Underway pH of seawater sampled during CCGS John P. Tully cruises in the northeast Pacific Ocean from Vancouver Island to Station P from 2019 to 2020

Website: https://www.bco-dmo.org/dataset/866582
Data Type: Cruise Results
Version: 1
Version Date: 2021-12-13

Project
» Constraining Upper-Ocean Carbon Export with Biogeochemical Profiling Floats (EXPORTS BGC Floats)

Contributors	Affiliation	Role
Lam, Phoebe J.	University of California-Santa Cruz (UCSC)	Principal Investigator
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Abstract
The pH (in situ, total scale) of near surface seawater was measured from the CCGS John P. Tully while underway during three Canadian Line P cruises conducted from 2019 through 2020. A prototype instrument, BGC-SUMO (Y. Takeshita, MBARI), was plumbed into the ship's seawater intake line to measure near surface pH while a collocated thermosalinograph measured near surface salinity and temperature from the same flow stream. This dataset provides information on these properties.

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Coverage

Spatial Extent: **N**:54.696 **E**:-123.206 **S**:48.252 **W**:-145.113
Temporal Extent: 2019-06-03 - 2020-02-23

Methods & Sampling

Underway measurements were made aboard the *CCGS John P. Tully* during three Canadian Line P cruises (2019-2020) in the northeast Pacific from Vancouver Island to Station P (50°N, 145°W).
Fisheries and Oceans Canada (DFO) Cruise numbers: 2019-006, 2019-008, 2020-001

pH

A prototype instrument (BGC-SUMO) developed by Dr. Yui Takeshita at MBARI was plumbed into the *CCGS John P. Tully* seawater intake (~5 m below the surface) line in the wet lab. Underway in situ pH on the total hydrogen ion concentration scale was measured with an ion-sensitive field-effect transistor (ISFET) pH sensor (Deep-Sea DuraFET; Johnson et al., 2016). The instrument was powered through an isolation transformer to prevent ground loop issues. The system was polled using a LabView interface and pH measurements were made every 10 milliseconds. pH sensor data were calibrated using discrete pH samples collected from the underway line (near BGC-SUMO) during the three cruises: 2019-006, 2019-008, and 2020-001 (n= 19, n= 5, n= 5, respectively)

Temperature and Salinity
Underway temperature and salinity were measured by a Sea-Bird Scientific SBE45 MicroTSG thermosalinograph located directly downstream (< 10 cm) of the BGC-SUMO pH sensor that was plumbed into the *CCGS John P. Tully* seawater intake (~5 m below the surface) line in the wet lab. Underway temperature and salinity were also measured with a *CCGS John P. Tully* thermosalinograph at the seawater intake location. These data were used to correct for warming between the seawater intake and the location where the instruments were plumbed into the underway line. The *CCGS John P. Tully* thermosalinograph data can be accessed through the Canadian Line P Program data archive (https://waterproperties.ca/linep/2019-001/index.php). The instrument was powered through an isolation transformer to prevent ground loop issues. The system was polled using a LabView interface and pH measurements were made every 10 milliseconds.

Data Processing Description

Underway pH
Discrete pH and BGC-SUMO pH data were converted from pH values measured at the BGC-SUMO TSG temperature to in situ pH values using the ship-board TSG intake temperature. This pH temperature conversion calculation was performed using the program CO2SYSv3 (*Lewis & Wallace,* 1998; *Sharp et al.,* 2020; *van Heuven et al.,* 2011). An average of discrete TA samples (QF as good), also collected during these cruises, was used in the CO2SYSv3 calculations. The following constants were chosen for CO2SYSv3 input: K_1K_2 of Lueker et al (2000); K_{SO4} of Dickson (1990); KF of Perez & Fraga (1987); TB of Lee (2010). The mean of pH residuals (BGC-SUMO pH – discrete pH, both at BGC-SUMO TSG temperature) was near zero for all cruises ($4.5x10^{-07}$, $-1.0x10^{-06}$, $-3.3x10^{-06}$; for cruises 2019-006, 2019-008, 2020-001, respectively).

