REPORT OF UNDERWAY pCO$_2$ MEASUREMENTS IN SURFACE WATERS
AND THE ATMOSPHERE DURING August 2000
TRANSIT PUNTA ARENAS, CHILE TO PANAMA CANAL

(RVIB Nathaniel B. Palmer Cruise 00/6)

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1. General

1-a) <u>The Cruise</u>:

The cruise starts in Punta Arenas, and the system began recording data near the Northern border of Chile near latitude of 41°S at 2317 UTC on 23 July 2000. Data ends at 0233 UTC on 6 August 2000. There is a period of 3 days where the flow of nitrogen was below the minimum acceptable value, and that period is ignored. Further, the air flow was never high enough to be acceptable, so there are no air observations.

In June 2014 we re-edited this file using techniques from 2014. Before JD 217, the Thermosalinograph (TSG) temperature was very unstable, and we used an estimated offset to the equilibration temperature (TEQ) from the last two days of data where the TSG was stable to estimate TSG/Sea Surface Temperature. This eliminated the need to offset the TSG temperature to account for the transit from the remote TSG sensor to the pCO$_2$ system.

1-b) <u>The pCO$_2$ data</u>:

The primary source of data are files created by the ships data acquisition system, (RVDAS). A program runs to combined pCO$_2$ data, TSG data, and several other parameters, such as latitude, longitude, windspeed, water-flow in the uncontaminated seawater line, etc. We used raw pCO$_2$, TSG temperature and salinity, and position from the ship's GPS data in the merged RVDAS file. These files have the name: NDP0001pco2.dXXX, where XXX is the yearday. They are stored in the rawdata subdirectory, and have been merged into rawdata.txt. We then edit rawdata.txt to remove extra observations after the last set of standards. Further, as the **procpco2.prg** program runs it identifies places where the number of standards is wrong. This did not find any problems in this file.

Thirty-three seawater and one air observation are made between standard sets. Each observation involves flowing the equilibration gas for 180 seconds. We also flow the

air for 180 seconds before stopping for an observation. Details on these and other aspects of the analysis system are explained later.

Standards:

Cylinder	Concentration (ppm)
Nitrogen (UHP)	0.0
CC02231	236.29
CC02218	109.95
CC15551	362.8
CA02205	495.18

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

Standards flow for about 70 seconds before an observation is made.

1-c) AIR data:

The air data is unacceptable because the flow was less than 14 ml/min throughout the cruise. Flow of at least 30 ml/min is needed to properly flush the sensor.

To calculate ΔpCO_2 we use the GlobalView CO2 database. Since the data ends at the end of 1996, we used an estimate. We added 6.0 ppm to each latitude band to account for the increase over 4 years. For each latitude, we look in the Globalview CO2 database for the appropriate latitude band, add our 6.0 ppm correction, then use the equilibrator barometric pressure to calculate pCO_2 of moist air.

1-d) Editing:

This is a very well behaved data set ignoring the 3 days where there was inadequate nitrogen flow. Only a few points required editing. The criteria here is usually spikes in temperature, particularly where the temperature warms sharply. This normally implies some sort of 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. Of the **9,005** observations of seawater pCO_2 we rejected **1,453**, which leaves **7,552** valid observations. The program **editpco2.prg** performs this editing operation.

To create a 0005sfc.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\NBP00_4\SURFACE\PCO2DATA. We add Thermosalinograph salinity and the ship's barometric pressure (from JGxxx.dat) files, and estimate the air value from the GlobalView CO2 South Pole database (as explained under 1-d) AIR data).

1-f) Estimating Temperatures:

During the period until julian date 216, there were long periods where the TSG temperature showed a very large deviation from the equilibrator temperature. Using the periods where the offset was more or less constant, we calculate an average offset, and use that to estimate TSG (and SST) temperature. The variable esttemp is set = 1 in the pco2data.dbf database for these observations.

1-g) Other Data:

As of this writing, we have no JGxxx.dat files. We use equilibrator pressure to calculate pCO_2 of air, rather than the ship's observation.

Even though no salinity processing was necessary, we used a file in the salinity directory to include in the final **0005sfc.dbf** file during the running of **make0005.prg**

Wind speed is in units of meters sec^{-1}.

