Dissolved concentrations of the trace metals Mn, Cd, Co, Cu, Ni, Zn, and Pb in vertical profile seawater samples from the upper 1,000 meters of the water column collected on R/V Roger Revelle cruise RR2004 in the south Pacific Ocean from Jan-Feb 2021

Website: https://www.bco-dmo.org/dataset/933773

Data Type: Cruise Results

Version: 1

Version Date: 2025-06-09

Project

» <u>Collaborative Research: Biogeochemical and Physical Conditioning of Sub-Antarctic Mode Water in the Southern Ocean</u> (Conditioning_SAMW)

Contributors	Affiliation	Role
Morton, Peter L.	Florida State University - National High Magnetic Field Lab (FSU - NHMFL)	Co-Principal Investigator
<u>Caprara,</u> <u>Salvatore</u>	University of South Florida (USF)	Scientist
<u>Hearn, Lauren</u>	Florida State University (FSU)	Student
Middleton, Jule	Woods Hole Oceanographic Institution (WHOI)	Student
<u>Tegler, Logan</u>	Woods Hole Oceanographic Institution (WHOI)	Student
Rauch, Shannon	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

Abstract

This dataset includes dissolved (<0.4 micrometers) concentrations of the trace metals Mn, Cd, Co, Cu, Ni, Zn, and Pb in vertical profile seawater samples (upper ~1000 meters), collected on cruise RR2004 (on R/V Roger Revelle) in the south Pacific Ocean from 30 degrees South latitude to 60 degrees South along the 150 degrees West meridian. Water was collected using nine 5-liter trace metal Niskin-X bottles, suspended from Kevlar line and triggered to close with Teflon messengers. Pressure depth and temperature were determined using a data logger secured to the deepest bottle. These data are part of the NSF project "Collaborative Research: Biogeochemical and Physical Conditioning of Sub-Antarctic Mode Water in the Southern Ocean", which focused on the biological, physical, and chemical surface water properties across the polar and subpolar fronts of the south Pacific Ocean, especially as they related to the phytoplankton communities of coccolithophores and diatoms. Samples were collected by Dr. Pete Morton (Florida State University), Dr. Jule Middleton (MIT/WHOI), Dr. Logan Tegler (MIT/WHOI), and Lauren Hearn (Florida State University). Samples were analyzed by Dr. Pete Morton with assistance from Dr. Salvatore Caprara (University of South Florida-St Petersburg) at the National High Magnetic Field Laboratory.

Table of Contents

- Coverage
- Dataset Description
 - Methods & Sampling
 - Data Processing Description
 - BCO-DMO Processing Description
- Data Files
- Supplemental Files
- Related Publications
- <u>Parameters</u>
- <u>Instruments</u>
- Deployments
- Project Information

Coverage

Location: South Pacific Ocean and Southern Ocean **Spatial Extent**: N:-32.2 **E**:-138.02 **S**:-60 **W**:-150.22 **Temporal Extent**: 2021-01-08 - 2021-02-08

Methods & Sampling

To characterize the nutritional values of Southeast Pacific Ocean waters and determine the limiting nutrient(s) in each regime, uncontaminated seawater samples (n=173) were drawn from 21 deployments of nine 5-liter (L) Niskin-X bottles suspended from Kevlar line at varying depths between 30 meters (m) and 1050 m.

Sampling procedure:

Niskin-X bottles were carried from a UNOLS trace-metal clean van to the starboard squirt boom, where they were secured by hand to the 1/4-inch Aracom Miniline using stainless steel hardware. The Niskins were attached incrementally so that each Niskin was lowered to its target depth when the deepest Niskin reached its target depth (~ 1000 m). Niskin bottles were allowed to sit at depth for ~ 5 minutes before triggered to close using a series of Teflon messengers.

The Niskins were recovered and returned to the trace metal clean van, where they were secured in PVC racks with wedges to keep the caps tight. A series of air lines were connected to the air ports at the top of the Niskins, which were then overpressured (\sim 6-8 psi) with filtered air using a Gast pump.

Unfiltered samples were drawn from each Niskin-X for salinity and major nutrient measurements (ODF). The remainder of the volume was filtered using 47-millimeter (mm), 0.4-micrometer (μ m) pore-size Isopore membrane filters installed in Advantec filter cartridges. The filtrate was collected into trace metal-cleaned (acidwashed) 125-milliliter (mL) LDPE bottles for dissolved trace metal concentrations.

