

# Surface fish dissolved metals (Ni, Mn, Pb, Ce, Y, La) from Leg 2 (Hilo, HI to Papeete, French Polynesia) of the US GEOTRACES PMT cruise (GP15, RR1815) on R/V Roger Revelle from Oct-Nov 2018

**Website:** <https://www.bco-dmo.org/dataset/876550>

**Data Type:** Cruise Results

**Version:** 1

**Version Date:** 2022-07-07

## Project

» [US GEOTRACES Pacific Meridional Transect \(GP15\)](#) (U.S. GEOTRACES PMT)

» [Collaborative Research: U.S. GEOTRACES PMT: Dissolved trace metal distributions and size partitioning](#) (PMT Dissolved Metals)

## Program

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

Contributors	Affiliation	Role
<a href="#">Till, Claire P.</a>	Humboldt State University	Principal Investigator
<a href="#">Fitzsimmons, Jessica N.</a>	Texas A&M University (TAMU)	Co-Principal Investigator
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## Abstract

This dataset includes concentrations of dissolved metals (Ni, Mn, Pb, Ce, Y, La) from surface fish tows conducted on Leg 2 (Hilo, HI to Papeete, French Polynesia) of the US GEOTRACES PMT cruise (GP15, RR1815) on R/V Roger Revelle from October to November 2018

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## Coverage

**Spatial Extent:** N:17.613 E:-152 S:-19.857 W:-152.258

## Methods & Sampling

### Sampling and analytical procedures:

Sample bottles were LDPE and were cleaned in accordance with the GEOTRACES cookbook (<http://www.geotraces.org/images/stories/documents/intercalibration/Cookbook.pdf>). Sample bottles were stored in dilute (~0.1 N) trace metal grade nitric acid, and were emptied before shipping. Fish surface samples were taken using an all-plastic "towed fish" pumping system as described in Bruland et al. (2005) at approximately 3 m depth. Samples were filtered through an Acropak-200 Supor capsule filter (0.2 µm pore size made of polyethersulfone), and sample bottles were rinsed three times before filling. Samples were acidified at sea with the equivalent of 2 mL optima 12M HCl per liter of seawater (resulting in pH 1.7-1.8). Samples were sitting acidified for several months before analysis back in

the laboratory.

Samples were analyzed with an adaptation of Biller and Bruland (2012) as described in Parker et al (2016). For this method, 24 mL of sample was pipetted into 30 mL teflon jars, and spiked with In to 5 nM (natural concentrations of In are sub pM, so this spike overwhelms the natural concentrations). This In spike was developed by Middag et al. (2015) and we used it as a check of consistent recovery across different resin columns and sampling days.

Samples were pre-concentrated on resin columns of Nobias-chelate PA1 resin (IDA and EDTA functional groups). We used 8 columns at a time, and therefore pre-concentrated 8 samples at a time. Columns were stored in dilute (~0.1N) nitric acid, and every day before samples were analyzed, the columns were cleaned with alternating pH 6 seawater, 1N nitric acid eluent, and pH 6 rinse/conditioning solution (0.05M NH<sub>4</sub>Ac).

Just before pre-concentration on resin columns, 8 samples were buffered to pH 5.7-6.2 with an NH<sub>4</sub>Ac buffer, inverted and weighed. For each set of samples, the columns were conditioned with the rinse/conditioning solution (to get the columns the correct pH before the sample arrives), then loaded with the sample (~40 minutes), then rinsed with the rinse/conditioning solution (to remove the salts) and then eluted with ~1 mL of 1M quartz-distilled nitric acid with 10 ppb Rh internal standard. The eluent vials were weighed before and after elution, and the (now empty) sample jars are weighed as well. This method results in a concentration factor of about 24.

