

REPORT OF UNDERWAY pCO₂ MEASUREMENTS IN SURFACE WATERS
AND THE ATMOSPHERE DURING January - February 2004

R/V Laurence M. Gould 04/1

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1. General

Cautionary note on salinity: The salinity observations reported in these data files are NOT calibrated, and not adjusted in any way. The few comparisons that have been made between the thermosalinograph observations, and measurements by more accurate systems (Autosal, etc.), show offsets of as much as 0.3 on the Practical Salinity Scale (PSS). In particular, this cruise, 04/1, salinities are about 1.4 units on the PSS below other transits of this same area. More explanation follows.

1-a) The Cruise:

This cruise was to service Palmer Station and conduct another cruise in the LTER series.. The ship departed Punta Arenas, Chile on 1 January 2004, arrived at Palmer Station on 4 January. This southbound track was an "XBT" leg with TCO₂ and salinity (measured by Autosal). The ship departed from Palmer Station on 5 January, conducting research north of the Palmer Peninsula and returned to Palmer Station on 2 February. She then departed Palmer Station on 3 February, and arrived in Punta Arenas on 7 February 2004. Generally our system performed well. There were some periods where the flow from the equilibrator dropped below the minimum acceptable level. The air data continues to be highly problematic. It is highly variable, and the low mean value is near 374, higher than the Globalview CO₂ value. The latter part of the cruise had particularly noisy air data. Finally the salinity data is unacceptable. The TSG was replaced, but the calibration constants were not changed in the software that reads the raw TSG data and converts to engineering units. Apparently, the raw data are not stored, so recovering the data has not been successful.

1-b) The pCO₂ data:

The primary source of data are files created by the ships data acquisition system, (RVDAS). A program runs to combined pCO₂ data, thermosalinograph (TSG) data, and several other parameters, such as latitude, longitude, windspeed, ship heading and speed, etc. We used raw pCO₂, TSG temperature and salinity, and position from the ship's GPS data in the merged RVDAS file. These files have the name: LMGpco2m.dxxx, where xxx is the 3 digit Julian Date.

The system performed very well, and the only editing a few periods where the equilibrator sample flow was below 20 ml/min. The thermosalinograph temperature data continues to have anomalous spikes. Even though the salinity data are unacceptable due to problems with the calibration constants, it appears that the remote temperature probe data are OK. The graph of equilibration chamber temperature versus thermosalinograph temperature shows several groups of data with slopes dramatically different from 1.0, as we have seen almost from the start of the program aboard Gould. These are eliminated, and a curve fit through the remaining data. This curve is used to estimate Sea Surface Temperature, and it is the temperature at which the pCO₂ at SST is calculated.

Thirty seawater and five air observations are made between standard sets. Each observation involves flowing the equilibration gas for 120 seconds. We also flow the air for 120 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
CC46457	150.19
CA02237	364.44
CC22986	252.0
CC46471	788.0
CC104439	384.075

A 4th order calibration curve is used with 5 standards, not including the Nitrogen, as described in Section 2.

Standards flow for about 120 seconds before an observation is made.

1-c) AIR data:

There are **2,164 air observations**. By applying a mean and standard deviation filter to the data, **1,237** were retained. These gave a mean of **373.34 ± 0.97 (N = 1237)**. This compares with a value from the GlobalView CO₂ database extrapolated from 2002 of 373.0. Our value contains a great deal of noise, but is just within 1 ppm of the GlobalView value.

To calculate ΔpCO₂ we use the Global View CO₂ data, extrapolated from the end of 2001 through 2002. The last observations in that file are for year 2001. A longterm 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 **L041sfc** database.

