

# Total dissolved sulfide (TDS) and carbonyl sulfide (OCS) from Leg 2 (Hilo, HI to Papeete, French Polynesia) of the US GEOTRACES Pacific Meridional Transect (PMT) cruise (GP15, RR1815) conducted on R/V Roger Revelle from October to November 2018

**Website:** <https://www.bco-dmo.org/dataset/873927>

**Data Type:** Cruise Results

**Version:** 1

**Version Date:** 2022-05-19

## Project

» [US GEOTRACES Pacific Meridional Transect](#) (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
<a href="#">Cutter, Gregory A.</a>	Old Dominion University (ODU)	Principal Investigator, Contact
<a href="#">Buckley, Nicole R.</a>	Old Dominion University (ODU)	Co-Principal Investigator
<a href="#">Rauch, Shannon</a>	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

## Abstract

This dataset includes total dissolved sulfide (TDS) and carbonyl sulfide (OCS) data from Leg 2 (Hilo, HI to Papeete, French Polynesia) of the US GEOTRACES Pacific Meridional Transect (PMT) cruise (GP15, RR1815) conducted on R/V Roger Revelle from October to November 2018.

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## Coverage

**Spatial Extent:** N:18.9 E:-152 S:-20 W:-155.3

**Temporal Extent:** 2018-10-25 - 2018-11-21

## Acquisition Description

### Methodology:

Total dissolved sulfide (TDS) and carbonyl sulfide (OCS) was determined at sea within 8 hours of collection using the Radford-Knoery and Cutter (1993) method. This method entails hermetically transferring 300 mL of seawater sample into a 300 mL gas stripping vessel and purging with helium, acidification to a pH of 1.6 using 1.5 M phosphoric acid, and then gas stripping and cryogenically trapping the sulfide gases, and subsequent quantification using a gas chromatograph coupled with a flame photometric detector.

### Sampling and analytical procedures:

Total dissolved sulfide (TDS) and carbonyl sulfide (OCS) were collected from the GTC GO-FLO bottles and the GeoFish, filtered through 0.2 µm AcroPak filter capsules and stored in 4 L polyethylene cubitainers. The cubitainers were rinsed 3 times with the sample before filling hermetically with approximately 1.5 L of seawater sample and stored in a

refrigerator until analyzed at sea usually within 8 hours of collection. Upon analysis, roughly 100 mL the seawater sample was used to rinse the gas stripping vessel, it was then filled with 300 mL of seawater sample and purged with helium (120 mL/min) for 2 minutes. After 2 minutes, the cryogenic trap was immersed in liquid nitrogen followed by injecting 1.5 M phosphoric acid and stripped/trapped the gases for 20 minutes before quantifying TDS and OCS using a gas chromatograph coupled with a flame photometric detector.

This method quantifies TDS as free ions and metal-sulfide complexes with detection limits of 0.2 pmol/L for TDS and 1.3 pmol/L for OCS for 300 mL samples (Radford-Knoery & Cutter, 1993). Dissolved sulfide water samples were mostly analyzed in duplicate, occasionally triplicate when time permitted. To ensure accuracy, the H<sub>2</sub>S and OCS gases are calibrated using permeation tubes whose permeation rates have been gravimetrically measured for 2 - 4 years. By trapping and measuring known amounts of permeated H<sub>2</sub>S and OCS over a range of times, linear calibration curves for each gas were assembled daily and applied to the unknown samples.

#### **Instruments:**

These samples were processed following the analytical apparatus first stated by Radford-Knoery and Cutter (1993). All details can be found in that publication.

A Hewlett Packard (HP) 5890 Series II gas chromatograph coupled with a HP flame photometric detector (model 19256A) was used in the quantification of TDS and OCS. The output signal from the detector was processed using a PeakSimple Chromatography Data System (model 333). Hydrogen (130 mL/min) and air (130 mL/min) are used for the flame photometric detector's flame while ultra-high purity helium is used as the carrier gas (30 mL/min) and the stripping gas (120 mL/min). While cylinders were used as the source of air and ultra-high purity helium, a VWR hydrogen generator (model H2PEM-165) was used for the hydrogen source. A VWR circulating water bath (model 1130S) was used to maintain 40°C for H<sub>2</sub>S and OCS permeation devices (Metronics) which were used to calibrate the instrument for H<sub>2</sub>S and OCS.

#### **Quality Flags:**

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

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

## **Processing Description**

#### **Data Processing:**

The output signal from the flame photometric detector was processed using a PeakSimple Chromatography Data System (model 333). The sulfide peaks were manually integrated in the PeakSimple software and converted to a value in pmol S/L using the slope calculated from the system's calibration immediately before or after processing the samples and the volume of seawater in the gas stripping vessel (300 mL).

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

- re-named fields to comply with BCO-DMO naming conventions;
- changed years of 2013 to 2018;
- added date/time columns in ISO8601 format.

