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MEASUREMENTS OF UNDERWAY fCO, IN THE EASTERN EQUATORIAL PACIFIC ON NOAA SHIPS *MALCOLM BALDRIGE* AND *DISCOVERER* FROM FEBRUARY TO SEPTEMBER, 1994

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# MEASUREMENTS OF UNDERWAY fCO<sub>2</sub> IN THE EASTERN EQUATORIAL PACIFIC ON NOAA SHIPS MALCOLM BALDRIGE AND DISCOVERER FROM FEBRUARY TO SEPTEMBER, 1994

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From February through September, 1994 underway ABSTRACT. measurements of the fugacity (partial pressure) of carbon dioxide (fCO<sub>2</sub>) were performed in the Eastern Equatorial Pacific as part of the Ocean Atmosphere Carbon Exchange Study (OACES) of the National Oceanographic and Atmospheric Administration (NOAA). The measurements were performed with semiautonomous instruments which measured the fugacity in the air and in the headspace of an equilibrator drawing water from the bow of the ship, from which the fCO<sub>2</sub> of the surface water is calculated. From the difference in fugacity in air and water, the CO<sub>2</sub> flux from the Equatorial Pacific can be estimated. On the NOAA ship MALCOLM BALDRIGE the system measured three reference standards, three air values, and eight water values per hour. The system on the DISCOVERER measured three standards, one 19-minute average air sample and one 20-minute average water sample per hour. This report contains a description of the methodology and reduction of the fCO<sub>2</sub> and ancillary measurements. The results from the cruises of the MALCOLM BALDRIGE in the Equatorial Pacific in the (boreal) spring and fall of 1994, and from the DISCOVERER along nominally 110 °W in the spring of 1994 are shown in a series of graphs with fCO<sub>2</sub> air and water versus latitude as top panel and temperature and salinity versus latitude as bottom panel. The full data sets and support measurements can be obtained either via anonymous FTP from: <ftp://ftp.aoml.noaa.gov/pub/ocd/carbon/uweqpac94> or via the World Wide Web: <a href="http://www.aoml.noaa.gov/ocd/oaces/">http://www.aoml.noaa.gov/ocd/oaces/</a>.

#### 1. INTRODUCTION

The underway component of the Ocean-Atmosphere Carbon Exchange Study (OACES) of NOAA's Climate and Global Change (C&GC) program performs surface water measurements to determine the oceanic source and sink regions for atmospheric CO<sub>2</sub>. The results are used to map air-water concentration differences to provide an estimate of the magnitude of the air-water CO<sub>2</sub> flux. Quasi-continuous measurements of the fugacity of CO<sub>2</sub> in air and surface water using an infrared analyzer have been performed on NOAA ships MALCOLM BALDRIGE and DISCOVERER from 1991 through 1996. The ships have performed yearly cruises to the Eastern Equatorial Pacific in support of the TOGA/TAO mooring array. This cruise schedule has facilitated a bi-annual record of CO<sub>2</sub> observations in this region. In addition to the Equatorial cruises, these ships have been used for the NOAA OACES/TRACERS long lines work with meridional sections in the Atlantic, Pacific and Indian Oceans. In this report we present the Equatorial observations and a long lines cruise along nominally 107 °W from 67 °S to 20 °N for 1994.

The Equatorial Pacific is the largest natural CO<sub>2</sub> source to the atmosphere. It has become increasingly apparent from historical and from current measurements that the CO<sub>2</sub> source is also highly variable (Keeling, 1965; Feely et al., 1987; Feely et al., 1994; Feely et al., 1995a; Wanninkhof et al., 1996). As pointed out by Feely et al. (1995b) El Niño conditions cause depressed fCO<sub>2</sub> values in the mixed layer. Decreased upwelling during El Niño periods causes less water containing high dissolved inorganic carbon concentrations to reach the surface and

lowers the surface fCO<sub>2</sub> levels. The latest El Niño conditions started in 1991/92. The coverage of fCO<sub>2</sub> on the NOAA Ships MALCOLM BALDRIGE, and DISCOVERER, and now the KA'IMIMOANA in the Equatorial Pacific has offered the opportunity to determine the evolution of the surface water fCO<sub>2</sub> signal with unsurpassed resolution.

Previous results, as discussed in Dandonneau (1995) and Wanninkhof et al. (1995), show that the surface water fCO<sub>2</sub> are influenced by the rate of upwelling, with decreased upwelling causing lower fCO<sub>2</sub> levels. Recent work suggests that sea surface temperature is an important parameter determining fCO<sub>2</sub>, as fCO<sub>2</sub> increases by about 4.2 % / °C (Takahashi et al., 1993) by a combination of decrease in solubility and repartitioning of the inorganic carbon pools favoring gaseous CO<sub>2</sub> at higher temperatures. For the Equatorial Pacific at the equator an opposite effect is observed with high fCO<sub>2</sub> corresponding with lower temperatures. This is caused by upwelling water containing high levels of dissolved inorganic carbon (DIC). The fCO2 values in the Equatorial Pacific are thus controlled by a complex interplay of upwelling, mixing, biological drawdown, and water temperature. This can be illustrated with a simple example. A water parcel which rises to the surface the water will be cold, and contain high DIC and nutrients due to remineralization of organic tissue at depth. It thus reaches the surface with high fCO<sub>2</sub>. Two competing processes takes place in the euphotic zone. Warming of the water will increase the fCO2 while biological drawdown will decrease the fCO<sub>2</sub> level. Since the response time of heating is generally shorter than biological productivity, the initial effect will be further increases in fCO2 which will be counteracted in time by net biological productivity. The strong zonal current structures, which are influenced by El Niño as well, will cause the upwelled water to move on the order of 1 m·s<sup>-1</sup> (or about 30 degrees longitude per month). Thus significant displacements of the water over time take place while the biological and physical processes influence fCO2 in the water parcel. The large variability in physical, biological, and chemical processes which take place thus cause large interannual variability in fCO<sub>2</sub> levels in the Equatorial Pacific. The biannual coverage of the Equatorial Pacific region has enabled us to start quantifying and parameterizing the processes involved in controlling fCO<sub>2</sub>.

The South Pacific cruise is part of the NOAA OACES/TRACERS long lines effort and was designated as a World Ocean Circulation Experiment/World Hydrographic Program, WOCE/WHP line (P18). The cruise transected the Equatorial region along 103/110 °W thereby giving additional coverage in the Eastern Equatorial Pacific during the (boreal) spring of 1994. The data from the cruise also confirmed the large Southeastern Pacific fCO<sub>2</sub> source region from 40 °S to 20 °S first observed in Murphy et al. (1991). This appears to be a robust feature and is unique to the Southeastern Pacific. The subtropical gyres in the Indian, Southwestern Pacific, and Atlantic Ocean are predominantly sink regions.

This data report presents the measurements from the MALCOLM BALDRIGE during the boreal spring and fall of 1994, and measurements taken on the DISCOVERER along 103/110 °W from 65 °S to 20 °N as part of the Climate and Global Change 1994 (CGC94) World Ocean Circulation Experiment (WOCE) P-18 cruise during March/April 1994. The cruise track in the spring included transects along 95 °W between 5 °N and 5 °S, 110 °W between 5 °N and 8 °S, 125 °W between 8 °N and 8 °S, and 140 °W between 9 °N and 9 °S. In the fall, coverage included transects from 8 °N to 8 °S along 95 °W, 110 °W, and 125 °W. The DISCOVERER Cruise included a deadhead from San Francisco to Puenta Arenas, and return along 103/110 °W (see Fig. 1).

### 2. UNDERWAY fCO<sub>2</sub> SYSTEM DESCRIPTIONS

Two slightly different underway fCO<sub>2</sub> measurement systems were used on the DISCOVERER and MALCOLM BALDRIGE. They are referred to as systems 1.0 and 1.5,

respectively. System 1.0 has been described in detail in Wanninkhof and Thoning (1993) and will only be briefly discussed here. System 1.5, which was a modification from the system 1.0 based on three years experience with the original system, was used for the first time during 1994 and will be discussed in greater detail below.

#### 2.1. Underway fCO<sub>2</sub> System Version 1.0 Description

System 1.0 was built at NOAA/Climate Monitoring and Diagnostics Laboratory using a LI-COR Non-Dispersive Infrared (NDIR) analyzer (LI-COR model LI-6251, Lincoln, NE) (LI-COR, 1990) and is described in Wanninkhof and Thoning (1993). The system runs on hourly cycle in which the first 15 minutes are dedicated to analyzing compressed gas standards, the next 22 minutes are used to measure air, and an equilibrator headspace is measured for the last 23 minutes. Compressed gas standards bracket the air and water values. The air sample is drawn through multilaminate tubing (Dekoron, Furon, Aurora, OH) from the bow of the ship to the laboratory (OCEA lab). The headspace of a shower equilibrator is measured to determine the fCO<sub>2</sub> in the surface water. Water is drawn from the bow pump, through 2" PVC tubing to the OCEA lab where it enters the equilibrator. The droplets and severe turbulence in the equilibrator cause the gases in the water to equilibrate with the gases in the semi-closed headspace such that the fCO<sub>2</sub> in the headspace will be the same as the water. Based on our results in the South Atlantic, we believe we can routinely obtain air values with a precision of 0.3 μatm and water values with a precision of 2 μatm.

#### 2.2. Underway fCO<sub>2</sub> System Version 1.5 Description

#### 2.2.1. Overview

For the MALCOLM BALDRIGE Equatorial Pacific cruises the underway fCO<sub>2</sub> system was slightly modified from system version 1.0 described above. The modified system is referred to as system 1.5. This system was used to determine the fCO<sub>2</sub> of surface water and overlaying air on a quasi-continuous basis. When in operation, seawater is drawn at a rate of 15 l·min<sup>-1</sup> from the uncontaminated seawater intake on the ship's bow bubble at 5 m below the sea surface to a 24 l shower head equilibrator, where the 16 l headspace reaches equilibrium with seawater on a short time scale (Fig. 2). At specific times during an hourly cycle, the content of the headspace is measured by the LI-COR infrared CO<sub>2</sub> analyzer. Air from the marine boundary layer is drawn continuously from the bow mast to the underway fCO<sub>2</sub> system through Dekoron tubing at a rate of 6 l·min<sup>-1</sup> and vented into the laboratory. At designated times, 100 ml·min<sup>-1</sup> of air is teed off into the LI-COR infrared CO<sub>2</sub> analyzer.

The CO<sub>2</sub> measurement are made by a LI-COR model LI-6251 NDIR CO<sub>2</sub> analyzer (LI-COR, 1990), which is based on the difference in absorption of 4.26 µm (IR) radiation passing through two gas sampling cells. The lowest of the three reference gas standards is continuously flowed through the reference cell at a rate of 15 ml·min<sup>-1</sup>. The sample cell is flushed with either one of three reference gas standards (calibrated in the laboratory of Dr. P. Tans at NOAA/CMDL), marine air, or headspace gas from the equilibrator. The analyzer is operated in stopped flow mode in which the flow of sample gas is stopped during analysis. In the hourly cycle, the first 12 minutes of every hour are devoted to calibration of the LI-COR CO<sub>2</sub> analyzer. Next, the headspace gas of the equilibrator is sampled for a total of 18 minutes. This is followed by bow air sampling for 12 minutes. Finally, the equilibrator headspace is sampled again, concluding the last 18 minutes of the hour.

The analog output of the LI-COR CO<sub>2</sub> analyzer is converted to a digital signal with a 12-bit A/D converter board (DASCON-1, Keithley MetraByte, Taunton, MA) and the data is stored on a computer. The three other A/D channels are used to read the water flow meter (Cole Parmer, Vernon Hills, IL) and to convert the analog thermistor readings recording the temperature of the sample cell within the LI-COR and water temperature within the equilibrator (YSI, Yellow Springs, OH). The computer also logs the ship's position using a Global Positioning System (Magellan Systems, San Dimas, CA) and atmospheric pressure using a barometer (Model 370, Setra Systems, Boxborough, MA) with a RS-232 interface through the communication ports. All of these readings aid in simpler and more accurate data interpretation. The GW-BASIC program controlling the operation of the underway fCO<sub>2</sub> system is designed for easy timing sequence modifications and peripheral instrument elimination in the event of failure. (The program is listed in Appendix A).

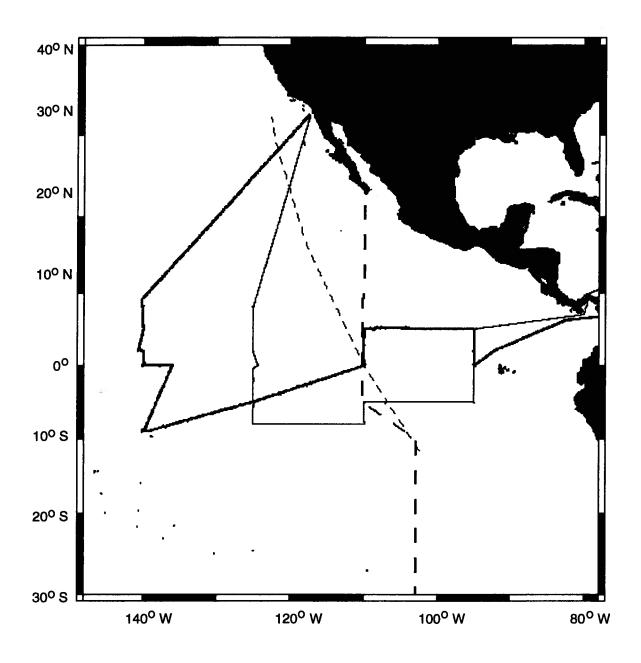
A schematic diagram of the flow pathways is given in Fig. 3. The standards, ambient air, and equilibrator air gases are diverted to the NDIR sample cell by switching the appropriate 3-way solenoid valves (Skinner valves, Honeywell, New Britain, CT) in the valve switching box. The ambient air is drawn from the bow through 70 m of 0.95 cm OD (3/8") Dekoron tubing using a rubber bellows pump (Air Cadet, Cole Parmer, Vernon Hills, IL). The air is passed through a water trap held at 7 °C to lower the water vapor content and a 1 µm PTFE filter (Gelman Sciences, Ann Arbor, MI) to remove particulates and aerosols. The head space of the equilibrator is circulated with a small diaphragm pump (Spectrex, Redwood City, CA) at 100 ml·min<sup>-1</sup> through 0.31 cm OD (1/8") stainless steel tubing. Like the marine air samples, the water vapor pressure of the equilibrator air is also decreased by passing it through a water trap held at 7 °C. This trap contains a float with a magnet which will trip a breaker deactivating power to the pumps if the water level in the traps reaches a critical level. This mechanism prevents flooding of the valves and the NDIR if the traps are not emptied or if water inadvertently enters the air lines. In the Equatorial Pacific the traps are emptied daily. The air is completely dried using Mg(ClO<sub>4</sub>)<sub>2</sub> (Magnesium perchlorate) downstream of the 3-way valves prior to entering the NDIR.

