

R/V Ronald H. Brown METADATA - 2005

Class of Data: Surface ocean and atmospheric carbon dioxide concentrations

Dataset Identifier: R/V Ronald H. Brown

One File: RHB2005

Statement of how to cite dataset:

Ron Brown website: http://www.aoml.noaa.gov/ocd/gcc/rvbrown_data2005.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 6 major cruises in the Atlantic and eastern Pacific Oceans for a total of 11 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:

Rik Wanninkhof
NOAA/AOML/Ocean Chemistry Division
4301 Rickenbacker Causeway
Miami, Florida 33149
Rik.Wanninkhof@noaa.gov

Contact person for this dataset:

Bob Castle
NOAA/AOML/Ocean Chemistry Division
4301 Rickenbacker Causeway
Miami, Florida 33149
Robert.Castle@noaa.gov

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: 12/29/2004 - 11/25/2005

Geographic area the dataset refers to:

65 S to 45 N
125 W to 20 W

2005 Cruises:

- RB200501T - CLIVAR A16S Transit
Valparaiso, Chile to Punta Arenas, Chile
December 29, 2004 to January 5, 2005
Chief Scientist - Kevin Sullivan
Operator - Jonathan Shannahoff
- RB200501A - CLIVAR A16S
Punta Arenas, Chile to Fortaleza, Brazil
January 11, 2005 to February 22, 2005
Chief Scientist - Rik Wanninkhof
Operator - Jonathan Shannahoff
- RB200502T - NTAS Moorings Transit
Fortaleza, Brazil to Bridgetown, Barbados
February 28, 2005 to March 6, 2005
Chief Scientist - N/A
Operator - Jonathan Shannahoff
- RB200502A - NTAS Moorings
Bridgetown, Barbados to Charleston, SC
March 10, 2005 to March 18, 2005
Chief Scientist - Al Plueddemann
Operator - Jonathan Shannahoff
- RB200503SB- Sea Beam Patch Testing
Charleston, SC to Woods Hole, MA
July 12, 2005 to July 15, 2005
Chief Scientist - N/A
Operator - Jonathan Shannahoff
- RB200503A - Ocean Explorations Lost City
Woods Hole, MA, to Punta Delgada, Azores
July 18, 2005 to August 4, 2005
Chief Scientist - Robert Ballard
Operator - Jonathan Shannahoff
- RB200503B - Ocean Explorations Stepping Stone
Punta Delgada, Azores to Woods Hole, MA
August 10, 2005 to September 3, 2005
Chief Scientist - Les Watling
Operator - Jonathan Shannahoff
- RB200504T - Western Boundary Time Series Transit
Woods Hole to Charleston, SC
September 6, 2005 to September 9, 2005
Chief Scientist - N/A
Operator - Jonathan Shannahoff

RB200504 - Western Boundary Time Series
 Charleston, SC to Miami, FL
 September 11, 2005 to September 24, 2005
 Chief Scientist - Chris Meinen
 Operator - Jonathan Shannahoff

RB200505 - Stratus Mooring
 Rodman, Panama to Arica, Chile
 October 4, 2005 to October 20, 2005
 Chief Scientist - Robert Weller
 Operator - Jonathan Shannahoff

RB200506 - TAO
 Arica, Chile to Rodman, Panama
 October 27, 2005 to November 25, 2005
 Chief Scientist - Andy Shepherd
 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.	PRES_EQUIL_hPa:	Barometric pressure in the lab in hectopascals (1 hectopascal = 1 millibar).
11.	PRES_SEALEVEL_hPa:	Barometric pressure corrected to sea level from the ship's barometer in hectopascals (1 hectopascal = 1 millibar).
12.	EqTEMP_C:	Temperature in equilibrator water in degrees centigade. Temperature in equilibrator measured with a calibrated thermistor.

13. SST(TSG)_C: Temperature from the ship's thermosalinograph in degrees centigrade.
14. SAL(TSG)_PERMIL: Salinity from the ship's thermosalinograph on the Practical Salinity Scale.
15. WATER_FLOW_L/MIN: Water flow rate through the equilibrator in liters per minute.
16. GAS_FLOW_IR_ML/MIN: Gas flow through the sample cell of the Licor IR analyzer in milliliters per minute.
17. TEMP_IR_C: Temperature in the Licor sample cell in degrees centigrade.
18. PRES_IR_hPa: Barometric pressure in the lab in hectopascals (1 hectopascal = 1 millibar). The Licor in this system does not include a pressure sensor so this field is the same as # 10 above.
19. SHIP_HEADING_TRUE_DEGREE: Ship's heading in true degrees from the ship's scientific computing system.
20. SHIP_SPEED_KNOT: Ship's speed in knots from the ship's scientific computing system.
21. WIND_DIR_REL_DEGREE: Relative wind direction in degrees from the ship's scientific computing system.
22. WIND_SPEED_REL_M/S: Relative wind speed in meters per second from the ship's scientific computing system.
23. fCO2W@SST_uatm: Fugacity of CO2 in sea water in microatmospheres calculated as outlined below.
24. QC_FLAG_WATER: Quality control flag for fCO2W@SST measurement. 2 = good, 3 = questionable, 4 = bad.
25. fCO2A_uATM: Fugacity of CO2 in air in microatmospheres calculated as outlined below.
24. QC_FLAG_AIR: Quality control flag for fCO2A measurement. 2 = good, 3 = questionable, 4 = bad.
27. dfCO2_uATM: Sea water fCO2 - air fCO2 in microatmospheres. This uses the average air value for the current hour.
28. FLUORO_uG/l: Measurement from the ship's Turner 10AU fluorometer in micrograms per liter.
29. WIND_SPEED_TRUE_M/S: True wind speed in meters per second from the ship's scientific computing system.
30. WIND_DIR_TRUE_DEGREE: True wind direction in degrees from the ship's scientific computing system.