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## **Related Publications**

Radford-Knoery, J., & Cutter, G. A. (1993). Determination of carbonyl sulfide and hydrogen sulfide species in natural waters using specialized collection procedures and gas chromatography with flame photometric detection. *Analytical Chemistry*, 65(8), 976–982. doi:[10.1021/ac00056a005](https://doi.org/10.1021/ac00056a005)  
*Methods*

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## Related Datasets

### Continues

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Cutter, G. A., Buckley, N. R. (2022) **Total dissolved sulfide (TDS) and carbonyl sulfide (OCS) 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 2022-05-06 <http://lod.bco-dmo.org/id/dataset/873908> [[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 in ISO8601 format: 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 in ISO8601 format: YYYY-MM-DDThh:mmZ	unitless
Start_Latitude	Latitude at start of sample collection	decimal degrees North
Start_Longitude	Longitude at start of sample collection	decimal degrees East
End_Latitude	Latitude at end of sample collection (not recorded)	decimal degrees North
End_Longitude	Longitude at end of sample collection (not recorded)	decimal degrees East
Event_ID	Event number	unitless
Sample_ID	GEOTRACES sample number	unitless
Sample_Depth	Sample depth	meters (m)
TDS_D_CONC_FISH_df1p8g	Total dissolved sulfide (TDS) determined from GeoFish samples	picomoles per liter (pmol/L)
SD1_TDS_D_CONC_FISH_df1p8g	One standard deviation of TDS_D_CONC_FISH_df1p8g	picomoles per liter (pmol/L)
Flag_TDS_D_CONC_FISH_df1p8g	Quality flag for TDS_D_CONC_FISH_df1p8g	unitless
TDS_D_CONC_BOTTLE_3yeqid	Total dissolved sulfide (TDS) determined from bottle samples	picomoles per liter (pmol/L)
SD1_TDS_D_CONC_BOTTLE_3yeqid	One standard deviation of TDS_D_CONC_BOTTLE_3yeqid	picomoles per liter (pmol/L)
Flag_TDS_D_CONC_BOTTLE_3yeqid	Quality flag for TDS_D_CONC_BOTTLE_3yeqid	unitless
OCS_D_CONC_FISH_a0azdg	Dissolved carbonyl sulfide (OCS) determined from GeoFish samples	picomoles per liter (pmol/L)
SD1_OCS_D_CONC_FISH_a0azdg	One standard deviation of OCS_D_CONC_FISH_a0azdg	picomoles per liter (pmol/L)
Flag_OCS_D_CONC_FISH_a0azdg	Quality flag for OCS_D_CONC_FISH_a0azdg	unitless
OCS_D_CONC_BOTTLE_ggwdgx	Dissolved carbonyl sulfide (OCS) determined from bottle samples	picomoles per liter (pmol/L)
SD1_OCS_D_CONC_BOTTLE_ggwdgx	One standard deviation of OCS_D_CONC_BOTTLE_ggwdgx	picomoles per liter (pmol/L)
Flag_OCS_D_CONC_BOTTLE_ggwdgx	Quality flag for OCS_D_CONC_BOTTLE_ggwdgx	unitless

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## Instruments

<b>Dataset-specific Instrument Name</b>	
<b>Generic Instrument Name</b>	GO-FLO Bottle
<b>Generic Instrument Description</b>	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.

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

<b>Dataset-specific Instrument Name</b>	Hewlett Packard (HP) 5890 Series II gas chromatograph
<b>Generic Instrument Name</b>	Hewlett Packard 5890 Series II gas chromatograph
<b>Generic Instrument Description</b>	A gas chromatograph that separates and analyses compounds that do not degrade or decompose in the gas phase. The sample is dissolved in a solvent and vaporised in the instrument. A chemically inert gas, (e.g. helium or nitrogen) carries the vaporised analyte through a stationary phase which is coated inside the capillary column that is maintained at an elevated temperature. The analyte mixture separates on the stationary phase leading to chromatographic separation of the molecules. The HP 5890 Series II is completely customisable depending on the application, with choices of inlets, columns, detectors, sampling systems, flow and pressure control components. Optional detectors include Flame Ionization Detector (FID), Nitrogen-Phosphorus Detector (NPD), Electron Capture Detector (ECD), Thermal Conductivity Detector (TCD), Photoionisation Detector (PID), Flame Photometric Detector (FPD) and mass spectrometer. The instrument was originally manufactured by Hewlett Packard (HP), but part of this business was sold to Agilent Technologies in 1999. This model is no longer in production.

<b>Dataset-specific Instrument Name</b>	HP flame photometric detector (model 19256A)
<b>Generic Instrument Name</b>	flame photometric detector
<b>Generic Instrument Description</b>	The determination of sulfur or phosphorus containing compounds is the job of the flame photometric detector (FPD). This device uses the chemiluminescent reactions of these compounds in a hydrogen/air flame as a source of analytical information that is relatively specific for substances containing these two kinds of atoms. The emitting species for sulfur compounds is excited S <sub>2</sub> . The lambda max for emission of excited S <sub>2</sub> is approximately 394 nm. The emitter for phosphorus compounds in the flame is excited HPO (lambda max = doublet 510-526 nm). In order to selectively detect one or the other family of compounds as it elutes from the GC column, an interference filter is used between the flame and the photomultiplier tube (PMT) to isolate the appropriate emission band. The drawback here being that the filter must be exchanged between chromatographic runs if the other family of compounds is to be detected.

<b>Dataset-specific Instrument Name</b>	VWR hydrogen generator (model H2PEM-165)
<b>Generic Instrument Name</b>	hydrogen generator
<b>Generic Instrument Description</b>	A gas generator that generates hydrogen gas.

<b>Dataset-specific Instrument Name</b>	VWR circulating water bath (model 1130S)
<b>Generic Instrument Name</b>	circulating water bath
<b>Generic Instrument Description</b>	A device designed to regulate the temperature of a vessel by bathing it in water held at the desired temperature. [Definition Source: NCI]

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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 (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.

## **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 than sulfide, providing overall context and novel capacity to fully understand trace element cycles in the ocean.

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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

Funding Source	Award
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1737342</a>

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