Series AS-P3

Underway pCO_2 System

INSTRUCTION MANUAL

V2024.6

Apollo SciTech, LLC
Carbon Analytical Instrument

Apollo SciTech, LLC
18 Shea Way, Suite 108 – 109
Newark, DE 19713 USA
Tel: +1 (302) 861-6557
Fax: +1 (302) 861-6582
http://www.apolloscitech.com
E-mail: admin@apolloscitech.com

CAUTION

PLEASE READ THE INSTRUCTION MANUAL BEFORE USING THE UNDERWAY *p*CO_2 SYSTEM.

THIS PRODUCT IS DESIGNED FOR INDOOR ENVIRONMENTS.

USE CORRECT VOLTAGE AND FUSE.

TABLE OF CONTENTS

A. UNPACKING AND INITIAL INSPECTION

A1. Inspect package

The underway water pCO_2 (partial pressure of carbon dioxide) system (referred to as the underway pCO_2 system, the pCO_2 system, or the system) was carefully packed in a rigid cardboard box, with cushioning materials to withstand shipping. Inspect the package for possible external damage upon receipt. If damage to the exterior of the package is apparent, contact the shipping company immediately. The analyzer is insured with its full price with the shipping company. Apollo SciTech LLC. will not be liable for damage caused by the shipping carrier.

A2. Unpack the package

Open the package carefully from the top and inspect for any sign of concealed shipping damage. In addition to contacting the shipping carrier, please forward a report of any damages to Apollo SciTech LLC.

When unpacking the instrument from the shipment, please make sure that you have all the items indicated on the Packing List. Please report any missing items promptly.

B. INSTALLATION

⚠ ***Caution:*** *Check the power supply voltage before connecting the power cord; incorrect power voltage may damage your instrument!*

B1. Preparation for your underway pCO_2 system installation

B1.1. CO_2 gas standards

Three tanks/cylinders of CO_2 reference gas (standard gas) are needed. More gases (up to five) with different CO_2 concentrations can be used for better accuracy. Air-balanced CO_2 gas standards should be used. Although LI-850 and LI-7000 work fine in both air-balanced and nitrogen balanced gases, LI-7815 and the Picarro analyzer do not function properly in nitrogen-balanced gases. Primary CO_2 standards (e.g., roughly 150, 350, 550, and 1000 ppm, depending on the pCO_2 range in your study) can be purchased from NOAA. Less precise and low-cost standards may be used for estuarine and coastal research, or they can be calibrated against the primary standards.

B1.2. Gas regulators

The gas tanks are operated with a stable delivery pressure of 15 psi (~ 1 atm). High-quality two-stage regulators with a full delivery pressure range of 0 – 30/50 psi are recommended for the CO_2 gas standards. Type CGA-590 gas regulators are needed for air-balanced gas tanks.

B1.3. Water pump

A water pump with a flow rate of 2.5 – 5 L/min and a pressure of about 60 psi should be used. The system is tested with a water flow rate of ~ 3.7 L/min and a pressure of 60 psi. Most research vessels have a water sample pump installed, which can be used for supplying source water if the flow rate and the pressure meet the criteria. A pressure regulator may be used to prevent variations in water supply when the source water is shared with other devices in the ship. The water pump needs to shut off or split before the water inlet to relieve the pressure when the shut-off valve in the pCO_2 system in engaged.

B1.4. Discharge

A piece of ¾" PVC pipe or soft hose is required for water discharge. Water flowing through the equilibrator inside the system discharges by gravity. Allow the outlet of the equilibrator to drain into a sink freely. If a tube or a pipe is attached to the outlet, ensure it is not pinched or restricted in any way.

B1.5. Computer

A computer running a Windows® 10 operation system and having USB ports is used to control the pCO_2 system.

B1.6. LI-COR and Picarro CO_2 Analyzers

The pCO_2 system and the software programs are set up to be compatible with different models of CO_2 analyzers from LI-COR and Picarro. Certain text in this manual may describe components not included in your system.

B1.6.1 CO_2 scrubber and filter for LI-7000

If an LI-7000 CO_2/H_2O Analyzer is to be connected to the pCO_2 system, install a CO_2 scrubber with appropriate chemicals and an air filter as shown in Figure 1. Make sure that air first passes through Ascarite II, and then magnesium perchlorate. Fill 1/3 to 1/2 of the tube with Ascarite II and the rest of the tube with magnesium perchlorate. Make sure the inlet of the air filter is connected to the CO_2 scrubber and the outlet to the inlet of cell A.

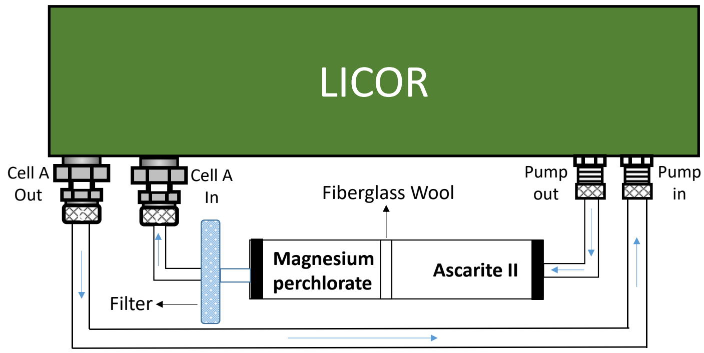


Figure 1. Diagram of CO_2 scrubber and air filter on the back of LI-7000

B1.6.2. LI-7815 Batteries

Two Li-ion batteries are either packed with the LI-7815 analyzer or installed in it. It is recommended to install the batteries in the LI-7815 analyzer while using it.

If batteries are not installed, they need to be charged to approximately 30% to 40% (2 bars will be displayed on the battery charge indicator) within 6 months of the shipping date and every 6 months thereafter. Batteries may fail if they are not maintained, requiring the delivery of replacement equipment.

If the LI-7815 analyzer is being stored for a long period of time, maintain each Li-ion battery per these recommendations to prevent premature failures.

B1.6.3. Picarro analyzer settings

If a Picarro analyzer is used, change the settings by following these steps.

1) When Picarro analyzer is taking measurements, go to its desktop, run the program Stop Instrument under the folder Diagnostics. Choose “Stop software but keep driver running”.
2) Run the program Setup Tool under the folder Picarro Utilities on the desktop.
3) In the tab Port Manager, change Command Interface to COM1. Click “Apply” to save. You need to click “Apply” in each tab to save the changes in that tab.
4) In the tab Command Interface, depending on the model, choose the available items in this list: CO2_dry, 12CO2_dry, 13CO2_dry, Delta_Raw, H2O, and CH4_dry. Some models of Picarro analyzers include 12CO2, 12CO2_dry, 13CO2, 12CO2_ppm, 12CO2_ppm_dry, 13CO2_ppm, and 13CO2_ppm_dry while leave out 13CO2_dry. For the sake of consistency, pick 12CO2_ppm_dry and 13CO2_ppm_dry instead. Click “Apply” to save.
   The list of parameters will be read by the pCO_2 program.
5) After exit the setup tool, run the program Start Instrument on the desktop.

B2. Familiarizing with your analyzer

Your underway pCO$_2$ system is composed mainly of four parts: electrical and mechanical control modules, water and gas equilibrators, a main control panel, and a data acquisition unit.

Figure 2. Front view of underway pCO$_2$ system

Figure 3. Right view

There are five reference gas ports marked with port numbers 1, 2, 3, 4, and 5, all of which are 1/8" stainless steel compression fittings, and one port for air, which is 1/4" stainless steel compression fitting on the right side of the system (Fig. 3). The second 1/4" stainless steel compression fitting port is for the connection to the CO_2 analyzer. RS-232 ports are for the Weather Station and GPS antennas. The USB port is for the communication with the computer; a USB-USB cable is included.

B3. Sample water connection

The system is tested with a flow rate of ~ 3.4 L/min and a pressure of 60 psi. The sample water flow rate of ~ 2.5 – 5 L/min is required. Connect a piece of ¾" PVC pipe to the outlet of the equilibrator, positioning the pipe so that the draining water exits into a sink or ground drain. The discharge pipe must be kept downward since the water flow is driven by gravity.

Adjust the water valve at the inlet to a proper position until water is evenly and gently sprayed.

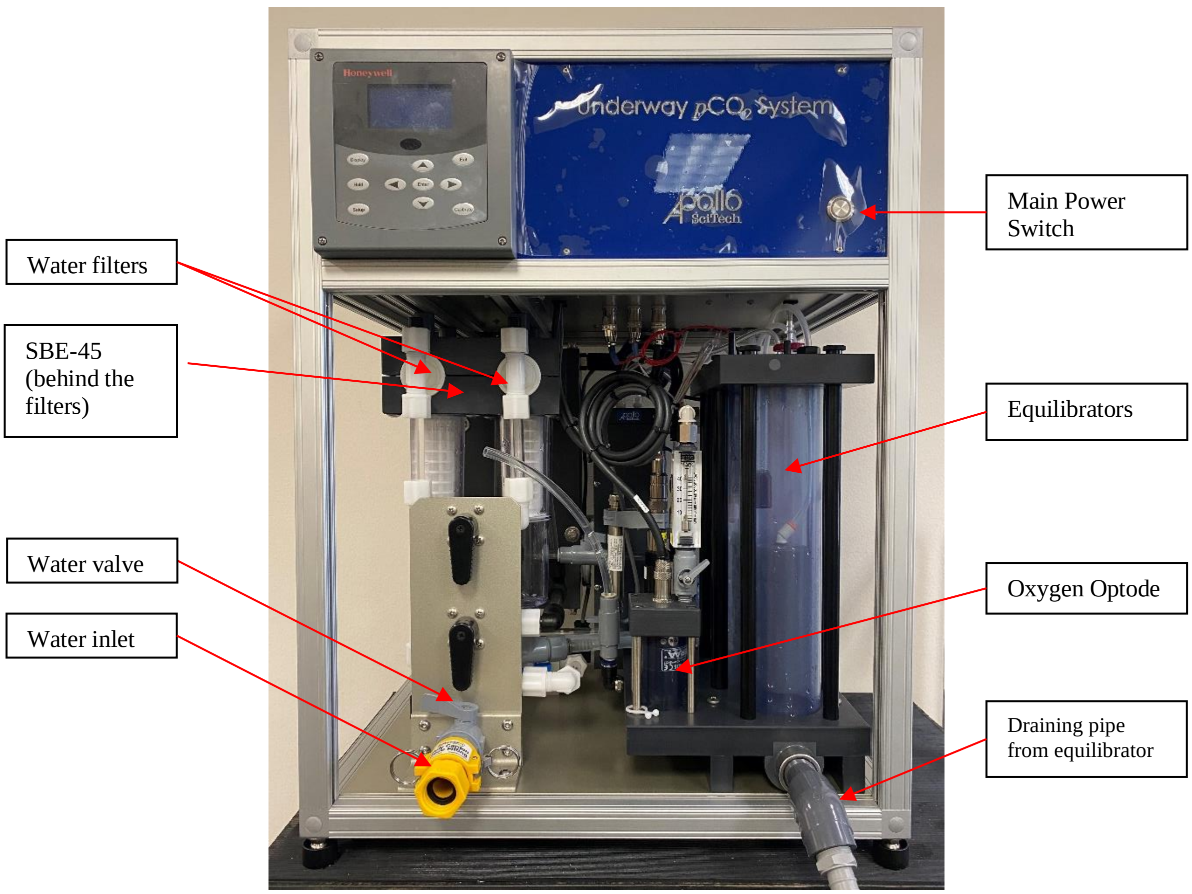


Figure 4. Underway pCO_2 system

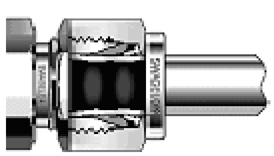
The yellow connector at the water inlet has been removed before packing. Make no more than 4 full turns when connecting it to the system. After 4 turns, it may feel that it still could be tightened. Stop here and do not overtighten it; otherwise, the O-ring may be compromised, and it may leak.

