# General Oceanics Underway pCO<sub>2</sub>

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# Outline

- Oceanographic Data Facility
- Underway pCO<sub>2</sub> systems
- General Oceanics (GO)
  - Design and options
- UCSD Ship Installations
  - R/V Sally Ride and Revelle
- Data Quality
  - Aux data needs
  - SOCAT



# Oceanographic Data Facility

- Specialized services in oceanography since 1972
- Current Team:
  - Chemists (Susan Becker, Melissa Miller, John Ballard)
  - Data analysts (Joseph Gum and Michael Kovatch)
  - Science Advisor (Todd Martz and Jim Swift)
- Nutrients, oxygen, salinity, chlorophyll analysis
- Rosette and CTD sensor setup, calibration, and QC
- GO-SHIP, SOCCOM, UCSD vessel operations, shore analysis, equipment loan, SIO teaching assistance, and PI contracted cruises
- Analytical methods, instrument, and software development

# Underway pCO<sub>2</sub> systems

- Measurement of carbon dioxide in surface seawater and atmosphere (Infrared analyzer, GC, or cavity ring down)
  - Ocean and atmosphere gas exchange
  - Significant parameter for global carbon budgets and modeling
- Normally frequent calibration with CO<sub>2</sub> standards
- Many custom built systems over past 30-40 years
- Effort to standardize data quality (ie: SOCAT)
  - Accuracy within 0.2 µatm (air) and 2 µatm (seawater)
- Supporting measurement accuracy crucial
  - Barometric pressure, equilibrator temperature, intake temperature

# General Oceanics

- Originally developed by Craig Neill (UW, Bergen, CSIRO)
  - Craig Neill still advises GO engineering decisions
- One of the first commercially available underway pCO<sub>2</sub> systems (2003?)
- Fully automated measurements with option of stand alone operation
  - Particularly useful on ships of opportunity
- NOAA/AOML installation guides and support

- 1/8" stainless steel gas tubing
- ½" Dekabon (Synflex) tubing
- Data cable
- Power cable (AC or DC)
  Pressurized air
  - 1 Water inlet
  - 2 Manual valve
  - 3 Safety valve
  - 4 Temperature sensor for intake temperature
  - 5 Anti fouling device
  - 6 Pump
  - 7 Thermosalinograph and/or manifold
- 8 pCO2 system wet box
- 9 pCO2 system dry box
- 10 Main switch for pump
- 11 Drain tank
- 12 Outlet
- 13 Inlet for outside air
- 14 Deck box
- 15 GPS antenna
- 16 Iridium antenna
- 17 Pressure inlet

