# Iron, manganese and nutrient data from four cruises in the eastern tropical North Pacific, 2012 to 2018

Website: https://www.bco-dmo.org/dataset/828183 Data Type: Cruise Results Version: 1 Version Date: 2020-11-02

#### Project

» <u>Development and Intercomparison of Methodologies to Measure Dissolved Ferrous Iron in Seawater</u> (Ferrous iron in seawater)

» <u>The role of cryptic nutrient cycling within sinking particles on trace element transport in oxygen minimum</u> <u>zones</u> (OMZ Nutrient Cycling)

Contributors	Affiliation	Role
Moffett, James W.	University of Southern California (USC)	Principal Investigator
Copley, Nancy	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

#### Abstract

Iron, manganese, temperature, salinity, oxygen, nitrates, and nitrites collected from NOAAV Ronald H. Brown (RB1603), R/V Sikuliaq (SKQ201617S), R/V Roger Revelle (RR1805), and Thompson (TN278) in the eastern tropical North Pacific off Mexico in the spring of 2012 and 2016 to 2018.

# **Table of Contents**

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

# Coverage

**Spatial Extent**: N:24.04018 **E**:-99.00134 **S**:14.99976 **W**:-113.00043 **Temporal Extent**: 2012-03-26 - 2018-04-17

### Methods & Sampling

Samples were collected and analyzed as described in Bolster et al. Briefly, samples were collected from a tracemetal clean rosette, sampled under filtered nitrogen pressure through acid-washed 0.2 µm polyethersulfone filters into acid-washed low-density polyethylene bottles. Iron(II) was measured using luminol chemiluminescence, using diethylenetriaminepentaacetic acid as a masking ligand to correct for interferents (Bolster et al., 2018). Total dissolved metal samples were acidified with Optima grade hydrochloric acid (final concentration 20 mM) and stored at room temperature for several months. Dissolved iron and manganese were determined using inductively coupled plasma mass spectrometry with an offline preconcentration system.

Additional hydrographic and nutrient data is provided for some samples. Temperature, salinity, and oxygen were measured using a CTD, and measurements of phosphate, nitrate, and nitrite were performed using a nutrient auto-analyzer onboard, as described in Selden et al.

Trace metal samples were collected in 5 L Teflon-coated external spring "Niskin-type" bottles (Ocean Test Equipment) mounted on a powder-coated trace metal clean rosette (Sea-Bird Electronics). Samples were preconcentrated using a seaFAST system (ESI), and quantified using isotope dilution for iron and standard additions for manganese. Analyses were performed on an inductively coupled mass spectrometer in medium resolution mode (Thermo Element 2), using indium as an internal standard. Trace metal quantification was performed using Microsoft Excel 2016.

Temperature, salinity, and oxygen were determined from a Sea-Bird SBE 11plus CTD and a model 43 dissolved oxygen sensor, attached to a sampling rosette for dissolved nutrient concentrations. Nutrients were measured using an Astoria-Pacific nutrient autoanalyzer.

A number of samples have no measured values for total dissolved iron and manganese, either because sample collection was not logistically possible, or because some of the samples were lost in transit.

### **Data Processing Description**

#### **BCO-DMO Processing Notes:**

- data submitted in csv file "ferrous iron seawater withdates.csv
- added conventional header with dataset name, PI name, version date
- renamed column time UTC to ISO DateTime UTC and formatted as yyyy-mm-ddTHH:MM:SSZ
- sorted records by ISO DateTime UTC and depth
- records were sorted by date
- reduced precision of fe, mn, temp, salinity, oxygen, no3, and no2 tp 3 digits

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

# **Data Files**

File Fe\_nuts.csv(Comma Separated Values (.csv), 24.66 KB) MD5:0592ff20de93a7290c131df3516150ef

Primary data file for dataset ID 828183

```
[ table of contents | back to top ]
```

# **Related Publications**

Bolster, K. M., Heller, M. I., & Moffett, J. W. (2018). Determination of iron(II) by chemiluminescence using masking ligands to distinguish interferences. Limnology and Oceanography: Methods, 16(11), 750–759. doi:<u>10.1002/lom3.10279</u> *Methods* 

Selden, C. R., Mulholland, M. R., Bernhardt, P. W., Widner, B., Macías-Tapia, A., Ji, Q., & Jayakumar, A. (2019). Dinitrogen Fixation Across Physico-Chemical Gradients of the Eastern Tropical North Pacific Oxygen Deficient Zone. Global Biogeochemical Cycles, 33(9), 1187–1202. doi:10.1029/2019gb006242 <u>https://doi.org/10.1029/2019GB006242</u> *Results* 

[ table of contents | back to top ]

# **Related Datasets**

#### IsSupplementedBy

Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2019-10-15 http://lod.bco-dmo.org/id/dataset/779185 [view at BCO-DMO]

