report	https://www.bodc.ac.uk/resources/inventories/cruise_inventory/report/17779/
Start Date	2021-05-01
End Date	2021-06-01
Description	See additional information from the British Oceanographic Data Centre (BODC): https://www.bodc.ac.uk/resources/inventories/cruise_inventory/report/17779/

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Project Information

Collaborative Research: Diatoms, Food Webs and Carbon Export - Leveraging NASA EXPORTS to Test the Role of Diatom Physiology in the Biological Carbon Pump (Diatoms and carbon export)

Coverage: Sub-Arctic Pacific, Ocean Station Papa

NSF Award Abstract:

This project focuses on a group of microscopic single-celled photosynthetic organisms in the ocean called diatoms. Diatoms float in the surface ocean as part of a group of organisms collectively called phytoplankton. There are thousands of different species of diatoms distributed across the global ocean. A famous oceanographer Henry Bigelow once said "All fish is diatoms" reflecting the importance of diatoms as the base of the food chain that supports the world's largest fisheries. Despite their small size, diatom photosynthesis produces 20% of the oxygen on earth each year. That's more than all of the tropical rain forests on land. The major objective of the research is to understand how the metabolic differences among diatom species affects the amount of diatom organic carbon that is carried, or exported, from the surface ocean to the deep ocean. As diatoms are photo-synthesizers like green plants, their biological carbon comes from converting carbon dioxide dissolved in seawater from the atmosphere into organic forms. Diatoms also require a series of other nutrients supplied by the ocean such as nitrogen and phosphorous and, uniquely for diatoms, the silicon used to construct their glass shells. This research will investigate how genetic and physiological differences among diatoms influence how each species react to changes in nutrient levels in the ocean and how those shifts affect the export of diatom carbon to the deep sea. The link between diatoms' physiological response and their carbon export comes about because shifts in physiology affect diatom attributes like how fast they sink and how tasty they are to predators. So if we can relate the physiological condition of different diatoms to the food-web pathways followed by different species, we can ultimately use knowledge of diatom physiological status and food web structure to predict how much diatom carbon gets to the deep sea. The research involves investigators with expertise in the physiology and genomics of diatoms and in the ocean's chemistry. The work will initially take place in the subarctic North Pacific in conjunction with the NASA Export Processes in the Ocean from RemoTe Sensing (EXPORTS) field program. The EXPORTS program is using a wide variety of methods to quantify the export and fate of photo-synthetically fixed carbon in the upper ocean. The research supports the training of undergraduate students, graduate students and a postdoctoral scholar. The research will also serve as the basis for activities aimed at K-12 and junior high school students.

The research will broadly impact our understanding of the biology of the biological pump (the transport of photo-synthetically fixed organic carbon to the deep sea) by forming a mechanistic basis for predicting the export of diatom carbon. It is hypothesized that the type and degree of diatom physiological stress are vital aspects of ecosystem state that drive export. To test this hypothesis, the genetic composition, rates of nutrient use and growth response of diatom communities will be evaluated and supported with measurements of silicon and iron stress to evaluate stress as a predictor of the path of diatom carbon export. The subarctic N. Pacific ecosystem is characterized as high nutrient low chlorophyll (HNLC) due to low iron (Fe) levels that are primary controllers constraining phytoplankton utilization of other nutrients. It has been a paradigm in low Fe, HNLC systems that diatoms grow at elevated Si:C and Si:N ratios and should be efficiently exported as particles significantly enriched in Si relative to C. However, Fe limitation also alters diatoms species composition and the high Si demand imposed by low Fe can drive HNLC regions to Si limitation or Si/Fe co-limitation. Thus, the degree of Si and/or Fe stress in HNLC waters can all alter diatom taxonomic composition, the elemental

composition of diatom cells, and the path cells follow through the food web ultimately altering diatom carbon export.

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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Program Information

EXPORT Processes in the Ocean from Remote Sensing (EXPORTS)

Website: <http://oceanexports.org/>

EXPORT Processes in the Ocean from Remote Sensing (EXPORTS) is a large-scale NASA-led field campaign that will provide critical information for quantifying the export and fate of upper ocean net primary production (NPP) using satellite observations and state of the art ocean technologies.

Ocean ecosystems play a critical role in the Earth's carbon cycle and the quantification of their impacts for both present conditions and for predictions into the future remains one of the greatest challenges in oceanography. The goal of the EXPORT Processes in the Ocean from Remote Sensing (EXPORTS) Science Plan is to develop a predictive understanding of the export and fate of global ocean net primary production (NPP) and its implications for present and future climates. The achievement of this goal requires a quantification of the mechanisms that control the export of carbon from the euphotic zone as well as its fate in the underlying "twilight zone" where some fraction of exported carbon will be sequestered in the ocean's interior on time scales of months to millennia. In particular, EXPORTS will advance satellite diagnostic and numerical prognostic models by comparing relationships among the ecological, biogeochemical and physical oceanographic processes that control carbon cycling across a range of ecosystem and carbon cycling states. EXPORTS will achieve this through a combination of ship and robotic field sampling, satellite remote sensing and numerical modeling. Through a coordinated, process-oriented approach, EXPORTS will foster new insights on ocean carbon cycling that maximizes its societal relevance through the achievement of U.S. and International research agency goals and will be a key step towards our understanding of the Earth as an integrated system.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1756816
NSF Division of Ocean Sciences (NSF OCE)	OCE-1756433
NSF Division of Ocean Sciences (NSF OCE)	OCE-1756442
NSF Division of Ocean Sciences (NSF OCE)	OCE-2424207

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