Description of Underway pCO_2 System on board the NOAA Ship *Discoverer* from 1992 through 1994

Overview: The CO₂ group at NOAA/PMEL installed and maintained an underway pCO₂ system onboard the NOAA Ship *Discoverer* for several cruises between August of 1992 through Spring of 1994.

September 1992 – December 1992

The National Oceanic and Atmospheric Administration's (NOAA) Ocean-Atmosphere Carbon Exchange Study (OACES) Program, in cooperation with the U.S. Joint Global Ocean Flux Study (U.S. JGOFS) Program, the Equatorial Pacific Ocean Climate Study (EPOCS) and Tropical Ocean Global Atmosphere (TOGA) Program, participated in a multifaceted oceanographic research cruise conducted aboard the NOAA Ship *Discoverer* from September 6 to December 8, 1992. The primary objective of this U.S. JGOFS/OACES effort was to determine the relative effects of biological fixation of carbon within equatorial upwelling, followed by vertical flux of that fixed carbon to abyssal depths, and of CO₂ outgassing. The cruise was focused on determining the concentrations of carbon species and describing ocean circulation in the upper ocean over the equatorial Pacific from 95°W to 140°W. This report includes a summary of the underway pCO₂ measurements collected during the cruise. Details of 1992 OACES/JGOFS/EPOCS/TOGA cruise can be found in Lamb et al., 1995 and Feely et al, 1995.

August 1992, March/April 1993, June 1994

In conjunction with the TOGA/TAO project, the CO₂ group at NOAA/PMEL installed and maintained an underway pCO₂ system on the *Discoverer* on three TOGA/TAO cruises between 1992 and 1994. The TOGA/TAO project is dedicated to maintaining the TAO buoy array (www.pmel.noaa.gov/tao/), in the equatorial Pacific. Details of the TOGA/TAO cruises between 1991 and 1995 are included in Johnson and Plimpton (1999).

March 1994

In the spring of 1994, NOAA participated in the Climate and Global Change (CGC94) World Ocean Circulation Experiment (WOCE) P-18 cruise on the *Discoverer*. Included in this report is a description of underway pCO₂ measurements collected along 103/110W as the ship transited between San Francisco and Punta Arenas, Chile. Details of the CGC94/WOCE P-18 cruise are included in Ho et al., 1997.

Data File					TAO Lines	System	Gas standards		
Name	Start Date	End Date	Start Port	End Port	Serviced	Operator	Low/Ref	Mid	High
DI1992_170.csv	20-Aug-92	27-Aug-92	Honolulu, HI	Hilo, HI	170°W, 155°W	Paulette	CC71615	CC71635	CC106646
						Murphy	352.67 ppm	417.6 ppm	488.51 ppm
DI1992_140.csv	6-Sep-92	9-Oct-92	Hilo, HI	Manzanillo	140°W, 125°W	Cathy	CC71615	CC71635	CC106646
DI1992_125.csv						Cosca	352.67 ppm	417.6 ppm	488.51 ppm
DI1992_110_95.csv	12-Oct-92	18-Nov-92	Manzanillo	Salinas, EQ	110°W, 95°W	Matt	CC71615	CC71635	CC106646
						Steckley	352.67 ppm	417.6 ppm	488.51 ppm
DI1993_155.csv	25-Feb-93	14-Mar-93	Hilo, HI	Samoa	170°W, 155°W	Dana	CC114944	CC111794	CC71635
DI1993_170.csv						Greeley	295.09 ppm	352.97 ppm	417.6 ppm
DI1994_110.csv	31-Mar-94	27-Apr-94	Easter Island	San Diego, CA	110°W	Matt	CC1782	CC1786	CC111790
						Steckley	355.83 ppm	419.1 ppm	482.23
DI1994_170.csv	3-Nov-94	21-Nov-94	Honolulu, HI	Honolulu, HI	170°W, 180	Cindy	CC111794	CC1786	CC111790
DI1994_180.csv						Venn	352.97 ppm	419.1 ppm	482.23 ppm

Principal Investigator:

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

System Installation, Maintenance, Troubleshooting, Data Processing and QC:

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

Ship Name: Discoverer Call Sign: WTEA Country: United States Ship Owner: National Oceanic and Atmospheric Administration (NOAA)

Location of data: www.pmel.noaa.gov/co2/uwpco2/

Experiment Name: Underway measurement of atmospheric and surface water pCO₂

Name/Model of pCO2 System: System 1.0, 1992. The system is described in detail in Wanninkhof and Thoning, 1993.

Analyzer: Li-COR 6251 (analog output) infrared (IR) analyzer

Method of analysis: Differential analyses relative to the low standard gas which flows continuously through the Li-COR reference cell. Measures dried air and equilibrator headspace gas. Gas flow is stopped prior to IR readings.

