

R/V Ronald H. Brown METADATA - 2002

Class of Data: Surface ocean and atmospheric carbon dioxide concentrations

Dataset Identifier: R/V Ronald H. Brown

One File: RHB2002

Statement of how to cite dataset:

Ron Brown website: http://www.aoml.noaa.gov/ocd/gcc/rvbrown_data2002.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 Atlantic and eastern Pacific Oceans for a total of 13 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: 11/18/09

Timestamp for the most recent update of dataset: 11/18/09

Timestamp period the dataset refers to: 1/15/2002 - 11/8/2002

Geographic area the dataset refers to:

15 S to 45 N
115 W to 30 W

2002 Cruises:

- RB200201T - Transit 2002A
Charleston, SC to Recife, Brazil
January 15, 2002 to January 27, 2002
Chief Scientist - N/A
Operator - Jonathan Shannahoff
- RB200201 - Tropical-Subtropical Interaction
Recife, Brazil to Bridgetown, Barbados
February 1, 2002 to February 23, 2002
Chief Scientist - Bob Molinari
Operator - Jonathan Shannahoff
- RB200202 - Plueddemann Moorings
Bridgetown, Barbados to Bridgetown, Barbados
March 3, 2002 to March 7, 2002
Chief Scientist - Albert J. Plueddemann
Operator - Jonathan Shannahoff
- RB200203 - Grenada Passage
Bridgetown, Barbados to St. Thomas, U.S. Virgin Islands
March 10, 2002 to March 18, 2002
Chief Scientist - Albert J. Plueddemann
Operator - Jonathan Shannahoff
- RB200204T - Transit 2002B
St. Thomas, U.S. Virgin Islands to Jacksonville, FL
March 25, 2002 to March 26, 2002
Chief Scientist - N/A
Operator - Jonathan Shannahoff
- RB200204 - Western Boundary Time Series
Jacksonville, FL, to Miami, FL
June 17, 2002 to June 29, 2002
Chief Scientist - Sonia Bauer
Operator - Jonathan Shannahoff
- RB200205A - Air Quality in Coastal New England Leg A
Charleston, SC to Portsmouth, NH
July 13, 2002 to July 26, 2002
Chief Scientist - Tim Bates
Operator - Jonathan Shannahoff
- RB200205B - Air Quality in Coastal New England Leg B
Portsmouth, NH to Charleston, SC
July 26, 2002 to August 11, 2002
Chief Scientist - Tim Bates
Operator - Jonathan Shannahoff

- RB200206 - South Florida Plume Study
 Charleston, SC to Miami, FL
 August 17, 2002 to August 23, 2002
 Chief Scientist - Jules Craynock
 Operator - Jonathan Shannahoff
- RB200207 - Ocean Exploration Hudson Canyon
 Miami, FL to New York, NY
 August 27, 2002 to September 15, 2002
 Chief Scientist - Peter Rona
 Operator - Jonathan Shannahoff
- RB200208T - Transit 2002C
 New York, NY to San Juan, Puerto Rico
 September 19, 2002 to September 24, 2002
 Chief Scientist - N/A
 Operator - Jonathan Shannahoff
- RB200208 - Ocean Exploration Puerto Rican Trench
 San Juan, Puerto Rico to San Juan, Puerto Rico
 September 24, 2002 to September 30, 2002
 Chief Scientist - Uri Ten Brick
 Operator - Jonathan Shannahoff
- RB200209 - TOGA/TAO 2002
 Balboa, Panama to Balboa, Panama
 October 8, 2002 to November 8, 2002
 Chief Scientist - Patrick A'Hearn
 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., RBYYYYnn 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 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 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 2002 field season were:

STANDARD	TANK #	CONCENTRATION	VENDOR
Low	CA04403	291.58	ESRL
Low	CC114999	275.63	ESRL
Low	CA01433	293.73	ESRL
Mid	CA02901	339.57	ESRL
Mid	CA05098	358.87	ESRL
High/Mid	CC71655	423.28	ESRL
High	CA03079	431.30	ESRL
High	CA03888	524.99	ESRL
High	CC71588	531.98	ESRL

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 2002 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 2 cruises (RB200201T & RB200201) were 291.58 ppm, 339.57 ppm, and 431.30 ppm. For the next 2 cruises (RB200202 & RB200203) the standards were 275.63 ppm, 339.57 ppm, and 431.30 ppm. For cruise RB200204T the standards were 275.63 ppm, 339.57 ppm, and 524.99 ppm. For cruises RB200204, RB200204, RB200204, RB200204, RB200204, and RB200204 the standards were 293.73 ppm, 358.87 ppm, and 423.28 ppm. For cruise RB200209 the standards were 293.73 ppm, 358.87 ppm, and 531.98 ppm.

