Description of Underway *p*CO_2 System onboard the NOAA Ship *Ka'imimoana* from 1996 through 2004

Overview: The CO_2 group at NOAA/PMEL installed an underway pCO_2 system onboard the NOAA Ship *Ka'imimoana* in June 1996, just prior to the ship's commissioning. The *Ka'imimoana* is designed and dedicated to maintaining the TAO buoy array (www.pmel.noaa.gov/tao/), in the equatorial Pacific.

The PMEL CO_2 group has maintained an underway pCO_2 system on the *Ka'imimoana* from 1996 to the present. This document describes the system that was on board from June 1996 through December 2004, and the underway data collected during 44 cruises during that time period. Details of the pCO2 system installed after 2004 is described in separate documents.

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Ship Name: Ka'imimoana
Call Sign: WTEU
Country: United States
Ship Owner: National Oceanic and Atmospheric Administration (NOAA)

Temporal Coverage:
44 cruises along TAO buoy lines between 10°N, 10°S and 165°E, 95°W
See table below for details on each cruise.

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

Experiment Name: Underway measurement of atmospheric and surface water pCO_2

Name/Model of pCO2 System: System 2.0, 1996. Built by PMEL engineering, LabView programming by Mike Stapp. The system is described in detail in Feely et al., 1998.

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 $Mg(ClO_4)_2$

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 re-circulated at 5 l/min.

Standards (number, concentrations, frequency): Three are used with concentrations ranging from 350 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.

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:

Minute	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	Event
0 to 9 (10 seconds)	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

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
GPS Latitude
GPS Longitude
Licor reading (averaged over stop flow time; 30 seconds)
Standard deviation for Licor readings (averaged over stop flow time; 30 seconds)
Licor cell temperature (averaged over stop flow time; 30 seconds)
Sea Surface temperature at the sea chest (averaged over flush and stop flow times; 288 seconds)
Equilibrator temperature (averaged over flush and stop flow times; 288 seconds)
TSG Salinity (averaged over flush and stop flow times; 288 seconds)
Barometric pressure (averaged over flush and stop flow times; 288 seconds)
Valco valve position
Flow rates for bow air, re-circulating equilbrator headspace, gas through Li-COR sample cell and reference cell
Flow rate of water to the equilibrator

Hardware details
Temperature measurements:
Equilibrator Temperature: YSI Seriess 700 Thermistor positioned in bottom of equilibrator, calibrated annually against a Guildline model 5010 platinum resistance thermometer with a NIST traceable probe. Temperatures are believed accurate to 0.02°C.
Sea Surface Temperature and Salinity: A Seabird SBE 21 thermosalinograph was mounted in the bow chamber 3 m from the intake at nominally 5-m depth. The unit was calibrated annually and provided SST accurate to 0.02 °C and salinity accurate to 0.1.
Pressure measurements: Paroscientific Model 760-16B barometer located next to the underway system an accuracy of ± 0.2 hPa. The equilibrator had two 0.5-cm ID vents, 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.
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

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.

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)
pCO_2 analytical system (includes valves and electronics), approximately 24” x 24” x 18”
Macintosh Computer

Paros barometer
Storage for tools, spare parts

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, H.B. Milburn, C.E. Cosca, M. Stapp, and P.P. Murphy, A new automated underway system for making high precision pCO_2 measurements onboard research ships, Analytica Chim. Acta, 377, 185-191, 1998.

Wanninkhof, R. and K. Thoning (1993) Measurement of fugacity of CO_2 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_2 in seawater. Nature 300: 511-513.

Table of NOAA Ship *Ka'imimoana* cruises with underway *p*CO2 data collected from 1996 through 2004