Problem report
Underway pH measurements during the sensor warm-up phase for each cruise were given a Quality Flag (QF) of 4 or 3, determined based on comparison with in-line temperature and salinity data. During the return transits for cruises 2019-006 and 2020-001, large discrepancies between BGC-SUMO and discrete pH data were observed. These underway pH data were assigned a QF = 3. Unrealistic pH data for this region (values > 8.4 and < 7.6) were also assigned a QF of 4. A moving mean filter with a sliding window of 200 (~2 second resolution) was applied to the pH data to identify irregular spikes, which were assigned a QF = 3. When ship TSG temperature or salinity values were missing, BGC-SUMO pH data were set to NaN.

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BCO-DMO Processing:

- Imported data from source file "combined_SUMO_data_FORMATTED.xlsx" into the BCO-DMO data system.
- Data file imported using missing data identifiers "NaN". The missing data identifier "NaN" in the original source file will be displayed as appropriate based on the type of file you download from the BCO-DMO data system. For example, missing data will be shown as blank (null) values in the csv files. In MATLAB .mat files it will be displayed as NaN. When viewing data at BCO-DMO the missing value will be shown as "nd" meaning "no data."
- Converted separate date and time fields to single datetime column with ISO8601 format.
- Added column for vessel/ship
- Added conventional header with dataset name, PI name, version date.
- Modified parameter (column) names to conform with BCO-DMO naming conventions. (The only allowed characters are A-Z,a-z,0-9, and underscores. No spaces, hyphens, commas, parentheses, or Greek letters).

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Data Files

File
underway_ph.csv (Comma Separated Values (.csv), 26.13 MB) MD5:702a425068701dd31ab21277a99c01b5 Primary data file for dataset ID 866582

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Related Publications

Dickson, A. G. (1990). Standard potential of the reaction: AgCl(s) + 1/2 H2(g) = Ag(s) + HCl(aq) and the standard acidity constant of the ion HSO4− in synthetic sea water from 273.15 to 318.15 K. The Journal of Chemical Thermodynamics, 22(2), 113–127. doi:10.1016/0021-9614(90)90074-z https://doi.org/10.1016/0021-9614(90)90074-Z
Methods

Johnson, K. S., Jannasch, H. W., Coletti, L. J., Elrod, V. A., Martz, T. R., Takeshita, Y., Carlson, R.J., and Connery, J. G. (2016). Deep-Sea DuraFET: A Pressure Tolerant pH Sensor Designed for Global Sensor Networks. Analytical Chemistry, 88(6), 3249–3256. doi:10.1021/acs.analchem.5b04653
Methods

Lee, K., Kim, T.-W., Byrne, R. H., Millero, F. J., Feely, R. A., & Liu, Y.-M. (2010). The universal ratio of boron to chlorinity for the North Pacific and North Atlantic oceans. Geochimica et Cosmochimica Acta, 74(6), 1801–1811. doi:10.1016/j.gca.2009.12.027
Methods

Lewis, E. R., & Wallace, D. W. R. (1998). Program Developed for CO2 System Calculations. Environmental System Science Data Infrastructure for a Virtual Ecosystem. https://doi.org/10.15485/1464255
Methods

Lueker, T. J., Dickson, A. G., & Keeling, C. D. (2000). Ocean pCO2 calculated from dissolved inorganic carbon, alkalinity, and equations for K1 and K2: validation based on laboratory measurements of CO2 in gas and seawater at equilibrium. Marine Chemistry, 70(1-3), 105–119. doi:10.1016/s0304-4203(00)00022-0 https://doi.org/10.1016/S0304-4203(00)00022-0
Methods

Perez, F. F., & Fraga, F. (1987). Association constant of fluoride and hydrogen ions in seawater. Marine Chemistry, 21(2), 161–168. doi:10.1016/0304-4203(87)90036-3
Methods