Special modifications to sampling operations:

- 1. A small Ronstan Series 60 Single Orbit block (model #7298755) was used instead of a larger metering block, which eliminated the risk of the line jumping the sheave and the need for a deck-mounted snatch block. The block was attached to the starboard squirt boom which allowed for the Niskin-X bottles to be attached to the Aracom line without having to lean too far over the side of the ship.
- 2. The Niskin-X bottles were deployed from the starboard side of the ship by securing the Hawboldt winch at an angle, just aft of the ResTech locker. This allowed the Aracom line to be threaded through the Ronstan block mounted to the squirt boom. Even in heavier seas, the Niskin-X bottles were deployed reliably and reproducibly due to this arrangement (which was designed by Matt Durham, UCSD ResTech).
- 3. In order to better estimate the depths at which the bottles were deployed, a miniature temperature and pressure sensor (centi-TD, 5-1500 m; Star Oddi) was secured to each Niskin-X bottle. These sensors recorded the temperature and pressure (i.e., depth) at preset intervals (every 60 seconds). These depths were double-checked by comparing the salinity and nutrient values determined in samples from each Niskin-X bottle against (1) the temperature and salinity values from the ship's CTD sensors and (2) discrete salinity and nutrient concentrations determined from the ship's bottles.

Analytical procedure (dissolved trace metals):

Filtered seawater samples were acidified to 0.024 M HCl using concentrated Fisher Optima HCl. The samples were allowed to sit for \sim 6 months to allow complete desorption of metals from the bottle walls, according to Jensen et al. 2020.

Aliquots of acidified seawater (~15 mL) were transferred to 30 mL FEP bottles (Savillex) for UV-oxidation (1.5 hours), according to Milne et al. 2010. The samples were then processed online using a SeaFAST S2 system (Elemental Scientific, Inc.), which includes online buffering with ammonium acetate buffer before passing over a 200-microliter (µL) column filled with Nobias Chelate PA-1. The extraction procedure captures trace metals from 10 mL of buffered seawater while allowing most of the major sea-salt cations (e.g., Na and Mg) to be directed to waste. The column is then eluted with 0.5 mL of 1.6 M HNO3 (Fisher Optima) to release the trace metals, and this eluate is introduced directly to the High Resolution-Inductively Coupled Plasma-Mass Spectrometer (Thermo ELEMENT 2) for analysis. By eliminating the major seasalts and concentrating the trace

metals by a factor of \sim 20 (10 mL sample loaded, 0.5 mL eluted), the matrix effects are minimized, and the metal detection limits are increased.

Metal concentrations were quantified upon comparison against external standards prepared in low metal surface seawater, which were processed identically to the samples. Blanks (n=93) were determined by running a complete loading-extraction-elution cycle without seawater (i.e., leaving the sample probe out of any sample or rinse solution, taking up only HEPA-filtered air). These blanks were applied to all samples and reference materials to determine any background metal contributions from the SeaFAST system, ICPMS sample introduction components, or reagent blanks.

Reference materials were included in every analytical run, including the GEOTRACES GS (n=9) and GD (n=3) consensus reference materials, as well as an in-house "daily check" sample of surface seawater collected from the Gulf of Mexico (n=18).

Details of the reference materials and daily check sample are included with the air blanks in the "QA/QC" summary file "BCO-DMO_SAMW_2021_dTM_QAQC_2024_06_04" (PDF and Excel formats provided; see Supplemental Files section of metadata).

Data Processing Description

Microsoft Excel

Elemental Scientific, Inc. autosampler control software

Thermo ELEMENT 2/XR software

Sample concentrations determined by normalizing all standards and samples to 1 ppb In, and then dividing the signal (cps) by the external calibration curve slope (cps/concentration).

Cd signal was corrected for any isobaric interferences from Mo oxides, by producing a set of Mo standards and monitoring the mass windows for "Cd-111" and "Cd-112" (Mo-95 and Mo-96 \pm O-16). The slope of signals from the Mo masses (95 and 96) vs the signals from the "Cd" masses (111 and 112) were used to estimate the contribution of MoO to the Cd signal. These estimated contributions were subtracted from the raw 111 and 112 signals before further quantification.

BCO-DMO Processing Description

- Imported original file "BCO-DMO SAMW 2021 dTM 2024 06 04.xlsx" into the BCO-DMO system.
- Renamed fields to comply with BCO-DMO naming conventions.
- Converted the Date collected field to YYYY-MM-DD format.
- Saved the final file as "933773 v1 rr2004 dissolved trace metals.csv".

