# Dissolved trace metal and macronutrient concentration data from incubation experiments conducted during the May 2021 EXPORTS North Atlantic cruise (DY131)

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#### Project

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

## Program

» EXport Processes in the Ocean from Remote Sensing (EXPORTS)

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## Abstract

This dataset includes trace metal (iron, manganese, cobalt, nickel, copper, zinc, cadmium, lead) and macronutrient (nitrate+nitrite, nitrite, phosphate, silicic acid) concentration data from incubation experiments conducted on board the RRS Discovery during the EXPORTS North Atlantic campaign at the Porcupine Abyssal Plain-Sustained Observatory (PAP-SO) site (DY131). In these experiments, additions of macronutrients (N, P, Si) and Fe were used to assess the level of Si, N, and Fe stress being experienced by the phytoplankton and to contextualize taxa-specific metatranscriptome responses for resolving gene expression profiles in the in-situ communities. This research project 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) Spatial Extent: N:49.5 E:-14.6 S:48.5 W:-15 Temporal Extent: 2021-05-01 - 2021-06-01

## Methods & Sampling

#### Incubation set-up

This work was funded by NSF and conducted in collaboration with the NASA EXPORTS campaign at 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. Three types of shipboard incubation experiments were conducted using trace metal clean techniques: Long-Term (LT), Short-Term (ST), and Grow-Out (GO) incubation experiments, for a total of eight incubations.

## Long-Term experiments

Surface water for LT experiments was collected using a trace metal clean towfish (Mellett and Buck 2020) while transiting at a speed of ~6 knots. Four treatments were used for the LT experiments: control (no additions), AllbutSi (+5 nM 57FeCl3, 20  $\mu$ M nitrate, 1.25  $\mu$ M phosphate), AllbutFe (+20  $\mu$ M silicic acid, 20  $\mu$ M nitrate, 1.25  $\mu$ M phosphate), and AllbutN (+5 nM 57FeCl3, 20  $\mu$ M silicic acid, 1.25  $\mu$ M phosphate). All Fe additions were made with an enriched standard of 57FeCl3 (ISOFLEX) to serve as a tracer of the added Fe. The nitrate and phosphate stocks were chelexed prior to use to remove metal contaminants. The silicic acid stock was made in an acid-cleaned Teflon bottle that was changed periodically to lower dissolved Fe concentrations and minimize metal contamination from this nutrient addition.

Triplicate 20 L polycarbonate (PC) carboys were used for each treatment. The carboys were filled in three rounds, with the first set of replicate carboys filled first, followed by the subsequent replicates. To facilitate homogenization, the carboys for each replicate round were filled in three passes, with each pass filling them to one-third of their final volume until full to the brim. For each treatment except the control, a 1 L PC bottle was also filled through the same sequence. Once filled, carboys and 1 L bottles were spiked with the treatments outlined above; a second 1 L PC bottle was filled from the treated carboys as a second check on the treatments. The 1 L bottles were sampled for post-spike time-zeroes of the incubation treatments and were identified as "T0.1"; these bottles were uniquely spiked with 10 nM 57FeCl3. The 1 L bottles sampled from the already treated carboys are identified as "T0.2" and had Fe additions of 5 nM 57FeCl3. Both sets of 1 L bottles were sacrificed in full for the time-zero samples. The LT 2 experiments were set up on the same day as the short-term experiment 2 (ST 2), and the time-zero Control treatments were sampled from one set of incubation bottles to represent both experiments. The treated carboys were placed in seawater-flowthrough deckboard incubators, covered with a mesh to allow 40% of surface photosynthetically active radiation (PAR) exposure, and harvested for final timepoint sampling after 6 (LT 1) or 5 (LT 2) days.

