R/V Ronald H. Brown METADATA - 2003

Class of Data: Surface ocean and atmospheric carbon dioxide concentrations

Dataset Identifier: R/V Ronald H. Brown

One File: RHB2003

Statement of how to cite dataset:

Ron Brown website: http://www.aoml.noaa.gov/ocd/gcc/rvbrown_data2003.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 9 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:

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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: 2/6/2003 - 11/21/2003

Geographic area the dataset refers to:

10 S to 65 N
115 W to 15 W

2003 Cruises:

RB200301 - Western Boundary Time Series
Charleston, SC to Miami, FL
February 4, 2003 to February 15, 2003
Chief Scientist – Chris Meinen
Operator – Jonathan Shannahoff

RB200302 - Puerto Rico Trench
Miami, FL to San Juan, Puerto Rico
February 19, 2003 to March 7, 2003
Chief Scientist – Uri ten Brink
Operator – Jonathan Shannahoff

RB200303 - Kick'em Jenny Volcano
San Juan, Puerto Rico to Charleston, SC
March 10, 2003 to March 28, 2003
Chief Scientist – Haraldur Sigurdsson
Operator – Jonathan Shannahoff

RB200304T - CO2/CLIVAR Transit
Charleston, SC to Reykjavik, Iceland
June 5, 2003 to June 14, 2003
Chief Scientist – Kevin Sullivan
Operator – Jonathan Shannahoff

RB200304A - CO2/CLIVAR Leg A (WOCE A16N)
Reykjavik, Iceland to Funchal, Madeira
June 19, 2003 to July 10, 2003
Chief Scientist – John Bullister
Operator – Jonathan Shannahoff

RB200304B - CO2/CLIVAR Leg B (WOCE A16N)
Funchal, Madeira, to Natal, Brazil
July 15, 2003 to August 10, 2003
Chief Scientist – John Bullister
Operator – Jonathan Shannahoff

RB200305 - Puerto Rico Trench
St. Maarten, Netherlands Antilles to St. Petersburg, FL
August 28, 2003 to September 4, 2003
Chief Scientist – Uri ten Brink
Operator – Jonathan Shannahoff

RB200306 - Harbor Branch Oceanographic Institution Bio-pharmaceuticals
St. Petersburg, FL to Panama City, FL
September 9, 2003 to September 19, 2003
Chief Scientist – John Reed
Operator – Jonathan Shannahoff

RB200307 - Gulf of Mexico Deep Sea Habitats
Panama City, FL to Gulfport, MS
September 21, 2003 to October 1, 2003
Chief Scientist – George P. Schmahl
Operator – Jonathan Shannahoff

RB200308 - U-166 Survey
Gulfport, MS to Pensacola, FL
October 6, 2003 to October 11, 2003
Chief Scientist – Robert Church
Operator – Jonathan Shannahoff

RB200309 - TOGA/TAO
Balboa, Panama to Balboa, Panama
October 27, 2003 to November 21, 2003
Chief Scientist – Ben Morre
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 fCO2a (or fCO2eq) is calculated assuming 100% water vapor content:

$$fCO2eq = xCO2eq(P-pH2O)\exp(B11+2*d12)P/RT$$

where fCO2eq is the fugacity in the equilibrator, pH2O 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^3·atm·deg^-1·mol^-1). The exponential term is the fugacity correction where B11 is the second virial coefficient of pure CO2

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

and d12 = 57.7 - 0.118 T is the correction for an air-CO2 mixture in units of cm^3·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:

$$fCO2(SST) = fCO2(eq) / \exp((Teq-SST) * [0.03107 - 2.7851E-4 * Teq - 1.8391E-3 * \ln(fco2eq * 1.0E-6)])$$

where SST is sea surface temperature and Teq 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 2003 field season were:

STANDARD	TANK #	CONCENTRATION	VENDOR
Low	CC71632	295.37	ESRL
Mid	CC91287	357.18	ESRL
High	CC71655	423.28	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 2003 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 all cruises were 295.37 ppm, 357.18 ppm, and 423.28 ppm.
3. Beginning with the second cruise (RB200302) additional data fields were reported. These data come from the ship's various meteorological sensors and include wind speed and direction (both true and relative), air temperature, fluorometer, barometric pressure corrected to sea level, course over ground (COG), and speed over ground (SOG). In addition, water and gas flow through the instrument are reported as well as QC flag fields for fCO2 water and air. Flags are in the WOCE format with 2 = good, 3 = questionable, and 4 = bad. No data was recorded for COG, SOG, and air temp during this year. Beginning with cruise RB200306 and continuing until the end of the year, no data from the ship's barometer was recorded. All missing data has been set to -999.99.

Comments related to the individual legs:

RB200301:
1. The Licor was not turned on for the first 49 hours and no data was collected during this time period.
2. There was no water flow from Feb. 11 at 1720 to 1904 and from 2150 on Feb. 11 to 0955 on Feb. 12. All water values during these time periods were removed.
3. The salinity readings from the ship's TSG were bad from Feb. 14 at 1804 to Feb. 15 at 1151 and were suspect for much of the rest of the cruise. They have been replaced with the YSI salinity - 0.2 for the entire data set where 0.2 is the approximate offset between the two sensors.

RB200302:
1. The TSG temperature and salinity readings were "stuck" at a constant value on Feb. 20 from 18:38 to 18:52 and on Feb. 26 from 12:30 to 15:15. I did a linear interpolation from the last "non-stuck" value to the next "non-stuck" value. The difference in fCO2 values should be much less than 1 hectopascal for these samples.

2. Some air values were removed because they were anomalously high or because of probable contamination by stack gas. Some air values were slightly higher than the baseline of approximately 376 ppm and the high values could not be attributed to stack gas. These values have been left in the data file and given a flag of 3 and are likely due to winds coming from the island of Puerto Rico.

RB200303: 1. The seawater flow was turned off three times: from March 21 at 20:40 to March 22 at 19:40; from March 24 at 10:22 to March 24 at 18:52; and from March 25 at 17:36 to March 26 at 14:00. No surface water measurements were included from these time periods.
2. From March 21 at 22:40 to March 22 at 15:40 all air values were removed due to probable contamination by stack gas.

RB200304T: 1. Seawater was turned off from June 7 @ 0950 to June 10 @ 2250 and from June 11 @ 1354 to June 12 @ 1720 (GMT) because no permission had been given to sample in Canadian and Danish waters respectively.
2. Early in the cruise air values that differed significantly from the baseline value of approximately 378 ppm were recorded. I believe these are caused by air from the North American continent and are real, so I have left them in and given them a QC flag of 3.

RB200304A: No problems of note.

RB200304B: No problems of note.

RB200305: 1. The system was down from September 2 at 00:20 to September 3 at 10:50 while passing through Cuban waters.
2. On September 1 and September 4, air values were measured that were above the normal baseline of approximately 372 ppm. Most of these could not be attributed to stack gas contamination and have been left in the data file with a QC flag of 3.

RB200306: 1. The survey tech who normally operates the system was not present on this cruise. This apparently had no effect as no significant problems were found in the data.

RB200307: 1. The survey tech who normally operates the system was not present on this cruise. This apparently had no effect as no significant problems were found in the data.
2. The sea water flow was turned off from September 22 at 15:15 to September 23 at 13:28. Water values in this period have been removed and given a QC flag of 9. Air values have been retained.

RB200308: 1. The survey tech who normally operates the system was not present on this cruise. This apparently had no effect as no significant problems were found in the data.

RB200309: No problems of note.