#### 2.2.2. Standard Gas Standardization/Conversion Polynomial

The first 12 minutes of every hour are devoted to calibration of the LI-COR CO<sub>2</sub> analyzer. Three different standard gases of known concentrations, covering the CO<sub>2</sub> range that is encountered on the cruise, are passed through the IR cell at 50 ml·min<sup>-1</sup> for 3.5 minutes each. The flow is then stopped for 10 seconds to let the pressure and temperature of the cell equilibrate with stagnant flow conditions. Then, the analog output of the detector is sampled five times over three seconds. A second order polynomial is determined by curve fitting of the three standard voltage values. This polynomial is used to convert air or water LI-COR voltage readings for the subsequent hour, to a mixing ratio (ppm). During the post cruise data reduction (see below), the reference gas output values from the LI-COR are averaged with ones from the next hour and used to calculate a second order polynomial to "bracket" CO<sub>2</sub> marine air and equilibrator reading during the period.

#### 2.2.3. Sampling/Data Set

After standards are measured, the headspace gas of the equilibrator is passed through the detector four times at 4.5 minutes each for a total of 18 minutes. The procedure is similar to that of reference gas analysis in which the sample gas flow is stopped at the end of each period after which 5 consecutive readings are taken. This is followed by three bow air samples at 4 minutes each, totaling 12 minutes, and finally the equilibrator headspace is sampled four more times at 4.5 minutes each, concluding the last 18 minutes of the hour.



**Fig. 1a.** Cruise tracks for the Equatorial Pacific, spring 1994. Solid lines = MALCOLM BALDRIGE; Dotted lines = DISCOVERER.

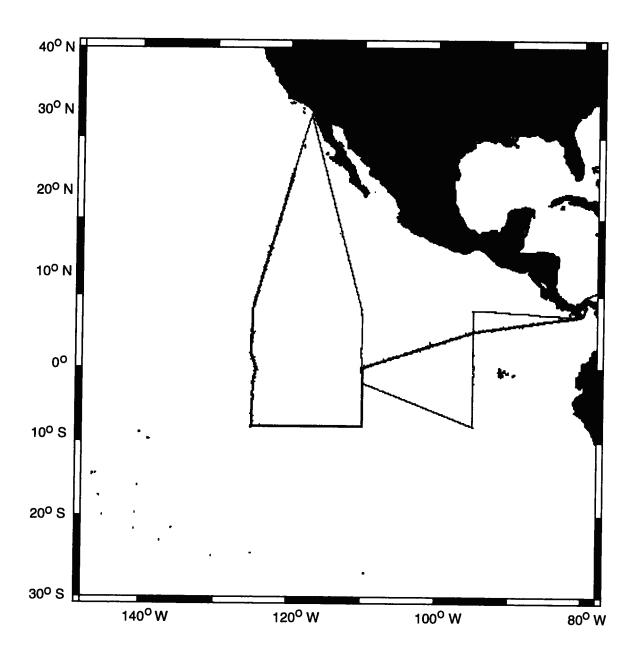


Fig. 1b. Cruise tracks for the MALCOLM BALDRIGE, Equatorial Pacific, fall 1994.

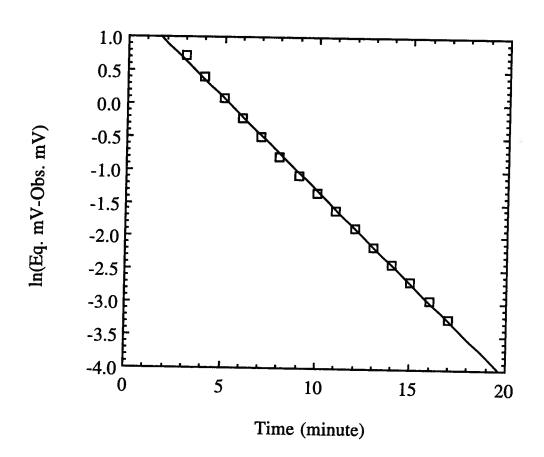


Fig. 2. Response of the IR after the headspace of the detector was flushed with nitrogen. The Y-axis gives the natural logarithm of the difference between the response of the detector at equilibrium conditions (Eq. mV) and the observed response (Obs. mV). The negative slope of the line is the equilibration time (3.6 minutes). From Wanninkhof and Thoning (1993).

# NOAA/AOML Underway pCO2 System Plumbing Block Diagram and Relay Schedule

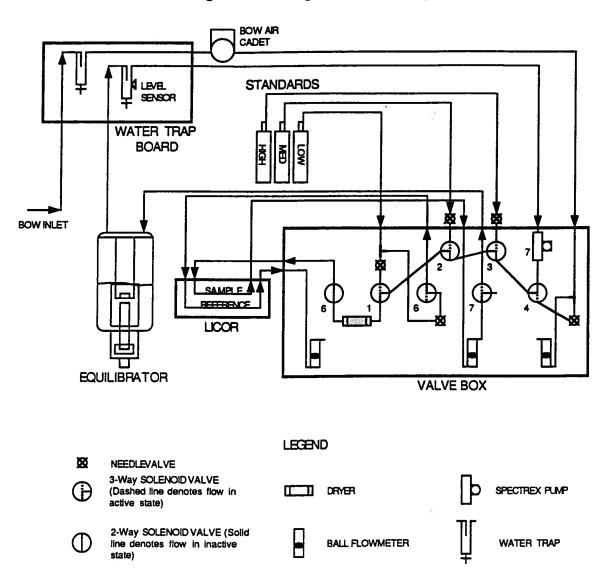


Fig. 3. Schematic of underway pCO<sub>2</sub> system used on the MALCOLM BALDRIGE Equatorial Pacific cruises in 1994.

Each sampling phase is done in the following manner: the sample is flushed through the system for 3.5 minutes (the equilibrator sample has a longer flushing time of 4 minutes to ensure complete flushing of new sample through the system). Then, flow stops and the system is vented to equilibrate with ambient pressure for 10 seconds. The four analog channels (LI-COR CO<sub>2</sub>, LI-COR temp, equilibrator temp., equilibrator water flow meter) are then scanned five times, taking about 3 seconds total. An average of these scans is printed on the screen and logged to a data file. The Magellan GPS and Setra barometer are also read at this time. A brief waiting period follows and then the next sample is introduced. During post cruise data reduction, the thermosalinograph (TSG) temperature and salinity data are incorporated into the fCO<sub>2</sub> data file.

#### 2.2.4. Screen Display

A comprehensive screen display facilitates on board quality control and error checking (Fig. 4). On the top line, the status of the system is displayed. The information includes: the current sample being measured (standard, "water" (= equilibrator headspace), or ambient air); whether the system is flushing the particular gas through the detector, waiting, or taking a reading; and a countdown (in seconds) of time remaining for the particular event. Displayed immediately below this status bar on the left hand corner are the mixing ratios of the standards (as calibrated by NOAA/CMDL) with the hourly updated detector response in millivolts (mV) listed below. To the right of this reading, the average mixing ratios of three air and eight equilibrator headspace readings of the previous hour along with their standard deviation are displayed. The main display contains the information taken during the current hourly cycle. It includes: the gas sampled; the time (in GMT); decimal latitude and longitude (from the GPS); the mixing ratio of CO<sub>2</sub> as determined from a polynomial through the standards measured the previous hour; the equilibrator temperature from the thermistor mounted in the bottom of the equilibrator; the LI-COR temperature from a plate thermistor mounted on the IR cell; and the ambient pressure measured with the Setra barometer; located immediately above the LI-COR, and the flow rate of water through the equilibrator. Inspection of the displayed readings along with knowledge of the default settings and atmospheric or oceanic CO<sub>2</sub> levels facilitates trouble shooting.

#### 3. DATA REDUCTION

The final data reduction occurs on shore utilizing several spreadsheet macros (Excel 5.0 Visual BASIC, Microsoft, Redmond, WA) for merging and calculation. The raw data files with relevant information of each 4.5 minute sample event logged on a separate line are stored on the hard drive of the computer. They are listed by month and downloaded to floppy disks or removable cartridges (SyQuest Technology, Fremont, CA).

The raw data files are in ASCII format and the columns are as follows:

- a) Phase
- b) Date
- c) Time
- d) Lat.
- e) Long.
- f) Standard Conc. (-99.99 for air and "water" samples)
- $CO_2 mV$

- h) CO<sub>2</sub> Concentration
- i) Li-COR Temperature (mV)
- j) Li-COR Temperature (°C)
- k) Equilibrator Temperature (mV)
- l) Equilibrator Temperature (°C)
- m) Equilibrator water flow rate (mA)
- n) Equilibrator water flow rate (L·min<sup>-1</sup>)
- o) Setra Barometric Pressure

This data is merged by time with sea surface temperature (SST) and salinity data obtained from the thermosalinograph (TSG) situated in the bow bubble. The TSG data is logged at 30 second intervals on the MALCOLM BALDRIGE shipboard computing system (SCS). The TSG and raw pCO<sub>2</sub> data are merged using a macro called "prepare raw file". Subsequently macros called "make bracket files" and "check for data gaps" will delete columns not used in the calculations and assure that every hour has 14 data points. If less data points are obtained because of instrument malfunction or shut down, the appropriate number of blank rows are manually inserted. The next macro "average xCO<sub>2</sub> mV values" averages the mV response of the standards before and after the hourly series of 14 samples and calculates a second order polynomial fit through these points. This fit is used to recalculate xCO<sub>2</sub> for air and water. These new xCO<sub>2</sub> values are visually checked against the original ones determined on board from a single set of standards. If values differ by more than 2 ppm, the cause is investigated. Frequently, the discrepancy is caused by an erroneous standard reading because a standard tank was turned off or because of an instrument malfunction. The ship's location is checked at this point as well. Occasionally, the Magellan GPS gives a wrong value because of electronic interference or antenna blockage by the ship's superstructure. Any errors are corrected by linear extrapolation, or if a large block of values are incorrect, the correct data are obtained from the SCS data files. Values are hand deleted as well when the water flow to the equilibrator is turned off or when the drying traps are changed. The equilibrator temperature and SST are compared to assure that they track each other (generally to within 0.2 °C). Deviations are caused by stopped flow through the equilibrator or an inadvertent mismatch between TSG files and underway files during merging. Missing thermosalinograph data is interpolated. The fCO<sub>2</sub> values are then calculated following the procedure below. In the final file the average air value for a given hour is matched with the water values for the hour and the difference ( $\Delta fCO_2$ ) is calculated with positive values denoting a net flux from the water. The sequence of individual macros assures that data is scrutinized, and where necessary, corrected at every step of the merging process and calculations.

#### 4. 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  $CO_2$  in surface seawater and water saturated air in order to determine the  $\Delta fCO_2$ . For ambient air and equilibrator headspace the  $fCO_{2a}$ , or  $fCO_{2eq}$  is calculated assuming 100 % water vapor content:

$$fCO_{2a/eq} = xCO_{2a/eq}(P - pH_2O)exp(B_{11} + 2\delta_{12})P / RT$$
 (2)

where  $fCO_{2a/eq}$  is the fugacity in ambient air or equilibrator,  $pH_2O$  is the water vapor pressure at the sea surface temperature, P is the atmospheric pressure (in atm), and T is the SST or equilibrator temperature (in K) and R is the ideal gas constant (82.057 cm<sup>3</sup>·atm·deg<sup>-1</sup>·mol<sup>-1</sup>). The exponential term is the fugacity correction where  $B_{11}$  is the second virial coefficient of pure  $CO_2$  ( $B_{11}$ =-1636.75+12.0408T-0.0327957T<sup>2</sup>+3.16528x10<sup>-5</sup>T<sup>3</sup>) and  $\delta_{12}$  (= 57.7 - 0.118 T) is the correction for an air- $CO_2$  mixture in units of cm<sup>3</sup>mol<sup>-1</sup> (Weiss, 1974). The calculation for the fugacity at SST involves a temperature correction term for the increase of  $fCO_2$  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).

$$\Delta \ln(\text{fCO}_2) = (t_{\text{eq}} - \text{SST})(0.0317 - 2.78510^{-4}t_{\text{eq}} - 1.83910^{-3}\ln(\text{fCO}_{\text{2eq}})$$
 (3)

where  $\Delta ln(fCO_2)$  is the difference between the natural logarithm of the fugacity at  $t_{eq}$  and SST, and  $t_{eq}$  is the equilibrator temperature in °C.

