Total dissolved metal concentrations measured during the 2017-2018 CICLOPS expedition

Website: https://www.bco-dmo.org/dataset/877466
Data Type: Cruise Results
Version: 1
Version Date: 2022-07-26

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

Contributors	Affiliation	Role
Saito, Mak A.	Woods Hole Oceanographic Institution (WHOI)	Principal Investigator
Kellogg, Riss	Woods Hole Oceanographic Institution (WHOI)	Student, Contact
Newman, Sawyer	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

Abstract

The Ross Sea and Amundsen Sea of Antarctica were sampled during the 2017-2018 CICLOPS (Cobalamin and Iron Co-Limitation of Phytoplankton Species) expedition for total dissolved concentrations of the trace metals Fe, Mn, Ni, Cu, Zn, and Cd. Water samples for dissolved trace metal analyses were collected at a total of 26 stations using a trace metal clean rosette suspended on a Kevlar line and equipped with twelve 8L X-Niskin bottles (Ocean Test Equipment) at depths ranging from 4.5 – 1209 m.

Table of Contents

Coverage

Spatial Extent: **N**:-70 **E**:-115 **S**:-80 **W**:160
Temporal Extent: 2017-12-30 - 2018-02-18

Methods & Sampling

Methodology:

Sampling and analytical procedures:

Study area and sample collection

Sample collection occurred during the CICLOPS (Cobalamin and Iron Co-Limitation of Phytoplankton Species) expedition (expedition code NBP18-01; chief scientist G.R. DiTullio) aboard the RVIB Nathaniel B. Palmer, December 11, 2017 – March 3, 2018 in the Amundsen Sea and Ross Sea of the Southern Ocean. Water samples were collected using trace metal sampling protocols described previously (Noble et al. 2012). A trace metal clean rosette suspended on a Kevlar line and equipped with twelve 8L X-Niskin bottles (Ocean Test Equipment) was used to collect seawater at depths ranging from 10 – 600 m.

Preparation of plasticware

Polyethylene and polycarbonate sampling and incubation bottles were rigorously cleaned to remove trace metal contaminants before use. Bottles with rinsed with Milli-Q water (Millipore), soaked for 72h in <1% Citranox detergent, rotated, soaked for an additional 72h, and then rinsed five times with Milli-Q water. Bottles were then filled with 10% HCl (Baker instra-analyzed) by volume and soaked for a minimum of one week, rotated, and soaked for another week. Bottles were then rinsed five times with dilute acid (HCl, pH 2) and stored double-bagged in plastic zip bags. All cleaning work was conducted in a Class 100 clean room.

Analyses of total dissolved Cd and Zn using isotope dilution

Samples for the analysis of total dissolved Zn, Cd, Fe, Mn, Cu and Ni concentrations were collected shipboard by pressure-filtering X-Niskin bottles through an acid-washed 142mm, 0.2µM Supor membrane filter (Pall) within 3 hours of rosette recovery using high purity (99.999%) N2 gas. Total dissolved water samples were collected into 250mL trace metal clean polyethylene bottles and were stored double-bagged in plastic zip bags. Seawater samples for 110Cd and 67Zn stable isotope uptake experiments were collected in the same way but without filtering. All sample collection occurred shipboard within a trace metal clean van containing laminar flow hoods and plastic sheeting. Samples for total dissolved metal analysis were acidified to pH 1.7 with high purity HCl (Optima, Fisher Scientific) within 7 months of sampling and were stored acidified at room temperature for over 1 year prior to analysis.

Quantification of dissolved metals in samples and reference seawater was performed for total dissolved Fe, Ni, Cu, Zn, and Cd using isotope dilution. 15mL of acidified seawater sample was spiked with 50µL of a stable isotope spike solution artificially enriched in 57Fe, 61Ni, 65Cu, 67Zn, and 110Cd. All stable isotopes were received in solid form (Oak Ridge National Laboratory). Initial dissolution and all subsequent dilutions were made using concentrated nitric acid (Optima, Fisher Scientific). Concentrations and spike ratios were verified by ICP-MS using a multi-element standard curve (SPEX CertiPrep). The composition of the isotope spike was made such that the 15mL spiked sample contained the following ratios: 57Fe/56Fe = 0.7, 61Ni/60Ni = 0.5, 65Cu/63Cu = 1, 67Zn/66Zn = 0.7, and 110Cd/114Cd = 1 and were verified with ICP-MS. These ratios were chosen to minimize the uncertainty introduced by error propagation through the isotope dilution equation (Wu and Boyle 1998; Rudge et al. 2009; Tan et al. 2020). Because it is monoisotopic, total dissolved Mn was calculated using a modified isotope dilution equation. This equation and its details can be found under the Supplemental Files section of this metadata landing page within the file titled, *Modified Isotope Dilution Equation.*