#### **Short-Term experiments**

Three short-term experiments were conducted: ST 1A, ST 1B, and ST 2. Surface seawater was collected for the ST experiments following the same approach outlined above for the Long-Term experiments: 20 L PC carboys were filled with the TMC Towfish in three rounds corresponding to each set of replicates, and in each round, the set of carboys were filled to one-third of the volume, consecutively until full to the brim. Each ST experiment had a different set of treatments: ST 1A included Control (no addition), +Fe (+ 5 nM 57FeCl3); ST 1B included Control (no addition), +N (+20  $\mu$ M silicic acid); ST 2 included Control (no addition), +N (+20  $\mu$ M

nitrate). T0.1 and T0.2 1 L bottles were collected the same way as described above for the LT experiments: the T0.1 bottles filled from the towfish and then spiked with 10 nM 57FeCl3, and the T0.2 bottles filled from subsampling the post-spike carboys that had already been spiked with 5 nM 57FeCl3. The same stock standards of 57FeCl3, silicic acid, and nitrate were used for these experiments as for the LT experiments. The ST 2 and LT 2 experiments were set up on the same day, and the time-zero Control treatments were sampled from one set of incubation bottles to represent both experiments. The treated carboys were placed in seawater-flowthrough deckboard incubators, covered with a mesh to allow 40% of surface photosynthetically active radiation (PAR) exposure, and harvested for final timepoint sampling after 22 hours for ST 1A, 40 hours for ST 1B, and 25 hours for ST 2.

#### **Grow-Out experiments**

Subsurface seawater for the grow-out (GO) experiments was collected with modified x-Niskin bottles (12L Ocean Test Equipment, Inc.) on a trace metal clean rosette (Cutter et al. 2017). Casts to collect the seawater were conducted between 11 am and 12 pm local time on the ship. Seawater was collected at depths of 47% and 12% of the surface photosynthetically active radiation (PAR), for a "High Light" and "Low Light" treatment, respectively. Seawater from the x-Niskins was transferred to 1 L PC incubation bottles that had been acid cleaned, Milli-Q conditioned, and rinsed three times with seawater before filling (Hollister et al., 2020; Burns et al., 2023). Three treatments were conducted for each light level: Control (no addition); +Fe (+5 nM 57FeCI3); +Fe+Si (+5 nM 57FeCI3, 20  $\mu$ M silicic acid); for GO 3, the Fe addition was +0.5 nM 57FeCI3. The same stock standards of 57FeCI3 and silicic acid were used for these experiments as for the LT and ST experiments. A replicate incubation bottle for all treatments was prepared in filtered (<0.2  $\mu$ m; Acropak) seawater and incubated wrapped in heavy duty black construction bags to allow for a dark control and an assessment of abiotic changes in trace metals including wall loss and precipitation.

The PAR intensity (47% and 12%) from the water column was maintained for the incubations by placing the 1-L incubation bottles in custom mesh screen bags designed to achieve the target light levels. All incubation bottles in their respective light treatment bags were placed in the seawater-flowthrough deckboard incubators, and harvested after 67 hours for GO experiment 1, 45 hours for GO experiment 2, and 70 hours for GO experiment 3.

#### Incubation sampling

All sampling occurred in a positive pressure hood of HEPA filtered air inside a trace metal clean van built into the RRS Discovery. Incubation sampling occurred at two timepoints: time-zero and time-final. For the LT and ST experiments, the T0.1 and T0.2 1 L bottles constituted the time-zeroes of the incubation treatments with additions. For time-final timepoints, the LT and ST experiments were subsampled from the 20 L PC carboys into 1 L PC bottles after carefully mixing. No sub-sampling was required for the GO experiments, which were conducted in 1 L PC bottles. In all cases, the incubation samples were filtered by vacuum using custom filtration rigs with Teflon dual-stage filter holders (Savillex ®) through two consecutive, acid cleaned polycarbonate track etched (PCTE) filters of 5  $\mu$ m and 0.4  $\mu$ m (Burns et al., 2023). The <0.4  $\mu$ m filtrate was collected for dissolved trace metals in acid-cleaned 125 mL low-density polyethylene (LDPE) bottles, and dissolved macronutrients in acid-cleaned 15 mL polypropylene tubes (Falcon). Dissolved trace metal samples were then acidified to 0.024 M with Optima HCl (pH~ 1.8; (Johnson et al., 2007)) and stored at room temperature until returned to the Buck lab at the University of South Florida for analyses. Dissolved macronutrient samples were stored frozen at -20 °C until returned to the Buck lab at the University of South Florida for analyses.

