

Dissolved trace metal concentrations, nickel speciation, and pH in shipboard incubations conducted on FeOA project cruise SKQ202209S on the R/V Sikuliaq between June 4 2022 to July 1 2022 in the NE Pacific.

Website: <https://www.bco-dmo.org/dataset/957607>

Data Type: Cruise Results

Version: 1

Version Date: 2025-07-09

Project

» [Collaborative Research: The Effect of Ocean Acidification on Fe Availability to Phytoplankton in Coastal and Oceanic Waters of the Eastern North Pacific](#) (pH-Fe availability)

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Abstract

This dataset includes the concentrations of total dissolved trace metals (manganese, iron, added iron-57, nickel, copper, zinc), of labile dissolved nickel, and pH measured in samples collected from phytoplankton shipboard incubation experiments conducted on the FeOA cruise SKQ202209S on R/V Sikuliaq in the NE Pacific from June to July 2022. This project investigates the effects of ocean acidification on the associations between iron and organic ligands in seawater and on iron bioavailability to marine phytoplankton communities. The project used a combination of shipboard incubation experiments and depth profiles to characterize iron speciation and cycling across coastal upwelling, oligotrophic open ocean, and iron-limited subarctic oceanographic regimes in the NE Pacific. Surface seawater was incubated at pH of 8.1, 7.6, and 7.1 with natural iron and with dissolved iron amendments in order to investigate interactions between pH and iron bioavailability across the different regimes. Understanding how pH influences iron and its relationship with ligands provides important information for assessing the impacts of ocean acidification on primary production and biogeochemical processes.

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Coverage

Location: Northeast Pacific Ocean; 35 to 55 N, -125 to -145 E (125 to 145 W)

Spatial Extent: N:50 E:-125.56 S:35 W:-145

Temporal Extent: 2022-06-10 - 2022-06-29

Methods & Sampling

Incubation Setup:

Surface water was collected for shipboard incubations in June 2022 aboard the R/V Sikuliaq using a trace metal clean surface pump “towfish” system (Mellett and Buck, 2020). Filtered (<0.2 μm , Acropak) seawater from the towfish was homogenized in three acid-cleaned and seawater rinsed 50-L carboys that were filled round-robin style (Burns et al., 2023). Each carboy was then bubbled overnight with a custom CO₂-air mixture to achieve the target pH levels of pH 8.1, 7.6, and 7.1, which was verified with shipboard spectrophotometric pH analyses using the Byrne MICA system (Adornato et al., 2016). Unfiltered surface seawater was then collected and homogenized in a fourth acid-cleaned and seawater-rinsed carboy using the trace metal clean towfish. Trace metal clean polycarbonate incubation bottles were then filled two-thirds with filtered seawater and one-third unfiltered seawater, amended for the nutrient and/or iron treatment, sealed with the caps/threads wrapped in parafilm and electrical tape, and delivered to deckboard flow-through seawater incubators that were covered in screening to mimic surface light levels. Once all incubation bottles were in the incubators, the time-zero sampling of each incubation began. Six incubations were conducted, two each at a coastal upwelling station (Inc 1, 2; 40.112 °N, 125.56 °W), in the oligotrophic central North Pacific (Inc 3, 4; 35 °N, 145 °W), and at Ocean Station PAPA (Inc 5, 6; 50 °N, 145 °W) in the subarctic North Pacific. For incubations 1-4, all incubation bottles were spiked with chelexed stocks of nitrate and phosphate, and aged (for trace metal cleanliness) silicic acid stocks, to target additions of 10 μM nitrate, silicic acid, and 0.8 μM phosphate; no macronutrients were added to Incs 5 and 6, which were already macronutrient replete. Replicates of pH treatment were additionally spiked with 1 nM ⁵⁷FeCl₃ as a dissolved iron addition. Incubation bottles were labeled according to treatment and were the same across light bottles all incubations: A = pH 8.1, B = pH 8.1 + Fe, C = pH 7.6, D = pH 7.6 + Fe, E = pH 7.1, F = pH 7.1 + Fe. Replicates of each treatment were also incubated in heavy duty black contractor bags to serve as dark controls (G = A, H = B, I = C, J = D, K = E, L = F), which were sampled on day final only.

