Benthic iron data on the Oregon Shelf from samples collected on R/V Oceanus cruise OC2107A during July to August 2021

Website: https://www.bco-dmo.org/dataset/894761
Data Type: Cruise Results
Version: 1
Version Date: 2024-04-22

Project
» Collaborative Research: Coupling of physical and chemical processes in the shelf to basin transport of iron and iodine off Washington and Oregon (Oregon shelf to basin transport)

Contributors	Affiliation	Role
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Abstract
These data were obtained on two cruises to the Oregon shelf in August and November 2021. They describe the release of dissolved iron (Fe) from the benthic boundary layer and show that a sizeable fraction of this Fe is present as soluble Fe(II). Hypoxia is increasing in strength and duration on the Oregon continental shelf. Intermediate waters of the North Pacific are also experiencing deoxygenation. Lower oxygen (O2) will lead to elevated Fe(II) release and persistence in the water column, increasing the role of the Oregon continental margin as an Fe source. Coastal Oregon and North Pacific Ocean waters are often iron-limited and this increased Fe source could act as a positive feedback to Pacific deoxygenation by increasing primary production and therefore carbon supply to hypoxic intermediate waters. Understanding and simulating continental margin Fe supply will provide helpful information for predicting the condition of the future coastal ocean. Intensive modeling and monitoring already occur for these waters due to their economic significance and an improved understanding of Fe, a critical nutrient in this region, will advance these efforts. Note this version of the dataset includes data only from the August 2021 cruise.

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Coverage

Spatial Extent: **N**:46.77694 **E**:-124.19801 **S**:43.81996 **W**:-126.0507
Temporal Extent: 2021-07-22 - 2021-08-08

Methods & Sampling

Sampling at the sediment-water interface was carried out using a benthic lander called Susane built at IFREMER by Joel Knoery (Knoery et al., 2019). It was deployed using a 0.322 cable from the port side squirt boom on the Oceanus. The lander was deployed at the seafloor and syringes sampled water at 10-centimeter (cm) intervals while it sat on the seafloor. Transfer of sampled water to the analytical system is described below.

Water column samples were collected using a Seabird Rosette equipped with an SBE50 pressure sensor and

an autofire module. It was pre-programmed and deployed on amsteel cable and fired at select depths). Bottles were 5 liter (L) Niskin-style acquired from Ocean Test Equipment. They were teflon-coated and had external teflon-coated springs.

All iron (Fe) samples were filtered using Pall Gelman Supor 0.45 micrometer (µm) polyethersulfone filters with either Millipore Swinnex polypropylene 25-millimeter (mm) filter holders or Advantec-MFS type PP47 47 mm polypropylene inline filter holders, as recommended by the GEOTRACES Cookbook version 3.0 (Cutter et al., 2017). Nitrogen (N2) gas was used to pressurize the Go-Flo bottles during filtration. Filtered fractions for Fe(II) measurement were transferred to a syringe using a three-way Luer-lock adaptor to prevent the introduction of air, then measured immediately. Fe(II) was measured via chemiluminescence with luminol, consisting of a continuous 2 milliliters per minute (mL min-1) flow of sample and luminol solution at a 1:1 ratio into a standard quartz flow cell with a Hamamatsu HC135 photon counter via a peristaltic pump. The signal value for each sample was determined as the mean of the signal for 30 seconds (n=50), once the signal reached a plateau. Because luminol chemiluminescence is not selective for Fe(II), each sample was also treated with diethylenetriamine pentaacetate (DTPA), a selective Fe(II) chelator used as a masking ligand. The DTPA-treated samples, with a final concentration of 0.5 millimolar (mM) DTPA, serve to correct for chemiluminescence caused by compounds besides Fe(II). DTPA-treated samples were processed with the exact same analytical train as untreated Fe(II) samples. The order of sample measurement was randomized to prevent systematic error due to sample oxidation. Fe(II) calibration was performed each time the system was powered on and calibration curves consisted of six or more concentrations within the appropriate working range of the measured Fe(II). These concentrations were created by spiking a seawater solution that aged for at least 24 hours in an amber bottle with an appropriate volume of 1 micromole (µM) Fe(II) working stock in milliQ water. This working stock was created fresh before calibration from a 0.01 mole (M) Fe(II) standard solution at pH 2, prepared monthly by dissolving Optima grade hydrochloric acid (Fisher) and ammonium ferrous sulfate (Fluka) in milliQ water. Luminol solutions were prepared first using a stock solution with 0.796 grams (g) of sodium luminol (Sigma), 250 mL of Optima grade ammonium hydroxide (Fisher), approximately 45 mL of Optima grade hydrochloric acid (Fisher), and milliQ water. The working luminol reagent was produced by diluting this stock to one-fourth of its starting concentration, then heating it at 50º Celsius for 9 to 12 hours. The DTPA solution was created by diluting 2.4584 g of DTPA (Millipore-Sigma) with sodium hydroxide (Aldrich, trace metal basis) in milliQ water for a final concentration of 50 mM DTPA and 200 mM NaOH. Additional details of this method including reagent preparation, instrumental settings, and procedures have been previously reported (Bolster et al., 2018).

