R/V Ronald H. Brown RB-10-02 (CLIVAR/A13.5) METADATA

Class of Data: Surface ocean and atmospheric carbon dioxide concentrations

Dataset Identifier: R/V *Ronald H. Brown*

One File: A13.5_2010_underway.csv

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

Cruise Information:

On March 8, 2010 the NOAA research vessel Ronald H. Brown left Cape Town, South Africa to begin the scientific leg of the RB-10-02 cruise. The cruise ended on April 17, 2010 when the ship arrived in Takoradi, Ghani. Dr. John Bullister was the chief scientist and Dr. Robert Key was the co-chief scientist. Mr. Kevin Sullivan was the scientist responsible for operating the pCO2 underway system throughout the cruise.

Project Information:

The RB-10-02 cruise was part of a decadal series of repeat hydrography sections jointly funded by NOAA-OGP and NSF-OCE as part of the CLIVAR/CO2/ hydrography/tracer program (http://ushydro.ucsd.edu).

Scientist responsible for technical quality of dataset:

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Timestamp for initial submission of dataset: 4/05/12

Timestamp for the most recent update of dataset: 4/05/12

Timestamp period the dataset refers to: 03/07/2010 – 04/17/2010

Geographic area the dataset refers to:

55 S to 5 N
4 W to 19 E

List of variables included in this dataset:

COLUMN	HEADER	EXPLANATION
1.	Group_Ship:	AOML_RBrown
2.	Cruise ID:	A13.5
3.	EXPOCODE	Expedition Code: 33RO20100308
4.	JD_GMT:	Decimal year day
5.	DATE_UTC_ddmmyyyy:	Date in European format
6.	TIME_UTC_hh:mm:ss:	GMT time
7.	LAT_dec_degree:	Latitude in decimal degrees (negative values are in the southern hemisphere)
8.	LONG_dec_degree:	Longitude in decimal degrees (negative values are in the western hemisphere)
9.	xCO2_EQU_ppm:	Mole fraction of CO2 in the equilibrator at equilibrator temperature
10.	xCO2_ATM_ppm:	Mole fraction of CO2 in air in parts per million (ppm)
11.	xCO2_ATM_interpolated_ppm:	Bracketing average air values interpolated to time of current Equ measurement
12.	PRES_EQU_hPa:	Barometric pressure in the equilibrator in hectopascals
13.	PRES_ATM@SSP_hPa:	Barometric pressure from ship’s barometer, corrected to sea level in hectopascals.
14.	TEMP_EQU_C:	Equilibrator water temperature in degrees centigrade
15.	SST_C:	Sea surface temperature in degrees centigrade
16.	SAL_permil:	Micro TSG in the Hydro Lab
17.	fCO2_SW@SST_uatm:	Fugacity of CO2 in sea water in microatmospheres corrected to sea surface temperatures given in column 14 above

18. fCO2_ATM_interpolated_uatm: Fugacity of CO2 in air in microatmospheres interpolated to time of Equ measurement

19. dfCO2_uatm: Fugacity of CO2 in sea water – fugacity of CO2 in air in microatmospheres

20. WOCE_QC_FLAG: Quality control flag for Equ fCO2 values and Atm xCO2 values (2 = good, 3 = questionable, 4 = bad)

21. QC_SUBFLAG: Subflag text string for values flagged as 3

The following fields have been QC'ed by the CO2 group:

Group_Ship
Cruise ID
JD_GMT
DATE_UTC_mmddyyyy
TIME_UTC_hh:mm:ss
LAT_dec_degree
LONG_dec_degree
xCO2W_EQU_ppm
xCO2_ATM_ppm
xCO2_ATM_interpolated_ppm
PRES_EQU_hPa
TEMP_EQU_C
fCO2_SW@SST_uatm
fCO2_ATM_interpolated_uatm
dfCO2_uatm
WOCE_QC_FLAG
QC_SUBFLAG

SST_C values are from the Seabird 21 TSG, which is immersed in the instrument chest of the ship located in the bow thruster space. Sal_permil values are from the Seabird 45 Micro TSG located in the Hydro Lab, next to the pCO2 instrument. PRES_ATM@SSP_hPa values are from a ship barometer located on the deck. The quality of these data cannot be verified.

