

# Dissolved cobalt concentrations measured by cathodic stripping voltammetry from the MetZyme cruise KM1128 on R/V Kilo Moana in October 2011

**Website:** <https://www.bco-dmo.org/dataset/647250>

**Data Type:** Cruise Results

**Version:** 4

**Version Date:** 2020-12-03

## Project

» [Connecting Trace Elements and Metalloenzymes Across Marine Biogeochemical Gradients](#) (MetZyme)

## Program

» [U.S. GEOTRACES](#) (U.S. GEOTRACES)

Contributors	Affiliation	Role
<a href="#">Saito, Mak A.</a>	Woods Hole Oceanographic Institution (WHOI)	Principal Investigator
<a href="#">Rauch, Shannon</a>	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

## Abstract

This dataset includes dissolved cobalt concentrations measured by cathodic stripping voltammetry. Samples were collected during the KM1128 METZYME research expedition (Metals and Enzymes in the Pacific) on the R/V Kilo Moana October 1-25, 2011 from Oahu, Hawaii to Apia, Samoa.

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## Coverage

**Spatial Extent:** N:17 E:-154.5 S:-15 W:-174.5

**Temporal Extent:** 2011-10-03 - 2011-10-24

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## Dataset Description

This dataset includes dissolved cobalt concentrations measured by cathodic stripping voltammetry. Samples were collected during the KM1128 METZYME research expedition (Metals and Enzymes in the Pacific) on the R/V Kilo Moana October 1-25, 2011 from Oahu, Hawaii to Apia, Samoa.

## Acquisition Description

Samples were collected during the KM1128 METZYME research expedition (Metals and Enzymes in the Pacific) on the R/V Kilo Moana October 1-25, 2011 from Oahu, Hawaii to Apia, Samoa, with Carl Lamborg and Mak Saito as Chief Scientists.

Dissolved trace metal samples were collected by an internally programmed standard SBE Rosette (Seabird Electronics Inc.) user-modified to serve as a trace metal clean system with 24 8 L X-Niskin bottles (Ocean Test Equipment), 12 X-Niskin bottles were attached to the rosette per deployment) with minimal exposed metal surfaces using 5000 m of non-metallic non-conducting line. Temperature, oxygen, and conductivity sensor data were collected using a SBE19plus V2 system (Seabird Electronics Inc.) attached to a CTD extension stand on the Trace Metal Rosette. All sensors were factory calibrated immediately prior to the expedition. X-Niskins were pressurized with ultra-high purity nitrogen gas and seawater was filtered through cleaned 47 mm 0.2 micron Supor membrane filters within a HEPA filtered cleanroom space aboard the ship. The volume filtered was calculated (X-Niskin volume minus small unfiltered samples) and the filters were stored in cleaned tubes and frozen for particulate metal analysis (see below). Acid-washed 60 mL LDPE bottles were filled entirely, leaving no headspace. Samples were stored at preserved in a heat-sealed bag containing gas absorbing satchels immediately after sample collection and kept at 4C until analysis in lab.

Sample storage and reagent bottles were soaked for >1 week in the acidic detergent Citranox, rinsed thoroughly with 18.2 M-Ohm Milli-Q water (Millipore), filled with 10% HCl to soak for 10 days, and rinsed thoroughly with Milli-Q water adjusted to pH 2 with TM-grade HCl. Reagent purification protocols were identical to those previously published (Saito and Moffett 2001).

Concentrations of total dissolved cobalt were determined using a previously described cathodic stripping voltammetry (CSV) method (Saito and Moffett 2001, Saito et al. 2004). Measurements were made using the Eco-Chemie  $\mu$ AutolabIII systems connected to Metrohm 663 VA Stands equipped with hanging mercury drop electrodes and Teflon sampling cups. Sample preparation was modified slightly to accommodate use of a Metrohm 837 Sample processor, operated with NOVA 1.8 software (Metrohm Autolab B.V.).

