

# Total Zn and Cd uptake rates of natural phytoplankton assemblages measured during the 2017-2018 CICLOPS expedition

**Website:** <https://www.bco-dmo.org/dataset/877681>

**Data Type:** Cruise Results

**Version:** 1

**Version Date:** 2022-08-03

## Project

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

Contributors	Affiliation	Role
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## Abstract

<sup>67</sup>Zn and <sup>110</sup>Cd tracer uptake experiments were conducted along the Amundsen Sea and Ross Sea shelves during the 2017-2018 CICLOPS expedition in order to quantify the movement of dissolved Zn and Cd into the phytoplankton particulate fraction (>3 $\mu$ m). Variations in these uptake rates with depth and time were examined to draw conclusions regarding the relative demand of these trace metals within the native phytoplankton bloom.

## Table of Contents

- [Coverage](#)
- [Dataset Description](#)
  - [Methods & Sampling](#)
  - [Data Processing Description](#)
- [Data Files](#)
- [Supplemental Files](#)
- [Related Publications](#)
- [Parameters](#)
- [Instruments](#)
- [Deployments](#)
- [Project Information](#)
- [Funding](#)

## 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 were 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, 0.2 $\mu$ M Supor membrane filter (Pall) within 3 hours of rosette recovery using high purity (99.999%) N<sub>2</sub> 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 <sup>110</sup>Cd and <sup>67</sup>Zn 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 50 $\mu$ L of a stable isotope spike solution artificially enriched in <sup>57</sup>Fe, <sup>61</sup>Ni, <sup>65</sup>Cu, <sup>67</sup>Zn, and <sup>110</sup>Cd. 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: <sup>57</sup>Fe/<sup>56</sup>Fe = 0.7, <sup>61</sup>Ni/<sup>60</sup>Ni = 0.5, <sup>65</sup>Cu/<sup>63</sup>Cu = 1, <sup>67</sup>Zn/<sup>66</sup>Zn = 0.7, and <sup>110</sup>Cd/<sup>114</sup>Cd = 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 are captured in the Supplemental Files dropdown on this metadata landing page, within the file titled, *Modified Isotope Dilution Equation*.

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 500 $\mu$ L (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 (ethylenediaminetriacetate 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 (<sup>115</sup>In, SPEX CertiPrep) added as an internal standard. Solutions were prepared with 18.2  $\Omega$  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 quadrupole 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  $R^2$  values were  $\geq 0.98$  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.

#### *Uptake experiments: $^{67}\text{Zn}$ and $^{110}\text{Cd}$ spiking, incubation, and sample collection*

$^{67}\text{Zn}$  and  $^{110}\text{Cd}$  and stable isotope uptake experiments were modelled after those conducted by Cox et al. 2014. Raw (unfiltered) seawater was collected shipboard over a depth range of 10 – 600m at each station into 250mL trace metal clean polycarbonate incubation bottles. All incubation bottles were filled with minimal headspace such that the total culture volume was  $\sim 275\text{mL}$ . Two incubation bottles per depth were filled with raw seawater— one was spiked with  $^{67}\text{Zn}$ , the other was spiked with  $^{110}\text{Cd}$ . The Cd and Zn isotope spikes were prepared by dissolving  $^{110}\text{CdO}$  and  $^{67}\text{ZnO}$  (Oak Ridge National Laboratory) in 5%  $\text{HNO}_3$  (Seastar Baseline) and were diluted using Milli-Q water to minimize added acidity. When added to the filled incubation bottles, the total added (spiked) concentration of Cd was 300 pM and the total added concentration of Zn was 2 nM. The chosen total added concentrations were based on the surface ratio of total dissolved Cd (dCd) to total dissolved Zn (dZn) reported previously for the Ross Sea (Fitzwater et al. 2000). Immediately after spiking, incubation bottles were sealed, inverted to mix, and transferred to flow-through on-deck incubators for 24hr. Incubators were shielded by black net neutral density screening to allow 20% ambient light penetration.

