Water column particulate metals from Hawaii Ocean Timeseries (HOT) R/V Kilo Moana cruises at station ALOHA, North Pacific Subtropical Gyre, from December 2020 to November 2023

Website: https://www.bco-dmo.org/dataset/962966
Data Type: Cruise Results
Version: 1
Version Date: 2025-05-29

Project
» Quantifying Iron Turnover in the Upper Ocean via Time-series Measurements at Station ALOHA (HOT Trace Metals)

Program
» Ocean Time-series Sites (Ocean Time-series)

Contributors	Affiliation	Role
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Abstract
We collected water column particulate metal samples onboard Hawaii Ocean Time-series (HOT) cruises between December 2020 and November 2023. All samples were collected at Station ALOHA. Samples were collected using a trace metal rosette and filtered onto 0.2 micron polyethersulfone (PES) filters (approx. 4L per sample). Approx. 11 depth samples were collected for each cruise within the upper 300 m of the water column. Filters were subject to a 2-stage digestion: 1) a "Berger" leach consisting of hydoxylamine and acetic acid, to dissolve labile trace metals, and 2) a digestion with nitric acid and hydrofluoric acid to dissolve recalcitrant metals. Dissolved metals for each leach were analyzed by inductively coupled plasma mass spectrometry at the University of Hawaii at Manoa using a Thermo Scientific iCAP-TQ mass spectrometer. This dataset is part of a larger study focused on the cycling of trace metals in the North Pacific Subtropical Gyre, and is embedded within the HOT program.

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Coverage

Location: Station ALOHA, North Pacific Subtropical Gyre, 22.75 N, 158.00 W
Spatial Extent: **Lat**:22.75 **Lon**:-158
Temporal Extent: 2020-12-18 - 2023-11-05

Methods & Sampling

Sample Collection

Samples were collected on 21 Hawaii Ocean Time-series (HOT) cruises, onboard the R/V *Kilo Moana* throughout 2020-2023. All samples were collected at Station ALOHA (22.45°N, 158.0°W) following trace metal clean procedures.

For all cruises except for October and December 2021, trace metal clean particle profile samples were collected using a powder-coated aluminum 12-place 'trace metal' rosette (Seabird) with 8 L external spring sampling bottles (Ocean Test Equipment), deployed using metal-free line (Amsteel). For the October and December 2021 cruises, samples were collected with C-Free bottles (Ocean Test Equipment) that were attached directly to the metal-free line and triggered with Teflon-coated messengers. Prior to sampling, sampling bottles were subjected to a ca. 18 hr soak in seawater collected at a test station near Oahu.

Upon recovery, sampling bottles were taken to a positive-pressure clean van onboard. Particle samples were collected onto acid-cleaned 25 mm diameter 0.2 mm polyethersulfone (Supor) filters using acid-cleaned filter holders and polyethylene tubing. Bottles were pressurized for sampling at 10-15 psi using compressed air and filtrate (~4 L) was collected for gravimetric measurement on land. Filters were stored in acid-cleaned centrifuge tubes and transported back to the lab.

Sample Processing and Measurement

In the lab, filters underwent a two-stage digestion to isolate 'labile' and 'recalcitrant' metal fractions. The 'labile' digestion followed the procedure outlined by Berger et al. (2008). Filters were submerged in 2 mL of a 25% acetic acid, 0.02 M hydroxylamine hydrochloride solution, with 10 ppb Indium added as an internal standard and recovery tracer. The filter and solution were heated in a water bath at 95C for 10 min, and allowed to return to room temperature. After a total contact time of 2 hrs, the filters were removed and the leachate was transferred to acid-cleaned PFA digestion vials (Savillex). To improve recovery, the filter was then rinsed with a few mL of high purity (18.2 M-ohm cm-1) water, which was then added back to the leachate. 100 uL of concentrated nitric acid was added to the leachate, which was then dried overnight at 110C. The sample was redissolved in 0.1 M HNO_3 for ICP-MS analysis.

