

Trace metals, hydrography, and fluorescence from CTD casts on the R/VIB Nathaniel B. Palmer (cruise NBP1704) in the Ross Sea, Antarctica from April to May 2017

Website: <https://www.bco-dmo.org/dataset/856009>

Data Type: Cruise Results

Version: 1

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Project

» [Impact of Convective Processes and Sea Ice Formation on the Distribution of Iron in the Ross Sea: Closing the Seasonal Cycle](#) (PIPERS)

Contributors	Affiliation	Role
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Abstract

Water column samples for analysis of trace elements (dissolved, soluble, and particulate), and continuous profiles of temperature, salinity, chlorophyll fluorescence, and dissolved oxygen concentration were collected from CTD casts on the R/VIB Nathaniel B. Palmer (cruise NBP1704) in the Ross Sea, Antarctica from April to May 2017.

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Coverage

Spatial Extent: N:-71.128 E:-179.956 S:-77.715 W:178.861

Temporal Extent: 2017-04-23 - 2017-05-28

Acquisition Description

Water-column sample collection and in-situ measurements: Water-column samples for analysis of trace elements (dissolved, soluble and particulate), and continuous profiles of temperature, salinity, chlorophyll fluorescence and dissolved oxygen concentration were collected using a trace-metal clean conductivity-temperature-depth sensor (SBE 19 plus, SeaBird Electronics) mounted on a custom-built

trace-metal clean carousel (SeaBird Electronics) fitted with custom-modified 5-L Teflon-lined external-closure Niskin-X samplers (General Oceanics), deployed using a non-metallic line with polymer jacket.

Shipboard processing of water-column samples: Upon recovery, the Niskin-X samplers were transferred into a shipboard Class-100 clean laboratory container, where seawater was filtered through pre-rinsed 0.2-micrometer (μm) pore AcroPak Supor filter capsules (Pall) into acid-cleaned 125 milliliter (mL) low-density polyethylene (LDPE) bottles (Nalgene) for shore-based dissolved trace element determinations, and, for selected samples, into acid-cleaned 60 mL LDPE bottles (Nalgene) for subsequent ultrafiltration through acid-rinsed 0.02 μm Anotop syringe filters (Whatman) following Ussher et al. (2010) for shore-based soluble trace element determinations. While drawing samples, the Niskin-X samplers were pressurized using 0.2 μm -filtered ultra-high purity compressed nitrogen gas. All samples used for dissolved- and soluble trace element determinations were acidified at sea to pH $\sim$ 1.8 with ultrapure hydrochloric acid (Fisher Optima grade) then stored at room temperature until post-cruise analysis at Old Dominion University. In addition, from selected samples, a pre-cleaned perfluoroalkoxy alkane (PFA) cylindrical reservoir (Savillex) was filled with approximately 1.8 liters (L) of unfiltered seawater, which was passed through sequential 2 μm - and 0.2 μm -pore acid-cleaned 47-mm diameter polycarbonate membrane filters (Poretics) mounted in an in-line PFA filter holder (Savillex) using overpressure from 0.2 μm -filtered compressed air. The filters were then rinsed with 200 mL of ultrapure deionized water (Barnstead Nanopure) that had been adjusted to pH 8 with ultrapure ammonium hydroxide solution (Fisher Optima grade), placed in pre-cleaned polystyrene Petri dishes (Fisher), then air-dried under a Class-100 clean-air bench. The dried filters were stored in the sealed Petri dishes inside a desiccator at room temperature until post-cruise analysis at the NOAA Pacific Marine Environmental Laboratory.