The flow meter on the front measures the water flow rate through the SBE-45. Turn the knob on the bottom of the flow meter to adjust the flow rate to 20 gallons per hour. The required flow rate by the manufacturer is 10 – 28 gallons per hour.

Figure 5. Adjust the flow rate through SBE-45

B4. Reference gases and Air sample connection

Secure all the standard gas tanks. Connect 1/8" OD stainless steel tubing (or copper tubing as a substitute) to the ports on the right-hand side of the system (Fig. 2). Insert the gas tubing into the nut and then the ferrules as shown below.

First, make sure the nut is finger tight. Second, while holding the fitting body with one wrench, tighten the nut with another wrench for three quarters of a turn. For the 1/8" tubing fitting, the wrench sizes are 1/2" for the body and 7/16" for the nut. For the 1/4" tubing fitting, wrench sizes are 5/8" and 9/16", respectively.

Use 1/4" OD or thicker gas tight tubing for air sampling. Depending on the design of the ship, attach the outlet of the air tubing to a secure location on or near the highest point of the research vessel. Do not make any sharp turns on the tubing to prevent it from squeezing. To keep water from entering the inlet of the air tubing, it is best to cover the inlet with an upside-down bottle or any device that can protect it from outside influences. Connect the other end to the port for air on the right side of the system (see Fig. 2).

B5. GPS antenna

The system records time in UTC and coordinates received from a GPS 19x-HVS antenna or the Airmar 200WX Weather Station. Install the antenna in an open area such as on or near the top of the ship. The GPS antenna or the Weather Station can be connected directly to the RS-232 port reserved for it on the right side of the $p\mathrm{CO}_2$ system (Fig. 2).

B6. Computer connection

A computer running a Windows® operating system is used to control the $p\mathrm{CO}_2$ system. The computer communicates with the $p\mathrm{CO}_2$ system via a USB-USB cable. The USB port on the system is connected to a USB-Serial adapter inside the $p\mathrm{CO}_2$ system.

After connecting the laptop and the $p\mathrm{CO}_2$ system, the USB-Serial adapter inside the system is recognized as a serial of COM ports. These COM ports can be seen in the “device manager” of the Windows® operating system, such as COM1 to COM8.

B7. Power supply connection

Before connecting the AC power cord from a wall outlet to the $p\mathrm{CO}_2$ system, make sure the push button switch of the main unit is not pushed in. The underway $p\mathrm{CO}_2$ system is designed for an AC power supply of either 110 V or 220 V according to your region. Please ensure that your power supply fits the requirement.

B8. Program installation

A USB flash drive with the system software is included in the package. Run the installer on a computer with a Windows 10 operating system. Send the product code to Apollo SciTech to obtain the activation code.

C. OPERATION

⚠ ***Caution:*** *The water sample flowing through the equilibrator* ***must be discharged freely under gravity.*** *If the discharge pipe is clogged, the measurements could be inaccurate, and it may damage the system. Make sure the discharge pipe is set properly.*

C1. Warming up

Before turning the power switch on, connect all reference gases and air supply to the *p*CO_2 system, and make sure there is no gas leakage. Connect the *p*CO_2 system and the computer with a USB cable.

Depending on the model of LI-COR CO_2 analyzer, minor variations in the start-up of the CO_2 analyzer may be present. In general, when the CO_2 analyzer is powered on, it takes 2 minutes to 1 hour, also dependent on the room temperature, to warm up and pass the self-test. Refer to their user's manuals if the analyzers do not start up properly.

Turn on the computer and open the underway *p*CO_2 program. **After connecting the GPS, the mouse may drift randomly because the GPS is recognized as a mouse in the Windows® operation system. If this happens, disconnect your GPS. Go to "device manager" of the Windows® operation system. Expand "Mice and other pointing devices" and disable GPS device, which is labeled "Serial balls…". After disabling it, reconnect your GPS to the *p*CO_2 system. The mouse drifting issue will be resolved.**

Let the CO_2 analyzer warm up overnight. Then let the *p*CO_2 system warm up for ~30 minutes before using. Turn the reference gases on to make sure the delivery pressure is at 15 psi (1 atm).

C2. Zero and span settings

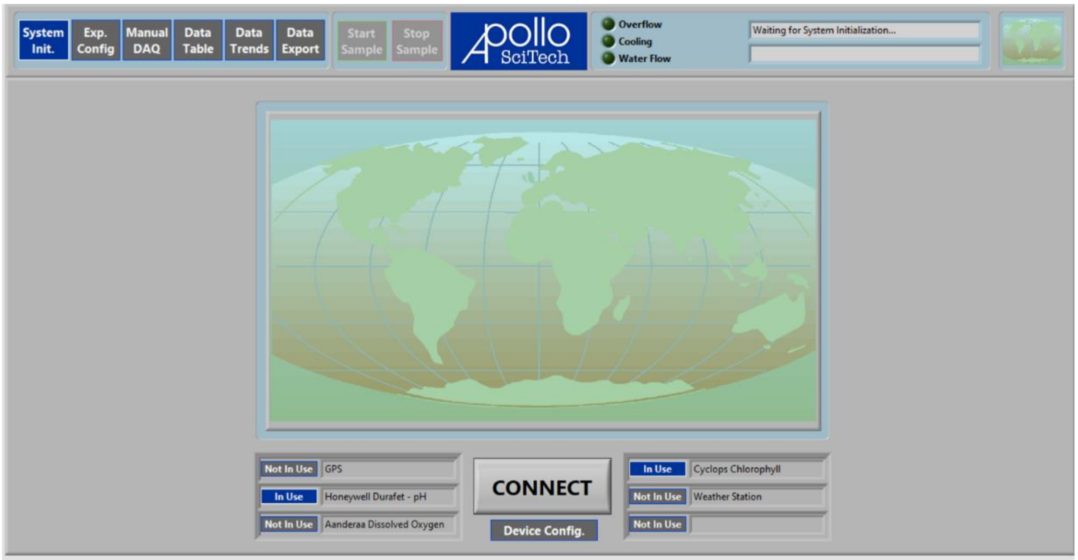
For LI-850 and LI-7000, we suggest that the user checks their performance through periodic zero and span calibrations following the instructions in their user's manuals. Calibrations should be conducted in lab before the system is used in the field. It is not recommended to conduct zero or span calibration during analysis at sea.

LI-7810 and LI-7815 are laser-based CO_2 analyzers and no regular user calibration is required. For details, refer to their user's manuals.

Compatible Picarro CO_2 analyzer models are also laser-based and no regular user calibration is required. For details, refer to their user's manuals.

C3. System initialization

Double click the Underway pCO2.exe icon on the desktop to open the pCO_2 system program.



Select the devices you want to use. Click the buttons "In Use" or "Not in Use" to change the choice. A CO_2 analyzer and an SBE-45 Thermosalinograph are always in use and cannot be excluded.

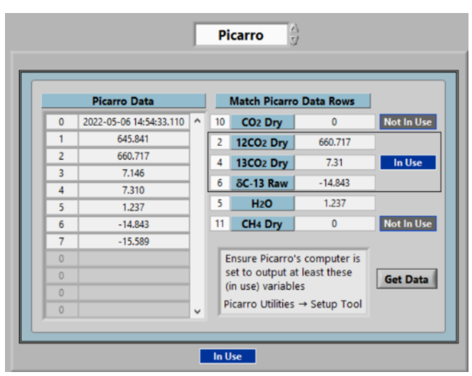
Click Device Config. for the settings of CO_2 analyzer model, GPS input, overflow alarm criteria, user calibrations of the chlorophyll sensor, and the time and frequency of the peristaltic pump.

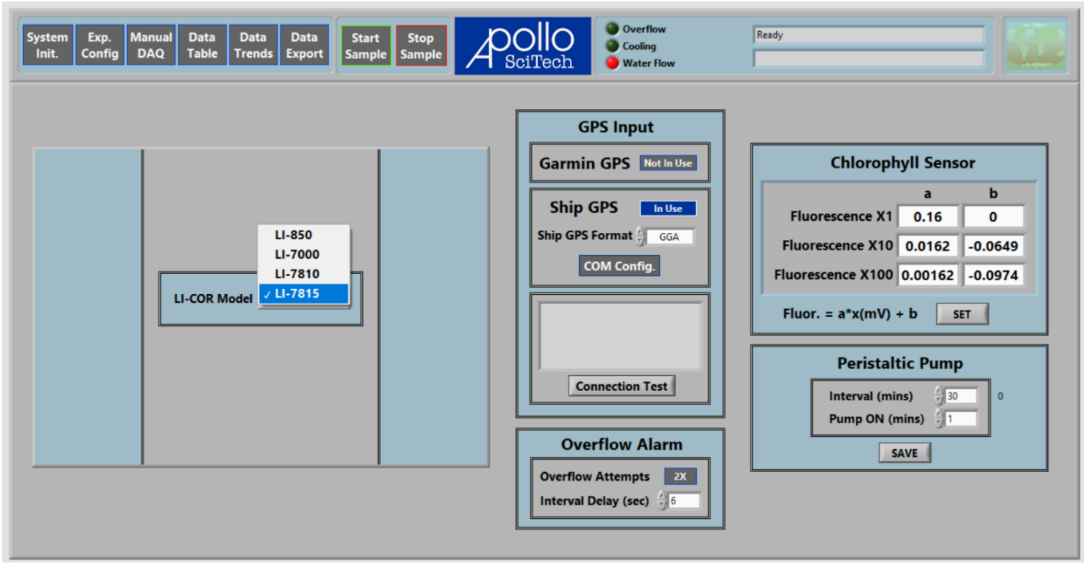
Click on LI-COR or Picarro to switch between the two groups of settings.

Under LI-COR, select the model being used and click the button Not In Use to change it to In Use. If no LI-COR analyzer is used, change the status to Not In Use.

Under Picarro, click Get Data to have a timestamp and the selected parameters displayed in the column Picarro Data. On the right, match the parameters in use with the correct row numbers on the left.

Either CO_2 dry or all of $12CO_2$ dry, $13CO_2$ dry, and δC-13 Raw can be in use. CH_4 dry can be selected if the Picarro model in use measures methane.





Only one of GPS source can be used. The program is compatible with GPS formats GGA, RMC, and GLL, if the ship GPS is used. Click "Connection Test" to acquire a test reading from the GPS.

Set the parameters for overflow alarm. There are two sets of parameters for the overflow alarm, while the basic set is inaccessible to the users. The basic parameters dictate when the overflow alarm is registered in the program. The advanced parameters in this tab dictate when the program aborts the measurements.