Column blanks were determined for each column by following the same procedure for samples, but loading a low-metal seawater for just 1 min rather than the 40 min a sample usually takes to load. Reagent blanks were determined to account for the reagents that were added directly to the sample. They were measure by analyzing low-metal seawater twice normally (rx1) and twice with double the reagents (rx2; reagent doubled include the acid used to originally acidify the sample, the buffer used to get the sample to pH 5.7-6.2, and the In spike). In this way, the rx2 sample was the correct pH for analysis, but contained twice the amount of blank from the reagents. The difference between the rx2 and rx1 was used as the reagent blank.

Standards were made by spiking low-metal seawater and analyzing the standards in the same manner as the samples. The resulting standard addition curve was compared with a standard curve made in clean eluent. This allowed us to calculate and monitor the percent recovery of each metal over time. We also had a Mo standard curve that allowed us to correct for the MoO interference on Cd.

#### **Detection Limits and Accuracy:**

Detection limits were calculated using 3 times the standard deviation of the column blanks. This was done across three analytical runs that focused on this dataset; the precision reported in this dataset are the average detection limit across those three analytical runs. See the Supplemental File "[Detection\\_limits.csv](#)".

For Mn, Ni, Cd, and Pb, accuracy is assessed by measuring reference samples and comparing with consensus values. For Sc, Y, Ce, and La, for which there are no consensus values, accuracy is assessed by measuring reference samples and comparing with values measured previously by the PI and by scrutinizing the blanks and standards for any anomalies. Though there has yet to be an official intercalibration of these metals, previously we have measured Sc, Y, and La depth profiles that are consistent with other published datasets. Official intercalibration of these datasets with other PMT analysts for as many metals as possible are to come.

#### **Known Issues/Problems:**

The northern half of the transect was analyzed without UV irradiating the samples, and the southern half of the transect was analyzed with UV irradiating the samples (2 hours in teflon jars with quartz lids). This is not expected to make a difference for any of the metals reported here and was only done to better analyze Cu and Co, for which it is necessary with this method (Biller and Bruland, 2012).

## **Data Processing Description**

#### **Data Processing:**

The XR dataset was normalized to a 10 ppb internal standard using the instrumental software. From there, the data was processed using microsoft excel. First, acid blanks were subtracted from all standards, samples and other blanks. The acid blanks were eluent ran directly on the XR. Then the concentration in the eluent vials were determined using the slopes of the standard addition curves. Then the nmol of each metal in each eluent vial was calculated using the mass of eluent and the metal concentrations. At this point, the column blanks and reagent blanks were subtracted. Next, the blank-subtracted nmol in the eluent bottles were converted to nmol/kg or pmol/kg, as appropriate for each metal, using the mass of sample loaded on the column.

#### **Quality Flags:**

Data were flagged using the SeaDataNet quality flag scheme. For more information on SeaDataNet flags, see: <https://www.geotraces.org/geotraces-quality-flag-policy/> and <https://www.seadatanet.org/Standards/Data-Quality->

## [Contro](#)

SeaDataNet quality flag definitions:

0 = No quality control;  
1 = Good value;  
2 = Probably good value;  
3 = Probably bad value;  
4 = Bad value;  
5 = Changed value;  
6 = Value below detection;  
7 = Value in excess;  
8 = Interpolated value;  
9 = Missing value;  
A = Value phenomenon uncertain.

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

- renamed fields to comply with BCO-DMO naming conventions;
- converted longitude values to be negative (West).

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## **Data Files**

File
<b>Surface_Fish_Diss_Metals_Leg2.csv</b> (Comma Separated Values (.csv), 3.48 KB) MD5:a7144a675dd1265ad1f6410e2dd206ea
Primary data file for dataset ID 876550

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## **Supplemental Files**

File
<b>Detection_limits.csv</b> (Comma Separated Values (.csv), 131 bytes) MD5:d9c7ca5f404601c8eed4023b9eb505d
Detection limits for Mn, Y, Ce, Pb, La, and Ni. Associated with datasets 876536 and 876550, GP15 Surface Fish Dissolved Metals (PI: Claire Till).

