REPORT OF UNDERWAY pCO_2 MEASUREMENTS IN SURFACE WATERS AND THE ATMOSPHERE DURING March 2002

R/V Laurence M. Gould 02/1B

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31 July, 2017

1. General

1) The programs used to process this cruise form the prototype for the rest of this year of Gould cruises. We use a 4th order response curve to convert millivolts to ppm, using all 5 standards in the processing. The rational is as follows:

2) We think we know the value of our standards to better than 1 ppm. When we fit the response curve to a quadratic form, we get residuals near 2 for the area around 350 ppm, exactly the area we want the best value. By using a 4th order curve, which exactly fits all 5 standards, we are accounting for any problems with the Licor analyzers response, particularly problems with the linearizing circuit. Naturally, this makes our residuals essentially zero.

3) Regarding SST (Thermosalinograph (TSG) Temperature). The TSG was unreliable, and we used equilbrator temperature to estimate SST. We use 1 scan offset to adjust the pCO_s timing.

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

This cruise was a mooring recovery cruise. The ship left Punta Arenas on 7 March 2002 and arrived back in Punta Arenas on 18 March 2002 after travelling across Drake Passage to the vicinity of Palmer Station, Antarctica. The northbound and southbound legs were XBT legs, and 30 stations were sampled for TCO_2 and PO_4.

1-b) The pCO_2 data:

The primary source of data are files created by the ships data acquisition system, (RVDAS). A program runs to combined pCO_2 data, thermosalinograph (TSG) data, and several other parameters, such as latitude, longitude, windspeed, ship heading and speed, etc. We used raw pCO_2 , TSG temperature and salinity, and position from the ship's GPS data in the merged RVDAS file. Reprocessing was necessary because the wrong constants were used in the ship's pco2 data acquisition program for equilibration pressure. Tim Newberger provided a simple algorithm to correct the barometric pressure.

We put the raw data files into the rawdata subdirectory, and ran an updated version of **procpco2.prg**.

Twenty seawater and two 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
CC51612	353.77
CC22986	251.79
CC46471	788.0

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

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

1-c) AIR data:

There are **135 air observations**., however, they are all greater than 372 ppm, and believed to be unusable. All were **rejected**.

To calculate ΔpCO_2 we use the Global View CO_2 data, extrapolated from the end of 2001 through the early part of 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 **L021sfc** database.

1-d) Editing:

a. The TSG temperature was not reliable for most of this cruise. We use a linear regression to estimate SST from equilibration temperature.
The equation is:

$$\textbf{Sea Surface Temperature} = -0.00682 \times \textbf{pCO}_2\ \textbf{Temperature} + 0.15$$

b. The system did not seem to recover properly from the standard runs, and the first five seawater observations after each set of standards were eliminated.

c. If the flow of air as recorded by the system fell below 20 ml min^{-1} we eliminated the observation.

d. The first 5 observations after each set of standards were rejected, as the system appeared to take that long to come to equilibrium.

Of the **3,948 observations** of seawater pCO_2 we **rejected 1,229**, **retaining 2,719 records.**

To create a **L021sfc**.dbf surface format file, we use only ACCEPTED pCO_2 values, but ALL the data are retained in the pco2data.dbf database.. We estimate the air value from the Globalview CO2database (as explained under 1-d) AIR data . The program **makeL021.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) Salinity:

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 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 **L021sfc.dbf.**

1-g) Total CO_2:

The northbound and southbound legs of this cruise were XBT legs, and 30 samples for TCO_2 and PO_4 were drawn. John Goddard ran the samples and a file called **tco2list.dbf** was created with these data. The program **maketco2.prg** runs to search the main station data file for the time stamps in the TCO_2 data file, and adds pCO_2, temperature, salinity, barometric pressure, latitude, and, longitude. A time from the pCO_2 file called pco2time records the average time from the pCO_2 file. These data are subsequently placed into the **l021sfc.dbf** database along with the PO_4 (below) with the TCO_2 time recorded as well.

