Dissolved trace metal concentrations for Incubation 3, initiated September 27th, 2016 on RVIB Nathaniel B. Palmer cruise NBP16-08 in the Southern Ocean

Website: https://www.bco-dmo.org/dataset/781841
Data Type: Cruise Results, experimental
Version: 1
Version Date: 2019-11-15

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

Contributors	Affiliation	Role
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Chappell, Phoebe Dreux	Old Dominion University (ODU)	Co-Principal Investigator
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Abstract
Dissolved trace metal concentrations for Incubation 3, initiated September 27th, 2016 on RVIB Nathaniel B. Palmer cruise NBP16-08 in the Southern Ocean.

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Coverage

Spatial Extent: **N**:-62.33418 **E**:-59.565 **S**:-62.46 **W**:-64.6477
Temporal Extent: 2016-09-24 - 2016-10-09

Dataset Description

Dissolved trace metal concentrations for Incubation 3, initiated September 27th, 2016 on RVIB Nathaniel B. Palmer cruise NBP16-08 in the Southern Ocean.

Related Datasets:
* NBP1608 TMs: stations https://www.bco-dmo.org/dataset/781773
* NBP1608 TMs: Incubation 1 https://www.bco-dmo.org/dataset/781759
* NBP1608 TMs: Incubation 2 https://www.bco-dmo.org/dataset/781827

Acquisition Description

Methodology:
The following methods are provided from a manuscript currently in preparation (Burns et al. in prep.).

Sampling and analytical procedures:

Sample Collection:

Seawater for the incubation was collected in austral spring 2016 aboard the R/V/I/B Nathaniel B. Palmer using a SeaBird GEOTRACES style SBE32 rosette system deployed on a conducting Kevlar line (Cutter and Bruland 2012) with OceanTestEquipment, Inc. X-Niskin samplers modified for trace element sampling.

The collected seawater was homogenized in trace metal clean, Milli-Q (18.2 MΩcm)-conditioned 50-L polypropylene carboys. The seawater from the 50-L carboys was then aliquoted into a series of acid-cleaned (10% hydrochloric acid (HCl), Fisher, Trace Metal Grade (TMG)), Milli-Q conditioned 4-L polycarbonate incubation bottles, which were assigned different treatments. The treatments were carried out in both light and dark conditions. The light bottles were continuously exposed to blue fluorescent light to simulate surface ocean light conditions during austral spring (Hopkinson et al. 2007; Buck et al. 2010). The dark bottles were placed in heavy duty black bags as controls for background heterotrophic bacterial

activity and trace metal adsorption to walls. The 4-L bottles were incubated in a temperature-controlled (2 ºC) incubation van onboard for approximately two weeks. All bottles were rinsed three times with sample seawater prior to filling.

For Incubation 3, the vessel returned to the same offshore location as used for Incubation 1, station 13 (-62º 20.051 N, -64º 38.863 E), and water was collected on September 26, 2016 at depths of 25-35 m. This seawater was used use in combination with filtered (AcroPakTM, 0.2 µm) inshore water previously collected from the location of Incubation 2, station 12 (-62.46 ºN, -59.565 ºE), in the Bransfield Strait on September 24, 2016. Only two treatments were carried out in the light and dark for this incubation: (1) +0 unamended offshore control and (2) a 50:50 mixture of unfiltered ACC offshore water and filtered inshore Bransfield Strait water. Treatment (1) thus linked incubation three with the +0 offshore control in incubation one, with a 15-day time lapse in offshore water sampling. Incubation 3 was carried out for 12 days, from September 27, 2016 to October 9, 2016. The light-exposed treatments for this incubation were sampled on days 0, 1, 3, 5, 7, 9, and 12. For each light-exposed treatment, three of the nine 4-L incubation bottles were randomly sampled per timepoint to yield three replicates per timepoint. Eight replicate bottles were sampled on the final day. Each dark treatment was sampled on days 1, 5, 7, 9, and 12, with only one of the two 4-L incubation bottles sampled per timepoint, except for the final day when both bottles were sampled.

Dissolved Trace Metals:

Samples for dissolved trace metals were filtered through sequential 3 µm and 0.4 µm acid-cleaned PCTE filters on Teflon dual-stage filter rigs (Savillex) connected to a custom-made, trace-metal-clean vacuum filtration system. The dissolved fraction (<0.4 µm) filtrate was collected in acid-cleaned 125-mL low-density polyethylene (LDPE) bottles. Bottles were rinsed three times with sample seawater prior to filling. Samples were acidified to pH 1.8 (0.024 M HCl, Fisher, Optima) and stored double bagged in buckets at room temperature until analyzed at the University of South Florida.