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## **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*

Bruland, K. W., Rue, E. L., Smith, G. J., & DiTullio, G. R. (2005). Iron, macronutrients and diatom blooms in the Peru upwelling regime: brown and blue waters of Peru. *Marine Chemistry*, 93(2-4), 81-103.  
doi:[10.1016/j.marchem.2004.06.011](https://doi.org/10.1016/j.marchem.2004.06.011)  
*Methods*

Cutter, Gregory, Casciotti, Karen, Croot, Peter, Geibert, Walter, Heimbürger, Lars-Eric, Lohan, Maeve, Planquette, Hélène, van de Flierdt, Tina (2017) Sampling and Sample-handling Protocols for GEOTRACES Cruises. Version 3, August 2017. Toulouse, France, GEOTRACES International Project Office, 139pp. & Appendices. DOI:  
<http://dx.doi.org/10.25607/OBP-2>  
*Methods*

Middag, R., Séférian, R., Conway, T. M., John, S. G., Bruland, K. W., & de Baar, H. J. W. (2015). Intercomparison of dissolved trace elements at the Bermuda Atlantic Time Series station. *Marine Chemistry*, 177, 476-489.  
<https://doi.org/10.1016/j.marchem.2015.06.014>  
*Methods*

Parker, C. E., Brown, M. T., & Bruland, K. W. (2016). Scandium in the open ocean: A comparison with other group 3

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## Related Datasets

### Continues

Freiberger, R., Fitzsimmons, J. N., Till, C. P. (2022) **Surface fish dissolved metals (Ni, Mn, Pb, Ce, Y, La) from Leg 1 (Seattle, WA to Hilo, HI) of the US GEOTRACES Pacific Meridional Transect (PMT) cruise (GP15, RR1814) on R/V Roger Revelle from September to October 2018.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2022-07-07 doi:10.26008/1912/bco-dmo.876536.1 [[view at BCO-DMO](#)]

*Relationship Description: GP15 was made up of two cruise legs, RR1814 (Leg 1) and RR1815 (Leg 2)*

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## Parameters

Parameter	Description	Units
Station_ID	Station ID number	unitless
Start_Date_UTC	Start date (not provided)	unitless
Start_Time_UTC	Start time (not provided)	unitless
End_Date_UTC	End date (not provided)	unitless
End_Time_UTC	End time (not provided)	unitless
Start_Latitude	Latitude at start of tow	decimal degrees North
Start_Longitude	Longitude at start of tow	decimal degrees East
End_Latitude	Latitude at end of tow (not provided)	decimal degrees North
End_Longitude	Longitude at end of tow (not provided)	decimal degrees East
Cast_number	Cast number (not provided)	unitless
Event_ID	Event number (not provided)	unitless
Sample_ID	GEOTRACES sample number	unitless
Sample_Depth	Sample depth	meters

Mn_D_CONC_FISH_caxnn7	Dissolved manganese	nmol/kg
SD1_Mn_D_CONC_FISH_caxnn7	Standard deviation of Mn	nmol/kg
Flag_Mn_D_CONC_FISH_caxnn7	Quality flag for Mn_D_CONC_FISH_caxnn7	unitless
Y_D_CONC_FISH_fxard3	Dissolved yttrium	pmol/kg
SD1_Y_D_CONC_FISH_fxard3	Standard deviation of Y	pmol/kg
Flag_Y_D_CONC_FISH_fxard3	Quality flag for Y_D_CONC_FISH_fxard3	unitless
Ce_D_CONC_FISH_9wwle2	Dissolved cerium	pmol/kg
SD1_Ce_D_CONC_FISH_9wwle2	Standard deviation of Ce	pmol/kg
Flag_Ce_D_CONC_FISH_9wwle2	Quality flag for Ce_D_CONC_FISH_9wwle2	unitless
Pb_D_CONC_FISH_mvgvvj	Dissolved lead	pmol/kg
SD1_Pb_D_CONC_FISH_mvgvvj	Standard deviation of Pb	pmol/kg
Flag_Pb_D_CONC_FISH_mvgvvj	Quality flag for Pb_D_CONC_FISH_mvgvvj	unitless
La_D_CONC_FISH_8kmndh	Dissolved lanthanum	pmol/kg
SD1_La_D_CONC_FISH_8kmndh	Standard deviation of La	pmol/kg
Flag_La_D_CONC_FISH_8kmndh	Quality flag for La_D_CONC_FISH_8kmndh	unitless
Ni_D_CONC_FISH_rfsphv	Dissolved nickel	nmol/kg
SD1_Ni_D_CONC_FISH_rfsphv	Standard deviation of Ni	nmol/kg
Flag_Ni_D_CONC_FISH_rfsphv	Quality flag for Ni_D_CONC_FISH_rfsphv	unitless

