

R/V Ronald H. Brown METADATA - 2001

Class of Data: Surface ocean and atmospheric carbon dioxide concentrations

Dataset Identifier: R/V Ronald H. Brown

One File: RHB2001

Statement of how to cite dataset:

Ron Brown website: http://www.aoml.noaa.gov/ocd/gcc/rvbrown_data2001.php

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

Cruise Information:

The Ron Brown conducted 9 major cruises in the Pacific Ocean for a total of 12 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 pCO₂ 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: 10/29/2009

Timestamp for the most recent update of dataset: 10/29/09

Timestamp period the dataset refers to: 2/7/2001 - 12/3/2001

Geographic area the dataset refers to:

20 S to 60 N
125 E to 70 W

2001 Cruises:

- RB200101 - Gasex 2001
Panama Canal to Honolulu, HI
February 7, 2001 to March 7, 2001
Chief Scientist - Dick Feely
Operator - Jonathan Shannahoff and Bob Castle

- RB200102 - ACE-Asia
Honolulu, HI to Yokosuka, Japan
March 15, 2001 to April 19, 2001
Chief Scientist - Tim Bates
Operator - Jonathan Shannahoff

- RB200103T - FOCI Transit
Yokosuka, Japan to Dutch Harbor, AK
April 28, 2001 to May 4, 2001
Chief Scientist - N/A
Operator - Jonathan Shannahoff

- RB200103A - FOCI Leg 1
Dutch Harbor, AK to Kodiak, AK
May 6, 2001 to May 23, 2001
Chief Scientist - William Floering/Nancy Kachel
Operator - Jonathan Shannahoff

- RB200103B - FOCI Leg 2
Kodiak, AK to Dutch Harbor, AK
May 26, 2001 to June 8, 2001
Chief Scientist - Ned Cokelet
Operator - Jonathan Shannahoff

- RB200104 - Haruphone/Tsunami
Dutch Harbor, AK to Victoria, BC, Canada
June 11, 2001 to June 22, 2001
Chief Scientist - Scott Stalin
Operator - Jonathan Shannahoff

- RB200105 - Ocean Exploration/Groundfish
Victoria, BC, Canada to Newport, OR
June 27, 2001 to July 12, 2001
Chief Scientist - Waldo Wakefield
Operator - Jonathan Shannahoff

- RB200106 - Vents/Ropos
Newport, OR to Victoria, BC, Canada
July 14, 2001 to July 31, 2001
Chief Scientist - Bob Embley
Operator - Jonathan Shannahoff

RB200107 - Pioneer Seamount
 Seattle, WA to San Diego, CA
 August 28, 2001 to September 2, 2001
 Chief Scientist - Christopher G. Fox
 Operator - Jonathan Shannahoff

RB200108A - Epic Leg 1
 San Diego, CA to Santa Cruz, Galapagos Islands
 September 10, 2001 to October 6, 2001
 Chief Scientist - Chris Fairall
 Operator - Jonathan Shannahoff

RB200108B - Epic Leg 2
 Santa Cruz, Galapagos Islands to Arica, Chile
 October 9, 2001 to October 25, 2001
 Chief Scientist - Robert Weller
 Operator - Jonathan Shannahoff

RB200109 - TAO
 Arica, Chile to Balboa, Panama
 October 30, 2001 to December 3, 2001
 Chief Scientist - Brian Lake
 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:

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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

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

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SST(TSG)_C
Sal(TSG)_Permil

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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 T_{eq} 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 CO₂ (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 CO₂ 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 CO₂ in surface seawater and water saturated air in order to determine the fCO₂. For ambient air and equilibrator headspace, the fCO_{2a} (or fCO_{2eq}) is calculated assuming 100% water vapor content:

$$fCO_{2eq} = xCO_{2eq}(P-pH_2O) \exp(B_{11}+2*d_{12})P/RT$$

where fCO_{2eq} is the fugacity in the equilibrator, pH_{2O} 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 cm³·atm·deg⁻¹·mol⁻¹). The exponential term is the fugacity correction where B₁₁ is the second virial coefficient of pure CO₂

$$B_{11} = -1636.75 + 12.0408T - 0.032795T^2 + 3.16528E-5 T^3$$

and d₁₂ = 57.7 - 0.118 T is the correction for an air-CO₂ mixture in units of cm³·mol⁻¹ (Weiss, 1974).

