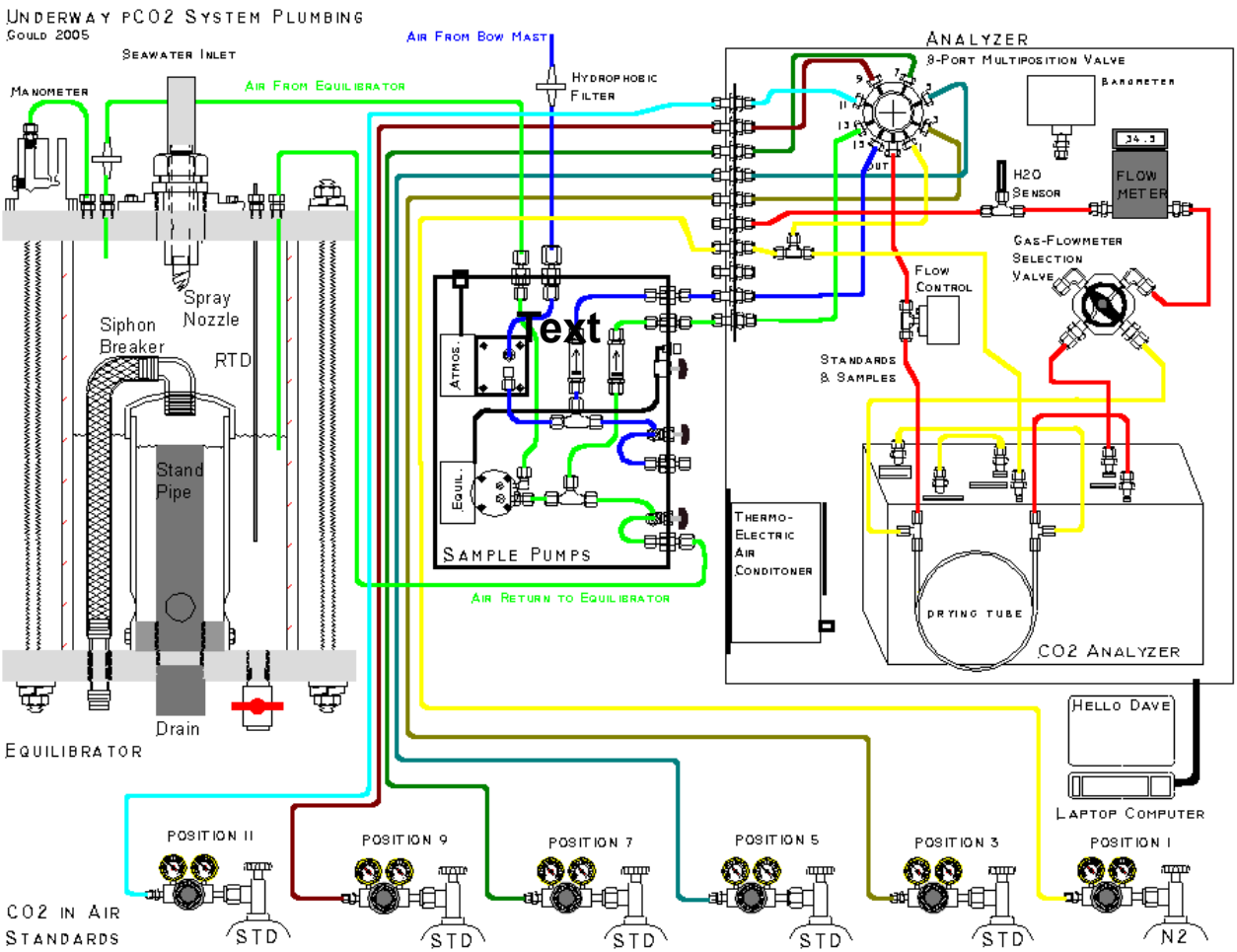
Underway PCO2 System Schematic and Description



Report Prepared for the Fleet Improvement Committee, UNOLS

The LDEO Underway Measurement System for Surface Water pCO_2

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(March 14, 2019)

This report describes the LDEO system for the underway continuous measurement of surface water pCO_2, which is a measure for the direction and intensity of sea-air CO_2 transfer across the sea surface. The purpose is to obtain the temporal and spatial variation of the amount of CO_2 gas being absorbed by the global oceans or released to the air. This information is important to the assessment of future climate change, in which CO_2 in the atmosphere plays a major role.