Determination of DFe, sFe, DMn, sMn, DNi, DCu, DZn: Concentrations of these dissolved and soluble transition metals were measured in 0.2 μm -filtered (dissolved fraction) or 0.02 μm -filtered (soluble fraction) acidified seawater samples using a sector-field inductively-coupled plasma mass spectrometer (Thermo Fisher Scientific ElementXR) with an in-line separation-preconcentration system (Elemental Scientific SeaFAST SP3), following a modification of the method of Lagerström et al. (2013). Calibration standards were prepared in low-analyte concentration seawater, for which initial concentrations were determined using the method of standard additions, and were introduced using the same in-line separation-preconcentration procedure as the seawater samples. Scandium was used as an internal standard. Analyses were performed on a volumetric basis, so concentrations are reported in units of nanomole per liter (nM). Analytical blank concentrations were assessed by applying the in-line separation-preconcentration procedure including all reagents except loading air in place of the seawater sample ("air blank"), with the following mean blank concentrations: 0.002 nM DFe, <0.001 nM DMn, 0.003 nM DNi, 0.001 nM DCu, 0.001 nM DZn. Limits of detection were defined as the concentration equivalent to 3 times the standard deviation on the mean blank ($n = 12$), as follows: 0.042 nM DFe and sFe, 0.003 nM DMn and sMn, 0.021 nM DNi, 0.006 nM DCu, and 0.018 nM DZn. Estimated analytical precision, expressed as percent relative standard deviation on the mean (%RSD), is the average value of the %RSD obtained for replicate (separate-day) analyses of 58 different samples, as follows: 8.0% for DFe and sFe, 1.8% for DMn and sMn, 3.0% for DNi, 2.5% for DCu, and 5.8% for DZn. In terms of external consistency, we obtained the following mean concentrations for the GEOTRACES GSP seawater consensus material: 0.187 ± 0.037 nM DFe ($n = 17$; consensus value 0.155 ± 0.045 nM), 0.789 ± 0.016 nM DMn ($n = 19$; consensus value 0.778 ± 0.034 nM), 2.59 ± 0.08 nM DNi ($n = 19$, consensus value 2.60 ± 0.10 nM), 0.581 ± 0.015 nM DCu ($n = 19$; consensus value 0.574 ± 0.053 nM), and 0.015 ± 0.003 nM DZn ($n = 3$; consensus value 0.030 ± 0.052 nM). Our reported GSP DZn concentration is for measurements in aliquots from a freshly-opened bottle of this consensus material; two other bottles yielded much higher concentrations and are therefore assumed to be contaminated.

Determination of pFe-large, pFe-small, pMn-large, pMn-small, pAl-large, pAl-small: The concentrations of Fe, Mn, and Al in suspended particles separated on 2 μm - and 0.2 μm -pore membrane filters (defined as large- and small-particulate fractions, respectively) were measured using energy dispersive X-ray fluorescence (ED-XRF), following the method of Buck et al. (2021). ED-XRF analysis was conducted under a vacuum atmosphere using thin-film principles on a Thermo Fisher Scientific Quant'X equipped with a rhodium target X-ray tube and an electronically-cooled, lithium-drifted solid-state detector. X-rays for primary sample excitation were passed through graphite and metal filters for optimum control of peak-to-background ratios, using the excitation conditions described by Buck et al. (2021). Four

separate quality assurance/quality control procedures were conducted: (1) daily energy adjustment was performed for an energy channel alignment of the Quant'X; (2) weekly calibration verification using a series of multi-element samples; (3) weekly analysis of the NIST 2783 standard reference material; and (4) monthly analysis of 10 acid-washed filter blanks. Calibrations were performed using commercially available thin-film standards (MicroMatter Inc.), as well as low-concentration standards for pFe and pMn (<1000 nanograms per square centimeter (ng cm⁻²)) that were prepared as described by Buck et al. (2021). Field blanks, for which acid-cleaned 0.2 µm- and 2 µm-pore polycarbonate membranes were mounted in the filtration assembly, rinsed with 200 mL of pH 8 ammonium hydroxide solution, then air-dried and stored as for the samples, yielded the following measured blank concentrations that were subtracted from corresponding sample values: 4.5/5.1 ng cm⁻² for Fe (0.2 µm/2 µm), below the minimum detection limit for Mn (0.2 µm/2 µm), and 11.78/11.77 ng cm⁻² for Al (0.2 µm/2 µm). The minimum detection limit (MDL) for individual elements using ED-XRF is defined as 3 times the square root of the background intensity measured from a standard of known concentration (Bertin, 2012; Buck et al., 2021), which yields the following MLD values: 0.95 ng cm⁻² Fe (equivalent to ~0.13 nM pFe), 1.27 ng cm⁻² Mn (equivalent to ~0.18 nM pMn), and 9.4 ng cm⁻² Al (equivalent to ~2.8 nM pAl). Analytical precision and accuracy of the ED-XRF method were assessed from analyses of the NIST-2783 standard reference material (air particulate on filter media). Mean recoveries ± one standard deviation for individual elements in NIST-2783 by ED-XRF were 108% ± 2.6% for Fe, 104% ± 2.5% for Mn, and 92% ± 3.5% for Al (n = 320).

Temperature: In-situ temperature was measured using a conductivity-temperature-depth sensor (SBE 19 plus, SeaBird Scientific), with data processed using the SBE Data Processing software.

Salinity: Salinity was calculated from in-situ conductivity, as measured using a conductivity-temperature-depth (CTD) sensor (SBE 19 plus, SeaBird Electronics), with data processed using the SBE Data Processing software.

Fluorescence: In-situ chlorophyll fluorescence was measured using a WET Labs ECO-FL(RT)D deep chlorophyll fluorometer with 125 micrograms per liter (µg L⁻¹) range mounted on the CTD rosette, with data processed using the SBE Data Processing software.

Dissolved Oxygen: In-situ dissolved oxygen concentration was measured using an SBE 43 Dissolved Oxygen Sensor mounted on the CTD rosette, with data processed using the SBE Data Processing software.

