Methods Used in Measuring Surface Seawater pCO_2 Aboard RVIB Nathaniel B. Palmer

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1. Introduction:

This documentation accompanies data files in the Lamont-Doherty pCO_2 web site (http:\\www.ldeo.columbia.edu\~pco2\palmer). We will describe our system and the processes we used to arrive at the value of pCO_2 in seawater that are reported in the data files. Each of the data files contains a heading which specifies the units of each variable.

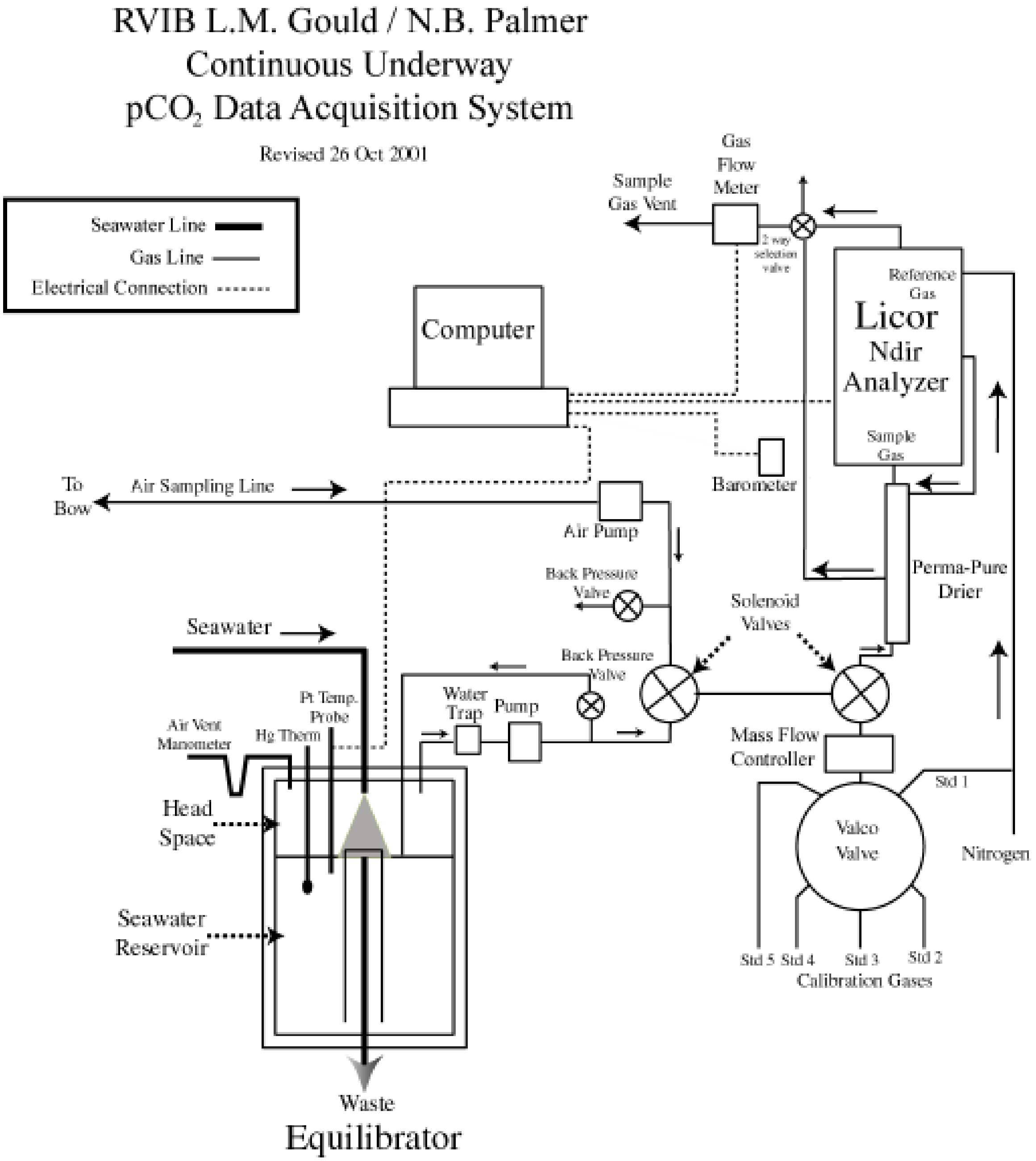
Each file beginning in 1999 also has as associated data report. In this data report we describe in more detail the specifics of a particular cruise. The actual value of the standard gases used; problems with the system; and, such items as whether and were temperatures were estimated where they are missing, and, a discussion of the CO_2 concentration in air that we measured.

The CO_2 in air data are not considered accurate enough to be included in these data files. It appears that there is a small (1-2 ppm) contamination from the ship which we cannot adequately account for.

2. 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.



3. 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.

4. 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 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.

5. <u>Data Logging System:</u>

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),
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, barometric pressure, water flow in the uncontaminated seawater line.

6. 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:

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

$(Vco_2)eq$ = 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):

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

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 $\underline{+}$1.5 uatm.

7. REFERENCES CITED

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