Monthly cross-shore transects of biogeochemical properties in La Jolla, CA

Website: https://www.bco-dmo.org/dataset/839175
Data Type: Cruise Results
Version: 1
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Project
» CAREER: Biogeochemical Modification of Seawater CO2 Chemistry in Near-Shore Environments: Effect of Ocean Acidification (Nearshore CO2)
» Collaborative Research: Iron Bioavailability in High-CO2 Oceans: New Perspectives on Iron Acquisition Mechanisms in Diatoms (Iron_CO2_Diatoms)

Contributors	Affiliation	Role
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Abstract
These data result from monthly cross-shore transects of biogeochemical properties in La Jolla, CA. In this study, discrete seawater samples were collected between 0-40m on a monthly transect extending from the coastline to ~2km offshore in La Jolla, CA. Seawater samples were collected for analysis of dissolved inorganic carbon chemistry parameters and dissolved inorganic nutrient concentrations. The study was designed to characterize the biogeochemical near-shore spatiotemporal variability in the Southern California Bight, and in particular, the influence of seasonal upwelling.

Table of Contents

- Coverage
- Dataset Description
  - Methods & Sampling
  - Data Processing Description
- Data Files
- Related Publications
- Parameters
- Instruments
- Deployments
- Project Information
- Funding

Coverage

Spatial Extent: **N**:32.865 **E**:-117.259 **S**:32.865 **W**:-117.2701
Temporal Extent: 2017-03-08 - 2018-09-27

Methods & Sampling

General study design:
In this study, seawater samples were collected between 0-40m on a monthly transect extending from the coastline to ~2km offshore in La Jolla, CA. Seawater samples were collected for analysis of dissolved carbonate chemistry parameters and inorganic nutrient concentrations. The study was designed to characterize the biogeochemical near-shore spatiotemporal variability in the Southern California Bight, and in particular, the influence of seasonal upwelling.

Methods description:
Seawater was collected with a 5 L Niskin bottle between the surface and bottom in 10 m intervals at four stations between the end of the SIO pier and ~2 km offshore. Transect stations were separated by ~400 m. Seawater carbonate chemistry samples were collected into 250 ml Pyrex Corning glass bottle and immediately poised with 100 µL $HgCL_2$ following standard protocols (Dickson et al., 2007). Inorganic nutrient samples were filtered through a 0.45 µm polycarbonate filter into 30 mL Falcon tubes and immediate placed on ice and kept frozen until analysis. Temperature, salinity, and dissolved oxygen were measured in the residual seawater in the Niskin bottle following seawater collection using a YSI multiprobe.

Analytical Methods:
Seawater samples were analyzed for DIC and TA at the Scripps Coastal and Open Ocean Biogeochemistry lab. DIC analyses were conducted with an automated infrared inorganic carbon analyzer (AIRICA, Marianda) and TA with an open-cell potentiometric acid titration system developed at Scripps Institution of Oceanography (SIO) by A. Dickson (Dickson et al. 2007).

Inorganic nutrient samples were analyzed for dissolved NO3, PO4, H4SIO4, NO2, and NH3 at the Ocean Data Facilities (ODF) at the Scripps Institution of Oceanography either spectrophotometrically or fluorometrically via an analytical continuous-flow autoanalyzer. For details see: https://scripps.ucsd.edu/ships/shipboard-technical-support/odf/documentation/nutrient-analysis.

Quality Control:
Samples for seawater carbon chemistry analysis were collected and analyzed following standard protocol (Dickson et al., 2007). The handheld YSI multiprobe was calibrated prior to each survey with and accuracy of ±0.2°C for temperature and 1% for salinity. The accuracy and precision for DIC and TA samples were 0.45 ± 1.57 and 0.93 ± 1.40, respectively and were evaluated using CRMs provided by the laboratory of A. Dickson at SIO. CRMs were analyzed every 5 samples for DIC and every 10 for TA.

Data Processing Description

BCO-DMO Processing:
-added UTC date/time field in ISO8601 format;
- converted longitude values from positive to negative.