Extraction and pre-concentration of the dissolved samples was performed using the seaFAST-pico system (Elemental Scientific) offline (Lagerström et al. 2013; Bown et al. 2017; Rapp et al. 2017). The commercially available Nobias-chelate PA1 resin (Sohrin et al. 2008; Sohrin and Bruland 2011; Biller and Bruland 2012) in the seaFAST preconcentration column concurrently extracts the trace metals of interest in this study: Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb. To sufficiently extract dissolved Co and Cu, ultraviolet (UV) oxidation of the dissolved samples was conducted prior to seaFAST extraction (Achterberg et al. 2001; Milne et al. 2010; Biller and Bruland 2012). To accomplish this, dissolved samples were poured into acid-cleaned Teflon™ 30-mL vials (Savillex) with Teflon™ caps custom-fitted with transparent quartz window, and UV oxidized for 90 minutes at ~20 mW cm-2 in a UVO-Cleaner® (Jelight Model No. 342) after a 30-minute system warm-up.

During the seaFAST extraction process, UV-oxidized samples were buffered to a target pH range of 6.0 to 6.5 (Lagerström et al. 2013). To conserve the buffer reagent, the seaFAST buffer flow rate was adjusted in the submethod from 400-650 to 400-350 sec-µL/min. To make the ammonium acetate (NH4Ac) buffer, a solution of 5.3 M glacial acetic acid (HAc, Fisher, Trace Metal Grade) and 2.6 M ammonium hydroxide (NH4OH, Fisher, Optima) in Milli-Q was adjusted to pH 7.4 ± 0.2 with small additions of either HAc or NH4OH.

For preconcentration of the extracted trace metals, the seaFAST software method was programmed to take up one 10-mL loop of sample seawater and elute the extracted trace metals with 400 µL of elution acid. The elution acid was 0.74 M triple-distilled nitric acid (HNO3) containing 10 ppb indium (In) and rhodium (Rh) internal standards. The HNO3 was triple-distilled using a Savillex DST-1000 Acid Purification System prior to use. The eluent was eluted into acid-cleaned, 2.0 mL PVDF vials (Elemental Scientific) with TeflonTM caps (Elemental Scientific). A 0.30 M HNO3 (Fisher, Trace Metal Grade) rinse for the seaFAST autosampler probe was used between each sample.

Quality control (QC) checks were included in seaFAST runs. GEOTRACES 2008 GS and SAFe 2004 D2 reference samples were measured to assess accuracy. Additionally, QC seawater samples were run approximately every 15 samples to monitor instrument precision over time. The first QC was offshore seawater from the Antarctic Circumpolar Current (ACC), acidified to pH 1.8 (0.024 M) with Optima (Fisher) HCl. The second QC was from offshore Eastern Pacific Zone seawater, acidified to pH 1.8 (0.024 M) with Optima (Fisher) HCl.

Two sets of standard curves were made for these analyses: one set in ACC QC seawater (acidified to 0.024 M with Optima HCl) and a second set in the elution acid (0.74 M triple-distilled HNO3 containing 10 ppb In and Rh). For the mixed metal standard curves, stock solutions were made in 1.49 M Optima (Fisher) HNO3 using 1,000 ppm standards (ULTRA Scientific) of Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb. Each curve was a minimum of six points and made to cover the concentration ranges of the dissolved trace metals in incubation samples.

The eluents from the seaFAST were analyzed on a Thermo Scientific magnetic sector Element XR High Resolution Inductively Coupled Plasma Mass Spectrophotometer (HR-ICP-MS). In between each sample, the autosampler probe was rinsed twice in 0.74 M TraceMetalGrade (Fisher) HNO3, to avoid sample carryover. To account for any interference of MoO+ on Cd counts, a three-point Mo calibration curve was made in elution acid and the slope of the Mo counts plotted against Cd counts was used to adjust Cd counts.

Trace metals were quantified by standard addition from the seawater standard curves. The average counts for each trace metal were normalized to the In internal standard counts per sample, to account for daily drift in ICP-MS measurements. Dissolved trace metal concentrations in each seawater sample were calculated from the seawater calibration curve slope. The In-normalized average trace metal counts were divided by the seawater standard

curve slope to yield the trace metal concentrations in each eluent.

Air blanks were measured with a minimum of three replicates per seaFAST and Element XR run. For the air blanks, the seaFAST method was run as usual, but taking up air instead of acidified seawater. For the dissolved trace metal concentrations presented here, the average air blank concentrations per seaFAST run were subtracted from the dissolved sample concentrations to account for the procedural blank.

Sample analyses for dissolved trace metals were performed by Shannon Burns (USF); ORCID ID: https://orcid.org/0000-0002-1569-3060.

Quality Flags: The standard Ocean Data View qualifying flags were used (reference all flags at https://www.bodc.ac.uk/data/codes_and_formats/odv_format/). Additional notes specific to the application of these flags to this project are noted in brackets […].

