

## **CW2005\_02 Readme File**

### **Principal Investigator/Organization:**

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### **Ship Name:** Columbus Waikato

Call Sign: DHCF2  
Country: Bremen, Germany  
Ship Owner: Alphaship (<http://www.alphaship.de>)

### **Temporal Coverage:**

Cruise Start: February 16, 2005; Los Angeles, California  
Cruise End: February 28, 2005; Auckland, New Zealand

**System Operator:** Laurie Juranek; University of Washington

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

**Dataset ID/Location:** cw2005\_02.csv ([www.pmel.noaa.gov/co2/uwpc2/waikato\\_data.html](http://www.pmel.noaa.gov/co2/uwpc2/waikato_data.html))

**Experiment Name:** Underway measurement of atmospheric and surface water pCO<sub>2</sub>

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

Westernmost Longitude: 177.545  
Easternmost Longitude: -119.907  
Northernmost Latitude: 31.245  
Southernmost Latitude: -34.411

### **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.  
CO<sub>2</sub> 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  $\pm 0.01^\circ\text{C}$ .

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  $\pm 0.01^{\circ}\text{C}$ .

Salinity: A Seabird SBE 21 thermosalinograph was mounted next to the underway pCO<sub>2</sub> 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  $\pm 0.15$  hPa. The equilibrator was passively vented to a secondary equilibrator, and the Licor sample output was vented to the laboratory when CO<sub>2</sub> 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 pCO<sub>2</sub> 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 CO<sub>2</sub> 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 xCO<sub>2</sub> values are reported in parts per million by volume (ppmv) and fCO<sub>2</sub> 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<sub>2</sub> in surface seawater and water saturated air in order to determine the fCO<sub>2</sub>. For ambient air and equilibrator headspace the fCO<sub>2a</sub>, or fCO<sub>2eq</sub> 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<sub>2a/eq</sub> is the fugacity in ambient air or equilibrator, pH<sub>2O</sub> 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<sup>3</sup>·atm·deg<sup>-1</sup>·mol<sup>-1</sup>). The exponential term is the fugacity correction where B<sub>11</sub> is the second virial coefficient of pure CO<sub>2</sub>

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

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

is the correction for an air-CO<sub>2</sub> mixture in units of cm<sup>3</sup>·mol<sup>-1</sup> (Weiss, 1974).

The calculation for the fugacity at SST involves a temperature correction term for the increase of fCO<sub>2</sub> 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).

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

where dln(fCO<sub>2</sub>) 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

	<b>COLUMN HEADER</b>	<b>DESCRIPTION</b>
1.	GROUP/SHIP:	PMEL/ColumbusWaikato
2.	CRUISE_ID:	CW<Year>_<Month>
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 CO <sub>2</sub> (dry) in the headspace equilibrator at equilibrator temperature (T <sub>eq</sub> ) in parts per million. Water comes from bow intake 2m below the water line.
10.	xCO2A_PPM:	Mole fraction of CO <sub>2</sub> in air in parts per million.
11.	xCO2A_INTERPOLATED_PPM:	xCO <sub>2</sub> atm_ppm averaged linearly to match up with measurements xCO <sub>2</sub> eq_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 CO <sub>2</sub> in sea water in microatmospheres calculated as outlined in the DOE Handbook.
18.	CO2A_uATM:	Fugacity of CO <sub>2</sub> in air in microatmospheres
19.	dfCO2_uatm:	Sea water fCO <sub>2</sub> - air fCO <sub>2</sub> 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  $\Delta T$  (EqT – SST)(  $\pm 1^\circ\text{C}$ )
  - 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<sub>2</sub> measurements onboard research ships, *Analytica Chim. Acta*, 377, 185-191, 1998.
- Wanninkhof, R. and K. Thoning (1993) Measurement of fugacity of CO<sub>2</sub> 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<sub>2</sub> in seawater. *Nature* 300: 511-513.

For questions or comments contact:

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