Following the 'labile' digestion, the filter was then subject to a total extraction following the procedures used by Planquette & Sherrell (2012). 2 mL of a digest solution containing 8 M HNO_3, 2.9 M HF, and 10 ppb Y (also applied as an internal standard and recovery tracer) was added to the filters in a 20 mL PFA vial (Savillex), which was heated for 4 hours at 110°C. The filters were then removed and the sample was evaporated to dryness. 100 ul of concentrated nitric acid was added and the sample was dried again before being redissolved in 0.1 M HNO_3.

Several blank filter and reagent blank analyses (containing no filter) were analyzed to estimate the metal contributions of the filters and reagents.

Digested samples were analyzed using a Thermo Scientific iCAP TQ ICP-MS at the University of Hawai'i at Mānoa. All elements were analyzed in triple-quadrupole mode with oxygen as the reactive gas (TQ-O2). A multi-element standard (Inorganic Ventures) was run multiple times throughout a run to monitor changes in instrument sensitivity over the course of a run.

Accuracy of particulate metals from the digestion protocol was assessed by digestion and measurement of certified reference materials BCR-414, PACS-3. Average recoveries for these standards ranged from 85-92% for Al, 80% for Ti, 79-93% for Mn, 83-93% for Fe, 70-80% for Zn, 122-139% for Cd, 97-113% for Ni, 79-84% for Cu, and 89-98% for Co.

Data Processing Description

Prior to calibration, ion intensities derived from the ICP-MS were corrected for matrix suppression and/or sample loss by 115-In ('labile' digestions) and 89-Y ('recalcitrant' digestions). Detection of 115-In in the recalcitrant digestions was used to infer and quantify any carry-over of 'labile' metals into the 'recalcitrant' digest, which were subtracted from the recalcitrant total. Metal contents from digestions of blank filters were subtracted from derived concentrations, and subsequent quantity in moles was then re-scaled to a concentration using the volume of seawater filtered (obtained gravimetrically).

Data were quality controlled by checking for oceanographic consistency across profiles. Samples with concentrations lower than the filter blank were corrected to 0.

BCO-DMO Processing Description

* Sheet 1 of submitted file "HOTpTM_QCflags_nM_v2.xlsx" was imported into the BCO-DMO data system for this dataset. Table will appear as Data File: 962966_v1_hot-watercolumn-particulate-metals.csv (along with other download format options).

* Data within sheet 2 "Flag Key" appeared redundant with already entered metadata so was not added (see Problems/Issues section for quality flag info)

* ISO DateTime with timezone (UTC) column added in ISO 8601 format.

* After discussion with the data submitter, Cruise ID changed to HOT-### to match the project convention

Problem Description

Quality flags were applied following the GEOTRACES policy (https://www.geotraces.org/geotraces-quality-flag-policy/), which recommends the SeaDataNet Scheme:

0 = no quality control;
1 = good value;
2 = probably good value;
3 = probably bad value;
4 = bad value;
5 = changed value;
6 = below detection limit; (used here for samples < filter blank)
7 = value in excess;
8 = interpolated value;
9 = missing value;
A = value phenomenon uncertain.

Major issues with this dataset are:

1. Likely contamination of particulate Zn concentrations, due to the use of Zn anodes on our rosette, or inadvertent contamination in the laboratory.

2. Many recalcitrant metal concentrations were not detectable, but are reported here for transparency.

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Data Files

File
962966_v1_hot-watercolumn-particulate-metals.csv (Comma Separated Values (.csv), 46.74 KB) MD5:a9e7262d392e0230103c02a5add21046
Primary data file for dataset ID 962966, version 1

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Related Publications

Bates, E. S., & Hawco, N. J. (2025). Dissolved Iron Seasonal Cycle and Residence Time in the North Pacific

Subtropical Gyre. Geophysical Research Letters, 52(21). Portico. https://doi.org/10.1029/2025gl118095
https://doi.org/10.1029/2025GL118095
Results