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 reference sample data.]
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. [Not used.]
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 data appeared anomalous.]
4: Bad Value: An obviously erroneous data value. [Not used.]
5: Changed Value: Data value adjusted during quality control. [Not used.]
6: Value Below Detection Limit: The level of the measured phenomenon was too small to be quantified by the technique employed to measure it. The accompanying value is the detection limit for the technique or zero if that value is unknown. [Not used. See Table 1 for detection limits.]
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. [Not 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.]

Processing Description

Data were processed using ESI SC version 2.9.0.380 software.

BCO-DMO Data Manager Processing Notes:
* Extracted data submitted in xlsx format as csv file.
* added a conventional header with dataset name, PI name, version date
* modified parameter names to conform with BCO-DMO naming conventions
** Multiple "FLAG" columns renamed to reflect the trace metal concentration they describe e.g. FLAG renamed to Mn_D_CONC_FLAG columns.
* blank values in this dataset are displayed as "nd" for "no data." nd is the default missing data identifier in the BCO-DMO system.
* Date format converted to ISO 8601 date format yyyy-mm-dd

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Related Publications

Achterberg, E. P., Braungardt, C. B., Sandford, R. C., & Worsfold, P. J. (2001). UV digestion of seawater samples prior to the determination of copper using flow injection with chemiluminescence detection. Analytica Chimica Acta, 440(1), 27–36. doi:10.1016/S0003-2670(01)00824-8

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Buck, K. N., Selph, K. E., & Barbeau, K. A. (2010). Iron-binding ligand production and copper speciation in an incubation experiment of Antarctic Peninsula shelf waters from the Bransfield Strait, Southern Ocean. Marine Chemistry, 122(1-4), 148–159. doi:10.1016/j.marchem.2010.06.002

Burns, S. M., R. M. Bundy, W. Abbott, Z. Abdala, A. R. Sterling, P. D. Chappell, B. D. Jenkins, and K. N. Buck. in prep. Biogeochemical feedbacks between trace metals and phytoplankton growth: Insights from Southern Ocean incubation experiments.

Cutter, G. A., & Bruland, K. W. (2012). Rapid and noncontaminating sampling system for trace

elements in global ocean surveys. Limnology and Oceanography: Methods, 10(6), 425–436. doi:10.4319/lom.2012.10.425

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

Milne, A., Landing, W., Bizimis, M., & Morton, P. (2010). Determination of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in seawater using high resolution magnetic sector inductively coupled mass spectrometry (HR-ICP-MS). Analytica Chimica Acta, 665(2), 200–207. doi:10.1016/j.aca.2010.03.027

Rapp, I., Schlosser, C., Rusiecka, D., Gledhill, M., & Achterberg, E. P. (2017). Automated preconcentration of Fe, Zn, Cu, Ni, Cd, Pb, Co, and Mn in seawater with analysis using high-resolution sector field inductively-coupled plasma mass spectrometry. Analytica Chimica Acta, 976, 1–13. doi:10.1016/j.aca.2017.05.008

Sohrin, Y., & Bruland, K. W. (2011). Global status of trace elements in the ocean. TrAC Trends in Analytical Chemistry, 30(8), 1291–1307. doi:10.1016/j.trac.2011.03.006

Sohrin, Y., Urushihara, S., Nakatsuka, S., Kono, T., Higo, E., Minami, T., … Umetani, S. (2008). Multielemental Determination of GEOTRACES Key Trace Metals in Seawater by ICPMS after Preconcentration Using an Ethylenediaminetriacetic Acid Chelating Resin. Analytical Chemistry, 80(16), 6267–6273. doi:10.1021/ac800500f

Standards and Reference Materials. (n.d.). GEOTRACES. Retrieved November 18, 2019, from http://www.geotraces.org/index.php/science/intercalibration/322-standards-and-reference-materials.

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Parameters

Parameter	Description	Units
DATE	GMT date when incubation sample was pulled from the incubation bottle for filtering, in format MM/DD/YY.	unitless
INCUBATION	Incubation identifier.	unitless
DAY	Day of incubation when sample was collected. Days start from 0 for the day the incubation was setup.	unitless
ID	Sample identifier for incubation bottle and treatment that sample was collected from.	unitless