Comments related to the individual legs:

RB200201T: 1. For the first 15 hours of the leg, there was no flow in either the mid standard or the high standard. For this time period I derived voltage values for mid and high standards by using a 2nd order curve fit between the low standard voltage and the other two based on the next 42 hours of values. For the mid standard (Std 2) I used the equation $S2V = -19.141 * S1V^2 + 2.8042 * S1V + 0.2021$ ($R^2 = 0.9974$) for the mid standard and $S3V = -57.415 * S1V^2 + 6.2084 * S1V + 0.5545$ ($R^2 = 0.9819$) for the high standard. Water values for this period were in the range of 335 - 365 ppm and air values were in the range of 377 - 381 ppm, both of which are close to the mid standard value of 340 ppm. For this reason I believe that the values in the file are within +/- 3 ppm of the actual value.

2. The feed from the ship's computer system was down for about 12 hours on Jan. 21 - Jan. 22 and for that period the system recorded no SST or salinity from the ship's TSG. I derived values for SST from the equilibrator thermistor and for salinity from the YSI probe for this time period. For SST, I used the equation $SST = EqT - 0.11$ based on approximately 42 hours worth of values where SST was above 27 degrees C. For salinity, I used the equation $S = YSI \text{ salinity} - 0.44$ based on all other data from this leg.

3. There were 3 data dropouts of approximately 30, 36, and 42 hours where the ship was not allowed to sample in certain territorial waters.

RB200201: No problems of note.

RB200202: 1. The low standard cylinder was changed on March 4 to 275.63. Some values were removed at this time because of the change. After the change, the air values increased by ~2 ppm. We have been unable to determine the cause of this and have left the values in the data file.

2. The equilibrator thermistor was reading incorrectly up until the time of the cylinder change. I have substituted a derived value for equilibrator temperature for the first part of the cruise using the YSI TSG temperature as follows: $EqT = 0.9401 * YSI \text{ T} + 1.334$ ($r^2 = 0.8904$). This equation was derived from values after the cylinder change where comparisons with SST and the YSI indicate the thermistor was reading correctly.

RB200203: No problems of note.

RB200204T: 1. Air values on this leg were high - in the range 382 - 386 ppm. No reason for the high readings could be found but they should be considered suspect. Normal air values for this region and time of year should be a little over 370 ppm.

RB200204: No problems of note.

RB200205A: 1. Seawater was turned off from July 15 at 0915 to July 16 at 0015 (GMT) due to dirty water in New York harbor. All surface water samples during that period have been removed.

2. Coastal air transects resulted in air concentration values varying from 350-405 ppm because of air masses originating from land.

3. The delta fCO2 values were determined using the highly variable air values.

RB200205B: 1. Seawater was turned off on August 9 from 0150 to 1830 (GMT) due to dirty water. All surface water samples during that period have been removed.

2. Coastal air transects resulted in air concentration values varying from 355-440 ppm because of air masses originating from land.
3. The delta fCO₂ values were determined using the highly variable air values.

- RB200206: 1. Seawater was turned off on August 19 from 1355 to 2046 (GMT) when the ship stopped in Miami. All surface water and air samples during that period have been removed.
- RB200207: 1. Seawater was turned off from September 1 at 1120 to September 3 at 2046 (GMT) when the ship entered New York harbor. All surface water and air samples during that period have been removed.
2. There were peaks in the air values on September 5 and September 11 which have been removed from the data file. We cannot attribute these to contamination by stack gases and assume they were caused by pollution from sources on land. Anyone interested in this data should contact Bob Castle at Robert.castle@noaa.gov.
- RB200208T: 1. On September 23, gas flow in the air phase dropped below 30 ml/min due to water in the line. Many air values were removed for that reason.
- RB200208: 1. The system was down from 9/25 at 2108 to 9/26 at 1145 (GMT) due to a suspected software glitch. No data was recorded during this time.
2. Gas flow in the air phase dropped to 0 on 9/25 at 1630 due to water clogging the line. From that time to the end of the file I extrapolated the average air value of 369.5 ppm.
- RB200209: 1. The TSG malfunctioned on this cruise, resulting in high variance in SST and salinity. The salinity data was particularly noisy. I believe this was at least in part due to the noise in the temperature signal. To check the values, I compared them to the data from 45 CTD casts, using the upcast values at 2 meters depth. The temperature values were close, but the CTD salinities were higher than the TSG values. For the values in this data file, I did a 15 minute running average of the TSG SST and salinity recorded by our system. I then matched these values up with the CTD temperature and salinity. For SST, I used the 15 minute average with no adjustments since the average difference of the values was -0.01416 degrees with a standard deviation of 0.1237 for n = 44 CTDs. For salinity, I corrected the 15 minute averaged TSG values by adding 0.194 to them. This is the average difference (CTD sal - TSG sal) for n = 45 CTDs, with a standard deviation of 0.034. All fCO₂ values are computed using the averaged and adjusted TSG data.