Total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP) of samples collected from rivers draining onto the West Florida Shelf and submarine groundwater wells on the Western coast of Florida from Nov 2022 to Mar 2024

Website: https://www.bco-dmo.org/dataset/989225
Data Type: Other Field Results
Version: 1
Version Date: 2025-11-20

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)

Contributors	Affiliation	Role
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Abstract
The West Florida Shelf (WFS) is oligotrophic, with inorganic N and P concentrations typically at or below detection limits, and yet significant rates of primary productivity, including blooms of the cyanobacterial diazotroph Trichodesmium spp. as well as the harmful algal species Karenia brevis, are observed there. Consequently, dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) are thought to be the primary sources of assimilative nutrients on the WFS. Here we report measurements of total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP) concentrations made on samples collected quarterly from rivers draining onto the WFS as well as from submarine groundwater wells on three transects extending from the Florida Nature Coast in the north to Venice Headland in the south. Elevated concentrations of TDN (>12 µM) and TDP (>0.5 µM) were observed in riverine and groundwater samples, as well as in the shallow, nearshore region, while to the west concentrations of both TDN and TDP decreased to values typically associated with oligotrophic North Atlantic waters (4 to 5 µM TDN and 0.05 to 0.1 µM TDP).

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Coverage

Location: West Florida Shelf
Spatial Extent: **N**:28.7669 **E**:-81.8474 **S**:26.3874 **W**:-83.0012
Temporal Extent: 2022-11-14 - 2024-03-08

Methods & Sampling

Riverine and estuarine samples were collected on land. Submarine groundwater samples collected on various shore boats by Co-PI Christopher Smith. Riverine, estuarine and submarine groundwater well samples were collected between November 2022 and March 2024 using a trace metal clean pump and filtered through a 0.2 µm Pall Acropak Super membrane filter capsule, collected into 60 mL HDPE bottles and frozen at -20 C until

analysis on land.

TDP concentrations were measured using a Shimadzu UV-1800 and a Shimadzu UV-1900i. All reagents were prepared in dedicated labware with high purity Milli-Q (>18.2 MΩ cm) water. Samples were calibrated using a 6 point calibration curve with concentrations that bracketed sample concentrations. Each run included multiple Milli-Q water and reagent blanks, as well as three internal standards including adenosine triphosphate, a polyphosphate compound, glyphosate, a polyphosphonate compound, and 0.2 μm filtered oligotrophic surface water from the Gulf to check the consistency of the TDP concentration analysis over time.

TDN concentrations were measured using a Thermo 42i NOx analyzer and a Teledyne T200 NOx analyzer and were calibrated with standards that bracketed the concentration range of samples. Additionally, as an internal check on the completeness of the persulfate oxidation method, DON standards were included as "unknowns" in each set of persulfate oxidation, in this case USGS 40 (L-glutamic acid) and IAEA600 (caffeine).

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

- Opened "BCO-DMO_STING_LandSampling_TDN_TDP_Conc_v2.xlsx" in Excel and moved 'NDA' values from the 'TDP_FLAG' and 'TDN_FLAG' fields to the 'TDP' and 'TDN' fields, respectively
- Replaced all 'NDA' values from the 'TDP_FLAG' and 'TDN_FLAG' with '9' to represent missing data, as described in the Data Processing section
- Saved file as "BCO-DMO_STING_LandSampling_TDN_TDP_Conc_v2_dm_adjust_keys.xlsx" and uploaded the file again to the submission
- Imported "BCO-DMO_STING_LandSampling_TDN_TDP_Conc_v2_dm_adjust_keys.xlsx" into the BCO-DMO system
- Removed the second "STING_ID" parameter, since it's values were the same as the first "STING_ID" parameter
- Renamed CRUISE_ID to CRUISE_TYPE to better describe the contents of the parameter
- Exported file as "989225_v1_sting_land_tdn_tdp.csv"

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Related Publications

Knapp, A. N., Sigman, D. M., & Lipschultz, F. (2005). N isotopic composition of dissolved organic nitrogen and nitrate at the Bermuda Atlantic Time-series Study site. Global Biogeochemical Cycles, 19(1). doi:<u>10.1029/2004gb002320</u>
Methods

Liang, Z., McCabe, K., Fawcett, S. E., Forrer, H. J., Hashihama, F., Jeandel, C., Marconi, D., Planquette, H., Saito, M. A., Sohm, J. A., Thomas, R. K., Letscher, R. T., & Knapp, A. N. (2022). A global ocean dissolved organic phosphorus concentration database (DOPv2021). Scientific Data, 9(1). https://doi.org/<u>10.1038/s41597-022-01873-7</u>
Methods

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Parameters

Parameter	Description	Units
CRUISE_TYPE	Sampling cruise; STING Estuary, STING River, STING Wells, or STING OFS. OSF stands for 'Offshore Sampling' and was only carried out in June and July 2023	unitless
SAMPLE_ID	Land-based sample identifier	unitless
STING_ID	Unique number assigned to each sampling event in STING project	unitless
DATE	Date the sample was collected	unitless
STATION	USGS station identifier for submarine ground water well samples, and station name for river and estuary samples; 'VH' = Venice Headlands transect; 'IRB' = Indian Rocks Beach transect; 'NC' = Nature Coast transect	unitless

