# Dissolved Macronutrient Concentrations from Depth Profiles and Incubation Experiments from STING I Cruise AE2305 on R/V Atlantic Explorer in the Gulf of Mexico from February to March 2023

**Website**: https://www.bco-dmo.org/dataset/929305
**Data Type**: Cruise Results
**Version**: 1
**Version Date**: 2024-06-04

**Project**
» Collaborative Research: Linking iron and nitrogen sources in an oligotrophic coastal margin: Nitrogen fixation and the role of boundary fluxes (Gulf of Mexico DON and Fe)


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|---|---|---|
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**Abstract**
Concentrations of inorganic dissolved macronutrients, including phosphate, nitrate plus nitrite (N+N), silicic acid, and nitrite, from phytoplankton shipboard incubation experiments and depth profiles collected on STING I cruise AE2305 on R/V Atlantic Explorer in the Gulf of Mexico from February to March 2023. This project investigates how groundwater discharge delivers important nutrients to the coastal ecosystems of the West Florida Shelf. Preliminary studies indicate that groundwater may supply both dissolved organic nitrogen (DON) and iron in this region. In coastal ecosystems like the West Florida Shelf that have very low nitrate and ammonium concentrations, DON is the main form of nitrogen available to organisms. Nitrogen cycling is strongly affected by iron availability because iron is essential for both photosynthesis and for nitrogen fixation. This study will investigate the sources and composition of DON and iron, and their influence on the coastal ecosystem. The team will sample offshore groundwater wells, river and estuarine waters, and conduct two expeditions across the West Florida Shelf in winter and summer.

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## Coverage

**Location**: Eastern Gulf of Mexico and West Florida Shelf
**Spatial Extent**: **N**:28.5 **E**:-82.5 **S**:26.3 **W**:-86.6
**Temporal Extent**: 2023-02-20 - 2023-03-05

### Methods & Sampling

Water column samples were collected in February and March 2023 aboard the R/V Atlantic Explorer using a trace metal clean rosette (SeaBird) outfitted with 12-L Niskin-X samplers (Ocean Test Equipment), a trace metal clean pump, or a custom surface pump “towfish” system (Mellett and Buck, 2020). Seawater samples for macronutrient analysis were filtered through 0.2 µm Pall Acropak Super membrane filter capsules, collected in acid-cleaned and triple-rinsed 15-mL Falcon tubes, and stored in ziplock bags in the fridge until analyzed shipboard following recommended practices (Becker et al., 2020), typically within 24 hours of collection.

Samples were analyzed shipboard for phosphate, nitrate+nitrite, silicate, and nitrite on a QuAAtro39 AutoAnalyzer (SEAL Analytical) according to standard colorimetric methods (Strickland and Parsons, 1972). All reagents were prepared in dedicated labware with high purity Milli-Q (>18 MΩ cm) water. Working standards were prepared fresh daily in an artificial seawater (ASW; 35 g/L sodium chloride, 0.5 g/L sodium bicarbonate) matrix using calibrated volumetric pipettes.

Nine-point standard curves were analyzed at the beginning of each run with multiple reagent blanks. Quality control checks were analyzed every twelfth sample with ASW blanks and standards. The highest standard from the calibration curve was analyzed approximately every twenty samples to check for drift during the runs. Subsamples of reference material for nutrients in seawater (Konso) were measured in each run (see Table 1 below).

Detection limits for each parameter were determined from three times the standard deviation of replicate lowest standards. Limits of detection were 0.035 µM for phosphate, 0.048 µM for nitrate+nitrite, 0.051 µM for silicate, and 0.012 µM for nitrite. Values below detection are reported as 0 µM with accompanying QC Flag 6.

Sample analyses for macronutrients were performed by USF MS student Caitlyn Parente. See the Supplemental File: 929305_v1_measured_and_certified_RMNS_results.csv and 929305_v1_measured_and_certified_RMNS_results_summary.csv for these figures and summary statistics.

### Data Processing Description

Data were flagged using the SeaDataNet quality flag scheme recommended by GEOTRACES (https://www.geotraces.org/geotraces-quality-flag-policy/) and described below. Notes specific to the application of these flags to this dataset 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. [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 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. [Values below detection are reported as 0.00 µM in the data file. Detection limits for each parameter are listed in the “methods and sampling” section of this form].

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**

- Spaces from column names replaced with underscores ("_")
- Special characters in column names replaced with plain text (i.e., "%" has been replaced with "percent")
- Date formats converted from %m/%d/%y to %Y-%m-%d
- Column "ISO_DateTime_UTC" created by merging the DATE_UTC and TIME_UTC columns

**Problem Description**

No problems or issues were reported with this dataset.