## Analysis of dissolved 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 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 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% HNO3 (Optima) with 1 ppb Indium as the internal standard. Upon loading the buffered sample (pH ~ 6.2 ± 0.2; Burns et al., 2023) in the resin column, the column was rinsed with Milli-Q ( $\geq$ 18.2 M $\Omega$ ·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, matrix-matched molybdenum (Mo), two Fe57 calibration curves, including an Fe57 calibration curve made in 5% HNO3 (Optima) and a matrix-matched Fe57 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  $\mu$ m) 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, Mo, and Fe57 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  $\mu$ g/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  $\mu$ g/mL Mo in H2O (SPEX CertiPrep), from which a Mo working stock was made by dilution with 5% HNO3 (Optima, Fisher). The Fe57 primary standard consisted of Fe57 oxide enriched to 96.64% (ISOFLEX), which was dissolved in HCl to make a concentrated stock of 57FeCl3. For this work, two working stocks of 186  $\mu$ M and 10  $\mu$ M 57FeCl3 were used to achieve Fe additions in 22 L and 1 L incubation bottles. Calibration curves for Fe57 were made with by dilution of the 10  $\mu$ M working stock in acid-cleaned, 125 mL LDPE bottles.

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, Mo, and Fe57 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).

#### 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. Values below these limits of detection are reported as 0  $\mu$ M 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: <u>https://www.geotraces.org/geotraces-quality-flag-policy/</u>). 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 2 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. [Used when all replicate measurements were too high to be consistent with real phenomena].

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. The accompanying value is the detection limit for the technique or zero if that value is unknown. [Instead of showing LOD values, "<LOD" was used in the data file. See Table 2 for detection limits of the dissolved trace metals].

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**

- Dates converted from %m/%d/%y to %Y-%M-%D format.
- Spaces removed from column names.

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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/<u>10.3389/fmars.2020.581790</u> *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/<u>10.1002/ino.12290</u> *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/<u>10.25607/OBP-2</u> *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:<u>10.1002/lno.11429</u> *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:<u>10.1016/j.marchem.2013.06.001</u> *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:<u>10.1016/j.aca.2010.03.027</u> *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 <a href="https://doi.org/10.1016/c2009-0-07774-5">https://doi.org/10.1016/c2009-0-07774-5</a> Methods

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## **Parameters**

Parameter	Description	Units
CRUISE_ID	Cruise identifier	unitless
EVTNBR	Event number for incubation setup water collection events, from ship log.	unitless
DATE_UTC	Date in UTC time when sample was collected, in format MM/DD/YY; ship time was set at UTC throughout cruise.	unitless
JULIAN_DAY	Julian Day when sample was collected.	unitless
EPOCH	Defined time block during the cruise, #1-3.	unitless
EPOCH_DAY	Day within the epoch time block.	unitless
LATITUDE	Ship position when incubation setup water was collected in decimal °N.	decimal degrees
LONGITUDE	Ship position when incubation setup water was collected in decimal °E.	decimal degrees
PLATFORM	Sampling system used for incubation setup water collection. TMC CTD = trace metal clean CTD. rosette. FISH = towfish	unitless

