R/V Ronald H. Brown METADATA - 1999

Class of Data: Surface ocean and atmospheric carbon dioxide concentrations

Dataset Identifier: R/V Ronald H. Brown

One File: RHB1999

Statement of how to cite dataset:

Ron Brown website: http://www.aoml.noaa.gov/ocd/gcc/rvbrown_data1999.php

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

Cruise Information:

The Ron Brown conducted 6 major cruises that took the ship through the Atlantic, Indian, and Pacific Oceans from Norfolk, VA east to San Diego, CA for a total of 11 legs.

Project Information:

The system was operated by personnel from AOML or PMEL (Pacific Marine Environmental Laboratory). 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: 09/15/08

Timestamp for the most recent update of dataset: 09/15/08

Timestamp period the dataset refers to: 1/14/1999 – 12/2/1999

Geographic area the dataset refers to:

35 S to 60 N
All except 95 W to 75 W

1999 Cruises:

RB199901 – ACE 99 Leg 1
Norfolk, VA to Capetown, South Africa
January 14, 1999 to February 8, 1999
Chief Scientist – Tim Bates
Operator – Bob Castle

RB199902 - ACE 99 Leg 2
Capetown, South Africa to Port Louis, Mauritius
February 11, 1999 to February 20, 1999
Chief Scientist – Tim Bates
Operator – Drew Hamilton

RB199903 - INDOEX 99 Leg 1
Port Louis, Mauritius to Male, Maldives Islands
February 21, 1999 to February 28, 1999
Chief Scientist – Tom Carsey
Operator – Drew Hamilton

RB199904 - INDOEX 99 Leg 2
Male, Maldives Islands to Male, Maldives Islands
March 4, 1999 to March 23, 1999
Chief Scientist – Tom Carsey
Operator – Drew Hamilton

RB199905 - INDOEX 99 Leg 3
Male, Maldives Islands to Male, Maldives Islands
March 26, 1999 to April 2, 1999
Chief Scientist – Tom Carsey
Operator – Drew Hamilton

RB199907 - JASMINE 99 Leg 2
Singapore to Darwin, Australia
April 30, 1999 to June 8, 1999
Chief Scientist – Christopher Fairall
Operator – Dana Greeley

RB199908 - Nauru 99
Darwin, Australia to Kwajalein
June 15, 1999 to July 18, 1999
Chief Scientist – Christopher Fairall
Operator – Jennifer Aicher

RB199911 - NOPP 99 Leg 1
Kwajalein to Honolulu, HI
September 13, 1999 to September 20, 1999
Chief Scientist – Jim Butler
Operator – Marilyn Roberts

RB199912 - NOPP 99 Leg 2
Honolulu, HI to Dutch Harbor, AK
September 26, 1999 to October 3, 1999
Chief Scientist – Hugh Milburn
Operator – Marilyn Roberts

RB199913 - NOPP 99 Leg 3
Dutch Harbor, AK to Seattle, WA
October 5, 1999 to October 23, 1999
Chief Scientist – Hugh Milburn/Marilyn Roberts
Operator – Marilyn Roberts

RB199914 - TAO 99
Seattle, WA to San Diego, CA
November 1, 1999 to December 2, 1999
Chief Scientist – Andrew J. Shepherd
Operator – Esa Peltola

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:

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 CO_2 in the headspace and the temperature in the chamber, the partial pressure (or fugacity) of CO_2 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 CO_2 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 CO_2 molecule. The LI-COR detector passes IR radiation through two 6" cells. The reference cell is flushed with a gas of known CO_2 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_2 (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_2 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_2 in surface seawater and water saturated air in order to determine the fCO_2. 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:

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

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 2.5) was an in-house prototype built by Jason Masters, Mike Shoemaker, and Bob Castle 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 1999 field season were:

STANDARD	TANK #	CONCENTRATION	VENDOR
Low	CA03372	283.26	CMDL
Low	CA01213	298.46	CMDL
Low	N/A	337.78	CMDL
Mid	CC106641	360.62	CMDL
Mid,High	CA03253	426.96	CMDL
High	N/A	523.27	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 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 1999 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. Before the first cruise, the Spectrex pump that pumped headspace gas from the equilibrator to the Licor was replaced with a KNF pump.
3. The standard gases at the start of the year were: low – 283.26 ppm, mid – 360.62 ppm, high – 426.96 ppm.

