CW2005_01_ANZ Readme File

Principal Investigator/Organization:
Dr. Richard Feely
NOAA/PMEL
7600 Sand Point Way NE
Seattle, WA 98115
(206) 526-6214
Richard.A.Feely@noaa.gov

Ship Name: Columbus Waikato
Call Sign: DHCF2
Country: Bremen, Germany
Ship Owner: Alphaship (http://www.alphaship.de)

Temporal Coverage:
Cruise Start: January 12, 2005; Melbourne, Australia
Cruise End: January 21, 2005; Auckland, New Zealand

System Operator: Bronte Tilbrook; CSIRO

Shoreside Support/Data Reduction: Cathy Cosca; NOAA/PMEL

Dataset ID/Location: cw2005_01_anz.csv (www.pmel.noaa.gov/co2/uwpco2/waikato_data.html)

Experiment Name: Underway measurement of atmospheric and surface water pCO2

Geographical Bounds (+ E, - W for Longitude; + N, - S for Latitude):

Westernmost Longitude: 144.676
Easternmost Longitude: 174.867
Northernmost Latitude: -34.020
Southernmost Latitude: -39.268

Method Description:
Equilibrator type/specifications: Showerhead, volume of ~0.5 L with a headspace of ~ 0.8 L.
Water Flow rate: 1.5 to 2 L/minute
Headspace gas flow rate: 60 ml/minute
Measurement method: Infrared absorption of dried gas.
CO2 Sensor: Licor 6262, Serial # IRG3-1261
Resolution/Uncertainty: 0.3 uatm for equilibrator measurements, 0.2 utam for atmospheric measurements.
Temperature measurements:
Equilibrator Temperature: Superlogics RTD module 8013 with an Omega RTD PR-11-2-100-1 temperature probe. Accurate to ± 0.01°C.

Sea Surface Temperature: A Seabird SBE 3 remote temperature probe was mounted in the sea chest approximately 5m below the sea surface. The SBE 3 was calibrated annually, with an accuracy of ± 0.01°C.
Salinity: A Seabird SBE 21 thermosalinograph was mounted next to the underway pCO2 system in the engine room. The unit was calibrated annually and provided salinity accurate to 0.1.
Pressure measurements: Pressure inside the equilibrator was measured with a Vaisala PTB210 pressure transducer, accurate to ± 0.15 hPa. The equilibrator was passively vented to a secondary equilibrator, and the Licor sample output was vented to the laboratory when CO2 measurements were made, thus equilibrator headspace pressure was assumed to be laboratory pressure.

The general principle of instrumental design and operation are described in:

Feely, R.A., R. Wanninkhof, H.B. Milburn, C.E. Cosca, M. Stapp, and P.P. Murphy, A new automated underway system for making high precision pCO2 measurements onboard research ships, Analytica Chim. Acta, 377, 185-191, 1998.

and

Wanninkhof and Thoning, Measurement of fugacity of Carbon Dioxide in surface water and air using continuous sampling methods, Marine Chemistry, 44, 189-205, 1993.

Standard gases:
Standard gases are supplied by NOAA's Climate Monitoring Diagnostics Laboratory in Boulder, CO, and are directly traceable to the WMO scale. Any value outside the range of the standards should be considered approximate, although the general trends should be indicative of the seawater chemistry.

Serial numbers and CO2 concentrations for the cylinders used on this cruise:

LL55868	296.35
LL55864	355.07
LL55867	397.48
LL55866	468.48

Sampling Cycle:
The system runs a full cycle in approximately 112 minutes. The cycle starts with 4 standard gases, then measures 10 atmospheric samples followed by 60 surface water samples. Each new gas is flushed through the Licor Analyzer for 4 minutes prior to a 10 second reading from the analyzer during which the sample cell is open to the atmosphere. Subsequent samples of the same gas are flushed through the Licor Analyzer for 30 seconds prior to a stop-flow measurement.

Units:
All xCO2 values are reported in parts per million by volume (ppmv) and fCO2 values are reported in microatmospheres (uatm) assuming 100 % humidity at the equilibrator temperature.