Incubation sampling:

Triplicate bottles from each incubation were sampled daily over the course of the experiments. Incubation bottles were brought in from the incubators into a clean lab bubble in the ship, where they were washed down with Milli-Q and transferred into a clean hood. After gently inverting to mix, each was subsampled for pH, chlorophyll *a*, and particulate organic nutrients. The remaining contents of each bottle were filtered in the bubble clean hood on a custom acrylic filtration rig outfitted with dual stage Teflon filtration holders (Savillex) that allows the filtrate to go directly into sample bottles after passing through consecutive 5 μm and 0.4 μm acid-cleaned polycarbonate track-etched (PCTE; Whatman) filters. Samples for dissolved trace metals were collected in acid-cleaned and triple-rinsed narrow mouth low density polyethylene bottles, acidified with 0.024 M ultrapure hydrochloric acid (to pH ~1.8), and stored for shore-based analysis at the University of Nagasaki (Yoshiko Kondo). Samples for dissolved iron and nickel speciation were collected in acid-cleaned, Milli-Q-conditioned, and triple-rinsed narrow mouth fluorinated high density polyethylene bottles (Nalgene) and analyzed shipboard for dissolved iron speciation (Lise Artigue, Kristen Buck lab) before freezing at -20 °C for shore-based dissolved nickel speciation analyses at Oregon State University (Matthew Koteskey, Kristen Buck lab). Samples for pH were analyzed shipboard (Drajed Seto, Mark Wells lab).

Sample analyses – dissolved trace metals:

The concentrations of dissolved iron, manganese, nickel, zinc, and copper were analyzed by high resolution inductively coupled plasma mass spectrometry (Thermo Scientific ELEMENT II) with a preconcentration flow injection system seaFAST-pico (Elemental Scientific Inc., ESI) at Nagasaki University (Yoshiko Kondo and Shigenobu Takeda). Acidified samples were measured without UV-oxidation, and dissolved copper

concentrations should be considered 'reactive Cu' as total recovery may have been hindered by organic complexation in these samples. Briefly, dissolved trace metals in the samples were preconcentrated on a Nobias-chelate PA1 resin, eluted with 2 M HNO₃, and quantified by calibration curve prepared with SAFe and GEOTRACES reference samples (S1, GS, and GD) (<https://www.geotraces.org/standards-and-reference-materials/>).

A subset of incubation samples were analyzed for total dissolved nickel concentrations by competitive ligand exchange-adsorptive cathodic stripping voltammetry following UV-oxidation of remaining volume in nickel speciation samples. Frozen seawater samples were thawed at room temperature in the lab at Oregon State University and UV-oxidized in Teflon jars (Savillex) with quartz lids for at least ninety minutes in a Jelight model 342 UVO cleaner. Following UV-oxidation, seawater sample aliquots were buffered with a borate-ammonium buffer and amended with 200 µM dimethylglyoxime to complex the dissolved nickel in the sample and form an electroactive complex, which was then measured by standard addition on a hanging mercury drop electrode (BioAnalytical Systems, Inc.).

Sample analyses – labile dissolved nickel:

The concentration of labile dissolved nickel concentrations was measured by competitive ligand exchange-adsorptive cathodic stripping voltammetry using the added ligand dimethylglyoxime (DMG; van den Berg and Nimmo 1987) and following a modification of previously described procedures (Saito et al. 2004; Boiteau et al. 2016). Briefly, seawater sample aliquots were buffered with a borate-ammonium buffer and equilibrated overnight with 200 µM DMG. Following equilibration, the amount of dissolved nickel in the samples that was bound to DMG was measured on a hanging mercury drop electrode and quantified by standard additions of dissolved nickel to the sample. All measurements, of the sample and of the standard additions, were conducted in triplicate. The concentration of labile dissolved nickel was determined from the slope of the standard curve and the triplicate measurements of the initial sample, and the results presented as averages and standard deviations of the three values.

Sample analyses – pH:

pH was measured using a USB4000 fiber optic spectrometer (Ocean Optics) with purified meta-Cresol Purple (mCP) as the pH indicator dye (Liu et al., 2011). The system comprised a open top, flow-thru cell positioned in a temperature controlled (20°C) water bath. The cell was zeroed by manually injecting a blank or reference sample (seawater without mCP) and recording the absorbance at 434, 578, and 700 nm (reference). For sample analysis, 1 µL of purified mCP indicator solution was drawn into a clean 3 ml syringe followed by 2 ml of seawater sample. The solution was mixed gently to ensure uniform distribution of the indicator while avoiding air bubble formation. The solution then was manually injected into the flow-thru cell (using excess volumes for rinse) and allowed to thermally equilibrate. Once absorbance values had stabilized (1-3 min) the values were recorded at 434, 578, and 700 nm. Seawater pH was calculated on the total scale using the absorbance ratio (578/434) according to Liu et al. (2011). All samples were analyzed in triplicate and the results presented as the averages and standard deviations of the three values.

