

**Investigators:** Wiley Evans (Hakai Institute), Katie Pocock (Hakai Institute), Carrie Weekes (Hakai Institute), and Alex Hare (Hakai Institute)

**Title:** High-resolution record of surface seawater CO<sub>2</sub> content from December 2014 to April 2016 collected in Hyacinthe Bay, British Columbia, Canada

**Abstract:** Quadra Island, at the northern terminus of the Salish Sea, has been a site for shore-based and high-resolution measurement of surface seawater CO<sub>2</sub> content since December 2014. Measurements of in situ temperature, salinity, and CO<sub>2</sub> partial pressure are made near-continuously on seawater drawn from a sample line with an intake 50 m from shore and a depth of 1 m in Hyacinthe Bay on the eastern side of Quadra Island. The effort to collect these data are part of the Hakai Institute's directive to advance the understanding of carbon cycling in northeast Pacific coastal settings with specific emphasis on ocean acidification. This data contribution consists of measurements from December 19, 2014 to April 5, 2016.

**Cite as:** Evans, W., K. Pocock, C. Weekes, and A. Hare. (2021). High-resolution record of surface seawater CO<sub>2</sub> content from December 2014 to April 2016 collected in Hyacinthe Bay, British Columbia, Canada. Version 2.0. Hakai Institute. Dataset. [access date].

**Type of Study:** Continuous data record

**Temporal Coverage:** December 19, 2014 to April 5, 2016

**Spatial Coverage:** Seawater drawn from 1-m depth approximately 50 m from shore in central Hyacinthe Bay; eastern Quadra Island; northern Salish Sea; 50.1160°N, 125.2220°W

**Geographic Names:** Quadra Island; Northern Salish Sea; British Columbia coast; North Pacific Ocean

**Expocode:** 189920141219

**Platforms:** Shore-side laboratory; Hakai Institute Quadra Island Field Station

**Version:** 2.0

**Submission Date:** January 14, 2021

**Change log:**

This submission was updated from version 1.0 to include columns for measurements made at the seawater intake in subsequent data files, columns for adjusted TSG-T (SST), pCO<sub>2</sub>, and fCO<sub>2</sub> values to account for warming between the seawater intake and the equilibrator, and columns for derived CO<sub>2</sub> system parameters computed using the regional alkalinity-salinity relationship published in Evans et al. (2019), the carbonic acid dissociation constants from Waters et al.

(2014), the bisulfate dissociation constant from Dickson et al. (1990), the hydrogen fluoride dissociation constant from Perez and Fraga (1987), and total boron concentration from Uppström (1974).

A correction for warming of seawater between the intake and the equilibrator was conducted by first compiling records of the temperature difference between these locations using measurements at the seawater intake from a Sea-Bird Electronics SBE 56 temperature sensor (accuracy = 0.002 °C) between October 2017 and December 2020 (consisting of time periods in late 2017, late 2019, and the latter half of 2020) and from a Van Essen Instruments CTD-Diver (unit 8975 and accuracy = 0.1 °C) for the first half of 2020. Both CTD-Diver units underwent calibration in our laboratory within tanks of temperature-controlled seawater and using a reference RBR Concerto CTD. CTD-Diver data provided as part of this data product are calibrated measurements with improved temperature accuracy of 0.02 °C. The compiled records of the temperature difference between the intake and the equilibrator were then averaged (mean  $\pm$  1 standard deviation =  $0.17 \pm 0.15$ ), and this average was used to correct the entire dataset from equilibrator temperature to in situ sea surface temperature. Equilibrator temperature is taken to be the temperature as recorded by the thermosalinograph (TSG), as this closely matched the temperature recorded by an RTD probe in the equilibrator (slope = 1.006, offset = 0.129; RMSE = 0.164). The RTD probe temperature at times was noisy and intermittent, and not included in version 2.0 of this dataset. The temperature offset between the TSG and the seawater intake records was also used to adjust the TSG temperature to SST.

**Filename:** QuadraSuperCO2\_5mindata\_Dec2014\_Apr2016\_v2.xlsx

**Data dictionary / header information:**

- (1) Yearday: numeral day of the year
- (2) Year: calendar year
- (3) Matlab Serial Date Number (days since Jan 1 0000): serial date number in Matlab format
- (4) Excel Serial Date Number (days since Jan 1 1990): serial date number in Excel format
- (5) TSG-T (deg C): SBE 45 TSG seawater temperature in degrees C
- (6) TSG-S (PSS-78): SBE 45 TSG seawater salinity in Practical Salinity Units
- (7) corrected xCO2 (ppm): corrected SW CO2 mole fractions in wet air (ppm)
- (8) equilibrator pressure (kPa): total pressure of equilibration (equilibrator differential pressure + LI840 cell pressure; kPa)
- (9) SWpCO2@TSG\_T (uatm)
- (10) SWfCO2@TSG\_T (uatm)
- (11) SBE56\_T (deg C)
- (12) DiverCTD8975\_Pressure (standard atm pressure removed, mbar)
- (13) DiverCTD8975\_T (deg C)
- (14) DiverCTD8975\_S (PSS-78)
- (15) DiverCTD8967\_Pressure (standard atm pressure removed, mbar)
- (16) DiverCTD8967\_T (deg C)
- (17) DiverCTD8975\_S (PSS-78)