The LDEO pCO_2 system has been operated successfully for multiple-years aboard research ships including R/V Sikuliaq, R/V N. L. Palmer, R/V L. M. Gould and USCGC Healy in polar and sub-polar oceans. Similar systems were also operated successfully aboard R/V Akademik Ioffe, R/V Ewing, R/V Langseth and the M/Y Turmoil. In this report, we 1) present the principle of pCO_2 measurements, 2) describe engineering aspects of the system, 3) address the requirements to host the pCO_2 system, and 4) discuss the data processing method and management.

1) Principle of pCO_2 measurements:

Carbon dioxide (CO_2) is dissolved in seawater in three forms: molecular CO_2 form and two ionized forms HCO_3^- and $CO_3^=$. The ionized forms are not exchanged directly with air above. The exchange of CO_2 between seawater and air takes place only in the molecular form, which is expressed as the partial pressure (or vapor pressure) of CO_2 (pCO_2). If seawater has pCO_2 less than that in the air, it absorbs CO_2 from air and is a sink for air CO_2; and if it is greater, seawater releases CO_2 to the air and is a source. The difference between the pCO_2 in the seawater and that of the overlying atmosphere determines the direction of CO_2 exchange (i.e. source or sink for CO_2) and the rate of transfer. This instrument is designed to measure pCO_2 continuously with a precision of ±2 uatm or better over the variable global ocean conditions. Surface water pCO_2 varies over a wide range from 50 uatm to 1200 uatm: in general, low values are observed in cold waters with intense biological activities in polar oceans, and high values are in warmer waters upwelled recently in mid- and low-latitude oceans.

2) Description of the LDEO pCO_2 system:

The pCO_2 system consists of several major components; a seawater/air equilibrator, the analysis enclosure (LI-COR 6251 infrared gas analyzer (IR), gas dryer, pressure sensor, A/D modules and gas stream selection valve), computer for system control and data logging, an enclosure holding a pair of air pumps for delivering the sample gas streams, 5 cylinders of CO_2 in air calibration mixtures, 1 cylinder of nitrogen gas. The analysis system is driven by a laptop computer using *Labview* programs to control, via separate A/D modules, switching of a multi-position selector valve, analog voltage output to drive the flow controller, reading of various

sensors (IR millivolts, IR cell temperature, equilibrator water temperature, air sample flow rate, equilibration pressure) and writing of data to files. The partial pressure of CO_2 is calculated using air pressure and water temperature in the equilibrator at the time of measurement. The pCO_2 system data are merged with vessel underway data that includes navigation, meteorological and surface seawater sensor data. The following table describes the various data fields and their sources for the underway pCO_2 system. Since the time intervals for these various data fields are not the same we use a common time stamp and some simple code to match and merge data sourced from the vessel to that produced by the pCO_2 system.