Bates, E. S., White, A. E., & Hawco, N. J. (2025). Variability and Export Timescales of Upper Ocean Particulate Trace Metals in the North Pacific Subtropical Gyre. Global Biogeochemical Cycles, 39(9). Portico. https://doi.org/10.1029/2025gb008657 https://doi.org/10.1029/2025GB008657
Results

European Virtual Institute for Speciation Analysis (EVISA) (2025). Material Database: BCR-414 - Trace elements in plankton. Available from https://speciation.net/Database/Materials/JRC--Joint-Research-Centre/BCR414--Trace-elements-in-plankton-;i195
Methods

Willie, S., Boyko, V., Brophy, C., Clancy, V., Pihillagawa Gedara, I., Grinberg, P., Kumkrong, P., Mercier, P. H. J., Mihai, O., Tyo, D. D., Jiang, C., Kingston, D. M., Maxwell, P., Meija, J., Mester, Z., Sturgeon, R., & Yang, L. (2013). *PACS-3: Marine Sediment Certified Reference Material for total and extractable metal content* (Version 1). National Research Council of Canada. https://doi.org/10.4224/CRM.2013.PACS-3
https://doi.org/10.4224/crm.2013.pacs-3
Methods

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Parameters

Parameter	Description	Units
Cruise	HOT Cruise number	unitless
Time	DateTime of rosette deployment (local HST time zone)	unitless
Time_UTC	DateTime with timezone of rosette deployment (UTC)	unitless
Longitude	Longitude of sampling	decimal degrees
Latitude	Latitude of rosette deployment	decimal degrees
Depth	Depth of rosette cast when sample was taken	meters (m)
pAl_labile	Labile particulate Aluminum concentration	nanomoles per liter (nmol/L)
pAl_labile_qc	Data flag for labile particulate Aluminum	unitless
pTi_labile	Labile particulate Titanium concentration	nanomoles per liter (nmol/L)
pTi_labile_qc	Data flag for labile particulate Titanium	unitless
pMn_labile	Labile particulate Manganese concentration	nanomoles per liter (nmol/L)

pMn_labile_qc	Data flag for labile particulate Manganese	unitless
pFe_labile	Labile particulate Iron concentration	nanomoles per liter (nmol/L)
pFe_labile_qc	Data flag for labile particulate Iron	unitless
pCo_labile	Labile particulate Cobalt concentration	nanomoles per liter (nmol/L)
pCo_labile_qc	Data flag for labile particulate Cobalt	unitless
pNi_labile	Labile particulate Nickel concentration	nanomoles per liter (nmol/L)
pNi_labile_qc	Data flag for labile particulate Nickel	unitless
pCu_labile	Labile particulate Copper concentration	nanomoles per liter (nmol/L)
pCu_labile_qc	Data flag for labile particulate Copper	unitless
pCd_labile	Labile particulate Cadmium concentration	nanomoles per liter (nmol/L)
pCd_labile_qc	Data flag for labile particulate Cadmium	unitless
pAl_recal	Recalcitrant particulate Aluminum concentration	nanomoles per liter (nmol/L)
pAl_recal_qc	Data flag for recalcitrant particulate Aluminum	unitless
pTi_recal	Recalcitrant particulate Titanium concentration	nanomoles per liter (nmol/L)
pTi_recal_qc	Data flag for recalcitrant particulate Titanium	unitless
pMn_recal	Recalcitrant particulate Manganese concentration	nanomoles per liter (nmol/L)
pMn_recal_qc	Data flag for recalcitrant particulate Manganese	unitless
pFe_recal	Recalcitrant particulate Iron concentration	nanomoles per liter (nmol/L)
pFe_recal_qc	Data flag for recalcitrant particulate Iron	unitless

pCo_recal	Recalcitrant particulate Cobalt concentration	nanomoles per liter (nmol/L)
pCo_recal_qc	Data flag for recalcitrant particulate Cobalt	unitless
pNi_recal	Recalcitrant particulate Nickel concentration	nanomoles per liter (nmol/L)
pNi_recal_qc	Data flag for recalcitrant particulate Nickel	unitless
pCu_recal	Recalcitrant particulate Copper concentration	nanomoles per liter (nmol/L)
pCu_recal_qc	Data flag for recalcitrant particulate Copper	unitless
pCd_recal	Recalcitrant particulate Cadmium concentration	nanomoles per liter (nmol/L)
pCd_recal_qc	Data flag for recalcitrant particulate Cadmium	unitless

