

CW2004_09 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: September 20, 2004; Los Angeles, CA

Cruise End: October 4, 2004; Auckland, New Zealand

System Operator: Andrea Pratt; University of Washington

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

Dataset ID/Location: cw2004_09.csv (www.pmel.noaa.gov/co2/uwpc2/waikato.html)

Experiment Name: Underway measurement of atmospheric and surface water pCO₂

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

Westernmost Longitude: -119.713

Easternmost Longitude: -163.319

Northernmost Latitude: 31.397

Southernmost Latitude: -17.444

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.

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 CO₂ in surface seawater and water saturated air in order to determine the fCO₂. For ambient air and equilibrator headspace the fCO_{2a}, or fCO_{2eq} is calculated assuming 100% water vapor content:

$$fCO_{2a/eq} = xCO_{2a/eq}(P - p_{H_2O}) \exp(B11 + 2d12)P/RT$$

where fCO_{2a/eq} is the fugacity in ambient air or equilibrator, p_{H₂O} 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 ($82.057 \text{ cm}^3 \cdot \text{atm} \cdot \text{deg}^{-1} \cdot \text{mol}^{-1}$). The exponential term is the fugacity correction where B11 is the second virial coefficient of pure CO₂

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

$$\text{and } d12 = 57.7 - 0.118 T$$

is the correction for an air-CO₂ mixture in units of $\text{cm}^3 \cdot \text{mol}^{-1}$ (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 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).

$$d\ln(f\text{CO}_2) = (t_{eq} - SST)(0.0317 - 2.7851E-4 t_{eq} - 1.839E-3 \ln(f\text{CO}_{2eq}))$$

where $d\ln(f\text{CO}_2)$ is the difference between the natural logarithm of the fugacity at t_{eq} and SST, and t_{eq} is the equilibrator temperature in degrees C.

File Format

	COLUMN HEADER	DESCRIPTION
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 ₂ (dry) in the headspace

equilibrator at equilibrator temperature (T_{eq}) 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 ($E_{qT} - SST$)($\pm 1^{\circ}C$)
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 pCO₂ measurements onboard research ships, *Analytica Chim. Acta*, 377, 185-191, 1998.
- 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.

For questions or comments contact:

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