Description of Underway pCO₂ System onboard the Ka'imimoana

Laboratory: NOAA/PMEL

Name/Vintage: System 2.0, 1996. Built by PMEL engineering, LabView programming by Mike Stapp.

Reference:

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 Chimica Acta.*, *377*, 185-191, 1998.

Where installed: NOAA Ship Ka'imimoana

Location of Data: <u>www.pmel.noaa.gov/uwpco2</u>, or by request to Richard Feely

Analyzer: Li-COR 6252 (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): Equilibrator purchased from Scripps Institution of Oceanography and patterned after a design by Weiss, with 17 liter water reservoir and 12 liter gaseous headspace. Water flow rate is 10 l/min. Headspace gas is recirculated at 5 l/min.

Standards (number, concentrations, frequency): Three are used with approximate concentrations of 350, 420, and 480 ppm. In the eastern equatorial Pacific, a high standard of approximately 500 is used instead of 480 ppm. 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.

Standard consumption: 2 tanks a year of low/reference standard; less than 1 tank a year for mid and high standards.

Operating cycle:

PMEL's underway pCO_2 system runs on an hourly cycle which is further divided into 12 five minute cycles. A Valco valve is utilized to determine the gas to be analyzed, and the lowest standard gas is always used as the reference for the Licor IR. The first 15 minutes of each hour are dedicated to calibrating the system with three gas standards. The remaining 45 minutes of the hour alternate between measuring the equilibrator air and the atmospheric air from the bow. Thus, each 5 minute cycle is distinguished by the gas being measured:

<u>Minute</u>	Gas
1 to 5	Low Standard
6 to 10	Mid Standard
11 to 15	High Standard
16 to 20	Equilibrator
21 to 25	Equilibrator
26 to 30	Equilibrator
31 to 35	Air
36 to 40	Air
41 to 45	Air
46 to 50	Equilibrator
51 to 55	Equilibrator
56 to 60	Equilibrator

The sampling routine during a 5 minute cycle (300 seconds) is identical for each gas:

Second 0 to 9 (10 seconds)	Event Valco sets valve position for gas to be measured; Time,
,	Date, Latitude, and Longitude are recorded during the first second
10 to 141 (132 seconds)	Gas is flushed through the system
142 (1 second)	Flow to reference and sample cells is stopped; the
	following values are recorded:
	4 Licor values (averaged over flush time; 1 value per 33 seconds)
	Licor cell temp (averaged over flush time; 132 seconds)
	Gas Flow 1-4 (averaged over flush time; 132 seconds)
143 to 268 (126 seconds)	System is stabilized after flow is stopped
269 to 298 (30 seconds)	Stop flow data is acquired
299 (1 second)	Data is saved (listed below)
	Note: If the high standard gas has been sampled, the
	polynomial is created during the second 299; if air or
	equilibrator gas has been sampled, the polynomial is
	applied during second 299 prior to saving data.

Parameters recorded/frequency :

PC date PC time SCS Latitude SCS Longitude SCS sea surface temperature SCS salinity SCS wind speed SCS wind direction Licor reading (averaged over stop flow time; 30 seconds) SD for Licor readings (averaged over stop flow time; 30 seconds) Licor cell temp (averaged over stop flow time; 30 seconds) Air temp (averaged over flush and stop flow times; 288 seconds) Sea temp – bow (averaged over flush and stop flow times; 288 seconds) EQ temp (averaged over flush and stop flow times; 288 seconds) TSG cond (averaged over flush and stop flow times; 288 seconds) TSG temp (averaged over flush and stop flow times; 288 seconds) Barometer (averaged over flush and stop flow times; 288 seconds) Valco valve position Flow rates for bow air, recirculating equilbrator headspace, gas through Li-COR sample cell and reference cell Flow rate of water to the equilibrator

<u>Hardware details</u>

Temperature measurements: Thermistor positioned in bottom of equilibrator, calibrated against a mercury thermometer once a year **Pressure measurements:** Paros barometer located next to the Li-COR **Circulation pathway:** Two KNF pumps (one for head space gas, one for bow air) routed through a Valco 8-port valve. The Licor sample output is vented to the atmosphere.

Computer: Macintosh Quadra 650 **Operating software:** Labview Version 4.1

Computer interface boards: National Instruments NB-MIO-16X, 4 port serial board

Sensors read:

A/D 16 bit- voltage LICOR CO2 channel (0-5 V)
A/D 16 bit- voltage LICOR temperature (0-5 V)
A/D 16 bit- Aalborg gas flow meter on equilibrator sample (0-5 V)
A/D 16 bit- Aalborg gas flow meter on air sample (0-5 V)
A/D 16 bit- Aalborg gas flow meter on reference side of Licor (0-5 V)
A/D 16 bit- Aalborg gas flow meter on sample side of Licor (0-5 V)
A/D 16 bit- 100 ohm platinum temperature probe - equilibrator (0-5 V)
A/D 16 bit- 100 ohm platinum temperature probe - air (0-5 V)
A/D 16 bit- Data Industrial water flow meter (0-5 V)

Paros barometer is read via RS-232 port SeaBird thermosalinograph with remote temperature sensor is read via RS-232 port Trimble GPS receiver is read via RS-232 port Analog Devices digital I/O board is controlled via RS-232 port

Approximate Size and Footprint

In wet lab:

Equilibrator: a plexiglass cylindrical tube approximately 9" in diameter and 3 feet high. It is mounted on a 4 foot marine plywood board, 2 feet off the ground and offset from the bulkhead by 2 inches.

Next to the equilibrator is a 4' x 4' marine plywood board. Two pumps and two water traps are mounted on this board.

A water cooling bath, 20" wide by 24" deep by 30" high is underneath the plywood board.

6 aluminum gas cylinders are mounted near the instrumentation in the wet lab.

In the computer lab: A 60" bench along the bulkhead directly opposite from the equilibrator in the wet lab houses the following: UPS (underneath the bench) pCO₂ analytical system (includes valves and electronics), approximately 24" x 24" x 18" Macintosh Computer Paros barometer Storage for tools, spare parts

"Unique" Hardware or operating principles worth highlighting:

- Magnetic float and reed switch that will turn off pumps if condenser fills with water (design borrowed from Rik Wanninkhof).

- Automatic water drains for condenser (operate every once/hour during standard cycle)

What improvements would you incorporate in this system?

Improve drying of the gas, add 2-way communication to acquire data and remotely adjust controls, increase sampling frequency of surface ocean pCO_2