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Instruments

Dataset-specific Instrument Name	Seabird SBE9plus CTD system with SBE32C
Generic Instrument Name	CTD Sea-Bird
Generic Instrument Description	A Conductivity, Temperature, Depth (CTD) sensor package from SeaBird Electronics. This instrument designation is used when specific make and model are not known or when a more specific term is not available in the BCO-DMO vocabulary. Refer to the dataset-specific metadata for more information about the specific CTD used. More information from: http://www.seabird.com/

Dataset-specific Instrument Name	
Generic Instrument Name	Thermo Fisher Scientific iCAP TQ inductively coupled plasma mass spectrometer
Generic Instrument Description	A benchtop triple quadrupole (TQ) inductively coupled plasma mass spectrometer (ICP-MS) with a four channel peristaltic pump, three plasma gas flow controllers, and four QCell mass flow controllers. The iCAP TQ utilises triple quadrupole technology which allows the analyte signal to be isolated from interferences, enabling the analysis of complex or high-matrix samples. The high frequency (4 MHz) quadrupole mass analyser has pre and post filters for isolation of wanted ions. The instrument features Peltier cooled high purity quartz or perfluoroalkoxy alkane (PFA), and low volume, baffled cyclonic or double pass spray chambers to efficiently filter out larger aerosol droplets for improved plasma stability. A reaction finder method development assistant aids easy method development. The plasma system is designed to rapidly adapt to changing matrices and provide robustness for challenging samples such as highly volatile organic solvents. The argon ICP ion source has a digital, solid state radiofrequency generator, and dynamic frequency impedance matching the plasma at 27 MHz. The iCAP TQ has applications in trace element analysis of solid or liquid (particularly sediment or sea water) samples. It has a nebuliser default flow rate of 400 uL/min.

Deployments

HOT_cruises

Website	https://www.bco-dmo.org/deployment/58879
Platform	Multiple Vessels
Report	http://hahana.soest.hawaii.edu/hot/
Start Date	1988-10-31
Description	Since October 1988, the Hawaii Ocean Time-series (HOT) program has investigated temporal dynamics in biology, physics, and chemistry at Stn. ALOHA (22°45' N, 158°W), a deep ocean field site in the oligotrophic North Pacific Subtropical Gyre (NPSG). HOT conducts near monthly ship-based sampling and makes continuous observations from moored instruments to document and study NPSG climate and ecosystem variability over semi-diurnal to decadal time scales.

Project Information

Quantifying Iron Turnover in the Upper Ocean via Time-series Measurements at Station ALOHA (HOT Trace Metals)

Coverage: North Pacific Subtropical Gyre

NSF Award Abstract:
Phytoplankton are the base of marine food webs but their ability to grow in the open ocean by photosynthesis is limited by the scarcity of key nutrients especially iron. To understand how phytoplankton respond to global environmental changes, it is essential to predict how the nutrient content of seawater will change as well. Iron is essential to the light-harvesting machinery of phytoplankton but is an extremely small fraction of seawater (1

part per billion) . Iron is much more abundant in soils and when dust storms blow these soils out to sea, the iron content of seawater increases. It is unknown how long the effects of these iron supply events last, which depends on how well the marine ecosystem can recover and reuse iron before it sinks to the seafloor. It is also unknown if human activities have added to the natural Fe supply. The proposed research will address these questions by conducting a 3 year time-series of iron measurements in the North Pacific Ocean. Here, dust supply from Asia occurs mainly during spring, allowing the loss of iron over the summer and fall months to be documented. Unique chemical signatures will be used to distinguish iron supply from the deposition of desert dust or from human sources. This record of the marine iron cycle will be important for validating ecosystem models that are used to predict how climate change will influence the growth of phytoplankton in the future. The research would make a scientific contribution to the Hawaii Ocean Time-Series, help improve biogeochemical iron models, student training at the graduate and undergraduate level, and support an early career scientist.

