# Water column GeoFish and bottle pH data 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

Website: https://www.bco-dmo.org/dataset/838157 Data Type: Cruise Results Version: 2 Version Date: 2021-05-06

#### Project

- » US GEOTRACES Pacific Meridional Transect (GP15) (U.S. GEOTRACES PMT)
- » US GEOTRACES PMT: hydrogen sulfide as a strong ligand affecting trace metal cycling (PMT Hydrogen Sulfide)

# Program

» U.S. GEOTRACES (U.S. GEOTRACES)

Contributors	Affiliation	Role
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#### Abstract

Water column GeoFish and bottle pH data 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.

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# Coverage

Spatial Extent: N:55.72 E:-152 S:19.68 W:-155.72 Temporal Extent: 2018-09-24 - 2018-10-21

# Methods & Sampling

# Methodology:

60 mL of unfiltered water was subsampled from 12L GO-Flo bottles on the GTC carousel for each pH measurement. They were analyzed at sea in primarily single analyses using an automated Ocean Optics UV-VIS spectrophotometric system that was modified from Carter et al. (2013) with pure m-cresol purple (mCP) indicator dye. They were usually analyzed within 3 hours of collection and the salinity and temperature dependent pH equation from Clayton and Byrne (1993) was applied.

# Sampling and analytical procedures:

Sampling followed the GEOTRACES cookbook sampling method. 60 mL of unfiltered water was subsampled from 12L GO-Flo bottles, mounted on the GTC carousel. The 60 mL polypropylene syringes were fitted with polycarbonate 3-way

valves to remove air bubbles and prevent exchange of CO2 prior to analysis and rinsed 3 times with unfiltered water. The sample syringes were then kept at room temperature in the dark until placed in a circulating water bath at 25°C for a minimum of 20 minutes to bring the samples close to analysis temperature.

Once at analysis temperature, each syringe was attached to one of the ports on the automated syringe pump that delivered sample and dye to a 10 cm cell with an inner volume of 10 mL for sample seawater. The cell is placed in a thermostated-holder that is temperature controlled by water continuously pumped from a circulating water temperature bath, so the sample remains at  $25\pm0.1^{\circ}$ C during analysis. The samples were analyzed at sea within 3 hours of collection and the automated measurement sequence was initiated in LabVIEW and required a total processing time of 5 minutes.

#### Instruments:

The temperature of the absorbance cell is controlled using deionized water pumped from a VWR circulating water bath (Cat. No. 89202-966) and through the water-jacketed CUV-10 cuvette holder with a 10 cm pathlength, 10 mL volume cuvette with quartz windows. QP400-1-UV-VIS premium fiber optic cables are used from the HL-2000-FHSA light source to the CUV UV 10 cm cuvette holder and then to the Optics STS-VIS-L-25-400-SMA miniature spectrophotometer. The automation and data processing are controlled from a computer program written in LabVIEW. A Norgren Kloehn Versa Pump 6 syringe pump with a 4-way valve and 48000 step resolution was controlled by the LabVIEW program that delivers the sample, then dye to the cuvette.

#### **Data Processing Description**

#### Data processing:

LabVIEW (version 16.0) was used to automate the syringe pump and read the R value obtained from the spectrophotometer and approximate pH value prior to corrections. Salinity corrections were later applied using corresponding GEOTRACES bottle data. Dye corrections were later applied using the method of Clayton and Byrne (1993) using intercalibration samples provided by Andrew Dickson's lab at UCSD.

Two reference materials (B162 and B164) from Andrew Dickson's lab at UCSD were used to evaluate the uncertainty of our pH results collected at sea. pH values of 7.9143±0.0065 and 7.5532±0.0030 were recorded, in comparison the reported values for these reference materials were 7.9100±0.0005 and 7.5407±0.0010, respectively (Bockman and Dickson, unpublished). This translates to a 99.95% agreement for B162 and a 99.83% agreement for B164.

#### Known Problems:

For all of Station 27 and half of Station 29, the pH measurements are not trustworthy due to an error with the light source resulting in greater fluctuations of the  $\lambda$ 434 absorbance reading (data are flagged 4). The integration time was increased, and the attenuator adjusted to fix this problem.

# Quality Flags:

The SeaDataNet scheme was used to assign data quality flags to samples. More information can be found at <a href="https://www.seadatanet.org/Standards/Data-Quality-Control">https://www.seadatanet.org/Standards/Data-Quality-Control</a>.

