Total dissolved cobalt and labile dissolved cobalt distributions measured by shipboard voltammetry in the Amundsen Sea, Ross Sea, and Terra Nova Bay during the CICLOPS expedition on RVIB Nathaniel B. Palmer (NBP1801) from Dec 2017 to Feb 2018

Website: https://www.bco-dmo.org/dataset/893487
Data Type: Cruise Results
Version: 1
Version Date: 2023-04-11

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

Contributors	Affiliation	Role
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Abstract
Cobalt (Co) is often a scarce but essential micronutrient for marine plankton in the Southern Ocean and coastal Antarctic seas where dissolved cobalt (dCo) concentrations can be extremely low. This dataset presents total dCo and labile dCo distributions measured via shipboard voltammetry in the Amundsen Sea, Ross Sea, and Terra Nova Bay during the CICLOPS (Cobalamin and Iron Co-Limitation of Phytoplankton Species) expedition on RVIB Nathaniel B. Palmer (NBP1801). The resulting profiles indicate that a significantly smaller dCo inventory was observed during the 2017/2018 CICLOPS expedition compared to the 2005/2006 CORSAC expeditions to the Ross Sea over a decade earlier. The dCo inventory loss (~10–20 pM) was present in both the surface and deep ocean and can be attributed to the loss of labile dCo, resulting in the near-100% strong ligand-bound complexation of dCo in the photic zone. This perturbation of the Southern Ocean cobalt biogeochemical cycle could signal changes in the nutrient limitation regimes, phytoplankton bloom composition, and carbon sequestration sink of the Southern Ocean.

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Coverage

Spatial Extent: **N**:-72.7507 **E**:-151.918 **S**:-76.7499 **W**:179.819
Temporal Extent: 2017-12-30 - 2018-02-08

Methods & Sampling

Samples were collected along the coastal Antarctic Shelf from the Amundsen Sea, Ross Sea, and Terra Nova Bay during the CICLOPS expedition on the RVIB Nathanial B. Palmer (cruise ID NBP-1801) from December 11,

2017 to March 3, 2018. Dissolved seawater was collected from full-depth station profiles using a trace metal clean sampling rosette deployed on a conducting synthetic line, both supplied by the U.S. Antarctic Program (USAP), and equipped with twelve 8-liter (L) X-Niskin bottles (Ocean Test Equipment), supplied by the Saito Laboratory. Real-time trace metal rosette operations allowed for the careful collection of seawater from 10 and 20 meters (m) above the ocean floor to study sediment-water interactions within a potential nepheloid layer. After deployment, the X-Niskin bottles were transported to a trace metal clean van and pressurized with high-purity N_2 gas. Seawater samples for dCo analysis were then filtered through acid-washed 0.2-micromole (µM) Supor polyethersulfone membrane filters (Pall Corporation, 142-millimeter (mm) diameter) within 3 hours of rosette recovery.

To minimize metal contamination of samples, all sample bottles were prepared using trace metal clean procedures, including soaking sample bottles for ~1 week in Citranox, an acidic detergent, rinsing with Milli-Q water (Millipore), soaking sample bottles for ~2 weeks in 10% trace metal grade HCl (Optima, Fisher Scientific), and rinsing with lightly acidic Milli-Q water (> 0.1% HCl).

Samples for dCo analysis were collected in 60-milliliter (mL) low-density polyethylene (LDPE) bottles and stored at 4^0C until analysis. Duplicate dCo samples were collected: one for at-sea analysis of labile dCo and total dCo, and another for preservation and total dCo analysis in the laboratory after the expedition. Preserved total dCo samples were stored with oxygen-absorbing satchels (Mitsubishi Gas Chemical, model RP-3K), which preserve the sample for long-term storage and future analysis (Noble et al. 2017; Bundy et al. 2020). Preserved dCo samples were stored in groups of 6 within an open (unsealed) plastic bag, which was then placed into a gas-impermeable plastic bag (Ampac) with one oxygen-absorbing satchel per 60 mL dCo sample. The outer bag was then heat-sealed and stored at 4°C until analysis.