Biomass was collected after 24hr by vacuum filtering the entire volume of each incubation sample at 34.5 kPa (5 psi) onto an acid-cleaned 3mm, 50mm Versapore filter (Pall) mounted on an acid-cleaned Teflon (Saville) filtration rig. Samples were 3mm filtered rather than 0.2mm in order to minimize filtration time (and thus time exposed to potential contamination) and to capture the bulk of eukaryotic phytoplankton biomass typically found in the Southern Ocean.  $\sim 1\text{ mL}$  of 0.2mm filtered surface (10m depth) seawater was used to rinse the sample before collecting the filter into an acid-cleaned 2mL cryovial using acid-rinsed plastic forceps. Filter blanks were duplicate 3mm acid-clean Versapore filters that were placed onto the filtration rig, rinsed with filtered surface seawater, collected, stored, and processed as samples were in order to correct for any contaminating metals present on the filters themselves. Blanks were collected at each station. Filters were stored frozen at  $-80^\circ\text{C}$  in acid-cleaned cryovials until analysis. The filtration rig was rinsed with pH 2 HCl between samples. Polycarbonate incubation bottles were cleaned between stations with a 10% HCl rinse and several rinses in Milli-Q water, followed by a brief soak in 10% HCl followed by a pH 2 HCl rinse. All spike addition and sample filtration procedures were completed in a fabricated shipboard positive-pressure clean room environment made of laminar flow hoods and plastic sheeting.

#### *Filter digestion and particulate ICP-MS analysis*

All work was performed in a Class 100 clean room under laminar flow hoods. Sample filters were retrieved from storage at  $-80^\circ\text{C}$ , removed from cryovials using plastic acid-washed forceps, and transferred into trace metal clean 15 mL PFA vials with 4 mL of 5%  $\text{HNO}_3$  (Optima) containing a 1 ppb Indium (In) internal standard. Filters were digested for  $\sim 3.5\text{h}$  at  $140^\circ\text{C}$  using a HotBlock® heating block (Environmental Express, USA) before the filters were removed and discarded, leaving behind the liquid extract. After evaporating the remaining solution to just dryness, the residue was resuspended in 2 mL of 5%  $\text{HNO}_3$  (Optima) by light vortexing. Process blank filters were digested and processed as sample filters were. Digests were analyzed in duplicate by ICP-MS using a Thermo ICAP-Q plasma mass spectrometer calibrated to a multi-element standard curve (Spex Certiprep) over a range of 1 – 20 ppb. Natural Cd and Zn isotope abundances of the standards were assumed to calculate concentrations of  $^{110}\text{Cd}$ ,  $^{111}\text{Cd}$ ,  $^{114}\text{Cd}$ ,  $^{67}\text{Zn}$ ,  $^{66}\text{Zn}$ , and  $^{68}\text{Zn}$ . Digests were analyzed in KED mode after an 85s sample uptake window and element mass windows were scanned 3 times during measurements. The 1 ppb In internal standard was used to correct for variation in sample delivery and plasma suppression between samples. Process blanks were subtracted from measured sample concentrations. Phosphorus concentrations were simultaneously measured by ICP-MS and were calibrated to a standard curve ranging from 100 – 3,200 ppb using a 1 ppm certified P stock (Alfa Aesar Specpure). The equation and its details used for the calculations described above are captured in the Supplemental Files section of this metadata landing page within the file titled, *Particulate Rates Metal Concentration Equation*.

The Zn spike and Cd spike were also analyzed by ICP-MS using a 1:9 dilution of spike solution into 5%  $\text{HNO}_3$  1 ppb In to determine isotopic compositions and concentrations. When added to filled incubation bottles (275mL total volume), the added concentrations were 288 pM  $^{110}\text{Cd}$ , 4.51 pM  $^{111}\text{Cd}$ , and 1.69 pM  $^{114}\text{Cd}$  for Cd spiked bottles, and were 1.91 nM  $^{67}\text{Zn}$ , 0.045 nM  $^{66}\text{Zn}$ , and 0.047 nM  $^{68}\text{Zn}$  for Zn spiked bottles.