#### 5. ESTIMATES OF PRECISION

Accuracy and precision are determined by instrument performance, gas calibration, and uncertainties in the calculations leading from instrument response to the fCO<sub>2</sub> value. Precision of the LI-COR infrared analyzer appears well within the factory specification of 0.2 ppm peak-to peak deviation for instantaneous reading at 350 ppm. The CO<sub>2</sub> reference gases are believed to be accurate to 0.1 ppm for standards in the range of 300 to 400 ppm based on the WMO-X93 scale. The standard with nominal mixing ratio of 520 ppm is accurate to an estimated  $\pm$  1 ppm.

The accuracy and precision of the measurements will also depend on changes in temperature and pressure in the IR cell between analysis of samples and standards. For an estimate of this effect the average LI-COR cell temperature and pressure for the three gas standards and the equilibrator and air analyses are compared for the start of the spring cruise from 4/15/95 until 4/30/94. The average difference in the hourly reading of pressure between standards and samples is -0.01 mB  $\pm$  0.28 mB (n=351) while the difference in temperature is -0.01 °C  $\pm$  0.28 °C (n=351). The distribution of temperature differences, shown in Fig. 5, is close to a log normal distribution. Thus there is no bias in the readings and variations in temperature and pressure will degrade the overall precision but not cause biases in the fCO<sub>2</sub> calculations. The influence of temperature and pressure variations on the LI-COR reading is primarily caused by expansion/contraction of gas in the sample cell and thus can be approximated assuming ideal gas behavior. If the standard deviation of the differences are used as a guide, the pressure variations contribute about 0.1 ppm to the uncertainty of the mixing ratio (0.28 mB /  $10\overline{1}3$  mB × 400 ppm) and the temperature variation about 0.3 ppm (0.21 K /  $300 \text{ K} \times 400 \text{ ppm}$ ). Since the response of the detector to standards before and after the hourly sample sequence is used, the uncertainty from pressure and temperature variations will decrease. Comparing the average temperature of the cell for the standard runs before and after the samples with the temperature during the sample run the average difference is  $0.00~^{\circ}\text{C} \pm 0.06~^{\circ}\text{C}$  (n=345) which translates into an uncertainty of 0.1 ppm. Thus under typical operating conditions the variation of cell temperature and pressure does not degrade the precision appreciably.

Gas in IR: Water	/ Start at : 22:24:	23 /	Status : flush	/ sec.	remaining: 40
GPS: 2544.08,N,08009.73	,w		LAST 60 MIN A	VG. AND ST	D. DEV
CO2 Standards Informati	ion		Sample P.P.M	Std. Dev	
STD # STD_1 STD_2	2 STD 3		WATER 350.53		
STD ppm 296.53 347.87	524.87		AIR 356.64		
STD mV -18.1 312.1	1126		WATER 350.34	0.34	
GAS TIME D.LAT	D.LON pCO2_PPM	IR_TEMP	EQ_TEMP E	Q_FLOW	PRESSURE
WAT 01:16:05 25.66	80.17 350.54	24.2	26.1	10	1014.53
WAT 01:20:05 25.66	80.17 350.49	24.2	26.2	10	1014.53
WAT 01:25:05 25.66	80.17 350.65	24.3	26.2	10	1014.53
WAT 01:29:05 25.66	80.17 350.51	24.2	26.3	10	1014.22
AIR 01:33:45 25.66	80.17 356.51	24.3	26.2	11	1014.89
AIR 01:37:45 25.66	80.17 356.99	24.3	26.4	11	1014.89
AIR 01:41:45 25.66	80.17 356.14	24.3	26.5	11	1014.89
WAT 01:46:45 25.66	80.17 349.88	24.2	26.2	10	1014.27
WAT 01:50:45 25.66	80.17 350.09	24.2	26.3	10	1014.82
WAT 01:55:45 25.66	80.17 350.77	24.3	26.4	10	1014.42
WAT 01:59:45 25.66	80.17 350.89	24.2	26.1	10	1014.22
10-14-1994 01:59:59			DOC	/NOAA/AOI	ML/OCD/CO2

Fig. 4. Screen display from the underway pCO2 system used on the MALCOLM BALDRIGE Equatorial Pacific cruises in 1994. (Description in the text).

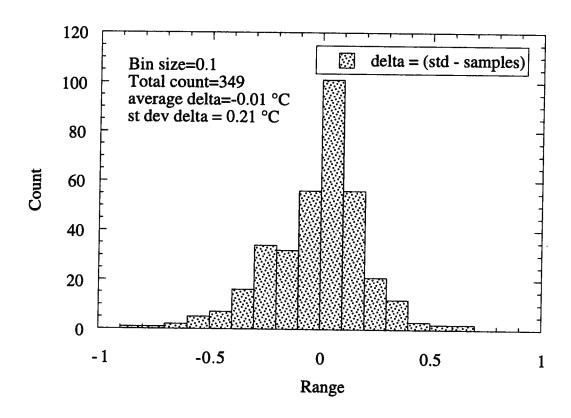


Fig. 5. Difference in the IR temperature during sampling of standards and air or water samples from 4/15 to 4/30/94. Since the response of the detector is dependent on the temperature, any systematic bias will influence the accuracy of the results, while the deviation will influence the precision. The influence of the IR temperature is roughly proportional to the absolute temperature. Thus the standard deviation of 0.21 °C is equivalent to 0.25 ppm in the CO<sub>2</sub> reading

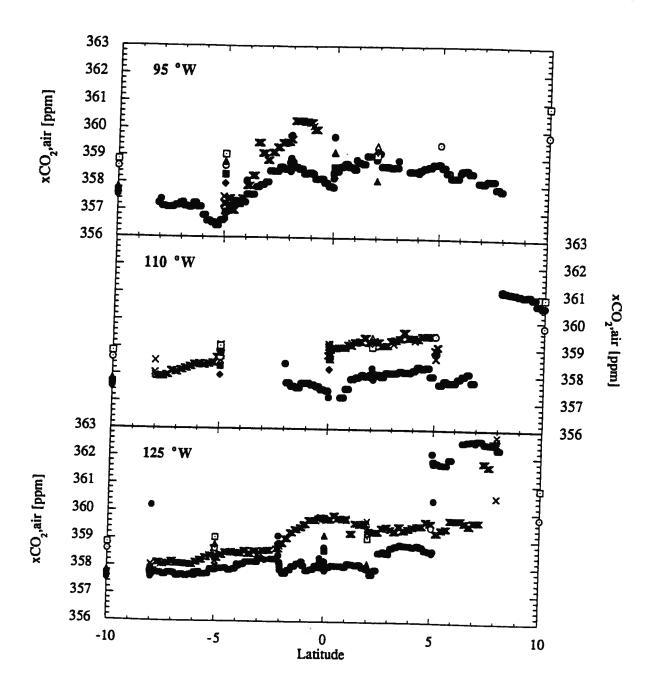


Fig. 6. Comparison of air values from the MALCOLM BALDRIGE cruise ( $\times$  = spring;  $\bullet$  = fall) with the monthly mean values obtained at the NOAA/CMDL flask network for 1994 ( $\circ$  = February;  $\square$  = March;  $\diamond$  = April;  $\triangle$  = May;  $\blacktriangle$  = July;  $\blacksquare$  = August;  $\diamond$  = September; Conway and Tans, personal communication, see http://www.cmdl.noaa.gov/). The values at 2 °N are from Christmas Island, while the other values are 5 ° averages from a commercial vessel en route from the West Coast of the United States to New Zealand with an equator crossing near the date line.

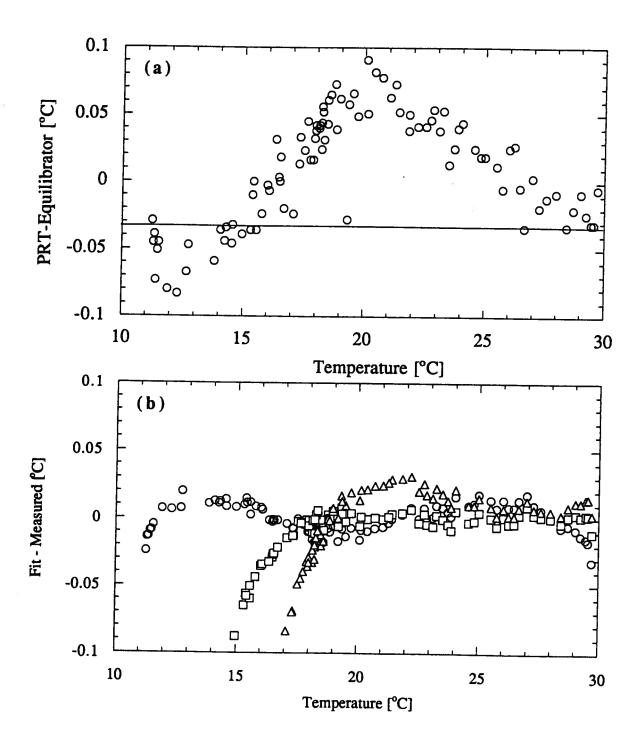


Fig. 7. (a) Comparison between the Guildline PRT with the thermometer mounted in the equilibrator and which was read every six-hours while the ship was underway. (b) Difference between the measured temperature with the Guildline PRT and the third order fit for three algorithms which were created from the calibrations (0 = 1/94 11-30 °C;  $\Box$  = 1/94 20-30 °C;  $\Delta$  = 7/94 20-30 °C). See text for details.

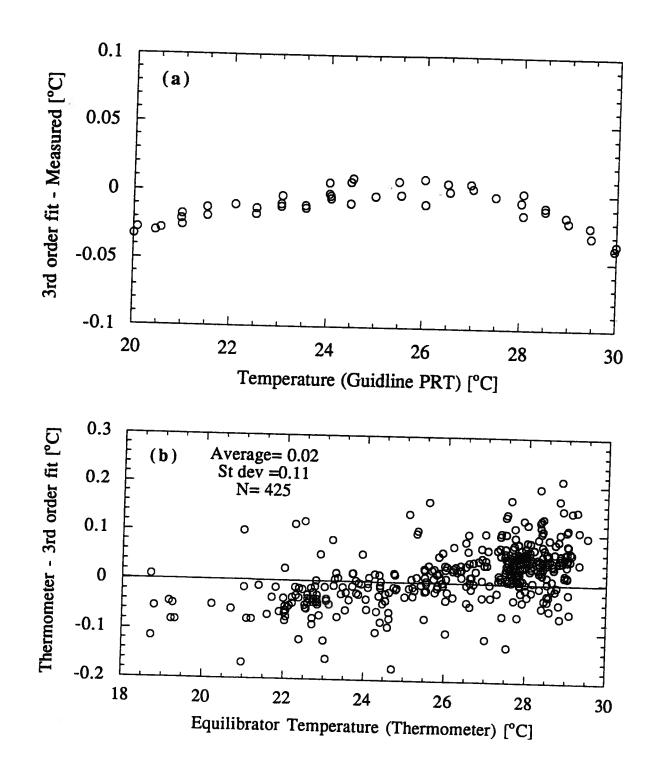


Fig. 8 (a) Comparison of the best fit algorithm and the calibration on 7/94 which shows that the thermistor did not drift appreciably during the Spring-94 cruise. (b) Comparison between the 6-hour thermometer reading in the equilibrator during the cruise and the thermistor temperature deduced from the algorithm listed in Eq 3.

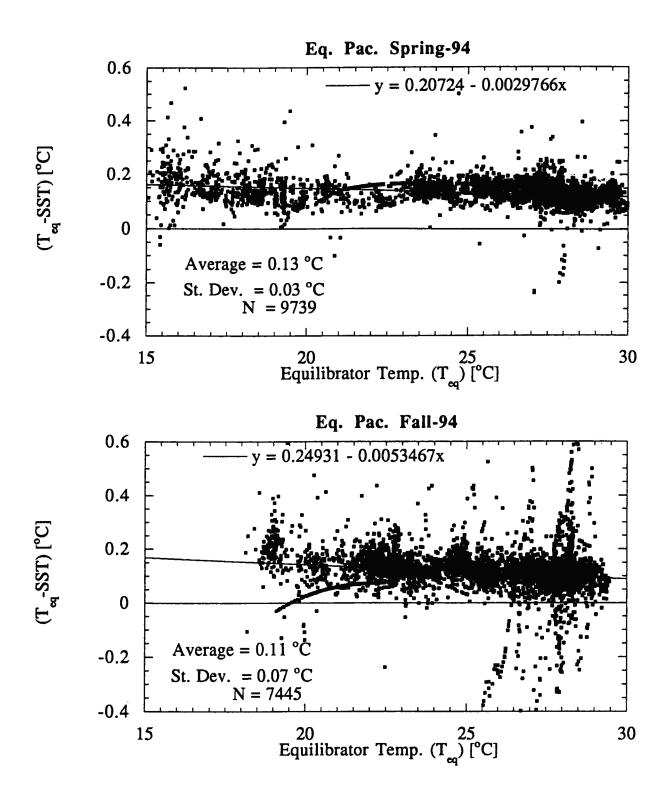


Fig. 9. Difference between the  $t_{eq}$  and SST for the spring and fall Equatorial Pacific cruises on the MALCOLM BALDRIGE. The temperature in the equilibrator is on average 0.2 °C warmer than the SST at the bow intake. High deviations occur when the flow is stopped.

The accuracy of the ambient air values for Equatorial Pacific cruises in 1992 and 1993 have been checked in Wanninkhof et al. (1996) by comparing 4 to 8° latitudinal band averages with values obtained from the NOAA/CMDL network suggesting that air values are accurate to within 1 ppm. Figures 6a-c show graphical comparisons of the air values obtained during Equatorial Pacific cruises in 1994 and monthly averaged values at Christmas Island (2°N, 157°W) and from flask samples taken on container vessels en route from San Francisco to Auckland, crossing the equator near the international date line. Although many flask sample values are missing and a zonal gradient in xCO<sub>2</sub> is likely, it appears that on average the air mixing ratios taken on the MALCOLM BALDRIGE are about 0.5 ppm lower than the NOAA/CMDL flask values.