Total dCo – the combined fractions of labile and ligand-bound dCo, hereafter simply dCo – and labile dCo concentrations were analyzed via cathodic stripping voltammetry (CSV) as described by Saito and Moffett (2001) and modified by Saito et al. (2010) and Hawco et al. (2016). CSV analysis was conducted using a Metrohm 663 VA and µAutolabIII systems equipped with a hanging mercury drop working electrode. All reagents were prepared as described in Chmiel et al. (2022). Most samples were analyzed at sea within 3 weeks of sample collection, and stations 57 and 60 were analyzed for labile dCo at sea and their duplicate preserved samples were analyzed for total dCo in November 2019 in the laboratory.

To measure total dCo concentrations, filtered seawater samples were first UV-irradiated in quartz tubes for one hour in a Metrohm 705 UV Digester to destroy natural ligand-bound Co complexes. 11 mL of sample was then added to a 15 mL trace metal clean polypropylene vial, and 100 microliters (µL) of 0.1 molar (M) dimethyglyoxime (DMG; Sigma Aldrich) ligand and 130 µL of 0.5 M N-(2-hydroxyethyl)piperazine-N-(3-propanesulfonic acid) (EPPS, Sigma Aldrich) buffer was added to each sample vial. A Metrohm 858 Sample Processor then loaded 8.5 mL of each sample into the electrode's Teflon cup and added 1.5 mL of 1.5 M $NaNO_2$ reagent (Merck). The mercury electrode performed a fast linear sweep from -1.4 volts (V) to -0.6 V at a rate of 5 volts per second ($V\ s^{-1}$) and produced a cobalt reduction peak at -1.15 V, the voltage at which the $Co(DMG)_2$ complex is reduced from Co(II) to Co(0) (Saito and Moffett 2001). The height of the Co reduction peak is linearly proportional to the amount of total dCo present in the sample. Peak heights were determined by NOVA 1.10 software. A standard curve was created with 4 additions of 25 picomoles(pM) dCo to each sample, and a type-I linear regression of the addition standard curve performed by the LINEST function in Microsoft Excel allowed for the calculation of the initial amount of Co present in the sample.

When analyzing labile dCo concentrations, samples were not UV-irradiated so as to only quantify the free or weakly bound dCo not bound to strong organic ligands. 11 mL of labile samples were instead allowed to equilibrate with the DMG ligand and EPPS reagent overnight (~8 hours) before analysis so as to allow time for the labile dCo present in the sample to bind to the DMG ligand via competitive ligand exchange (K > 10^16.8). Labile dCo samples were then loaded onto the Sample Processor and analyzed electrochemically using identical methods as described above for total dCo samples.

Known Issues/Problems:
Many of the dCo and labile dCo values measured were unusually low and below the analytical detection limit of 4 pM. In cases where no dCo or labile dCo were detected (i.e. when no peak was measurable and/or the dCo value predicted was < 0 pM), values of 0 pM were assigned for the purposes of plotting and select statistical analysis and were flagged as not detected (n.d.) as well as <DL in the dataset; although these concentrations are not detectable with our methodology, we believe the incredibly low concentrations of dCo and labile dCo observed on this expedition were meaningful, and that removing these values from our analysis misrepresents the data and would skew the results to appear higher than was observed.

Data Processing Description

Data Processing:
The height of the Co reduction peak is linearly proportional to the amount of total dCo present in the sample. Peak heights were determined by NOVA 1.10 software. A standard curve was created with 4 additions of 25 pM dCo to each sample, and a type-I linear regression of the addition standard curve performed by the LINEST function in Microsoft Excel allowed for the calculation of the initial amount of Co present in the sample.

Analytical blank measurements for each reagent batch (a unique combination of DMG, EPPS, and NaNO2 reagent batches) were measured to determine any Co contamination due to reagent impurities. Blanks were prepared in triplicate with UV-irradiated surface seawater passed through a column with Chelex 100 resin beads (Bio-Rad) to remove metal contaminants, then UV-irradiated again. Chelex beads were prepared as described in Price et al. (2013) to remove organic impurities from leaching into the eluent. For the 5 batches of reagents used on this expedition, the analytical blanks were found to be 2.3 pM, 4.0 pM, 10.1 pM, 15.6 pM, and 8.6 pM dCo, with an average of 8.1 pM Co. The analytical blank detected for the laboratory-run total dCo samples was 1.0 pM. It should be noted that blank values above 10 pM are considered high for this method. Analytical blank values were subtracted from the measured Co values determined with the respective reagent batch. The average standard deviation within each triplicate batch of blanks (1.3 pM) was used to estimate the analytical limit of detection (3 * blank standard deviation) of 4 pM. When detectable dCo concentrations were found below the 4 pM detection limit, their values were preserved in the dataset and flagged as below the detection limit (<DL).