In this equation, 55Mnspl and 57Fespl refer to the blank corrected counts per second (cps) of 55Mn and 57Fe in the spiked sample, 57Fe spike is the concentration of 57Fe spike, 57Feslope is the slope of the external standard calibration curve (SPEX curve) relating 57Fe cps to ppb, and 55Mnslope is the slope of the external calibration curve (SPEX curve) relating 55Mn cps to ppb. Due to the acidification of seawater prior to ICP-MS analysis, Mn ICP-MS measurements do not include contributions from humic-type Mn(III)-ligand complexes (Oldham et al. 2021). Until the inclusion of Mn(III) is resolved and intercalibrated, we report these Mn values as Mn(II) and note that they are consistent with prior studies employing the same acidification technique (Sedwick et al. 2000; Noble et al. 2013; Gerringa et al. 2020).

Preconcentration of spiked seawater samples for total dissolved metal analysis was performed using the automated solid phase extraction system seaFAST-pico (Elemental Scientific) in offline concentration mode with an initial volume of 15mL and elution volume of 500µL (Bown et al. 2017; Rapp et al. 2017; Jackson et al. 2018; Wuttig et al. 2019). The seaFAST contains a Nobias-chelate PA1 resin column (ethylenediaminetriacete and iminodiacetate) suitable for the simultaneous preconcentration of several trace metals (Fe, Mn, Zn, Cu, Co, Cd, Ni) with high sensitivity and quantitative recovery (Sohrin et al. 2008; Biller and Bruland 2012). Adjusted seaFAST software settings were a 17 second load loop time and a single 10mL load cycle. Process blanks consisted of pH 2 HCl (Optima, Fisher Scientific) and were processed as samples were to account for any contamination introduced by instrument processing.

Reagents consisted of a 1.5M ammonium acetate pH 6.0 buffer made using glacial acetic acid and ammonium hydroxide (20-22%) of the highest purity (Optima, Fisher Chemical), a 1% nitric acid rinse solution (Optima grade, Fisher Chemical), and a 10% nitric acid elution buffer (Optima grade, Fisher Chemical) with 10 ppb indium (115In, SPEX CertiPrep) added as an internal standard. Solutions were prepared with 18.2 Ω Milli-Q water (Millipore). Polypropylene 15mL centrifuge tubes used in sample processing were made trace metal clean by soaking in 10% HCl for 5 days and rinsing with pH 2 HCl prior to use.

Following offline seaFAST preconcentration, multielemental quantitative analysis was performed using an iCAP-Q inductively coupled plasma-mass spectrometer (ICP-MS) (Thermo Scientific). Oxide interference on metal isotopes was minimized through the use of a cooled spray chamber and helium collision gas. Analytes were measured in single quadruple mode (kinetic energy discrimination [KED]). Concentrations of Mn, Fe, Ni, Cu, Zn and Cd were determined using a six-point external standard curve of a multi-element standard (SPEX CertiPrep), diluted to range from 1-10 ppb in 5% nitric acid. An indium standard (SPEX CertiPrep) was similarly added to these standard stocks, diluted to range 1-10 ppb. Instrument injection blanks consisted of 5% nitric acid in Milli-Q. Standard curve R2 values were ≥0.98 for all metals monitored. Method accuracy and precision were assessed using the 2009 GEOTRACES coastal surface seawater (GSC) standard which produced values consistent with consensus results.

Data Processing Description

Data Processing Notes from Researcher:

For analysis of dissolved metal data, method accuracy and precision were assessed using the 2009 GEOTRACES coastal surface seawater (GSC) standard which produced values consistent with consensus results.

BCO-DMO Processing Notes:

- Renamed column titled yyyy-mm-dd hh:mm to Collection_date
- Rounded latitude and longitude fields to 6 positions after the decimal point

[table of contents | back to top]

Data Files

File
totaldissolvedmetals_forbcodmo-1.csv(Comma Separated Values (.csv), 26.51 KB) MD5:e3c0c1ea9fdc7ffba2ddaacac9751394 Primary data file for dataset ID 877466

[table of contents | back to top]

Supplemental Files

File
Modified Isotope Dilution Equation filename: CICLOPS_Modified_Isotope_Dilution_Equation.pdf(Portable Document Format (.pdf), 111.02 KB) MD5:12f6d5fb8788de199d3080e0020ea68a

[table of contents | back to top]

Related Publications

Biller, D. V., & Bruland, K. W. (2012). Analysis of Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in seawater using the Nobias-chelate PA1 resin and magnetic sector inductively coupled plasma mass spectrometry (ICP-MS). Marine Chemistry, 130-131, 12–20. doi:10.1016/j.marchem.2011.12.001
Methods