Data Processing Description

Data were flagged using the SeaDataNet quality flag scheme recommended by GEOTRACES (<https://www.geotraces.org/geotraces-quality-flag-policy/>) and described below. Notes specific to the application of these flags to this dataset are noted in brackets [...].

0 = No Quality Control: No quality control procedures have been applied to the data value. This is the initial status for all data values entering the working archive. [Not used].

1 = Good Value: Good quality data value that is not part of any identified malfunction and has been verified as consistent with real phenomena during the quality control process. [Used for analyses that included replicates and/or reference samples].

2 = Probably Good Value: Data value that is probably consistent with real phenomena, but this is unconfirmed or data value forming part of a malfunction that is considered too small to affect the overall quality of the data object of which it is a part. [Used when no replicates or reference samples were available to further verify the quality of the data].

3 = Probably Bad Value: Data value recognized as unusual during quality control that forms part of a feature that is probably inconsistent with real phenomena. [Not used].

4 = Bad Value: An obviously erroneous data value. [Used when value was flagged high].

5 = Changed Value: Data value adjusted during quality control. Best practice strongly recommends that the value before the change be preserved in the data or its accompanying metadata. [Not used].

6 = Value Below Detection Limit: The level of the measured phenomenon was less than the limit of detection (LOD) for the method employed to measure it. The accompanying value is the detection limit for the technique or zero if that value is unknown. [Not used].

7 = Value in Excess: The level of the measured phenomenon was too large to be quantified by the technique employed to measure it. The accompanying value is the measurement limit for the technique. [Not used].

8 = Interpolated Value: This value has been derived by interpolation from other values in the data object. [Not used].

9 = Missing Value: The data value is missing. Any accompanying value will be a magic number representing absent data [When sample was not collected the notation 'na' for 'not applicable' was used; when sample was collected but there is no result for this parameter, the notation 'nda' for 'no data available' was used].

A = Value Phenomenon Uncertain: There is uncertainty in the description of the measured phenomenon associated with the value such as chemical species or biological entity. [Not used]

BCO-DMO Processing Description

* Created ISO Date-Time column from original DATE_SHIP and TIMESTART_SHIP and TIMESTOP_SHIP

* Added latitude & longitude of stations to dataset

* Converted pH row 285 from 7,58 to 7.58

* Adjusted values in column BTLNBR_INC after discussion with submitter, row 168: '105 (108 is chl?)' to 105 and row 184: '118 (113 is chl?)' to 118

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Data Files

File
957607_v1_tracemetals.csv (Comma Separated Values (.csv), 88.70 KB) MD5:0b416a65f44c325c0f5f2d227298674a
Primary data file for dataset ID 957607, version 1

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Parameters

Parameter	Description	Units
FeOA_NBR	Unique sample number for the FeOA cruise project	unitless
EVTNBR	Event number; 'nda' for 'no data available' or missing information; 'na' for 'not applicable' to that sample	unitless
DATE_SHIP	Date on ship time when sample was collected, in format MM/DD/YY, AKDT (Alaska Daylight) timezone	unitless
TIMESTART_SHIP	Ship time when sample collection started, in format HH:MM; 'nda' for 'no data available' or missing information; 'na' for 'not applicable' to that sample. , AKDT (Alaska Daylight) timezone	unitless

TIMESTOP_SHIP	Ship time when sample collection started, in format HH:MM; 'nda' for 'no data available' or missing information; 'na' for 'not applicable' to that sample. , AKDT (Alaska Daylight) timezone	unitless
LATITUDE	Ship position when sample was collected in decimal °N; south is negative. 'nda' for 'no data available' or missing information; 'na' for 'not applicable' to that sample	decimal degrees
LONGITUDE	Ship position when sample was collected in decimal °E; west is negative. 'nda' for 'no data available' or missing information; 'na' for 'not applicable' to that sample	decimal degrees
PLATFORM	Sampling system used. TMC CTD = trace metal CTD rosette. FISH = tow fish. TM PUMP = trace metal pump. INC = incubation.	unitless
STNNBR	Station number; 'na' for 'not applicable' to that sample	unitless
INCNBR	Number assigned to incubation experiment as a series	unitless
INCDAY	Day after start of incubation that sample was collected (day 0 is initiation of incubation)	unitless
INCTREATMENT	Incubation treatment. A and G: pH 8.1; B and H: pH 8.1 + Fe; C and I: pH 7.6; D and J: pH 7.6 + Fe; E and K: pH 7.1; F and L: pH 7.1 + Fe. Treatments A-F incubated in screened light, treatments G-L incubated in dark	unitless
BTLNBR_INC	Unique number assigned to incubation bottle; bottles were reused between experiments but number remained the same, allowing for follow of any bottle effects	unitless
INCLABEL	Label used to describe incubation number and day.	unitless
pH	pH of field samples. 'na' for 'not applicable' used when no sample was collected for this parameter. 'nda' for 'no data available' used when sample was collected but no data has been obtained for this parameter.	unitless
pH_FLAG	Quality flag for pH.	unitless
Fe_D_noUV_CONC_INC	Concentrations of total dissolved iron (Fe) in incubation samples; samples were not UV-oxidized prior to measurement.	Nanomoles per kilogram (nmol/kg)