Total dissolved Fe (dFe) samples were collected into 500 mL LDPE bottles. Within one month of collection, these samples were acidified to a pH of approximately 1.7 by adding 1 mL of hydrochloric acid (Optima, Fisher Scientific) per 500 mL of seawater. After one year of storage, samples were prepared in triplicate using the seaFAST-pico (Elemental Scientific) offline method, where 10 mL of acidified sample was added to a Nobias resin chelation column and then eluted with ultra-pure, distilled 5% nitric acid (Optima, Fisher Scientific) for a final volume of 0.5 mL. This method is similar to the method described in Jackson et al. (2018) and Rapp et al. (2017). Fe concentrations were quantified with a Finnegan Element 2 (Thermo Scientific) Inductively Coupled Plasma-Mass Spectrometer and Apex desolvation system in medium resolution. A 1 part per billion (ppb) indium eluent is used during sample preparation as an internal standard to correct for instrument drift. Instrument optimization and tuning are performed daily with a 1 ppb indium and uranium tuning solution. Procedural blanks were prepared in triplicate from pH 1.7 hydrochloric acid to correct for contamination during acidification of samples. Sample concentration of Fe was determined via the isotopic dilution method in which acidified samples were spiked with a multi-element standard, including 57Fe, enriching it over the natural isotopic abundances.

Oxygen (O2) concentrations from the benthic boundary gradient sampler were measured less than an hour from recovery using a Presens TX-3 microoptode in a flow cell fitted to the sampling syringe outlets. Between each O2 measurement, brief flushes of nitrogen gas were also used to check for calibration shifts and remove contamination between samples. The order of sample measurement was randomized to reduce the influence of any contamination post-recovery.

Data Processing Description

Data Processing:
MATLAB R2018B (The MathWorks, Inc., 2018) was used to read in and average signal values for Fe(II) measurement. The calibration curve for Fe(II) using this method follows a second-order polynomial, so the "nllsqr" function (Glover et al., 2011) was used to fit this data. Sample concentrations were calculated by first subtracting the DTPA signal and then applying the "vpasolve" command with the given calibration curve. The

uncertainty in measured Fe(II) concentrations was calculated using the standard error of the signal plateau (n=50). For Fe(II) samples measured in duplicate, the uncertainty consists of this standard error and the standard deviation of the two measurements added in quadrature.

BCO-DMO Processing Description

- Imported the original Excel file "Processed Fe2 data_OC2107A.xlsx" into the BCO-DMO system.
- Removed 'NaN' as the missing data identifier (missing values are blank in the final CSV file).
- Separated the Cruise ID from the "Fe Only" column.
- Renamed fields to comply with BCO-DMO naming conventions.
- PI Moffett provided a revised file "fe2_oc2107a_with dates.csv" including dates.
- Converted the Date field to YYYY-MM-DD format.
- Changed years of "2023" to "2021".
- PI Moffett provided a revised file "894761_v1_benthic_iron_oregon_AF.csv", which included additional dissolved Fe data.
- Removed 'N/A' as the missing data identifier (missing values are blank in the final CSV file).
- Saved the final file as "894761_v1_benthic_iron_oregon.csv".

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Related Publications

Bolster, K. M., Heller, M. I., & Moffett, J. W. (2018). Determination of iron(II) by chemiluminescence using masking ligands to distinguish interferences. Limnology and Oceanography: Methods, 16(11), 750–759. doi:10.1002/lom3.10279
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

Evans, N. et al., (2023) The role of seasonal hypoxia and benthic boundary layer exchange on margin-derived iron cycling (submitted).
Results

Jackson, S. L., Spence, J., Janssen, D. J., Ross, A. R. S., & Cullen, J. T. (2018). Determination of Mn, Fe, Ni, Cu, Zn, Cd and Pb in seawater using offline extraction and triple quadrupole ICP-MS/MS. Journal of Analytical Atomic Spectrometry, 33(2), 304–313. https://doi.org/10.1039/c7ja00237h
Methods

Knoery, J., Cossa, D., Thomas, B., Gregory, G., & Rigaud, S. (2019). Susane, a device for sampling chemical gradients in the benthic water column. Limnology and Oceanography: Methods. Portico. https://doi.org/10.1002/lom3.10317
Methods