The greatest source of uncertainty is the equilibration efficiency of the equilibrator and correction of the fCO<sub>2w</sub> to SST. As shown in Chen et al. (1995) (pages 21-24) the equilibration efficiency is a function of water flow rate because of entrainment of bubbles through the water drain which is made up by introduction of marine air through the vents. During the Equatorial Pacific 1994 cruises the flow rate was nominally 15 l·min<sup>-1</sup> and based on previous test this would cause a maximum deviation towards ambient air values of 0.5 ppm.

The correction to SST is important because this is where biases, in addition to random error, can be introduced if the temperature probes are not adequately calibrated. The thermosalinograph was calibrated in October 1993 and November 1994 by Seabird Electronics and the two sets of calibration coefficients yielded a maximum deviation in salinity and temperature of 0.005 and of 0.005 °C, respectively (which is insignificant). The equilibrator temperature was measured with a YSI glass bead thermistor encapsulated in a 1/8" stainless steel probe. The resistance was converted to temperature using an empirical 3rd-order polynomial algorithm determined from calibrations before and after the spring cruise using a Guildline 9540 platinum resistance thermometer (PRT). The combination of the pre-cruise and post-cruise calibrations yielded a fit of:

$$t_{eq} = 73.6908 - 0.0383166R + 0.0000085113R^2 - 0.000000007868R^3$$
 (3)

where  $t_{eq}$  is in °C and R is the resistance in Ohm. The post cruise (new) calibration was only performed from 20 to 30 °C. Figures 7 and 8 show the results of laboratory calibrations. Fig. 7a compares the Guildline PRT with the thermometer mounted in the equilibrator and which was read every six hours while the ship was underway. The agreement is within 0.05 °C but there does appear to be a systematic trend with the thermometer reading up to 0.08 °C low from 18-23 °C and about 0.02 °C high at 30 °C. Fig. 7b shows the difference between the measured temperature with the PRT and the third order fit for three algorithms which were created from the calibrations. The one labeled 1/94 is the algorithm used to determine t<sub>eq</sub> on the cruise. The other two are algorithms created in the range from 20 to 30 °C from calibration on 1/94 and 7/94. In the range of measurement all three algorithms show good agreement but deviation becomes large outside the range of measurement. Fig. 8a gives a comparison of the best fit algorithm and the calibration on 7/94 which shows that the thermistor did not drift appreciably during the Spring-94 cruise. Fig. 8b compares the 6-hour thermometer reading in the equilibrator during the cruise with the thermistor temperature deduced from the algorithm listed above. Twenty five data points which disagreed more than  $\pm$  0.25 °C are not plotted and presumed to be reading errors. The average difference of 0.02 °C, again indicating that the thermistor did not drift during the cruise, and the standard deviation of 0.11 °C is likely due to reading errors of the analog thermometer mounted in the equilibrator. The thermometer readings were not used because the measurements were only performed every six hours and probably have a reading error of at least 0.05 °C. The calibration comparisons suggest that biases in  $t_{eq}$  are less than 0.05 °C (or equivalent of 1  $\mu$ atm).

Figs. 9a,b shows the difference between the  $t_{eq}$  and SST for the cruises. The temperature in the equilibrator is on average 0.2 °C warmer than the SST at the bow intake. The larger deviations are during periods when the flow to the equilibrator was restricted, or when the air conditioning system in the laboratory malfunctioned. The slight trend in the data of smaller differences at higher temperatures is because heating in the lines is partly offset by temperatures in the laboratory being lower than SST.

#### 6. EXPLANATION OF COLUMNS IN THE DATA SET

A sample of the underway fCO2 data for the Spring and Fall 1994 Equatorial Pacific data are given in Appendix B. Here is an explanation of the column headers:

Ъ	Julian Day
Date	Date (month, day, year)
Time	Greenwich Mean Time
Lat	Latitude (decimal degrees)
Long	Longitude (decimal degrees)
xCO2,w	mixing ratio of CO <sub>2</sub> (dry) in headspace of equilibrator. Water comes from
	a bow intake 5 m below the water line (in ppm)
xCO2,a	mixing ratio of CO <sub>2</sub> (dry) from the bow of the ship (15 m above water)
Eq Temp	temperature in equilibrator measured with a calibrated thermistor (in °C)
Pressure	pressure in OCEA laboratory (in mB)
SST (TSG)	sea surface temperature measured at the water intake (5 m below water
	line) (in °C)
Sal (TSG)	salinity measured at the water intake (5 m below water line)
fCO2w, eq	fugacity of water in equilibrator calculated according to DOE (1994) (in
fCO2 in situ	μatm)
fCO2w, in situ	fugacity of water at SST calculated from algorithm of Weiss et al. (1982)
fCO2a	fugacity of CO <sub>2</sub> in air
ΔfCO2	water- air fugacity difference

#### Notes:

Columns have a default value of -999.99 in case of instrument malfunction or erroneous readings. Furthermore, if a suspicious xCO<sub>2</sub> value, pressure or temperature value is encountered which cannot be readily extrapolated, the fCO<sub>2</sub> is not calculated

For the spring cruise the air pump failed during the 140 °W transit. The xCO<sub>2</sub> values from 125°W at the appropriate latitude were used instead. The 125 °W transect occurred 2-weeks to a month earlier and air values show a seasonal cycle, particularly in the Northern hemisphere. To assess the possible error introduced by this extrapolation the air values at 125 °W were compared with the northern hemisphere values along 110 °W at the same latitude but occupied a month later, immediately after the 140 °W transect. The agreement from 0 to 5 °N is within 1 ppm. The correspondence between xCO<sub>2</sub> at 125 °W and at 140 °W when the air pump was working is good

as well. At 21 °N, the xCO<sub>2</sub>a value was 362.82 at 140 °W and 363.96 at 125 °W; at 8 °S the 140 °W value was 358.21 and at 125 °W it was 357.79. The *in situ* SST, salinity, and pressure values were used to calculate the corresponding fCO<sub>2</sub>a values along 140 °W.

# 7. SUPPORT MEASUREMENTS

Discrete samples were taken for DIC, O<sub>2</sub>, chlorophyll a and nutrients at nominally one degree spacing along the north-south transects. Near the equator the spacing was decreased to one half degree spacing between 1 °N and 1 °S, and 1/4 degree spacing from 0.5 °N and 0.5 °S. The samples were stored for shore based analyses, or in the case of oxygen and chlorophyll they were stored up to a week and analyzed aboard the ship. The storage and lack of expertise of the operators degraded the sample analysis compared to routine operation on dedicated long line cruises but because of the large natural variability in the Equatorial Pacific area, the analyses yield spring and fall cruises are given in Table 1 and 2. Upwelling near the equator is manifested by high DIC, AOU (apparent oxygen utilization), and nutrient values. Sea surface temperatures and oxygen values are low. Furthermore, an east-west trend is observed with higher DIC, and nutrient values towards the coast.

#### 7.1. DIC Determination

Samples for dissolved inorganic CO<sub>2</sub> (DIC) analysis were drawn from 10-L Niskin bottles or from the underway line into 500 ml Pyrex bottles using Tygon tubing. Each sample had 0.2 ml of a saturated HgCl<sub>2</sub> solution added as preservative. The sample bottles were sealed with glass stoppers lightly covered with Apiezon grease (DOE, 1994). The samples were then stored in darkness at ambient (room) temperature for a maximum of two month prior to being analyzed on shore.

DIC analysis was performed by extracting the inorganic carbon from a 20 ml aliquot of sea water sample by acidification and subsequent displacement of the gaseous CO<sub>2</sub> into a coulometer cell using an automated SOMMA system. Details concerning this system and procedures are presented in Johnson (1992), and Johnson et al. (1993). Precision and accuracy based on replicates and analyses of certified reference materials is estimated at 3 µmol·kg<sup>-1</sup>, or about twice as great as analysis under optimal conditions

## 7.2. Oxygen Measurements

The oxygen samples were collected, in 150 ml ground-glass stoppered sample bottles from the surface Niskin bottle or from the underway line. Reagents were added and the samples were stored in the dark with the stopper submerged under water. They were analyzed using the method described by Carpenter (1965), with computer-controlled colorimetric endpoint determination as described in Friederich et al. (1984) on a weekly basis. Oxygen samples that have been collected and analyzed using the above methodology with prolonged storage have a precision of about 2-3 percent.

Table 1. EQUARTORIAL PACIFIC SPRING 1994 SUPPORT MEASUREMENTS

ı		ı																																					
total Chi			0.17	0.23	0.25	0.47	0.25	0.27	0.30	0.26	0.34	14.1	0.49	0.35		0.30	0.34	0.19	0.27	0.23	0.26	0.23	0.43	0.24	0.36	0.36	0.23	0.34	0.25	0.17	0.38	0.30	0.18	0.17	0.22	0.22	0.25		0.26
phao	(ug-l-1)	0.05	9	0.05	9	0.11	0.07	0.05	000	0.05	0.10	0.17	0.10	0.08		90.0	0.10	0.02	0.05	0.02	0.07	0.07	0.12	0.07	90:0	0.08	0.11	0.11	0.0	0.03	0.00	0.00	0.03	0.05	0.05	0.07	0.0		90:0
Chl a	(ue·]-1)	0.20	0.13	0.18	0.20	0.36	0.19	0.22	0.23	0.21	0.24	1.24	0.39	0.27		0.24	0.24	0.17	0.22	0.20	0.19	0.16	0.31	0.17	0:30	0.28	0.12	0.24	0.20	0.14	0.29	0.23	0.15	0.12	0.17	0.15	0.20		0.20
DIC	(umol·kg-1)	1812	1826	1842	1869	2066		2071		2079	2063				2015		1761	1921		2003	2006	2017	2027		2026		2013	2008	1984	2000	1932	1909		1929	1956			1960	1983
SiO	(mol·l·l)	0.0	0.0	0.0	0.0	4.2		3.3		3.0	2.1			0:0	8.0		0.0	0.0	0.0		8.0	0.0	1.0		6.0										0.0			0.0	0.7
NO,	(umol·l·l)	0.0	0.0	0.0	0.0	7.4		7.6		8.3	6.8			1.8	5.0		2.0	3.3	3.4		3.5	3.4	2.7		2.4										0.8			1.1	2.5
NO	(umol·l·1)	0:0	0.0	0.0	0.0	1.9		2.5		2.5	1.6			2.0	1.0		0.3	0.7	9.0		9.0	6.0	2.5		2.7										0.0			0.0	0.0
AOU	(µmol·l·¹)	2	æ	5	-	18	∞	31	15	35	7			-10	1-		-1	3	3	3	5	-7	2	-1	9	6	00	7	••	4	0	9		7					
o	(µmol·l·1)	200	198	197	203	197	210	186	206	181	<b>504</b>			215	210		203	198	199	199	196	210	200	207	201	200	200	198	194	199	199	195		198					
Temp.	(၁)	28.67	28.88	28.50	27.54	23.99	23.06	23.39	22.43	23.58	25.03			56.69	27.46		27.64	27.96	27.70	27.78	27.68	27.22	26.57	26.27	25.98	25.60		26.64	27.46	27.64	28.72	28.23		28.58	28.52	28.30		28.13	27.61
Salinity		32.04	32.43	32.69	33.02	35.00	35.00	35.18	35.15	35.22	35.12			35.11	35.12		34.85	35.19	35.12	35.16	35.14	35.19	35.19		35.11	35.03		34.74	34.74	34.71	34.40	34.13		34.45	34.72	34.78		34.78	34.92
Latitude Longitude		94.99	95.00	95.00	95.02	94.98	95.00	94.94	94.97	94.98	94.96	95.00	95.00	95.03	110.02	110.00	109.97	125.00	124.93	125.02	125.00	124.90	124.99	125.00	124.32	124.51	124.67	125.08	125.02	125.01	125.00	124.93	140.00	139.98	140.22	140.46	140.00	140.02	139.85
Latitude		5.03	4.00	3.00	2.00	1.01	0.51	-0.03	-0.55	-1.00	-2.01	-3.00	4.00	4.98	4.98	-5.00	-8.00 -8.00	-8.00	4.97	-3.98	-3.00	-2.02	-1.00	-0.50	0.02	0.47	1.00	1.96	3.00	4.00	5.08	8.15	00.6	5.02	4.00	3.00	2.00	1.97	1.00
Time	(GMT)	20:10	03:20	09:22	05:15	12:31	15:05	18:30	23:08	05:00	08:02			04:38	23:15		02:18	21:38	21:35	03:41	09:18	15:04	19:56	23:30	04:30	05:53	10:31	05:38	12:17	18:15	00:47	03:15		04:42	10:36	15:11		08:00	13:41
Date		4/19/94	4/20/94	4/20/94	4/21/94	4/21/94	4/21/94	4/21/94	4/21/94	4/22/94	4/22/94	4/22/94	4/22/94	4/23/94	4/26/94	4/27/94	4/28/94	4/30/94	5/1/94	5/2/94	5/2/94	5/2/94	5/2/94	5/2/94	5/3/94	5/3/94	5/3/94	5/4/94	5/4/94	5/4/94	5/5/94	5/6/94	5/24/94	5/25/94	5/25/94	5/25/94	5/25/94	5/26/94	5/26/94