Fe_D_noUV_FLAG	Quality flag for Fe_D_noUV_CONC.	unitless
ADD_57Fe_D_noUV_CONC_INC	Concentrations of added dissolved iron (Fe) as 57Fe in incubation samples; represents concentration of 57Fe spike in samples. 'na' for 'not applicable' used for treatment samples where no 57Fe was added. Samples were not UV-oxidized prior to measurement.	Nanomoles per kilogram (nmol/kg)
ADD_57Fe_D_noUV_FLAG	Quality flag for ADD_57Fe_D_noUV_CONC.	unitless
Mn_D_noUV_CONC_INC	Concentrations of dissolved manganese (Mn) in incubation samples; samples were not UV-oxidized prior to measurement.	Nanomoles per kilogram (nmol/kg)
Mn_D_noUV_FLAG	Quality flag for Mn_D_noUV_CONC.	unitless
Ni_D_noUV_CONC_INC	Concentrations of dissolved nickel (Ni) in incubation samples; samples were not UV-oxidized prior to measurement.	Nanomoles per kilogram (nmol/kg)
Ni_D_noUV_FLAG	Quality flag for Ni_D_noUV_CONC.	unitless
Zn_D_noUV_CONC_INC	Concentrations of dissolved copper (Cu) in incubation samples; samples were not UV-oxidized prior to measurement.	Nanomoles per kilogram (nmol/kg)
Zn_D_noUV_FLAG	Quality flag for Cu_D_noUV_CONC.	unitless
Cu_D_noUV_CONC_INC	Concentrations of dissolved zinc (Zn) in incubation samples; samples were not UV-oxidized prior to measurement. 'nda' for 'no data available' used when sample was collected but no data has been obtained for this parameter.	Nanomoles per kilogram (nmol/kg)
Cu_D_noUV_FLAG	Quality flag for Zn_D_noUV_CONC.	unitless
Ni_D_UV_CONC_INC	Concentrations of dissolved nickel (Ni) in incubation samples, measured by voltammetry after UV-oxidation. 'nda' for 'no data available' used when sample was collected but no data has been obtained for this parameter.	Nanomoles per liter (nmol/L)
Ni_D_UV_STDEV	Standard deviation of replicate dissolved nickel (Ni) measurements of incubation samples that were measured by voltammetry after UV-oxidation. 'na' used for 'not applicable'.	Nanomoles per liter (nmol/L)
Ni_D_UV_COUNT	Number of replicate measurements averaged for Ni_D_UV_CONC. 'na' used for 'not applicable'.	unitless

Ni_D_UV_FLAG	Quality flag for Ni_D_UV_CONC.	unitless
Ni_DL_CONC_INC	Concentrations of labile dissolved nickel (Ni) in field samples. 'na' for 'not applicable' used when no sample was collected for this parameter. 'nda' for 'no data available' used when sample was collected but no data has been obtained for this parameter.	Nanomoles per liter (nmol/L)
Ni_DL_STDEV	Standard deviation of replicate labile dissolved nickel (Ni) measurements of incubation samples. 'na' used for 'not applicable'.	Nanomoles per liter (nmol/L)
Ni_DL_COUNT	Number of replicate measurements averaged for Ni_DL_CONC. 'na' used for 'not applicable'.	unitless
Ni_DL_FLAG	Quality flag for Ni_DL_CONC.	unitless
ISO_DateTime_STARTSHIP.UTC	description	unitless
ISO_DateTime_STOPSHIP.UTC	description	unitless

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Instruments

Dataset-specific Instrument Name	Towfish
Generic Instrument Name	Discrete water sampler
Dataset-specific Description	Seawater for the incubations was collected with a custom surface sampling system, "towfish" (Mellett and Buck 2020), comprised of acid cleaned Bev-A-Line-IV tubing and an Almatec Double PTFE Diaphragm Pump.
Generic Instrument Description	A device that collects an in-situ discrete water sample from any depth and returns it to the surface without contamination by the waters through which it passes, such as a water bottle.

