

REPORT OF UNDERWAY pCO₂ MEASUREMENTS IN SURFACE WATERS
AND THE ATMOSPHERE DURING
THE AMUNDSEN AND BELLINGHAUSEN SEA CRUISE,
FEBRUARY – MARCH 2000
(RVIB Nathaniel B. Palmer Cruise 00/1)

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16 May, 2017

1. General

We have re-evaluated the validity of this data set and find that it does not pass muster compared with other cruises. The failure of one standard gas, the complete failure of the equilibrator temperature sensor and the extreme spiking in the TSG temperature compromise this cruise beyond repair.

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1-a) The Cruise:

RVIB Nathaniel B. Palmer departed the ice edge near McMurdo Station, Antarctica on 15 February 2000, and arrived at Palmer Station, Antarctica on 29 March 2000. Our surface pCO₂ system was started soon after departure at 1222 UTC 16 February (yearday 47) and operated continuously until 0420 UTC 30 March 2000 (yearday 90). A total of 28,303 seawater and 882 air observations were recorded. After extensive editing, a total of 26,474 seawater observations remain. The ship's thermosalinograph (TSG) was operating as well, and the 1-minute sampled data was merged with our raw pCO₂ data into a set of RVDAS files which form the source for these observations. Shipboard measurements of wind speed, wind direction, barometric pressure, position, and heading were also included in these files. There was an eastbound transit of the Ross Sea at the start of the cruise. For the remainder the ship operated near the continent in an easterly direction until arrival at Palmer Station.

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 pCO₂ data one scan earlier.

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, TSG data, and several other parameters, such as latitude, longitude, windspeed, water-flow in the uncontaminated

seawater line, 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: 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.

There was a long period, beginning at yearday 54.8841 (23 Feb) until yearday 82.7098 (22 Marcy) where the standard cylinder CC02231, 236.29 ppm, flow dropped below 40 ml/min. This is not enough to properly flush the Li-Cor cell, so for that period only 4 standards (including UHP N₂) were used to calculate VCO₂ from millivolts. These 4 data points were time-drifted to derive a 3rd order polynomial response curve. For the rest of the time, 5 standards are used to derive a time-drifted 4th order curve.

There was also a problem with a faulty temperature sensor in the pCO₂ equilibrator for much of the cruise. We estimate equilibration temperature from TSG temperature for that period (see editing, below).

Standards:

Cylinder	Concentration (ppm)
Nitrogen (UHP)	0.0
CC02231	236.39
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:

There may be some structure to the VCO₂ of air, but it is within the error of about ±0.3 ppm, so we use a constant 367.3 ppm. The data had typical scatter in the raw observations. These we attribute to stack gas blowing across our intake, even though it is at the furthest forward part of the ship. When working in ice, the ship often has to maneuver, and stack gas can easily blow across our intake. These positive spikes are usually ignored, and a minimum value is estimated.

1-d) Editing:

Equilibration Temperature (Teq):

Big problems here. As the cruise progressed, the difference between Teq and TSG temperature gradually became larger, with the Teq drifting down. After day 68 it even got below -1.9°C . Jay Ardai cleaned the contacts on the top of the temperature sensor of the salt deposit, and the delta temperature (Teq – TSG) jumped right back to within 0.02°C of what it was at the start. The first 209 records give $+0.48^{\circ}$, and the last few days from day 88.0 to the end give $+0.52^{\circ}\text{C}$. With this information, beginning with yearday 48, (17 Feb), until Jay replaced the cleaned sensor at yearday 85.725 (1755 UTC 25 March) we estimated equilibration temperature (Teq) by TSG temperature + 0.50°C .

Generally, several criteria were used to reject data points:

- a. When the water flow dropped below 48 l/min.
- b. When the salinity jumped more than 0.05 ppm from a running average.
- c. When the TSG temperature jumped more than 0.30°C from a running average.

There were a few other points which did not quite meet these criteria, and after day 85 there is too much real variation for this system to work. There are, therefore, about 6 periods where data were rejected “by hand.”

To create a 0001sfc.dbf surface format file, we use only ACCEPTED pCO₂ values, but ALL the data are retained in the pco2data.dbf database in the subdirectory:
 \NBPALMER\NBP00_1\SURFACE\PCO2DATA.

1-f) Temperature Calibration:

Jay Ardai did some simple calibration experiments with the various thermometers with the following results. These experiments were performed on 29 March 2000 after cleaning and reinstalling the RTD sensor into the pCO₂ equilibrator.