2. MEASUREMENTS OF pCO_2 IN SURFACE WATERS

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

The system for underway measurements of pCO_2 in surface waters consists of a) a water-air equilibrator, b) a non-dispersive infra-red CO_2 gas analyzer and c) 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 1 - The underway pCO$_2$ system used for the measurements of pCO$_2$ in surface
waters during the Southern Ocean JGOFS (AESOP) Program.
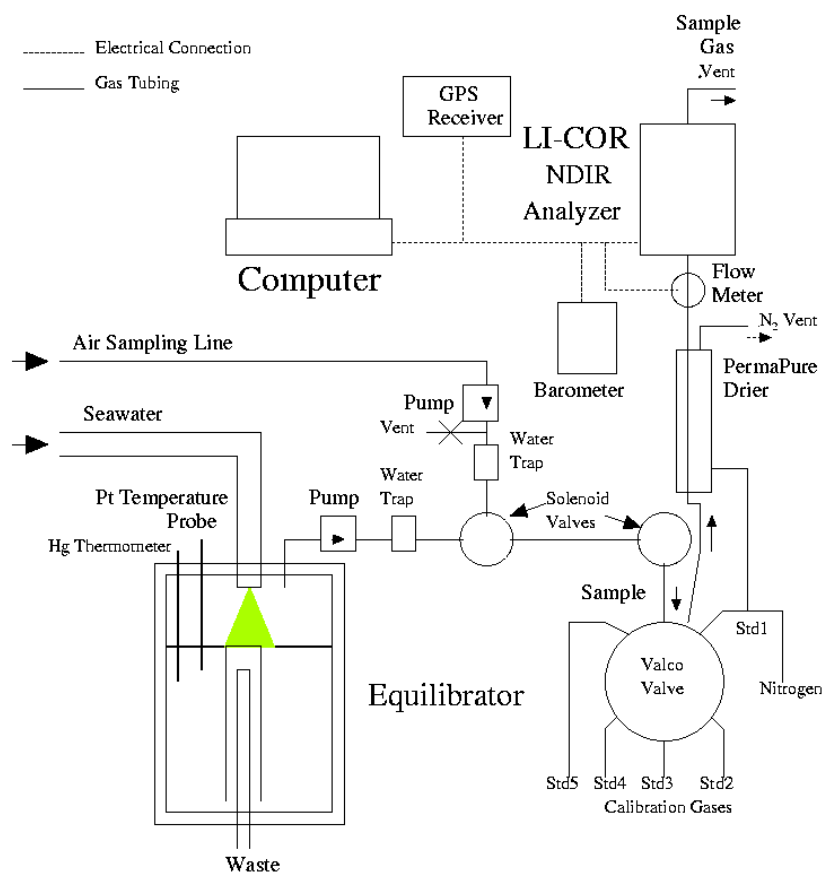
2-b) <u>Water-air Equilibrator:</u>

The equilibrator has a total volume of about 30 liters and is equipped with a specially designed drain which maintains automatically the level of water in the equilibrator at a constant level at about half the height of the equilibrator leaving about 15 liters of headspace. 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 drawn into the chamber by a diaphragm pump, and exchanges CO_2 with a continuous flow of seawater sprayed into the chamber through a shower head. 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 operating conditions, the carrier gas in the equilibration chamber is pumped into the infra-red gas analyzer at a rate of about 50 ml/min. 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 is always in equilibrium with water. 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 is chosen in order to have a large thermal inertia of 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 recorded on the data logging computer. A calibrated mercury thermometer is also inserted in the equilibrator for testing the performance of the platinum thermometer.

At the gas intake end of the equilibrator, a flow indicator based on U-tube manometer is attached. This gives a visual confirmation for the fact that marine air is taken into the equilibration chamber at a desired flow rate. Since we operate the system with the equilibration chamber at the same pressure as the ambient room pressure, the total pressure, at which the gas was equilibrated, is measured using a precision electronic barometer (Setra Model 270, Action, MA) outside the equilibrator. 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 report temperature data has been estimated to be about 0.005 ^{o}C.