- (18) SBE 37 T (deg C)
- (19) SBE 37 S (PSS-78)
- (20) SST (TSG-T minus mean delta-T)
- (21) SWpCO<sub>2</sub>@SST (uatm): SW CO<sub>2</sub> partial pressure in wet air (uatm)
- (22) SWfCO<sub>2</sub>@SST (uatm): SW CO<sub>2</sub> fugacity in wet air (uatm)
- (23) TA (umol/kg; from Evans et al., 2019 relationship)
- (24) TCO<sub>2</sub> (umol/kg; Waters et al constants)
- (25) pH\_T (total scale; Waters et al constants)
- (26) Omega\_arag (Waters et al constants)
- (27) Omega\_calc (Waters et al constants)
- (28) Revelle factor (Waters et al constants)
- (29) Date and Time: in GMT yyyy-mm-dd hh:mm:ss
- (30) Latitude (deg N): degrees north
- (31) Longitude (deg W): degrees west

**Researcher Contact:** Please direct questions regarding these data to Wiley Evans (wiley.evans@hakai.org).

**Researcher institution:** Hakai Institute

#### **Core Measured Variables:**

*Partial pressure of carbon dioxide*

**Abbreviation:** SWpCO<sub>2</sub>@SST

**Unit:**  $\mu\text{atm}$

**Observation type:** measurements from continuously flowing seawater stream

**In-situ/Manipulation/Response variable:** In situ observation

**Measured or calculated:** calculated from measured CO<sub>2</sub> mole fractions (xCO<sub>2</sub>) and ambient atmospheric pressure.

**Sampling instrument:** Sunburst Sensors Shipboard Underway pCO<sub>2</sub> Environmental Recorder (with showerhead equilibrator)

**Analyzing instrument:** Sunburst Sensors Shipboard Underway pCO<sub>2</sub> Environmental Recorder uses a LI-COR LI-840A non-dispersive infrared detector

**Detailed sampling and analyzing information:** Seawater pCO<sub>2</sub> data were calculated from corrected measurements of CO<sub>2</sub> mixing ratio (xCO<sub>2</sub>) made using a Sunburst Sensors Shipboard Underway pCO<sub>2</sub> Environmental Recorder (SUPERCO<sub>2</sub>) following many recommended protocols by Pierrot et al. (2009) with the system theory and calculations described in detail elsewhere (Hales et al., 2004; Evans et al., 2015; Evans et al., 2019). Seawater continuously flowed at 1 GPM first through a Sea-Bird Electronics SBE 45 MicroTSG Thermosalinograph and then to the equilibrator (showerhead). Carrier gas (marine air) is pumped into the equilibrator from the electronics box of the SUPERCO<sub>2</sub> at  $\sim 100 \text{ ml min}^{-1}$ . Full equilibration was verified by injecting high and low CO<sub>2</sub> gas standard into the equilibration chamber and verifying carrier gas concentrations returned to the same pre-disturbance xCO<sub>2</sub>. These tests also revealed the response time of the equilibrator to be  $\sim 5$  mins. Equilibrated carrier gas is then supplied to a

non-dispersive infrared gas analyzer (LI-COR LI840A CO<sub>2</sub>/H<sub>2</sub>O) housed within the electronics box. Carrier gas is then recirculated through the system, minimizing the need for make-up air in the equilibrator. Pressure and temperature were continuously measured in the equilibrator using a Honeywell ASCX Microstructure Pressure Sensor and an Omega Fast Response RTD, respectively. Equilibrated carrier gas, three standard gases of known mixing ratio (nominally 150, 450, and 750 ppm), and unaltered marine air were all plumbed to provide gas flow to the electronics box. The system is controlled using National Instruments LabVIEW software. The software controls data acquisition from the thermosalinograph, the pressure and temperature sensors, and the LI-COR; while also controlling Valco Instruments Co. Inc. (VICI) multi-port actuators that cycle between the gas streams plumbed to the electronics box. None of the gas streams were dried prior to analysis, and all measurements were made at 2 Hz. The prescribed measurement scheme controlled by the software was to supply equilibrated carrier gas from the equilibrator to the LI-COR continuously for 720 minutes, then cycle the actuators to consecutively allow for the standard gas streams and unaltered marine air to be measured for 90 s each at 100 ml min<sup>-1</sup> before returning to sample the carrier gas equilibrated with seawater xCO<sub>2</sub>. From each sequence of standard gas measurements, the final 20 s of data in the 80 s interval before the actuator changed position were used to construct calibration functions that were then interpolated in time between standard gas sequences. These functions were subsequently used to calibrate the xCO<sub>2</sub> measurements of seawater equilibrated carrier gas. Corrected seawater xCO<sub>2</sub> was then adjusted for under- or over-pressurization in the equilibrator using the ratio of equilibrator to vented LI-COR cell pressure, and then converted to pCO<sub>2</sub> using atmospheric pressure measured by the LI-COR. The 2 Hz seawater pCO<sub>2</sub>, temperature and salinity data were quality controlled by removing questionable measurements, and then averaged in 5-min interval bins. Finally, pCO<sub>2</sub> at the equilibrator temperature was adjusted to sea surface temperature using the average temperature difference measured between the seawater intake and the equilibrator (see Change Log note). Uncertainty in SWpCO<sub>2</sub>@SST was computed by adding the component uncertainties in quadrature: LI840A uncertainty (1 ppm, according to manufacturer), calibration uncertainty (0.5 ppm, by comparison with WMO traceable standard from ESRL), equilibrator temperature uncertainty (0.164 degrees C, by comparison between RTD probe and the TSG temperature), equilibrator pressure uncertainty (2 hPa), and uncertainty in the warming correction (0.15 degrees C, 1 standard deviation of the average difference between intake and TSG temperatures). Computed at a pCO<sub>2</sub> of 400 uatm, this equates to  $\sqrt{1^2 + 0.5^2 + 2.76^2 + 0.79^2 + 2.513^2} = 3.98$  uatm.

