

R/V Ronald H. Brown METADATA - 2000

Class of Data: Surface ocean and atmospheric carbon dioxide concentrations

Dataset Identifier: R/V Ronald H. Brown

One File: RHB2000

Statement of how to cite dataset:

Ron Brown website: [http://www.aoml.noaa.gov/ocd/gcc/rvbrown\\_data2000.php](http://www.aoml.noaa.gov/ocd/gcc/rvbrown_data2000.php)

These data are made freely available to the public and the scientific community in the belief that their wide dissemination will lead to greater understanding and new scientific insights. The availability of these data does not constitute publication of the data. We rely on the ethics and integrity of the user to assure that AOML receives fair credit for our work. Please send manuscripts using this data to AOML for review before they are submitted for publication so we can insure that the quality and limitations of the data are accurately represented.

Measurement platform identifier: NOAA research vessel Ronald H. Brown (R104)

Cruise Information:

The Ron Brown conducted 7 major cruises in the Pacific Ocean for a total of 9 legs.

Project Information:

The system was operated by personnel from AOML or PMEL (Pacific Marine Environmental Laboratory) or by the Ron Brown's Chief Survey Tech, Jonathan Shannahoff. The work was sponsored by the Underway pCO<sub>2</sub> on Ships project of the NOAA climate program.

Scientist responsible for technical quality of dataset:

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Timestamp for initial submission of dataset: 09/18/08

Timestamp for the most recent update of dataset: 09/18/08

Timestamp period the dataset refers to: 3/18/2000 - 11/13/2000

Geographic area the dataset refers to:

10 S to 60 N  
170 W to 94 W

2000 Cruises:

- RB200001 - Tsunami Vents  
Seattle, WA to Newport, OR  
March 17, 2000 to March 22, 2000  
Chief Scientist - Scott Stalin  
Operator - Bob Castle
- RB200002 - Vents 2000  
Newport, OR to Seattle, WA  
March 24, 2000 to April 9, 2000  
Chief Scientist - N/A  
Operator - Jonathan Shannahoff
- RB200003 - Haruphone/Tsunami  
Seattle, WA to Seattle, WA  
May 22, 2000 to June 4, 2000  
Chief Scientist - Matt Fowler, Lt. Keith Roberts  
Operator - Jonathan Shannahoff
- RB200004 - Vents Leg 1  
Seattle, WA to Newport, OR  
June 17, 2000 to June 27, 2000  
Chief Scientist - Robert Embley  
Operator - Jonathan Shannahoff
- RB200005 - Vents Leg 2  
Newport, OR to Seattle, WA  
June 29, 2000 to July 18, 2000  
Chief Scientist - Robert Embley  
Operator - Jonathan Shannahoff
- RB200006 - Vents Leg 3  
Victoria, BC, Canada to Seattle, WA  
July 20, 2000 to August 4, 2000  
Chief Scientist - Ed Baker  
Operator - Jonathan Shannahoff
- RB200007 - FOCI 2000  
Dutch Harbor, AK to Dutch Harbor, AK  
September 16, 2000 to September 23, 2000  
Chief Scientist - Ed Cokelet  
Operator - Jonathan Shannahoff
- RB200008 - NOPP 2000  
Dutch Harbor, AK to San Diego, CA  
September 27, 2000 to October 9, 2000  
Chief Scientist - Bill Parker  
Operator - Jonathan Shannahoff

RB200009 - TAO 2000  
San Diego, CA to Panama Canal  
October 16, 2000 to November 13, 2000  
Chief Scientist - N/A  
Operator - Jonathan Shannahoff

List of variables included in this dataset:

COLUMN	HEADER	EXPLANATION
1.	GROUP/SHIP:	AOML_Brown for all underway data from the Ron Brown.
2.	CRUISE_DESIGNATION:	Cruise ID (e.g., RBYYYn where RB = Ron Brown, YYYY = the four digit year, and nn = the cruise number for that year).
3.	JD_GMT:	Decimal year day.
4.	DATE_DDMMYYYY:	GMT date. The date format has been changed to comply with the IOCCP recommendations.
5.	TIME_HH:MM:SS:	GMT time.
6.	LAT_DEC_DEGREE:	Latitude in decimal degrees (negative values are in the southern hemisphere).
7.	LONG_DEC_DEGREE:	Longitude in decimal degrees (negative values are in the western hemisphere).
8.	xCO2W_PPM:	Mole fraction of CO2 (dry) in the equilibrator headspace at equilibrator temperature (Teq) in parts per million.
9.	xCO2A_PPM:	Mole fraction of CO2 in air in parts per million.
10.	EqTEMP_C:	Temperature in equilibrator water in degrees centigade. Temperature in equilibrator measured with a calibrated thermistor.
11.	PRES_EQUIL_hPa:	Barometric pressure in the lab in hectopascals (1 hectopascal = 1 millibar).
12.	SST(TSG)_C:	Temperature from the ship's thermosalinograph in degrees centigrade.
13.	SAL(TSG)_PERMIL:	Salinity from the ship's thermosalinograph on the Practical Salinity Scale.
14.	fCO2w,eq:	Fugacity of CO2 in the equilibrator in microatmospheres calculated as outlined below.
15.	fCO2W@SST_uatm:	Fugacity of CO2 in sea water in microatmospheres calculated as outlined below.
16.	fCO2A_uATM:	Fugacity of CO2 in air in microatmospheres calculated as outlined below.

17. dfCO2\_uatm: Sea water fCO2 - air fCO2 in microatmospheres. This uses the average air value for the current hour.

The following fields have been QC'ed by the CO2 group:

GROUP/SHIP  
CRUISE\_DESIGNATION  
JD\_GMT  
DATE\_DDMMYYYY  
TIME\_HH:MM:SS  
LAT\_DEC\_DEGREE  
LONG\_DEC\_DEGREE  
xCO2W\_PPM  
xCO2A\_PPM  
EqTEMP\_C  
PRES\_EQUIL\_hPa  
fCO2w,eq  
fCO2W@SST\_uatm  
fCO2A\_uATM  
dfCO2\_uatm

The following fields are from the ship's onboard systems and the quality of this data cannot be verified:

SST(TSG)\_C  
Sal(TSG)\_Permil

Narrative description of system design:

#### CO2 ANALYTICAL SYSTEM:

The concentration of carbon dioxide (CO2) in surface ocean water is determined by measuring the concentration of CO2 in gas that is in contact with the water. Surface water is pumped ~ 100 m through 7/8" Teflon tubing from an inlet in the ship's bow to the equilibration chamber. Water comes from the bow intake ~4.2 m below the water line and the TSG is located close to the inlet. When the SST is below about 20 °C, friction in the pipes and from the pump cause heating and the Teq is higher than SST. When the SST is higher than about 25 °C, the ship's air conditioning cools the water and the Teq is lower than SST. The equilibration chamber has an enclosed volume of gas, or headspace, and a pool of seawater that continuously overflows to a drain. As the water flows through the chamber, the dissolved gases (like CO2) partition between the water and the headspace. At equilibrium, the ratio of CO2 in the water and in the headspace is influenced most by temperature, and that relationship is known. By measuring the concentration of CO2 in the headspace and the temperature in the chamber, the partial pressure (or fugacity) of CO2 in the surface water can be calculated.

#### INSTRUMENT DESCRIPTION

The general principle of instrumental design can be found in Wanninkhof and Thoning (1993), Ho et al. (1995), and Feely et al. (1999). The concentration of CO2 in the headspace gas is measured using the adsorption of infrared (IR) radiation, which results from changes in the rotational and vibrational energy state of the CO2 molecule. The LI-COR detector passes IR radiation through two 6" cells. The reference cell is flushed with a gas of known CO2 concentration. The sample cell is flushed with the headspace gas. A vacuum-sealed, heated filament is the

broadband IR source. The IR radiation alternates between the two cells via a chopping shutter disc. An optical filter selects an adsorption band specific for CO<sub>2</sub> (4.26 micron) to reach the detector. The solid state (lead selenide) detector is kept at -12 degrees °C for excellent stability and low signal noise (less than 0.2 ppm).