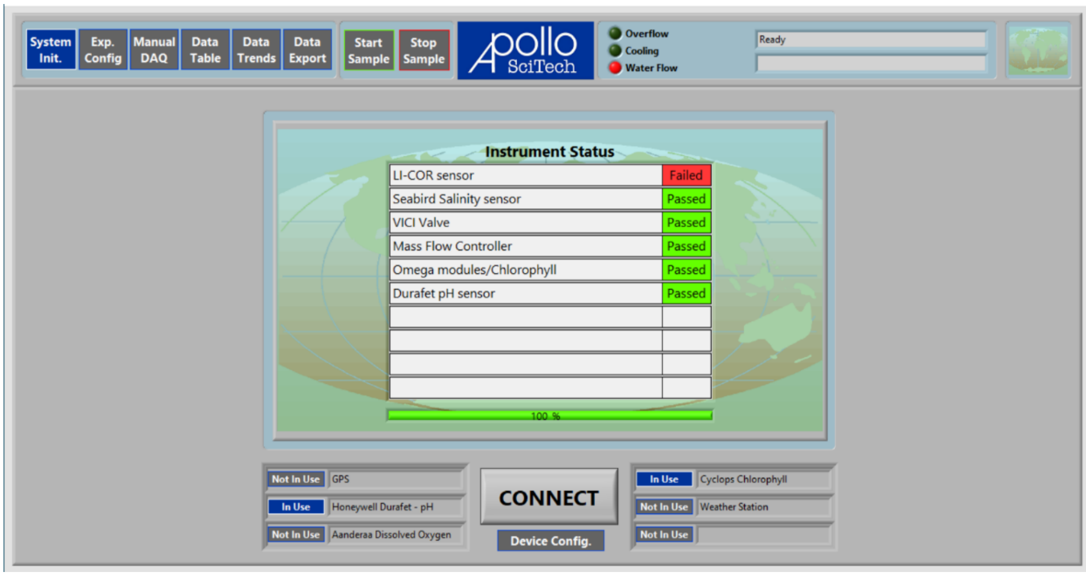
The basic parameters are set to stop the water intake if the water level is too high for 4 seconds continuously. Then if the overflow attempts button is set to 1X in the device configuration tab, it stops the water flow by engaging the shut-off valve AND aborts the measurements. However, if the overflow attempts button is set to 2X, it only engages the shut-off valve and ignores the overflow for 6 seconds before it checks the status. The measurements continue normally during this 6-second delay. If the water level is still too high after water has been allowed to drain for 6 seconds, the program aborts the measurements, and the shut-off valve is left engaged. The maximum delay allowed is 20 seconds.

Regardless of the overflow attempts, an audible alarm is always played as long as the water level is high enough to trigger the physical alarm inside the equilibrator.

Input the coefficients for the relationship between voltage readings and fluorescence for all three gains. Refer to Appendix I for the determination of these coefficients.

Input the time interval and the length of the peristaltic pumps to be on. With the settings in the screenshot blow, the peristaltic pumps are turned on for 1 minute every 30 minutes. They are always turned on after the button Start Sample is clicked, and the 30-minute countdown starts at this point.

Click System Init. to escape the settings. Click Connect to establish communication between the selected device and the program. It will display the status of each device.



C4. Manual Data Acquisition and Devices

Click Manual DAQ to access the tab where the user can manually control the pumps and the gas source. In general, this tab should not be used to collect data. This tab may be useful in troubleshooting or testing that each device updates properly. In rare cases, the user can manually switch different gas sources to collect data, but an automatic sequence of standard gases, air, and seawater can be realized with the automatic measurements; see section 5.1 for more details.

In the Pump Control pane, each pump can be turned on or off by clicking the button beside it. The current status is displayed in the button.

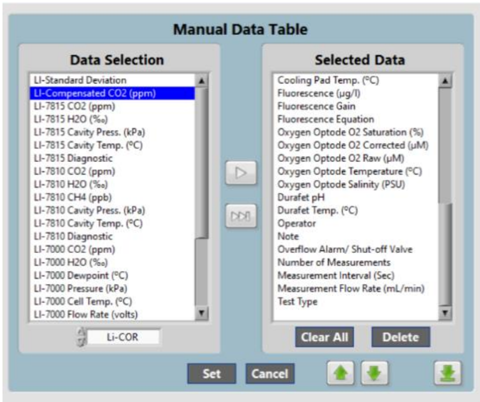
Select the gas source from air, seawater, or any standard port in the drop-down menu for sources.

Set the gas flow rate controlled by the mass flow controller.

Select the device to read. Click Read to get one reading from that device. Results are displayed in the corresponding tab to the right.

Select either a single reading or a series of readings with a set time interval. Click Start Manual DAQ on the bottom left to start reading from all devices. Results are tabulated in the table to the right.

Click the gear icon on the bottom right corner to change the column headers in this table.



Click the drop-down menu below the left column to show parameters from a certain device; the current selection, LI-COR, calls for all models of the LI-COR analyzers. Click any item in the left column to select. Press and hold Shift and click to select all items a continuous series of items. Press and hold Ctrl and click to select a discontinuous series of items.

Click  to add the selected items to the right column, which are displayed in the data table. If no items are selected in the left column, click  to add all items to the right column. In the right column, click on any item to select, then click the appropriate green arrow to move it up or down for one. The green bar arrow auto-sorts the headers in order.

Click Set to save the current the selection and click Cancel to escape.

C4.1. LI-COR and Picarro CO_2 Analyzers

In the Device Config. tab, click on the drop-down menu to select the correct model of the LI-COR CO_2 analyzer, if applicable. Note that the LI-COR or Picarro tab under Manual DAQ will update accordingly. For details of each parameter output by the LI-COR or Picarro analyzer, refer to their user’s manuals.

C4.2. Seabird SBE-45 Temperature and Salinity

The water flow rate through the SBE-45 thermosalinograph cannot exceed 0.48 gal/min or 1.8 L/min. Refer to section B.3 to set its water flow rate to about 1.3 L/min (20 gph).

C4.3. VICI Gas Selection Valve

Only ports 3 to 7 can be connected to standard gases.

C4.4. Sensirion SFC5500 Mass Flow Controller (MFC)

The minimum gas flow rate is 100 mL/min. This is restricted by the minimum gas flow rate required by LI-7815.

C4.5. Omega Modules and Cyclops-7F Fluorescence

The Peltier Cooler Temperature should remain within the range 6 to 9°C.

The Cyclops-7F Fluorescence sensor is an optional sensor that can measure chlorophyll concentration (µg/L).

The sensor has three gain settings: X1, X10, and X100, which refers to the sensitivity configuration of the sensor. As the gain increases, the sensitivity increases and the concentration range decreases. The X10 gain is for samples representing typical conditions. It is desirable to obtain a signal from the sample that is significantly higher than a blank sample (de-ionized water or filtered aged offshore seawater), but not a signal that is close to the maximum of 5 Volts. If the sample signal is high, use the X1 gain to avoid going over scale. If the sample signal is very low, the X100 gain setting may be used to achieve higher sensitivity but a smaller measurable range.

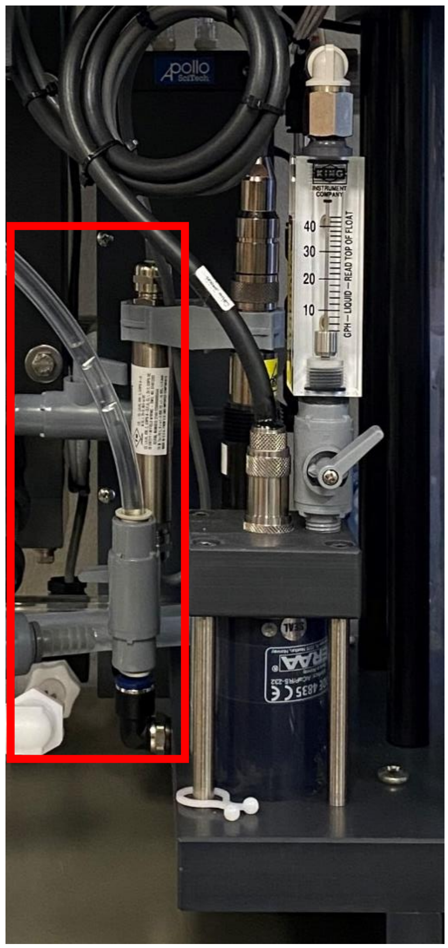
The gain can be set to auto-select and the program will determine the best gain, and its corresponding equation, with approximate coefficients, is displayed. The coefficients are user input in the tab Device Config. accessible from the tab System Init. Refer to Appendix I for the determination of these coefficients.

Note: to calibrate the chlorophyll sensor, the user should have at least one chlorophyll standard. Turner Designs also supplies a matching solid-state secondary standard, which can be used in place of a primary liquid standard once a correlation between a primary standard and the solid standard is established. This solid standard can be used to check stability and/or check for loss in sensitivity. Detailed information can be found in Appendix I.

C4.6. Honeywell Durafet® III pH

The Durafet® III pH electrode is an optional sensor that measures the pH.

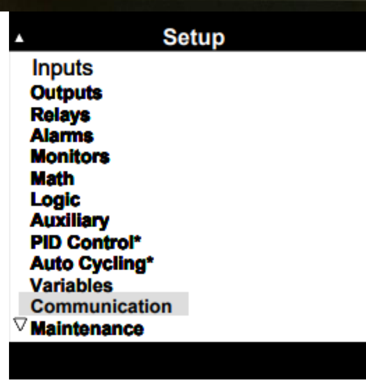
When the pH sensor is not in use, keep the sensor head space hydrated at all times with distilled water inside the cap or flow through chamber. Add distilled water via the soft tube and maintain a water level same as the top surface of the PVC plate where the pH, chlorophyll a, and DO sensors are mounted, or higher.



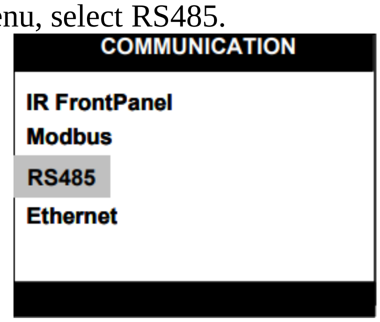
While the Durafet® III pH electrode is known for its long-term stability, it is not precisely calibrated. Therefore, appropriate calibration is needed. You may first use buffers to check the pH, which is generally quite close to the true values. During the analysis, you should take water samples occasionally and measure pH values from time to time to adjust the possible small pH drift. These calibration measurements can be done in one of the several methods. 1) Most precisely, use a spectrophotometric pH analytical instrument, such as the Apollo SciTech's Spec-pH analyzer. 2) Use a high precision Orion Ross glass pH electrode. 3) Calculate pH from two other measured carbonate system parameters such total dissolved inorganic carbon (DIC) and total alkalinity (TAlk).

In addition, a UDA2182 Universal Dual Analyzer is connected to the Durafet® III pH electrode to achieve precise monitoring during application. The following figure shows the front panel of this UDA2182 analyzer.

Set up the analyzers following these steps:
Step 1: on the front panel, select the *communication* menu option in the *setup* menu.



Step 2: In the *Communication* menu, select RS485.



You will see the following Parameters: Port Reset, Address, Baud Rate.

Step 3: Set the Address to a unique address on your RS485 link.
Set the Baud Rate to 9600. Scroll to Port Reset at the top of the menu, and press enter. Change the value to Enable and press enter to lock the values into the communication card.

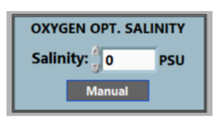
For calibration procedures, refer to the instrument manual for the instrument you are using with the electrode. For best results, Durafet® III pH electrodes should be calibrated periodically. The detailed calibration and maintenance information for this electrode is in Appendix II."

C4.7. Aanderaa 4835/4831 Dissolved Oxygen (DO)

The Aanderaa Oxygen Optode 4835/4831 is optional sensor that measures the dissolved oxygen.