For dissolved cobalt analyses, samples were UV-irradiated for 1 h prior to analysis in a Metrohm 705 UV digester to degrade the organic ligands that bind cobalt, enabling full chelation by the added electroactive ligand, dimethylglyoxime (DMG). 11 ml of sample was pipetted into 15ml polypropylene tubes. Recrystallized DMG (0.1M in methanol) was added to a final concentration of 400  $\mu$ M and purified N-(2-hydroxyethyl)piperazine-N-(3-propanesulfonic acid) (EPPS) buffer (0.5 M in Milli-Q water) was added to a final concentration of 3.8 mM. Tubes were inverted several times before being placed in the autosampler queue, where 8.5 ml of the mixture was dosed into the teflon analysis cup using a 800 Dosino automated burette (Metrohm). 1.5 ml of purified sodium nitrite (1.5M in Milli-Q water) was added directly to the Teflon cup using a dedicated 800 Dosino burette. Once loaded, samples were purged with high purity (>99.99%) N<sub>2</sub> for 3 min and cobalt concentrations were determined by standard addition, with triplicate measurement of the sample followed by four 25 pM cobalt additions. 5 nM Co stock was diluted from a certified 1ppm reference (SPEX) and added to the analysis cup via a third Dosino burette.

The analytical blank was determined by analyzing seawater that had been UV-irradiated for 1 h, equilibrated overnight with prepared Chelex 100 resin beads (Bio-Rad), and UV-irradiated a second time to degrade any leached synthetic ligands. Mean blank was 4.6 +/- 0.7 pM, and the detection limit was calculated as triple the standard deviation of the blank, 2.1 pM. A portion of this dataset was published previously in Saito et al. 2014; the blank for those samples was 3.5 pM.

The Saito laboratory has participated in the GEOTRACES intercalibration effort using this electrochemical Co method. Acidified standards were neutralized with concentrated ammonium hydroxide (Seastar), mixing the entire sample between drops, prior to UV digestion. We report our laboratory values for the GEOTRACES and SAFe standard analyses using this electrochemical method, including those conducted during analysis of the EPZT samples to be:

SAFe D1 = 48.5 +/- 2.4 (n=3, at sea),  
SAFe D2 = 45.0 +/- 2.7 (n=7),  
GEOTRACES GSP = 2.5 +/- 2.0 (n=10),  
GEOTRACES GSC = 77.7 +/- 2.4 (n=4).

These results are in good agreement with those from the GEOTRACES intercalibration effort for Co and demonstrate that the methodologies employed to produce this dataset detect concentrations within the standard deviation of current consensus values for UV irradiated samples, which can be found on the [International GEOTRACES Program website](#)

## Processing Description

Peak height (in nA) was measured relative to a linear baseline for the Co reduction peak ca. -1.15V. All seven scans (3 baseline and 4 standard additions) were used to determine a sample specific sensitivity (nA/pM Co added, mean  $r^2 = 0.998$ ). Cobalt concentrations were calculated from the baseline peak height, divided by the sensitivity and corrected from volume changes from sodium nitrite addition, followed by subtraction of the mean blank for at sea, or in lab analyses.

Analyses were characterized with mild electrical inference that required additional processing before peak height could be reliably measured. We adopted a simplified least squared fitting routine included in the NOVA software package that conducted a 15-point weighted moving average according to a second order polynomial. This method did not distort cobalt concentrations when noise was low.

On occasion, analyses were repeated due to obvious electrode malfunction or to confirm oceanographic consistency of measured values. If the repeated measurement was similar to the initial, the initial value is reported. If the repeated analysis was more oceanographically consistent with adjacent values in the water column, that analysis was used instead.

## Quality Flags:

Quality flags for dissolved Cobalt follow the SeaDataNet scheme (<https://www.geotraces.org/geotraces-quality-flag-policy/>):

- 1) Good value;
- 2) Probably Good Value;
- 3) Probably Bad Value;
- 6) Value Below detection;
- 9) Missing Value.

