REPORT OF UNDERWAY pCO_2 MEASUREMENTS IN SURFACE WATERS AND THE ATMOSPHERE DURING April - May 2004

RVIB Nathaniel B. Palmer Cruise 04/3

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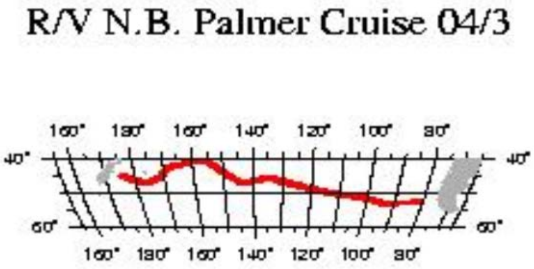
1. General

1-a) The Cruise:

This was a transit from Lyttleton, New Zealand to Punta Arenas, Chile. Our data begins on 16 April and ends on 7 May 2004. There was NO editing required on our sea water pCO_2 data, and a few hours of missing thermosalinograph (TSG) data early in day 116 are the only problem. The atmospheric data may be problematic with the mean dry-air CO_2 mixing ratio remaining about 2 ppm above the GlobalView CO2 estimate. The old atmospheric tubing from the bow mast to the pCO_2 analyzer was replaced after this cruise.



This cruise continued to use the new pCO_2 sampling system that was installed in December 2003 (Figure 2). The design changes incorporated into the new underway pCO_2 system included: simplifying the flow path by the removal of the solenoid valves; constructing the major units of the system modularly for ease of maintenance and repair; and, upgrading the software to drive the new system and to provide a better real time user interface. The latter section of this report describes additional details of the system.

We have applied the revised algorithm for correcting for the time lag between water passing the remote temperature probe and arriving at our equilibrator. We move the pCO_2 data one scan earlier.

1-b) The pCO_2 data:

A program on the vessel's RVDAS computer data collection system merges the pCO_2 system data with specific fields of the shipboard navigational and meteorological data. The fields added to the pCO_2 data stream include: a date/time stamp, latitude, longitude, sea surface temperature, sea surface salinity, flourometer, windspeed, wind direction, barometric pressure, seawater-flow in the uncontaminated seawater line, speed over ground and course made good. We used raw pCO_2 , sea surface temperature and salinity, and position from the ship's GPS data in the merged RVDAS file. These files have the name: NDP0403pco2_m.dxxx, where xxx is the 3 digit Julian Date. They are stored in the rawdata subdirectory, and have been merged into rawdata.txt. We then edit rawdata.txt to remove extra observations both before the first set of standards, and after the last one.

This cruise used 4 gas standards of CO_2 in air and Nitrogen (0 ppm). The program **procpco2.prg** was used to recalculate the concentration of CO_2 from the raw millivolt value using a 4th order polynomial to fit the response curve exactly through all the standards.

Thirty seawater and five air observations are made between standard sets. Each observation involves flowing the equilibrated gas for 120 seconds through the IR analyzer with a nominal rate of 55 ml/min. This means a standard set is run approximately every 75 minutes. We also flow the marine air sample for 120 seconds at a similar rate. The flow is stopped for a few seconds before the reading is taken. Details on these and other aspects of the analysis system are explained later.

<u>Standards:</u>

Cylinder	CO2 Concentration (ppm)
Nitrogen (UHP)	0.00
CC02231	236.29
CC51988	450.05
CC58080	151.67
CC15551	362.80

A 4^{th} order calibration curve is used with all 5 standards, as described in Section 2.

Standards flow for 120 seconds at the nominal rate of 60 ml/min, and flow is stopped for 10 seconds before millivolt readings are taken.

1-c) AIR data:

As with the surface pCO_2 observations, with the benefit of an additional 10 years of observations, we have had to generally reject air observations from this ship. It is not possible to locate the observations contaminated by the ships exhaust systems, primarily from the main engines. Even with the benefit of accurate wind data, and trying to use a nearly head-on relative wind, we still get severe spikes in the air data. (added 03 Mar 2015).

There is some noise and spikiness in the air data. Much of this is due to stack gas contamination of the air sample stream. We made **1,554** individual observations of air, and rejected 424. The remaining data give and average of **375.30 ± 1.70 (N=1,130)**.