Sharp, J. D., Pierrot, D., Humphreys, M. P., Epitalon, J.-M., Orr, J. C., Lewis, E. R., & Wallace, D. W. R. (2020). CO2SYSv3 for MATLAB (v3.0.1) [Computer software]. Zenodo. https://doi.org/10.5281/ZENODO.3952803 https://doi.org/10.5281/zenodo.3952803
Software

Van Heuven, S., Pierrot, D., Rae, J. W. B., Lewis, E., & Wallace, D. W. R. (2011). MATLAB Program Developed for CO2 System Calculations. ORNL/CDIAC-105b. Carbon Dioxide Information Analysis Center (CDIAC). https://doi.org/10.3334/CDIAC/OTG.CO2SYS_MATLAB_V1.1 https://doi.org/10.3334/CDIAC/otg.CO2SYS_MATLAB_v1.1
Software

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Related Datasets

IsRelatedTo

Fassbender, A. J., Johannessen, S., Long, J. S., Wright, C. (2021) **Dissolved and particulate carbon and nitrogen data from seawater collected during CCGS John P. Tully cruises in the northeast Pacific Ocean from Vancouver Island to Station P from 2018 to 2020.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2021-12-07 doi:10.26008/1912/bco-dmo.865893.1 [view at BCO-DMO]

Johannessen, S., Fassbender, A. J., Long, J. S., Wright, C. (2021) **DOC and TOC of seawater collected during CCGS John P. Tully cruises in the northeast Pacific Ocean from Vancouver Island to Station P from 2018 to 2020.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2021-12-06 doi:10.26008/1912/bco-dmo.865829.1 [view at BCO-DMO]

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Parameters

Parameter	Description	Units
ISO_DateTime_UTC	Date and time in ISO8601 standard format (YYYY-MM-DDThh:mm:ssZ)	unitless
Vessel	Vessel	unitless
Cruise_ID	Cruise	unitless
Latitude	Latitude of sample collection	decimal degrees
Longitude	Longitude of sample collection	decimal degrees
pH_in_situ	In situ pH value calculated using program CO2SYSv3 with conversion of discrete pH and SUMO pH data	unitless
pH_QF	pH measurement quality flag where 2=acceptable; 3=questionable; 4=bad; 6=mean of replicate; 8=sample lost; 9=not sampled	unitless
Temperature	Underway temperature as measured with TSG	degrees Celsius
Salinity	Underway salinity as measured with TSG from the ship's intake about 5 meters below the surface	practical salinity unit (PSU)
Date	Date of sample collection	unitless

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Instruments

Dataset-specific Instrument Name	Deep-Sea DuraFET (DSD) sensor
Generic Instrument Name	pH Sensor
Dataset-specific Description	pH was measured using a Deep-Sea Durafet (DSD) sensor
Generic Instrument Description	An instrument that measures the hydrogen ion activity in solutions. The overall concentration of hydrogen ions is inversely related to its pH. The pH scale ranges from 0 to 14 and indicates whether acidic (more H+) or basic (less H+).

Dataset-specific Instrument Name	BGC-SUMO
Generic Instrument Name	pH Sensor
Dataset-specific Description	A prototype instrument (BGC-SUMO; Y. Takeshita - yui@mbari.org) for measuring seawater pH on underway ships was plumbed into the CCGS John P. Tully seawater intake line
Generic Instrument Description	An instrument that measures the hydrogen ion activity in solutions. The overall concentration of hydrogen ions is inversely related to its pH. The pH scale ranges from 0 to 14 and indicates whether acidic (more H+) or basic (less H+).

