DS06STAR Readme File

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Ship Name: David Starr Jordan
Call Sign: WTDK
Country: United States
Ship Owner: National Oceanic and Atmospheric Administration (NOAA)

Temporal Coverage:
Cruise Start: August 6, 2006; San Diego, CA
Cruise End: December 7, 2006; San Diego, CA
Ports: Mazatlan, Mx; Punta Arenas, CR; Quezta, GT; Acapulco, MX

System Operator: Kim Belveal, NOAA

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

Dataset ID/Location: DS06STAR.csv (www.pmel.noaa.gov/co2/uwpco2)

Experiment Name: Underway measurement of atmospheric and surface water pCO2

Geographical Bounds (+ E, - W for Longitude; + N, - S for Latitude):
Westernmost Longitude: -78.1148
Easternmost Longitude: -118.793
Northernmost Latitude: 32.2563
Southernmost Latitude: 3.602

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
CO2 Sensor: Licor 6262, Serial # IRG3-951
Thermosalinograph: Seabird 21, Serial #2647, calibrated on 09-Feb-2006

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 and Salinity: A Seabird SBE 21 thermosalinograph was mounted in the bow chamber approximately 5m below the sea surface. The unit was calibrated annually and provided SST accurate to 0.02 °C and 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.

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:


and


**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:
- LL63974  318.15
- LL55858  350.75
- LL55881  485.02
- LL70585  551.85

**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 applying a time-weighted linear fit 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 fCO2a, or fCO2eq is calculated assuming 100% water vapor content:

\[
f_{\text{CO2a/eq}} = x_{\text{CO2a/eq}}(P-p_{\text{H2O}})\exp(B_{11}+2d_{12})P/RT
\]

where \( f_{\text{CO2a/eq}} \) is the fugacity in ambient air or equilibrator, \( p_{\text{H2O}} \) 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 cm\(^3\)·atm·deg\(^{-1}\)·mol\(^{-1}\)). The exponential term is the fugacity correction where \( B_{11} \) is the second virial coefficient of pure CO2

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

and \( d_{12} = 57.7 - 0.118 T \)

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 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).

\[
d\ln(f_{\text{CO2}}) = (t_{\text{eq}}-\text{SST})(0.0317-2.7851E-4 t_{\text{eq}} - 1.839E-3 \ln(f_{\text{CO2eq}}))
\]

where \( d\ln(f_{\text{CO2}}) \) is the difference between the natural logarithm of the fugacity at teq and SST, and \( t_{\text{eq}} \) is the equilibrator temperature in degrees C.

**File Format**

<table>
<thead>
<tr>
<th>COLUMN HEADER</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. GROUP/SHIP:</td>
<td>PMEL/DavidStarrJordan</td>
</tr>
<tr>
<td>2. CRUISE_ID:</td>
<td>DS&lt;Year&gt;_&lt;nth Cruise of Year&gt;</td>
</tr>
<tr>
<td>3. JD_GMT:</td>
<td>Decimal year day</td>
</tr>
<tr>
<td>4. Date_MM/DD/YYYY</td>
<td>Date in the format MM/DD/YYYY</td>
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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 pCO₂ measurements onboard research ships,


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