Bown, J., Laan, P., Ossebaar, S., Bakker, K., Rozema, P., & de Baar, H. J. W. (2017). Bioactive trace metal time series during Austral summer in Ryder Bay, Western Antarctic Peninsula. Deep Sea Research Part II: Topical

Studies in Oceanography, 139, 103–119. doi:10.1016/j.dsr2.2016.07.004
Methods

Gerringa, L. J. A., Alderkamp, A. C., van Dijken, G., Laan, P., Middag, R., & Arrigo, K. R. (2020). Dissolved Trace Metals in the Ross Sea. Frontiers in Marine Science, 7. https://doi.org/10.3389/fmars.2020.577098
Methods

Jackson, S. L., Spence, J., Janssen, D. J., Ross, A. R. S., & Cullen, J. T. (2018). Determination of Mn, Fe, Ni, Cu, Zn, Cd and Pb in seawater using offline extraction and triple quadrupole ICP-MS/MS. Journal of Analytical Atomic Spectrometry, 33(2), 304–313. https://doi.org/10.1039/c7ja00237h
Methods

Noble, A. E., Lamborg, C. H., Ohnemus, D. C., Lam, P. J., Goepfert, T. J., Measures, C. I., … Saito, M. A. (2012). Basin-scale inputs of cobalt, iron, and manganese from the Benguela-Angola front to the South Atlantic Ocean. Limnology and Oceanography, 57(4), 989–1010. doi:10.4319/lo.2012.57.4.0989
Methods

Noble, A. E., Moran, D. M., Allen, A. E., & Saito, M. A. (2013). Dissolved and particulate trace metal micronutrients under the McMurdo Sound seasonal sea ice: basal sea ice communities as a capacitor for iron. Frontiers in Chemistry, 1. https://doi.org/10.3389/fchem.2013.00025
Methods

Oldham, V. E., Chmiel, R., Hansel, C. M., DiTullio, G. R., Rao, D., & Saito, M. (2021). Inhibited Manganese Oxide Formation Hinders Cobalt Scavenging in the Ross Sea. Global Biogeochemical Cycles, 35(5). Portico. https://doi.org/10.1029/2020gb006706 https://doi.org/10.1029/2020GB006706
Methods

Rudge, J. F., Reynolds, B. C., & Bourdon, B. (2009). The double spike toolbox. Chemical Geology, 265(3-4), 420–431. doi:10.1016/j.chemgeo.2009.05.010
Methods

Sedwick, P. N., DiTullio, G. R., & Mackey, D. J. (2000). Iron and manganese in the Ross Sea, Antarctica: Seasonal iron limitation in Antarctic shelf waters. Journal of Geophysical Research: Oceans, 105(C5), 11321–11336. Portico. https://doi.org/10.1029/2000jc000256 https://doi.org/10.1029/2000JC000256
Methods

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
Methods

Tan, D., Xu, W., Zhu, Z., Li, S., Wu, G., & Qin, H. (2020). Optimizing the ratio of the spike to sample for isotope dilution analysis: a case study with selenium isotopes. Acta Geochimica, 39(2), 192–202. https://doi.org/10.1007/s11631-019-00390-6
Methods

Wu, J., & Boyle, E. A. (1998). Determination of iron in seawater by high-resolution isotope dilution inductively coupled plasma mass spectrometry after Mg(OH)2 coprecipitation. Analytica Chimica Acta, 367(1–3), 183–191. https://doi.org/10.1016/s0003-2670(98)00145-7 https://doi.org/10.1016/S0003-2670(98)00145-7
Methods

Wuttig, K., Townsend, A. T., van der Merwe, P., Gault-Ringold, M., Holmes, T., Schallenberg, C., Latour, P., Tonnard, M., Rijkenberg, M. J. A., Lannuzel, D., & Bowie, A. R. (2019). Critical evaluation of a seaFAST system for the analysis of trace metals in marine samples. Talanta, 197, 653–668. https://doi.org/10.1016/j.talanta.2019.01.047
Methods

[table of contents | back to top]