The direct measurement signal for the DO sensor is the partial pressure of O_2 (pO_2), which can be expressed in percent saturation relative to the air saturated value. The oxygen reading in percent saturation can then be converted to concentration, in µmol/L or µmol/kg, based on the Henry's law of solubility, i.e., $[O_2] = K*pO_2$. The solubility constant (K) is a function of salinity and temperature. The salinity value is either read from the SBE-45 salinity sensor or by manual input.

If SBE-45 is connected to the pCO_2 system, the user can let the software read the current salinity from SBE-45 by clicking the button Manual to change it to From SBE-45. Alternatively, the user can set the salinity manually and enter the salinity value in the text box. This setting applies only to manual data acquisition. In the automatic measurement, it always takes the salinity readings from SBE-45.



Note: to obtain the highest accuracy, the sensors to be calibrated should be submerged in water at least 24 – 48 hours prior to the calibration. If a sensor dries out, it could lead to a bias in the readings of up to 2%. This effect disappears when the sensor is submerged in the water.

C4.8. Airmar 220WX WeatherStation®

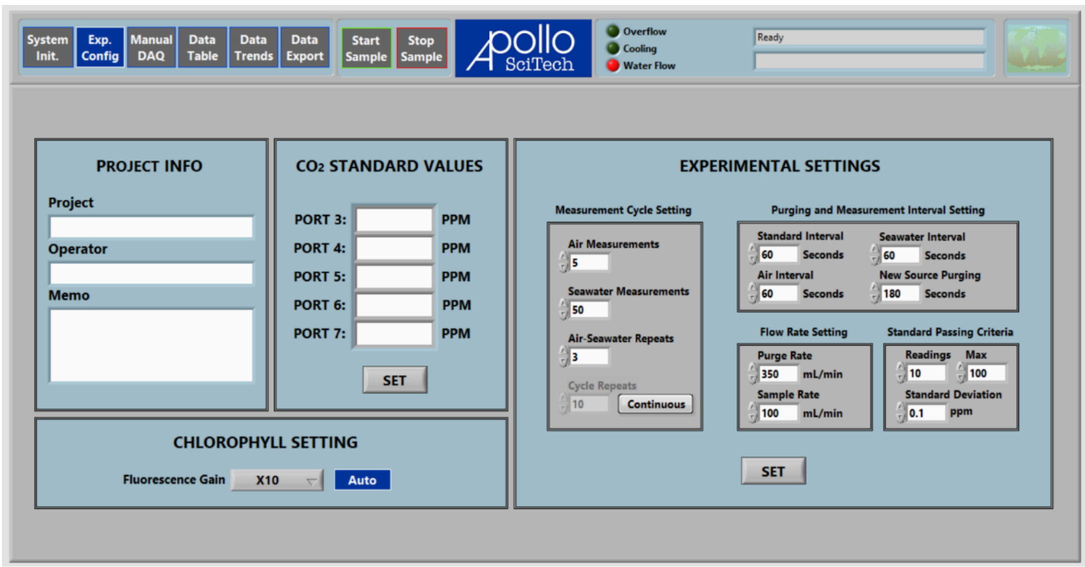
The Airmar 220WX WeatherStation® is an optional sensor to be incorporated in the pCO_2 system. The software program is under development.

C5. Measurement Sequences

Click the button “Exp. Config” to go to the Experiment Configuration tab.
Here, the user can set up the measurement sequence and parameters for CO_2 standards, air, and seawater samples.

C5.1. Configure the measurement sequence

The $p$$CO_2$ system can measure CO_2 concentration of standard gases, atmospheric air, and seawater consecutively or separately.



The three text boxes for basic information such as project, operator, and memo are saved together with each data file. The boxes for project and memo are only recorded at the start of a new data file, which can be at the start of the automatic measurement sequence and after 1000 rows of data, while operator is recorded on each data row.

To set up the parameters for the measurements, input appropriate numbers in the following boxes.

1. Enter the CO_2 concentrations of the standard gases into the blanks of “CO_2 Standard Values”. Up to 5 CO_2 standard gases are allowed. It is not recommended to use a zero-CO_2 air as one of the reference gases because it takes too long for the analyzers to reach the true zero value. Thus, a low CO_2 air (such as 120 ppm) should serve as the lowest CO_2 reference.

2. Input the number of measurements for each source and the number of repeated cycles of both air and seawater before the next group of standards are analyzed. This option may be preferred when frequent calibration is not needed.

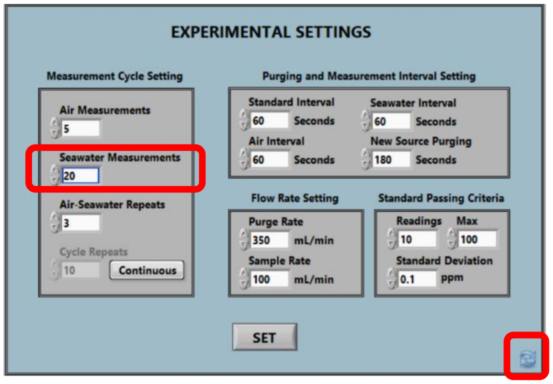
For example, set 5 for air, 50 for water, AND 2 for air-seawater repeats, the measurement sequence is standards (meeting the standard passing criteria input), air (5 measurements), water (50 measurements), air (5 measurements), water (50 measurements), standards, and so on. In the open ocean, since the seawater pCO_2 is relatively stable, the user can take relatively more measurements of air. While in coastal waters, where pCO_2 changes very rapidly, the user may choose to take more measurements of water.

The default setting is to measure the above sequence continuously until the user clicks the button Stop Sample. Click the button Continuous to change it to cycles. Then, with the current settings, the program will stop the measurements after 10 cycles.

3. Set the duration of each measurement and the interval between the different sources. When the valve is switched to a new source, i.e., atmosphere, water, or standard gases, it takes a relatively long time to refresh the system. Thus, no data are recorded while the system is being flushed. The default time to allow the system to be thoroughly flushed with a new air source is 240 seconds (180 seconds minimum recommended). Set it to a larger value if necessary. For every single analysis, the default setting is 60 seconds for air, water, and the standard. This setting determines the frequency of measurements. The user can adjust it to a larger or smaller value to change the recording frequency.

4. Set the standard passing criteria. The default setting requires a standard deviation no more than 0.1 ppm for the first 10 readings of the standard after the all the purging. If the standard deviation is over 0.1 ppm for the first 10 readings, it takes more readings and as soon as the last 10 readings yield a standard deviation within 0.1 ppm, the average is recorded as the reading of this standard gas. It takes a maximum of 100 readings accepting the average of the last 10 readings.

When a number box in the CO_2 standard values or the experimental settings is changed, its frame turns blue. Click SET in the corresponding box to save the changes. Click the circling arrows at the bottom right corner of the box to revert to the last saved values.



Start the measurement sequence:

Once all values are set, click the “Start Sample” button to start the measurement sequence.

Three alarms, Overflow, Cooling and Water Flow, are to the left of the status fields. The alarm for overflow is on when the water level is high for 4 seconds continuously. The alarm for the cooling is on when the temperature in the cooler is below 0°C or above 10°C. The alarm for water flow is on when the water flow rate drops to below 1 L/min.

Stop the measurement sequence:

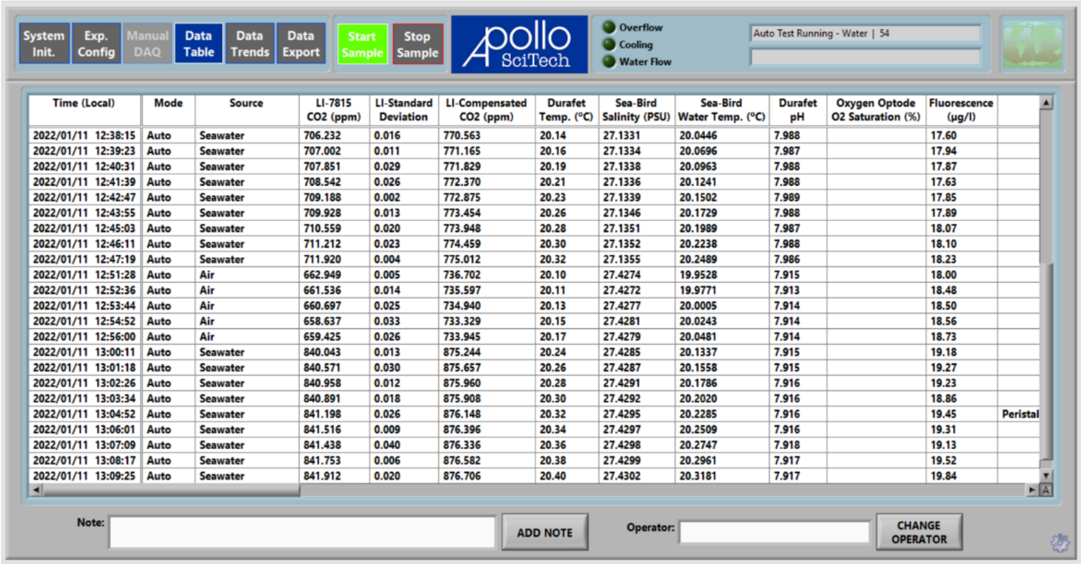
Press the button “Stop Sample” to stop the measurement.

It will finish making the current reading and abort the sequence. Then a pop-up message allows the user to either run a set of standards or stop all measurements. If there is no response for 2 minutes, it will proceed with a set of standards.

C5.2. Data Table

Click the button “Data Table” to bring up the data in the current test.

The status field displays the current step and a countdown timer.



Time (Local)	Mode	Source	LI-7815 CO2 (ppm)	LI-Standard Deviation	LI-Compensated CO2 (ppm)	Durafet Temp. (°C)	Sea-Bird Salinity (PSU)	Sea-Bird Water Temp. (°C)	Durafet pH	Oxygen Optode O2 Saturation (%)	Fluorescence (µg/l)	
2022/01/11 12:38:15	Auto	Seawater	706.232	0.016	770.563	20.14	27.1331	20.0446	7.988		17.60	
2022/01/11 12:39:23	Auto	Seawater	707.002	0.011	771.165	20.16	27.1334	20.0696	7.987		17.94	
2022/01/11 12:40:31	Auto	Seawater	707.851	0.029	771.829	20.19	27.1338	20.0963	7.988		17.87	
2022/01/11 12:41:39	Auto	Seawater	708.542	0.026	772.370	20.21	27.1336	20.1241	7.988		17.63	
2022/01/11 12:42:47	Auto	Seawater	709.188	0.002	772.875	20.23	27.1339	20.1502	7.989		17.85	
2022/01/11 12:43:55	Auto	Seawater	709.928	0.013	773.454	20.26	27.1346	20.1729	7.988		17.89	
2022/01/11 12:45:03	Auto	Seawater	710.559	0.020	773.948	20.28	27.1351	20.1989	7.987		18.07	
2022/01/11 12:46:11	Auto	Seawater	711.212	0.023	774.459	20.30	27.1352	20.2238	7.988		18.10	
2022/01/11 12:47:19	Auto	Seawater	711.920	0.004	775.012	20.32	27.1355	20.2489	7.986		18.23	
2022/01/11 12:51:28	Auto	Air	662.949	0.005	736.702	20.10	27.4274	19.9528	7.915		18.00	
2022/01/11 12:52:36	Auto	Air	661.536	0.014	735.597	20.11	27.4272	19.9771	7.913		18.48	
2022/01/11 12:53:44	Auto	Air	660.697	0.025	734.940	20.13	27.4277	20.0005	7.914		18.50	
2022/01/11 12:54:52	Auto	Air	658.637	0.033	733.329	20.15	27.4281	20.0243	7.914		18.56	
2022/01/11 12:56:00	Auto	Air	659.425	0.026	733.945	20.17	27.4279	20.0481	7.914		18.73	
2022/01/11 13:00:11	Auto	Seawater	840.043	0.013	875.244	20.24	27.4285	20.1337	7.915		19.18	
2022/01/11 13:01:18	Auto	Seawater	840.571	0.030	875.657	20.26	27.4287	20.1558	7.915		19.27	
2022/01/11 13:02:26	Auto	Seawater	840.958	0.012	875.960	20.28	27.4291	20.1786	7.916		19.23	
2022/01/11 13:03:34	Auto	Seawater	840.891	0.018	875.908	20.30	27.4292	20.2020	7.916		18.86	
2022/01/11 13:04:52	Auto	Seawater	841.198	0.026	876.148	20.32	27.4295	20.2285	7.916		19.45	Peristal
2022/01/11 13:06:01	Auto	Seawater	841.516	0.009	876.396	20.34	27.4297	20.2509	7.916		19.31	
2022/01/11 13:07:09	Auto	Seawater	841.438	0.040	876.336	20.36	27.4298	20.2747	7.918		19.13	
2022/01/11 13:08:17	Auto	Seawater	841.753	0.006	876.582	20.38	27.4299	20.2961	7.917		19.52	
2022/01/11 13:09:25	Auto	Seawater	841.912	0.020	876.706	20.40	27.4302	20.3181	7.917		19.84	