The most common reason for a Quality flag of 2 was a lower than normal  $r^2$  of standard additions ( $0.98 < r^2 < 0.99$ ) or a moderate difference in replicate analyses (order 10 pM). Quality Flags of 3 were assigned based on poor  $r^2$  of standard addition, disagreement between triplicate baseline scans, or lack of oceanographic consistency). Quality flags of 6 were assigned for values below 3 pmol/L.

## BCO-DMO Processing:

- modified parameter names.
- replaced blanks (missing data) with "nd" ("no data").
- 2016-06-30 (v2) - corrected typo in one station number per request from PI.
- 2017-08-01 (v3) - un-restricted the full dataset and made corrections to the time values in stations 5 and 10.
- 2020-12-03 (v4; current) - replaced with GEOTRACES DOoR-formatted version.

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## Related Publications

Cutter, G. A., & Bruland, K. W. (2012). Rapid and noncontaminating sampling system for trace elements in global ocean surveys. *Limnology and Oceanography: Methods*, 10(6), 425–436.

doi:[10.4319/lom.2012.10.425](https://doi.org/10.4319/lom.2012.10.425)

*Methods*

Noble, A. E., Saito, M. A., Maiti, K., & Benitez-Nelson, C. R. (2008). Cobalt, manganese, and iron near the Hawaiian Islands: A potential concentrating mechanism for cobalt within a cyclonic eddy and implications

for the hybrid-type trace metals. *Deep Sea Research Part II: Topical Studies in Oceanography*, 55(10-13), 1473–1490. doi:[10.1016/j.dsr2.2008.02.010](https://doi.org/10.1016/j.dsr2.2008.02.010)

*General*

Saito, M. A., & Moffett, J. W. (2001). Complexation of cobalt by natural organic ligands in the Sargasso Sea as determined by a new high-sensitivity electrochemical cobalt speciation method suitable for open ocean work. *Marine Chemistry*, 75(1-2), 49–68. doi:10.1016/s0304-4203(01)00025-1

[https://doi.org/10.1016/S0304-4203\(01\)00025-1](https://doi.org/10.1016/S0304-4203(01)00025-1)

*Methods*

Saito, M. A., McIlvin, M. R., Moran, D. M., Goepfert, T. J., DiTullio, G. R., Post, A. F., & Lamborg, C. H. (2014). Multiple nutrient stresses at intersecting Pacific Ocean biomes detected by protein biomarkers. *Science*, 345(6201), 1173–1177. <https://doi.org/10.1126/science.1256450>

*Results*

Saito, M. A., Moffett, J. W., & DiTullio, G. R. (2004). Cobalt and nickel in the Peru upwelling region: A major flux of labile cobalt utilized as a micronutrient. *Global Biogeochemical Cycles*, 18(4), n/a–n/a. doi:10.1029/2003gb002216 <https://doi.org/10.1029/2003GB002216>

*Methods*

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## **Parameters**

Parameter	Description	Units
Station_ID	Station identifier	unitless
Start_Date_UTC	Date at start of sample collection; format: MM/DD/YYYY	unitless
Start_Time_UTC	Time (UTC) at start of sample collection; format: hh:mm:ssZ	unitless
Start_ISO_DateTime_UTC	Date and time (UTC) at start of sample collection formatted to ISO8601 standard: YYYY-MM-DDThh:mm:ssZ	unitless
End_Date_UTC	Date at end of sample collection; format: MM/DD/YYYY	unitless
End_Time_UTC	Time (UTC) at end of sample collection; format: hh:mm:ssZ	unitless
End_ISO_DateTime_UTC	Date and time (UTC) at end of sample collection formatted to ISO8601 standard: YYYY-MM-DDThh:mm:ssZ	unitless
Start_Longitude	Longitude at start of event	degrees East
Start_Latitude	Latitude at start of event	degrees North
End_Longitude	Longitude at end of event	degrees East
End_Latitude	Latitude at end of event	degrees North
CAST_ID	Cast identifier	unitless
Event_ID	BODC event ID number	unitless
Sample_ID	BODC bottle ID number	unitless
Sample_Depth	Sampling depth	meters (m)
Co_D_CONC_BOTTLE_dbqwt	The total concentration of cobalt in a 0.22 um filtered sample, determined following a 1hr UV oxidation procedure that removes organic ligands.	picomoles per liter (pmol/L)
SD1_Co_D_CONC_BOTTLE_dbqwt	One standard deviation of Co_D_CONC_BOTTLE_dbqwt	picomoles per liter (pmol/L)
Flag_Co_D_CONC_BOTTLE_dbqwt	Quality flag for Co_D_CONC_BOTTLE_dbqwt. Refer to 'Processing Description' section of metadata for flag definitions.	unitless