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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*

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
*Methods*

Strickland, J. D. H. and Parsons, T. R. (1972). A Practical Hand Book of Seawater Analysis. Fisheries Research Board of Canada Bulletin 157, 2nd Edition, 310 p.
*Methods*

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## Parameters

| Parameter | Description | Units |
|---|---|---|
| EVTNBR | Event number; ‘nda’ for ‘no data available’ or missing information; ‘na’ for ‘not applicable’ to that sample. | unitless |
| ISO_DateTime_UTC | UTC datetime when sample was collected. | unitless |
| DATE_UTC | UTC date when sample was collected. | unitless |
| TIME_UTC | UTC time when sample was collected, in format HH:MM; ‘nda’ for ‘no data available’ or missing information; ‘na’ for ‘not applicable’ to that sample. | unitless |
| DATE_GMT | GMT date when sample was collected. | unitless |
| TIME_GMT | GMT time when sample was collected, in format HH:MM; ‘nda’ for ‘no data available’ or missing information; ‘na’ for ‘not applicable’ to that sample. | unitless |
| LATITUDE | Position when sample was collected in decimal decimal degrees, where a positive value indicates a Northern coordinate; ‘nda’ for ‘no data available’ or missing information; ‘na’ for ‘not applicable’ to that sample. | decimal degrees |
| LONGITUDE | Position when sample was collected in decimal degrees where positive values represent an Eastern coordinate; ‘nda’ for ‘no data available’ or missing information; ‘na’ for ‘not applicable’ to that sample. | decimal degrees |
| PLATFORM | Sampling system used. TMC CTD = trace metal CTD rosette. FISH = tow fish. TM PUMP = trace metal pump. INC = incubation. | unitless |
| CASTNBR | Cast number; ‘na’ for ‘not applicable’ to that sample. | unitless |
| STNNBR | Station number; ‘na’ for ‘not applicable’ to that sample. | unitless |
| BTLNBR | CTD rosette bottle number; ‘na’ for ‘not applicable’ to that sample. | unitless |
| DEPTH | Sample collection depth below sea surface; ‘no data available’ or missing information; ‘na’ for ‘not applicable’ to that sample. | meters (m) |
| NO3_NO2 | Concentrations of dissolved nitrate+nitrite. | micromoles per liter (uM) |

| | | |
|---|---|---|
| NO3_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) |
| NO3_NO2_FLAG | Quality flag for NO3_NO2. Refer to the Data Processing Description for more details about flags. | unitless |
| PO4 | Concentrations of dissolved phosphate. | micromoles per liter (uM) |
| 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) |
| PO4_FLAG | 6 = below the limit of detection. | unitless |
| SiO4 | Concentrations of dissolved silicate. | micromoles per liter (uM) |
| 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) |
| SiO4_FLAG | Quality flag for SiO4. | unitless |
| NO2 | Concentrations of dissolved nitrite. | micromoles per liter (uM) |
| 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) |
| NO2_FLAG | Quality flag for NO2. | unitless |
| STING_ID | need from submitter | unitless |
| NO3_NO2_percentRSD | Percent relative standard deviation of replicate nitrate+nitrite concentration measurements. Calculated as NO3_NO2_STDEV divided by NO3_NO2 and multiplied by 100; ‘na’ for ‘not applicable’, used when value of 0 assigned to concentrations <LOD. | unitless |
| PO4_percentRSD | Percent relative standard deviation of replicate phosphate concentration measurements. Calculated as PO4_STDEV divided by PO4 and multiplied by 100; ‘na’ for ‘not applicable’, used when value of 0 assigned to concentrations <LOD. | unitless |

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|---|---|---|
| SiO4_percentRSD | Percent relative standard deviation of replicate silicate concentration measurements. Calculated as SiO4_STDEV divided by SiO4 and multiplied by 100. | unitless |
| NO2_percentRSD | Percent relative standard deviation of replicate nitrite concentration measurements. Calculated as NO2_STDEV divided by NO2 and multiplied by 100;  'na' for 'not applicable', used when value of 0 assigned to concentrations <LOD. | unitless |

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## Instruments

| | |
|---|---|
| **Dataset-specific Instrument Name** | Towfish |
| **Generic Instrument Name** | Discrete water sampler |
| **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 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. |