31. AIR_TEMP_C: Outside air temperature from the ship's scientific computing system.

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
WATER_FLOW_L/MIN
GAS_FLOW_L/MIN
TEMP_IR_C
PRES_IR_hPa
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
PRES_SEALEVEL_hPa
SHIP_HEADING_TRUE_DEGREE
SHIP_SPEED_KNOT
WIND_DIR_REL_DEGREE
WIND_SPEED_REL_M/S
FLUORO_uG/l
WIND_SPEED_TRUE_M/S
WIND_DIR_TRUE_DEGREE
AIR_TEMP_C

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 2005 field season were:

STANDARD	TANK #	CONCENTRATION	VENDOR
Low	CA05395	315.25	ESRL
Low	CA05760	303.23	ESRL
Mid	CA05398	370.90	ESRL
Mid,high	CA05344	411.42	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 or other sensors, 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 2005 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 4 cruises (RB200501T-RB200502A) were 315.25 ppm, 411.42 ppm, and 531.98 ppm. The standards for the last 7 cruises (RB200503SB-RB200506) were 303.23 ppm, 370.90 ppm, and 411.42 ppm.

Comments related to the individual legs:

- RB200501T: 1. Extremely high pCO₂ values were encountered in the first two days of the cruise. These are apparently due to upwelling and have been left in the data file since there is no indication of problems with the system.
2. Air values have been removed in three periods: from 0740 to 1550 on December 30, from 0840 to 1550 on January 2, and from 2345 on January 3 to 0940 on January 4. In the last two cases these high values are likely due to stack gas contamination. In the first case, it is possible that they are due to shore-based sources. Some of these have been left in and given QC flags of 3.
3. The Seabird TSG was not working during this leg and the temperature and salinity from it should not be considered valid. Instead, the temperature and salinity from the ship's TSG or the equilibrator temperature should be used.
- RB200501A: 1. AC power problems occurred on Jan. 14 from 1344 to 1830, on Jan. 15 from 2000 to 2300, and on Jan. 16 from 144 to 1544. During these periods, most water and air values have been removed.
2. Also during the periods of power problems, the equilibrator thermistor gave bad readings. A relationship was derived between the Seabird temperature and the equilibrator temperature ($E_{qT} = (0.0129 *$

SBT) - 0.2932, $R^2 = .9282$) and was used to replace the bad equilibrators temperatures.

RB200502T: No problems of note.

RB200502A: No problems of note.

RB200503SB: 1. There was no water flow from the beginning of the cruise until July 12 at 1230. All water values were removed through July 12 at 1330.

RB200503A: 1. A severe drop in gas flow in the water phase occurred on July 25 at around 0600. This was probably caused by an obstruction in the gas line. About half of the water values from July 25 at 0600 until July 27 at 1200 were removed and all water values after noon on July 27 were removed.

RB200503B: 1. There was insufficient gas flow in the water phase from the beginning of the cruise until about 2245 on August 18. Almost all water values in this time period have been removed.

RB200504T: No problems of note.

RB200504A: No problems of note.

RB200505: 1. There was no gas flow in the water phase from October 5 at 1357 to October 6 at 1253. All water values during this time have been removed.
2. The salinity readings from the ship's TSG were bad from October 13 at 0019 to October 15 at 1703. They were replaced with values from the Seabird TSG near the underway system using the equation $SCS\ sal = SBE\ sal - 0.16$, which was derived from the period when both sensors were working correctly.

RB200506: 1. There was a problem with the ship's salinity sensor and all values before October 28 at 1645 and after November 21 at 1530 were replaced. The new values were equal to the salinity from the Seabird Micro TSG - 0.077 where 0.077 was the average difference between the ship's TSG and the Seabird Micro TSG when the ship's TSG was giving good values.
2. The gas flow in the water phase dropped to near zero on November 10 from 0420 to 1304 and from November 22 at 0501 to November 23 at 1327. Almost all water values during these time periods have been removed.