2-c) <u>Infra-red CO_2 Gas Analyzer:</u>

The equilibrated gas was passed through a water trap (to collect aerosols and condensates), mass flow controller and a reverse flow naphion dryer (PermaPure flushed with pure nitrogen gas) to remove water vapor (to a level of -20°C), 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 about 3 minutes of

purging period, the gas flow was stopped and readings were recorded on the computer. Although an electronic circuit was provided by the manufacturer in order to linearize the CO_2 response, it exhibited a few inflexions that deviated from linearity by a few ppm. Therefore, we chose not to use the outputs from the linearization circuit supplied by the manufacturer. Instead, we used five standard gas mixtures (one pure nitrogen and four CO_2-air mixtures) during the expeditions, and established response curves using the raw output from the analyzer. 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, each of the standard gas mixtures was passed through the analyzer for 70 to 90 seconds at a rate of about 60 ml/min. This replaced the IR analyzer cell completely with the new gas. The flow was stopped for 5 seconds and then a millivolt reading from the analyzer was taken and recorded. Samples of equilibrated air and marine air were pumped through the analyzer for 180 seconds (3 minutes) at a rate of about 50 ml/min to purge the previous sample in the IR cell. The flow was stopped for 5 seconds and a reading for the analyzer output 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 slow flow rates used for samples were required for the removal of water vapor using the PermaPure membrane dryer. Between two sets of calibration runs using the five standard gases, 6 to 20 samples were analyzed depending upon the stability of the IR analyzer.

2-d) **Data Logging System:**

The following values were recorded on a laptop computer. The sample locations were derived from a GPS positioning unit that is a part of our surface water pCO_2 system. The CO_2 readings for samples were recorded once every 3 minutes (180 seconds), and those for the standard gas mixtures once every 1.5 minutes.

Date,
Time (GMT),
Latitude,
Longitude,
Sample ID (standard gas cylinder numbers, seawater CO_2, atmospheric CO_2)
Barometric pressure in the laboratory (to 0.1 mb)
IR cell temperature,
Gas flow rate in the IR cell (to 0.1 ml/min),
Temperature of equilibration (to 0.01 ^{o}C),
Analyzer output (millivolts to 0.1 mv)
CO_2 concentration in dry gas sample (preliminary based on the last response curve), and
pCO_2 (preliminary value based on the last response curve).

2-e) Data Deduction Procedures:

The concentration of CO_2 in the sample was computed by the following way 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 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 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:

$$(pCO_2)sw @ Teq = (Vco_2)eq \ x \ (Pb - Pw), ...[1]$$

$(Vco_2)eq$ = the mole fraction concentration (ppm) of CO_2 in the dried equilibrated carrier gas;
Pb   = the barometric pressure (that is equal to the total pressure of equilibration) in atmospheres; and
Pw   = the equilibrium water vapor pressure at Teq (^{o}C) and salinity.

The water vapor pressure was computed using the following formulation;

$$Pw \ (atm) = (1/760) x (1 - 5.368x10^{-4} x \ Sal)$$
$$x \ EXP\{[0.0039476 - (1/TK)]/1.8752x10^{-4}\}, ... [2]$$

where Sal is salinity in PSU measured using the ship's thermosalinograph, and TK is the temperature of equilibration in ^{o}K.

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

$$(pCO_2)sw @ Tin \ situ \ = (pCO_2)sw @ Teq \ x \ EXP[0.0423 \ x \ (Tin \ situ - Teq)].$$

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 Tin situ by 0.5 ~ 0.8 ^{o}C. 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 ± 1.5 uatm.

3. MEASUREMENTS OF pCO_2 IN THE ATMOSPHERE

3-a) Measurements:

The air measurement system is shown schematically in Fig. 1. Uncontaminated marine air samples were collected about 10 m above the sea surface using a DEKORON tubing (1/4" i.d., Calco Inc., PA), a thin-wall aluminum tubing protected by plastic casing. The intake was located at the middle of the foremast about 10 m above the sea surface. A KNF Neuberger air pump that was 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, the pump was on all the time to keep the air flowing through the sampling line. For the analysis, the air sample was passed through a water trap and a drying column to remove water vapor (the same PermaPure column as used for the equilibrated gas) and introduced into the IR cell for CO_2 analysis at a rate of about 50 ml/min. After 3 minutes of purging the cell, the flow was stopped for 5 seconds and the IR millivolt output reading was recorded.

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:

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

$(Vco_2)air$ = 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 Tin situ (^{o}C) 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

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