Table 1. EQUARTORIAL PACIFIC SPRING 1994 SUPPORT MEASUREMENTS

Time Latitude Longitude Salinity Temp. O, AOU	Temp. O <sub>2</sub>	Temp. O <sub>2</sub>	emp. O <sub>2</sub>		PΟ	Þ	NO,	, ON	SiO,	DIC	Chl A	a Page	17.
(CMT) ("C) (µmol·l·¹) (µmol·l·¹)	(µmol·l·¹)	(µmol·l·¹)	(µmol·l·¹)		Omri)	( <del>1</del> -1-1	(umol·l·1)	(umol·l·1)	(I-Mod-1)	(I-molebo-1)		puido (1.1.1)	
139.97 35.06 26.67	35.06 26.67	26.67	,	1	,		7	1	1	(MINOLERE)		(Light)	(Hg·l.,)
0.01 139.94 35.05 26.85	35.05 26.85 192	26.85 192	192		13		0.2	4.6	-	1100	0.31	0.08	0.40
0.02		196	196	196			0.2	4.6	<u> </u>	3006	,,	8	
137.75 35.07 28.06	35.07 28.06 167	28.06 167	167		33		}	) :	]	C007	0.32	0.08	0.40
130.00					i								
	35.01 27.74	27.74		201	_		0	8 4	40	7001	0.18	0.05	0.23
120.00					•		?	2	C.O	1994	0.20	0.08	0.28
-1.67 115.01	35.07		25.61	22							0.09	0.02	0.11
0.00 110.02 35.08 25.15	35.08 25.15	25.15		197	01		-	7.3	(		0.18	0.08	0.26
110.01 34.99	34.99 25.41	25.41		205	(1 V		7.0	Ç,	3.5	2029	0.21	0.08	0.30
1.01 110.03 34.00 25.30	34 00 25 30	25.20		507	٠ ٢		ć	,			0.16	0.08	0.23
207 11013 2414 2722	34.14	77.73		CI CCI	3 0		0.2	0.0	1.9	2016	0.23	0.10	0.33
2.00 110.00 24.14 27.23	24.14 27.23	27.72		0	>		0:0	0.1	0.0	1939	0.21	0.09	0.30
3.00 110.05 24.14 21.23	24.05	27.1.7			•		,	,			0.24	0.02	0.26
3.00 110.00 54.20 27.53	54.20 27.53	27.73		207	7		0.0	8.	0.0	1941	0.17	0.05	0.21
4.01 110.01 33.86	33.86 28.19	28.19		195	9		0:0	0.5	0.0	1904	0.17	0.03	0.20
109.94 33.35 28.12	33.35 28.12	28.12		198 4	4			0.0	0.0	1879	0.19	0.05	0.24
5.05 95.00 33.76 27.88	33.76 27.88	27.88		199 2	7		0.0			1908	0.19	0.08	0.27
2.99 95.00 34.77	34.77 24.73	24.73		198 14	14						0.27	800	98.0
3.00 95.00	34.77		24.73								12	8 6	0.30
2.01 95.01	34.84 23.62 192	23.62 192	192		24		00	8.2	,	2044	7.0	0.0	0.25
1.00 94.97 35.00 23.44 186	35.00 23.44 186	23.44 186	186		· ~		2	}	7. F	1407	0.20	0.00	0.26
94.96 35.00 23.59 186	35.00 23.59 186	23.59 186	186		5 8						0.22	0.05	0.27
001 9490 3512	35 12 22 23	22.73	167		3 5		ć	į,			0.25	0.04	0.28
101 67:07 70:00	101 67:07	104	104		75	ı	0.7	8.7	3.4	2053	0.23	0.03	0.26

Table 2. EQUARTORIAL PACIFIC FALL 1994 SUPPORT MEASUREMENTS

Doto	Time	Latitude	Latitude Longitude	Salinity	Temp.	0,	AOU	NO2	NO <sub>3</sub>	SiO <sub>3</sub>	PO4	DIC
Dake	(GMT)		<b>D</b>	•	(Ç)	(µmol·l·1)	(µmol·l·¹)	(µmol·l·¹)	(µmol·l <sup>-1</sup> )	(µmol·l <sup>-1</sup> )	(µmol·l·¹)	(µmol·kg <sup>-1</sup> )
8/8/94	6:10	7.94	-94.95	33.76	26.14	161	17					
8/8/94	6:10	7.94	-94.95	33.76	26.14	191	17					1932
8/8/94	12:08	66.9	-94.98	33.74	26.95							1913
8/8/94	12:08	6.99	-94.98	33.74	26.95			(	,	Ġ	30.0	1912
8/8/94	17:45	5.99	-94.99	33.73	27.12	197	<b>∞</b>	0.0	0.1	0.0	0.35	7/91
8/8/94	22:23	4.92	-94.99	33.73	26.75	205	7	0.0	0.1	0.0	0.37	8681
8/9/94	4.44	4.00	-95.00	33.98	26.93	199	9	0.0	0. <b>1</b>	0:0	0.47	1921
8/0/07	10.50	3.01	-95.01	33.92	26.42	198	10	0.0	0.1	0.0	0.46	1914
8/10/94	4.14	2.00	-94.00	33.93	25.39	204	7	0.0	0.5	0.0	0.45	1915
8/10/94	10:35	1.00	-94.98	34.64	21.43	199	25	0.2	8.4	3.4	0.98	2019
8/10/94	12:55	0.49	-94.94	34.95	19.80	197	34	0.3	14.2	7.1	1.24	2070
8/10/94	13.57	0.26	-94.93	35.06	19.54	190	42	0.3	18.4	9.2	1.45	2100
8/10/94	19:06	-0.02	-94.94	35.11	19.09	184	49	0.3	16.5	4.1	1.41	2092
8/10/04		-0.02	-94.94	35.11	19.09			0.3	18.0	4.4	1.45	2091
8/10/04	21.16	-0.26	-94.93	35.03	18.70			0.2	14.7	0.0	1.47	2076
8/10/04		-0.54	-94.93	34.89	18.87	198	37	0.3	15.8	2.2	1.33	2080
0/10/2		1.00	-94.95	35.12	19.92	205	25	0.2	12.5	0.0	1.23	2080
8/11/94		-1.99	-95.03	35.06	18.92	506	53	0.2	10.5	1.8	0.95	2060
8/12/94		-1.97	-95.00	35.09	19.63				;	,	Ö	000
8/12/94	7:20	-3.00	-95.00	35.14	20.13	200	53	0.1	11.3	0.0	0.90	2070
8/12/94		-4.00	-95.01	35.36	22.24	203	18	0.1	11.9	6.5	0.94 4.00	2063
8/12/94	18:57	-5.00	-95.03	35.46	22.82			0.2	12.1	7.7		7607
8/13/94		-6.00	-95.01	35.46	22.75	210	6	0.2	11.9	1.5	1.20	2026
8/13/94	1 7:30	-7.00	-95.00	35.55	22.75	207	11	0.2	11.7	1.6	1.24	2027
8/13/94	•	-7.96	-95.06	35.46	22.62	506	10	0.3	12.8	1.8	1.27	//07
8/13/94			-95.06	35.46	22.62	209	=	0.3	11.7	6.0	1.18	2029
8/17/94			-110.02	34.82	22.12	190	32	0.2	11.6	4.0	1.13	2038
8/17/94			-110.03	34.81	21.98	184	38	0.1	10.2	3.2	1.01	2034
8/17/94			-110.02	34.75	21.91	179	43	0.2	12.7	6.3	1.22	2033
8/17/94			-110.02	34.81	21.87				,	(	ć	0000
8/11/94		0.01	-110.02	34.76	21.90	183	39	0.1	10.2	5.3	0.93	2038
8/17/94			-110.02	34.76	21.90		37	0.2	10.3	8.4	0.98	2038
8/17/94			-110.06	34.69	22.74			0.0	11.5	7.1	0.99	6107
8/18/94			-110.08	34.54	24.45	198	15	0.0	4.9	0.4	0.09	1761

Table 2. EQUARTORIAL PACIFIC FALL 1994 SUPPORT MEASUREMENTS

		.g.																																		
	DIC	(µmol·kg-1)	1956	1951		1881	1868	1880	1821	1848	1842	1912	1912	1935	1948	1957	2018	2007	1998	1998	2000	2003	2001	2006	2024	2035	2038	2037	2034	2035	2033	2025	2022	2026	2023	2026
	ro,	(µmol·l·¹)	0.43	0.57			0.37	0.35	0.37	0.35	0.40	0.07	0.12	0.42	0.34	0.55	0.94	0.85	0.93	1.02	0.94	1.07	1.09	1.07	1.22	0.93	0.92	0.84	0.83	0.74	0.83	0.58	89.0	0.93	69.0	0.70
Č		('-I-lomu')	3.2	0.4			2.1	0.0	0.0	0.0	1.2	6.4	5.8	0.3	0.4	0.3	2.3	2.5	3.9	4.7	4.2	4.0	5.2	5.3	5.3	8.2	8.2	4.9	7.1	4.6	1.9	3.8	3.7	0.0	6.2	5.8
CN		( Liouri)	2.5	2.6			0.1	0.1	0.1	0.2	0.1	0.0	0.0	0.1	6:0	2.2	6.7	∞ ∞.	8.1	9.8	7.9	9.3	8.6	10.0	12.1	11.9	11.7	10.3	8.6	9.0	9.2	5.7	6.7	7.4	6.5	7.9
ON	(11mol-1-1)	( FIGURE)	0.0	0.0		6	0.0	0.0	0.0	0:0	0:0	0.0	0.0	0.0	0.0	0.0	0.0	0:0	0:0	0.1	0.1	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.1	0.0	0:0	0.0	0.0	I.0	0:0
AOU	(IImol-l-1)	21	7 -1	-	:	11	d	×o d	δ.	c	o P	0 1	<b>`</b> o	o	c	ν <u>-</u>	† (	7 7	†				ç	10	36	27	)(	7	C t	•	,	۶ ک	، ۵	, <sub>(</sub>	4	
O,	(umol·l-1)	190	198	27	102	661	105	195	661	211	117	1 2	105	221	197	218	210	216	710				700	<b>t</b> 07	181	181	101	200	202	602	700	186	210	205	3	
Temp.		25.37	25.73	26.32	27.47	27.70	28.00	27.81	27.01	27 98	27.97	27 97	27.41	26.74	26.42	24.36	24.70	24.78	24.71	24.60	24 53	24 53	24.25	23.81	23.51	22.95	23.35	23.91	24 66	25.35	25.72	25.80	25.89	25.99	25.63	
Salinity		34.01	34.32	34.04	33.48	33,35	33.24	32.48	32.92	32.89	34.13	34.13	34.59	34.64	34.67	34.83	34.72	34.64	34.36	34.67	34.68	34.68	34.69	34.76	34.86	34.89	34.89	34.87	35.19					•	35.28	
Latitude Longitude		-110.11	-110.15	-110.05	-110.02	-109.97	-110.00	-110.00	-110.10	-110.13	-124.91	-124.91	-124.95	-125.02	-125.01	-125.04	-125.10	-124.73	-124.58	-124.50	-124.47	-124.47	-124.47	-124.50	-124.63	-124.90	-124.88	-124.88	-124.91	-124.93	-124.98	-124.99	-124.99	-125.02	-125.02	
Latitude		1.49	2.01	3.52	4. 40.	5.00	9009	7.00	7.50	8.04	8.15	8.15	00.9	5.08	4.00	3.00	1.98	1.00	0.47	0.26	0.00	0.00	-0.24	-0.50	-1.00	-2.08	-3.00	-4.00	-4.80	-5.99	-7.00	-7.99	-7.99	-7.98	-7.97	
Time	(CMT)	6:35	11:11	10:20	12:41	17:20	0:05	4:51	7:55	13:27	18:20	18:20	98:3	12:00	10:08	16:15	23:19	9:00	8:56	10:05	12:51	12:51	8:12	10:10	13:37	8:09	14:10	20:00	2:35	8:41	14:55	7:20	7:20	20:50	21:11	
Date		8/18/94	8/18/94	8/19/94	8/19/94	8/19/94	8/20/94	8/20/94	8/20/94	8/20/94	9/4/94	9/4/94	9/5/94	9/5/94	9/6/94	9/6/94	9/6/94	9/7/94	9/7/94	9/7/94	9/7/94	977/94								9/10/94		_	_	_	9/12/94 2	

Table 2. EQUARTORIAL PACIFIC FALL 1994 SUPPORT MEASUREMENTS

,																						
	DIC	(µmol·kg <sup>-1</sup> )	, , , ,	2007		2066		7007	2063	1700	764	2038		2046	2062	7007	2062	2064		2057	2060	2064
2	2	(Limol-i')	1 23	7.7	1.00	1.31	5	20.1	1.01	5	CO.1	1.16		0.89	1.22		1.30	1.15				
Cio		(mmol·l-1)	90	); (	6.0	2.1	10		8.7	00	2.	3.6	:	7.11	4.7	27	C.D	16.2				
CN		(mol·l·)	15.6	) · ·	2.11	15.3	12.1		12.9	0	3	12.1	717	<del>*</del>	14.0	15.5	C.C.I	15.6				
ON	(1.1.0.1.1.1)	( Linual)	0.0		7.0	0.2	0.1		0.0	0.2		0.3	00	) i	0.5	50	9	0.0				
AOU	(1.Telemin)	(humori )	0	·	1 1	n	<b>∞</b>	-	7	v	71	10	25	ì		36	2 6	28	33	1	9	940
ó	(t-lifomit)	( LIONING	217	215	9 6	717	<b>50</b> 2	216	7	506	5	2	196			186	101	104	190	1	0	182
Temp.	່ ຄ		23.27	23.27	32.10	23.10	23.28	23.77		23.98	27.76	77.10	22.27	21.63	75.17	21.89	21 02	61.73	22.02	20 00	00 10	71.00
Salinity			35.25	35.25	35.01	12.55	35.17	35.34		35.53	34 90	2	34.87	34 01	14.71	34.90	34 80	01:0	34.87	34.87	34 06	24:30
Latitude Longitude		1000	-109.97	-109.97	-100 08	00.001	-109.98	-110.00	10000	-109.98	-109 97	10100	-109.99	110.00	00.01	-110.01	-110.02	10001	-109.98	-109.98	-10014	102.11
Latitude		8	-9.00	-8.00	00 8-	8	9.0	-4.97	3.00	57.0-	-3.01		-2.01	00 0-		-0.48	-0.25	9 6	0.02	0.02	0.31	
Time	(CML)	9.40	2.40	3:40	9:36	16.06	13:23	21:47	3.06	9.6	8:45	14.00	14:33	20:32		22:35	23:45		7:13	7:13	6:44	
Date	_	0/16/04	7110174	9/16/94	9/16/94	0/15/04	7/10/74	9/16/94	0/17/04	711174	9/17/94	70/17/07	7/11/2	9/17/94	70170	7/1//94	9/17/94	70/01/0	7/18/74	9/18/94	9/19/94	

#### 7.3. Nutrient Analysis Methods

Nutrient samples were collected from 10-L Niskin bottles or from the underway line in aged 60 ml linear polyethylene bottles after three complete seawater rinses. They were flash frozen by submerging the bottle in a salt/ice mixture and stored in the dark at -10 °C until analysis, several months after collection. Concentrations of dissolved inorganic nitrite (NO<sub>2</sub>), dissolved inorganic nitrate (NO<sub>3</sub>), and silicate (SiO<sub>4</sub>), reported in  $\mu$ mol·l·l·, were determined using an AlpKem RFA/2 Auto-Analyzer on shore.