TREATMENT	Incubation treatment identifier. Treatments Q-R were exposed to light, treatments V-W were kept in the dark. Treatments were as follows: Q and V = +0, control; R and W = 50:50 mixture of unamended (+0, control) unfiltered water used for Q and unamended (+0, control) filtered water used for Incubation 2. The R-Q, and R-R bottles were the same light treatments as Q and R, respectively, in replicate R-labeled 4-L incubation bottles. The notation “NONE” refers to no treatment, used to describe samples collected from the carboys of experimental seawater prior to allocation into 4L incubation bottles and treatment additions. The notation “NONE, FILTERED” refers to the sample collected from the untreated carboy of filtered seawater used in the experiments. One of the incubation bottles was filled with water from the NONE, FILTERED carboy and incubated as a control with no treatment, described as “FILTERED CONTROL”.	unitless
BTLNBR	Incubation bottle identifier. Each 4-L incubation bottle was assigned a unique number from 1-99 across all shipboard incubations, with the exception of the R bottles, which are noted as “R-” followed by treatment identifier. The 50-L homogenization carboys used to prepare the incubations were labeled “X”, “Y”, and “Z”.	unitless
Mn_D_CONC	Concentration of dissolved manganese (Mn).	nanomoles per liter (nM)
Mn_D_CONC_FLAG	Quality flag for the concentration of dissolved manganese (Mn). The standard Ocean Data View qualifying flags were used. Additional notes specific to the application of these flags to this project are noted in the Acquisition Description metadata section.	unitless
Fe_D_CONC	Concentration of total dissolved iron (Fe) in a sample (ambient Fe + added 57Fe).	nanomoles per liter (nM)

Fe_D_CONC_FLAG	Quality flag for the concentration of dissolved iron (Fe). The standard Ocean Data View qualifying flags were used. Additional notes specific to the application of these flags to this project are noted in the Acquisition Description metadata section.	unitless
Co_D_CONC	Concentration of dissolved cobalt (Co).	picomoles per liter (pM)
Co_D_CONC_FLAG	Quality flag for the concentration of dissolved cobalt (Co). The standard Ocean Data View qualifying flags were used. Additional notes specific to the application of these flags to this project are noted in the Acquisition Description metadata section.	unitless
Ni_D_CONC	Concentration of dissolved nickel (Ni).	nanomoles per liter (nM)
Ni_D_CONC_FLAG	Quality flag for the concentration of dissolved nickel (Ni). The standard Ocean Data View qualifying flags were used. Additional notes specific to the application of these flags to this project are noted in the Acquisition Description metadata section.	unitless
Cu_D_CONC	Concentration of dissolved copper (Cu).	nanomoles per liter (nM)
Cu_D_CONC_FLAG	Quality flag for the concentration of dissolved copper (Cu). The standard Ocean Data View qualifying flags were used. Additional notes specific to the application of these flags to this project are noted in the Acquisition Description metadata section.	unitless
Zn_D_CONC	Concentration of dissolved zinc (Zn).	nanomoles per liter (nM)
Zn_D_CONC_FLAG	Quality flag for the concentration of dissolved zinc (Zn). The standard Ocean Data View qualifying flags were used. Additional notes specific to the application of these flags to this project are noted in the Acquisition Description metadata section.	unitless

Cd_D_CONC	Concentration of dissolved cadmium (Cd).	picomoles per liter (pM)
Cd_D_CONC_FLAG	Quality flag for the concentration of dissolved cadmium (Cd). The standard Ocean Data View qualifying flags were used. Additional notes specific to the application of these flags to this project are noted in the Acquisition Description metadata section.	unitless
Pb_D_CONC	Concentration of dissolved lead (Pb).	picomoles per liter (pM)
Pb_D_CONC_FLAG	Quality flag for the concentration of dissolved lead (Pb). The standard Ocean Data View qualifying flags were used. Additional notes specific to the application of these flags to this project are noted in the Acquisition Description metadata section.	unitless

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Instruments

Dataset-specific Instrument Name	SeaFAST pico
Generic Instrument Name	Ion Chromatograph
Generic Instrument Description	Ion chromatography is a form of liquid chromatography that measures concentrations of ionic species by separating them based on their interaction with a resin. Ionic species separate differently depending on species type and size. Ion chromatographs are able to measure concentrations of major anions, such as fluoride, chloride, nitrate, nitrite, and sulfate, as well as major cations such as lithium, sodium, ammonium, potassium, calcium, and magnesium in the parts-per-billion (ppb) range. (from http://serc.carleton.edu/microbelife/research_methods/biogeochemical/ic....)

Dataset-specific Instrument Name	Element XR Inductively Coupled Plasma Mass Spectrophotometer
Generic Instrument Name	Mass Spectrometer
Generic Instrument Description	General term for instruments used to measure the mass-to-charge ratio of ions; generally used to find the composition of a sample by generating a mass spectrum representing the masses of sample components.

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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

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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.

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Funding

Funding Source	Award
NSF Office of Polar Programs (formerly NSF PLR) (NSF OPP)	OPP-1443483
NSF Office of Polar Programs (formerly NSF PLR) (NSF OPP)	OPP-1443474
NSF Office of Polar Programs (formerly NSF PLR) (NSF OPP)	OPP-1443646

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