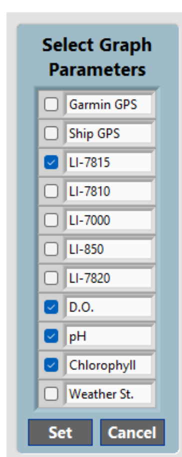
To select the parameters to display in the table or to change the order of the parameters, click the gear icon on the bottom right corner. The pop window works similarly to that in the manual data acquisition tab (cf. page 17).

C5.3. Data Plot

Click the button "Data Trends" to bring up the plots. In each pane, choose the data file (current or historical) in the list first, then choose the parameter to plot in the drop-down menu. The project title will be displayed to the right of the date and time of the file (not shown in this example; refer to C5.4 for an example). When the current data file is selected, the plot will automatically update when new data points are recorded.

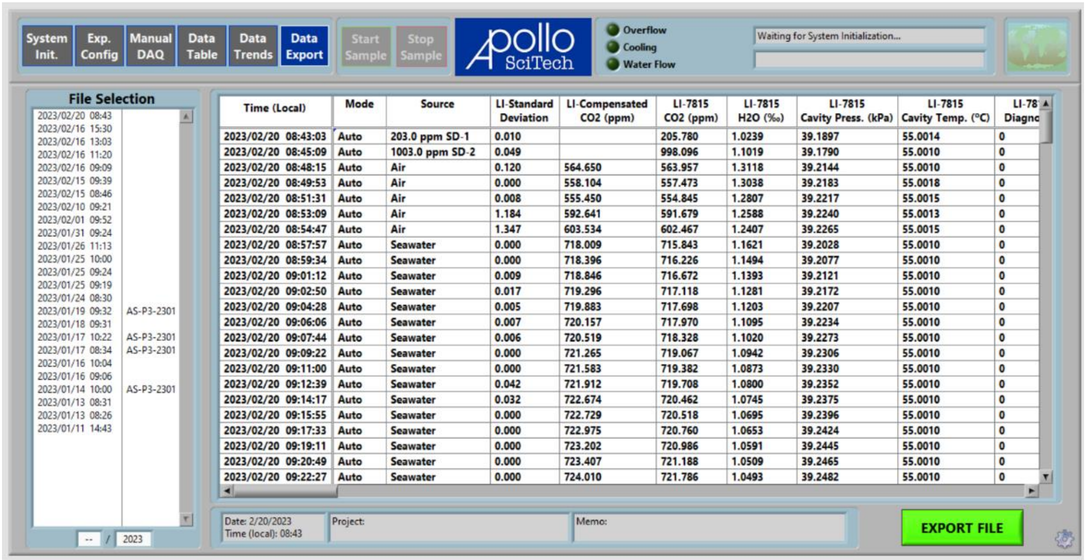
The auto-scale is defaulted to be on for both axes when a new item is chosen to be plotted. If one needs to change the range of either axis, right click on the plot, turn off the auto-scale, and then change the range. Or use the built-in zoom and drag functions near the bottom right corner of each plot (red box in screenshot). Latitude and longitude are plotted as numbers in degrees.

Click the gear icon at the bottom left corner to select the devices. Parameters not checked in this list will not show up in the drop-down menus for the plots.

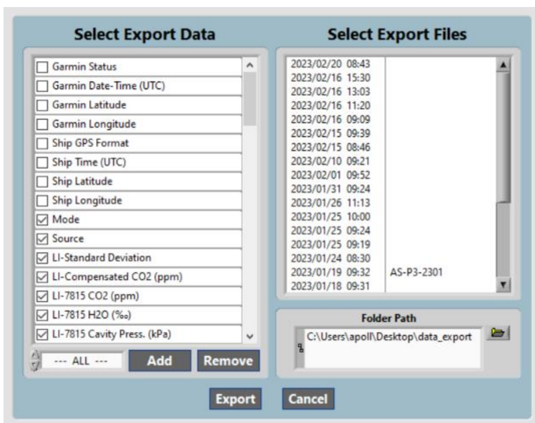


C5.4. Data Export

Data files are ordered by the date and time the files were created and the project titles are displayed in the right column (AS-P3-2301 in this example). This tab displays all the historical data files.



Click "Export File" to bring the pop-up window to select which files to export.



Under "Select Export Data", click "ALL" to choose all parameters or only the parameters from a certain device. Click "Add" or "Remove" to check or uncheck all of the parameters from the specified device. The checked parameters will be the data columns exported to the CSV files.

Under "Select Export Files", you may select one or multiple files to export. Press and hold Shift and click to select consecutive files. Press and hold Ctrl and click to select non-consecutive files.

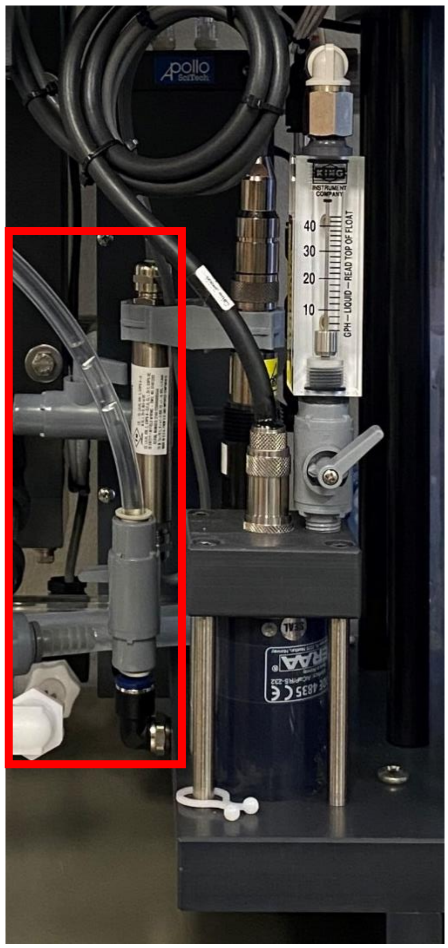
Under "Folder Path", choose the location where the export files are saved.

Click "Export" to export the selected files. Click "Cancel" to close this pop-up window.

C6. After seawater measurement

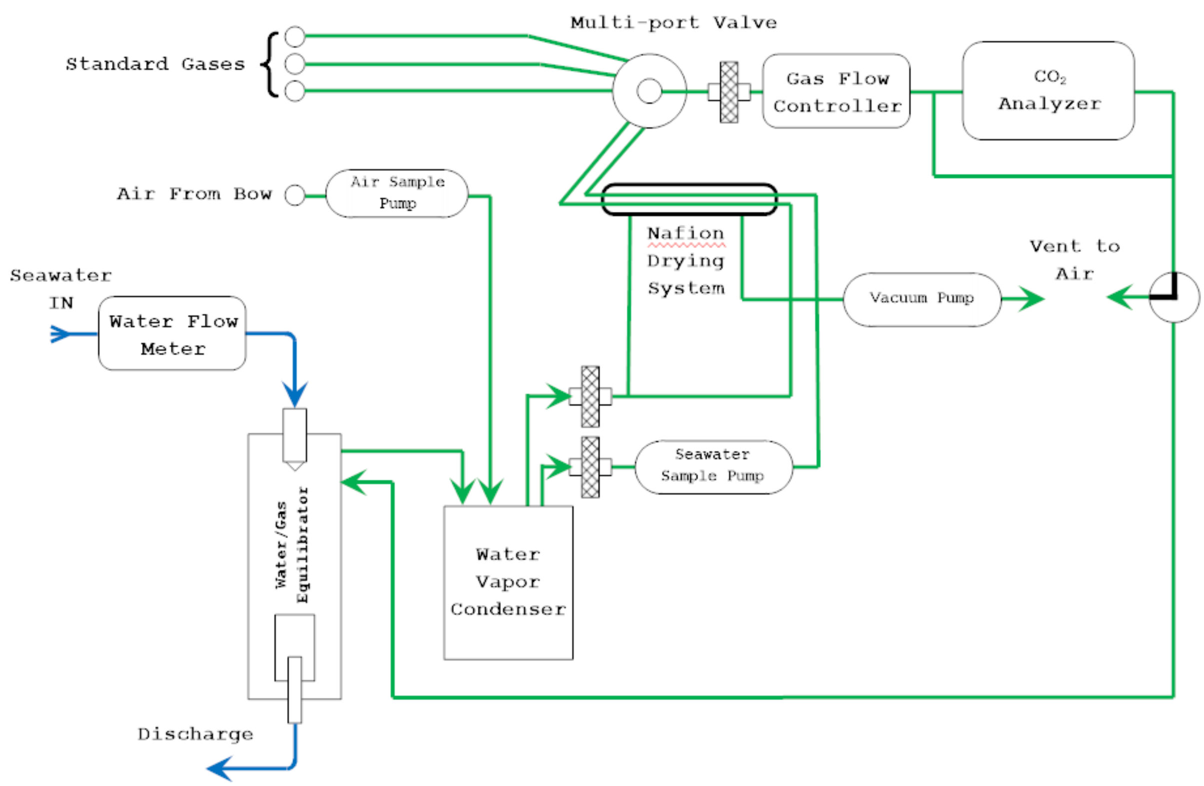
Run DI water for a couple of minutes before shutting down the system to remove seawater from the system. Wipe away any water spilled on the base plate of the system.

In order to drain the seawater in the channel for the pH, chlorophyll, and DO sensor, hold the tube in the box and gently turn it down. Open the valve to release the water. After seawater is drained, add DI water via the soft tube until the pH sensor is submerged. Close the valve after DI water reaches the required level.