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## Instruments

<b>Dataset-specific Instrument Name</b>	towed fish
<b>Generic Instrument Name</b>	GeoFish Towed near-Surface Sampler
<b>Dataset-specific Description</b>	Fish surface samples were taken using an all-plastic "towed fish" pumping system as described in Bruland et al. (2005)
<b>Generic Instrument Description</b>	The GeoFish towed sampler is a custom designed near surface (

<b>Dataset-specific Instrument Name</b>	Thermo Element XR high-resolution ICP-MS
<b>Generic Instrument Name</b>	Inductively Coupled Plasma Mass Spectrometer
<b>Dataset-specific Description</b>	After preconcentration, the Thermo Element XR high-resolution ICP-MS at the University of California Santa Cruz was used to analyze the seawater extracts (as in Biller and Bruland, 2012).
<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.

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## Deployments

### RR1815

<b>Website</b>	<a href="https://www.bco-dmo.org/deployment/776917">https://www.bco-dmo.org/deployment/776917</a>
<b>Platform</b>	R/V Roger Revelle
<b>Report</b>	<a href="https://datadocs.bco-dmo.org/docs/geotraces/GEOTRACES_PMT/casciotti/data_docs/GP15_Cruise_Report_with_ODF_Report.pdf">https://datadocs.bco-dmo.org/docs/geotraces/GEOTRACES_PMT/casciotti/data_docs/GP15_Cruise_Report_with_ODF_Report.pdf</a>
<b>Start Date</b>	2018-10-24
<b>End Date</b>	2018-11-24
<b>Description</b>	Additional cruise information is available from the Rolling Deck to Repository (R2R): <a href="https://www.rvdata.us/search/cruise/RR1815">https://www.rvdata.us/search/cruise/RR1815</a>

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## Project Information

### US GEOTRACES Pacific Meridional Transect (GP15) (U.S. GEOTRACES PMT)

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

**Coverage:** Pacific Meridional Transect along 152W (GP15)

A 60-day research cruise took place in 2018 along a transect from Alaska to Tahiti at 152° W. A description of the project titled "*Collaborative Research: Management and implementation of the US GEOTRACES Pacific Meridional Transect*", funded by NSF, is below. Further project information is available on the [US GEOTRACES website](#) and on the [cruise blog](#). A detailed [cruise report is also available](#) as a PDF.

*Description from NSF award abstract:*

GEOTRACES is a global effort in the field of Chemical Oceanography in which the United States plays a major role. The

goal of the GEOTRACES program is to understand the distributions of many elements and their isotopes in the ocean. Until quite recently, these elements could not be measured at a global scale. Understanding the distributions of these elements and isotopes will increase the understanding of processes that shape their distributions and also the processes that depend on these elements. For example, many "trace elements" (elements that are present in very low amounts) are also important for life, and their presence or absence can play a vital role in the population of marine ecosystems. This project will launch the next major U.S. GEOTRACES expedition in the Pacific Ocean between Alaska and Tahiti. The award made here would support all of the major infrastructure for this expedition, including the research vessel, the sampling equipment, and some of the core oceanographic measurements. This project will also support the personnel needed to lead the expedition and collect the samples.