A 3 year time-series of iron (Fe) measurements is proposed to constrain the magnitude of external Fe input and Fe recycling in the open ocean. Near-monthly observations will be conducted in the North Pacific Subtropical Gyre onboard Hawaii Ocean Timeseries cruises, which receives regular dust input during springtime and is minimally influenced by deep mixing. Water column profiling of dissolved and particulate Fe concentrations – combined with the flux of Fe recorded in trace-metal-clean sediment traps – will define a residence time of Fe in the upper water column. Iron uptake rates will be quantified through short-term incubations using a novel stable isotope technique and will be used to derive a turnover time with respect to biological uptake. Finally, the isotopic composition of dissolved and particulate Fe in the mixed layer will be measured to evaluate the potential importance of anthropogenic and Hawaiian Fe sources, which are poorly constrained. Together, these measurements will define the tempo and variability of the open ocean Fe cycle and provide a means to validate models that simulate the biogeochemistry of this key micronutrient.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

See more information about the Hawaii Ocean Time Series (HOT) on the related project page: https://www.bco-dmo.org/project/2101

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Program Information

Ocean Time-series Sites (Ocean Time-series)

Coverage: Bermuda, Cariaco Basin, Hawaii

Program description text taken from Chapter 1: Introduction from the **Global Intercomparability in a Changing Ocean: An International Time-Series Methods Workshop** report published following the workshop held November 28-30, 2012 at the Bermuda Institute of Ocean Sciences. The full report is available from the workshop Web site hosted by US OCB: http://www.whoi.edu/website/TS-workshop/home

Decades of research have demonstrated that the ocean varies across a range of time scales, with anthropogenic forcing contributing an added layer of complexity. In a growing effort to distinguish between natural and human-induced earth system variability, sustained ocean time-series measurements have taken on a renewed importance. Shipboard biogeochemical time-series represent one of the most valuable tools scientists have to characterize and quantify ocean carbon fluxes and biogeochemical processes and their links to changing climate (Karl, 2010; Chavez et al., 2011; Church et al., 2013). They provide the oceanographic community with the long, temporally resolved datasets needed to characterize ocean climate, biogeochemistry, and ecosystem change.

The temporal scale of shifts in marine ecosystem variations in response to climate change are on the order of several decades. The long-term, consistent and comprehensive monitoring programs conducted by time-series sites are essential to understand large-scale atmosphere-ocean interactions that occur on interannual to decadal time scales. Ocean time-series represent one of the most valuable tools scientists have to characterize and quantify ocean carbon fluxes and biogeochemical processes and their links to changing climate.

Launched in the late 1980s, the US JGOFS (Joint Global Ocean Flux Study; http://usjgofs.whoi.edu) research program initiated two time-series measurement programs at Hawaii and Bermuda (HOT and BATS, respectively) to measure key oceanographic measurements in oligotrophic waters. Begun in 1995 as part of the US JGOFS Synthesis and Modeling Project, the CARIACO Ocean Time-Series (formerly known as the CArbon Retention In A Colored Ocean) Program has studied the relationship between surface primary production, physical forcing variables like the wind, and the settling flux of particulate carbon in the Cariaco Basin.

The objective of these time-series effort is to provide well-sampled seasonal resolution of biogeochemical variability at a limited number of ocean observatories, provide support and background measurements for process-oriented research, as well as test and validate observations for biogeochemical models. Since their creation, the BATS, CARIACO and HOT time-series site data have been available for use by a large community of researchers.

Data from those three US funded, ship-based, time-series sites can be accessed at each site directly or by selecting the site name from the Projects section below.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-2022969

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