Drying method: Bow air and equilibrator headspace gas pass through a water trap cooled to 5° C and subsequently through a column of Mg(ClO₄)₂

Equilibrator (setup, size, flows): Weiss style Plexiglass showerhead equilibrator, with 17 liter water reservoir and 12 liter gaseous headspace. Water flow rate of 15 l/min, pumped from the bow of the ship through a clean sampling line. Headspace gas re-circulated at 5 l/min.

Standards (number, concentrations, frequency): Three are used with concentrations ranging from 300 ppm to 500 ppm. See table for specific concentrations. Standards are run once per hour.

Source of calibration and accuracy: All standards come from NOAA's Climate Monitoring and Diagnostics Laboratory (CMDL) and are traceable to the WMO scale. Stated accuracy of the standards is 0.07 ppm from 330 to 420 ppm and 0.2 ppm for higher or lower standards.

Sampling Cycle

The system runs on an hourly cycle during which three standard gases, one air sample from the bow mast and two surface water samples (from the equilibrator head space) are analyzed on the following schedule:

Minutes after the hour	Sample
4	Low Standard
8	Mid Standard
12	High Standard
30	Water
42	Air
60	Water

The two water values are averaged to yield a single hourly value which is merged with the air value to determine the air-water difference in fugacity (delta fCO_2). The time stamp and location are for the top of the hour after the air and two water sample analyses.

Units: All xCO_2 values are reported in parts per million(ppm)and are for dry gas and fCO₂ values are reported in microatmospheres (uatm) assuming 100% humidity at the equilibrator temperature.

Data reported:

COLUMN HEADER		DESCRIPTION		
1.	Group:	PMEL		
2.	JD_GMT:	Decimal year day		
3.	Date	The date format has been changed to comply with the IOCCP recommendations (DDMMYYYY)		
4.	Time:	GMT time		
5.	Latitude:	Latitude in decimal degrees (negative values are in southern hemisphere).		
6.	Longitude:	Longitude in decimal degrees (negative values are in western latitudes).		
7.	xCO2w_ppm:	Mole fraction of CO_2 (dry) in the headspace equilibrator at equilibrator temperature (Teq) in parts per million. Water comes from bow intake ~ 2 m below the water line.		
8.	xCO2a_ppm:	Mole fraction of CO ₂ in air in parts per million		
9.	Pres_sealevel_mB:	Barometric pressure at sea level, in millibars		
10.	EqTemp_C:	Temperature in equilibrator water in degrees centigrade. Temperature in equilibrator measured with a calibrated thermistor.		
11.	SST(TSG)_C:	Temperature from the ship's thermosalinograph in degrees centigrade.		
12.	Sal(TSG)_Permil:	Salinity from the ship's thermosalinograph on the Practical Salinity Scale		
13.	fCO2W@SST_uatm:	Fugacity of CO ₂ in sea water in microatmospheres.		
14.	fCO2a_uatm:	Fugacity of CO ₂ in air in microatmospheres.		
15.	dfCO2_uatm:	Sea water fCO_2 - air fCO_2 , microatmospheres		

using the average air value for the current hour.

16.	pCO2W@SST_uatm:	Partial pressure of CO ₂ in sea water in microatmospheres.
17.	pCO2a_uatm:	Partial pressure of CO ₂ in air in microatmospheres.
18.	dpCO2_uatm:	Sea water pCO_2 - air pCO_2 in microatmospheres.
* * * * *	* * * * * * * * * * * * * * * * * * * *	using the average air value for the current hour.

Data processing and Quality Control:

Carbon measurements at PMEL undergo the data processing and quality control procedures outlined in the DOE Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water (DOE, 1994).

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, C.E. Cosca, P.P. Murphy, M.F. Lamb, and M.D. Steckley (1995): CO₂ distributions in the equatorial Pacific during the 1991–1992 ENSO event. *Deep-Sea Res. Pt. II*, 42(2–3), 365–386.
- 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.
- Johnson, E.S., and P.E. Plimpton (1999): TOGA/TAO shipboard ADCP data report, 1991–1995. NOAA Data Report ERL PMEL-67, NTIS: PB2002-101766, NOAA/Pacific Marine Environmental Laboratory, 23 pp.
- Lamb, M.F., T. Lantry, J. Hendee, K.E. McTaggart, P.P. Murphy, R.A. Feely, R. Wanninkhof, F.J. Millero, R.H. Byrne, E.T. Peltzer, and D. Frazel (1995): Chemical and hydrographic measurements from the equatorial Pacific during boreal autumn, 1992. NOAA Data Report ERL PMEL-56, NTIS: PB95-274809, 166 pp.
- 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.