To calculate the sea-air pCO_2 difference we use the Global View CO_2 data for the atmospheric CO_2 concentration, extrapolated from the end of 2002 through the early part of 2004. The last observations in that file are for year 2002. A long term trend is fitted to these observations, then extrapolated forward. Naturally, there is some uncertainty in this extrapolation, but it should be less than ±0.5 ppm . This value goes into the "vco2_air" and "gvvco2_air" variables in the **0403sfc** database

1-d) Editing:

With the benefit of 10 plus years of observations, editing, and analysis, we have rejected the running mean as a criteria for rejecting "outliers." These systems just do not work. It is impossible to account for the rapid changes occurring naturally in open ocean systems, with eddies, meandering of currents, local weather, and mesoscale weather and still retain valid observations. Essentially the file is hand edited.

To create a **0403sfc.dbf** surface format file, we use only ACCEPTED pCO_2 values, but ALL the data are retained in the pco2data.dbf database in the subdirectory: \NBPALMER\2004\NBP04_3\SURFACE\PCO2DATA. We estimate the air value from the Globalview CO2 database (as explained under 1-d) AIR data . The program **make0403.prg** performs this process. The program also adds salinity from the edited salinity file **saldata.dbf** in the salinity subdirectory (see other data below).

All of the **9,463** observations of seawater pCO_2 for this cruise all were accepted as we observed no anomalies. The program editpco2.prg performs this editing operation.

The documentation below in italics is, therefore, obsolete. I have chosen to retain it for continuity.

Generally, several criteria were used to reject data points:

a. *When the flow of the sample gas falls below 24 ml/min, and 3 additional scans afterward.*
b. *When the TSG temperature, equilibration temperature, or the difference between them fall outside a specified value from running mean temperature.*
c. *Manually selected observations, such as spikes, outliers, noisiness.*

We used a mean and standard deviation based analysis technique. A running total of 9 data points are used to calculate mean and standard deviation of the three parameters, Teq, TSG temperature, and Teq - TSG Temperature. A minimum standard deviation of 0.1°C is assigned where its calculated value is smaller. This allows times when the temperature is very steady followed by more variation to be preserved. First all values are used to calculate mean and standard deviation. Then we go back through the file, rejecting *data points where the temperatures are above the mean by at least one standard deviation (or 0.1°C). Then we also reject 4 additional data points after each instance of rejecting, to ensure that the system is back to equilibrium.*

After these editing passes there are still values that are outliers, and individual observations and groups of observations are rejected. The criteria here is usually spikes in temperature, particularly where the temperature warms sharply. This normally implies some sort of water flow problem, beyond what the water flow sensor is reporting. Salinity spikes also show flow and bubble problems, and that variable is used in a decision to reject observations. All of the 9,463 observations of seawater pCO_2 *for this cruise all were accepted as we observed no anomalies. The program editpco2.prg performs this editing operation.*

1-f) Other Data:

Salinity: There is a program, **procsal.prg** in the subdirectory salinity, which performs editing of the salinity data. The system uses a mean and standard deviation of 15 data points. There are five passes through the data. Three passes calculate mean and standard deviation and two passes perform edits. After each of the first 2 calculation passes, data points are rejected if outside 1 standard deviation. A minimum standard deviation of 0.02 is assigned. After the second editing pass (4th through the data), mean and standard deviation of the remaining data are calculated using only accepted values. Between accepted values the mean is unchanged. This file **saldata.dbf** is then used as the source for salinity in the master file **0403sfc.dbf**. There was a brief period at the start of day 116 where the salinity data was missing, and these were assigned the -999.9 missing value in the final database.