DEPTH	Depth in meters of incubation setup water collection.	meters (m)
INCLIGHT	Target light level of incubation treatment.	percentage of reference intensity (% I0)
INCVOL	Volume of incubation bottles used in each experiment.	liters (L)
INCNBR	Unique identification number assigned to each incubation experiment (see Table 1; methods).	unitless
INCDAY	Day of incubation experiment when sample was collected.	unitless
INCTREATMENT	Treatment identification within each incubation (see Table 1).	unitless
INCTREATMENT_ID	Identification number assigned to treatment samples within each incubation experiment.	unitless
NO3_NO2_CONC_INC	Concentrations of dissolved nitrate+nitrite in incubation samples. 'na' for 'not applicable' is used when no sample was collected for this parameter.	micromoles per liter (um/L)
NO3_NO2_STDEV	Concentrations of dissolved nitrate+nitrite in incubation samples. 'na' for 'not applicable' used when no sample was collected for this parameter.	micromoles per liter (um/L)
NO3_NO2_FLAG	Quality flag for NO3_NO2.	unitless
PO4_CONC_INC	Concentrations of dissolved phosphate in incubation samples. 'na' for 'not applicable' used when no sample was collected for this parameter.	micromoles per liter (um/L)
PO4_STDEV	Standard deviation of replicate phosphate concentration measurements. If only 2 replicates, the difference about the mean was used to calculate error.	micromoles per liter (um/L)
PO4_FLAG	Quality flag for PO4.	unitless
SiO4_CONC_INC	Concentrations of dissolved silicic acid in incubation samples. 'na' for 'not applicable' used when no sample was collected for this parameter.	micromoles per liter (um/L)
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SiO4_STDEV	Standard deviation of replicate silicate concentration measurements. If only 2 replicates, the difference about the mean was used to calculate error.	micromoles per liter (um/L)
SiO4_FLAG	Quality flag for SiO4.	unitless
NO2_CONC_INC	Concentrations of dissolved nitrite in incubation samples. 'na' for 'not applicable' used when no sample was collected for this parameter.	micromoles per liter (um/L)
NO2_STDEV	Standard deviation of replicate nitrate+nitrite concentration measurements. If only 2 replicates, the difference about the mean was used to calculate error.	micromoles per liter (um/L)
NO2_FLAG	Quality flag for NO2.	unitless
Mn_D_CONC_INC	Concentrations of dissolved manganese (Mn) in incubation samples.	nanomoles per liter (nmol/L)
Mn_D_STDEV	Standard deviation of replicate dissolved manganese (Mn) measurements. If only 2 replicates, the difference about the mean was used to calculate error.	nanomoles per liter (nmol/L)
Mn_D_FLAG	Quality flag for Mn_D_CONC.	unitless
Fe_D_CONC_INC	Concentrations of total dissolved iron (Fe) in incubation samples.	Nanomoles per liter (nmol/L)
Fe_D_STDEV	Standard deviation of replicate total dissolved iron (Fe) measurements. If only 2 replicates, the difference about the mean was used to calculate error.	Nanomoles per liter (nmol/L)
Fe_D_FLAG	Quality flag for Fe_D_CONC.	unitless
BKGDFe_D_CONC_INC	Concentrations of total dissolved iron (Fe) corrected for 57Fe spike in incubation samples; represents background (BKGD) dissolved iron concentrations. 'nda' for 'no data available' used when sample was collected but no data has been obtained for this parameter.	Nanomoles per liter (nmol/L)
BKGDFe_D_STDEV	Standard deviation of replicate background (BKGD) dissolved iron (Fe) measurements. If only 2 replicates, the difference about the mean was used to calculate error.	Nanomoles per liter (nmol/L)
BKGDFe_D_FLAG	Quality flag for BKGDFe_D_CONC.	unitless

ADD_57Fe_D_CONC_INC	Concentrations of added dissolved iron (Fe) as 57Fe in incubation samples; represents concentration of 57Fe spike in samples. 'na' for 'not applicable' used for treatment samples where no 57Fe was added.	Nanomoles per liter (nmol/L)
ADD_57Fe_D_STDEV	Standard deviation of replicate background (BKGD) dissolved iron (Fe) measurements. If only 2 replicates, the difference about the mean was used to calculate error.	Nanomoles per liter (nmol/L)
ADD_57Fe_D_FLAG	Quality flag for ADD_57Fe_D _CONC.	unitless
Co_D_UV_CONC_INC	Concentrations of dissolved cobalt (Co) in incubation samples, measured after UV-oxidation. 'nda' for 'no data available' used when sample was collected but no data has been obtained for this parameter.	Picomoles per liter (pmol/L)
Co_D_UV_STDEV	Standard deviation of replicate dissolved cobalt (Co) measurements in samples that were UV-oxidized. If only 2 replicates, the difference about the mean was used to calculate error.	Picomoles per liter (pmol/L)
Co_D_UV_FLAG	Quality flag for Co_D_UV_CONC.	unitless
Co_D_noUV_CONC_INC	Concentrations of dissolved cobalt (Co) in incubation samples; samples were not UV-oxidized prior to measurement. 'nda' for 'no data available' used when sample was collected but no data has been obtained for this parameter.	Picomoles per liter (pmol/L)
Co_D_noUV_STDEV	Standard deviation of replicate dissolved cobalt (Co) measurements in samples that were not UV-oxidized. If only 2 replicates, the difference about the mean was used to calculate error.	Picomoles per liter (pmol/L)
Co_D_noUV_FLAG	Quality flag for Co_D_noUV_CONC.	unitless
Ni_D_UV_CONC_INC	Concentrations of dissolved nickel (Ni) in incubation samples, measured after UV-oxidation. 'nda' for 'no data available' used when sample was collected but no data has been obtained for this parameter.	Nanomoles per liter (nmol/L)
Ni_D_UV_STDEV	Standard deviation of replicate dissolved nickel (Ni) measurements in samples that were UV-oxidized. If only 2 replicates, the difference about the mean was used to calculate error.	Nanomoles per liter (nmol/L)
Ni_D_UV_FLAG	Quality flag for Ni_D_UV_CONC.	unitless
Ni_D_noUV_CONC_INC	Concentrations of dissolved nickel (Ni) in incubation samples; samples were not UV-oxidized prior to measurement.	Nanomoles per liter (nmol/L)