Narrative description of system design:

INSTRUMENT DESCRIPTION AND CONFIGURATION

The general principle of operation of the instrument can be found in Wanninkhof and Thoning (1993), Ho et al. (1995), Feely et al. (1998), and Pierrot et al. (2009). Seawater flows through an equilibrator chamber where CO2 exchanges between water and the air above it. Small changes in seawater CO2 concentration are rapidly translated into changes in CO2 concentration in the air of the chamber (headspace). The mole fraction of CO2 in the headspace gas is measured using a non-dispersive infrared (NDIR) analyzer from LICOR®.

The effects of water vapor on the signal are compensated for by the analyzer but are also kept to a minimum by removing as much water as possible. The water is first condensed out of the gas stream by cooling. Then it is further removed using Nafion® gas dryers before reaching the IR analyzer. Typical water content of the gas streams are less than 3 millimoles/mole with approximately 90% of the water removed.

The infrared analyzer is calibrated regularly using four standard gases (284.75 - 545,88 ppm CO2 in air) from ESRL in Boulder, CO. Before and after use in the field, the standards are calibrated using primary reference gases from the laboratory of Dr. Charles P. Keeling, which are directly traceable to the WMO scale.

The system also measures the CO2 content of the atmospheric air, which is drawn from an inlet on the bow mast through tubing to the analytical system located in the Hydro Lab. A Seabird Micro TSG (SBE-45) in the Hydro Lab is connected directly to the underway system and provides temperature and salinity measurements. The GPS data comes from the ship's SCS system. The atmospheric pressure comes from the deck barometer.

The sequence of continuous analyses was:

STEP	TYPE	REPETITIONS
1	Zero gas	1
2	Span gas	1
3	Standards (all four)	1
4	ATM	5
5	EQU	50
6	Repeat steps from step 3 nine mores times	
7	Restart from Step 1	

The amount of time between analyses depends on whether the analyses are of the same type of gas (e.g., STD, ATM, EQU) or not. When switching between different gases, the connecting tubes and analyzer are flushed for an initial interval called the 'PRE-FLUSH' time plus an interval called the 'REGULAR FLUSH' time. Between successive measurements of the same type of gas, the system is flushed for only the 'REGULAR FLUSH' time. The gas flow is then stopped. After the 'STOP FLOW' time interval, which is 10 seconds for all analyses, the output of the NDIR analyzer is read. The pre-flush time is set to 180 seconds and the regular flush time is set to 60 seconds for standard and air analyses. Both the pre-flush and regular flush times are 120 seconds for equilibrator headspace analyses. With these settings, a complete set of standards and the atmospheric analyses are done every 3 hours and a full day contains about 480 analyses of the equilibrator headspace.

Narrative statement identifying measurement method for each required parameter:

CALCULATIONS:

The measured xCO2 values are linearly corrected for instrument response using the standard measurements (see Pierrot et al., 2009).

For ambient air and equilibrator headspace the fCO2a or fCO2eq is calculated assuming 100% water vapor content:

$$fCO2 = xCO2\ P\ (1-pH2O)\ \exp[(B11+2d12)P/RT]$$

where fCO2 is the fugacity in ambient air or equilibrator, pH2O is the water vapor pressure at the sea surface or equilibrator temperature, P is the equilibrator or outside 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 first virial coefficient of pure CO2

$$B11 = -1636.75 + 12.0408\ T - 0.0327957\ T^2 + 3.16528E\text{-}5\ T^3$$

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 fugacity as measured in the equilibrator is corrected for any temperature difference between sea surface temperature and equilibrator chamber using the empirical correction outlined in Takahashi et al. (1993).

$$fCO2(SST) = fCO2(teq)\exp[0.0423(SST-teq)]$$

where fCO2(SST) is the fugacity at the sea surface temperature and fCO2(teq) is the fugacity at the equilibrator temperature. SST and teq are the sea surface and equilibrator temperatures in degrees C, respectively.