1-h) Phosphate (PO_4):

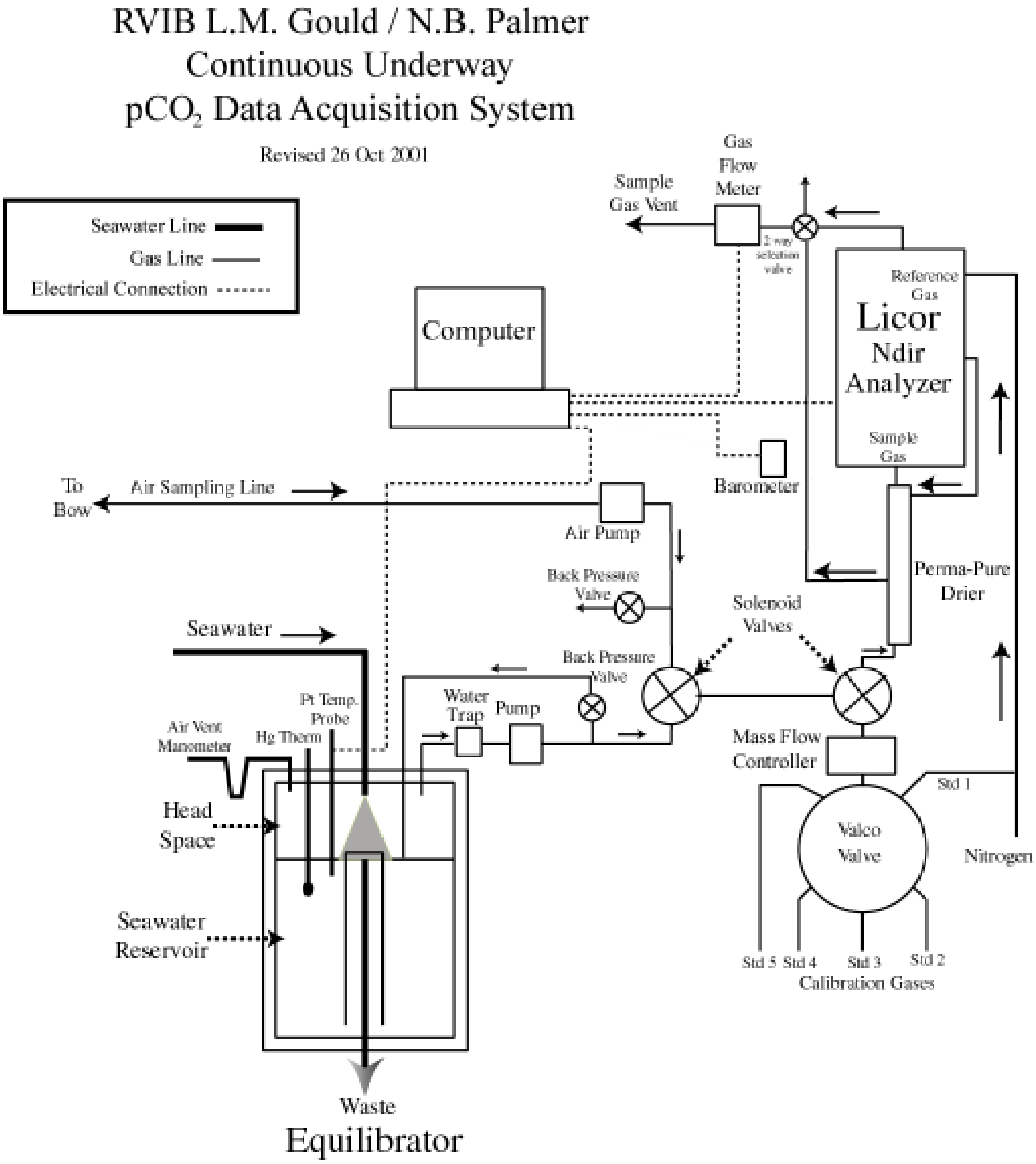
Phosphate is also measured in the total CO_2 bottles and included in the **tco2list** database.

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) Water-air Equilibrator:

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) Infra-red CO_2 Gas Analyzer:

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^{o}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 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 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 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.

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 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 ^oC),
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).

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 directiion, and, barometric pressure.

2-e) Data Reduction 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:

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

$(Vco_2)eq$ = 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 (^oC) and salinity.

The water vapor pressure was computed using the following formulation;

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

where Sal is salinity in PSU 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):

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

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 ^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 ±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 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 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:

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

(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 (^oC) and salinity given by Eq. [2].

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

4. REFERENCES CITED

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