BCO-DMO Processing:
- removed "NaN" as a missing data indicator (represented as blank/no value in the .csv data file);
- replaced "n.d." with "not detected";
- renamed fields to comply with BCO-DMO naming conventions;
- converted date/time field to ISO 8601 format.

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Data Files

File
ciclops_dissolved_cobalt.csv (Comma Separated Values (.csv), 22.24 KB) MD5:7b87fd92ac3ccd6cf8acae572c6ed382 Primary data file associated with dataset ID 893487

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Related Publications

Bundy, R. M., Tagliabue, A., Hawco, N. J., Morton, P. L., Twining, B. S., Hatta, M., … Saito, M. A. (2020). Elevated sources of cobalt in the Arctic Ocean. Biogeosciences, 17(19), 4745–4767. doi:10.5194/bg-17-4745-2020
Methods

Chmiel, R., Lanning, N., Laubach, A., Lee, J.-M., Fitzsimmons, J., Hatta, M., Jenkins, W., Lam, P., McIlvin, M., Tagliabue, A., & Saito, M. (2022). Major processes of the dissolved cobalt cycle in the North and equatorial Pacific Ocean. Biogeosciences, 19(9), 2365–2395. https://doi.org/10.5194/bg-19-2365-2022
Methods

Hawco, N. J., Ohnemus, D. C., Resing, J. A., Twining, B. S., & Saito, M. A. (2016). A dissolved cobalt plume in the oxygen minimum zone of the eastern tropical South Pacific. Biogeosciences, 13(20), 5697–5717. doi:10.5194/bg-13-5697-2016
Methods

Noble, A. E., Ohnemus, D. C., Hawco, N. J., Lam, P. J., & Saito, M. A. (2017). Coastal sources, sinks and strong organic complexation of dissolved cobalt within the US North Atlantic GEOTRACES transect GA03. Biogeosciences, 14(11), 2715–2739. https://doi.org/10.5194/bg-14-2715-2017
Methods

Saito, M. A., & Moffett, J. W. (2001). Complexation of cobalt by natural organic ligands in the Sargasso Sea as

determined by a new high-sensitivity electrochemical cobalt speciation method suitable for open ocean work. Marine Chemistry, 75(1-2), 49–68. doi:10.1016/s0304-4203(01)00025-1
Methods

Saito, M. A., Goepfert, T. J., Noble, A. E., Bertrand, E. M., Sedwick, P. N., & DiTullio, G. R. (2010). A seasonal study of dissolved cobalt in the Ross Sea, Antarctica: micronutrient behavior, absence of scavenging, and relationships with Zn, Cd, and P. Biogeosciences, 7(12), 4059–4082. doi:10.5194/bg-7-4059-2010
Methods

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Parameters

Parameter	Description	Units
Station	Station ID	unitless
Longitude	Longitude of sampling location (West is negative)	decimal degrees East
Latitude	Latitude of sampling location (South is negative)	decimal degrees North
Bottle_Number	Trace metal rosette niskin bottle number	unitless
Depth_m	Depth of trace metal rosette when sample was collected	meters (m)
Bottom_Depth_m	Station bottom seafloor depth	meters (m)
ISO_DateTime_UTC	Trace metal rosette start date and time in UTC in ISO 8601 format	unitless
Temperature	Temperature of seawater from trace metal CTD temperature sensor	degrees Celsius
Conductivity	Conductivity of seawater from trace metal CTD conductivity sensor	millisiemens per centimeter (mS/cm)
dO2_mg_L	Concentration of dissolved oxygen from trace metal CTD oxygen sensor	milligrams per liter (mg/L)
Fluorescence	Fluorescence of seawater from trace metal CTD fluorometer	milligrams per cubic meter (mg/m^3)
Percent_Transmisson	Beam Transmission from trace metal CTD Transmissometer	unitless (percent)
PAR	Photosynthetically Active Radiation (PAR) from trace metal CTD PAR sensor	watts per square meter (W/m^2)