Several steps are taken to reduce interferences and to increase the accuracy of the measurements. After the equilibration chamber, the headspace travels through a drying trap to remove water vapor. During each analysis, the headspace gas is compared to a reference gas of known concentration. To improve the accuracy of the measurements, three different gaseous standards for CO<sub>2</sub> are analyzed once an hour instead of the headspace gas.

Analyzer: LI-COR 6251 (analog output) infrared (IR) analyzer.

Method of Analysis: Differential analyses relative to the low standard. Measures dried equilibrator headspace gas. Gas flow is stopped prior to IR readings.

Drying Method: The equilibrator headspace sample gas first goes through a glass condenser cooled to ~ 5 °C. The sample and standard gases pass through a short column of magnesium perchlorate before reaching the analyzer.

Equilibrator (setup, size, flows): The equilibrator is based on a design by R. Weiss and was fabricated from a plexiglass housing with ~8 L water reservoir and ~16 L gaseous headspace. Water flow rate is ~11 L/min. Headspace recirculation rate is ~200 ml/min.

Additional sensors:

Thermistor mounted in the bottom of the equilibrator.

Setra Barometer Model 370

YSI Model 600R thermosalinograph with temperature, salinity, and dissolved oxygen sensors. This TSG is mounted in the Hydro lab sink near the equilibrator and the two are teed off the uncontaminated seawater feed.

The dissolved oxygen measurements are not reported in the final data file.

Narrative statement identifying measurement method for each required parameter:

CALCULATIONS:

The mixing ratios of ambient air and equilibrated headspace air are calculated by fitting a second-order polynomial through the hourly averaged millivolt response of the detector versus mixing ratios of the standards. Mixing ratios of dried equilibrated headspace and air are converted to fugacity of CO<sub>2</sub> in surface seawater and water saturated air in order to determine the fCO<sub>2</sub>. For ambient air and equilibrator headspace, the fCO<sub>2a</sub> (or fCO<sub>2eq</sub>) is calculated assuming 100% water vapor content:

$$fCO_{2eq} = xCO_{2eq}(P-pH_{2O}) \exp(B_{11}+2*d_{12}) P/RT$$

where fCO<sub>2eq</sub> is the fugacity in the equilibrator, pH<sub>2O</sub> is the water vapor pressure at the sea surface temperature, P is the atmospheric pressure (in atm), T is the SST or equilibrator temperature (in K) and R is the ideal gas constant (82.057 cm<sup>3</sup>·atm·deg<sup>-1</sup>·mol<sup>-1</sup>). The exponential term is the fugacity correction where B<sub>11</sub> is the second virial coefficient of pure CO<sub>2</sub>

$$B11 = -1636.75 + 12.0408T - 0.032795T^2 + 3.16528E-5 T^3$$

and  $d12 = 57.7 - 0.118 T$  is the correction for an air-CO<sub>2</sub> mixture in units of cm<sup>3</sup>·mol<sup>-1</sup> (Weiss, 1974).

The calculation for the fugacity at SST involves a temperature correction term for the increase of fCO<sub>2</sub> due to heating of the water from passing through the pump and through 5 cm ID PVC tubing within the ship. The empirical temperature correction from equilibrator temperature to SST is:

$$fCO_2(SST) = fCO_2(eq) / \text{Exp}((T_{eq}-SST) * [0.03107 - 2.7851E-4 * T_{eq} - 1.8391E-3 * \ln(fco2eq * 1.0E-6)])$$

where SST is sea surface temperature and T<sub>eq</sub> is the equilibrator temperature in degrees °C.

#### Sampling Cycle:

The system runs on an hourly cycle during which 3 standard gases, 3 air samples from the bow tower and 8 surface water samples (from the equilibrator head space) are analyzed on the following schedule:

Mins. after hour	Sample
4	Low Standard
8	Mid Standard
12	High Standard
16.5	Water
21	Water
25.5	Water
30	Water
34	Air
38	Air
42	Air
46.5	Water
51	Water
55.5	Water
60	Water

#### NOTES ON DATA:

Columns have a default value of -999.99 in case of instrument malfunction, erroneous readings or missing data. Furthermore, if a suspicious xCO<sub>2</sub> value, pressure or temperature value is encountered, the fCO<sub>2</sub> is not calculated.