Dataset-specific Instrument Name	SBE45 MicroTSG thermosalinograph
Generic Instrument Name	Sea-Bird SBE 45 MicroTSG Thermosalinograph
Dataset-specific Description	Underway temperature and salinity were measured near the pH sensor by an SBE45 MicroTSG thermosalinograph
Generic Instrument Description	A small externally powered, high-accuracy instrument, designed for shipboard determination of sea surface (pumped-water) conductivity and temperature. It is constructed of plastic and titanium to ensure long life with minimum maintenance. It may optionally be interfaced to an external SBE 38 hull temperature sensor. Sea Bird SBE 45 MicroTSG (Thermosalinograph)

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Deployments

Line-P_cruises

Website	https://www.bco-dmo.org/deployment/744516
Platform	CCGS John P. Tully
Description	Line P is an oceanic transect of 26 periodically sampled stations running from southern Vancouver Island to "Ocean Station Papa", situated at 50°N 145°W. Ocean (Weather) Station Papa, station P26, was originally operated as an ocean weather station from December of 1949 through 1981. After 1981, the Line-P / Station-P program was then taken over by the Institute of Ocean Sciences from Fisheries and Oceans Canada (DFO). While hydrographic (CTD-based) measurements are made at all of the 26 sites, water chemistry (bottle rosettes) and plankton (bongo) samples are only made at stations P4, P8, P12, P16, P20, and P26. Of those expanded sampling variables sites, all but P8 are featured in this web summary. See: https://www.st.nmfs.noaa.gov/copepod/time-series/ca-50903/ https://www.waterproperties.ca/linep/index.php

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Project Information

Constraining Upper-Ocean Carbon Export with Biogeochemical Profiling Floats (EXPORTS BGC Floats)

Coverage: Eastern Subarctic Pacific near Ocean Station Papa (50°N, 145°W)

OCE-1756932 Start Date: 2018-03-01
OCE-2032754 Start Date: 2020-05-28

NSF abstract:
A goal in chemical oceanography is to advance our understanding of the global carbon cycle, specifically to quantify the transfer of carbon from the surface ocean to depth through the sinking of particles produced by marine organisms. Yet, modern global estimates of this process (commonly called carbon export) differ by over 100%. These estimates are often derived from regional relationships between ocean measurements and satellite observations that are then applied globally. Persistent differences between the satellite and field-based estimates of carbon export have been found throughout the ocean, suggesting that improvements are needed. This project will determine whether profiling floats equipped with chemical sensors can be used to estimate the export of carbon in the ocean. Floats will be deployed at Ocean Station Papa, but the approach is scalable in nature and could be used to validate and improve the satellite algorithms used for global carbon export determinations. The project will support a female, early career scientist and a postdoc, as well as facilitate international collaboration with Canadian scientists. Additionally, the results may assist the National Aeronautics and Space Administration (NASA) EXPORTS campaign as well as other satellite carbon export development efforts.

Modern global estimates of the biological pump differ by over 100% (~5 to >12 Pg C yr-1) making it challenging to determine the role of marine biogeochemical (BGC) cycling in modern climate and climate variability. Global carbon export estimates are often derived from regional empirical relationships between field and satellite observations that are then applied globally. Persistent discrepancies between unique satellite algorithms and unique geochemical approaches suggest that accurately quantifying the biological pump remains a fundamental research goal. This project will assess the capability of using BGC profiling floats to estimate the export of distinct biogenic carbon pools (dissolved and particulate organic carbon, and particulate inorganic carbon). By using BGC floats to close multiple upper ocean tracer budgets this project will address two known issues common to other geochemical approaches: assumptions about (1) dissolved organic carbon cycling and (2) the integration depth used for annual carbon export assessments. The method will be tested at Ocean Station Papa, but is scalable in nature and could be used to develop a carbon export database suitable for the validation and training of satellite algorithms required for global carbon export determinations. Results from the floats will be compared to satellite carbon export algorithm estimates over the 5-year float lifetimes. Ten years of existing BGC data from profiling floats and a mooring in the region will also be used to provide further context about interannual variability.

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-2032754
NSF Division of Ocean Sciences (NSF OCE)	OCE-1756932

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