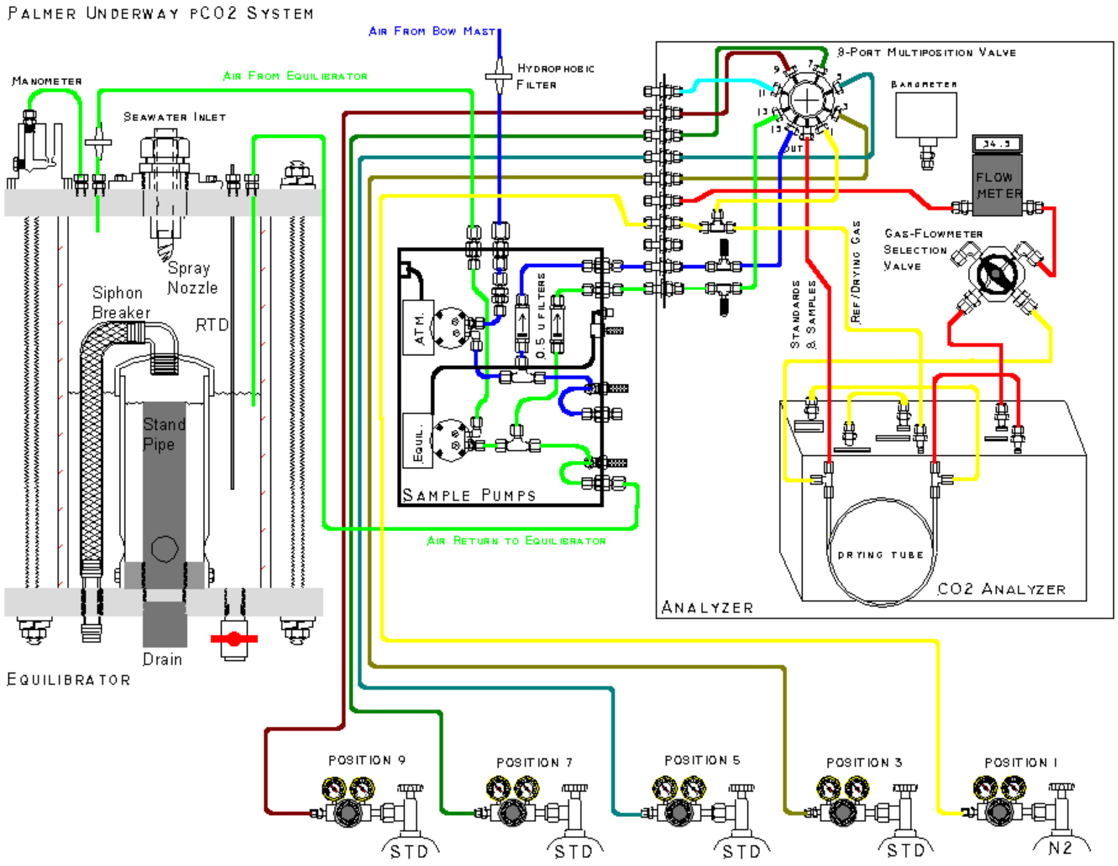
Wind speed units are meters $seconds^{-1}$ measured at the foremast height of about 15 meters.

2. MEASUREMENTS OF pCO_2 IN SURFACE WATERS

2-a) The LDEO Underway System for Surface Water pCO_2 Measurements:

The underway pCO_2 measurement system for surface waters consists of a) a water-air equilibrator, b) an analyzer system based on a non-dispersive infra-red CO_2 gas analyzer, c) sample pumps, d) 5 calibration standards and e) a data logging system. The measurement system is schematically shown in Fig. 1, and is similar with the one described in Bates et al. (1998). Each of these units and the data reduction procedures used will be described below.

Figure 2: Diagram of the underway pCO_2 system used for surface water pCO_2 measurements during NBP04-03.



2-b) Water-air Equilibrator:

The equilibrator has a total volume of about 30 liters and is equipped with a standpipe that is isolated from the headspace and automatically maintains a constant water level at about half the height of the equilibrator leaving about 15 liters of headspace (Figure 2). Seawater from the ship's uncontaminated water line is continuously pumped into the equilibrator at a rate of about 10 liters/min, giving a mean residence time of water in the equilibrator of about 1.5 minutes. The headspace above the water serves as an equilibration chamber. A carrier gas (commonly marine air) is continuously circulated to and from the head space in a closed loop by a diaphragm pump, and exchanges CO_2 with the continuous flow of seawater sprayed into the chamber through a spiral cone spray nozzle. Because of large gas-water contact areas created by fine water droplets as well as gas bubbles in the pool of water, CO_2 equilibration between the carrier gas and seawater is achieved rapidly with a e-folding time of 2 to 3 minutes. Under normal sampling conditions, about 50 ml/min of this sea water equilibrated air is directed into the infra-red gas analyzer. The air drawn for analysis is replaced by a controlled leak into the equilibrator through the water manometer. At this rate, the residence time of the carrier gas in the equilibration chamber is about 300 minutes, that is about 100 times as long as the equilibration time. Therefore, the carrier gas in the head space should always be in equilibrium with the seawater. The over all response time of the equilibrator system has been estimated to be of an order of several minutes. The large volume of water in the equilibrator was chosen to provide a large thermal inertia in the equilibrator, so that the effects of room temperature changes on the equilibration temperature may be minimized. The temperature of water in the equilibrator is monitored continuously using a Guildline platinum resistance thermometer (readable to 0.05 ^{o}C and regularly calibrated against a mercury thermometer traceable to N.I.S.T.) and recorded on the data-logging computer.

The water manometer is attached to the gas intake end of the equilibrator (Figure 2) and provides a visual confirmation that marine air is being returned to the equilibration chamber at the same flow rate that it is being diverted to the CO2 analyzer. The manometer also isolates the equilibrator head space from free exchange with the ambient marine air. The low head of the water manometer ensures that the equilibration chamber pressure is nearly identical to ambient atmospheric pressure. The total pressure at which the gas was equilibrated, can then be measured outside the equilibrator using a precision electronic barometer (Setra Model 270, Action, MA). This equilibration pressure is also logged on the computer.