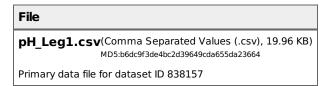
- The reported codes for flagged data are:
- 0 = no quality control;
- 1 = good value;
- 2 = probably good value;
- 3 = probably bad value;
- 4 = bad value;
- 5 = changed value;
- 6 =value below detection;
- 7 = value in excess;
- 8 = interpolated value;
- 9 = missing value.

For intercalibration procedures, refer to the dataset's GEOTRACES Intercalibration Report (PDF).

# **BCO-DMO Processing:**

modified parameter names;
added date/time fields in ISO8601 format.
Version history:
2021-05-06 (v2; current) - version 2 processed & published; includes corrections to event and sample numbers.
2021-01-26 (v1) - version 1 processed & published.

# Data Files



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# Supplemental Files

File
GP15 pH Total Leg 1 Intercalibration Report filename: RR1814-pH_TOT-multiple-param-intercal-report.pdf(Portable Document Format (.pdf), 530.04 KB) MD5:daace64e43417767e786b1dd7040cf3f
GEOTRACES Intercalibration Report for the GP15 Leg 1 total pH data reported by Greg Cutter.

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# **Related Publications**

Carter, B. R., Radich, J. A., Doyle, H. L., & Dickson, A. G. (2013). An automated system for spectrophotometric seawater pH measurements. Limnology and Oceanography: Methods, 11(1), 16–27. doi:<u>10.4319/lom.2013.11.16</u> *Methods* 

Clayton, T. D., & Byrne, R. H. (1993). Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. Deep Sea Research Part I: Oceanographic Research Papers, 40(10), 2115–2129. doi:<u>10.1016/0967-0637(93)90048-8</u> *Methods* 

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# **Related Datasets**

#### IsContinuedBy

Cutter, G. A., Buckley, N. R. (2021) Water column GeoFish and bottle pH data from Leg 2 (Hilo, HI to Papeete, French Polynesia) of the US GEOTRACES Pacific Meridional Transect (PMT) cruise (GP15, RR1815) on R/V Roger Revelle from October to November 2018. Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 2) Version Date 2021-05-06 doi:10.26008/1912/bco-dmo.838173.2 [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 number	unitless
Start_Date_UTC	Date (UTC) at start of sample collection; format: DD/MM/YYYY	unitless
Start_Time_UTC	Time (UTC) at start of sample collection; format: hh:mm	unitless
		•

Start_ISO_DateTime_UTC	Date and time (UTC) at start of sample collection; formatted to ISO8601 standard: YYYY-MM-DDThh:mmZ	unitless
 End_Date_UTC	Date (UTC) at end of sample collection; format: DD/MM/YYYY	unitless
End_Time_UTC	Time (UTC) at end of sample collection; format: hh:mm	unitless
End_ISO_DateTime_UTC	Date and time (UTC) at end of sample collection; formatted to ISO8601 standard: YYYY-MM-DDThh:mmZ	unitless
Start_Latitude	Latitude at start of sample collection	degrees North
Start_Longitude	Longitude at start of sample collection	degrees East
End_Latitude	Latitude at end of sample collection	degrees North
End_Longitude	Longitude at end of sample collection	degrees East
Event_ID	Event number	unitless
Sample_ID	GEOTRACES sample number	unitless
Sample_Depth	Sample depth	meters (m)
PH_TOT_BOTTLE_gr5eba	pH, referred to total scale from bottle samples	unitless
SD1_PH_TOT_BOTTLE_gr5eba	One standard deviation of PH_TOT_BOTTLE_gr5eba	unitless
Flag_PH_TOT_BOTTLE_gr5eba	Quality flag for PH_TOT_BOTTLE_gr5eba	unitless
PH_TOT_FISH_8srxc6	pH, referred to total scale from GeoFish samples	unitless
SD1_PH_TOT_FISH_8srxc6	One standard deviation of PH_TOT_FISH_8srxc6	unitless
Flag_PH_TOT_FISH_8srxc6	Quality flag for PH_TOT_FISH_8srxc6	unitless

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# Instruments

Dataset-specific Instrument Name	
Generic Instrument Name	GeoFish Towed near-Surface Sampler
Generic Instrument Description	The GeoFish towed sampler is a custom designed near surface (

Dataset- specific Instrument Name	
Generic Instrument Name	GO-FLO Bottle
	GO-FLO bottle cast used to collect water samples for pigment, nutrient, plankton, etc. The GO-FLO sampling bottle is specially designed to avoid sample contamination at the surface, internal spring contamination, loss of sample on deck (internal seals), and exchange of water from different depths.