The calculation for the fugacity at SST involves a temperature correction term for the increase of fCO₂ 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:

$$fCO_2(SST) = fCO_2(eq) / \exp((T_{eq}-SST) * [0.03107 - 2.7851E-4 * T_{eq} - 1.8391E-3 * \ln(fco_{2eq} * 1.0E-6)])$$

where SST is sea surface temperature and T_{eq} 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 xCO₂ value, pressure or temperature value is encountered, the fCO₂ 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 xCO₂eq measurements are believed accurate to 0.1 ppm. The fCO₂@SST measurements are believed to be precise to 0.2 ppm.

List of calibration gases used:

The standards used during the 2001 field season were:

STANDARD	TANK #	CONCENTRATION	VENDOR
Low	CA04453	296.11	CMDL
Low	CA04403	291.58	CMDL
Low, Mid	CC01782	357.58	CMDL
Mid, High	CA03182	400.95	CMDL
High	CA03888	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 System Research Laboratory and are directly traceable to WMO 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 xCO₂ values are reported in parts per million (ppm) and fCO₂ 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 pCO₂ 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 fCO₂ 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 CO₂ 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 CO₂ in seawater. *Nature* 300: 511-513.

Comments related to all 2001 data:

1. xCO₂ 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. The standard gases for the first cruise were 357.58 ppm, 400.95 ppm, and 524.99 ppm. For the next 7 cruises the standards were 296.11 ppm, 357.58 ppm, and 400.95 ppm. For cruise RB200107 the low standard was replaced with a 291.58 ppm standard. For the last 3 cruises, the standard gases were 291.58 ppm, 400.95 ppm, and 524.99 ppm.

Comments related to the individual legs:

- RB200101: 1. Data collection did not begin until Feb. 7, 2001 after the ship was outside the 200 mile limit of the Galapagos Islands.
- RB200102: 1. From 13:50 to 19:25 on March 20, seawater flow was shut down in order to perform system maintenance. Data from this period have been removed.
- RB200103T: No problems of note.
- RB200103A: No problems of note.
- RB200103B: No problems of note.

- RB200104: No problems of note.
- RB200105: 1. The system was down from July 3 at 1333 GMT to July 4 at 0100 GMT due to a touch-and-go in Astoria, Oregon.
- RB200106: 1. All water values from July 16 at 0415 to July 16 at 0800 were removed due to no water flow through the equilibrator.
- RB200107: 1. The system was shut down for approximately 7 hours from 8/30 at 2200 GMT to 8/31 at 0530 GMT while the ship did a touch-and-go inport at San Francisco.
- RB200108A: 1. The system was shut down for approximately 6-2/3 days from Sep. 14 to Sep. 20 because of a mechanical failure.
2. On Sep. 27 at 2230, gas flow in the air phase dropped to zero because of clogged tubing. For the remainder of the cruise I have inserted air values from the CO2 rug file of Pieter P. Tans and Thomas J. Conway of the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL). This file gives atmospheric CO2 concentrations by latitude band through 2000. The replaced air values were derived by adding 1.6 ppm to the Sep. 30, 2000 values for each latitude band. The value of 1.6 ppm is the average increase from 2000 to 2001 (personal communication from Tom Conway).
- RB200108B: 1. On Sep. 27 at 2230, gas flow in the air phase dropped to zero because of clogged tubing. For this entire cruise leg I have inserted air values from the CO2 rug file of Pieter P. Tans and Thomas J. Conway of the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL). This file gives atmospheric CO2 concentrations by latitude band through 2000. The replaced air values were derived by adding 1.6 ppm to the values for each latitude band after matching the time of year. The value of 1.6 ppm is the average increase from 2000 to 2001 (personal communication from Tom Conway).
- RB200109: 1. On Sep. 27 at 2230, gas flow in the air phase dropped to zero because of clogged tubing. For this entire cruise leg I have inserted air values from the CO2 rug file of Pieter P. Tans and Thomas J. Conway of the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL). This file gives atmospheric CO2 concentrations by latitude band through 2000. The replaced air values were derived by adding 1.8 ppm to the values for each latitude band after matching the time of year. The value of 1.8 ppm is the average increase from 2000 to 2001 (personal communication from Tom Conway).