Rapp, I., Schlosser, C., Rusiecka, D., Gledhill, M., & Achterberg, E. P. (2017). Automated preconcentration of Fe, Zn, Cu, Ni, Cd, Pb, Co, and Mn in seawater with analysis using high-resolution sector field inductively-coupled plasma mass spectrometry. Analytica Chimica Acta, 976, 1–13. doi:10.1016/j.aca.2017.05.008
Methods

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Parameters

Parameter	Description	Units
Cruise	Cruise ID	unitless

Date	Date of sampling (local time zone)	unitless
Fe_only	Indicates a trace metal cast where only dissolved Fe was measured (i.e. not Fe(II))	unitless
Station	Station number	unitless
Latitude	Latitude of sample collection (positive = North)	degrees North
Longitude	Longitude of sample collection (positive = East)	degrees East
Cast	Cast number	unitless
Cast_type	Type of cast: BBG = using a benthic boundary gradient sampler with 50 mL syringes on OC2107A. Note that instead of depth, this variable now refers to height above seafloor in centimeters; CTD = using a traditional 10 or 14 L bottle mounted on a rosette; TMC= using a trace metal clean 5 L bottle mounted on a trace metal clean rosette following Geotraces protocols; TMC dFe only = Trace metal cast and only dissolved Fe was measured (i.e. not Fe(II))); these are the stations where dFe was measured the first time but Fe(II) wasn't, so we resampled and got the Fe(II).	unitless
Depth	Sample depth	meters (m)
Sample_number	Sample number	unitless
Fe_II	Fe(II) concentration	nanomolar (nM)
Fe_II_std	Fe(II) standard deviation	nanomolar (nM)
Fe_II_flag	Fe(II) measurement flag: 0 = Final dilution and order of magnitude specified; 1 = Order of magnitude specified ; 2 = Final dilution specified ; 3 = Neither final dilution and order of magnitude specified.	unitless
Fe_II_err_flag	Fe(II) uncertainty flag: 0 = single measurement with uncertainty; 1 = doublet averaged and propagated with uncertainty.	unitless
dFe	Dissolved Fe concentration	nanomolar (nM)
Sampling_time_local	Time (local time zone) when sample was collected	unitless

Measurement_time_local	Time (local time zone) when sample was analyzed	unitless
pH	pH	unitless (pH scale)
Potential_density	Potential density	kilogram per cubic meter (kg m-3)
O2	Oxygen concentration	micromoles per kilogram (umol kg-1)
Bottom_depth	Bottom depth	meters (m)
Temperature	Water temperature	degrees Celsius
Salinity_practical	Practical salinity	unitless
Comments	Comments or notes	unitless

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Instruments

Dataset-specific Instrument Name	SUSANE
Generic Instrument Name	benthic lander
Dataset-specific Description	Refer to Knoery, et al. (2019) for a description of the benthic lander nicknamed "SUSANE", which stands for "System for Underwater SAmpling of beNthic Environments". In short, this sampler was designed to simultaneously collect 16 discrete water column samples at a centimeter-scale vertical resolution. The small device (40 × 40 × 60 cm) is deployed from a small boat using a cable or a Scuba diver. The device can contribute to the characterization of vertical concentration gradients in benthic water columns.
Generic Instrument Description	A benthic lander is an autonomous research platform used in marine research to take measurements directly on the seafloor. Benthic landers are carrier systems to which different measuring and sampling devices can be attached. They transport these devices to the seafloor and back up again. Autonomous means that the lander is not connected to the ship via a cable. It can thus work independently on the seafloor for a long period of time.

Dataset-specific Instrument Name	Seabird Rosette
Generic Instrument Name	CTD Sea-Bird
Generic Instrument Description	Conductivity, Temperature, Depth (CTD) sensor package from SeaBird Electronics, no specific unit identified. This instrument designation is used when specific make and model are not known. See also other SeaBird instruments listed under CTD. More information from Sea-Bird Electronics.

Dataset-specific Instrument Name	Finnegan Element 2 (Thermo Scientific) Inductively Coupled Plasma-Mass Spectrometer
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Generic Instrument Description	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.

Dataset-specific Instrument Name	5-liter Niskin-style bottles from Ocean Test Equipment
Generic Instrument Name	Niskin bottle
Generic Instrument Description	A Niskin bottle (a next generation water sampler based on the Nansen bottle) is a cylindrical, non-metallic water collection device with stoppers at both ends. The bottles can be attached individually on a hydrowire or deployed in 12, 24, or 36 bottle Rosette systems mounted on a frame and combined with a CTD. Niskin bottles are used to collect discrete water samples for a range of measurements including pigments, nutrients, plankton, etc.