[table of contents | back to top]

Data Files

File
la_jolla_biogeochem.csv (Comma Separated Values (.csv), 28.44 KB) MD5:efa50ab1f2df08d0d434f3c8a193abbf Primary data file for dataset ID 839175

[table of contents | back to top]

Related Publications

Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007. Guide to Best Practices for Ocean CO2 Measurements. PICES Special Publication 3, 191 pp https://isbnsearch.org/isbn/1-897176-07-4
Methods

Kekuewa, S. A. (2020). Seawater CO2-Chemistry Variability in the Near-Shore Environment of the Southern California Bight. UC San Diego. ProQuest ID: Kekuewa_ucsd_0033M_19412. Merritt ID: ark:/13030/m5md47st. Retrieved from https://escholarship.org/uc/item/5ng2r1p5
Results

Kekuewa, S. A. H., Courtney, T. A., Cyronak, T., & Andersson, A. J. (2022). Seasonal nearshore ocean acidification and deoxygenation in the Southern California Bight. Scientific Reports, 12(1). https://doi.org/10.1038/s41598-022-21831-y

Parameters

Parameter	Description	Units
Sample	Sample number for reference	unitless
Station	Station number along transect	unitless
Date	Date of the survey (local time; PST); format: MM/DD/YYYY	unitless
Time	Time of survey in local time (PST; GMT-7/-8); format: hh:mm	unitless
ISO_DateTime_UTC	Date and time of survey (UTC) in ISO8601 format: YYYY-MM-DDThh:mmZ	unitless
Lat	Latitude of survey station	degrees North
Long	Longitude of survey station	degrees East
Depth	Depth of seawater sample	meters (m)
Temp	Temperature of seawater	degrees Celsius
Salinity	Salinity of seawater	PSU
DO	Dissolved oxygen of seawater	micromoles per kilogram (umol/kg)
DIC	Dissolved inorganic carbon of seawater	micromoles per kilogram (umol/kg)
TA	Total alkalinity of seawater	micromoles per kilogram (umol/kg)
pH	pH of seawater	unitless
Ar	Aragonite saturation state of seawater	unitless
NO3	Dissolved Inorganic nitrate concentration of seawater	micromoles per kilogram (umol/kg)

PO4	Dissolved Inorganic phosphate concentration of seawater	micromoles per kilogram (umol/kg)
SIL	Dissolved Silicate (H4SiO4) concentration of seawater	micromoles per kilogram (umol/kg)
NO2	Dissolved Nitrite concentration of seawater	micromoles per kilogram (umol/kg)
NH3	Dissolved Nitrite concentration of seawater	micromoles per kilogram (umol/kg)

[table of contents | back to top]