#### 7.3.1. Nitrate and Nitrite

The automated colorimetric procedures and methodologies used in the analysis of nitrite and nitrate are similar to those described by Armstrong et al. (1967), with modifications described in Atlas et al. (1971). Standardizations were performed prior to each sample run with working solutions from pre-weighed "Baker Analyzed" reagent-grade standards. Nitrite was determined by diazotizing with sulfanilamide and coupling with N-1 napthylethelendiamine dihydrochloride to form an azo dye. The color produced is proportional to the nitrite concentration. Samples for nitrate analysis were passed through a copperized cadmium column, which reduces nitrate to nitrite and the resulting nitrite concentration was then determined as described above. The detection limits for nitrite and nitrate were 0.1  $\mu$ mol·l-1 and 0.4  $\mu$ mol·l-1, respectively. The precision of duplicate standards measurements was  $\pm 4\%$  at 8  $\mu$ mol·l-1 for nitrite and  $\pm 4\%$  at 40  $\mu$ mol·l-1 for nitrate. The accuracy for both analyses was assumed to be  $\pm 10\%$  since no absolute standards are available.

#### 7.3.2. Silicates

The analytical procedures and methodologies used in the analysis of silicate are similar to those described by Armstrong et al. (1967), with modifications described in Atlas et al. (1971). Silicate was determined from the reduction of silicomolybdate in acidic solution to molybdenum blue by ascorbic acid. The color produced is proportional to the concentration of silicate in the sample, with a detection limit of  $0.4~\mu mol \cdot l^{-1}$ .

### 7.4. Chlorophyll Extraction and Analysis

Chlorophyll a and phaeopigments were determined by the fluorometric technique using a Turner Designs Model 10-AU-005 R fluorometer that was calibrated with commercial chlorophyll a (Sigma). Samples for determination of plant pigments were filtered onto 25 mm Whatman GF/F glass fiber filters and extracted in 90% acetone in a freezer for between 24 and 30 hours (Venrick and Hayward, 1984). Other than the modification of the extraction procedure, the method used is the conventional fluorometric procedure of Holm-Hansen et al. (1965) and Lorenzen (1966).

#### 8. NOAA SHIP DISCOVERER CRUISES

The first leg of the Discoverer CGC94 cruise departed Seattle, WA on January 26, 1994 to begin the transit to Punta Arenas, Chile. Underway measurements were conducted for pH, pCO2, nitrous oxide, methyl bromide, salinity and temperature from the ship's underway sea water system. The second leg (Leg 2) departed Punta Areas on February 22, 1994 The ship steamed from the entrance of the Strait of Magellan to the first station at 67 °S, 103 °W. Seventy-eight stations were occupied along 103 °W, following WOCE Hydrographic Program (WHP) protocol.

The last station occupied on Leg 2 was at 26 °S, 103 °W, and the ship docked in Isla de Pascua, Chile on March 24. The third leg (Leg 3) departed Isla de Pascua on March 29, 1994 and proceeded to 25°30' S, 103°W, where 30 nautical mile spacing was resumed along 103 °W to 10 °S. Stations were occupied along a dog-leg from 10 °S, 103 °W to 5 °S, 110°20' W over the East Pacific Rise. The 30-nautical mile spacing was resumed from 5 °S to 3 °S along 110°20' W; from 3 °N to 22 °30' N stations were occupied at 30 nautical mile intervals, except from 12 °N to 16 °N, where spacing was increased to 40 nautical mile. A gradual shift in longitude from 110°20' W to 110 °W was made between 8 °N and 10 °N. North of 22°30' N, station spacing was reduced to as little as 3 nautical mile over the rapidly shoaling bathymetry approaching Cabo San Lucas. The last station occupied was at 22°51' N, 110 °W, and the cruise ended in San Diego on April 27, 1994.

Underway pCO2 measurements were made using the non-dispersive infrared method discussed in detail in Wanninkhof and Thoning (1993). Temperature and pressure corrections were made using the methods described by Murphy et al. (1993; 1994). The precision of the method is  $\pm$  1.0  $\mu atm$ . The thermistors used on the CGC94 cruise were calibrated against a NIST-traceable mercury thermometer (Brooklyn Thermometers Co, Farmingdale, NY). The thermistors were calibrated from 18 to 30 °C in 1° increments during the cruise on April 29, 1994.