C7. Surface water pCO_2 measurement principle

In natural water, the species of dissolved inorganic carbon are CO_2+H_2CO_3, HCO_3^-, and CO_3^{2-}. The partial pressure of dissolved molecular CO_2 (i.e., CO_2+H_2CO_3), or pCO_2, is defined thermodynamically as the CO_2 gas pressure in an air parcel that is in equilibrium with the water. This is a thermodynamic definition and thus does not require a physical reality, i.e., a gas phase does not necessarily exist in the water. In practice, such an equilibrium phase can be established via a gas-water equilibrator. The equilibrator used in the AS-P3 Underway pCO_2 System follows the design principle of the pCO_2 system described in Wanninkhof and Thoning, 1993 and Feely et al., 1998 and detailed in Pierrot et al., 2009.



Flowchart of the underway pCO_2 Analyzer

The equilibrated air from the equilibrator is drawn through a Nafion dryer tube to reduce water vapor to almost zero before entering the CO_2 analyzer for quantification.

The LI-7815 CO_2/H_2O analyzer is a laser-based gas analyzer. It is very precise and stable under good maintenance. A low-flow kit has been added in the LI-7815 analyzer to limit the intake gas flow to 70 mL/min. For more detailed information about the LI-7815 CO_2/H_2O analyzer, refer to its instruction manual.

C8. Final data processing

C8.1. Correct xCO_2 measured by the CO_2 analyzers

The values in the column "Compensated CO_2 (ppm)" are those corrected following the procedures described in section 8.1. The procedures are included here for reference.

The measured xCO_2 (mole fraction concentration of seawater/atmospheric/standard CO_2 in the dried sample gas flow [units: ppm]) needs to be corrected based on the measured values of the standards. It is recommended that the concentration range of the standard gases covers the range of the measured pCO_2 values to generate accurate corrections.

The equation shown below gives an example of how to correct the measured xCO_2 to accurate values using the measured standard xCO_2 values and the assigned standard xCO_2 values:

$$xCO_{2(Corr)} = (xCO_{2(Raw)} - xCO_{2(R1)}) \times (xCO_{2(S2)} - xCO_{2(S1)}) / (xCO_{2(R2)} - xCO_{2(R1)}) + xCO_{2(S1)}$$

where the subscript Corr means the value after correction, Raw stands for raw data measured by the CO_2 analyzers, S is the assigned/true CO_2 value of the standard gas, and R is the measured CO_2 value of the standard gas by CO_2 analyzers.

For instance, 3 standards and 2 different sample gases are measured, with the results listed in the table below.

Source	Standard xCO_2	CO_2 reading	Calibrated Sample CO_2
Standard 1	200	202.1	
Standard 2	360	362.0	
Standard 3	550	551.3	
Equilibrator		350.7	(348.7)
Air		386.4	(384.5)

For the sample gases measured from the equilibrator, the values fall between the first and the second standards. So, use these two standard values for the correction.

$$xCO_{2(Corr)} = (350.7 - 202.1) / (362.0 - 202.1) \times (360 - 200) + 200 = 348.7$$

The final xCO_2 value is 348.7 ppm.

For the air sample gas, the value falls between the second and the third standard values. Use these two standards for the correction. The final result is 384.5 ppm.

C8.2. Convert xCO_2 to 100% humidity pCO_2

The user needs to do the calculations in sections C8.2 and C8.3.

The partial pressure of CO_2 in seawater at the temperature of equilibration (inside the equilibrator), pCO_2 (eq) in µatm, is calculated as:

$$pCO_2\,(eq) = xCO_2\,(water) \times [P_b\,(eq) - P_w\,(eq)]$$

where xCO_2 (water) is the mole fraction concentration of seawater CO_2 in the dried sample gas flow read by the LI-7000 (after correction) in ppm; P_b (eq) is the barometric pressure at equilibration in atm; and P_w (eq) is the water vapor pressure at equilibration in atm that is calculated using salinity and temperature of equilibration, which is assumed to be equal to the salinity and temperature measured by the SBE-45. While there is a thermometer installed inside the equilibrator, it is not as accurately calibrated as that of the SBE-45.

Atmospheric xCO_2 should be measured once every 2 – 4 hours using the same CO_2 system. The inlet of the atmospheric CO_2 pipe should be set up on or near the highest platform in front of the ship. In order to avoid possible contamination from the ship's stack gases, atmospheric xCO_2 data should be used only when the ship is moving and the wind is blowing from the bow. The partial pressure of CO_2 in the air, pCO_2 (air) in µatm, is then calculated as:

$$pCO_2\,(air) = xCO_2\,(air) \times [P_b\,(sea\ surface) - P_w\,(sea\ surface)]$$

where xCO_2 (air) is the mole fraction concentration of the atmospheric CO_2 in the dried sample gas flow in ppm, P_b (sea surface) is the barometric pressure at the sea surface in atm, and P_w (sea surface) is the water vapor pressure at sea surface in atm calculated from the temperature and salinity measured at the ship's water intake. In a small vessel our SBE-45 data can be used instead.

C8.3. Normalize measured pCO_2 to in-situ surface seawater temperature

The partial pressure of CO_2 in seawater at the in-situ temperature can be calculated as (*Takahashi et al.*, 2002):

$$pCO_2\,(water) = pCO_2\,(eq) \times \exp[0.0423 \times (SST - T_{eq})]$$

where SST is the in-situ sea surface temperature measured at the ship's water intake point in °C and T_{eq} is the temperature at equilibration in °C. In the small vessel our SBE-45 data can be used instead.

References

Feely, R. A., R. Wanninkhof, H. B. Milburn, C. E. Cosca, M. Stapp, and P. P. Murphy (1998), A new automated underway system for making high precision pCO_2 measurements onboard research ships, *Anal. Chim. Acta*, *377*, 185–191.

Pierrot, D., C. Neill, K. Sullivan, R. Castle, R. Wanninkhof, H. Lüger, …, C. Cosca (2009), Recommendations for autonomous underway pCO_2 measuring systems and data-reduction routines. *Deep Sea Res. II: Top. Stud. Oceanogr.*, *56*: 512–522.

Takahashi, T., S. C. Sutherland, C. Sweeney, A. Poisson, N. Metzl, B. Tilbrook, N. Bates, R. Wanninkhof, R. A. Feely, C. Sabine, J. Olafsson, and Y. Nojiri (2002), Global sea-air CO_2 flux based on climatological surface ocean pCO_2, and seasonal biological and temperature effects, *Deep Sea Res. II: Top. Stud. Oceanogr.*, 49, 1601–1622.

Wanninkhof, R., and K. W. Thoning (1993), Measurement of fugacity of CO_2 in surface water using continuous and discrete sampling methods, *Mar. Chem.*, *44*, 189–205.

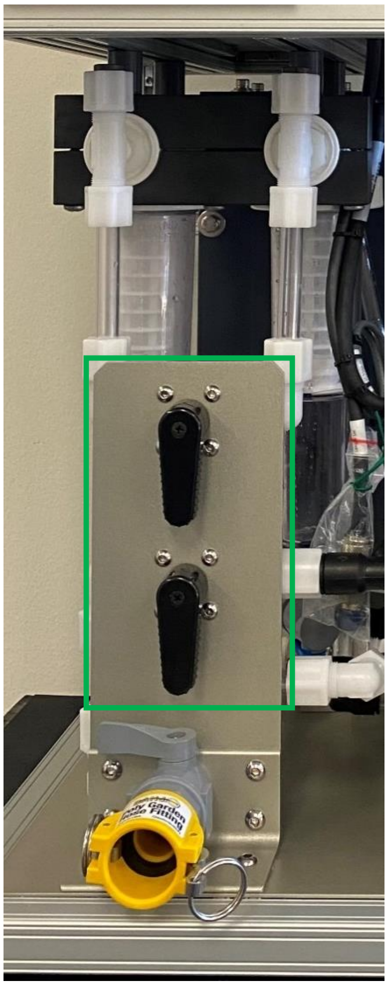
D. SPECIFICATIONS

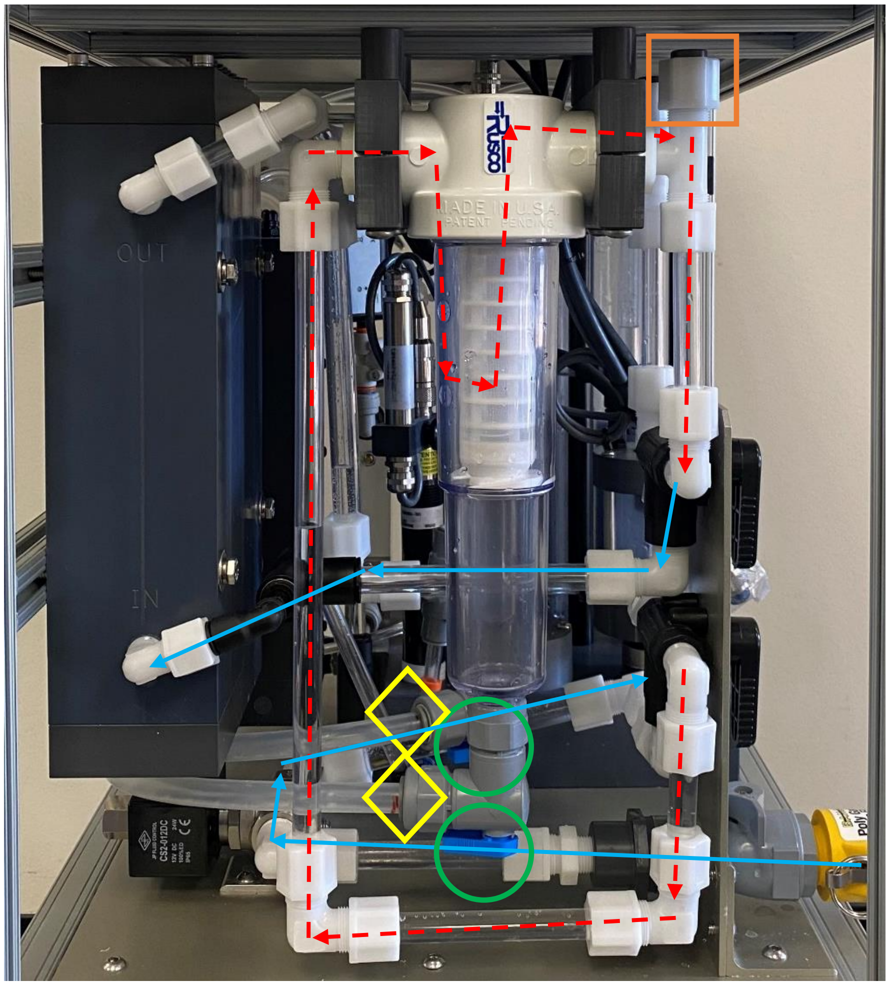
Power supply:	220 VAC
Power fuse:	3-Amp slow blow
Reference gases:	Depends on the sample *p*CO_2; should cover the sample concentration range; three to five standard gases are used
Repeatability:	better than 1 ppm
PC system:	Windows® 10
Communication:	USB
Environment Required:	Indoor
Operation Temperature:	Room temperature
Humidity:	up to 85%
Positioning:	Horizontal use only (**NEVER turn the system upside down**)
Dimension:	27” × 20” × 16” (H × W × D, main unit) (69 cm × 51 cm × 41 cm)
Net weight:	95 lb (43 kg)
Storage Temperature:	0°C (32 °F) to 50 °C (122 °F)

E. MAINTENANCE

E1. pCO_2 analyzer water filter cleaning

The analyzer has two water filters (mesh 40). Check the filter if the water flow rate drops and clean it if necessary.





