Soluble Mn speciation from CTD casts in the Ross Sea, Southern Ocean taken during RVIB Nathaniel B. Palmer cruise NBP1801 in Jan-Feb 2018

Website: https://www.bco-dmo.org/dataset/850300
Data Type: Cruise Results
Version: 1
Version Date: 2021-04-26

Project
» Collaborative Research: Defining the Role of Biologically Produced Reactive Oxygen Species in Dark Mercury Cycling (ROS in Hg Cycling)
» Collaborative Research: Cobalamin and Iron Co-Limitation Of Phytoplankton Species in Terra Nova Bay (CICLOPS)

Contributors	Affiliation	Role
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Abstract
Soluble Mn speciation from CTD casts in the Ross Sea, taken in Jan-Feb 2018. Speciation was performed using a porphyrin ligand substitution method with a 100 cm pathlength cell in a UV-Vis spectrophotometer.

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Coverage

Spatial Extent: **N**:-74.7407 **E**:170.374 **S**:-76.4544 **W**:164.005
Temporal Extent: 2018-01-26 - 2018-02-14

Dataset Description

Submitted for publication to Global Biogeochemical Cycles (Table S2):
Oldham, V.E., Chmiel, R., Hansel, C.M., DiTullio, G.R., Rao, D., and Saito, M.

Methods & Sampling

Location: Ross Sea Polynya

Sampling

Ten stations in the Ross Sea polynya, including stations in in the western Ross Sea and Terra Nova Bay, were sampled during the NBP-1801 expedition aboard the RV/IB N.B. Palmer from February-March 2018. Stations numbers for Mn sampling were less frequent than expedition stations and were numbered sequentially and correspond to expedition stations as described in Table S1 (Stations Mn-1 to Mn-10). Measurements were made for soluble phase Mn speciation using a 12-bottle (X-Niskin bottles) trace metal clean CTD (Conductivity, Temperature and Depth) rosette sampling system equipped with SeaBird equipment for salinity, temperature, dissolved oxygen, conductivity and fluorometry. Sampling depths were selected based on the down-cast profile of salinity, fluorescence and dissolved oxygen. For most stations, 8 depths were selected for soluble Mn speciation. Upon retrieval, Niskin bottles were transported with gloved hands to a trace metal clean van and sampled into acid-washed 1 L PTFE bottles. Bottles were triple rinsed before filling and were overflowed to prevent oxygen contamination. The seawater was immediately filtered in the main laboratory through 0.2 µm PES Millipore filters using acid washed Savillex vacuum-filtration rigs. One 10 mL volume of filtrate was immediately amended with 1 µM hydroxylamine hydrochloride for total MnT (over 10 times excess predicted total dMn concentration), and one volume was immediately analyzed for soluble Mn(II) + Mn(III)-Lw

Shipboard Mn speciation and concentrations

Speciation of soluble Mn(II) and Mn(III)-L was carried out using the spectrophotometric competitive ligand assay first described by Madison et al. (2011) and modified for low-level analysis by Oldham et al. (2017). In brief, a meso-soluble porphyrin ligand α, β, γ, δ-tetrakis(4-carboxyphenyl) porphine (T(4-CP)P) is added to the sample, complexes Mn(II), and rapidly oxidizes to form Mn(III)-T(4-CP)P in the presence of oxygen. This complex is quantified spectrophotometrically at 468 nm. For complete determination of Mn speciation, a separate sample aliquot is completely reduced to Mn(II) by addition of hydroxylamine and quantified similarly. The difference in these two parallel measurements permits determination of total Mn, Mn(II) and strongly bound Mn(III)-L by difference (Oldham et al., 2017).

Filtered samples were immediately analyzed for Mn speciation shipboard using UV/Vis spectrophotometry. One aliquot of sample was amended with 1 µM hydroxylamine and allowed to react overnight at 4 ^{o}C before analysis (total dissolved Mn [dMn]). A second aliquot was analyzed immediately; the unreduced fraction represents Mn(II), but as the reaction proceeds for over an hour, it is likely that this fraction also contained some weakly bound Mn(III)-L complexes (Mn(III)-Lw), so our reported Mn(III)-L is a conservative estimate. Samples were added to a solution containing T(4-CP)P, CdCl2 (which complexes T(4-CP)P, opening its ring structure), and imidazole tetraborate buffer (pH=8.2) at a 1:12 dilution factor to avoid chloride interference (Madison et al., 2011). The samples were then heated for 60 minutes in a 90 ^{o}C hot water bath, cooled to room temperature, then injected by syringe into the spectrophotometric setup. The analytical setup uses a 100 cm liquid waveguide capillary cell (World Precision Instruments) coupled with an Ocean Optics UV/Vis spectrophotometer in which a mini deuterium halogen light source (DT-Mini-2-GS) is coupled with a USB2000+ fiber optic spectrometer, controlled with SpectraSuite software. The Mn(III)-T(4-CP)P complex is measured at its absorbance maximum against appropriate reagent blanks. The detection limit for this method is 0.5 nM.