Dataset-specific Instrument Name	Elemental Scientific seaFAST-pico system
Generic Instrument Name	SeaFAST Automated Preconcentration System
Dataset-specific Description	Elemental Scientific seaFAST-pico system was used to preconcentrate dissolved trace metals from project samples for the ICPMS analyses.
Generic Instrument Description	The seaFAST is an automated sample introduction system for analysis of seawater and other high matrix samples for analyses by ICPMS (Inductively Coupled Plasma Mass Spectrometry).

Dataset-specific Instrument Name	Ocean Optics USB4000 fiber optic spectrometer
Generic Instrument Name	Spectrometer
Dataset-specific Description	Ocean Optics USB4000 fiber optic spectrometer for pH measurements.
Generic Instrument Description	A spectrometer is an optical instrument used to measure properties of light over a specific portion of the electromagnetic spectrum.

Dataset-specific Instrument Name	
Generic Instrument Name	Thermo Fisher Scientific ELEMENT 2 inductively coupled plasma mass spectrometer
Dataset-specific Description	ThermoScientific Element II high resolution inductively coupled plasma mass spectrometer was used to measure dissolved metal concentrations.
Generic Instrument Description	The Thermo Scientific Element 2 ICP-MS is a double-focussing magnetic-sector-field Inductively Coupled Plasma Mass Spectrometer equipped with a discrete dynode detector system, linear over nine orders of magnitude - from ppq to ppm concentrations. Other features include: Sensitivity (Concentric Nebuliser) greater than 1×10^9 counts per second (cps)/ppm In; Dark noise less than 0.2 cps; Mass resolution 300, 4,000, 10,000 (10 percent valley, equivalent to 5 percent height), 600, 8,000, 2,000 (FWHM); Signal stability better than 1 percent RSD over 10 minutes or 2 percent RSD over 1 hour; Mass stability: 25 ppm / 8 hours; Magnetic scan speed: m/z 7 to 240 to 7 in less than 150 ms, Electronic scan speed: 1 ms/jump, independent of mass range.

Dataset-specific Instrument Name	Epsilon Eclipse
Generic Instrument Name	Voltammetry Analyzers
Dataset-specific Description	BioAnalytical Systems Inc. controlled growth mercury electrode and Epsilon Eclipse voltametric analyzer were used for the labile dissolved nickel concentration measurements.
Generic Instrument Description	Instruments that obtain information about an analyte by applying a potential and measuring the current produced in the analyte.

Deployments

SKQ202209S

Website	https://www.bco-dmo.org/deployment/945379
Platform	R/V Sikuliaq
Start Date	2022-06-04
End Date	2022-07-01
Description	Additional information is available from R2R: https://www.rvdata.us/search/cruise/SKQ202209S

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Project Information

Collaborative Research: The Effect of Ocean Acidification on Fe Availability to Phytoplankton in Coastal and Oceanic Waters of the Eastern North Pacific (pH-Fe availability)

Coverage: North East Pacific, Ocean Station PAPA

NSF Award Abstract:

Iron is an important nutrient for algae in the ocean. Different forms of iron and their availability to algae are influenced by many factors including the acidity of seawater (or pH). This research project focuses on understanding the effects of ocean acidification (low pH) on the associations between iron and chemical substances that bind with iron in seawater. The investigators will work in coastal and oceanic waters of the Pacific Ocean. These waters are characterized by substances that have weak and strong associations with iron. Samples will be collected from coastal waters off Washington State, the northern edge of the North Pacific gyre, and Ocean Station PAPA in the northeast subarctic Pacific. Water samples will be collected to test phytoplankton responses to light, pH, forms of iron, and the composition of the substances that bind with iron. This project will support graduate and undergraduate students. The investigators will participate in a range of education and outreach activities.

This study addresses oceanic responses to rising anthropogenic CO₂ and is broadly relevant to ocean biogeochemistry. The investigators will study the role of ocean acidification on iron availability in the Eastern North Pacific Ocean. The study location is characterized as a high nutrient low chlorophyll (HNLC) region of the ocean, where phytoplankton may be particularly sensitive to iron availability. The study region is also characterized by gradients in ligand composition and binding strength. This study will investigate how the associations between iron and different ligands (organic compounds that bind with iron) are influenced by pH and how this, in turn, influences primary production and microbial community structure in the ocean. The investigators will use batch cultures, at pH 8.1 and 7.6, and under high and low light regimes, to examine the iron demand of phytoplankton. Understanding how pH influences iron and its relationship with ligands will provide important information for assessing the impacts of ocean acidification on primary production and biogeochemical processes.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1830029
NSF Division of Ocean Sciences (NSF OCE)	OCE-1829753

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