Processing Description

Inductively-coupled plasma mass spectrometer: Instrumental data were collected using ElementXR processing software (Thermo Fisher Scientific), and post-analysis calculations were performed using Microsoft Excel.

Energy dispersive X-ray fluorescence spectrometer: Instrumental data were processed using Quant'X processing software (Thermo Fisher Scientific), and post-analysis calculations were performed using Microsoft Excel.

CTD sensors: Primary and derived data from the CTD sensors (temperature, conductivity, depth, in-situ chlorophyll fluorescence, dissolved oxygen) were processed using the SBE Data Processing software (SeaBird Scientific).

Known problems: The measured values from the dissolved oxygen concentration sensor were systematically low compared to sensor measurements from a conventional CTD (verified by discrete bottle sample measurements), and are not considered to be quantitatively reliable. We suspect that the sensor membrane was damaged due to exposure to sub-freezing temperatures during deployment and recovery.

Data quality flags were assigned as follows:

- 1 = good;
- 2 = good; an average of at least two determinations on different days;
- 3 = possibly contaminated; determination anomalously high;

4 = sample signal outside the range of calibration standards;

5 = values were systematically low compared to sensor measurements from conventional CTD, and are therefore not considered to be quantitatively reliable.

"BDL" is used to indicate values that are below detection limits. See Acquisition Description for detection limits.

BCO-DMO processing description:

- Converted dates to ISO date format (yyyy-mm-dd)
- Adjusted field/parameter names to comply with BCO-DMO naming conventions
- Missing data identifier "ND" (not determined) replaced with 'nd' (BCO-DMO's default missing data identifier)
- Added a conventional header with dataset name, PI names, version date

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Related Publications

Ackley, S. F., Stammerjohn, S., Maksym, T., Smith, M., Cassano, J., Guest, P., ... Parno, J. (2020). Sea-ice production and air/ice/ocean/biogeochemistry interactions in the Ross Sea during the PIPERS 2017 autumn field campaign. *Annals of Glaciology*, 61(82), 181–195. doi:[10.1017/aog.2020.31](https://doi.org/10.1017/aog.2020.31)

Results

Buck, N. J., Barrett, P. M., Morton, P. L., Landing, W. M., & Resing, J. A. (2021), ED-XRF methodology and analysis of suspended particulate matter in seawater for trace element compositions and an intercomparison with HR ICP-MS. *Limnology and Oceanography: Methods*, in press.

Methods

Lagerström, M. E., Field, M. P., Séguet, 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](https://doi.org/10.1016/j.marchem.2013.06.001)

Methods

Ussher, S. J., Achterberg, E. P., Sarthou, G., Laan, P., de Baar, H. J. W., & Worsfold, P. J. (2010). Distribution of size fractionated dissolved iron in the Canary Basin. *Marine Environmental Research*, 70(1), 46–55. doi:[10.1016/j.marenvres.2010.03.001](https://doi.org/10.1016/j.marenvres.2010.03.001)

Methods

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Parameters

Parameter	Description	Units
Station	PIPERS cruise station number	unitless
Sample_ID	unique identifier for each water sample	unitless
Depth	sample collection depth (below surface)	meters
Latitude	latitude of CTD recovery in decimal degrees North	decimal degrees
Longitude	longitude of CTD recovery in decimal degrees East (West is negative)	decimal degrees
Date	Date of CTD recovery in ISO8601 format (YYYY-MM-DD)	unitless
Bottom_Depth	approximate seafloor depth	meters

DFe	dissolved Fe (	nanomole per liter
DFe_Flag	data quality flag that applies to DFe (Refer to Processing Description for flag definitions)	unitless
sFe	soluble Fe (	nanomole per liter
sFe_Flag	data quality flag that applies to sFe (Refer to Processing Description for flag definitions)	unitless
pFe_large	>2 µm particulate Fe concentration	nanomole per liter
pFe_small	0.2-2 µm particulate Fe concentration	nanomole per liter
DMn	dissolved Mn (	nanomole per liter
DMn_Flag	data quality flag that applies to DMn (Refer to Processing Description for flag definitions)	unitless
sMn	soluble Mn (	nanomole per liter
sMn_Flag	data quality flag that applies to sMn (Refer to Processing Description for flag definitions)	unitless
pMn_large	>2 µm particulate Mn concentration	nanomole per liter
pMn_small	0.2-2 µm particulate Mn concentration	nanomole per liter
pAl_large	>2 µm particulate Al concentration	nanomole per liter
pAl_small	0.2-2 µm particulate Al concentration	nanomole per liter
DNi	dissolved Ni (	nanomole per liter
DNi_Flag	data quality flag that applies to DNi (Refer to Processing Description for flag definitions)	unitless
DCu	dissolved Cu (	nanomole per liter
DCu_Flag	data quality flag that applies to DCu (Refer to Processing Description for flag definitions)	unitless
DZn	dissolved Zn (	nanomole per liter
DZn_Flag	data quality flag that applies to DZn (Refer to Processing Description for flag definitions)	unitless
Temperature	in-situ temperature from CTD	degrees celsius
Salinity	salinity calculated from CTD conductivity	unitless
Fluor	in-situ chlorophyll fluorescence (uncalib)	milligrams per cubic meter (mg m-3)
Sigma_Theta	density calculated as sigma-theta	unitless
Oxygen	in-situ dissolved oxygen from CTD	micromole per kilogram
Oxygen_Flag	data quality flag that applies to Oxygen (Refer to Processing Description for flag definitions)	unitless