Cruise Name	Data File Name	Start Date	End Date	Start Port	End Port	TAO Line Serviced	Gas standards		
							Low/Ref	Mid	High
GP3-96-KA	KA1996_03.csv	19-Jun-96	16-Jul-96	Honolulu, HI	Kwajalein	165°E, 180°	CC01782 358.4 ppm	CC01790 418.73 ppm	CC02158 487.48 ppm
GP4-96-KA	KA1996_04.csv	19-Jul-96	14-Aug-96	Kwajalein	Honolulu, HI	170°W, 155°W	CC01782 358.4 ppm	CC01790 418.73 ppm	CC02158 487.48 ppm
GP5-96-KA	KA1996_05.csv	25-Aug-96	24-Sep-96	Honolulu, HI	San Diego, CA	140°W, 125°W	CC01782 358.4 ppm	CC01790 418.73 ppm	CC02158 487.48 ppm
GP6-96-KA	KA1996_06.csv	29-Sep-96	28-Oct-96	San Diego, CA	Manzanillo	110°W, 95°W	CC02184 347.4 ppm	CC01790 418.73 ppm	CC02158 487.48 ppm
GP7-96-KA	KA1996_07.csv	22-Nov-96	18-Dec-96	Honolulu, HI	Honolulu, HI	170°W, 155°W	CC02184 347.4 ppm	CC01790 418.73 ppm	CC02158 487.48 ppm
GP1-97-KA	KA1997_01.csv	3-Feb-97	4-Mar-97	Manzanillo	San Diego, CA	110°W, 95°W	CA01910 353.24 ppm	CC01790 418.73 ppm	CC02158 487.48 ppm
GP2-97-KA	KA1997_02.csv	25-Mar-97	A[r 23, 97	San Diego, CA	Honolulu, HI	140°W, 125°W	CA01910 353.24 ppm	CC01790 418.73 ppm	CC02158 487.48 ppm
GP3-97-KA	KA1997_03.csv	6-May-97	3-Jun-97	Honolulu, HI	Kwajalein	170°W, 155°W	CA01998 348.96 ppm	CC01790 418.73 ppm	CC02158 487.48 ppm
GP4-97-KA	KA1997_04.csv	8-Jun-97	3-Jul-97	Kwajalein	Honolulu, HI	165°E, 180°	CA01998 348.96 ppm	CC01790 418.73 ppm	CC02158 487.48 ppm
GP5-97-KA	KA1997_05.csv	31-Jul-97	30-Aug-97	Manzanillo	San Diego, CA	110°W, 95°W	CA01998 348.96 ppm	CC01790 418.73 ppm	CC02158 487.48 ppm
GP6-97-KA	KA1997_06.csv	27-Sep-97	30-Oct-97	San Diego, CA	Honolulu, HI	140°W, 125°W	CA01998 348.96 ppm	CC01790 418.73 ppm	CC02158 487.48 ppm
GP7-97-KA	KA1997_07.csv	6-Nov-97	16-Dec-97	Honolulu, HI	Honolulu, HI	165°E, 180°, 170°W	CA02823 348.43 ppm	CC01790 418.73 ppm	CC02158 487.48 ppm
GP1-98-KA	KA1998_01.csv	5-Feb-98	13-Mar-98	San Diego, CA	San Diego, CA	110°W, 95°W	CA02823 348.43 ppm	CC01790 418.73 ppm	CC02158 487.48 ppm
GP2-98-KA	KA1998_02.csv	18-Apr-98	20-May-98	San Diego, CA	Honolulu, HI	140°W, 125°W	CA02862 345.12 ppm	CC01790 418.73 ppm	CC02158 487.48 ppm
GP3-98-KA	KA1998_03.csv	2-Jun-98	3-Jul-98	Honolulu, HI	Kwajalein	170°W, 155°W	CA02862 345.12 ppm	CC01790 418.73 ppm	CC02158 487.48 ppm
GP4-98-KA	KA1998_04.csv	7-Jul-98	3-Aug-98	Kwajalein	Honolulu, HI	165°E, 180°	CA02846 346.18 ppm	CC01790 418.73 ppm	CC02158 487.48 ppm
GP5-98-KA	KA1998_05.csv	5-Sep-98	10-Oct-98	Honolulu, HI	Honolulu, HI	140°W, 125°W	CC111794 352.97 ppm	CA02858 423.79 ppm	CA02813 483.65 ppm
GP7-98-KA	KA1998_07.csv	19-Oct-98	13-Nov-98	Honolulu, HI	Suva, Fiji	170°W, 155°W	CA03392 347.79 ppm	CA02858 423.79 ppm	CA02813 483.65 ppm
GP8-98-KA	KA1998_08.csv	18-Nov-98	11-Dec-98	Suva, Fiji	Honolulu, HI	170°W, 180°	CA02809 346.22 ppm	CA02858 423.79 ppm	CA02813 483.65 ppm
GP1-99-KA	KA1999_01.csv	22-Jan-98	23-Feb-98	Honolulu, HI	San Diego, CA	140°W, 125°W	CA01910 345.68 ppm	CA02858 423.79 ppm	CA02813 483.65 ppm
GP2-99-KA	KA1999_02.csv	30-Apr-98	5-Jun-98	San Diego, CA	San Diego, CA	110°W, 95°W	CA01924 345.55 ppm	CA02858 423.79 ppm	CA02813 483.65 ppm
GP3-99-KA	KA1999_03.csv	30-Jun-98	31-Jul-98	Honolulu, HI	Kwajalein	170°W, 155°W	CA01998 346.13 ppm	CA02858 423.79 ppm	CA02813 483.65 ppm
GP1-00-KA	KA2000_01.csv	1-Feb-00	4-Mar-00	Honolulu, HI	San Diego, CA	140°W, 125°W	CA03927 350.1 ppm	CA02858 423.79 ppm	CC02000 490.84 ppm