1-d) Editing:

The group of individual days were concatenated together and edited under the name **rawdata.txt**. Periods where the system was interrupted before a standard run was complete, those where the data are unreadable, etc. are edited at this level.

a. The TSG temperature was not reliable for most of this cruise. We use an equation derived by matlab to estimate SST. The equation uses the data where equilibration temperature is > 0.5 degrees, and the difference between equilibration temperature and TSG temperature is < 0.1°C. The result is:

$$\text{SST} = 1.0061 * \text{Equilibration Temperature} - 0.0699$$

b. Of the **12,975 observations** of seawater pCO₂, we **rejected 419, retaining 12,556 records**. The program **editpco2.prg** performs this editing operation.

c. There was a period where the equilibrator gas flow was below 20 ml/min, which was eliminated. There were a couple of other small spikes which were eliminated.

d. To create a **L041sfc.dbf** surface format file, we use only ACCEPTED pCO₂ values, but ALL the data are retained in the pco2data.dbf database in the subdirectory: \LMGOULD\2004\img04_1\SURFACE\PCO2DATA. We estimate the air value from the Globalview CO2database (as explained under 1-d) AIR data . The program **makeL041.prg** performs this process. The program also adds salinity from the edited salinity file saldata.dbf in the salinity subdirectory (see other data below).

1-f) Other Data:

Salinity:

The technical staff aboard L.M. Gould changed the thermosalinograph instrument from serial number 3208 to serial number 1789, but did not change the constants in the calculation software. Thus, the salinities are wrong. The error seems about 1.5 units on the Practical Salinity Scale (PSS), with the observations too low by that amount. Using Matlab, we attempted to convert the data from one set of constants to another, but this only changed the values about about 0.1 unit. The data in this file are the original values. **GREAT CAUTIONS MUST BE USED IN INTERPRETING THESE VALUES.** The offset appears to be fairly constant, so the structure of the data is probably quite good, with a fairly constant offset of about -1.46 units.

We determine this offset by examining the values for 12 samples measured by Autosal during the southbound transit, 2-5 January. A linear regression between the Autosal and TSG values yields the following:

$$\text{Autosal} = 1.0637 \text{ X TSG} - 0.5944$$

By another analysis, the average offset is:

$$\text{TSG - Autosol} = -1.46 \pm 0.11 \text{ (N=12)}$$

In past cruises we have noticed that the offset of the TSG instrument has drifted about 0.3 units during the first week or so of the cruise. There is some indication of this action in the above data, but there are not enough data points to define this adequately, so we assume a constant offset.

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 calculate mean and standard deviation, two 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 **L041sfc.dbf**.