## Calculating zinc and cadmium uptake using $^{67}\text{Zn}$ and $^{110}\text{Cd}$

Total Zn and Cd uptake was calculated using Eq. (3) and Eq. (4), respectively. These equations can be found under the Supplemental Files section of this metadata landing page, within the file titled, *Metal Uptake Rate Equations*.  $^{110}\text{Cd}_{\text{Sample}}$  and  $^{67}\text{Zn}_{\text{Sample}}$  are the particulate  $^{110}\text{Cd}$  and  $^{67}\text{Zn}$  measured by ICP-MS analysis of the 3 $\mu\text{m}$  sample filter, normalized to the total culture volume (275 mL) and 24hr of incubation.  $^{110}\text{Cd}_{\text{Sample}}$  and  $^{67}\text{Zn}_{\text{Sample}}$  already in the particulate fraction (that is, the pCd and pZn that existed in the water column upon collection of the raw seawater samples) was accounted for by subtracting the particulate blank,  $^{110}\text{Cd}_{\text{Blank}}$  and  $^{67}\text{Zn}_{\text{Blank}}$ .  $^{110}\text{Cd}_{\text{Blank}}$  and  $^{67}\text{Zn}_{\text{Blank}}$  will hereafter be referred to as “pre-existing particulate  $^{110}\text{Cd}$  and  $^{67}\text{Zn}$ ”. The pre-existing particulate blank value for  $^{110}\text{Cd}$  was obtained from incubation bottles that had Zn added, but no Cd spike. Likewise, the pre-existing particulate blank value for  $^{67}\text{Zn}$  was obtained from incubation bottles that had Cd added, but no Zn spike. The  $^{67}\text{Zn}$  spike solution was confirmed to contain virtually no  $^{110}\text{Cd}$ ,  $^{111}\text{Cd}$ ,  $^{114}\text{Cd}$ . The  $^{110}\text{Cd}$  spike was likewise confirmed to contain virtually no  $^{67}\text{Zn}$ ,  $^{64}\text{Zn}$ ,  $^{66}\text{Zn}$ . As a result, we assumed that the added  $^{67}\text{Zn}$  spike did not affect the pre-existing Cd, nor did the  $^{110}\text{Cd}$  spike affect the pre-existing Zn. It is assumed that the pre-existing particulate blank was in steady state, i.e. that it represented the Cd or Zn already in the particulate fraction and any possible natural uptake that could occur during incubation for 24h was negligible. The total dissolved pool of each metal isotope (denominator of each equation) is the sum of the dissolved  $^{110}\text{Cd}$  or  $^{67}\text{Zn}$  added as the spike ( $^{110}\text{Cd}_{\text{Spike}}$ ,  $^{67}\text{Zn}_{\text{Spike}}$ ) plus the natural, pre-existing dissolved  $^{110}\text{Cd}$  or  $^{67}\text{Zn}$  that was in the raw seawater ( $^{110}\text{Cd}_{\text{Natural}}$ ,  $^{67}\text{Zn}_{\text{Natural}}$ ) collected at each depth. To calculate  $^{110}\text{Cd}_{\text{Natural}}$  and  $^{67}\text{Zn}_{\text{Natural}}$ , the total dissolved Cd or Zn measured by isotope dilution-ICP-MS ( $\text{Cd}_{\text{Total}}$ ,  $\text{Zn}_{\text{Total}}$ ) was multiplied by the natural abundance of  $^{110}\text{Cd}$  and  $^{67}\text{Zn}$  (12.49% and 4.10%, respectively). Dividing the particulate  $^{110}\text{Cd}$  and  $^{67}\text{Zn}$  by the total dissolved  $^{110}\text{Cd}$  and  $^{67}\text{Zn}$  yields the fraction of these metal isotopes that moved from the dissolved pool to the particulate pool per day.