**Replicate information:** N/A

**Standardization description:** xCO<sub>2</sub> calibration functions developed during periodic sequential analysis of gas standards of known concentration (nominally 150, 450, and 750 ppm)

**Standardization frequency:** Every 720 minutes.

**CRM manufacturer:** Scott-Marrin Inc.

**Poison name:** N/A

**Poison volume:** N/A

**Poison correction:** N/A

**Uncertainty:** < 1% or 3.976 μatm at 400 uatm

**Quality flag convention:** no quality flag applied

**Method reference:** Hales, B., D. Chipman, and T. Takahashi (2004), High-frequency measurements of partial pressure and total concentration of carbon dioxide in seawater using microporous hydrophobic membrane contactors, *Limnology and Oceanography: Methods*, 2, 356-364; Pierrot, D., C. Neill, K. Sullivan, R. Castle, R. Wanninkhof, H. Lüger, T. Johannessen, A. Olsen, R. A. Feely, and C. E. Cosca (2009), Recommendations for autonomous underway pCO<sub>2</sub> measuring systems and data-reduction routines, *Deep Sea Research Part II: Topical Studies in Oceanography*, 56(8-10), 512-522, doi:10.1016/j.dsr2.2008.12.005; Evans, W., Mathis, J.T., Ramsay, J., and Hetrick, J. (2015). On the Frontline: Tracking Ocean Acidification in an Alaskan Shellfish Hatchery. *PLoS One* 10, e0130384; Evans, W., Pocock, K., Hare, A., Weekes, C., Hales, B., Jackson, J., Gurney-Smith, H., Mathis, J.T., Alin, S.R., and Feely, R.A. (2019). Marine CO<sub>2</sub> Patterns in the Northern Salish Sea. *Frontiers in Marine Science* 5, doi: 10.3389/fmars.2018.00536.

**Researcher name:** Wiley Evans

**Researcher institution:** Hakai Institute

#### *Sea surface temperature*

**Abbreviation:** SST

**Unit:** °C, ITS-90 scale

**Observation type:** measurements from continuously flowing seawater stream

**In-situ/Manipulation/Response variable:** In situ observation

**Measured or calculated:** calculated as the measured seawater temperature within the laboratory as determined by the TSG adjusted to sea surface temperature using the average difference in temperature between the TSG and the intake temperature records.

**Sampling instrument:** N/A

**Analyzing instrument:** Sea-Bird SBE 45 MicroTSG Thermosalinograph

**Detailed sampling and analyzing information:** 1 Hz data captured using National Instruments LabVIEW software

**Replicate information:** N/A

**Standardization description:** N/A

**Standardization frequency:** N/A

**CRM manufacturer:** N/A

**Poison name:** N/A

**Poison volume:** N/A

**Poison correction:** N/A

**Uncertainty:** 0.002°C

**Quality flag convention:** no quality flag applied

**Method reference:**

**Researcher name:** Wiley Evans

**Researcher institution:** Hakai Institute

#### *Salinity*

**Abbreviation:** Salinity

**Unit:** 1978 Practical Salinity Scale

**Observation type:** measurements from continuously flowing seawater stream

**In-situ/Manipulation/Response variable:** In situ observation

**Measured or calculated:** calculated from conductivity and temperature measurements

**Sampling instrument:** N/A

**Analyzing instrument:** Sea-Bird SBE 45 MicroTSG Thermosalinograph

**Detailed sampling and analyzing information:** 1 Hz data captured using National Instruments LabVIEW software

**Replicate information:** N/A

**Standardization description:** N/A

**Standardization frequency:** N/A

**CRM manufacturer:** N/A

**Poison name:** N/A

**Poison volume:** N/A

**Poison correction:** N/A

**Uncertainty:** 0.003 S/m

**Quality flag convention:** no quality flag applied

**Method reference:**