

Size-fractionated Fe speciation

Website: <https://www.bco-dmo.org/dataset/1010687>

Version: 1

Version Date: 2026-10-23

Project

» [Collaborative Research: Investigating Iron-binding Ligands in Southern Ocean Diatom Communities: The Role of Diatom-Bacteria Associations](#) (Diatom_Bacteria_Ligands)

Contributors	Affiliation	Role
Buck, Kristen Nicole	Oregon State University (OSU)	Principal Investigator, Contact, Data Manager
Chappell, Phoebe Dreux	University of South Florida (USF)	Co-Principal Investigator
Jenkins, Bethany D.	University of Rhode Island (URI)	Co-Principal Investigator
Caprara, Salvatore	Oregon State University (OSU)	Scientist
Freiberger, Robert Ben	Oregon State University (OSU)	Scientist
Mahieu, Léo	Oregon State University (OSU)	Scientist
Moore, Laura Ellen	Oregon State University (OSU)	Scientist
Rauch, Shannon	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

Abstract

This dataset includes the concentrations of in-situ dissolved (< 0.2 micrometers (μm)) and soluble (< 0.02 μm) iron, iron bound to electroactive humic-like substances, total electroactive iron-binding humic-like substances, and total organic iron-binding ligands from discrete depth profile samples collected on the NBP16-08 cruise on the R/V IB Nathaniel B. Palmer in the Southern Ocean on 10 October 2016. This project investigates the impact of iron-binding humic-like substances and total iron-binding organic ligands on dissolved iron (Fe) size fractionation in the Drake Passage. The project used depth profile samples to characterize the partitioning of Fe-binding humic-like substances and total Fe-binding organic ligands between the soluble and colloidal fractions and assess their impact on Fe fractionation in different parts of the water column. Understanding the distributions and fractionation of Fe-binding humic-like substances and organic Fe-binding ligands provides insight into their contribution to Fe stabilization.

Table of Contents

- [Coverage](#)
- [Dataset Description](#)
 - [Methods & Sampling](#)
 - [Data Processing Description](#)
 - [BCO-DMO Curation Notes](#)
- [Parameters](#)
- [Deployments](#)
- [Project Information](#)
- [Funding](#)

Coverage

Location: Drake Passage

Methods & Sampling

Water column sampling:

The full water column at the site named Station 21 in the Drake Passage was sampled on 10 October 2016 aboard the R/V IB Nathaniel B. Palmer. 12-liter (L) Niskin bottles (OceanTestEquipment, Inc.) mounted on a trace metal clean rosette sampling system (SBE32, Seabird; TMC CTD) were used to collect depth profile samples.

Samples for dissolved humic-like substances, total dissolved organic iron-binding ligands, and dissolved iron were filtered through pre-cleaned 0.2-micrometer (μm) polyethersulfone membrane filters (Acropak 200, Pall Corporation) from the trace metal clean rosette (Sterling et al., 2023). Samples for soluble humic-like substances, soluble total organic iron-binding ligands, and soluble iron were additionally filtered through 0.02 μm filters (Anopore; Fitzsimmons and Boyle 2014) on a custom vacuum filtration setup (Burns et al., 2023). Prior to sample collection, each 0.02 μm filter was rinsed with three ~ 50 -milliliter (mL) aliquots of Milli-Q (18.2 MW cm) followed by three ~ 30 -mL rinses with the seawater sample; a new filter was used for each sample. Humic-like substance and total organic ligand samples were collected in acid-cleaned, narrow mouth 500 mL fluorinated high-density polyethylene bottles (FLPE; Nalgene) and stored at -20 degrees Celsius ($^{\circ}\text{C}$) until shore-based analyses at Oregon State University. Samples for iron were collected into 125 mL acid-cleaned low-density polyethylene bottles (LDPE; Nalgene), acidified to 0.024 M final concentration with ultrapure hydrochloric acid (HCl; Optima, Fisher), then stored at room temperature prior to shore-based analysis.

Sample analyses - dissolved and soluble humic-like substances:

Electroactive, Fe-binding humic-like substances were measured using adsorptive cathodic stripping voltammetry based on the method first developed by Laglera et al. (2007), updated by Sukekava et al. (2018), and described in Moore et al. (in review). Samples were analyzed using a polarographic 797 VA Computrace (Metrohm) stand equipped with a hanging mercury drop electrode, Ag/AgCl reference electrode, platinum rod auxiliary electrode, and an acid-cleaned Teflon analytical cell. Briefly, frozen samples were set out to thaw overnight at room temperature in the dark. The following day, samples were inverted several times to homogenize, and 10 mL sub-samples were aliquoted into each of 2 paired acid-cleaned, pre-conditioned 50 mL polypropylene vials (MetalFree, Labcon). Boric acid buffer (7.5 mM final concentration; Mahieu et al., 2024) was added to maintain a solution pH of 8.2. Iron standard was added into vial "B" (final concentration 60 nanomolar (nM)) to saturate all the Fe-binding ligands in the solution, whereas vial A remained with ambient Fe conditions. Vial A represented the ambient concentration of Fe bound to humic-like substances in situ, and vial B represented the total concentration of Fe-binding electroactive ligands in the sample. Both aliquots were left to equilibrate for a minimum of 14 hours.