[table of contents | back to top]

Data Files

File

933773_v1_rr2004_dissolved_trace_metals.csv(Comma Separated Values (.csv), 12.87 KB)

MD5:36a4757ae10a44dea208b4f6b4cf0f23

Primary data file for dataset ID 933773, version 1

[table of contents | back to top]

Supplemental Files

File

BCO-DMO SAMW 2021 dTM QAQC 2025_06_08.pdf

(Portable Document Format (.pdf), 403.56 KB) MD5:f20034db3dff8d8fcf5df56a382e911d

Supplemental file for dataset ID 933773, version 1. Converted to PDF format by BCO-DMO (same content as Excel file). QA/QC data includes daily summaries of:

Air blanks and detection limits (3x standard deviation of the blanks)

Replicate sample precision (n=3)

Reference material recoveries (GEOTRACES GS and/or GD)

In-house check standards (Gulf of Mexico surface water)

BCO-DMO SAMW 2021 dTM QAQC 2025_06_08.xlsx

(Microsoft Excel, 15.10 KB)

MD5:6233aa0b2abf0bb29d7133bb9bef0890

Supplemental file for dataset ID 933773, version 1. Excel format (same content as PDF file). QA/QC data includes daily summaries of: Air blanks and detection limits (3x standard deviation of the blanks)

Replicate sample precision (n=3)

Reference material recoveries (GEOTRACES GS and/or GD)

In-house check standards (Gulf of Mexico surface water)

[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

Jensen, L. T., Wyatt, N. J., Landing, W. M., & Fitzsimmons, J. N. (2020). Assessment of the stability, sorption, and exchangeability of marine dissolved and colloidal metals. Marine Chemistry, 220, 103754. doi:10.1016/j.marchem.2020.103754

Methods

Milne, A., Landing, W., Bizimis, M., & Morton, P. (2010). Determination of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in seawater using high resolution magnetic sector inductively coupled mass spectrometry (HR-ICP-MS). Analytica Chimica Acta, 665(2), 200–207. doi:10.1016/j.aca.2010.03.027

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

[table of contents | back to top]

Parameters

Parameter	Description	Units
Station	station identification number	unitless
Lat	latitude, degrees N	decimal degrees
Lon	longitude, degrees E	decimal degrees
Date_collected	date of sample collection (UTC)	unitless

Depth	depth, in meters below surface	meters (m)
Mn	dissolved manganese concentration	nanomoles per liter (nmol/L)
Mn_SD	standard deviation of replicate (n=3) manganese analyses of aliquots of the same sample	nanomoles per liter (nmol/L)
Cd	dissolved cadmium concentration	picomoles per liter (pmol/L)
Cd_SD	standard deviation of replicate (n=3) cadmium analyses of aliquots of the same sample	picomoles per liter (pmol/L)
Со	dissolved cobalt concentration	picomoles per liter (pmol/L)
Co_SD	standard deviation of replicate (n=3) cobalt analyses of aliquots of the same sample	picomoles per liter (pmol/L)
Cu	dissolved copper concentration	nanomoles per liter (nmol/L)
Cu_SD	standard deviation of replicate (n=3) copper analyses of aliquots of the same sample	nanomoles per liter (nmol/L)
Ni	dissolved nickel concentration	nanomoles per liter (nmol/L)
Ni_SD	standard deviation of replicate (n=3) nickel analyses of aliquots of the same sample	nanomoles per liter (nmol/L)
Zn	dissolved zinc concentration	nanomoles per liter (nmol/L)
Zn_SD	standard deviation of replicate (n=3) zinc analyses of aliquots of the same sample	nanomoles per liter (nmol/L)
Pb	dissolved lead concentration	picomoles per liter (pmol/L)
Pb_SD	standard deviation of replicate (n=3) lead analyses of aliquots of the same sample	picomoles per liter (pmol/L)
Notes	notes	unitless
	· ·	I.

Instruments

Dataset- specific Instrument Name	High Resolution-Inductively Coupled Plasma-Mass Spectrometer (Thermo ELEMENT 2)
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	5-L Niskin-X bottles
Generic Instrument Name	Niskin bottle
Dataset- specific Description	Niskin 5 L, internally Teflon coated, with Teflon-coated external springs (General Oceanics 101005XTM)
	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	SeaFAST S2 system (Elemental Scientific, Inc.)
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).