Rocap, G., Devol, A. (2018) Water temperature, salinity, and other data from CTD taken from the RV Sikuliaq in the Pacific Ocean between San Diego, California and Manzanillo, Mexico from 2016-12-21 to 2017-01-13. Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2018-03-27 http://lod.bco-dmo.org/id/dataset/732092 [view at BCO-DMO]

[ table of contents | back to top ]

# Parameters

Parameter	Description	Units
cruise	ship for sampling; ship name (brown; sikuliaq; revelle; thompson)	unitless
station	station on cruise	unitless
cast	cast on cruise	unitless
ISO_DateTime_UTC	UTC date and time; formatted as yyyy-mm-ddTHH:MM:SSZ	unitless
depth	sample depth	meters
latitude	station latitude; north is positive	decimal degrees
longitude	station longitude; east is positive	decimal degrees
fe2	dissolved iron(II) concentration	picomoles/liter
fe	total dissolved iron concentration	nanomoles/liter
mn	total dissolved manganese concentration	nanomoles/liter
temp	water temperature	degrees Celsius
salinity	water salinity	practical salinity units (PSU)
oxygen	dissolved oxygen concentration	micromoles/liter
no3	dissolved nitrate concentration	micromoles/liter
no2	dissolved nitrite concentration	micromoles/liter

[ table of contents | back to top ]

# Instruments

Dataset- specific Instrument Name	
Generic Instrument Name	CTD Sea-Bird SBE 911plus
Dataset- specific Description	Used to measure temperature, salinity, and depth.
Generic Instrument Description	The Sea-Bird SBE 911 plus is a type of CTD instrument package for continuous measurement of conductivity, temperature and pressure. The SBE 911 plus includes the SBE 9plus Underwater Unit and the SBE 11plus Deck Unit (for real-time readout using conductive wire) for deployment from a vessel. The combination of the SBE 9 plus and SBE 11 plus is called a SBE 911 plus. The SBE 9 plus uses Sea-Bird's standard modular temperature and conductivity sensors (SBE 3 plus and SBE 4). The SBE 9 plus CTD can be configured with up to eight auxiliary sensors to measure other parameters including dissolved oxygen, pH, turbidity, fluorescence, light (PAR), light transmission, etc.). more information from Sea-Bird Electronics

Dataset- specific Instrument Name	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	Astoria-Pacific nutrient autoanalyzer
Generic Instrument Name	Nutrient Autoanalyzer
Generic Instrument Description	Nutrient Autoanalyzer is a generic term used when specific type, make and model were not specified. In general, a Nutrient Autoanalyzer is an automated flow-thru system for doing nutrient analysis (nitrate, ammonium, orthophosphate, and silicate) on seawater samples.

Dataset-specific Instrument Name	
Generic Instrument Name	Sea-Bird SBE 43 Dissolved Oxygen Sensor
Dataset-specific Description	Used to measure oxygen concentrations
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	
Generic Instrument Name	Trace Metal Bottle
Dataset-specific Description	5 L Teflon-coated external spring "Niskin-type" bottles (Ocean Test Equipment)
Generic Instrument Description	Trace metal (TM) clean rosette bottle used for collecting trace metal clean seawater samples.

# [ table of contents | back to top ]

# Deployments

# RR1805

Website	https://www.bco-dmo.org/deployment/779193
Platform	R/V Roger Revelle
Start Date	2018-04-14
End Date	2018-05-02
Description	More information is available at R2R: <u>https://www.rvdata.us/search/cruise/RR1805</u>

#### TN278

Website	https://www.bco-dmo.org/deployment/733752
Platform	R/V Thomas G. Thompson
Start Date	2012-03-17
End Date	2012-04-23
Description	Additional cruise data are available from the Rolling Deck to Repository (R2R): <u>http://www.rvdata.us/catalog/TN278</u>

# SKQ201617S

<u> </u>	
Website	https://www.bco-dmo.org/deployment/828218
Platform	R/V Sikuliaq
Start Date	2016-12-20
End Date	2017-01-16
Description	Cruise DOI: 10.7284/907444 See more cruise information from the Rolling Deck to Repository (R2R): <u>https://www.rvdata.us/search/cruise/SKQ2016175</u>

# RB1603

Website	https://www.bco-dmo.org/deployment/828215
Platform	NOAA Ship Ronald H. Brown
Start Date	2016-03-27
End Date	2016-04-24

# **Project Information**

# Development and Intercomparison of Methodologies to Measure Dissolved Ferrous Iron in Seawater (Ferrous iron in seawater)

Coverage: Southern Mexico; Catalna Island USA

#### NSF Award Abstract:

The trace metal iron is a key micronutrient throughout the oceans that plays an important role in regulating primary production. Iron (chemical symbol Fe) can exist in different ionization states in the environment, primarily as the reduced form Fe(II) and the oxidized form Fe(III), which impacts its chemical behavior within the water column, and ultimately the ability of researchers to accurately measure its abundance. There is an urgent need in the chemical oceanography community for accurate measurements of Fe(II) in the water column, as currently used methods may overestimate concentrations in water samples collected from certain depths. In this study, researchers from the University of Southern California will significantly redevelop an underutilized methodology to measure Fe(II), and carry out an evaluation and inter-comparison between the two methodologies. This work will enable the refinement of estimates of Fe(II) concentration, present a robust methodology for future use, and clarify conditions where the current methodology can be used effectively. This project will involve strong undergraduate research opportunities, and the research will be conducted in collaboration with an international researcher from India.