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| **Dataset-specific Instrument Name** | 12-L X-Niskin bottles (Ocean Test Equipment) |
| **Generic Instrument Name** | Niskin bottle |
| **Dataset-specific Description** | 12-L trace metal clean modified X-Niskin bottles (Ocean Test Equipment) mounted on a trace metal clean rosette with a programmable autofire module (Seabird) and deployed on 1/4" 12-strand Spectra synthetic line to collect depth profile seawater samples. |
| **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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| **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. |

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| **Dataset-specific Instrument Name** | TM Pump |
| **Generic Instrument Name** | Pump |
| **Dataset-specific Description** | Wilden Pro-Flo Series P100 PTFE Diaphram Pump was deployed on 1/4” 12-strand Spectra synthetic line to collect surface and depth profile seawater samples at stations with water depth |
| **Generic Instrument Description** | A pump is a device that moves fluids (liquids or gases), or sometimes slurries, by mechanical action. Pumps can be classified into three major groups according to the method they use to move the fluid: direct lift, displacement, and gravity pumps |

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## Deployments

**AE2305**

| | |
|---|---|
| **Website** | https://www.bco-dmo.org/deployment/929020 |
| **Platform** | R/V Atlantic Explorer |
| **Start Date** | 2023-02-18 |
| **End Date** | 2023-03-07 |
| **Description** | Start and End port: St. Petersburg, Florida |

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## Project Information

**Collaborative Research: Linking iron and nitrogen sources in an oligotrophic coastal margin: Nitrogen fixation and the role of boundary fluxes (Gulf of Mexico DON and Fe)**

**Coverage**: Gulf of Mexico, West Florida Shelf

**NSF Award Abstract:**
This project will investigate how groundwater discharge delivers important nutrients to the coastal ecosystems of the West Florida Shelf. Preliminary studies indicate that groundwater may supply both dissolved organic

nitrogen (DON) and iron in this region. In coastal ecosystems like the West Florida Shelf that have very low nitrate and ammonium concentrations, DON is the main form of nitrogen available to organisms. Nitrogen cycling is strongly affected by iron availability because iron is essential for both photosynthesis and for nitrogen fixation. This study will investigate the sources and composition of DON and iron, and their influence on the coastal ecosystem. The team will sample offshore groundwater wells, river and estuarine waters, and conduct two expeditions across the West Florida Shelf in winter and summer. Investigators will participate in K-12 and outreach activities to increase awareness of the project and related science. The project will fund the work of six graduate and eight undergraduate students across five institutions, furthering NSF's goals of education and training.

Motivated by preliminary observations of unexplained, tightly-correlated DON and dissolved iron concentrations across the West Florida Shelf (WFS), the proposed work will quantify the flux and isotopic signatures of submarine groundwater discharge (SGD)-derived DON and iron to the WFS, and evaluate the bioavailability of this temporally-variable source using four seasonal near-shore campaigns sampling offshore groundwater wells, estuarine, and riverine endmembers and two cross-shelf cruises. The work will evaluate whether SGD stimulates nitrogen fixation on the WFS, and the potential for the stimulated nitrogen fixation to further modify the chemistry of DON and dissolved iron in the region. The cross-shelf cruises will investigate hypothesized periods of maximum SGD and Trichodesmium abundance (June), and reduced river discharge and SGD (February), thus comparing two distinct biogeochemical regimes. The concentrations and isotopic compositions of DON and dissolved iron, molecular composition of DON, and the concentration and composition of iron-binding ligands will be characterized. Nitrogen fixation rates and Trichodesmium spp. abundance and expression of iron stress genes will be measured. Fluxes of DON and iron from SGD and rivers will be quantified with radium isotope mass balances. The impacts of SGD on nitrogen fixation and DON/ligand production will be constrained with incubations of natural phytoplankton communities with submarine groundwater amendments. Two hypotheses will be tested: 1) SGD is the dominant source of bioavailable DON and dissolved iron on the WFS, and 2) SGD-alleviation of iron stress changes the dominant Trichodesmium species on the WFS, increases nitrogen fixation rates and modifies DON and iron composition. Overall, the work will establish connections between marine nitrogen and iron cycling and evaluate the potential for coastal inputs to modify water along the WFS before export to the Atlantic Ocean. This study will thus provide a framework to consider these boundary fluxes in oligotrophic coastal systems and the relative importance of rivers and SGD as sources of nitrogen and iron in other analogous locations, such as coastal systems in Australia, India, and Africa, where nitrogen fixation and SGD have also been documented.

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-2326719 |


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