Ice-water Bath (29 Mar 2000):

Platinum Therm.	Glass (#62774)	RTD	TSG
0.007 to 0.011	0.020	0.25 to 0.26	
0.005	0.015	0.26	

At date_time 2000088.4541:

0.78	0.96	0.63 (1105 UTC, day 088)
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Across Drake Passage:

2.54	2.69	2.391
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NO adjustments have been made to reflect these data.

1-g) Other Data:

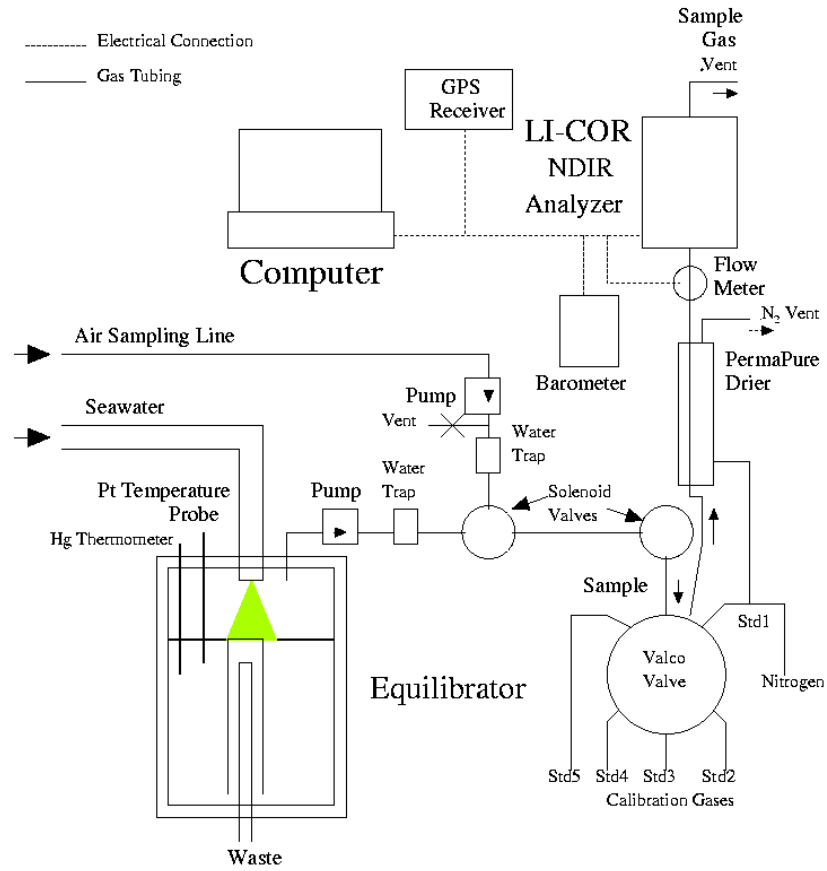
The subdirectory navdata contains the merged jgXXX.dat files. These contain barometric pressure and wind speed as observed by the ship's sensors. We merged these data into the master file using julian date, and using the julian date just BEFORE our pCO₂ data were observed. This formed an offset of about 30 seconds between the barometric pressure and wind speed and the pCO₂ observation. Ship's barometric pressure was 1.8 ± 0.2 mbar higher on average than the equilibrator barometric pressure. This ship's barometric pressure was used with observed sea surface temperature, and salinity to calculate pCO₂ of air assuming 100% relative humidity. Delta pCO₂ is the difference between our pCO₂ at SST and this pCO₂ of wet air.

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 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 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 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 °C.

2-c) Infra-red CO₂ 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°C), 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 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 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 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 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 pCO₂ system. The CO₂ 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 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).

2-e) Data Deduction 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;

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

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 T_{in 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 $p\text{CO}_2$ _{sw} values has been estimated to be about ± 1.5 μatm .

3. MEASUREMENTS OF $p\text{CO}_2$ 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, $(p\text{CO}_2)_{\text{air}}$, was computed in the unit of microatmospheres (μatm) in the same way as that for seawater using Eq. [3] below:

$$(p\text{CO}_2)_{\text{air}} = (V_{\text{CO}_2})_{\text{air}} \times (P_b - P_w), \dots \dots \dots [3]$$

$(V_{\text{CO}_2})_{\text{air}}$ = the mole fraction concentration (ppm) of CO_2 in the dried air sample;
 P_b = the barometric pressure at sea surface in atmospheres; and
 P_w = the equilibrium water vapor pressure at $T_{\text{in situ}}$ ($^{\circ}\text{C}$) and salinity given by Eq. [2].

The precision of the atmospheric $p\text{CO}_2$ values have been estimated to be about ± 1 μatm .

4. REFERENCES CITED

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