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# A: BASIC PROGRAM FOR OPERATION OF UNDERWAY SYSTEM VERSION 1.5'

```
10 '*************************
  11 '*
  12 '*
                    HELCOME TO NORA AOML UNDERWAY PCO2 GROUP
  13 '*
     ***********************
  14
 15 '
 16
    'THIS PROGRAM IS MADE FOR AOML UNDERWAY PCO2 SYSTEM.
 17
 18
 19 'NAME OF PROGRAM: UMPCO2.BAS
 20 '
 21 'VERSION: 1.5, MARCH, 1994
 22 '
 100
 110
 120 ' SECTION 1. INITIALIZATION
     '-----
 130
 140 '
 150 KEY OFF: CLS
 160 'Contract BASIC working space to 64k
 170 CLEAR, 60000!
 180 DEF SEG =0
 190 'Find start of BASIC's segment
 200 SG=256*PEEK(&H511)+PEEK(&H510)
 210 DEF SEG
    'Initialize offset variable (DASCON1) into CALL routine to zero
 220
 230 DASCON1=0
240 'Work out segment to load DASCON1.BIN at end of working place
250 SG=(32768!/16)+SG
260 'Initialize call parameters and declare DIOX, ADX and other arrays
270 DIM DIOX(8), ADX(8)
280 DIM STD(3), STDMU(3)
290 DIM SAMP(4), TIR(4), TMS1(4), TMS2(4), PRES(4) 300 'Fetch base address from DASCON1.ADR file
    OPEN "I", #1, "DASCON1.ADR": INPUT#1, BASADR%: CLOSE #1
310
320
    'Load DASCON1.BIN
330 SG=&H5000
340 DEF SEG =SG
350 BLOAD "DASCON1.BIN",0
400
410
   'SECTION 2. MAIN CONTROL LOOP OF PROGRAM
420
430
     '-----
440
450 LOFPRT=11 : 'STARTLINE FOR PRINT ON SCREEN
460 STD(1)=296.53 : STD(2)=347.87: STD(3)=524.87 : 'Standard CO2 in ppm, when
   replacing standard tank, please change relative CO2 ppm value on this
470 X1%=0 : GOSUB 7190 : 'reset system
480 GOSUB 5290
490 CN=CN+1
500 ' TIME CONTROL LOOP
```

```
510
          TP0$=TIME$
    520
          TP1$=MID$(TP0$,4,2)
    530
          TP2$=RIGHT$(TP0$,2)
    540 TP=UAL(TP1$)+UAL(TP2$)/60
    550 IF CN<=1 GOTO 580
    560 IF TP>=RT GOTO 710
   570 LOCATE 1,1 : PRINT "START TIME IS"; RT; ", PRESENT TIME IS ";
       RIGHT$(TIME$,5): LOCATE 1,51 : PRINT "PLEASE WAIT." : GOTO 510
   580
   590 RT=12
              : NW=4 : IF TP<RT
                                GOTO 490
   600 RT=16.5 : NW=3 : IF TP<RT
                               GOTO 490
   610 RT=21
              : NW=2 : IF TP<RT
   620 RT=25.5 : NW=1 : IF TP<RT
                               GOTO 490
                               GOTO 490
   630 RT=30
             : NA=3 : IF TP<RT
                               GOTO 490
   640 RT=34
             : NA=2 : IF TP<RT
                               GOTO 490
   650 RT=38
             : NA=1 : IF TP<RT
                               GOTO 490
   660 RT=42
              : NW=4 : IF TP<RT
                               GOTO 490
   670 RT=46.5 : NH=3 : IF TP<RT
                               GOTO 490
   680 RT=51
             : NW=2 : IF TP<RT
  690 RT=55.5 : NU=1 : IF TP<RT
                              GOTO 490
  700 RT=59.97 : GOTO 490
                               GOTO 498
  710
  720 IF RT=59.97 GOTO 770
  730 IF RT<=25.5 GOTO 790
  740 IF RT>=30 AND RT<=38 GOTO 810
  750 IF RT>=42 AND RT<=55.5 GOTO 830
  769 '
  770 GOSUB 1000 :
                          'starting standard measurement section
  780 NU=4 :
                          'NU is total measurements in one water section
  790 GOSUB 2000 :
                          'Starting water sample measurement section
  800 NA=3
                          'NA is total measurements in one air section
 810 GOSUB 3000 :
                         'Starting air sample measurement section
 820 NU=4 :
                        'NU is total measurements in one water section
 830 SN=1 : GOSUB 2000 :
                      'SN is the # of finished water section in this hour
 840 ' TIME RESET LOOP
 850
       TP0$=TIME$
 860
       TP1$=MID$(TP0$,4,2)
 878
       TP2$=RIGHT$(TP0$,2)
 880 TP=UAL(TP1$)+UAL(TP2$)/60
 890 IF TP<=55.5 GOTO 770
 900 GOTO 850
 910 '
     ·-----
 920
    'SECTION 3. SUBROUTINES
 930
940 '----
960 '
970 ' SECTION 3-1. SUBROUTINES FOR MEASUREMENTS OF STANDARDS, WATER, AND AIR
980 '-----
1000 'SECTION 3-1-1. SUBROUTINE FOR STANDARD MEASUREMENTS
     .
1020 SN=0 ; 'SN is the # of finished water section in this hour
1030 CLS : GOSUB 5290
1040 LOFPRT=11 : 'STARTLINE FOR PRINT ON SCREEN
1050 SAMPHAM$="STD
1060 FOR I=1 TO 3
1070 STDSUM=0 : TIRSUM=0 : TMS1SUM=0 : TMS2SUM=0
```

```
1080 X=1+2^I
 1090 X1X=X
              : GOSUB 7190
 1100 TIMPOINTS=TIMES
 1110 RTIME1$=MID$(TIMPOINT$,4,2)
 1120 RTIME2$=RIGHT$(TIMPOINT$,2)
 1130 INTUAL=210 : STATUS$="FLUSH"
 1140 RTIME=UAL(RTIME1$)*60+UAL(RTIME2$)
 1150 GOSUB 6120
 1160 X1X=0
              : GOSUB 7190
 1170 INTURL=220 : STATUS$="PR_EQ" : GOSUB 6120
            : GOSUB 7190
 1172 X1X=65
 1180 LOCATE 1,49 : PRINT "SCAN "
 1190 GOSUB 7030
 1200 FOR J=1 TO 3
 1210 TI=2 : GOSUB 6030
 1220 GOSUB 7110
 1230 STDSUM=STDSUM+AD%(0) : TIRSUM=TIRSUM+AD%(1)
 1240 TMS1SUM=TMS1SUM+AD%(2) : TMS2SUM=TMS2SUM+AD%(3)
 1250 NEXT J
 1260 X1X=0
              : GOSUB 7190
 1270 J=J-1
 1280 MURUE=STDSUM/J : TIRAUE=TIRSUM/J
 1290 THS1AUE=THS1SUM/J : THS2RUE=THS2SUM/J
 1300 STDMU(I)=MUAUE
 1310 GOSUB 4030
 1320 GOSUB 4230
 1330 GOSUB 4510
1340 X=STD(I) :CHL0=STD(I) :CHL1=TIR :CHL2=TMS1 :CHL3=TMS2
1350 GOSUB 5030
1360 LOCATE 8,11
1370 PRINT USING "**** ** *** *** *** *** ; STDMU(1);STDMU(2);STDMU(3)
1380 INTUAL=236 : STATUS$="SAVE " : GOSUB 6120
1390 NEXT I
1400 RETURN
1410
1420
2000 'SECTION 3-1-2. SUBROUTINE FOR WATER MEASUREMENT
      2010
2020 SAMPNAM$="UAT
2030 TSAMP=0 : TTIR=0 : TTMST=0 : TTMS2=0 : TPRES=0
2040 DSAMP=0 : DTIR=0 : DTMS4=0 : DTMS2=0 : DPRES=0
2050
2060 FOR M=1 TO NU
2070 N=4-NU+M
2080 TEND=12+30*SN+4.5*N
2090 X1%=129 : GOSUB 7190
     TIMPOINT$=TIME$
2100
2110
     RTIME1$=MID$(TIMPOINT$,4,2)
2120 RTIME2$=RIGHT$(TIMPOINT$,2)
2130 INTUAL=240 : STATUS$="FLUSH"
2140 RTIME=UAL(RTIME1$)*60+UAL(RTIME2$) : GOSUB 6120
2150 X1%=0
           : GOSUB 7190
2160 INTUAL=250 : STATUS$="PR_EQ" : GOSUB 6120
2162 X1%=65 : GOSUB 7190
2170 LOCATE 1,49 : PRINT "SCAN "
2180 GOSUB 7030
2190 SAMPSUM=0 : TIRSUM=0 : TMS1SUM=0 : TMS2SUM=0
2200 'SCANNING
```

```
2210 FOR J=1 TO 3
  2220 TI=2 : GOSUB 6030
  2230 GOSUB 7110
  2240 SAMPSUM-SAMPSUM+AD%(0) : TIRSUM-TIRSUM+AD%(1) : TMS1SUM-TMS1SUM+AD%(2) :
     TMS2SUM=TMS2SUM+AD%(3)
  2250 NEXT J
  2252 X1X=0
              : GOSUB 7190
  2260 J=J-1
  2270 MURUE=SAMPSUM/J :TIRAUE=TIRSUM/J :TMS1AUE=TMS1SUM/J :TMS2AUE=TMS2SUM/J
  2280 GOSUB 4030
  2290 GOSUB 4120
  2300 GOSUB 4230
  2310 GOSUB 4510
 2320 X=-99.99 :CHL0=SAMP :CHL1=TIR :CHL2=TMS1 :CHL3=TMS2
 2330 GOSUB 5030
 2340 SAMP(M)=SAMP : TIR(M)=TIR : TMS1(M)=TMS1 :TMS2(M)=TMS2 : PRES(M)=PRES
 2350 TSAMP=TSAMP+SAMP : TTIR=TTIR+TIR : TTMS1=TTMS1+TMS1 : TTMS2=TTMS2+TMS2 :
     TPRES=TPRES+PRES
 2360 STATUS$="SAVE
 2370 GOSUB 5210
 2380 TP0$=TIME$ : TP1$=MID$(TP0$,4,2) : TP2$=RIGHT$(TP0$,2):
     TP=UAL(TP1$)+UAL(TP2$)/60
 2390 DIFF=(TEND-TP)*60 :IF TEND>55.5 AND DIFF<=4 GOTO 2440
 2400 IF DIFF<=0 THEN 2440 ELSE 2410
 2410 LOCATE 1,1 : PRINT "GAS IN IR: ";SAMPNAM$;"/ START AT: ";TIMPOINT$; "/ STATUS: ";STATUS$;"/ SEC. REMAINING: ";FIX(DIFF)
 2420 COLOR 0,7 : LOCATE 23,1 : PRINT " ";DATE$;" ";TIME$;" " : COLOR 7,0
 2430 GOTO 2380
 2440 NEXT M
 2450
 2460 M=M-1
 2470 MSAMP=TSAMP/M : WMSAMP=MSAMP : AMSAMP=-99.99 : MTIR=TTIR/M :
    MTMS1=TTMS1/M : MTMS2=TTMS2/M : MPRES=TPRES/M
 2480 FOR I=1 TO M
2490 DSAMP=DSAMP+(SAMP(I)-MSAMP)^2 : DTIR=DTIR+(TIR(I)-MTIR)^2 :
    DTMS1=DTMS1+(TMS1(I)-MTMS1)^2 : DTMS2=DTMS2+(TMS2(I)-MTMS2)^2 :
    DPRES=DPRES+(PRES(I)-MPRES)^2
2500 NEXT I
2510 IF M=1 THEN M=2 ELSE M=M
2520 STSAMP=SQR(DSAMP/(M-1)) : USTSAMP=STSAMP : ASTSAMP=-99.99 :
    STTIR=SQR(DTIR/(M-1)) : STTMS1=SQR(DTMS1/(M-1)) : STTMS2=SQR(DTMS2/(M-
    1)):STPRES=SQR(DPRES/(M-1))
2530 GOSUB 5100
2540 IF SN>=1 THEN 2580 ELSE 2550
2550 LOCATE 6,58 : PRINT USING " ### ##
                                             ***. ##"; MSAMP; STSAMP
2560 UATPPM1=MSAMP : UATSTD1=STSAMP
2570 GOTO 2600
2580 LOCATE 8,58 : PRINT USING " ***, **
                                             *** ** ; MSAMP; STSAMP
2590 WATPPM2=MSAMP : WATSTD2=STSAMP
2600 RETURN
2610
2620
3000 'SECTION 3-1-3. SUBROUTINE FOR AIR MEASUREMENT
     3010
3020 SAMPHAM$="AIR
3030 TSAMP=0 : TTIR=0 : TTMS1=0 : TTMS2=0 : TPRES=0
3040 DSAMP=0 : DTIR=0 : DTMS1=0 : DTMS2=0 : DPRES=0
3050 '
```

```
3060 FOR M=1 TO NA
3070 N=3-NA+M
3080 TEND=30+4*N
3090 X1%=17 : GOSUB 7190
3100 TIMPOINTS=TIMES
3110 RTIME1$=MID$(TIMPOINT$, 4, 2)
3120 RTIME2$=RIGHT$(TIMPOINT$,2)
3130 INTUAL=210 : STATUS$="FLUSH"
3140 RTIME=UAL(RTIME1$)*60+UAL(RTIME2$) : GOSUB 6120
3150 X1%=0
            : GOSUB 7190
3160 INTUAL=220 : STATUS$="PR_EO" : GOSUB 6120
3162 X1x=65 : GOSUB 7190
3170 LOCATE 1,49 : PRINT "SCAN "
3180 GOSUB 7030
3190 SAMPSUM=0 : TIRSUM=0 : TMS1SUM=0 : TMS2SUM=0
3200
     'SCANNING
3210 FOR J=1 TO 3
3220 TI=2 : GOSUB 6030
3230 GOSUB 7110
3240 SAMPSUM-SAMPSUM+ADX(0) : TIRSUM-TIRSUM+ADX(1) : TMS1SUM-TMS1SUM+ADX(2)
      TMS2SUM=TMS2SUM+AD%(3)
3250 NEXT J
3252 X1%=0
            : GOSUB 7190
3260 J=J-1
3270 MUAUE=SAMPSUM/J :TIRAUE=TIRSUM/J :TMS1AUE=TMS1SUM/J :TMS2AUE=TMS2SUM/J
3280 GOSUB 4030
3290 GOSUB 4120
3300 GOSUB 4230
3310 GOSUB 4510
3320 X=-99.99 :CHL0=SAMP :CHL1=TIR :CHL2=TMS1 :CHL3=TMS2
3330 GOSUB 5030
3340 SAMP(M)=SAMP : TIR(M)=TIR : TMS1(M)=TMS1 :TMS2(M)=TMS2 : PRES(M)=PRES
3350 TSAMP=TSAMP+SAMP : TTIR=TTIR+TIR : TTMS1=TTMS1+TMS1 : TTMS2=TTMS2+TMS2 :
    TPRES=TPRES+PRES
3360 STATUS$="SAUE '
3370 GOSUB 5210
3380 TP0$=TIME$ : TP1$=MID$(TP0$,4,2) : TP2$=RIGHT$(TP0$,2) :
   TP=UAL(TP1$)+UAL(TP2$)/60
3390 DIFF=(TEND-TP)*60 : IF DIFF<=0 THEN 3430 ELSE 3400
3400 LOCATE 1,1 : PRINT "GAS IN IR: "; SAMPNAM$; "/ START AT: "; TIMPOINT$; "/
    STATUS: ";STATUS$;"/ SEC. REMAINING: ";FIX(DIFF)
3410 COLOR 0,7 : LOCATE 23,1 : PRINT " ";DATE$;" ";TIME$;" " : COLOR 7,0
3420 GOTO 3380
3430 NEXT M
3440
3450 M=M-1
3460 MSAMP=TSAMP/M : AMSAMP=MSAMP : WMSAMP=-99.99 : MTIR=TTIR/M :
   MTMS1=TTMS1/M : MTMS2=TTMS2/M : MPRES=TPRES/M
3470 FOR I=1 TO M
3480 DSAMP=DSAMP+(SAMP(I)-MSAMP)^2 : DTIR=DTIR+(TIR(I)-MTIR)^2 :
   DTMS1=DTMS1+(TMS1(I)-MTMS1)^2 : DTMS2=DTMS2+(TMS2(I)-MTMS2)^2 :
   DPRES=DPRES+(PRES(I)-MPRES)^2
3490 NEXT I
3500 IF M=1 THEN M=2 ELSE M=M
3510 STSAMP=SQR(DSAMP/(N-1)) : ASTSAMP=STSAMP : USTSAMP=-99.99 :
   STTIR=SQR(DTIR/(M-1)) : STTMS1=SQR(DTMS1/(M-1)) : STTMS2=SQR(DTMS2/(M-1))
   : STPRES=SQR(DPRES/(M-1))
3520 GOSUB 5100
```

```
###.##"; MSAMP; STSAMP
 3530 LOCATE 7,58 : PRINT USING " ***. **
 3540 AIRPPM=MSAMP : AIRSTD=STSAMP
3550 RETURN
3560
3570 '
4000 'SECTION 3-2. INTERFACE BETWEEN THERMISTERS, GPS AND BAROMETER
4020 '
4030 'SECTION 3-2-1. THERMISTERS mu--CENTIGRADE CONVERSION
4050 'Temperature of IR cell
4060
     TIR=-.058558+.05057*TIRAUE+1.5527E-07*(TIRAUE)^2
4070 'Temperature of Equilibrator
4072
4073
4074
4075 ' THIS IS THE EQUATION TO CHANGE UPON COMPLETING A NEW
4076 '
                TEMPERATURE CALIBRATION
4077
4080 TMS1=73.6908-.0.0383166*TMS1AUE+8.5113E-06*TMS1AUE^2-7.868E-10*TMS1AUE^3
4090 'Flow rate of equilibrator
4100 TMS2=30/(4260-852)*(TMS2AUE-852)
4110 RETURN
4120
4130 '
4140 'SECTION 3-2-2. CONVERT SAMPLE MU TO PPM BY INTERCEPTION
     4160 IF STDMU(1)=0 THEN 4170 ELSE 4180
4170 STDMU(1)=38 : STDMU(2)=460 : STDMU(3)=950
4180 A=((STDMU(1)-STDMU(2))/(STDMU(1)-STDMU(3))*(STD(3)-STD(1))-(STD(2)-
   STD(1)))/((STDMU(1)-STDMU(2))*(STDMU(2)-STDMU(3)))
4190 B=((STD(1)-STD(2))-A*(STDMU(1)^2-STDMU(2)^2))/(STDMU(1)-STDMU(2))
4200 C=STD(1)-B*STDMU(1)-A*STDMU(1)^2
4210 SAMP=A*MUAUE^2+B*MUAUE+C
4220 RETURN
4230
4240
4250
     'SECTION 3-2-3. LATITUDE AND LONGITUDE FROM GPS
4260
     4270 'IN CASE OF GPS FAILURE, REMOVE SIGN ('), GOTO LINE "RETURN".
4280 'PRINT CHR$(10)
4290 OPEN "COM2:9600,n,8,1,RS,CS,DS,CD" AS #2
4300 B$=CHR$(36)+CHR$(80)+CHR$(77)+CHR$(71)+CHR$(76)+CHR$(73)+CHR$(44)+
   CHR$(48)+CHR$(48)+CHR$(44)+CHR$(66)+CHR$(48)+CHR$(48)+CHR$(44)+CHR$(49)+
   CHR$(44)+CHR$(65)+CHR$(44)+CHR$(48)+CHR$(48)+CHR$(13)+CHR$(10)
4310 PRINT #2,B$
4320 G$=INPUT$(34,#2)
4330 GPS$=MID$(G$,15,20)
4340 'PRINT GPS$
4350 'PRINT CHR$(10)
4360 CLOSE #2
4370 OPEN "COM2:9600,n,8,1,RS,CS,DS,CD" AS #2
4380 LOCATE 3,1 : PRINT "GPS: ":GPS$
4390 CLOSE #2
4400 LATD$=LEFT$(GPS$,2) : LATM$=MID$(GPS$,3,2)
4410 LATS$=MID$(GPS$,6,2) : LATI$=MID$(GPS$,9.1)
4420 IF LATI$="N" THEN LATI=1 ELSE LATI=-1
```

```
4448 LOGD$=MID$(GPS$,11,3) : LOGM$=MID$(GPS$,14,2)
 4450 LOGS$=MID$(GPS$,17,2) : LOGI$=RIGHT$(GPS$,1)
 4460 IF LOGI$="E" THEN LOGI=1 ELSE LOGI=-1
     LONG=LOGI*(UAL(LOGD$)+UAL(LOGM$)/60+UAL(LOGS$)/3600)
 4480 RETURN
 4490
 4500 '
 4510 'SECTION 3-2-4. PRESSURE (mB) FROM BAROMETER
 4530 'GOTO 4610 : 'IN CASE OF BARO. FAILURE, REMOUE SIGN ', GOTO LINE "RETURN"
 4540 OPEN "com1:2400,n,8,1,RS" AS #3
 4550 C$=CHR$(80)
 4560 PRINT #3,C$
 4570 P$=INPUT$(20,#3)
 4580 PP$=MID$(P$,2,7)
 4590 PRES=UAL(PP$)
 4600 CLOSE #3
 4610 RETURN
 4620
 4630
 4640
5000 'SECTION 3-3. OUTPUT DATA TO DATAFILES IN DISK AND SHOW DATA ON SCREEN
5010 '-----
5020 '
5030 'SECTION 3-3-1. SAUE LATEST DATA TO DATAFILE "UMMMYY" (e.g. UM0394)
     5040
5050 FILENAME$="UW"+LEFT$(DATE$,2)+"94"
5060 OPEN FILENAME$ FOR APPEND AS #3
5070 PRINT #3, SAMPNAM$; DATE$;" "; TIME$;" "; LAT; LONG;" "; X; MUAUE;
CHL0; TIRAUE; CHL1; TMS1AUE; CHL2; TMS2AUE; CHL3; PRES
5080 CLOSE #3
5090 RETURN
5100
5110
5120 'SECTION 3-3-2. SAUE AUG. & STDEU. TO DATAFILE "UUMMYAUG" (e.g. UU034AUG)
5130 '.....
5140 FILENAME$="UW"+LEFT$(DATE$,2)+"5"+"AUG"
5150 OPEN FILENAME$ FOR APPEND AS #3
5160 PRINT #3, SAMPHAM$; DATE$;" "; TIME$; " "; LAT; LONG; MTIR; STTIR;
   MTMS1; STTMS1; MTMS2; STTMS2; MPRES; STPRES; UMSAMP; USTSAMP; AMSAMP;
   STSAMP
5170 CLOSE #3
5180 RETURN
5190 '
5200
5210 'SECTION 3-3-3. SHOW LATEST DATA ON SCREEN
522B
     5230
     LOFPRT=LOFPRT+1
5240
     LOCATE LOFPRT, 1 :PRINT SAMPNAM$; TIME$;
     PRINT USING " ***, ** ***, ** ***, ***
                                      ***, *** ** ***
   AT; LONG; CHL0; CHL1; CHL2; CHL3; PRES
5260
    RETURN
5270 '
5280 '
5290 'SECTION 3-3-4. SHOW STANDARD INFORMATION ON SCREEN
                    5310 COLOR 0,7 : LOCATE 5,1
5320 PRINT " CO2 STANDARDS INFORMATION " : COLOR 7,0
```

```
5330 LOCATE 7,1 : PRINT "STD ppm" : LOCATE 8,1 : PRINT "STD mU"
  5340 LOCATE 6,1 : PRINT "STD #
                                 STD_1
                                         STD_2
                                                STD 3"
  5350 LOCATE 7,11
 5360 PRINT USING "####,## ####,## ####,##"; STD(1);STD(2);STD(3)
  5370 LOCATE 8,11
 5380 PRINT USING "**** ## ### ### ; STDMU(1);STDMU(2);STDMU(3)
 5390 COLOR 0,7 : LOCATE 11,1 : PRINT "GAS TIME
 5400 LOCATE 11,15
 5410 PRINT "D. LAT
                  D. LON pCO2_PPM IR_TEMP EQ_TEMP EQ_FLOW PRESSURE "
 5420 COLOR 7,0
 5430
 5440 '
 5450 'SECTION 3-3-5. SHOW LAST 60 MIN. AUG. AND STD DEV. ON SCREEN
 5460 '.....
 5470 LOCATE 3,48: PRINT "LAST 60 MIN AUG. AND STD. DEU"
 5480 COLOR 0,7 : LOCATE 5,49 : PRINT " SAMPLE
                                          P.P.M STD. DEV * : COLOR
    7,0
 5490 LOCATE 6,50 : PRINT " WATER"
 5500 LOCATE 6,58 : PRINT USING " ### ##
                                        ###.##"; WATPPM1; WATSTD1
 5510 LOCATE 7,50 : PRINT "
                          AIR"
 5520 LOCATE 7,58 : PRINT USING " ###.##
                                        ###.##"; AIRPPM; AIRSTD
 5530 LOCATE 8,50 : PRINT " WATER"
 5540 LOCATE 8,58 : PRINT USING " ### ##
                                       ***, **"; WATPPM2; WATSTD2
 5550 COLOR 0,7 : LOCATE 23,54 : PRINT " DOC/NOAA/AOML/OCD/CO2 " : COLOR 7,0
 5560 RETURN
 5570
 5580 '
 5590 '
6000 'SECTION 3-4. TIME CONTROL AND TIME ALLOCATION
6010 '-----
6020 '
6030 'SECTION 3-4-1. ABSOLUT TIME INTERVAL CONTROL
     6040
6050 U=TIMER
6060 T=TIMER
6070 IF T-U < 0 THEN U=-1*(86400!-U)
6080 IF T-U < TI THEN 6060
6090 RETURN
6100
6110 '
6120 'SECTION 3-4-2. TIME ALLOCATION BY CLOCK
6130 '.....
6140 TPOINT$=TIME$
6150 FACTOR1$=MID$(TPOINT$,4,2)
6160 FACTOR2$=RIGHT$(TPOINT$,2)
6170 FACTOR=UAL(FACTOR1$)*60+UAL(FACTOR2$)
6180 IF FACTOR=RTIME GOTO 6140
6190 IF FACTOR<RTIME THEN 6200 ELSE 6210
6200 FACTOR=FACTOR+3600
6210 LOCATE 1,1
6220 PRINT "GAS IN IR: "; SAMPNAM$; "/ START AT: "; TIMPOINT$; "/ STATUS: ";
   STATUS$;"/ SEC. REMAINING: ";INTUAL-(FACTOR-RTIME)
6230 COLOR 0,7 : LOCATE 23,1 : PRINT " "; DATE$; " "; TIME$; " " : COLOR 7,0
6240 IF FACTOR-RTIME<INTUAL GOTO 6140
6250 RETURN
6260 '
6270 '
6280 '
```

```
7000 'SECTION 3-5. SUBROUTINES FOR RELAYBOARD AND SCANING CONTRAL
7010 '----
7020
7030
     'SECTION 3-5-1. SUBROUTINE FOR A/D FREE RUN TO COLLECT DRTA ON INTERRUPT
7040
     7050
     'test5
7060 CH2%=5 : MD2%=5
7070 CRLL DASCON1 (MD2%, CH2%, AD%(0), AD%(1), BASADR%)
7080 RETURN
7090
7100
7110 'SECTION 3-5-2. SUBROUTINE FOR COLLECTING DATA FROM INTERRUPT
7120
     7130 'test6
7140 CH2%=0 : MD2%=6
7150 CALL DASCON1 (MD2%, CH2%, AD%(0), AD%(1), BASADR%)
7170 '
7180 '
     'SECTION 3-5-3. SUBROUTINE FOR RELAYBOARD CONTROL
7190
7200
    7210 'test9----- Select desired configuration -----
7220 A$="1" : 'INPUT Desired configuration number <0-5>
7230 IF A$="" THEN CHX=0:GOTO 7250
7240 CH%=UAL(A$)
7245 DEF SEG=&H5000
7248 BLOAD "dascon1.bin",0
7250 IF CHX<0 OR CHX>5 THEN GOTO 7410
7260 ON (CHX+1) GOTO 7270,7290,7320,7330,7340,7380
7270 DIOX(0)=X1X : 'INPUT"PB output data <0-255>"
7280 GOTO 7410
7290 DIOX(0)=X1X : 'INPUT"PB output data <0-255>"
7300 DIOX(1)=0 : 'INPUT"PC output data <0-15>"
7310 GOTO 7410
7320 GOTO 7410
7330 DIOx(1)=0 : 'INPUT"PC output data <0-15>"
7340 CLS: LOCATE 25,1:PRINT"D/A mode 9 - Digital output mode"
7350 LOCATE 1,1:PRINT:PRINT:PRINT"In strobed output mode PC0-3 function as
   follows:-"
7360 DIOX(0)=X1X : 'INPUT"PB output data <0 - 255>"
7370 GOTO 7410
7380 CLS:LOCATE 25,1:PRINT"D/A mode 9 - Digital output mode"
7390 LOCATE 1,1:PRINT:PRINT:PRINT"In strobed input mode PC0-3 function as
   follows: - "
7400 GOTO 7410
7410 MDx=9
7420 DEF SEG=&H5000
7430 '----- Enter call routine -----
7440 CALL DASCON1 (MDx, CHx, DIOx(0),DIOx(1), BASADRx)
7450 'CLS: LOCATE 25,1:PRINT"D/A mode 9 - Digital output mode":LOCATE 2,1
7460 IF DIOX(8) <> 0 THEN PRINT:PRINT"!!!!!!! ERROR!!!!!!!":GOTO 7470
7470 'LOCATE 23,1
7480 RETURN
7490 END
```