Parameters

Parameter	Description	Units
Station	Station number	unitless

Lat_deg_N	Latitude	decimal degrees North
Lon_deg_E	Longitude	decimal degrees East
Collection_datetime	Datetime of sampling	unitless; %Y-%m-%d %H:%M
Bottle	Bottle ID	unitless
Depth_m	Depth of sampling	meters
Fe_D_CONC_BOTTLE	Dissolved iron concentration. This parameter follows GEOTRACES vocabulary for concentrations of dissolved metal	nanomoles per liter (nM)
Fe_D_CONC_BOTTLE_FLAG	Quality flag for dissolved iron concentration. 1= good value, 2= probably good value, 3= probably bad value, 4=bad value, 6=value below detection and changed to 0. Flags are based on GEOTRACES quality flag policy https://www.geotraces.org/geotraces-quality-flag-policy/.	unitless
Mn_D_CONC_BOTTLE	Dissolved manganese concentration	nanomoles per liter (nM)
Mn_D_CONC_BOTTLE_FLAG	Quality flag for dissolved iron concentration. 1= good value, 2= probably good value, 3= probably bad value, 4=bad value, 6=value below detection and changed to 0. Flags are based on GEOTRACES quality flag policy https://www.geotraces.org/geotraces-quality-flag-policy/.	unitless
Ni_D_CONC_BOTTLE	Dissolved nickel concentration	nanomoles per liter (nM)
Ni_D_CONC_BOTTLE_FLAG	Quality flag for dissolved iron concentration. 1= good value, 2= probably good value, 3= probably bad value, 4=bad value, 6=value below detection and changed to 0. Flags are based on GEOTRACES quality flag policy https://www.geotraces.org/geotraces-quality-flag-policy/.	unitless
Cu_D_CONC_BOTTLE	Dissolved copper concentration	nanomoles per liter (nM)
Cu_D_CONC_BOTTLE_FLAG	Quality flag for dissolved iron concentration. 1= good value, 2= probably good value, 3= probably bad value, 4=bad value, 6=value below detection and changed to 0. Flags are based on GEOTRACES quality flag policy https://www.geotraces.org/geotraces-quality-flag-policy/.	unitless

Zn_D_CONC_BOTTLE	Dissolved zinc concentration	nanomoles per liter (nM)
Zn_D_CONC_BOTTLE_FLAG	Quality flag for dissolved iron concentration. 1= good value, 2= probably good value, 3= probably bad value, 4=bad value, 6=value below detection and changed to 0. Flags are based on GEOTRACES quality flag policy https://www.geotraces.org/geotraces-quality-flag-policy/.	unitless
Cd_D_CONC_BOTTLE	Dissolved cadmium concentration	nanomoles per liter (nM)
Cd_D_CONC_BOTTLE_FLAG	Quality flag for dissolved iron concentration. 1= good value, 2= probably good value, 3= probably bad value, 4=bad value, 6=value below detection and changed to 0. Flags are based on GEOTRACES quality flag policy https://www.geotraces.org/geotraces-quality-flag-policy/.	unitless

[table of contents | back to top]

Instruments

Dataset-specific Instrument Name	iCAP-Q inductively coupled plasma-mass spectrometer (ICP-MS) (Thermo Scientific)
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Dataset-specific Description	Following offline seaFAST preconcentration, multielemental quantitative analysis was performed using an iCAP-Q inductively coupled plasma-mass spectrometer (ICP-MS) (Thermo Scientific).
Generic Instrument Description	An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer.

Dataset-specific Instrument Name	Twelve 8L X-Niskin bottles (Ocean Test Equipment)
Generic Instrument Name	Niskin bottle
Dataset-specific Description	Water samples were collected using trace metal sampling protocols described previously (Noble et al. 2012). A trace metal clean rosette suspended on a Kevlar line and equipped with twelve 8L X-Niskin bottles (Ocean Test Equipment) was used to collect seawater at depths ranging from 10 – 600 m.
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	Automated solid phase extraction system seaFAST-pico
Generic Instrument Name	SeaFAST Automated Preconcentration System
Dataset-specific Description	Preconcentration of spiked seawater samples for total dissolved metal analysis was performed using the automated solid phase extraction system seaFAST-pico (Elemental Scientific) in offline concentration mode with an initial volume of 15mL and elution volume of 500µL (Bown et al. 2017; Rapp et al. 2017; Jackson et al. 2018; Wuttig et al. 2019). The seaFAST contains a Nobias-chelate PA1 resin column (ethylenediaminetriacete and iminodiacetate) suitable for the simultaneous preconcentration of several trace metals (Fe, Mn, Zn, Cu, Co, Cd, Ni) with high sensitivity and quantitative recovery (Sohrin et al. 2008; Biller and Bruland 2012). Adjusted seaFAST software settings were a 17 second load loop time and a single 10mL load cycle. Process blanks consisted of pH 2 HCl (Optima, Fisher Scientific) and were processed as samples were to account for any contamination introduced by instrument processing.
Generic Instrument Description	The seaFAST is an automated sample introduction system for analysis of seawater and other high matrix samples for analyses by ICPMS (Inductively Coupled Plasma Mass Spectrometry).

[table of contents | back to top]

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

[table of contents | back to top]

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.

[table of contents | back to top]

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

[table of contents | back to top]