The temperature and salinity of seawater at the *in situ* conditions were measured using a SeaBird Model SBE-21 thermosalinograph aboard the N. B. Palmer and a SIO/ODF thermosalinograph unit based on Neil Brown sensors aboard the R. Revelle. The precision of the reported temperature data has been estimated to be about 0.005 ^{o}C.

2-c) Infra-red CO_2 Gas Analyzer:

The equilibrated gas was passed through a water trap (to collect condensate,) and, and a reverse flow naphion dryer (PermaPure flushed with pure nitrogen gas) to remove water vapor (to a level of –20^{o}C dewpoint), and was introduced into the IR sample cell at a rate of about 50 ml/min for CO_2 determinations. A LI-COR infra-red gas analyzer

(Model 6251, Lincoln, NB) was used. After a 2-minute purging period, the gas flow was stopped and readings were recorded on the computer. Although the CO2 analyzer has an electronic circuit to linearize the CO_2 response, it exhibited a few inflexions that deviated from linearity by a few ppm. Therefore, the pCO_2 system has been designed to use the raw voltage output of the CO2 analyzer to establish our own calibration curves using five standard gas mixtures (one pure nitrogen and four CO_2-air mixtures). The CO_2 concentrations in the gas mixtures were calibrated using the SIO standards determined by C. D. Keeling's group using the manometric method. The concentrations of CO_2 in the standard gas mixtures were summarized above.

During normal operations approximately every 75 minutes each of the standard gas mixtures was passed through the analyzer for 120 seconds at a rate of about 60 ml/min. This flow rate and time was redundantly sufficient to completely purge the IR analyzer cell with the new gas. The flow was stopped for 10 seconds to allow the pressure in the cell to equilibrate to atmospheric pressure and the average of 20 separate millivolt readings from the analyzer was recorded. Following the five standard gases, samples of seawater-equilibrated air and ambient marine air were pumped through the analyzer for 120 seconds (2 minutes) each at rates of about 50 ml/min and 60 ml/min respectively to purge the previous sample in the IR cell. The flow was stopped for 10 seconds and the average of 20 separate millivolt readings from the analyzer was recorded. This procedure was intended to eliminate errors due to fluctuations of the dynamic pressure within the IR cell by irregular gas flow rates. The relatively slow flow rates used for seawater-equilibrated air samples were required for the removal of water vapor using the PermaPure membrane dryer. We analyze 30 seawater-equilibrated air samples and 5 ambient marine air samples between two sets of calibration runs using the five standard gases.

2-d) Data Logging System:

The following values were recorded on a laptop computer. The sample locations were derived from the ships Global Positioning System (GPS). The CO_2 readings for seawater equilibrated air samples were recorded approximately every 3 minutes, and those for the standard gas mixtures approximately every 90 minutes.

Time/Date stamp (GMT),
CO_2 analyzer voltage output (to 0.1 mv)
Analyzer cell temperature (to 0.1 C)
Barometric pressure (pCO_2 system barometer) (to 0.1 mbar)
CO_2 concentration (to 0.1 ppm, preliminary value based on the last response curve)
Equilibrator temperature (to 0.01 ^oC)
pCO_2 (uatm, preliminary value based on the last response curve)
Gas flow rate (to 0.1 cc/min)
Selector valve position (integer)
Sample ID (standard gas cylinder numbers, seawater CO_2, atmospheric CO_2)

The ships RVDAS system adds several other data elements from various sensors and equipment including: Latitude, Longitude, Thermosalinograph temperature, thermosalinograph salinity, fluorometer voltage, wind speed, wind direction, barometric pressure (at ships instrument mast), water flow in the uncontaminated seawater line.

2-e) Data Reduction Procedures:

The concentration of CO_2 in the sample was computed in the following manner based on the millivolt reading and time of the reading. The millivolt reading taken for each of the five standard gases at the time of sample measurement was computed by linearly interpolating as a function of time using the readings taken before and after the respective standard gases were analyzed. This yields an interpolated millivolt reading for each of the five standard gases at the time when the sample was analyzed. These five values were fit to a fourth-order polynomial equation (with five constants to be determined). This serves as the response curve. The CO_2 concentration in the sample was computed using the response curve that was established at the time of each sample analysis. This method has been demonstrated to yield more reliable CO_2 values compared with those computed, for example, using a least-squares fit of a quadratic or cubic functions to the five calibration points. The method described above yields atmospheric CO_2 values that are consistent (within 1.5 ppm) with those reported for the South Pole and the Cape Grim by the Climate Monitoring and Diagnostics Laboratory/NOAA in Boulder, CO.