After the equilibration period, vial A was added to the Teflon voltametric cell with an addition of 500 microliters (μL) of 0.4M KBrO_3^- catalyst. The sample was then purged for 300 seconds with high-purity N_2 gas, and then electrochemical analysis was performed with a 60-120 second deposition period with stirring at -0.1 volts (V) followed by linear sweep voltammetry (-0.1 to -1V , scan rate 50 millivolts per second (mV s^{-1})). Vial B was analyzed immediately following vial A under the same conditions and deposition time, then three successive standard additions of Fe-saturated Suwannee River Fulvic Acid (SRFA, International Humic Substance Society #2S101F) standard were added. Default standard additions were 0.1, 0.2, and 0.3 mg SRFA per liter. A 70 s N_2 purge was included after each addition to ensure oxygen removal. Triplicate scans were performed for all measurements. Teflon analytical cell and polypropylene vials were rinsed thoroughly with Milli-Q water between samples to minimize carryover.

Peak heights were extracted from scans using ECDSOFT software (Omanović, 2025; Omanović and Branica, 1998). The peak heights from vial A and vial B were converted into ambient Fe-bound humic-like substance and total Fe-binding humic-like substance concentrations, respectively in μg SRFA eq per liter using the slope of curve generated by the three standard additions. Units were then converted to nM Fe eq using the measured binding capacity of SRFA in seawater $14.6 \pm 0.7 \text{ nmol Fe mg}^{-1} \text{ SRFA}$ (Sukekava et al., 2018).

Sample analyses: dissolved and soluble iron:

Dissolved and soluble Fe measurements were performed as described in Lagerström et al., (2013) and Burns et al., (2023). Trace metal analyses were performed using an automated SeaFAST pico in line with a Thermo Scientific iCAP-RQ Quadrupole CCT ICP-MS. Quantification was performed with external nine-point calibration curves and matrix match. Subsamples of internal standards and reference materials were measured at each run including NASS-7 (consensus Fe = $6.29 \pm 0.47 \text{ nM}$; measured value = $5.19 \pm 0.44 \text{ nM}$, $n = 14$), GSC (consensus Fe = 2.07 nM ; measured value = $1.97 \pm 0.02 \text{ nM}$, $n = 3$), SAFE D1 (consensus Fe = $0.69 \pm 0.04 \text{ nM}$; measured value = $0.61 \pm 0.00 \text{ nM}$, $n = 3$), SAFE D2 (consensus Fe = $0.96 \pm 0.02 \text{ nM}$; measured value = $1.03 \pm 0.02 \text{ nM}$, $n = 3$)

The detection limit for Fe was determined from three times the standard deviation of replicate lowest standards and was equivalent to 0.048 nM.

Sample analyses: dissolved and soluble total organic iron-binding ligands:

Samples were analyzed using competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-adCSV; Buck et al., 2012, 2007; Mahieu et al., 2024; Rue and Bruland, 1995). The samples were thawed overnight at room temperature in the dark prior to analysis. Thawed samples were inverted several times to homogenize, then 10 mL was aliquoted into each of 16 conditioned tubes (50 mL, MetalFree, Labcon) along with 7.5 millimolar (mM) boric acid-ammonium hydroxide buffer (Mahieu et al., 2024). Iron standard (prepared by dilution of atomic absorption spectrometry grade, AA; Fisher Chemical™ in 0.024 M trace metal grade HCl) was then added to aliquots to final concentrations 0, 0, 0.1, 0.25, 0.5, 0.75, 1, 1.5, 2, 2.5, 3, 4, 5, 7.5, 10, and 15 nM. After at least 2 hours of equilibration, salicylaldoxime (98 + %, TCI America™) solution made in methanol (LC/MS Grade Optima, Fisher Chemical™) was added to each vial for a final concentration of 25 micromolar (μM) and left to equilibrate for at least 15 minutes before analysis.