Cruise Name	Data File Name	Start Date	End Date	Start Port	End Port	TAO Line Serviced	Gas standards		
							Low/Ref	Mid	High
GP2-00-KA	KA2000_02.csv	11-Apr-00	20-May-00	San Diego, CA	Honolulu, HI	110°W, 95°W	CA03948 352.37 ppm	CA02858 423.79 ppm	CA01906 505.08 ppm
GP3-00-KA	KA2000_03.csv	13-Jun-00	14-Jul-00	Honolulu, HI	Kwajalein	170°W, 155°W	CA03948 352.37 ppm	CA02858 423.79 ppm	CA01906 505.08 ppm
GP4-00-KA	KA2000_04.csv	20-Jul-00	10-Aug-00	Kwajalein	Honolulu, HI	165°E, 180°	CA03946 349.13 ppm	CA02858 423.79 ppm	CA01906 505.08 ppm
GP5-00-KA	KA2000_05.csv	30-Aug-00	1-Oct-00	Honolulu, HI	Honolulu, HI	140°W, 125°W	CA03946 349.13 ppm	CA02858 423.79 ppm	CA01906 505.08 ppm
GP6-00-KA	KA2000_06.csv	14-Oct-00	10-Nov-00	Honolulu, HI	Kwajalein	170°W, 155°W	CA03913 351.34 ppm	CC01904 488.44 ppm	CA01906 505.08 ppm
GP8-00-KA	KA2000_08.csv	15-Nov-00	10-Dec-00	Kwajalein	Honolulu, HI	165°E, 180°	CA03913 351.34 ppm	CC01904 488.44 ppm	CA01906 505.08 ppm
GP1-01-KA	KA2001_01.csv	14-Jan-01	15-Feb-01	Honolulu, HI	San Diego, CA	140°W, 125°W	CA03913 351.34 ppm	CA02827 423.38 ppm	CA01906 505.08 ppm
GP2-01-KA	KA2001_02.csv	28-Mar-01	4-May-01	San Diego, CA	San Diego, CA	110°W, 95°W	CA03913 351.34 ppm	CA02827 423.38 ppm	CA01906 505.08 ppm
GP1-02-KA	KA2002_01.csv	1-Mar-02	4-Apr-02	San Diego, CA	Manzanillo	110°W, 95°W	CA04957 372.37 ppm	CC01789 466.95 ppm	CA01906 505.08 ppm
GP2-02-KA	KA2002_02.csv	8-Apr-02	13-May-02	Manzanillo	Honolulu, HI	140°W, 125°W 110°W	CA04957 372.37 ppm	CC01789 466.95 ppm	CA01906 505.08 ppm
GP3-02-KA	KA2002_03.csv	29-May-02	30-Jun-02	Honolulu, HI	Kwajalein	170°W, 155°W	CA04440 351.55 ppm	CC01789 466.95 ppm	CA01906 505.08 ppm
GP5-02-KA	KA2002_05.csv	16-Aug-02	16-Sep-02	Honolulu, HI	Honolulu, HI	140°W	CA04440 351.55 ppm	CC01789 466.95 ppm	CA01906 505.08 ppm
GP7-02-KA	KA2002_07.csv	3-Oct-02	26-Oct-02	Honolulu, HI	Kwajalein	170°W, 155°W	CC121961 360.31 ppm	CC01789 466.95 ppm	CA01906 505.08 ppm
GP1-03-KA	KA2003_01.csv	6-Jan-03	13-Feb-03	Honolulu, HI	San Diego, CA	140°W, 125°W	CA05018 347.87 ppm	CC01789 466.95 ppm	CA02829 505.58 ppm
GP2-03-KA	KA2003_02.csv	24-Mar-03	25-Apr-03	San Diego, CA	Manzanillo	110°W, 95°W	CA05049 347.55 ppm	1721 414.00 ppm	CA02829 505.58 ppm
GP5-03-KA	KA2003_05.csv	21-Aug-03	Sep 28. 03	Honolulu, HI	Honolulu, HI	140°W, 125°W	CA05508 346.38 ppm	1721 414.00 ppm	CA02829 505.58 ppm
GP7-03-KA	KA2003_07.csv	16-Oct-03	14-Nov-03	Honolulu, HI	Kwajalein	170°W, 155°W	CA05508 346.38 ppm	1721 414.00 ppm	CA02829 505.58 ppm
GP8-03-KA	KA2003_08.csv	17-Nov-03	13-Dec-03	Kwajalein	Honolulu, HI	165°E, 180°	CA05508 346.38 ppm	1721 414.00 ppm	CA02829 505.58 ppm
GP1-04-KA	KA2004_01.csv	24-Mar-04	26-Apr-04	San Diego, CA	Manzanillo	110°W, 95°W	CA05517 346.32 ppm	1721 414.00 ppm	CA02829 505.58 ppm
GP2-04-KA	KA2004_02.csv	27-Apr-04	2-Jun-04	Manzanillo	Honolulu, HI	140°W, 125°W	CA05517 346.32 ppm	1721 414.00 ppm	CA02829 505.58 ppm
GP3-04-KA	KA2004_03.csv	15-Jun-04	17-Jul-04	Honolulu, HI	Kwajalein	170°W, 155°W	CA05517 346.32 ppm	1721 414.00 ppm	CA02829 505.58 ppm
GP4-04-KA	KA2004_04.csv	17-Jul-04	17-Aug-04	Kwajalein	Honolulu, HI	165°E, 180°	CA05504 346.66 ppm	1721 414.00 ppm	CA02829 505.58 ppm