#### Analytical Instrument Manufacturer/Model:

The Ron Brown system (version 2.6) was built by Craig Neill in 1999. The analyzer is a LI-COR 6251 (analog output) infrared analyzer.

**Standard Gases and Reference Gas:** The three standard gases came from CMDL in Boulder and are directly traceable to the WMO scale. While individual data points above the high standard gas concentration or below the low standard gas concentration may not be accurate, the general trends should be indicative of the seawater chemistry.

#### Description of any additional environmental control:

The system is located in the Hydro Lab of the Ron Brown. The room is air-conditioned with little temperature fluctuation.

Resolution of measurement:

The resolution of the instrument is better than 0.1 ppm.

Estimated overall uncertainty of measurement:

The xCO<sub>2</sub>eq measurements are believed accurate to 0.1 ppm. The fCO<sub>2</sub>@SST measurements are believed to be precise to 0.2 ppm.

List of calibration gases used:

The standards used during the 2000 field season were:

STANDARD	TANK #	CONCENTRATION	VENDOR
Low	CA03334	298.47	CMDL
Low	CA03332	281.16	CMDL
Mid	CA03539	346.71	CMDL
Mid	CA03880	356.99	CMDL
High	CA01407	417.67	CMDL
High	CA03877	420.47	CMDL
High	N/A	524.99	CMDL

Traceability to an internationally recognized scale (including date/place of last calibration made):

All standards are obtained from NOAA/CMDL, now called the Global Monitoring Division of the Earth Research Laboratory and are directly traceable to WHO scale.

Uncertainty of assigned value of each calibration gas:

The uncertainty based on pre and post cruise calibrations is less than 0.05 ppm.

Pressure/Temperature/Salinity:

For information about the ship's thermosalinograph, contact Chief Survey Tech Jonathan Shannahoff at jonathan.shannahoff@noaa.gov.

Units:

All xCO<sub>2</sub> values are reported in parts per million (ppm) and fCO<sub>2</sub> values are reported in microatmospheres (uatm) assuming 100% humidity at the equilibrator temperature.

Bibliography:

- DOE (1994). Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2. DOE.
- Feely, R. A., R. Wanninkhof, H. B. Milburn, C. E. Cosca, M. Stapp and P. P. Murphy (1998). A new automated underway system for making high precision pCO<sub>2</sub> measurements onboard research ships. *Analytica Chim. Acta* 377: 185-191.
- Ho, D. T., R. Wanninkhof, J. Masters, R. A. Feely and C. E. Cosca (1997). Measurement of underway fCO<sub>2</sub> in the Eastern Equatorial Pacific on NOAA

- ships BALDRIGE and DISCOVERER, NOAA data report ERL AOML-30, 52 pp., NTIS Springfield.
- Wanninkhof, R. and K. Thoning (1993). Measurement of fugacity of CO<sub>2</sub> in surface water using continuous and discrete sampling methods. Mar. Chem. 44(2-4): 189-205.
- Weiss, R. F. (1970). The solubility of nitrogen, oxygen and argon in water and seawater. Deep-Sea Research 17: 721-735.
- Weiss, R. F. (1974). Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Mar. Chem. 2: 203-215.
- Weiss, R. F., R. A. Jahnke and C. D. Keeling (1982). Seasonal effects of temperature and salinity on the partial pressure of CO<sub>2</sub> in seawater. Nature 300: 511-513.

Comments related to all 2000 data:

1. xCO<sub>2</sub> values outside the range of the standard gases (i.e. below the low standard or above the high standard) are not as accurate as values within the range. However, the general trends should be indicative of the seawater chemistry.
2. A new system built by Craig Neill (System 2.6) was installed for this field season. Side-by-side tests were conducted in the laboratory of systems 2.5 and 2.6. The average difference in computed CO<sub>2</sub> concentration between them was 0.2723 ppm with a standard deviation of 0.43575 (n = 289). The main difference between the two systems is that the Licor infrared analyzer is now installed in a temperature controlled rack. In addition, KNF pumps are now being used for both air and equilibrator headspace gas.
3. The standard gases for the first 2 cruises were 298.47 ppm, 346.71 ppm, and 417.67 ppm. For the next 6 cruises the standards were 281.16 ppm, 356.99 ppm, and 420.47 ppm. For the last cruise the high standard was replaced with a 524.99 ppm standard due to the high CO<sub>2</sub> concentrations in the study area.