Instruments

Dataset-specific Instrument Name	Seal Analytical continuous-flow AutoAnalyzer 3
Generic Instrument Name	Continuous Flow Analyzer
Dataset-specific Description	For NO3: Instrument utilizes an analytical method where N-1-N (NEDD) and sulfanilamide are reacted with the sample to form a red dye, which is measured at an absorbance of 520-540 nm. For nitrate analysis, the nitrate is first reduced to nitrite by the sample being mixed with a buffer solution (ie., Ammonium Chloride or Imidazole) and passed over a cadmium column that has been treated with copper sulfate, which catalyzes the reduction reaction. The resulting nitrite is then analyzed and the final output for the 'nitrate' channel is a sum of both nitrate and nitrite. It is important therefore to analyze nitrite separately so that nitrate can be determined by subtracting from the total nitrate plus nitrite concentration (Becker et al., 2019). For analysis of PO4 in seawaters acidic solution of molybdate is added, followed by the addition of a reducing compound (dihydrazine sulfate or ascorbic acid) to form a phospho-molybdenum blue complex with the absorbance measured at approximately 820 or 880nm, depending on the method and availability of filters (Becker et al., 2019). For analysis of SIL, acidified ammonium molybdate is added to a seawater sample to produce silicomolybdic acid, which is then reduced to a silicomolybdenum blue complex following the addition of stannous chloride or ascorbic acid, and measured at 660nm for stannous chloride or 820nm for ascorbic acid (Becker et al., 2019). For NO2: Instrument utilizes an analytical method where N-1-N (NEDD) and sulfanilamide are reacted with the sample to form a red dye, which is measured at an absorbance of 520-540 nm. For nitrate analysis, the nitrate is first reduced to nitrite by the sample being mixed with a buffer solution (ie., Ammonium Chloride or Imidazole) and passed over a cadmium column that has been treated with copper sulfate, which catalyzes the reduction reaction. The resulting nitrite is then analyzed and the final output for the 'nitrate' channel is a sum of both nitrate and nitrite. It is important therefore to analyze nitrite separately so that nitrate can be determined by subtracting from the total nitrate plus nitrite concentration (Becker et al., 2019). For NH3: In the fluorometric method, without using any membrane diffusion, the sample is combined with a working reagent made up of OPA, sodium sulfite, a borate buffer, and then heat to 75°C. Fluorescence proportional to the ammonium concentration is measured at 460nm following excitation at 370nm (Becker et al., 2019).
Generic Instrument Description	A sample is injected into a flowing carrier solution passing rapidly through small-bore tubing.

Dataset-specific Instrument Name	AIRICA (Marianda)
Generic Instrument Name	Inorganic Carbon Analyzer
Dataset-specific Description	The Automated Infra Red Inorganic Carbon Analyzer (AIRICA) utilizes infrared detection of CO2 gas purged from an acidified seawater sample. A pump extracts the seawater sample, acidifies the sample with phosphoric acid, and analyzes the gas released with an infrared light analyzer (LICOR). The CO2 signal is integrated for four individual peaks for each sample and the three closest integrated peaks are averaged for a single given sample.
Generic Instrument Description	Instruments measuring carbonate in sediments and inorganic carbon (including DIC) in the water column.

Dataset-specific Instrument Name	AFT-pH (SAMI, Sunburst)
Generic Instrument Name	Titrator
Dataset-specific Description	Over a 5 minute time period, the AFT-pH uses a pump and extracts 10 mL of the seawater sample, introduces the sample with mCP indicator dye and is spectrophotometrically analyzed within a pH range of 7.4 to 8.5.
Generic Instrument Description	Titrators are instruments that incrementally add quantified aliquots of a reagent to a sample until the end-point of a chemical reaction is reached.

Dataset-specific Instrument Name	Open-cell potentiometric acid titrator
Generic Instrument Name	Titrator
Dataset-specific Description	The open-cell potentiometric acid titration system was developed by the laboratory of A.G. Dickson. Briefly, a known amount of seawater is added to an open cell temperature controlled beaker. Hydrochloric acid (0.1 N) is added using a Methrom Dosimat to a pH of 3.5-4.0. Following equilibration, small increments of hydrochloric acid are then added to the seawater until pH equals ~ 3.0. The titration is monitored by a glass electrode and the total alkalinity of the sample is calculated using a non-linear least-squares method following Dickson et al. (2007).
Generic Instrument Description	Titrators are instruments that incrementally add quantified aliquots of a reagent to a sample until the end-point of a chemical reaction is reached.

Dataset-specific Instrument Name	YSI Professional Plus handheld multi-parameter instrument (YSI 6600 V2)
Generic Instrument Name	Water Quality Multiprobe
Dataset-specific Description	The instrument was used to measure in situ temperature (±0.2°C), salinity (± 1%), and DO (both mg/L and %; ± 2%).
Generic Instrument Description	An instrument which measures multiple water quality parameters based on the sensor configuration.