Aliquots were analyzed in a fluorinated ethylene propylene cell (FEP; Princeton Applied Research) on a controlled mercury growth electrode (CGME) from BioAnalytical Systems, Inc. (BASi) equipped with a platinum wire counter electrode, a Ag/AgCl reference electrode, and quadruple-distilled elemental mercury (Bethlehem Apparatus) as working electrode. Analyses were run in Static Mercury Drop Electrode (SMDE) mode with a size 14 drop. The CGME was controlled by an ECLipse potentiostat (BASi) or an Epsilon E2 electrochemical analyzer (BASi; 2 systems were used simultaneously). The following parameters were applied through the software EpsilonEC (BASi): differential pulse adsorptive cathodic stripping voltammetry (DP-AdCSV), deposition at +0.05 V while stirring, 15 seconds of equilibration (no stirring), stripping from 0 to -0.85 V with a 6 mV step, 50 mV amplitude, 35 milliseconds (ms) pulse width, and 200 ms pulse period (Mahieu et al., 2024).

The reduction peak heights were determined using an automated procedure presented in Mahieu et al. (2024). Briefly, the 4th derivative of the scan was produced through the software ECDSOft (Omanović and Branica, 1998), and then the peak height was defined using a linear baseline on the adaptive scan. The peak heights were then compiled in a custom-made Excel spreadsheet, and the data fitted on the software ProMCC (Omanović et al., 2015) using complete complexation fitting model and detection window α_{AL} of 79 e.g. Buck et al. (2007).

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. [Not used].

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 replicates or reference samples were available to further verify the quality of the data; used for most data here].

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. [used when variability in triplicate scans exceeded measured value, suspected bottle misfire at 2000 m, and for low-quality total ligand titrations].

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. [Not used].

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 unsuccessfully analyzed 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 Curation Notes

currently being processed

[[table of contents](#) | [back to top](#)]

Parameters

Parameters for this dataset have not yet been identified

[[table of contents](#) | [back to top](#)]

Deployments

NBP1608

Website	https://www.bco-dmo.org/deployment/742174
Platform	RVIB Nathaniel B. Palmer
Start Date	2016-09-07
End Date	2016-10-14
Description	See additional information at R2R: https://www.rvdata.us/search/cruise/NBP1608

[[table of contents](#) | [back to top](#)]

Project Information

Collaborative Research: Investigating Iron-binding Ligands in Southern Ocean Diatom Communities: The Role of Diatom-Bacteria Associations (Diatom_Bacteria_Ligands)

Coverage: Southern Ocean, Western Antarctic Peninsula 60-65 S, 63 W

This project focuses on an important group of photosynthetic algae in the Southern Ocean (SO), diatoms, and the roles associated bacterial communities play in modulating their growth. Diatom growth fuels the SO food web and balances atmospheric carbon dioxide by sequestering the carbon used for growth to the deep ocean on long time scales as cells sink below the surface. The diatom growth is limited by the available iron in the seawater, most of which is not freely available to the diatoms but instead is tightly bound to other compounds. The nature of these compounds and how phytoplankton acquire iron from them is critical to understanding productivity in this region and globally. The investigators will conduct experiments to characterize the relationship between diatoms, their associated bacteria, and iron in open ocean and inshore waters. Experiments will involve supplying nutrients at varying nutrient ratios to natural phytoplankton assemblages to determine how diatoms and their associated bacteria respond to different conditions. This will provide valuable data that can be used by climate and food web modelers and it will help us better understand the relationship between iron, a key nutrient in the ocean, and the organisms at the base of the food web that use iron for photosynthetic growth and carbon uptake. The project will also further the NSF goals of training new generations of scientists and of making scientific discoveries available to the general public. The project

supports early career senior investigators and the training of graduate and undergraduate students as well as outreach activities with middle school Girl Scouts in Rhode Island, inner city middle and high school age girls in Virginia, and middle school girls in Florida.

The project combines trace metal biogeochemistry, phytoplankton cultivation, and molecular biology to address questions regarding the production of iron-binding compounds and the role of diatom-bacterial interactions in this iron-limited region. Iron is an essential micronutrient for marine phytoplankton. Phytoplankton growth in the SO is limited by a lack of sufficient iron, with important consequences for carbon cycling and climate in this high latitude regime. Some of the major outstanding questions in iron biogeochemistry relate to the organic compounds that bind >99.9% of dissolved iron in surface oceans. The investigators' prior research in this region suggests that production of strong iron-binding compounds in the SO is linked to diatom blooms in waters with high nitrate to iron ratios. The sources of these compounds are unknown but the investigators hypothesize that they may be from bacteria, which are known to produce such compounds for their own use. The project will test three hypotheses concerning the production of these iron-binding compounds, limitations on the biological availability of iron even if present in high concentrations, and the roles of diatom-associated bacteria in these processes. Results from this project will provide fundamental information about the biogeochemical trigger, and biological sources and function, of natural strong iron-binding compound production in the SO, where iron plays a critical role in phytoplankton productivity, carbon cycling, and climate regulation.

[[table of contents](#) | [back to top](#)]

Funding

Funding Source	Award
NSF Office of Polar Programs (formerly NSF PLR) (NSF OPP)	OPP-1443483

[[table of contents](#) | [back to top](#)]