Field	Data	Units	
1	RVDAS time tag		From vessel data logger
2	pCO_2 time tag (decimal is fractional time of day)	yyyyddd.ttt	From pco2 system
3	Raw voltage (IR)	mV	From pco2 system
4	Cell temperature	°C	From pco2 system
5	Barometer	MBar	From pco2 system
6	Flow rate	ml / min	From pco2 system
7	Concentration	ppm	From pco2 system
8	pCO_2 pressure	microAtm	From pco2 system
9	Equilibrated temperature	°C	From pco2 system
10	Sea Water Temp	1 or 2 digits	From pco2 system
11	Valve position	°C	From pco2 system
12	Flow source (Equil = pCO_2 measurement)	text	From pco2 system
13	RVDAS latitude	degrees	From vessel GPS
14	RVDAS longitude	degrees	From vessel GPS
15	TSG external temperature	°C	From vessel remote temperature probe
16	TSG salinity	PSU	From vessel TSG
17	Fluorometer	V	From vessel sensor if available
18	RVDAS true wind speed	m/s	From vessel Met data
19	RVDAS true wind direction	degrees	From vessel Met data
20	Barometric Pressure	mBars	From vessel Met data
21	Uncontaminated seawater pump flow rate	l/min	From vessel sensor if available
22	Speed over ground	knots	From vessel Nav data
23	Course made good	degrees	From vessel Nav data
24	Oxygen	µM	From vessel sensor if available

2-a) Equilibrator:

The heart of the pCO_2 system is an air-seawater "equilibrator", in which an isolated volume of air is exposed to a high volume of seawater to bring the partial pressure of CO_2 in the air to the same pCO_2 of the seawater (i.e. equilibration). To achieve rapid exchange of CO_2, seawater is sprayed into an equilibration chamber in order to increase surface area of contact. Because of the large volume of seawater, its pCO_2 remains unchanged by the exchange of CO_2 with small volume of air. The "equilibrated" air sample is pumped into an infrared gas analyzer for CO_2 concentration measurement, and the pCO_2 in the "equilibrated" air (hence the pCO_2 of

water) is computed. The instrument also measures the CO_2 in the overlying atmosphere, which is obtained through a long tube that leads to the top of the bow mast on the vessel. The difference between the pCO_2 in seawater and air gives the direction and rate of CO_2 transfer across the sea surface.

The equilibration chamber can be designed in a variety of ways. Our orginal equilibrators were made of clear acrylic plastic (~1/2-inch thick). We discovered that this type of equilibrator exchanged heat between the water sample and laboratory room by conduction through the wall. When the water temperature is much lower than the room temperature (as in the polar oceans), temperature of seawater and air sample may not be homogeneous in the equilibrator especially near the chamber wall, thus affecting the accuracy of pCO_2 measurements. In order to minimize the heat exchange, the equilibrator is covered with a thermal shield especially for the units operated primarily in polar oceans (i.e. ones on the Palmer, Gould and Healy). Other equilibrators such as the one currently operated on the R/V Sikuliaq were built using a large insulated beverage cooler for the equilibration chamber (Figure 1). Additionally all of the equilibrators have internal plumbing that ensures that the air sample is withdrawn away from any external chamber walls.

Figure 1: Insulated beverage cooler type equilibrator as installed on the R/V Sikuliaq

2-b) Calibration of CO_2 analyzer:

The infrared CO_2 analyzer is calibrated at regular intervals using certified reference gas mixtures, so that the results are compatible with the CO_2 standard scale of the World Meteorology Organization (WMO), which is used for atmospheric CO_2 measurements. Three to five calibration mixtures of various CO_2 concentrations (ranging 100 ppm to 900 ppm CO_2 by volume in air, and pure nitrogen gas) in compressed gas cylinders are used to calibrate the response of the infrared gas analyzer approximately every 90 minutes. A computer program performs the valve control, captures the data from the various sensors, performs preliminary pCO_2 calculations and stores the data in files. The data are displayed in real time on the computer's GUI. The instrument is designed to operate while the vessel is underway and acquires a measurement about every 3 minutes. The five calibration gas mixtures typically last for five years of normal operation and the nitrogen purge and drying gas cylinder lasts for one month of operation.

3) Requirements to host pCO_2 system:

The accurate underway SST, Salinity and barometric data are needed for the correcting the pCO_2 values to in-situ conditions. A well calibrated TSG unit on each ship is essential.