Comments related to the individual legs:

RB199901:
1. Data prior to 1/16 @ 1730 (about 1 day's worth) was removed due to a clog in one of the vent lines leading to the equilibrator which was causing bad readings.
2. On 1/17 from 0430 to 0630 the system was down for repairs to one of the solenoids.
3. On 1/26 from 1630 to 1830 the system was down for installation of a new version of the software (version 2.6) and other minor repairs.
4. On 1/27 from 2000 to 2130 the system was down for resurfacing and recalibration of the YSI dissolved oxygen sensor.

RB199902: No problems of note.

RB199903: No problems of note.

RB199904:
1. The system was down for approximately 8 hours beginning on March 14 at 0750 for calibration of the YSI TSG.
2. The system was down for approximately 8 hours beginning on March 18 at 0450 while the ship took on fuel at Diego Garcia.

3. The Air Cadet that pumps ambient air from the bow mast began to fail on March 18 at 2030. Flow through the Licor IR analyzer dropped steadily for the rest of the leg and for the last day there were no usable air measurements. When possible, I used the third of each group of three air readings, but in some cases complete flushing of the sample cell did not occur. Since the second half of the leg was spent steaming south from Male to about 13S and then turning around and steaming north back to Male, I used average air xCO2 values from the southbound section and pasted them into northbound spots that corresponded in latitude. This allowed me to match the gradient from 2N to 5S where xCO2 levels dropped about 2 ppm. The north and south bound sections were no more than 3 degrees of longitude apart.

4. The PC clock was reset prior to this leg to match GMT as it had become off by about 3 minutes. However, this PC has an annoying habit of changing the date when the time is reset and in the raw data file dates went from 2/9 to 2/28. I changed these to the correct dates in the final data file.

5. The low standard tank was changed on March 10 at 0700 from 283.26 to 298.46 ppm.

6. On several occasions, large changes in water xCO2 values were observed. I believe these were caused by intermittent air leaks in the uncontaminated seawater line feeding the equilibrator. This problem recurred 2 months later in a non-intermittent form. I removed about 130 water values that I suspected were bad. I left in 1 water xCO2 spike (on March 18 at 1425) that was likely real due to rapid changes in temperature and fluorometer readings.

RB199905: 1. The system was down for approximately 13 hours beginning on March 28 at 1320 when the PC froze up.

2. The Air Cadet that pumps ambient air from the bow mast had failed on the previous leg and never pumped enough air to flush the Licor IR analyzer during this leg. All air values for this leg were discarded. I inserted air xCO2 values by using the base value 371.8 ppm at 4N which was taken from the values observed on the previous leg. I then added 0.15 * (measurement_latitude - 4) to the base value to arrive at an xCO2 value for each air measurement. The number 0.15 comes from the CO2 rug file for 1981 - 1995 and is an approximation of how much air xCO2 values tend to rise per degree of latitude in the latitude range for this cruise leg.

3. Large variations in water xCO2 values cause me to suspect a serious air leak in the water line leading into the equilibrator. I removed a large number of data points from the final file. Further, periods of low xCO2 variability seem to coincide with times late at night when few if any people would have been in the lab.

RB199907: 1. The cruise began on April 30, 1999 but we were not allowed to sample in Indonesian waters. The data begins on May 4, 1999 at 0000 GMT and ends on May 31, 1999 at 2259 GMT when the ship entered Indonesian waters again. After exiting Indonesian waters the second time, data starts again on June 5 at 1800 GMT and ends upon arrival at Darwin on June 7 at 0600 GMT.

2. No data was collected on leg 1 of the Jasmine cruise.

3. The system developed an air leak in the condensor on May 24 at 2246 GMT. This was repaired on May 27 at 1300 GMT. The air leak caused high variability in water phase xCO2 measurements and therefore all water measurements during this period were removed.