Dataset-specific Instrument Name	automated Ocean Optics UV-VIS spectrophotometric system	
Generic Instrument Name	Spectrophotometer	
Generic Instrument Description	An instrument used to measure the relative absorption of electromagnetic radiation of different wavelengths in the near infra-red, visible and ultraviolet wavebands by samples.	

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# Deployments

#### RR1814

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Website	https://www.bco-dmo.org/deployment/776913
Platform	R/V Roger Revelle
Report	https://datadocs.bco- dmo.org/docs/geotraces/GEOTRACES_PMT/casciotti/data_docs/GP15_Cruise_Report_with_ODF_Report.pdf
Start Date	2018-09-18
End Date	2018-10-21
Description	Additional cruise information is available from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/RR1814

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# **Project Information**

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

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

Coverage: Pacific Meridional Transect along 152W (GP15)

A 60-day research cruise took place in 2018 along a transect form 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 <u>US GEOTRACES website</u> and on the <u>cruise blog</u>. A detailed <u>cruise report is also available</u> 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.

# US GEOTRACES PMT: hydrogen sulfide as a strong ligand affecting trace metal cycling (PMT Hydrogen Sulfide)

#### NSF Award Abstract:

Trace metals like iron and zinc are essential for the growth of the microscopic plants (phytoplankton) that dominate photosynthesis in the sunlit surface ocean. Other trace metals like copper or mercury are highly toxic to these same organisms. Even at concentrations of as low as one gram in a trillion grams of seawater, trace elements can alter the community consumption of carbon dioxide and the production of oxygen by ocean ecosystems. The resulting beneficial and/or toxic response depends on the chemical form of each trace metal. Dissolved in seawater, these metals can exist either as individual, free ions or attached to other dissolved chemical compounds, generically called ligands. Complexation is the process by which trace metals become chemically attached to ligands. This project will study the complexation of six biologically important trace metals with a ligand known as hydrogen sulfide. Data from work done during an expedition in the Pacific Ocean from Alaska to Tahiti will provide new scientific insight on hydrogen sulfide's importance in controlling essential and toxic metal bioavailability in various marine waters and thus have scientific impact on ocean carbon and ecosystem models. A graduate student will play a leading role in the project. Educational opportunities will be greatly enhanced by working alongside other world-class scientists as a participant in a large collaborative program. Additional graduate learning and outreach will include communicating experiences and research findings with the public with a blog and by interactions with undergraduate students as a teaching assistant.

In the oxygenated ocean, hydrogen sulfide is biologically produced in sunlit surface waters and emitted from hydrothermal vents on ocean ridges. It can then complex dissolved trace metals or react with them to form insoluble metal sulfides. In both cases, the abundance and cycling of essential trace elements would be affected and the importance of these reactions are currently not known. These sulfide - trace metal studies will be conducted as part of the 2018 US GEOTRACES Pacific Meridional Transect (PMT), a cruise track that allows sampling of productive coastal waters, low nutrient surface waters, and plumes of metal- and sulfide-rich hydrothermal waters near the bottom. The dissolved ions of hydrogen sulfide will be measured at sea soon after collection. Metal sulfides contained in and on particles will also be filtered and analyzed. This project will address several specific scientific questions. To what degrees does sulfide complexation vary as a function of the various biological and chemical regimes encountered? Are essential metals removed by precipitating with hydrogen sulfide in the upper water column? Does the reaction of metals with hydrogen sulfide in hydrothermal waters stabilize these dissolved complexes and allow long range transport? Related study will develop from close collaborations with other GEOTRACES scientists studying trace metals and their complexation with ligands other that sulfide, providing overall context and novel capacity to fully understand trace element cycles in the ocean.

# **Program Information**

**U.S. GEOTRACES (U.S. GEOTRACES)** 

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

Coverage: Global

**GEOTRACES** is a <u>SCOR</u> sponsored program; and funding for program infrastructure development is provided by the <u>U.S. National Science Foundation</u>.

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

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-1737342</u>

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