The components of the system (air-seawater equilibrator (Figure 1), sample pump box, analyzer box (Figure 2) and gas cylinders (Figure 3) are best installed by wall mounting near the uncontaminated seawater source. The laptop computer can be located in the same area or connected to the system from a more remote location.

The underway system requires about 20 liters per minute of seawater flow pumped continuously from near the surface of the ocean (~ 5 meters deep) from the vessel's uncontaminated seawater system. The water passes through the equilibrator and out a gravity drain that is sufficient to remove this same flow of water without being stored and discharged through the ship's water handling system. *The discharged water is unaltered seawater (nothing is added or extracted), and may be discharged directly to the ocean.*

The atmospheric sample pump draws about 4 liters per minute of air from a long tube that terminates at a high point on the bow mast of the vessel.

Figure 2: Air sample pump enclosure (left) and gas analysis enclosure (right) as installed on the R/V Sikuliaq. The laptop computer (not shown) normally resides on the wooden table directly under the enclosures but could be installed at a remote location as well.

Figure 3: Calibration gas mixtures (smaller cylinders) and the nitrogen purge and drying gas (larger cylinders) as installed on the R/V Sikuliaq.

4) Data processing method and management:

The raw data files, which list the parameters listed below, are received at Lamont either daily or at end of each leg (depending on ship) and examined by Stew Sutherland for mutual consistencies among the measured parameters. After the end of the cruise, a response curve from the calibration values and its time-drift are calculated to the time of each sample, and this curve is used to recalculate CO_2 concentration. The pCO_2 value in sample water is computed using the recalculated concentration of CO_2 in equilibrated air, the temperature of water and air pressure in the equilibration chamber. The pCO_2 at the equilibration temperature (Teq) is corrected to the value at in-situ SST using the ship's TSG temperature data. A major source of uncertainty for in-situ pCO_2 data is the fluctuations in the transit time of water through the pump and long water delivery pipe. This affects the time-lag between the time of TSG and time of pCO_2 measurement, and hence the temperature correction of pCO_2 to SST. The efficiency of the equilibration is also affected by flow rate changes. In the LDEO program, the mean time-lag is statistically assessed for each leg and used for estimating the pCO_2 correction for the (SST – Teq) difference. The method of correction is fully described in a public document "CDIAC Report. (2015) Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, doi: 10.3334/CDIAC/OTG.LDEO_CORR**.".**

The quality-controlled pCO_2 and associated data (time, position, SST, SSS, pCO_2 etc.) are submitted each year to the National Centers for Environmental Information (NCEI) at NOAA for public access and permanent archive.

List of Parameters Commonly Received from the Ships for Surface Water pCO_2 Program

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LATITUDE – Position. LONGITUDE – Position.
CMG – Course made good – actual course over ground (deg True).
SOG – Speed over ground (knots)'
WIND_SPEED – in Knots.
WIND_DIR – in degrees true.
BARO – Atmospheric Barometric Pressure (millibar).
SST – Sea Surface Temperature (Deg C).
SSS – Sea Surface Salinity (PSS).
CHL_A – chlorophyll A (mg/l).
WATER_FLOW – in volume/time units unique to each ship.
OXY – Oxygen concentration in ml/l (not on all ships).

ID - alpha-numeric containing time and date.
RAWMV - the millivolt value from the Licor .
CELLT - temperature of the Licor cell.
EQ_PBARO - Barometric pressure of the equilibrator vessel.
FLOW - gas flow from either the air pump or the equilibrator vessel.
VCO2 – concentration of CO2 in sample as measured by interim
      calibration curve.
pCO2_OBS – partial pressure of CO2 from VCO2, Temp in Equilibrator
      and equilibrator barometric pressure.
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PCO2_TEMP – Temperature measured in equilibrator vessel.
VALVE_POSN – Valve to select source of gas to the Licor.
ID – alphanumeric name of source (Equil, Atmos, Standard gas ID)

END March 14, 2019