[table of contents | back to top]

Deployments

La_Jolla_2017-18

Website	https://www.bco-dmo.org/deployment/839192
Platform	small boat - Boston Whaler 17’ SIO7/9
Start Date	2017-03-01
End Date	2018-09-30
Description	Monthly cruises from March 2017 to September 2018 on SIO's 17' Boston Whaler. Latitude: 32.865 Longitude: 117.259 to 117.2701 Depth: 0 to 40 m

[table of contents | back to top]

Project Information

CAREER: Biogeochemical Modification of Seawater CO2 Chemistry in Near-Shore Environments: Effect of Ocean Acidification (Nearshore CO2)

Coverage: San Diego, California; Bermuda; Oahu, Hawaii

NSF Award Abstract:
Because of well-known chemical principles, changes in the CO2 chemistry of seawater in the open ocean as a result of rising atmospheric CO2 can be predicted very accurately. On the other hand, in near-shore environments, these projections are much more difficult because the CO2 chemistry is largely modified by biogeochemical processes operating on timescales of hours to months. To make predictions on how near-shore seawater CO2 chemistry will change in response to ocean acidification (OA), it is critical to consider the relative influence of net ecosystem production (NEP) and net ecosystem calcification (NEC), and how these processes might change in response to this major perturbation. Understanding how future OA will alter near-shore seawater CO2 chemistry and variability was identified as a major critical knowledge gap at the recent IPCC WG II/WG I workshop on impacts of ocean acidification on marine biology and ecosystems in January of 2011, and also at the International Ocean Acidification Network workshop in Seattle in June of 2012.

With funding from this CAREER award, a researcher at the Scripps Institute of Oceanography and his students will study how biogeochemical processes and the relative contributions from NEP and NEC modify seawater CO2 chemistry in near-shore environments influenced by different benthic communities under well-characterized environmental and physical conditions, and how these processes might change in response to OA. The team will investigate a limited number of contrasting habitats in subtropical (reef crest, back/patch reef, lagoon, seagrass bed, algal mat) and temperate (kelp bed, inter- and sub-tidal, marsh) environments during summer and winter, employing a method that evaluates the function and performance of the carbon cycle of a system using a stoichiometric vector approach based on changes in total dissolved inorganic carbon (DIC) and total alkalinity (TA). These field studies will be complemented by controlled mesocosm experiments with contrasting and mixed benthic communities under different OA scenarios.

The project has two educational components: (1) developing a research-driven OA and biogeochemistry course based on inquiry-, experience-, and collaborative-based learning; and (2) working with the Ocean Discovery Institute (ODI) to engage individuals from a local underrepresented minority community in science through educational activities focused on OA, and also providing a moderate number of internships for high school and college students to engage in this research project.

Broader Impacts: This project will directly support one PhD student, one junior research technician, and two high school and college interns from underrepresented minorities (URM) each summer of the project. It will contribute to the education of 80 undergraduate and graduate students participating in the research based ocean acidification/biogeochemistry course offered four times throughout the duration of the project at

SIO/UCSD. Education and curricular material on the topics of OA, including hands-on laboratories, classroom and field-based activities will be developed through the collaboration with the ODI and brought to hundreds of URM students and their teachers in the City Heights area, a community with the highest poverty and ethnic diversity in the San Diego region. This collaboration will enable URM students to directly engage in a rapidly evolving field of research that has high relevance at both the local and global scales. To ensure broad dissemination of this project and the topic of OA, the research team will work with the Google Ocean team to incorporate information and educational material in the Google Ocean Explorer.

Collaborative Research: Iron Bioavailability in High-CO2 Oceans: New Perspectives on Iron Acquisition Mechanisms in Diatoms (Iron_CO2_Diatoms)