Ni_D_noUV_STDEV	Standard deviation of replicate dissolved nickel (Ni) measurements in samples that were not UV-oxidized. If only 2 replicates, the difference about the mean was used to calculate error.	Nanomoles per liter (nmol/L)
Ni_D_noUV_FLAG	Quality flag for Ni_D_noUV_CONC.	unitless
Cu_D_UV_CONC_INC	Concentrations of dissolved copper (Cu) in incubation samples, measured after UV-oxidation.	Nanomoles per liter (nmol/L)
Cu_D_UV_STDEV	Standard deviation of replicate dissolved copper (Cu) measurements in samples that were UV-oxidized. If only 2 replicates, the difference about the mean was used to calculate error.	Nanomoles per liter (nmol/L)
Cu_D_UV_FLAG	Quality flag for Cu_D_UV_CONC.	unitless
Cu_D_noUV_CONC_INC	Concentrations of dissolved copper (Cu) in incubation samples; samples were not UV-oxidized prior to measurement.	Nanomoles per liter (nmol/L)
Cu_D_noUV_STDEV	Standard deviation of replicate dissolved copper (Cu) measurements in samples that were not UV-oxidized. If only 2 replicates, the difference about the mean was used to calculate error.	Nanomoles per liter (nmol/L)
Cu_D_noUV_FLAG	Quality flag for Cu_D_noUV_CONC.	unitless
Zn_D_CONC_INC	Concentrations of dissolved zinc (Zn) in incubation samples. 'nda' for 'no data available' used when sample was collected but no data has been obtained for this parameter.	Nanomoles per liter (nmol/L)
Zn_D_STDEV	Standard deviation of replicate dissolved zinc (Zn) measurements. If only 2 replicates, the difference about the mean was used to calculate error.	Nanomoles per liter (nmol/L)
Zn_D_FLAG	Quality flag for Zn_D_CONC.	unitless
Cd_D_CONC_INC	Concentrations of dissolved cadmium (Cd) in incubation samples.	Picomoles per liter (pmol/L)
Cd_D_STDEV	Standard deviation of replicate dissolved cadmium (Cd) measurements. If only 2 replicates, the difference about the mean was used to calculate error.	Picomoles per liter (pmol/L)
Cd_D_FLAG	Quality flag for Cd_D_CONC.	unitless
Pb_D_CONC_INC	Concentrations of dissolved lead (Pb) in incubation samples.	Picomoles per liter (pmol/L)

Pb_D_STDEV	Standard deviation of replicate dissolved lead (Pb) measurements. If only 2 replicates, the difference about the mean was used to calculate error.	Picomoles per liter (pmol/L)
Pb_D_FLAG	Quality flag for Pb_D_CONC.	unitless

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## Instruments

Dataset-specific Instrument Name	Seabird SBS 32
Generic Instrument Name	Discrete water sampler
Dataset-specific Description	Seabird SBS 32 trace metals frame and rosette sampling system were used for depth profile sample collection.
Generic Instrument Description	A device that collects an in-situ discrete water sample from any depth and returns it to the surface without contamination by the waters through which it passes, such as a water bottle.

Dataset- specific Instrument Name	ThermoScientific Element II
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Dataset- specific Description	A 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	Towfish
Generic Instrument Name	towed unmanned submersible
Dataset- specific Description	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): <a href="https://www.bodc.ac.uk/resources/inventories/cruise_inventory/report/17779/">https://www.bodc.ac.uk/resources/inventories/cruise_inventory/report/17779/</a>

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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 nurtrients 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)	<u>OCE-1756816</u>
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-1756433</u>
NSF Division of Ocean Sciences (NSF OCE)	OCE-1756442

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