Dataset-specific Instrument Name	Presens TX-3 microoptode
Generic Instrument Name	Optode
Generic Instrument Description	An optode or optrode is an optical sensor device that optically measures a specific substance usually with the aid of a chemical transducer.

Dataset-specific Instrument Name	Hamamatsu HC135 photon counter
Generic Instrument Name	Photon Counter
Generic Instrument Description	Photon counting is a technique in which individual photons are counted using some single-photon detector (SPD).

Dataset-specific Instrument Name	SBE50 pressure sensor
Generic Instrument Name	SBE 50 pressure sensor
Generic Instrument Description	The SBE 50 digital oceanographic pressure sensor is a high-accuracy, high-resolution (16 Hz sampling) pressure sensor, intended for towed vehicle, ROV, AUV, or other autonomous profiling applications. It has titanium housing rated for depths to 7000 meters. It is offered in seven full-scale ranges from 0 to 20/100/350/1000/2000/3500/7000 meters. Its initial accuracy 0.1% of full-scale range, it has a typical Stability 0.004% of full-scale range per month, and a resolution 0.002% of full-scale range.

Dataset-specific Instrument Name	
Generic Instrument Name	syringe
Generic Instrument Description	A device used to inject fluids into or withdraw them from something; consists of a hollow barrel fitted with a plunger and a hollow needle.

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Deployments

OC2107A

Website	https://www.bco-dmo.org/deployment/894768
Platform	R/V Oceanus
Start Date	2021-07-21
End Date	2021-08-12
Description	See additional information from R2R: https://www.rvdata.us/search/cruise/OC2107A

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Project Information

Collaborative Research: Coupling of physical and chemical processes in the shelf to basin transport of iron and iodine off Washington and Oregon (Oregon shelf to basin transport)

NSF Award Abstract:
The boundary between productive coastal waters and relatively non-productive offshore waters is not a simple function of distance from the coast, but is determined by a complex interplay between biology, chemistry, and ocean physics. This interplay is a fundamental property that controls the oceanic contribution to the food supply and the global carbon cycle. During summer months when waters are warmer with low oxygen, biological decomposition near the seafloor consumes available oxygen and releases iron from sediments into overlying seawater. In deeper parts of the ocean, canyons and other rugged surface features influence currents and create turbulence that rapidly moves iron from the shelf offshore. This iron in turn can enhance biological productivity miles away. This project will investigate (1) how decomposition processes on the continental shelf seafloor release elements like iron required for ocean life and (2) how ocean currents interact with the continental shelf and slope to move waters overlying the shelf offshore to enhance productivity. Based on model simulations from the California and Oregon coasts done over 20 years that show transport of

iron via plumes from the shelf to the open ocean, scientists will collect and analyze samples for iron and iodine to prove the findings of the model. Iodine has been included in the study because it can track inputs from low oxygen sediments to the shelf. In addition, results from the study will be used to improve assumptions used in the current model. The project will support the research in whole or in part of four graduate students and several undergraduate students. The scientists are involved with High School student mentoring, through Project COOL (Chemical Oceanography Outside the Lab) and the Students on Ice Foundation.

Scientists from the University of Southern California and the University of California, Los Angeles will study iron (Fe) and iodine (I) geochemistry along the Washington and Oregon Coasts, where high organic matter oxidation rates, low dissolved oxygen concentrations, and high sedimentary Fe fluxes on the continental shelf occur. This project hypothesizes that a shelf-to-basin shuttle controls the supply of Fe from the Fe-rich shelf into the interior of the North Pacific Ocean. Simulations of a Regional Oceanic Modeling System (ROMS) coupled with the Biogeochemical Elemental Cycling model (BEC) run between 2007-2017 showed that this coastline is a major source of Fe to the ocean basin, exhibiting both deep and shallow Fe plumes that arise from subsurface eddies generated by poleward undercurrents. Results from this model will be used to predict how the distribution of Fe evolves seasonally and guide sampling during two cruises in 2021 to the region. According to the ROMS-BEC model, the Fe inventory is highest in late summer, when bottom water oxygen is lowest, and the inventory is lowest in winter and early spring. Model-generated deep plumes resemble those reported off Namibia, Peru and the Gulf of Alaska. This work will sample depths up to 4500m and look for such plumes. Deep plumes are important in global Fe budgets and because they may outcrop in high latitude waters that are Fe limited. Iodine will also be measured because, like Fe, it accumulates at the sediment water interface and is released under reducing conditions. Plumes of iodine arising from shelf sediments will be used as a semi-conservative tracer for lateral Fe advection. The cruises will also assess the relative importance of direct inputs from rivers (especially the Columbia River) versus reducing sediments, since these inputs are decoupled seasonally

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.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-2023708

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