Coverage: Eastern Subtropical Pacific waters, 33 N 120 W

NSF Award Abstract:
Iron is critically needed for growth of all marine phytoplankton, the microscopic plants at the base of the ocean food chain. Consequently, lack of iron in large regions of the global ocean limits phytoplankton growth and commercial fisheries. Ocean acidification (OA) is the ongoing decrease in seawater pH due to the ocean absorbing carbon dioxide from the atmosphere. OA is predicted to affect seawater chemistry by reducing the concentration of carbonate ions. Carbonate ions are required for phytoplankton to take up iron from their environment, which suggests that OA might inhibit iron nutrition. Further complicating the scenario, pH changes affect iron chemistry in seawater, such that OA is predicted to shift the relative abundance of various forms of iron. But despite these expectations, little is known about how the changes in ocean chemistry due to OA will impact the availability of iron to phytoplankton. Changes in phytoplankton iron uptake and associated growth rates would likely have large effects on how the ocean captures atmospheric carbon dioxide (CO2). This has important consequences for ecosystem productivity and for global cycles of critical chemical elements, such as carbon and nitrogen, and their chemistry. This project aims to help us understand how shifts in seawater pH and the chemistry of dissolved inorganic carbon will affect both iron uptake rates and iron acquisition strategies in the laboratory and in natural communities. This project also includes development of educational outreach activities which target primary school students in the areas of microbiology, biogeochemical cycles and current global change topics. These science outreach activities benefit from collaborations with the following San Diego-based organizations: the League of Extraordinary Scientists and Engineers (LXS), The Birch Aquarium at Scripps (BAS), and The Ocean Discovery Institute (ODI).

This project seeks to understand the differential sensitivity of diatom iron acquisition strategies to changes in seawater pH and carbonate chemistry. Ultimately a more thorough and detailed mechanistic understanding of diatom iron uptake pathways will facilitate a much-improved ability to forecast the impact of anticipated changes in ocean pH and inorganic carbon chemistry on rates of iron uptake by diatoms. This critical biogeochemical issue is addressed through trace metal clean manipulation experiments incorporating state-of-the-art analytical methodology to probe phytoplankton cellular physiology and biogeochemistry in laboratory cultures and natural communities. In the first year, laboratory experiments with a model pennate diatom leverage a collection of targeted knockout transgenic lines to evaluate the substrate specificity and relative importance of distinct iron assimilation pathways under a range of pCO2 and iron availability conditions. Additionally, quantitation of mRNA and proteins for key diatom iron assimilation pathways in natural communities in the Southern California Current further clarify the relative importance and sensitivity of distinct iron assimilation pathways in relation to pCO2 and iron availability. In year two a Lagrangian study of iron uptake rates and associated mRNA and protein abundance is performed on upwelled high pCO2 water over the course of offshore advection. Additionally, the investigators are conducting mesocosm experiments using naturally elevated high pCO2 seawater as well as laboratory experiments on multiplex knockout lines. Year three is dedicated to data analyses and overall project synthesis. Overall aims of the research activities include, 1) development and validation of a refined conceptual model of iron uptake in key marine phytoplankton and subsequent utilization of the model to characterize the sensitivity of distinct iron uptake pathways to the effects of ocean acidification, and 2) determination of the effects of acidification on iron uptake, and quantification of the relative contribution of distinct iron acquisition pathways in high pCO2 phytoplankton communities.

Related Datasets:
NSF award OCE-1756860 (PI: Katherine Barbeau) partially supported several students on CCE LTER process cruise P1908 to generate datasets for water column samples for dissolved Fe and biogenic Si that are pertinent to this funded project. These datasets, cited below, are available from the EDI Data Portal.

California Current Ecosystem LTER and K. Barbeau. 2023. Measurements, from CCE LTER process cruises in the California Current region, of dissolved inorganic concentrations of nutrient iron and of iron limitation at selected stations and depths, 2006 - 2019 (ongoing). ver 6. Environmental Data Initiative. https://doi.org/10.6073/pasta/50a0a46193bc6cbe7eaa1ba7510278e3.

California Current Ecosystem LTER and K. Barbeau. 2023. Vertical profiles of in-situ biogenic silica (bSi) from discrete rosette bottle samples from CCE-LTER starting with cruise P1706. ver 2. Environmental Data Initiative. https://doi.org/10.6073/pasta/265091f2b7435d010e69ab27b7a0aa47.

[table of contents | back to top]

Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1255042
NSF Division of Ocean Sciences (NSF OCE)	OCE-1756860

[table of contents | back to top]