NOTES ON DATA: Columns have a default value of −9 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 pCO2 underway system aboard the R/V Ronald H. Brown was built by General Oceanics. The analyzer is a LI-COR 6262 infrared analyzer with pressure sensor and water channel.

Standard Gases and Reference Gas: The four standard gases came from ESRL 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 xCO2_EQU measurements are believed accurate to 0.1 ppm. The fCO2_SW@SST measurements are believed to be precise to 0.2 ppm.

List of calibration gases used:

The standards used were:

STANDARD	TANK #	CONCENTRATION	VENDOR
Low	CA06709	284.75	ESRL

Mid	CA02813	363.24	ESRL
High	CA07291	423.57	ESRL
High	CC07931	545.88	ESRL

Traceability to an internationally recognized scale:

All standards are obtained from NOAA/ESRL (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:

The SST temperature measurements are from the Seabird 21 TSG, which is immersed in the instrument chest of the ship in the bow thruster space. The equilibrator temperature measurements were made by a Hart thermometer Model 1523 and a 10kOhm thermistor, the calibration of which is traceable to NIST. The salinity measurements are from the Seabird 45 Micro TSG (SBE-45). Atmospheric pressure values are from a ship barometer located on the deck.

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 for water measurements, or sea surface temperature for the air measurements.

References:

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.

Pierrot, D., C. Neill, K. Sullivan, R. Castle, R. Wanninkhof, R., H. Lüger, T. Johannessen, A. Olsen, R. A. Feely, C. E. Cosca, 2009. Recommendations for autonomous underway pCO2 measuring systems and data reduction routines, Deep Sea Research II, 56: 512-522.

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.

Takahashi, T., J. Olafsson, J. G. Goddard, D. W. Chipman, and S. C. Sutherland (1993). Seasonal variation of CO2 and nutrients in the high-latitude surface oceans: a comparative study, Global Biogeochem. Cycles, 7, 843-878.

Comments related to all data:

During this cruise several upgrades to the system were installed and tested. For most of the upgrades, the data acquisition was interrupted while the ship was maintaining station, but the first upgrade was done before the ship left Cape Town.

A new main equilibrator that includes a water jacket was installed. This concentric enclosure around the vertical walls of the main equilibrator was flushed with a seawater flow of approximately 1.5 liters/minute. This water jacket improves the stability and accuracy of the temperature measured in the main equilibrator, especially during analyses of very cold waters.

Additional upgrades were associated with the firmware and software used to control the hardware. On March 12, a new version of the software was installed and worked well. On April 2, a new firmware chip and the necessary newer software were installed. Both software upgrades yielded a more stable and adaptable analytical system. On April 9 the GPS signal was switched from the dedicated deck box that comes with the GO system to the ship's GPS that is broadcast through the ship. Other than these planned service events, the system ran continuously during the entire cruise.

During the processing of the data, it was determined that there is a 2 minute offset between the SST data record (i.e. SBE21 in the instrument chest) and the equilibrator temperature data record. The water takes about 2 minutes to travel from the inlet at the hull and the analytical equilibrator.

There were several air analyses that were flagged as questionable because they were not representative of the marine boundary layer concentrations. Some of these analyses were likely due to contamination from the ship's exhaust; however, some were likely influenced by land-based sources.

For this cruise, we used the atmospheric pressure values measured from the barometer in the deck box of the GO system that was situated on a rail aft of the Hydro Lab, instead of the ship’s barometer which showed strange patterns. A correction based on height of the deck relative to sea surface of 10-m was applied to the deck atmospheric pressure to calculate sea level pressure (hPa). This correction was about 1 hPa.