Fe(II) is thermodynamically unstable in seawater in the presence of oxygen or nitrate, yet its presence has been reported both in surface waters and in oxygen minimum zones. A rigorous assessment of Fe(II) measurements is important because its chemistry and bioavailability are so different than Fe(III). Fe(II) forms weak complexes, is weakly hydrolyzed and highly soluble in seawater. Fe(III) forms strong complexes, is sparingly soluble and strongly hydrolyzed. The presence of even a modest fraction of Fe as Fe(II) under Fe-limited conditions could increase bioavailability by orders of magnitude. The most widely used methodology to determine Fe(II) at nanomolar to sub-nanomolar levels involves the Fe(II) catalyzed oxidation of luminol, a chemiluminescent (CL) reaction. There are potential artifacts with this methodology, especially in the euphotic zone, where other reduced species might interfere. Researchers will develop a new, modified version of a published alternative method to CL involving the preconcentration of Fe(II) complexed by a synthetic chelator. While this alternative method is prone to artifacts and contamination that has limited its value in the open ocean, new approaches create a plausible path to an accurate and sensitive protocol that is independent of the luminol method. Following the new method development, this project will implement inter-comparisons with the CL approach, which will be conducted in the laboratory, in an anoxic mesocosm system, at a coastal time-series station off the California coast, and in the Eastern Tropical North Pacific.

# The role of cryptic nutrient cycling within sinking particles on trace element transport in oxygen minimum zones (OMZ Nutrient Cycling)

### Coverage: Eastern Tropical North Pacific

#### NSF Award Abstract:

The major process controlling the internal cycling of biologically active trace metals in the oceans is through uptake onto and remineralization from sinking particles. Uptake can occur through active biological uptake into living cells as micronutrients, or chemical adsorption onto sinking materials. This latter process is often referred to as scavenging. The relative importance of these processes is often unclear, especially for elements that are both biologically active and also "particle reactive." The latter characteristic is associated with sparing solubility in seawater and the formation of strong complexes with surface sites, with examples such as iron. Recent evidence suggests that the simplistic view of a sinking particle as a passive surface for metal complexation may require some revision. Investigators James Moffett and Seth John propose to study the chemistry of transition metals within large sinking particles and the resultant effects on metal biogeochemical cycling. They will collaborate with a group at the University of Washington, recently funded to study the microbiology and molecular biology of these particles. The central hypothesis of this project is that reducing microbial microenvironments within large particles support high rates of nitrogen and sulfur cycling, greatly enhancing the particles' influence on metal chemistry. The investigators will study these processes in the

Eastern Tropical North Pacific Oxygen Minimum Zone (OMZ). This regime was selected because of the wide range of redox conditions in the water column, and strong preliminary evidence that microenvironments within sinking particles have major biogeochemical impacts.

The primary objective is to investigate the interactions of metals with particles containing microenvironments that are more highly reducing than the surrounding waters. Such microenvironments arise when the prevailing terminal electron acceptor (oxygen, or nitrate in oxygen minimum zones) becomes depleted and alternative terminal electron acceptors are utilized. Within reducing microenvironments metal redox state and coordination chemistry are different from the bulk water column, and these microenvironments may dominate metal particle interactions. For example, reduction of sulfate to sulfide could bind metals that form strong sulfide complexes, such as cadmium and zinc, processes previously thought to be confined to sulfidic environments. Reducing microenvironments may account for the production of reduced species such as iron(II), even when their formation is thermodynamically unfavorable in the bulk water column. Tasks include observational characterization of dissolved and particulate trace metals and stable isotopes in the study area, sampling and in situ manipulation of particles using large-dimension sediment traps, shipboard experimental incubations under a range of redox conditions, and modeling, providing insight from microscopic to global scales. The metal chemistry data will be interpreted within a rich context of complimentary data including rates of nitrogen and sulfur cycling, phylogenetics and proteomic characterization of the concentration of key enzymes. Broader impacts include training of a postdoctoral scientist, international collaborations with Mexican scientists, and involvement of undergraduate students in the research.

# [ table of contents | back to top ]

# Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1356056
NSF Division of Environmental Biology (NSF DEB)	DEB-1542240
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-1459584</u>
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-1636332</u>

[ table of contents | back to top ]