Comments related to the individual legs:

- RB200001: 1. Water values before March 18 at 1900 GMT were removed due to high variability in the readings. This was caused by air leaks in the water lines.
2. The system was down from 2130 GMT on March 18 to 0300 GMT on March 19 except for 1/2 hour while work was done on the plumbing connections.
3. The system was down from 2015 GMT to 2358 on March 20 for software modifications.
4. Data from 2045 GMT to 2400 on March 21 was discarded because system work corrupted the readings.
5. The system was down from 0430 to 0500 GMT on March 22 to replace a tube in the equilibrator.
- RB200002: 1. Due to problems getting the system running, no data was collected before April 1. Data in this file covers the period from April 1 at 0000 GMT through April 4 at 0246 GMT.
2. The regulator on the mid standard tank failed and there was no gas flow in that phase for the entire cruise. Examination of the Licor voltage response during the previous cruise showed a relationship between mid standard voltage response and voltage response in the low and high standard phases. This relationship is  $(VM - VL)/(VH - VL) = 0.421$  where VL, VM, and VH are voltages in the low, mid and high standard phases respectively. Using this equation, a synthetic mid standard voltage was created and applied to the previous cruise. The



difference between using the real and synthetic voltages for the previous cruise was less than 0.5 ppm. All concentrations for the current cruise were computed using this synthetic mid standard voltage.

- RB200003: 1. A high cyclical variation in air xCO<sub>2</sub> values caused me to suspect a leak. I therefore replaced all air xCO<sub>2</sub> values with 376.00, which I derived from climatology records provided by CMDL in Boulder. I used values from Cold Harbor, Alaska and Cape Meares, Oregon from 1993 to 1997. For each year I averaged all values in the period from late May to early June and plotted them by year. I used a linear fit to extrapolate each station's values to the year 2000 to arrive at the value of 376.00. This matches fairly closely with minimum air xCO<sub>2</sub> values observed during the cruise which fell in the range of 374.50 to 377.00.
- RB200004: 1. Due to high variation in air xCO<sub>2</sub> values I replaced all air xCO<sub>2</sub> values with 375.00, which I derived from climatology records provided by CMDL in Boulder. I used values from the station in Cold Harbor, Alaska from 1994 to 1998. For each year I averaged all readings taken between June 17 and June 27 and plotted them by year. I used a linear fit to extrapolate to the year 2000 to arrive at the value of 375.00.
- RB200005: 1. Due to high variation in air xCO<sub>2</sub> values I replaced all air xCO<sub>2</sub> values with 366.50, which I derived from climatology records provided by CMDL in Boulder. I used values from the station in Cape Meares, OR from 1989 to 1997. I removed values for 1992 and 1993 because they ruined the linear curve fit. There were no good values for 1995 and 1996. For each year I averaged all readings taken between June 29 and July 18 and plotted them by year. I used a linear fit to extrapolate to the year 2000 to arrive at the value of 366.50. This value is in close agreement with the minimum air values observed during the cruise.
- RB200006: 1. Due to high variation in air xCO<sub>2</sub> values I replaced all air xCO<sub>2</sub> values with 363.00, which I derived from climatology records provided by CMDL in Boulder. I used values from the station in Cape Meares, OR from 1989 to 1997. There were no good values for 1993 and 1995. For each year I averaged all readings taken between July 20 and August 4 and plotted them by year. I used a linear fit to extrapolate to the year 2000 to arrive at the value of 363.00. This value is in close agreement with the minimum air values observed during the cruise.  
2. On July 29 at approximately 1800 GMT the difference between the equilibrator temperature (EqT) and SST drops about 0.11 degrees C (from ~ 0.42 to ~ 0.31) and stays that way for the remainder of the cruise. EqT is measured at the equilibrator in the Hydro Lab and SST is measured at the seawater intake in the bow of the ship. For SST in the range of 16-17 degrees C, the normal difference is about 0.4 degrees.
- RB200007: No problems of note.
- RB200008: No problems of note.
- RB200009: No problems of note.