Salinity	Salinity derived from conductivity measurements	PSU
PO4_uM	Concentration of dissolved phosphate	micromolar (uM)
NO3_NO2_uM	Concentration of dissolved nitrate plus dissolved nitrite	micromolar (uM)
Silicate_uM	Concentration of dissolved silicate	micromolar (uM)
NO2_uM	Concentration of dissolved nitrite	micromolar (uM)
NH4_uM	Concentration of dissolved ammonia	micromolar (uM)
dCo_pM	Concentration of total dissolved cobalt	picomolar (pM)
dCo_Flag	Quality flags for total dissolved cobalt measurement. When detectable dCo concentrations were found below the 4 pM detection limit, their values were preserved in the dataset and flagged as below the detection limit (<DL).	unitless
Labile_dCo_pM	Concentration of labile dissolved cobalt	picomolar (pM)
Labile_dCo_Flag	Quality flags for labile dissolved cobalt measurement. When detectable dCo concentrations were found below the 4 pM detection limit, their values were preserved in the dataset and flagged as below the detection limit (<DL).	unitless

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Instruments

Dataset-specific Instrument Name	Metrohm 858 Sample Processor
Generic Instrument Name	Laboratory Autosampler
Dataset-specific Description	Metrohm 858 Sample Processor - autosampler that introduces 11 mL of the sample, 1.5 mL of a 1.5 M NaNO2 reagent, and 25 pM standard dCo additions into the sample cup for electrochemical analysis by the 663 VA and µAutolabIII.
Generic Instrument Description	Laboratory apparatus that automatically introduces one or more samples with a predetermined volume or mass into an analytical instrument.

Dataset-specific Instrument Name	Metrohm 663 VA
Generic Instrument Name	Metrohm 663 VA Stand mercury electrode
Dataset-specific Description	Metrohm 663 VA and µAutolabIII - Voltammetry analyzer equipped with a hanging mercury drop working electrode. The instrument performed a fast linear sweep from -1.4 V to -0.6 V at a rate of 5 V s-1 and produced a cobalt reduction peak at -1.15 V, the voltage at which the Co(DMG)2- complex is reduced from Co(II) to Co(0). The height of the Co reduction peak is linearly proportional to the amount of total dCo present in the sample.
Generic Instrument Description	The Metrohm 663 VA stand forms the wet chemical part of a polarographic and voltammetric analytical system. It features a mercury electrode, an Ag/AgCl reference electrode and a glassy carbon counter electrode. The size of the mercury drop and the stirrer speed are set manually on the VA Stand. The VA Stand can be operated in Dropping Mercury Electrode (DME), Hanging Mercury Drop Electrode (HMDE) and Static Mercury Drop Electrode (SMDE) modes. The VA Stand can be controlled by a potentiostat in conjunction with the Metrohm IME663 interface.

Dataset-specific Instrument Name	X-Niskin
Generic Instrument Name	Niskin bottle
Dataset-specific Description	Dissolved seawater was collected from full-depth station profiles using a trace metal clean sampling rosette deployed on a conducting synthetic line, both supplied by the U.S. Antarctic Program (USAP), and equipped with twelve 8-liter X-Niskin bottles (Ocean Test Equipment), supplied by the Saito Laboratory.
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	Metrohm 705 UV Digester
Generic Instrument Name	UV Digester
Dataset-specific Description	Metrohm 705 UV Digester - To measure total dCo concentrations, filtered seawater samples were first UV-irradiated in quartz tubes for one hour in a Metrohm 705 UV Digester to destroy natural ligand-bound Co complexes.
Generic Instrument Description	Digestion instrument for UV photolysis of water samples

Dataset-specific Instrument Name	µAutolabIII
Generic Instrument Name	Voltammetry Analyzers
Dataset-specific Description	Metrohm 663 VA and µAutolabIII - Voltammetry analyzer equipped with a hanging mercury drop working electrode. The instrument performed a fast linear sweep from -1.4 V to -0.6 V at a rate of 5 V s-1 and produced a cobalt reduction peak at -1.15 V, the voltage at which the Co(DMG)2- complex is reduced from Co(II) to Co(0). The height of the Co reduction peak is linearly proportional to the amount of total dCo present in the sample.
Generic Instrument Description	Instruments that obtain information about an analyte by applying a potential and measuring the current produced in the analyte.

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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: 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 Office of Polar Programs (formerly NSF PLR) (NSF OPP)	OPP-1644073
NSF Office of Polar Programs (formerly NSF PLR) (NSF OPP)	OPP-1643684
NSF Office of Polar Programs (formerly NSF PLR) (NSF OPP)	OPP-1643845

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