## 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
- Detailed equations are captured within the Supplemental Files section of this metadata landing page

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

## Data Files

File
<b>zncduptakerates_forbcodmo-1.csv</b> (Comma Separated Values (.csv), 16.84 KB) MD5:b25d77af030db4da7bb25a5e75139a25
Primary data file for dataset ID 877681

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

## Supplemental Files

File	
<b>Metal Uptake Rate Equations</b> filename: CICLOPS_Zn_Cd_Uptake_Rates_Metal_Uptake_Equations.pdf	(Portable Document Format (.pdf), 121.72 KB) MD5:ad9acab94eb01e54a4a066aac5f64587
<b>Modified Isotope Dilution Equation</b> filename: CICLOPS_Modified_Isotope_Dilution_Equation.pdf	(Portable Document Format (.pdf), 111.02 KB) MD5:12f6d5fb8788de199d3080e0020ea68a
<b>Particulate Metal Concentration Equation</b> filename: CICLOPS_Zn_Cd_Part particulate_Rates_Metal_Concentration_Equation.pdf	(Portable Document Format (.pdf), 92.65 KB) MD5:505053c13f6abe680d20984c84501c84

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

## Related Publications

Billar, 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](https://doi.org/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](https://doi.org/10.1016/j.dsr2.2016.07.004)

*Methods*

Fitzwater, S. E., Johnson, K. S., Gordon, R. M., Coale, K. H., & Smith, W. O. (2000). Trace metal concentrations in the Ross Sea and their relationship with nutrients and phytoplankton growth. *Deep Sea Research Part II: Topical Studies in Oceanography*, 47(15-16), 3159-3179. [https://doi.org/10.1016/S0967-0645\(00\)00063-1](https://doi.org/10.1016/S0967-0645(00)00063-1)

[https://doi.org/https://doi.org/10.1016/S0967-0645\(00\)00063-1](https://doi.org/https://doi.org/10.1016/S0967-0645(00)00063-1)

*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](https://doi.org/10.4319/lo.2012.57.4.0989)

*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*

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](https://doi.org/10.1016/j.aca.2017.05.008)

*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](https://doi.org/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>

*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](https://doi.org/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)<sub>2</sub> 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](#) ]

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## Parameters

Parameter	Description	Units
Station	Station number	unitless
Lat_deg_N	Latitude in decimal degrees; positive values indicate North	unitless
Lon_deg_E	Longitude in decimal degrees; negative values indicate West	unitless
Collection_datetime	Time of sampling; %Y-%M-%D %H:%M	unitless
Depth_m	Depth of sampling	Meters (m)
Bottle	Bottle ID	unitless
Zn_UR_pmolLd	Total zinc uptake rate	picomoles per liter per day (pmol/L/d)
Cd_UR_pmolLd	Total cadmium uptake rate	picomoles per liter per day (pmol/L/d)

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

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## Instruments

<b>Dataset-specific Instrument Name</b>	iCAP-Q inductively coupled plasma-mass spectrometer (ICP-MS) (Thermo Scientific)
<b>Generic Instrument Name</b>	Inductively Coupled Plasma Mass Spectrometer
<b>Dataset-specific Description</b>	Following offline seaFAST preconcentration, multielemental quantitative analysis was performed using an iCAP-Q inductively coupled plasma-mass spectrometer (ICP-MS) (Thermo Scientific).
<b>Generic Instrument Description</b>	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.

<b>Dataset-specific Instrument Name</b>	Twelve 8L X-Niskin bottles (Ocean Test Equipment)
<b>Generic Instrument Name</b>	Niskin bottle
<b>Dataset-specific Description</b>	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.
<b>Generic Instrument Description</b>	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.

<b>Dataset-specific Instrument Name</b>	Automated solid phase extraction system seaFAST-pico (Elemental Scientific)
<b>Generic Instrument Name</b>	SeaFAST Automated Preconcentration System
<b>Dataset-specific Description</b>	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 (ethylenediaminetriacetate 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.
<b>Generic Instrument Description</b>	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

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

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

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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.

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

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## Funding

<b>Funding Source</b>	<b>Award</b>
<a href="#">NSF Office of Polar Programs (formerly NSF PLR) (NSF OPP)</a>	<a href="#">OPP-1644073</a>
<a href="#">NSF Office of Polar Programs (formerly NSF PLR) (NSF OPP)</a>	<a href="#">OPP-1643684</a>
<a href="#">NSF Office of Polar Programs (formerly NSF PLR) (NSF OPP)</a>	<a href="#">OPP-1643845</a>

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