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## Instruments

<b>Dataset-specific Instrument Name</b>	X-Niskin bottles (Ocean Test Equipment)
<b>Generic Instrument Name</b>	Niskin bottle
<b>Dataset-specific Description</b>	Dissolved trace metal samples were collected by an internally programmed standard SBE Rosette (Seabird Electronics Inc.) user-modified to serve as a trace metal clean system with 24 8 L X-Niskin bottles (Ocean Test Equipment).
<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>	Metrohm 663 VA Stands
<b>Generic Instrument Name</b>	Metrohm 663 VA Stand mercury electrode
<b>Dataset-specific Description</b>	Measurements were made using the Eco-Chemie $\mu$ AutolabIII systems connected to Metrohm 663 VA Stands equipped with hanging mercury drop electrodes and Teflon sampling cups. Sample preparation was modified slightly to accommodate use of a Metrohm 837 Sample processor, operated with NOVA 1.8 software (Metrohm Autolab B.V.).
<b>Generic Instrument Description</b>	The Metrohm 663 VA stand forms the wet chemical part of a polarographic and voltammetric analytical system. It features a mercury electrode, an Ag/AgCl reference electrode and a glassy carbon counter electrode. The size of the mercury drop and the stirrer speed are set manually on the VA Stand. The VA Stand can be operated in Dropping Mercury Electrode (DME), Hanging Mercury Drop Electrode (HMDE) and Static Mercury Drop Electrode (SMDE) modes. The VA Stand can be controlled by a potentiostat in conjunction with the Metrohm IME663 interface.

<b>Dataset-specific Instrument Name</b>	Eco-Chemie $\mu$ AutolabIII
<b>Generic Instrument Name</b>	Voltammetry Analyzers
<b>Dataset-specific Description</b>	Measurements were made using the Eco-Chemie $\mu$ AutolabIII systems connected to Metrohm 663 VA Stands equipped with hanging mercury drop electrodes and Teflon sampling cups. Sample preparation was modified slightly to accommodate use of a Metrohm 837 Sample processor, operated with NOVA 1.8 software (Metrohm Autolab B.V.).
<b>Generic Instrument Description</b>	Instruments that obtain information about an analyte by applying a potential and measuring the current produced in the analyte.

<b>Dataset-specific Instrument Name</b>	SBE19plusV2
<b>Generic Instrument Name</b>	CTD Sea-Bird SBE SEACAT 19plus
<b>Dataset-specific Description</b>	Temperature, oxygen and conductivity sensor data were collected using a SBE19plusV2 system (Seabird Electronics Inc.) attached to a CTD extension stand on the Trace Metal Rosette.
<b>Generic Instrument Description</b>	Self contained self powered CTD profiler. Measures conductivity, temperature and pressure in both profiling (samples at 4 scans/sec) and moored (sample rates of once every 5 seconds to once every 9 hours) mode. Available in plastic or titanium housing with depth ranges of 600m and 7000m respectively. Minature submersible pump provides water to conductivity cell.