Front view **Side view**

When both handles point down in the green box, the filter on the left is used; when both handles point to the right, the filter on the right is used. When the filter is being used, water from the on/off valve (entering from the bottom-right corner in the side view) flows in the direction of the blue and red arrows. The blue arrows (solid line) are for paths shared by the two filters and the red ones (dashed line) are for paths specific to either filter. When one filter is clogged, turn both handles on the front to the other filter so that the measurements do not need to stop.

When it measures CO_2 standards, it is possible to stop the seawater flow to clean the clogged filter. Turn both handles to the filter in question and turn the small blue handle underneath the filter (green circle) to drain the water. If the line is filled with water, it may be difficult to drain.

Loosen the cap (orange square) slightly to let in some air. After all of the water drains, tighten the cap in the orange square before pumping water into the filter. The filter is designed to be cleaned by flowing water.

If that is not satisfactory, it is possible to remove the filter from the system. First, open the blue handle valve to drain the remaining water from the filter. Then, disconnect the tube (yellow diamond) from the elbow-shaped connector below the filter. Push the gray ring on the connector evenly with two fingers towards the elbow while pulling the tube away from the elbow. Hold the top of the transparent cup and unscrew it from the 3-way Rusco connector. Pull the filter downward to remove it from the system. Move the filter and the cup together to move them out of the box. Then clean the clogged filter and install it back. Apply some grease on the O-ring inside the Rusco connector and the tube to be inserted in the elbow-shaped connector. Push the tube into the connector to the red mark on the tube. Turn the small handle underneath the filter to stop the water from draining.

Spare water filters of different meshes are provided together with the system.

E2. LI-COR and Picarro CO_2 analyzers maintenance

Refer to their respective instruction manuals.

F. TROUBLESHOOTING

F1. Common conditions

The *p*CO_2 analyzer was completely checked during and after manufacturing and assembly operations. It was carefully packed to prevent damage during shipment. Should you feel that the analyzer is not functioning properly, check for the following common conditions first:

Are all cables connected correctly and securely?

Are there any gas and/or water leaks?

Does the power supply match the required value?

F2. Troubleshooting guide

F2.1. Alarm triggered

1. Check if the water flow rate is too high.

   Check the discharge pipe. Find out if there are any blockages in the pipe or if the outlet is positioned too high.

2. For water condenser accumulation problems, go to the Manual DAQ tab and turn the peristaltic pump on. Check if all peristaltic pumps run normally.

F2.2. LI-COR and Picarro analyzers problems

Refer to their respective instruction manuals.

F2.3. Gas flow rate too low on water *p*CO_2 measurement

Turn the VICI valve to port 2. Start the sample pump in the tab Manual DAQ. Set the flow rate to 100 mL/min. Under normal conditions, the reading from the MFC should be around 100 mL/min. If the reading is significantly lower than the setpoint, part of the system is not functioning properly. Check if water is trapped or frozen inside the tubing that blocks the gas flow. It is possible that there is leakage due to a loosened or broken tube connector.

F2.4. The program does not run

If the problem is in communication, please check the connection cable and make sure there is a good connection.

The program uses serial ports to communicate with the system. A USB-serial port converter is adopted inside the system with an 8-COM-port output. The USB-serial port converter driver should be installed on the computer to use the converter. The driver can be found under "C:\Program Files (x86)\ coolgear USB RS232 driver". It can be reinstalled if necessary.

There are several RS232C serial communication devices in the underway pCO_2 system. The program automatically checks the COM ports for all devices. If any device is not communicating with the computer, check whether the COM ports are recognized by the Windows operating system in Device Manager, under Ports (COM & LPT). Restart the computer and the pCO_2 system if some devices can communicate with the program but others cannot.

F2.5. Cooling system does not work properly

1. Make sure the ambient temperature is not too high.

2. Check the cooling fans and see if they are blocked by foreign objects or dust.

F2.6. Reference gas measurements cannot pass

1. Check the reference gas and see if the pressure is too low. Make sure the pressure is about 15 psi (1 atm). It cannot open the mass flow controller's valve if the pressure is too low, or it will burst the system if the pressure is too high.

2. Make sure the regulator valves for the reference gases are open enough to supply a flow rate of 100 mL/min. The standard gas may be contaminated by air when being measured if too little standard gas is supplied.

3. The pressure of the reference gases should be stable with no pressure fluctuations.

4. Check the CO_2 analyzers. Make sure it is in good condition. If the CO_2 analyzers are not stable, the uncertainty of the final reading will be too large. The CO_2 analyzers may need to be serviced. However, a temporary solution is letting the program accept the measurements by increasing the max standard deviations of the CO_2 readings allowed in the Exp. Config tab (cf. section C5.1).

G. WARRANTY

Apollo SciTech offers one-year full warranty on the Underway Partial Pressure of Carbon Dioxide Analyzer against defects in parts and workmanship from the date of purchase. Apollo SciTech's sole obligation under this warranty shall be to repair or replace any part of the instrument which Apollo SciTech's examination discloses to have been defective in material or workmanship without charge and only under the following conditions:

1. The defects are reported to Apollo SciTech in writing within one year after the shipping date of the instrument.
2. The instrument has not been maintained, repaired, or altered by anyone who was not approved by Apollo SciTech.
3. The instrument was used in the normal, proper, and ordinary manner and has not been abused, altered, misused, neglected, involved in an accident or damaged by act of God or other casualty.
4. The purchaser packs and ships or delivers the instrument to Apollo SciTech within 20 days after Apollo SciTech has received the written notice of the defect.
5. No-charge repair parts may be sent at Apollo SciTech's sole discretion to the purchaser for installation by purchaser.
6. Apollo SciTech's liability is limited to repair or replace any part of the instrument without charge if Apollo SciTech's examination disclosed that part to have been defective in material or workmanship.

This warranty defines the obligation of Apollo SciTech and no other warranties expressed or implied are recognized.

Appendices

Appendix I CYCLOPS-7F® chlorophyll sensor calibration

Appendix II Durafet® pH sensor calibration and maintenance

Appendix III Oxygen Optode 4835 sensor calibration and maintenance

Appendix I CYCLOPS-7F® chlorophyll sensor calibration

The CYCLOPS-7F® sensor has been calibrated using the standard solution, P/N 2100-320, from Turner Designs, following the next 5 steps as per recommendations by its manufacturer. However, the standard solution based on rhodamine is only accurate to ± 30%. It is best to create calibration curves using the expected algal groups and concentration with the probe installed in the pCO_2 system, which would eliminate a constant offset caused by the deviation in the distance between the container and the sensor from that shown in Fig. A1.

1. Remove the CYCLOPS-7F® sensor from the pCO_2 system but keep the cable connected. Find a non-florescent container. Use a 1 L glass beaker and place the beaker on a non-reflective black surface (Fig. A1). Do not use plastic containers, as they may interfere with the sample's fluorescence. Leave the CYCLOPS-7F® sensor submerged in DI water. Ensure that the sensor is more than 3 inches above the bottom of the container and that the sensor is in the center of the container and has more than 2 inches clearance between the circumference of the sensor and the beaker.

Figure A1. Calibration setup

2. Read the fluorescence as a voltage in the pCO_2 program. Connect the pCO_2 program to the pCO_2 system. In the Manual DAQ tab, select the Omega modules and the chlorophyll sensor. Manually choose the gain X1. Start continuous measurements and the readings should update in the table.
3. Repeat step 2 for gains X10 and X100.
4. Change the DI water to the Chlorophyll standard solution (40 μg/L) and repeat steps 2 and 3. After obtaining both voltage outputs for the blank and the standard for gain X1 and X10, a correlation between the chlorophyll concentration and the voltage output has been established. The chlorophyll concentration at gain X1 and X10 is calculated following:

$$C_{sample} = \frac{C_{standard} \times (Volt_{sample} - Volt_{blank})}{(Volt_{standard} - Volt_{blank})}$$

or

$$C_{sample} = \frac{C_{standard}}{(Volt_{standard} - Volt_{blank})} \times Volt_{sample} + \frac{C_{standard} \times (-Volt_{blank})}{(Volt_{standard} - Volt_{blank})}$$

where C stands for concentration, and Volt stands for the voltage output.

We define:

$$a = \frac{C_{standard}}{(Volt_{standard} - Volt_{blank})} \text{ and } b = \frac{C_{standard} \times (-Volt_{blank})}{(Volt_{standard} - Volt_{blank})},$$

then we have

$$C_{sample} = a \times Volt_{sample} + b$$

The gain X100 only works for concentration 0 – 5 μg/L and needs to scale from the readings at the gain X10. The chlorophyll concentration at gain X100 is calculated following:

$$C_{X100\ sample} = \frac{C_{standard} \times (Volt_{X100\ sample} - Volt_{X100\ blank})}{10 * (Volt_{X10\ standard} - Volt_{X10\ blank})}$$

where the subscripts denote the gain setting and the material where the voltage is read.
Similarly,

$$a_{X100} = \frac{C_{standard}}{10 * (Volt_{X10\ standard} - Volt_{X10\ blank})} \text{ and } b_{X100} = \frac{C_{standard} \times (-Volt_{X100\ blank})}{10 * (Volt_{X10\ standard} - Volt_{X10\ blank})},$$

5. For each gain of X1, X10, and X100, calculate a and b based on the voltage outputs in DI water and the standard solution and input them in the parameter window in the Test Config tab (cf. section C4).

In practice, these caveats should be noted.

1. The CYCLOPS-7F® sensor is linear up to 500 μg/L at X1 gain, 50 μg/L at X10 gain, and 5 μg/L at X100 gain. Beyond these limits, a quenching effect is observed. As the concentration increases above the respective values, the light emitted by the sensor gets attenuated by the algae, which causes the measured concentration to decrease.

2. When the CYCLOPS-7F® sensor is installed in the pCO_2 system, it is less than 3 inches from the bottom of the plate. Therefore, the chlorophyll concentration reading is not 0 when DI water is measured. This is caused by the constant offset in the voltage. This offset should be subtracted from the voltage readings in the samples.

An optional secondary solid standard, not included in the package, is available from Turner Designs. The part number is 2100-900. It can be used in place of the liquid standard after the correlation between the two kinds of standard is established. It also can be used to check the stability and/or check for loss in sensitivity.

Appendix II Durafet® III pH sensor calibration and maintenance

Calibration:

This Calibration technique is recommended for best accuracy in most applications.
Calibration material needed:

- Two standard buffer reference solutions that are at least 2 pH apart from one another.
- A container for each buffer that is large enough to immerse the electrode to measuring depth.
- Distilled water or de-ionized water to rinse the electrode.

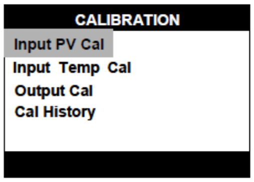
The UDA2182 Universal Dual Analyzer contains information on several commonly used buffer solution standards in three groups (shown in Table A1 below), including the pH versus temperature characteristics of each. By command, the instrument will automatically select one of these buffers in the selected group and use its values in the calibration process. Automatic checks are included to ensure that reasonable and correct values are entered.