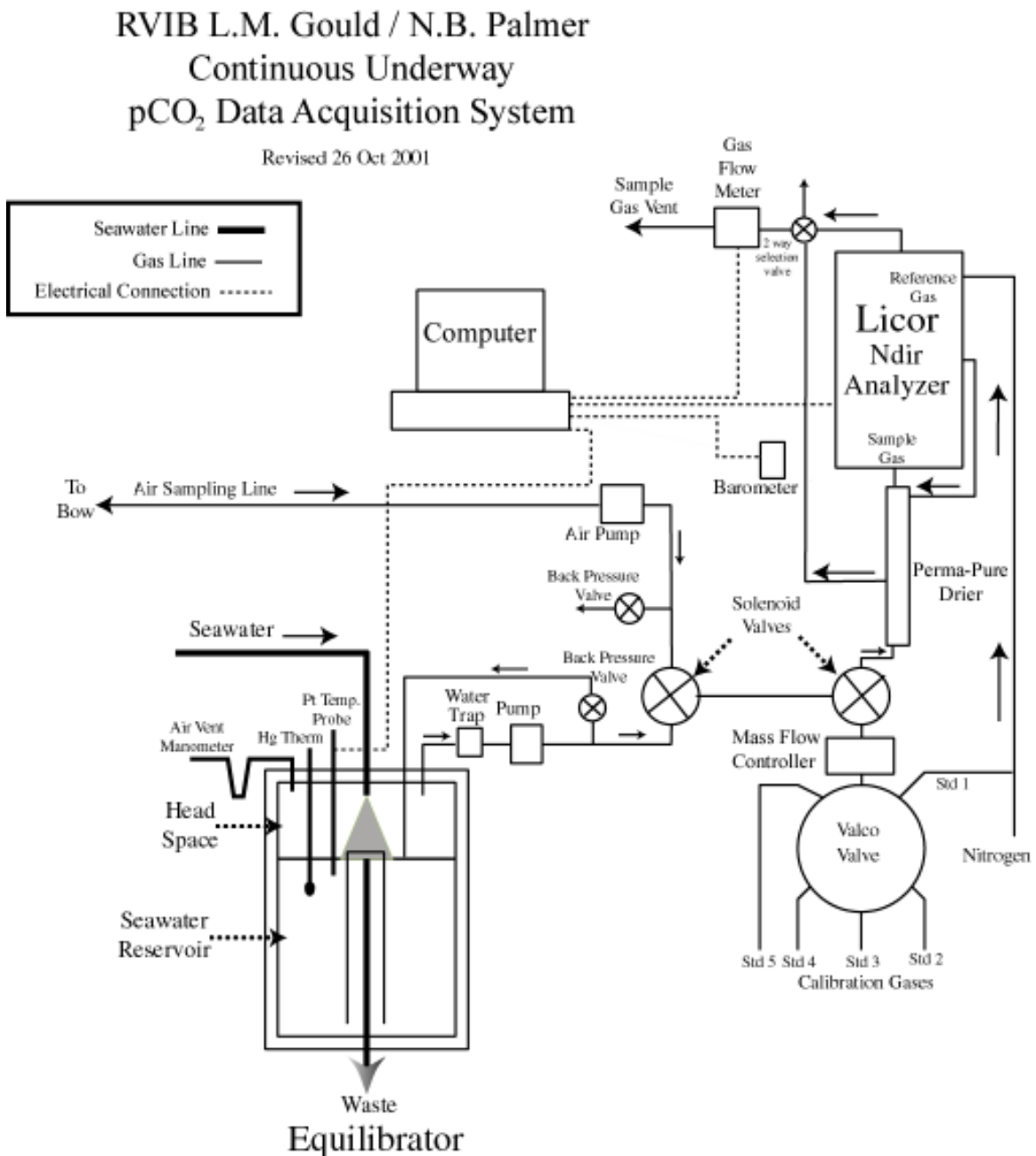
Wind speed units are meters seconds⁻¹.

2. MEASUREMENTS OF pCO₂ IN SURFACE WATERS

2-a) The LDEO Underway System for Surface Water pCO₂ Measurements:

The system for underway measurements of pCO₂ in surface waters consists of a) a water-air equilibrator, b) a non-dispersive infra-red CO₂ 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 pCO₂ system used for the measurements of pCO₂ in surface waters during the Southern Ocean JGOFS (AESOP) Program.



2-b) Water-air Equilibrator:

The equilibrator has a total volume of about 30 liters and is equipped with a standpipe drain which automatically maintains 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 CO₂ 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, CO₂ 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 °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 a 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 and ensures that two way air exchange does not occur. 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 °C.

2-c) Infra-red CO₂ Gas Analyzer:

The equilibrated gas was passed through a water trap (to collect aerosols and condensates), a reverse flow naphion dryer (PermaPure flushed with pure nitrogen gas) to remove water vapor (to a level of -20°C dewpoint), and was introduced into the IR sample cell at a rate of about 50 ml/min for CO₂ determinations. A LI-COR infra-red gas

analyzer (Model 6251, Lincoln, NB) was used. After about 2 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 CO₂ 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 CO₂-air mixtures) during the expeditions, and established response curves using the raw millivolt output from the analyzer. The CO₂ 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 CO₂ in the standard gas mixtures were summarized above.