This project would support the essential sampling operations and infrastructure for the U.S. GEOTRACES Pacific Meridional Transect along 152° W to support a large variety of individual science projects on trace element and isotope (TEI) biogeochemistry that will follow. Thus, the major objectives of this management proposal are: (1) plan and coordinate a 60 day research cruise in 2018; (2) obtain representative samples for a wide variety of TEIs using a conventional CTD/rosette, GEOTRACES Trace Element Sampling Systems, and in situ pumps; (3) acquire conventional CTD hydrographic data along with discrete samples for salinity, dissolved oxygen, algal pigments, and dissolved nutrients at micro- and nanomolar levels; (4) ensure that proper QA/QC protocols are followed and reported, as well as fulfilling all GEOTRACES intercalibration protocols; (5) prepare and deliver all hydrographic data to the GEOTRACES Data Assembly Centre (via the US BCO-DMO data center); and (6) coordinate all cruise communications between investigators, including preparation of a hydrographic report/publication. This project would also provide baseline measurements of TEIs in the Clarion-Clipperton fracture zone (~7.5°N-17°N, ~155°W-115°W) where large-scale deep sea mining is planned. Environmental impact assessments are underway in partnership with the mining industry, but the effect of mining activities on TEIs in the water column is one that could be uniquely assessed by the GEOTRACES community. In support of efforts to communicate the science to a wide audience the investigators will recruit an early career freelance science journalist with interests in marine science and oceanography to participate on the cruise and do public outreach, photography and/or videography, and social media from the ship, as well as to submit articles about the research to national media. The project would also support several graduate students.

#### **Collaborative Research: U.S. GEOTRACES PMT: Dissolved trace metal distributions and size partitioning (PMT Dissolved Metals)**

**Coverage:** Central Pacific Ocean along 152 W from 55 N to 20 S

##### *NSF Award Abstract:*

The goal of the international GEOTRACES program is to understand the distributions of trace chemical elements and their isotopes in the oceans. Many trace metals, which are by definition present in very low amounts, are essential for life and thus considered nutrients for phytoplankton growth. Other elements can be useful for tracing other ocean processes, and some (such as lead) are important because they are pollutants. The primary goal of this project is to measure the concentrations of iron, manganese, zinc, copper, cadmium, nickel, lead, and scandium dissolved in seawater along a line of full-depth ocean stations extending south from Alaska to Tahiti in the Pacific Ocean. Specialized sampling and filtration techniques will also enable these investigators and their colleagues to determine the distribution of these metals on very small particles. A graduate student and several undergraduate students will take part in the project.

The U.S. GEOTRACES Pacific Meridional Transect, planned for the fall of 2018, aims to systematically and thoroughly determine the distribution of trace elements and isotopes on a cruise transect that spans zonal bands of sedimentary, atmospheric, and hydrothermal metal supplies; intersects several zonal biological production and oxygenation regimes; traverses the complex equatorial upwelling system; and encompasses the oldest known deep waters in the ocean. The primary goal of this proposal is to determine the concentrations of dissolved (<0.2 micron-filtered) micronutrient metals Fe, Mn, Zn, Cu, Cd, and Ni, as well as tracers Pb and Sc, on every water column and surface sample collected, using two well-established multi-element analytical methods that will be intercalibrated internally to maximize data quality. Many of these are "key elements" required for analysis on GEOTRACES cruises. Ultrafiltration will also be completed on all samples to determine the "truly soluble" (<0.003 micron) concentrations of these elements and to calculate, by difference, the colloidal (0.003-0.2 micron) fraction. The overarching goal of the proposed research is to understand the ocean fluxes and processes that control the distributions of micronutrient trace metals, which themselves modulate primary production and oceanic carbon dioxide uptake, in the Pacific Ocean. The proposed research will allow for an estimate of the meridional influence of each of these metal source fluxes and processes in the Pacific, which is poorly constrained to date due to the mostly zonal Pacific cruise transects in the past. Colloidal distributions are specifically targeted in order to derive additional information on the reactivity (with respect to both scavenging and bioavailability) of distinct dissolved metal pools, as well as to provide a basic constraint on metal physicochemical speciation, which is poorly defined for many of the eight metals.

## 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.

## Funding

Funding Source	Award
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1736875</a>