Dataset- specific Instrument Name	centi-TD (5-1500 m; Star Oddi)
Generic Instrument Name	Star-Oddi DST centi-TD Temperature and Depth Recorder
	A miniature underwater temperature-pressure recorder with a range of depth ratings from 30 meters (m) to 3000 m. Temperature resolution is 0.032 degrees Celsius (C), with an accuracy of ± 0.1 degrees C over a range -2 degrees C to 40 degrees C. Depth resolution is 0.03% of selected range, with an accuracy of $\pm 0.4\%$ of selected range for 30 m to 270 m range and $\pm 0.6\%$ of selected range for 800 m to 3000 m range. See https://www.bodc.ac.uk/data/documents/nodb/223482/ for further details.

Deployments

small mesoscale eddy (Eddy C) which contained a highly focused, high-reflectance core that we had observed in satellite imagery for several weeks. We performed one VPR tow and one hydrographic survey along one diameter across the small eddy and left Eddy C with VPR in tow, to do a repeat crossing of Eddy A, then onward to a high-reflectance meander of the SubAntarctic Front for collection of water for the fourth experiment and documentation of the conditions of the SAF. We then headed for the portion of the meridional survey where we had seen low levels of coccolithophores three weeks prior. This region had remained cloud-covered for weeks, thus we had little idea of what awaited us. Shortly after leaving the Meander station, the estimates of acid-labile backscattering (an optical proxy for PIC) began rising and for the next 400 nautical miles saw PIC concentrations three times higher than anything we had seen previously along the 150°W meridian (or elsewhere for that matter). References: Fine, R. A. (2011), Observations of CFCs and SF 6 as ocean tracers, Annual Review of Marine Science, 3, 173-195, doi:10.1146/annurev.marine.010908.163933.

[table of contents | back to top]

Project Information

Collaborative Research: Biogeochemical and Physical Conditioning of Sub-Antarctic Mode Water in the Southern Ocean (Conditioning_SAMW)

NSF Award Abstract:

Cold surface water in the southern Indian Ocean sinks to about 500 meters and travels in the dark for thousands of miles before it resurfaces some 40 years later near the equator in the other ocean basins. This major water mass is named the Sub-Antarctic Mode Water (SAMW). Nutrients it contains when it warms and rises into the sunlit subtropical and tropical waters are estimated to fuel up to 75% of the microscopic plant growth there. Before it sinks, the chemical properties of the SAMW are modified by the growth and distinct physiology of two common phytoplankton; diatoms with shells made of silica, and coccolithophores with carbonate shells. Local physical dynamics influence where and how fast these two phytoplankton classes grow. Consequently, differing nutrient and trace chemical fingerprints are established at the point of SAMW formation. This project is an exceptionally detailed field and modeling effort that will document and quantify the remarkable, interconnected processes that chemically connect two important oceanic ecosystems half a world apart. The scientists leading the project will study the complexity of the biological and chemical conditioning of the SAMW and thus provide critical data about the large-scale oceanic controls of the biological carbon pump that removes atmospheric carbon dioxide to the deep ocean over millennial timescales. Scientific impact from this project will stem from significant peer-reviewed publications and improved predictive models. Societal benefits will develop from training of a range of scholars, including high school, undergraduate, and graduate students, as well as technical and post-doctoral participants. A high school teacher and science communication specialist will go to sea with the project and share experiences from the ship with students on shore via social media and scheduled web interactions.

To examine how SAMW formation and subduction controls the productivity of global waters well to the north, two January expeditions to the SE Indian Ocean will identify, track, and study the unique mesoscale eddies that serve as discrete water parcels supporting rich populations of either coccolithophores or diatoms plus their associated microbial communities. The eddies will be tracked with Lagrangian Argo drifters and observations will be made of exactly how SAMW is chemically conditioned (i.e. Si, N, P, Fe, and carbonate chemistry) over time scales of months. Using data obtained on the feedback between ecological processes and nutrient, trace metal, and carbonate chemistry in these eddies and on related transect cruises, the project will have three main goals: (1) determine the rates at which SAMW coccolithophores and diatoms condition the carbonate chemistry plus nutrient and trace metal concentrations, as well as assess taxonomic and physiological diversity in the study area with traditional methods plus next-generation sequence DNA/RNA profiling, (2) explore growth limitations by iron, silicate and/or nitrate in controlling algal assemblages and genetic diversity, and (3) combine these findings with the Ekman- and eddy-driven subduction of SAMW to examine biogeochemical impact on a basin scale, using both observations and global numerical models. A meridional survey from 30 to 60 degrees south latitude will be used to characterize the larger-scale variability of carbonate chemistry, nutrient distributions, productivity, genetics and biomass of various plankton groups as SAMW is subducted and proceeds northward.

[table of contents | back to top]

Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1735436

[table of contents | back to top]