Data Processing Description

BCO-DMO data manager processing notes:
* Imported two sheets from Excel file BCODMO_Mn_Data.xlsx. The first one was the Mn speciation data (geochemsitry) which is the main dataset served from this page. The second was a station list which I attached as a supplemental file.
* Joined the station list with geochemistry data on key station ID to add sample date and bottom depth to the dataset.
* Renamed columns to fit the BCO-DMO naming convention (only underscores, aZ0-9).
* Converted date to ISO 8601 yyyy-mm-dd
* Switched column names for Lat and Long since they were switched.

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Data Files

File
ctd_mn_speciation.csv (Comma Separated Values (.csv), 9.39 KB) MD5:b7d19d8345ca21866faf36f8e2b1817f Primary data file for dataset ID 850300

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Supplemental Files

File
Station list for CTD Manganese speciation dataset filename: ctd_mn_station_info.csv (Comma Separated Values (.csv), 482 bytes) MD5:48d3fb6198e1d33e1b55fb070b95e01b Station list for CTD Manganese speciation dataset. Parameters: Station_number, Station number Station_ID, Station identifier (used at BCODMO) Longitude, Longitude (west is negative), decimal degrees Latitude, Latitude, decimal degrees Bottom_Depth, Bottom depth, meters Date_Sampled, Date sampled in ISO8601 format yyyy-mm-dd

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Related Publications

Madison, A. S., Tebo, B. M., & Luther, G. W. (2011). Simultaneous determination of soluble manganese(III), manganese(II) and total manganese in natural (pore)waters. Talanta, 84(2), 374–381. doi:10.1016/j.talanta.2011.01.025
Methods

Oldham, V. E., Mucci, A., Tebo, B. M., & Luther, G. W. (2017). Soluble Mn(III)–L complexes are abundant in oxygenated waters and stabilized by humic ligands. Geochimica et Cosmochimica Acta, 199, 238–246. doi:10.1016/j.gca.2016.11.043
Methods

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Parameters

Parameter	Description	Units
Station_ID	Station identifier	unitless
Depth	Sample depth	meters
Bottom_Depth	Bottom depth	meters

Date_Sampled	Sample date in ISO 8601 format yyyy-mm-dd	unitless
Long	Longitude	decimal degrees
Lat	Latitude (south is negative)	decimal degrees
Temperature	Temperature	degrees Celsius
dO2	Dissolved oxygen	milligrams per liter (mg/L)
Fluorescence	Fluorescence	milligrams per liter (mg/L)
Transmisson_pcnt	Transmission	percent
PAR	Photosynthetically Active Radiation (PAR)	W/m2
Salinity	Salinity	ppt
PO4	Phosphate	micromolar (uM)
N_plus_N	Nitrate (NO3) plus nitrite (NO2)	micromolar (uM)
Silicate	Silicate	micromolar (uM)
NO2	Nitrite	micromolar (uM)
NH4	Ammonium	micromolar (uM)
Mn2_mean	Dissolved Mn(II) mean	nanomolar (nM)
Mn2_stdev	Dissolved Mn(II) standard deviation	nanomolar (nM)
MnT_mean	Total dissolved Mn mean	nanomolar (nM)
MnT_stdev	Total dissolved Mn standard deviation	nanomolar (nM)
Mn3_percent	Mn(3) percent. Calculated by the difference between MnT and Mn2	percent (%)

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Instruments

Dataset-specific Instrument Name	
Generic Instrument Name	CTD - profiler
Dataset-specific Description	Measurements were made for soluble phase Mn speciation using a 12-bottle (X-Niskin bottles) trace metal clean CTD (Conductivity, Temperature and Depth) rosette sampling system equipped with SeaBird equipment for salinity, temperature, dissolved oxygen, conductivity and fluorometry.
Generic Instrument Description	The Conductivity, Temperature, Depth (CTD) unit is an integrated instrument package designed to measure the conductivity, temperature, and pressure (depth) of the water column. The instrument is lowered via cable through the water column. It permits scientists to observe the physical properties in real-time via a conducting cable, which is typically connected to a CTD to a deck unit and computer on a ship. The CTD is often configured with additional optional sensors including fluorometers, transmissometers and/or radiometers. It is often combined with a Rosette of water sampling bottles (e.g. Niskin, GO-FLO) for collecting discrete water samples during the cast. This term applies to profiling CTDs. For fixed CTDs, see https://www.bco-dmo.org/instrument/869934.

Dataset-specific Instrument Name	12-bottle (X-Niskin bottles)
Generic Instrument Name	Niskin bottle
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.

