

REPORT OF UNDERWAY pCO₂ MEASUREMENTS IN SURFACE WATERS
AND THE ATMOSPHERE DURING THE ANTARCTIC PACK ICE SEALS
EXPEDITION, DECEMBER 1999 – JANUARY 2000, IN THE ROSS AND
AMUNDSEN SEAS - (RVIB Nathaniel B. Palmer Cruise 99/9)

Taro Takahashi, Colm Sweeney, S. C. Sutherland

Lamont-Doherty Earth Observatory of Columbia University
Palisades, NY 10964

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1. General

1-a) The Cruise:

RVIB Nathaniel B. Palmer departed Lyttleton, New Zealand on 20 December 1999, (yearday 354) and arrived at the ice-edge off McMurdo Station, Antarctica on 10 February 2000 (yearday 41). Surface pCO₂ data was collected from the time the ship reached 200 miles off New Zealand until arrival at McMurdo. Our pCO₂ system was energized, and began recording data at 0855 UTC on 21 December (yearday 355) and shut down at 1803 UTC on 9 February 2000 (yearday 40). A total of 33,050 seawater, and 986 air VCO₂ observations were recorded during this time. After editing, these 27,547 seawater values remained. The ship's thermosalinograph (TSG) was operating during this time, and the 1-minute sampled data were used to measure surface temperature and salinity. Shipboard measurements of wind speed, wind direction, barometric pressure, position, and heading were also obtained from the ship's main data acquisition system (RVDAS). This cruise crossed the Antarctic Circumpolar current along 175°E longitude, and entered the Ross Sea near 65°S and 175°E. The bulk of the cruise covered the Amundsen Sea between 160°W and 120°W, remaining south of 65°S. The last part was a transit across the Ross Sea near latitude 77°S.

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. For this cruise there were 2 days (yeardays 357 and 358, 23 & 24 December 2000), where TSG data was missing from the RVDAS files. We used raw pCO₂ and TSG data files for this period, and the position is from our GPS receiver in the pCO₂ system computer.

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	236.39
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.

After rather extensive editing, 27,547 seawater observations were retained. A FoxPro program (editpco2.prg) performed the editing process.

1-c) AIR data:

The raw VCO₂ of air shows many positive excursions, and also a latitude gradient across the Antarctic Front. North of 58°N we estimated a constant value of 368.2 from the raw data. South of 67°S we estimated a constant value of 367.2. In between across the Antarctic Front, we used the equation: $VCO_2 = 0.13 * \text{Latitude} + 376.1$.

Then using the SST, salinity (34.0 where no salinity is available), and barometric pressure, we calculate pCO₂ of air, and ΔpCO₂ (seawater – air).

1-d) Editing:

Nitrogen flow dropped to near zero for an extended period from yearday 23.82140 (23 Jan) through yearday 24.78520. Because this flow also passes through the drying column, we had to reject the data for the entire period. The gas could not be assumed to be dry.

We rejected the data where the equilibrated gas flow dropped below 27 ml/min. This occurred several times, for extended periods:

 yearday 359.62110 to yearday 360.00092

 yearday 360.69882 to yearday 361.13248

Also for shorter periods during the time from yearday 3 through yearday 15.

Thermosalinograph and “SST:” Generally the thermosalinograph temperature is used as the sea surface temperature. From yearday 1.98348 until yearday 2.03165 we used the equilibration temperature and a constant offset of –0.61°C using the observations before and after the data dropout. Another period from yearday 37.00114 until 37.99903 an offset of –0.51°C was used, again using the observations before and after the data dropout.

Waterflow less than 40 l/min also resulted in data being rejected. This occurred for only brief periods, less than a few minutes duration.

There is a period where Equilibration temperature was faulty. This was apparently due to a short across the leads of the electronic temperature probe. It began on yearday 20.74886, and was corrected at 26.24412. During this period, equilibration temperature is estimated using the TSG temperature and a constant offset of +0.42°C. We use the period before and after the TSG temperature dropout to estimate the offset.

After all these procedures, there still about 59 periods that were rejected by inspecting the data. The criteria were generally that the system had not returned to equilibrium as observed by the VCO₂ value settling to a more constant value. Further, there are periods where the temperature spikes up, indicating an interruption in the waterflow. While not observed in the waterflow data, they were still enough to effect the VCO₂ data, and it is not clear whether the system was in equilibrium during these brief periods. They are generally 5-10 observations wide, but some are as narrow as a single observation. The program editpco2.prg contains all of these edits.

Salinity was edited in only a rudimentary manner. The system here is very sensitive to bubbles in the water stream, and even when all the temperature anomalies are eliminated, there may be some salinity spikes remaining. I did apply a simple filter rejecting values below 33.25 and above 34.50, but that is the only salinity-specific editing that was performed.

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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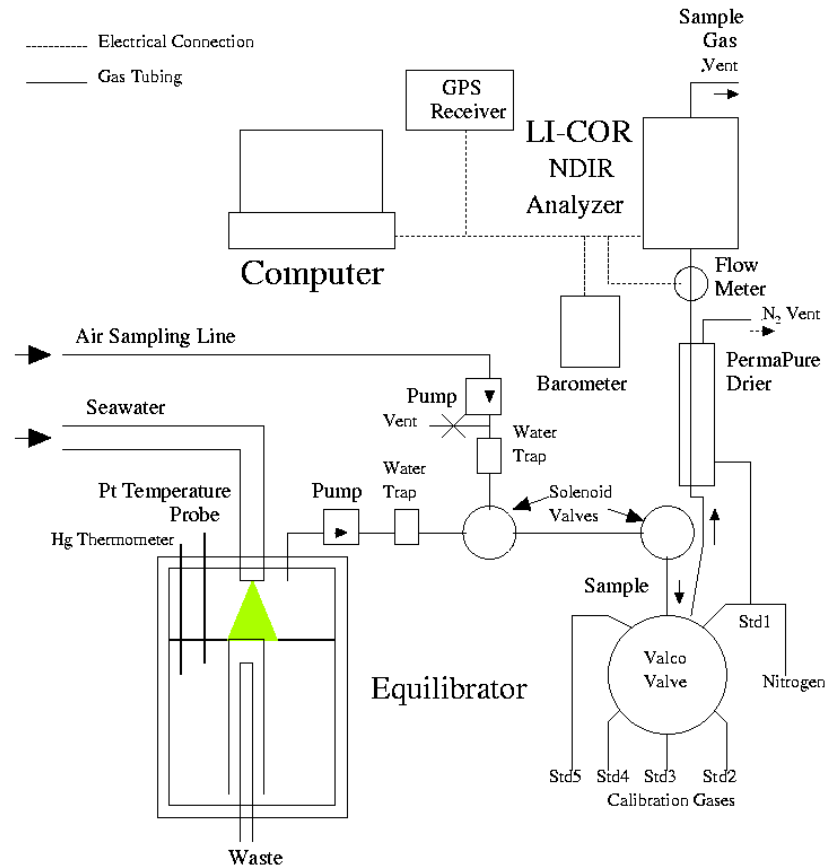
2. MEASUREMENTS OF pCO₂ IN SURFACE WATERS

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 (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 (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 CO₂ 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 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 T_{in 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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