4. On May 24, the system was down from 0830 to 0900 while the YSI TSG was recalibrated.
5. When the system was restarted on June 5, data from the ship's computer system (SCS) was no longer recorded in the data file. I have been unable to obtain this data so I derived SCS temperature and salinity from equilibrator temperature and YSI TSG salinity respectively. I used data from leg 2A of this cruise for that purpose, determining linear equations in both cases that are given in the notes below.
6. For temperature the equation used was: SCS T = (1.009546 * EqT) - 0.463015 with R^2 = 0.991904.
7. For salinity I used only the data from leg 2A that occurred after the calibration of the YSI TSG on May 24. The equation used was SCS Sal = (1.009276 * YSI Sal) - 1.061172 with R^2 = 0.994521.
8. On June 6 from 0150 to 0340, approximately 1-1/2 hours of data were not recorded while the system operator installed a patch in the program.

RB199908: 1. On July 2, the system's computer crashed, resulting in the erasure of the July data file. Data from the beginning of July until July 2 at 0620 GMT was lost.
2. The system was shut down from 0000 GMT to 0220 GMT on June 18 in order to recalibrate the YSI TSG.

RB199911: 1. I removed the first 2 hour's worth of data because of unstable voltage readings in the Standard gas phases.
2. The system was not operated during the previous KWAJEX cruise (legs RB199909 and RB199910).

RB199912: 1. The system was shut down for 2 hours beginning on October 2 at 0325 in order to remount the mercury thermometer in the equilibrator. When the system came back up, a drop of 40 ppm in water xCO_2 values was observed. I believe this drop was real because voltage response of the Licor in the water phase also dropped, salinity dropped about 0.15, and the fluorometer reading also rose 0.7 FSU. I can find no indication of leaks prior to the thermometer remount that would have caused elevated xCO_2 readings in the water phase.
2. The low standard tank at the beginning of the cruise was changed to 337.38 ppm. On October 2 at 2200 it was changed back to 298.46 ppm.

RB199913: 1. The uncontaminated seawater intake was shut down 5 times due to rough weather. The outages occurred on October 12 at 2111 (7 hrs), October 13 at 1459 (2 1/2 hrs), October 13 at 2059 (3 1/2 hrs), October 15 at 0341 (13 hrs), and October 16 at 1025 (9 hrs). All water xCO_2 values for these time periods have been removed. In some cases when the pCO_2 system was left on during an outage, I have retained the air xCO_2 values.
2. On October 20 at 1550 the seawater intake was shut down for maintenance for 4 hours. The underway system was also shut down during this period.
3. On October 14 at 0616 the low standard tank was changed from 298.46 to 283.26 ppm because the tank was near empty.
4. The last 3 hours (coming in to Seattle) have very high water xCO_2 values. Because temperature and salinity were both changing rapidly, I left these in the final data file. However, a sharp rise in the voltage response of the low standard gas indicates that the Licor sample cell was not being flushed completely. Since the water xCO_2

values are well above the high standard gas concentration, the numbers given in the data file are probably not entirely accurate.

RB199914: 1. The system was shut down on 11/6 at 0050 GMT (310.032-310.753) for 17 hours while the ship made a pick up in San Diego.
2. The system was shut down on 11/6 at 2020 GMT (310.854-314.083) for 3-1/4 days while the ship was in Mexican waters.
3. The system was shut down on 12/2 at 2033 GMT (336.857) when the ship entered Mexican waters. It was not turned on again during this leg.
4. On 2 occasions, low gas flow in the standard phases resulted in the incomplete flushing of the Licor sample cell. The first of these went from November 21 at 1803 to November 28 at 0559 and the second from November 29 at 1425 to the end of the cruise. In the first case, I averaged voltage response in the standard phases for the period from November 20 at 0803 to November 21 at 1703 (n=34) and replaced the bad values with the average values. In the second case, I averaged voltage response in the standard phases for the period from November 27 at 1803 to November 29 at 1503 (n=46) and replaced the bad values with the averages. Statistics for each of the averages are given below:

n	34	46
LoStdAvg	0.073247	0.073247
LoStdSD	0.001764	0.001837
MidStdAvg	0.491197	0.482420
MidStdSD	0.001668	0.003944
HiStdAvg	0.905697	0.896917
HiStdSD	0.002312	0.002658