During normal operations, each of the standard gas mixtures was passed through the analyzer for 120 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 10 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 120 seconds (2 minutes) at a rate of about 50 ml/min to purge the previous sample in the IR cell. The flow was stopped for 10 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. We analyze 20 seawater and two air samples between two sets of calibration runs using the five standard gases. (the current setup is 30 seawater samples, 5 atmospheric)

2-d) Data Logging System:

Our laptop records the following data and writes it via a serial port to the ship's RVDAS system.

Date,
Time (GMT),
Sample ID (standard gas cylinder numbers, seawater CO₂, atmospheric CO₂)
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 °C),
Analyzer output (millivolts to 0.1 mv)
CO₂ concentration in dry gas sample (preliminary based on the last response curve), and
pCO₂ (preliminary value based on the last response curve).

The ships RVDAS system adds several other data elements from various sensors and equipment. The list is:

Latitude, Longitude, Thermosalinograph temperature, thermosalinograph salinity, fluorometer voltage, wind speed, wind direction, and, barometric pressure.

2-e) Data Reduction Procedures:

The concentration of CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ in seawater, (pCO₂)_{sw}, at the temperature of equilibration, T_{eq}, in the unit of microatmospheres (µatm) was computed using the expression:

$$(pCO_2)_{sw} @ T_{eq} = (V_{CO_2})_{eq} \times (P_b - P_w), \dots \dots \dots [1]$$

- (V_{CO₂})_{eq} = the mole fraction concentration (ppm) of CO₂ in the dried equilibrated carrier gas;
- P_b = the barometric pressure (that is equal to the total pressure of equilibration) in atmospheres; and
- P_w = the equilibrium water vapor pressure at T_{eq} (°C) and salinity.

The water vapor pressure was computed using the following formulation;

$$P_w \text{ (atm)} = (1/760) \times (1 - 5.368 \times 10^{-4} \times \text{Sal}) \times \text{EXP}\{[0.0031476 - (1/TK)]/1.8752 \times 10^{-4}\}, \dots \dots [2]$$

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

The (pCO₂)_{sw} at the in situ temperature, T_{in situ}, was computed using a constant value of 0.0423 % per °C for the effect of temperature (Takahashi et al., 1993):

$$(pCO_2)_{sw} @ T_{in \text{ situ}} = (pCO_2)_{sw} @ T_{eq} \times \text{EXP}[0.0423 \times (T_{in \text{ situ}} - T_{eq})].$$

The value for T_{in situ} is taken to be the seawater temperature measured by the ship's thermosalinograph at the time of pCO₂ measurements. T_{eq} is generally warmer than

Tin situ by 0.5 ~ 0.8 °C. Hence the temperature correction is normally less than 3% of pCO₂ values.

The over all precision of the reported pCO₂)_{sw} values has been estimated to be about ±1.5 uatm.

3. MEASUREMENTS OF pCO₂ 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 (3/8 " 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 directed to the analyzer , 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 drying column to remove water vapor (the same PermaPure column as used for the equilibrated gas) and introduced into the IR cell for CO₂ analysis at a rate of about 50 ml/min. After 2 minutes of purging the cell, the flow was stopped for 10 seconds and the IR millivolt output reading was recorded.

3-b) Data Processing:

The partial pressure of CO₂ in the air, (pCO₂)_{air}, was computed in the unit of microatmospheres (µatm) in the same way as that for seawater using Eq. [3] below:

$$(pCO_2)_{air} = (V_{CO_2})_{air} \times (P_b - P_w), \dots \dots \dots [3]$$

- (V_{CO₂})_{air} = the mole fraction concentration (ppm) of CO₂ in the dried air sample;
- P_b = the barometric pressure at sea surface in atmospheres; and
- P_w = the equilibrium water vapor pressure at Tin situ (°C) and salinity given by Eq. [2].

The precision of the atmospheric pCO₂ values have been estimated to be about ± 1 µatm.

4. REFERENCES CITED

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