Table A1:

Temperature °C		**0**	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**
Group	***Buffer***											
NIST/USP	**1.68**	1.67	1.67	1.67	1.67	1.68	1.68	1.68	1.69	1.69	1.70	1.71
	4.01	4.01	4.00	4.00	4.00	4.00	4.01	4.01	4.02	4.03	4.04	4.06
	6.86	6.98	6.95	6.92	6.90	6.88	6.86	6.85	6.84	6.84	6.83	6.83
	9.18	9.46	9.40	9.33	9.28	9.23	9.18	9.14	9.10	9.07	9.04	9.01
	12.45	13.42	13.21	13.01	12.80	12.64	12.45	12.30	12.13	11.99	11.84	11.71
USA	**2.00**	2.01	2.01	2.01	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
	4.00	4.01	3.99	4.00	3.99	4.00	4.00	4.01	4.02	4.03	4.04	4.06
	7.00	7.13	7.10	7.07	7.05	7.02	7.00	6.99	6.98	6.97	6.97	6.97
	10.00	10.34	10.26	10.19	10.12	10.06	10.00	9.94	9.90	9.85	9.82	9.78
	12.00	12.60	12.44	12.28	12.14	12.00	11.88	11.79	11.66	11.53	11.43	11.32
Europe	**1.00**	0.98	0.98	0.99	0.99	1.00	1.00	1.01	1.01	1.01	1.01	1.02
	3.00	3.02	3.02	3.02	3.02	3.00	3.00	2.99	2.99	2.98	2.98	2.97
	6.00	6.03	6.02	6.01	6.00	6.00	6.00	6.00	6.01	6.02	6.04	6.05
	8.00	8.15	8.11	8.07	8.03	8.00	7.97	7.94	7.91	7.88	7.87	7.86
	10.00	10.22	10.17	10.12	10.05	10.00	9.95	9.90	9.86	9.82	9.78	9.74
	13.00	13.81	13.60	13.39	13.19	13.00	12.83	12.68	12.53	12.38	12.25	12.11

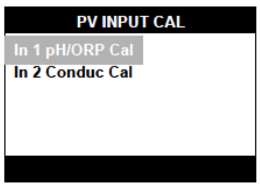
The procedure for using the automatic buffer recognition feature in an actual calibration:

1. Prepare containers of two standard reference solutions.
2. Press "Calibration"



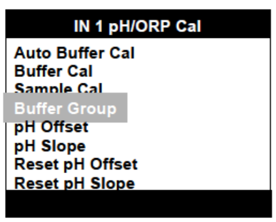
Use ▲▼ to select
Input PV Cal

3. Press "Enter"



Use ▲▼ to select
Input 1 or 2 pH/ORP Cal

4. Press "Enter"

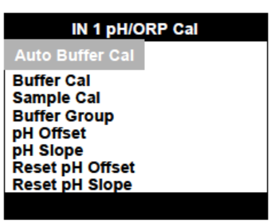


Use ▲▼ to select
"Buffer Group"

5. Press "Enter"

Use ▲▼ to select
NIST/USP (default)
USA, or
Europe

6. Press "Enter"



Use ▲▼ to select
"Auto Buffer Cal"

7. Put the unit in "Hold"; remove the electrode from the process; rinse the electrode thoroughly with distilled or de-ionized water
8. Calibrating the pH Offset
   Press "Enter", follow the prompts at the top and bottom of the screen.
   "Place probe in Buffer 1" The display will show the pH of the buffer 1 solution as measured by the electrode system.

The reading will be automatically adjusted to match the known pH value stored in the UDA2182 memory.
"Press Enter when stable"

9. Once the reading is stable, press "Enter"
   "Buffer 1 stability check"
   Use ▲▼ to change the value of the Buffer.
   "Up/Down changes Buffer"
10. Rinse the electrode thoroughly with distilled or de-ionized water
11. Calibrating the Slope,
    Press "Enter", follow the prompts at the top and bottom of the screen.
    "Place probe in Buffer 2"
    The display will show the pH of the buffer 2 solution as measured by the electrode system. The reading will be automatically adjusted to match the known pH value stored in the UDA2182 memory.
    "Press Enter when stable"
12. Once the reading is stable, press "Enter"
    "Buffer 2 stability check"
    Use ▲▼ to change the value of the Buffer.
    "Up/Down changes Buffer"
13. If the calibration fails, an error message will be displayed across the bottom stripe of the screen. Make necessary adjustments and re-calibrate.

Storage & Maintenance:

Periodic maintenance is required to ensure that the electrode does not dry out after prolonged shelf storage. Stored electrodes should be checked every 6 months to ensure that the water is still in the storage cap.

The procedure below should be performed annually for stored electrodes.
1. Remove the electrode from its storage box and remove the plastic cap from the sensing end.
2. Remove any excess crystals on sensor area by rinsing with warm tap water.
3. Refill the cap with distilled water.
4. Replace the cap on the electrode.
5. Place electrode in its storage box.
6. Mark the date on the box.

ATTENTION
Do not store electrode below –10 °C (+14 °F) or above 50 °C (122 °F).

Appendix III Oxygen Optode 4835 sensor calibration and maintenance

Calibration material preparation:

Prepare a suitable container with freshwater. Aerate the water using an ordinary aquarium pump together with an air stone, and let the temperature stabilize, which might take hours. Prepare a zero-oxygen solution by dissolving 5 grams of sodium sulfite (Na_2SO_3) in 500 mL of water. Other substances that remove oxygen can also be used.

NOTE: To obtain the highest accuracy the sensor(s) to be calibrated should be submerged into water at least 24 – 48 hours prior to the calibration. If a sensor is allowed to dry out this could lead to a bias in the readings of up to 2 %. This effect disappears when the sensor is submerged into the water.

NOTE: Stripping of the oxygen with N_2 gas is also possible but not recommended, since it is uncertain when an absolute zero oxygen level is reached or if ever it can be reached using this method.

Communication:

Connect the sensor to a PC by use of the Sensor Cable 3855 (RS232 communication). Start a terminal program, i.e., the HyperTerminal or Tera Terminal with the following set-up:

9600 Baud, 8 Data bits, 1 Stop bit, No Parity, and Xon/Xoff Flow Control

NOTE: Select one of the options 'Sent line ends with line feeds' or 'Echo line ends with line feeds' in the Hyper Terminal. If using Tera Terminal Pro, after setting up the com port according to settings above please select "Terminal" in the "Set up" menu and click "Local echo" also select "CR+LF" for both "Receive" and "Transmit" under "New line".

Calibration:

1. Submerge the Optode into the aerated water. Set the Interval property to e.g. 30 seconds. Enter the save command and wait until both the temperature and the phase measurements have stabilized:
   Set Passkey(1000)
   Set Interval(30)
   Save
2. Store calibration values by typing:
   Set Passkey(1000)
   Do CollectCalDataSat
   The save command is automatically performed when you type Do CollectCalDataSat.
3. Set the CalDataAPress property to the actual air pressure in hPa at the site.
   Set Passkey(1000)
   Set CalDataAPress (..)
   Save

NOTE: for maximum accuracy do not compensate the air pressure for height above sea level.

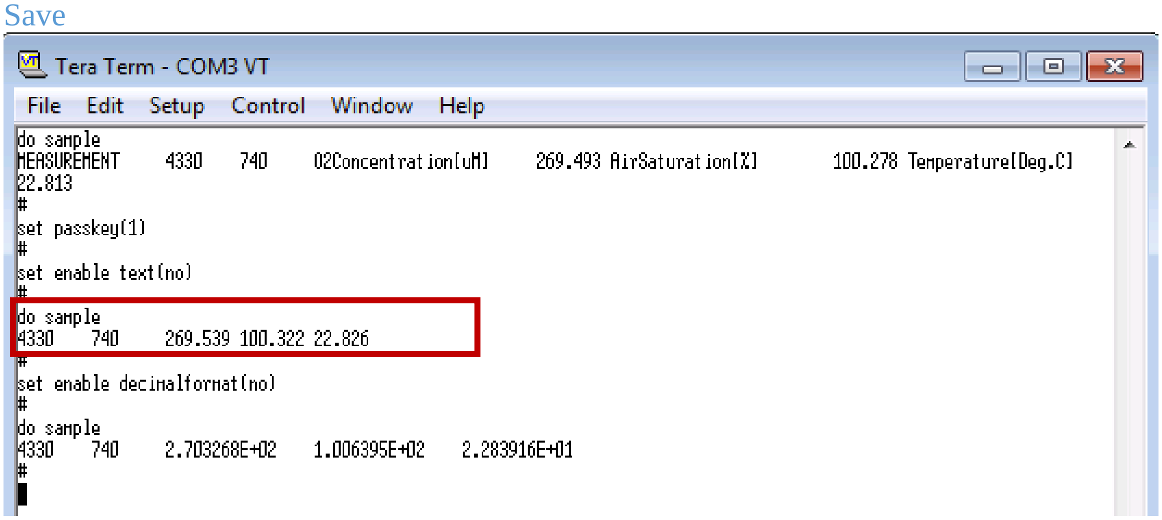
Submerge the Optode in the zero solution. Make sure that the sensing foil is free from air bubbles. Wait until both the temperature and the phase measurements have stabilized.

4. Enter the Do CollectCalDataZero command to store calibration values. The save command is automatically performed.
   Set Passkey(1000)
   Do CollectCalDataZero
5. Enter the Do Calibrate command to effectuate the new calibration and store the new coefficients in the sensor memory. The save command is automatically performed.
   Set Passkey(1000)
   Do Calibrate
6. Check
   Check that the sensor is working properly by taking it up into the air and rinse off, flush the sensor well to remove all Zero Oxygen water to not have cross contamination of your saturated sample. In dry air, the sensor should show close to 100% oxygen saturation at sea level. Put the sensor back into the anoxic water; the reading should drop to zero.

Communication:

NOTE: for failure of communication, please check it following steps shown below:

1. Find the right COM port and open it using Tera Terminal to with the following set-up: Select "Terminal" in the "Set up" menu and click "Local echo" also select "CR+LF" for both "Receive" and "Transmit" under "New line".
2. Check data output format:
   Do sample
   If the results turn out to be only numbers like shown below, then type:
   Set enable text(yes)
   Save



3. Close tera terminal. Go back to main user interface and try to connect again.

Maintenance:

The Oxygen Optode requires very little maintenance. When the membranes on traditional oxygen consuming sensors (based on electrochemical principles), often called Clark sensors, are fouled the water mixing in front of the sensor membrane becomes poorer, which influences the measurement directly. Since the Optode consumes no oxygen, the ability to diffuse gas has no influence on the measurement accuracy.

However, if the fouling is in the form of algae that produce or consume oxygen, the measurement might not reflect the oxygen concentration in the surrounding water correctly. Also the response time of the measurements might increase if the sensing foil is fouled. Therefore, the sensor should be cleaned at regular intervals depending on the fouling condition at the site. Field experiences have demonstrated that AADI Optodes typically are a factor of 2-4 more fouling resistant than electrochemical oxygen sensors from other manufacturers and then the AADI conductivity sensors.

The Optode housing can be cleaned using a brush and clean water. Carefully, use a wet cloth to clean the sensing foil. In all cases the cleaning procedure should be done with caution so that the protective foil coating (applies to slower responding foils) is not removed.

Figure A3. Oxygen Optode 4835 components.

If the fouling is calcareous, it can normally be dissolved with 7% household vinegar. Another substance that can be used is commercially called muriatic acid, which is a 5% HCl solution (dilute solution by 50% should be tested to see how well it dissolves growth before using a stronger concentration). If needed, use cotton covered Q-tips (normally for cleaning of ears) to gently wipe of the remains after it has been softened by soaking in vinegar/HCl. Optode can be submerged in vinegar/HCl overnight, or longer. After cleaning the sensor, it should be rinsed well in clean tap water before storing or reuse. Do not use any organic solvents such as: Acetone, Chloroform and Toluene since these and others will damage the foil.