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Instruments

Dataset-specific Instrument Name	Niskin-X samplers (General Oceanics)
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	SBE 19 plus, SeaBird Scientific
Generic Instrument Name	CTD Sea-Bird
Dataset-specific Description	Calibrated prior to the cruise by SeaBird Scientific
Generic Instrument Description	Conductivity, Temperature, Depth (CTD) sensor package from SeaBird Electronics, no specific unit identified. This instrument designation is used when specific make and model are not known. See also other SeaBird instruments listed under CTD. More information from Sea-Bird Electronics.

Dataset-specific Instrument Name	Fluorometer (in-situ chlorophyll fluorescence) WET Labs ECO-FL(RT)D deep chlorophyll fluorometer
Generic Instrument Name	Fluorometer
Dataset-specific Description	Calibrated prior to the cruise by SeaBird Scientific
Generic Instrument Description	A fluorometer or fluorimeter is a device used to measure parameters of fluorescence: its intensity and wavelength distribution of emission spectrum after excitation by a certain spectrum of light. The instrument is designed to measure the amount of stimulated electromagnetic radiation produced by pulses of electromagnetic radiation emitted into a water sample or in situ.

Dataset-specific Instrument Name	ElementXR (Thermo Fisher Scientific), with SeaFAST SP3 in-line separation-preconcentration system and autosampler (Elemental Scientific)
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
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	SBE 43 dissolved oxygen sensor, SeaBird Scientific
Generic Instrument Name	Sea-Bird SBE 43 Dissolved Oxygen Sensor
Dataset-specific Description	Calibrated prior to the cruise by SeaBird Scientific
Generic Instrument Description	The Sea-Bird SBE 43 dissolved oxygen sensor is a redesign of the Clark polarographic membrane type of dissolved oxygen sensors. more information from Sea-Bird Electronics

Dataset-specific Instrument Name	Energy dispersive X-ray fluorescence spectrometer Quant'X (Thermo Fisher Scientific)
Generic Instrument Name	Spectrometer
Generic Instrument Description	A spectrometer is an optical instrument used to measure properties of light over a specific portion of the electromagnetic spectrum.

Dataset-specific Instrument Name	in-line separation-preconcentration system (Elemental Scientific SeaFAST SP3)
Generic Instrument Name	SeaFAST Automated Preconcentration System
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).

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Deployments

NBP1704

Website	https://www.bco-dmo.org/deployment/856022
Platform	RVIB Nathaniel B. Palmer
Start Date	2017-04-10
End Date	2017-06-14
Description	See additional cruise information from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/NBP1704

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Project Information

Impact of Convective Processes and Sea Ice Formation on the Distribution of Iron in the Ross Sea: Closing the Seasonal Cycle (PIPERS)

Website: <https://www.usap-dc.org/view/project/p0010032>

Coverage: Ross Sea, Antarctica (ca. 66°S-78°S, 165°E-175°W)

NSF Award Abstract

The waters of the Ross Sea continental shelf are among the most productive in the Southern Ocean, and likely comprise a significant oceanic sink for atmospheric carbon dioxide. In this region, primary production can be limited by the supply of dissolved iron to surface waters during the growing season.

A range of biogeochemical measurements and activities are to be carried out in the late summer-autumnal- early winter time frame in the Ross Sea in order to better understand phytoplankton dynamics, along with carbon export. These biogeochemical parameters include elements such as Fe, C and S believed to be important to Antarctic ecosystems. As well as there being interest in the functioning of the Ross Sea ecosystem leading up to the impending polar night, there is also uncertainty as to what drives the biogeochemical redistribution undergone by micronutrient Fe species during the extensive sea-ice formation at this time of year.

The field setting and remote conditions that accompany the proposed study present several possibilities for STEM education and training at the K-12, undergraduate and graduate levels, as well as for public outreach. At the K-12 level, the project seeks to support the development of educational outreach materials targeting elementary and middle school students, pre-service science teachers, and in-service science teachers.

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Funding

Funding Source	Award
NSF Office of Polar Programs (formerly NSF PLR) (NSF OPP)	ANT-1543483

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