Calculations:

The mixing ratios of ambient air and equilibrated headspace air are calculated by fitting a second-order polynomial through the hourly averaged 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 fCO_{2a}, or fCO_{2eq} is calculated assuming 100% water vapor content:

$$fCO_{2a/eq} = xCO_{2a/eq}(P-pH_2O)\exp(B_{11}+2d_{12})P/RT$$

where $fCO_{2a/eq}$ is the fugacity in ambient air or 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 ($82.057\ cm^3 \cdot atm \cdot deg^{-1} \cdot mol^{-1}$). The exponential term is the fugacity correction where B_{11} is the second virial coefficient of pure CO_2

$$B_{11} = -1636.75 + 12.0408T - 0.032795T^2 + 3.16528E\text{-}5\ T^3$$

and $d_{12} = 57.7 - 0.118\ T$

is the correction for an air-CO_2 mixture in units of $cm^3 \cdot mol^{-1}$ (Weiss, 1974).

The calculation for the fugacity at SST involves a temperature correction term for the increase of fCO_2 due to heating of the water from passing through the pump and through 5 cm ID PVC tubing within the ship. The water in the equilibrator is typically 0.2 °C warmer than sea surface temperature. The empirical temperature correction from equilibrator temperature to SST is outlined in Weiss et al. (1982).

$$d\ln(fCO_2)=(teq-SST)(0.0317-2.7851E\text{-}4\ teq - 1.839E\text{-}3\ \ln(fCO_{2eq}))$$

where $d\ln(fCO_2)$ is the difference between the natural logarithm of the fugacity at teq and SST, and teq is the equilibrator temperature in degrees C.

File Format

	COLUMN HEADER	DESCRIPTION
1.	GROUP/SHIP:	PMEL/ColumbusWaikato
2.	CRUISE_ID:	CW<Year>_<Month>_ANZ
3.	JD_GMT:	Decimal year day
4.	Date_MM/DD/YYYY	Date in the format MM/DD/YYYY

5.	Date_DDMMYYYY	Date in the format DDMMYYYY
6.	TIME_HH:MM:SS:	GMT HH:MM:SS
7.	LAT_DEC_DEGREE:	Latitude in decimal degrees (negative values are in southern hemisphere).
8.	LONG_DEC_DEGREE:	Longitude in decimal degrees (negative values are in western latitudes).
9.	xCO2W_PPM:	Mole fraction of CO2 (dry) in the headspace equilibrator at equilibrator temperature (Teq) in parts per million. Water comes from bow intake 2m below the water line.
10	xCO2A_PPM:	Mole fraction of CO2 in air in parts per million.
11.	xCO2A_INTERPOLATED_PPM:	xCO2atm_ppm averaged linearly to match up with measurements xCO2eq_ppm
12.	PRES_EQUIL_hPa:	Barometric pressure in the equilibrator
13.	PRES_SEALEVEL_hPa:	Barometric pressure in the atmosphere
14.	EqTEMP_C:	Temperature in the equilibrator water.
15.	SST(TSG)_C:	Temperature from the ship's bow intake.
16.	SAL(TSG)_PERMIL:	Thermosalinograph salinity
17.	fCO2W@SST_uATM:	Fugacity of CO2 in sea water in microatmospheres calculated as outlined in the DOE Handbook.
18.	CO2A_uATM:	Fugacity of CO2 in air in microatmospheres
19.	dfCO2_uatm:	Sea water fCO2 - air fCO2 in microatmospheres.
20.	QC_FLAG:	Quality control flag 2 = Good value 3 = Questionable value 4 = Bad value

21. QC_SUBFLAG: Descriptive quality control flag used when a value receives a “3” QC flag

1 = Outside of Standard Range
2 = Questionable/interpolated SST
3 = Questionable EQU temperature
4 = Anomalous ΔT (EqT – SST)(± 1°C)
5 = Questionable Sea Surface Salinity
6 = Questionable pressure
7 = Low EQU gas flow
8 = Questionable air value
9= Interpolated standard value
10 = Other, see metadata

References

DOE (1994). Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2. A.G. Dickson and C. Goyet, eds., ORNL/CDIAC-74.

Feely, R.A., R. Wanninkhof, H.B. Milburn, C.E. Cosca, M. Stapp, and P.P. Murphy, A new automated underway system for making high precision pCO_2 measurements onboard research ships, Analytica Chim. Acta, 377, 185-191, 1998.

Wanninkhof, R. and K. Thoning (1993) Measurement of fugacity of CO_2 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 CO_2 in seawater. Nature 300: 511-513.

For questions or comments contact:

Cathy Cosca
NOAA/PMEL
7600 Sand Point Way NE
Seattle, WA 98115
206-526-6183
cathy.cosca@noaa.gov