Dataset-specific Instrument Name	Ocean Optics UV/Vis spectrophotometer
Generic Instrument Name	Spectrophotometer
Dataset-specific Description	The analytical setup uses a 100 cm liquid waveguide capillary cell (World Precision Instruments) coupled with an Ocean Optics UV/Vis spectrophotometer in which a mini deuterium halogen light source (DT-Mini-2-GS) is coupled with a USB2000+ fiber optic spectrometer, controlled with SpectraSuite software.
Generic Instrument Description	An instrument used to measure the relative absorption of electromagnetic radiation of different wavelengths in the near infra-red, visible and ultraviolet wavebands by samples.

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Deployments

NBP1801

Website	https://www.bco-dmo.org/deployment/778919
Platform	RVIB Nathaniel B. Palmer
Report	https://service.rvdata.us/data/cruise/NBP1801/doc/NBP1801DATA.pdf
Start Date	2017-12-16
End Date	2018-03-03
Description	Start Port: Punta Arenas, Chile End Port: Hobart, Australia

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Project Information

Collaborative Research: Defining the Role of Biologically Produced Reactive Oxygen Species in Dark Mercury Cycling (ROS in Hg Cycling)

Coverage: Coastal North Atlantic

NSF Abstract:

Mercury (Hg) is a toxic trace element that bioaccumulates into marine food webs, imposing a health threat to humans through the consumption of seafood. However, controls on the cycling of Hg in the ocean are poorly understood. Most research to date has focused on sun-lit and/or Hg-laden environments, where light-induced chemical and mercury resistance reactions, respectively, have been identified as dominant pathways for Hg cycling. The paradigm that dark Hg reactions are irrelevant is fading and it is now apparent that dark redox reactions, both reduction and oxidation, are important in the cycling of Hg. In this study, researchers at the Woods Hole Oceanographic Institution and Colorado School of Mines will obtain a better understanding of the biogeochemical reactions responsible for dark redox transformations of mercury (Hg) in marine systems. The researchers will explore the relationship between microbial activity, reactive oxygen species, and Hg speciation in a series of laboratory- and field-based investigations to obtain a mechanistic understanding of dark Hg cycling. By identifying new controls on the redox cycling of Hg in the ocean, this research will help inform global and ecosystem models used to predict Hg bioavailability.

Broader Impacts: The proponents plan to educate high school teachers from Boston Green Academy in South Boston on mercury biogeochemistry and have one teacher participate in the summer research cruises, as well as develop science curricula to engage the underrepresented students at the school in science. One postdoc and one graduate student from Woods Hole Oceanographic Institution and one graduate student from the Colorado School of Mines would be supported and trained as part of this project. It is anticipated that undergraduate students would have the opportunity to participate in the study as summer interns.

Collaborative Research: Cobalamin and Iron Co-Limitation Of Phytoplankton Species in Terra Nova Bay (CICLOPS)

Coverage: Amundsen Sea, Ross Sea, Terra Nova Bay

NSF abstract:
Phytoplankton blooms in the coastal waters of the Ross Sea, Antarctica are typically dominated by either diatoms or Phaeocystis Antarctica (a flagellated algae that often can form large colonies in a gelatinous matrix). The project seeks to determine if an association of bacterial populations with Phaeocystis antarctica colonies can directly supply Phaeocystis with Vitamin B12, which can be an important co-limiting micronutrient in the

Ross Sea. The supply of an essential vitamin coupled with the ability to grow at lower iron concentrations may put Phaeocystis at a competitive advantage over diatoms. Because Phaeocystis cells can fix more carbon than diatoms and Phaeocystis are not grazed as efficiently as diatoms, the project will help in refining understanding of carbon dynamics in the region as well as the basis of the food web webs. Such understanding also has the potential to help refine predictive ecological models for the region. The project will conduct public outreach activities and will contribute to undergraduate and graduate research. Engagement of underrepresented students will occur during summer student internships. A collaboration with Italian Antarctic researchers, who have been studying the Terra Nova Bay ecosystem since the 1980s, aims to enhance the project and promote international scientific collaborations.

The study will test whether a mutualistic symbioses between attached bacteria and Phaeocystis provides colonial cells a mechanism for alleviating chronic Vitamin B12 co-limitation effects thereby conferring them with a competitive advantage over diatom communities. The use of drifters in a time series study will provide the opportunity to track in both space and time a developing algal bloom in Terra Nova Bay and to determine community structure and the physiological nutrient status of microbial populations. A combination of flow cytometry, proteomics, metatranscriptomics, radioisotopic and stable isotopic labeling experiments will determine carbon and nutrient uptake rates and the role of bacteria in mitigating potential vitamin B12 and iron limitation. Membrane inlet and proton transfer reaction mass spectrometry will also be used to estimate net community production and release of volatile organic carbon compounds that are climatically active. Understanding how environmental parameters can influence microbial community dynamics in Antarctic coastal waters will advance an understanding of how changes in ocean stratification and chemistry could impact the biogeochemistry and food web dynamics of Southern Ocean ecosystems.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1355720
NSF Office of Polar Programs (formerly NSF PLR) (NSF OPP)	OPP-1644073
NSF Office of Polar Programs (formerly NSF PLR) (NSF OPP)	OPP-1643684

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