## APPENDIX B: EXAMPLE OF UNDERWAY fCO2 DATA FILE

AfCO2	33.06		33.41	33.64	34.32	33.62	34.01	33.97	32.70	32.35	32.62	33.34	32.88	32.53	32.19	32.27	33.48	32.89	32.62	31.75	30.13	29.74	29.41	29.21	28.46	28.79	29.24	29.91	31.69	30.75	29.85	28.50	28.14	27.72	7.83
fC02a	344 15	344.15	344.15	344.15	344.15	344.15	344.15	344.15	343.54	343.54	343.54	343.54		343.54	343.54	343.54	343.45				343.45	343.45		343.45		343.16	343.16	343.16	343.16			343.16			•
fCO2w, in situ	377.21	377.21	377.56	377.79	378.47	377.77	378.16	378.12										376.34											374.85	373.91 3	373.01 3			370.22 3	370.33
fCO2w, eq	379.56	379.38	379.65	379.65	379.94	380.07	380.23	380.22	378.41	378.19	378.52	379.13	378.73	378.41	378.27	378.12	378.58	378.22	377.41	376.50	375.38	375.13	374.84	374.68	374.04	373.36	373.09	373.03	375.56	375.05	374.06	372.97	371.60	371.30	371.38
Sal (TSG)	36.29	36.30	36.32	36.34	36.43	36.43	36.40	36.34	36.17	36.15	36.14	36.12	36.10	36.07	36.04	36.00	35.99	35.96	35.93	35.93	35.78	35.75	35.74	35.75	35.70	35.54	35.47	35.55	36.16	36.29	36.29	36.29	36.25	36.24	36.24
SST (TSG)	26.92	26.94	26.96	26.99	27.12	27.08	27.06	27.06	26.92	26.91	26.87	26.84	18.02	20.78	26.72	26.70	26.81	26.81	26.88	26.95	26.96	26.97	26.96	26.95	26.84	70.87	27.04	27.19	27.54	27.57	27.62	27.66	27.78	æί.	27.85
Pressure	1010.48	1010.44	1010.62	1010.45	30.010.	1010.91	1011.06	1011.20	1011.31	1011.35	101.40	4.1.01	1011.00	1011.70	1011.//	1011.02	1011.90	1011.93	1011.93	98. LL01	1012.11	1012.13	10.2101	1012.12	1012.25	1012.13	1012.20	1012.09	1012.00	1011.96	1012.00	1011.93	- ,		97.110
Еq Тетр	27.09	27.09	27.10	21.72	27.12	27.24	12.72	12.72	27.07	27.07	50.75	26.00	26.97	26.04	26.90	26.00	20.92	40.04	76.97	27.04	27.09	07.10	27.10				27.00	27.13	27.00	27.65	61.72		. 68.72	'n	26.72
xCO2,a	358.41	358.41	358.41	508.41	200.4	250.41	350.41	536.41	957.04	357.34	357.34	357.34	357.34	357 34	357.34	357.03	257.23	357.63	357.23	357.23	357.23	357.63	357.23	257.20	357.28	357.28	357.20	357.20	957.50	357.75	007.700	337.78	357.24		4
xCO2,w	395.36		393.42				305 00	303.00	303.04	393.87	394 46	393.94	393.55	393.35	393.16	393 70	303.24	_																	
Long		74.67				-74 72	-74 74	-74.79	-74.80	-74 83	-74.84	-74.89	-74.90	-74.93	-74.94	-74 99	-75 00	75.00	-75.04	-75.09	-75 10	-75 12			-75.20	-75.22	-75.24			-75.33	75.94	75.04	-75.41	75.43	) }
Lat		41.78	11 70	11 76	11 76	11 75	11 74	11 72	11.71	11.70	11.70	11.68	11.67	11.67	11.66	11.64	11.64	11.64	11.63	11.60	11.60	11.59	65		11.57			11.53				ı a		. ~	
Time	0:16:05	0.25.47	0.29.47	0:46:17	0:50:47	0:55:17	0:59:47	1:16:05	1:20:47	1:25:17	1:29:47	1:46:17	1:50:47	1:55:17	1:59:46	2:16:05	2:20:47	2:25:17	2:29:47	2:46:17	2:50:47	2:55:17	2:59:47	3:16:05	3:20:47	3:25:17	3:29:47	3:46:17	3.50.47	3:55:17	3.59.47	4.16.05	4:20:47	4:25:17	: : :
Date	8/1/94		8/1/9	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	8/1/94	4	
9	213.011	213.018	213.021	213.032	213.035	213.038	213.042	213.053	213.056	213.059	213.062	213.074	213.077	213.080	213.083	213.095	213.098	213.101	213.104	213.115	213.119	213.122	213.125	213.136	213.139	213.143	213.146	213.157	213,160	213.163	213.167				
															,	^																			

## APPENDIX C: PLOTS OF fCO2a, fCO2w, SST AND SAL VS. LATITUDE

This section contains results from the cruises of the NOAA ship MALCOLM BALDRIGE in the Equatorial Pacific in the (boreal) spring and fall of 1994; and from the DISCOVERER along nominally 110 °W in the spring of 1994 in a series of plots with  $fCO_2$  air and water versus latitude as top panel ( $\Phi = fCO_2w$ ;  $\Box = fCO_2a$ ) and temperature and salinity versus latitude as bottom panel ( $\times = SST$ ; O = Salinity).

The full data set can be obtained via anonymous FTP from: <a href="ftp://ftp.aoml.noaa.gov/pub/ocd/carbon/uweqpac94">ftp://ftp.aoml.noaa.gov/pub/ocd/carbon/uweqpac94</a>

or via the World Wide Web: <a href="http://www.aoml.noaa.gov/ocd/oaces/">http://www.aoml.noaa.gov/ocd/oaces/</a>