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## Deployments

### KM1128

<b>Website</b>	<a href="https://www.bco-dmo.org/deployment/59053">https://www.bco-dmo.org/deployment/59053</a>
<b>Platform</b>	R/V Kilo Moana
<b>Start Date</b>	2011-10-01
<b>End Date</b>	2011-10-25
<b>Description</b>	This is a MetZyme project cruise. The original cruise data are available from the NSF R2R data catalog.

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## Project Information

### Connecting Trace Elements and Metalloenzymes Across Marine Biogeochemical Gradients (MetZyme)

**Coverage:** Tropical North Pacific along 150 degrees West from 18 degrees North to the equator

MetZyme project researchers will determine the role of enzymatic activity in the cycling of trace metals. Specifically the research will address the following questions: (1) degradation of sinking particulate organic material in the Tropical North Pacific can be influenced by the ability of microbes to synthesize zinc proteases, which in turn is controlled by the abundance or availability of zinc, and (2) methylation of mercury is controlled, in part, by the activity of cobalt-containing enzymes, and therefore the supply of labile cobalt to the corrinoid-containing enzymes or co-factors responsible for methylation. To attain their goal, they will collect dissolved and particulate samples for trace metals and metalloenzymes from three stations along a biogeochemical gradient in the Tropical North Pacific (along 150 degrees West from 18 degrees North to the equator). Sinking particles from metal clean sediment traps will also be obtained. The samples will also be used to carry out shipboard incubation experiments using amendments of metals, metal-chelators, B12, and proteases to examine the sensitivity and metal limitation of heterotrophic,

enzymatic degradation of organic matter within the oceanic "Twilight Zone" (100-500 m). This study will result in a novel metaproteomic/metalloenzyme datasets that should provide insights into the biogeochemical cycling of metals, as well as co-limitation of primary productivity and controls on the export of carbon from the photic zone. In addition to the final data being contributed to BCO-DMO, an online metaproteomic data server will be created so the community has access to the raw data files generated by this research.

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## Program Information

### U.S. GEOTRACES (U.S. GEOTRACES)

**Website:** <http://www.geotraces.org/>

**Coverage:** Global

**GEOTRACES** is a [SCOR](#) sponsored program; and funding for program infrastructure development is provided by the [U.S. National Science Foundation](#).

GEOTRACES gained momentum following a special symposium, S02: Biogeochemical cycling of trace elements and isotopes in the ocean and applications to constrain contemporary marine processes (GEOSECS II), at a 2003 Goldschmidt meeting convened in Japan. The GEOSECS II acronym referred to the Geochemical Ocean Section Studies To determine full water column distributions of selected trace elements and isotopes, including their concentration, chemical speciation, and physical form, along a sufficient number of sections in each ocean basin to establish the principal relationships between these distributions and with more traditional hydrographic parameters;

- \* To evaluate the sources, sinks, and internal cycling of these species and thereby characterize more completely the physical, chemical and biological processes regulating their distributions, and the sensitivity of these processes to global change; and
- \* To understand the processes that control the concentrations of geochemical species used for proxies of the past environment, both in the water column and in the substrates that reflect the water column.

GEOTRACES will be global in scope, consisting of ocean sections complemented by regional process studies. Sections and process studies will combine fieldwork, laboratory experiments and modelling. Beyond realizing the scientific objectives identified above, a natural outcome of this work will be to build a community of marine scientists who understand the processes regulating trace element cycles sufficiently well to exploit this knowledge reliably in future interdisciplinary studies.

Expand "Projects" below for information about and data resulting from individual US GEOTRACES research projects.

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## Funding

<b>Funding Source</b>	<b>Award</b>
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1031271</a>
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1337780</a>
Gordon and Betty Moore Foundation (GBMF)	<a href="#">GBMF3934</a>
<a href="#">Gordon and Betty Moore Foundation: Marine Microbiology Initiative (MMI)</a>	<a href="#">GBMF3782</a>

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