The partial pressure of CO_2 in seawater, $(pCO_2)sw$, at the temperature of equilibration, Teq, in the unit of microatmospheres (μatm) was computed using the expression:

$$(pCO_2)sw \ @ \ Teq = (VCO_2)eq \ \text{x} \ (Peq - Pw), \text{.... ....[1]}$$

$(VCO_2)eq$ = the mole fraction concentration (ppm) of CO_2 in the dried equilibrated carrier gas;
Peq = the barometric pressure (that is equal to the total pressure of equilibration) in atmospheres; and
Pw = the equilibrium water vapor pressure at Teq (^oC) and salinity.

The water vapor pressure was computed using the following formulation;

$$Pw\ (atm) = (1/760)\text{x}(1 - 5.368\text{x}10^{-4}\text{x Sal}) \\ \text{x EXP}\{[0.0039476 - (1/TK)]/1.8752\text{x}10^{-4}\}, \text{....... [2]}$$

where Sal is salinity on the Practical Salinity Scale and measured using the ship's thermosalinograph, and TK is the temperature of equilibration in ^oK.

The $(pCO_2)sw$ at the *in situ* temperature, T *in situ*, was computed using a constant value of 0.0423 % per ^oC for the effect of temperature (Takahashi et al., 1993):

$$(pCO_2)sw\ @\ T\mathit{in\ situ} = (pCO_2)sw\ @\ Teq \times EXP[0.0423 \times (T\mathit{in\text{-}situ} - Teq)].$$

The value for Tin situ is taken to be the seawater temperature measured by the ship's thermosalinograph at the time of pCO_2 measurements. Teq is generally warmer than T*in-situ* by 0.5 ~ 0.8 ^oC. Hence the temperature correction is normally less than 3% of pCO_2 values.

The over all precision of the reported $(pCO_2)sw$ values has been estimated to be about $\pm$1.5 uatm.

3. MEASUREMENTS OF pCO_2 IN THE ATMOSPHERE

3-a) Measurements:

The air measurement system is also shown schematically in Fig. 1. Uncontaminated marine air samples were collected about 10 m above the sea surface using a 1/4" i.d. thin-walled aluminum tubing protected by an exterior plastic casing and an internal plastic film lining (Synflex, Calco Inc., PA). The air intake was located at the middle of the foremast about 10 m above the sea surface. A KNF Neuberger air pump located near the IR analyzer was used to pump air through the tubing and into the IR analyzer. Even when air samples were not analyzed, air was continually flowing through the sampling line to continuously purge the long Synflex tubing with fresh marine air. For analysis, the air sample was passed through a 0.5 micron filter to remove aerosols and a drying column to remove water vapor (the same PermaPure column as used for the seawater-equilibrated air) and introduced into the IR cell for CO_2 analysis at a rate of about 60 ml/min. For each sample the cell was purged for 120 seconds, the flow was stopped for 10 seconds and the average of 20 IR millivolt output readings was recorded on the computer.

3-b) Data Processing:

The partial pressure of CO_2 in the air, $(pCO_2)air$, was computed in the unit of microatmospheres (μatm) in the same way as that for seawater using Eq. [3] below:

$$(pCO_2)air = (Vco_2)air \times (Pb - Pw), \ldots. \ldots\ldots\ldots\ldots\ldots\ldots[3]$$

$(Vco_2)air$ = the mole fraction concentration (ppm) of CO_2 in the dried air sample;
Pb = the barometric pressure at sea surface in atmospheres; and
Pw = the equilibrium water vapor pressure at T*in situ* (^oC) and salinity given by Eq. [2].

The precision of the atmospheric pCO_2 values have been estimated to be about $\pm$ 1 μatm.

4. REFERENCES CITED

Bates, N. R., Takahashi, T., Chipman, D. W. and Knapp, A. H. (1998). Variability of pCO_2 on diel to seasonal time scales in the Sargasso Sea. Jour. Geophys. Res., 103, 15567-15585.

CO_2 Group, Lamont-Doherty Earth Observatory. (2004) “Underway pCO_2 System Users Manual”, LDEO of Columbia University, Palisade, NY, pp.23.

Takahashi, T., Olafsson, J., Goddard, J., Chipman, D. W. and Sutherland, S. C., (1993). Seasonal variation of CO_2 and nutrients in the high-latitude surface oceans: A comparative study. Global Biogeochemical Cycles, 7, 843-878.