SAMPLE	Type of sample, where 'SW' stands for 'surface water sample collected over a submarine groundwater well'; 'BW' stands for 'water collected just above the sediment/water interface about a submarine groundwater well', and 'GD' and 'GS' stand for 'water collected from a submarine groundwater well'; 'BW Fe' and 'SW Fe' indicate these were either 'Bottom Water' (BW) or 'Surface water' (SW) seawater samples that were collected using the same methods as samples collected for iron (Fe) and other trace metal analysis	unitless
TYPE	Type of land based sampling: submarine groundwater well, river, seawater, or estuarine	unitless
LATITUDE	Position when sample was collected in decimal degrees; a positive value indicates a Northern coordinate	decimal degrees
LONGITUDE	Position when sample was collected in decimal degrees; a negative value indicates a Western coordinate	decimal degrees
TDP	Concentrations of total dissolved phosphorus	micromoles per liter (µM)
TDP_STDEV	Standard deviation of replication total dissolved phosphorus measurements. If only 2 replicates, the difference about the mean was used to calculate error	micromoles per liter (µM)
TDP_COUNT	Number of TDP analytical replicates performed	unitless
TDP_FLAG	Quality flag for TDP measurements. See the 'Data Processing Description' section of the BCO-DMO metadata page for this dataset for full data quality flag details	unitless
TDN	Concentrations of total dissolved nitrogen	micromoles per liter (µM)
TDN_STDEV	Standard deviation of replication total dissolved nitrogen measurements. If only 2 replicates, the difference about the mean was used to calculate error	micromoles per liter (µM)
TDN_COUNT	Number of TDN analytical replicates performed	unitless
TDN_FLAG	Quality flag for TDN measurements. See the 'Data Processing Description' section of the BCO-DMO metadata page for this dataset for full data quality flag details	unitless

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Instruments

Dataset-specific Instrument Name	Thermo 42i NOx analyzer
Generic Instrument Name	Chemiluminescence NOx Analyzer
Dataset-specific Description	TDN concentrations were measured using a Thermo 42i NOx analyzer and a Teledyne T200 NOx analyzer and were calibrated with standards that bracketed the concentration range of samples.
Generic Instrument Description	The chemiluminescence method for gas analysis of oxides of nitrogen relies on the measurement of light produced by the gas-phase titration of nitric oxide and ozone. A chemiluminescence analyzer can measure the concentration of NO/NO2/NOX. One example is the Teledyne Model T200: https://www.teledyne-api.com/products/nitrogen-compound-instruments/t200

Dataset-specific Instrument Name	Teledyne T200 NOx analyzer
Generic Instrument Name	Chemiluminescence NOx Analyzer
Dataset-specific Description	TDN concentrations were measured using a Thermo 42i NOx analyzer and a Teledyne T200 NOx analyzer and were calibrated with standards that bracketed the concentration range of samples.
Generic Instrument Description	The chemiluminescence method for gas analysis of oxides of nitrogen relies on the measurement of light produced by the gas-phase titration of nitric oxide and ozone. A chemiluminescence analyzer can measure the concentration of NO/NO2/NOX. One example is the Teledyne Model T200: https://www.teledyne-api.com/products/nitrogen-compound-instruments/t200

Dataset-specific Instrument Name	Trace metal clean pump
Generic Instrument Name	Pump
Dataset-specific Description	Riverine, estuarine and submarine groundwater well samples were collected using a trace metal clean pump and filtered through a 0.2 µm Pall Acropak Super membrane filter capsule, collected into 60 mL HDPE bottles and frozen at -20 C until analysis on land.
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

Dataset-specific Instrument Name	Shimadzu UV-1800
Generic Instrument Name	UV Spectrophotometer-Shimadzu
Dataset-specific Description	TDP concentrations were measured using a Shimadzu UV-1800 and a Shimadzu UV-1900i.
Generic Instrument Description	The Shimadzu UV Spectrophotometer is manufactured by Shimadzu Scientific Instruments (ssi.shimadzu.com). Shimadzu manufacturers several models of spectrophotometer; refer to dataset for make/model information.

Dataset-specific Instrument Name	Shimadzu UV-1900i
Generic Instrument Name	UV Spectrophotometer-Shimadzu
Dataset-specific Description	TDP concentrations were measured using a Shimadzu UV-1800 and a Shimadzu UV-1900i.
Generic Instrument Description	The Shimadzu UV Spectrophotometer is manufactured by Shimadzu Scientific Instruments (ssi.shimadzu.com). Shimadzu manufacturers several models of spectrophotometer; refer to dataset for make/model information.

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-2148989
NSF Division of Ocean Sciences (NSF OCE)	OCE-2506248

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