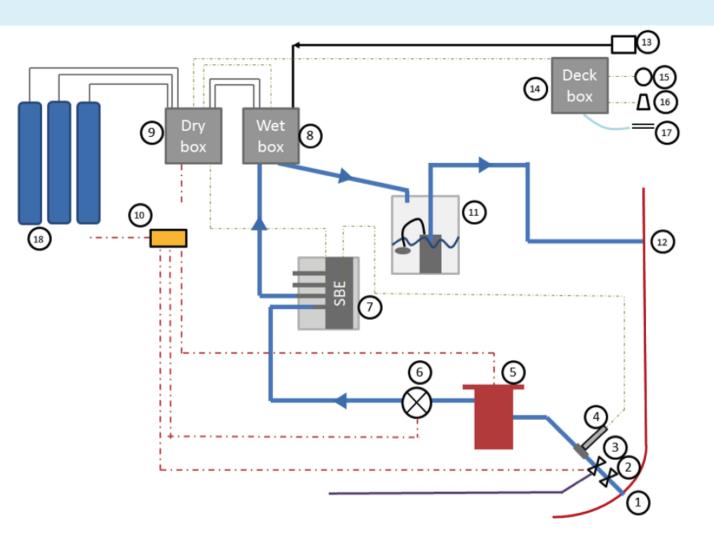
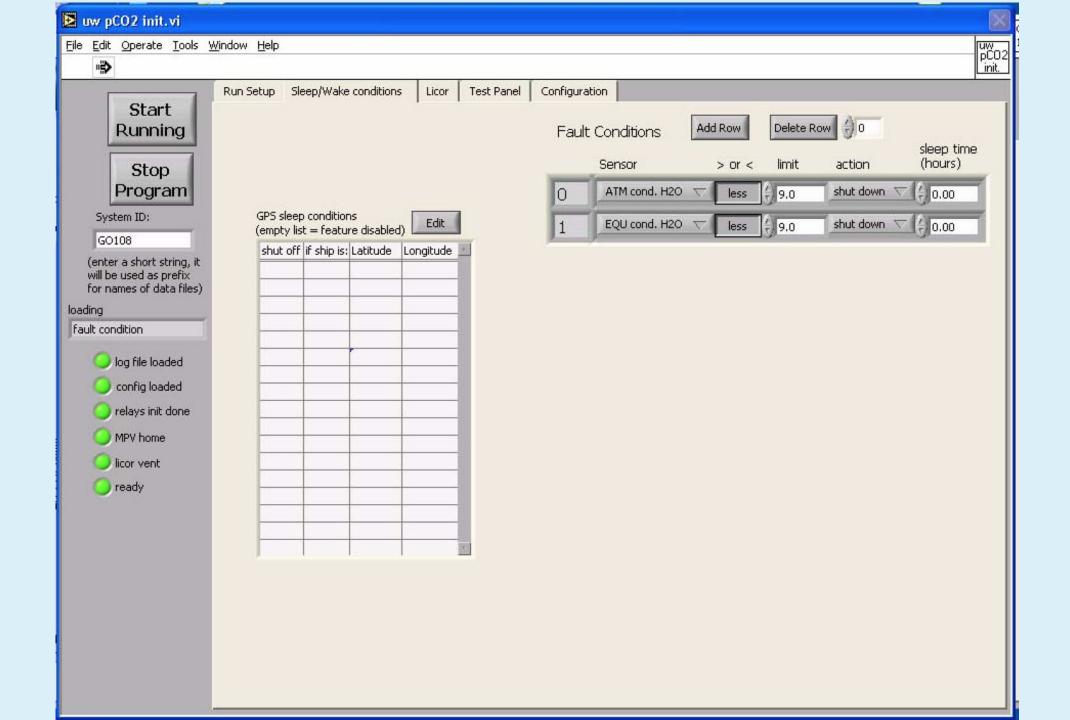


Figure 1. Schematic overview of the full installation of an autonomous underway *p*CO<sub>2</sub> system.

# General Oceanics

- Three main components:
  - Wet Box Seawater gas exchange
  - Dry Box CO<sub>2</sub> analyzer, control laptop
  - Deck Box GPS, barometric pressure, Iridium antenna
- Optional external sensor interface
  - pH, oxygen, temperature, salinity, turbidity, fluorometer
- Labview based control software
  - Serial inputs handled through ethernet switch to laptop
  - GPS based Sleep/Wake conditions
  - Moisture sensors and shut off valve
  - Additional shut off valve control

https://www.generaloceanics.com/pc02-monitoring/



### **Documentation and Support**

- Dennis Pierrot, AOML
- Rik Wanninkhov, AOML
- Kevin Sullivan, RSMAS
- Peter Quesada, General Oceanics
- Craig Neill, CSIRO

NOAA Technical Report, OAR-AOML-50 https://doi.org/10.25923/ffz6-0x48



**Instruction Manual** 

**Model 8050** 

Automated Flowing pCO<sub>2</sub> Measuring System

Installation of Autonomous Underway *p*CO<sub>2</sub> Instruments onboard Ships of Opportunity

#### Recommendations for Autonomous Underway *pCO*<sub>2</sub> Measuring Systems and Data Reduction Routines

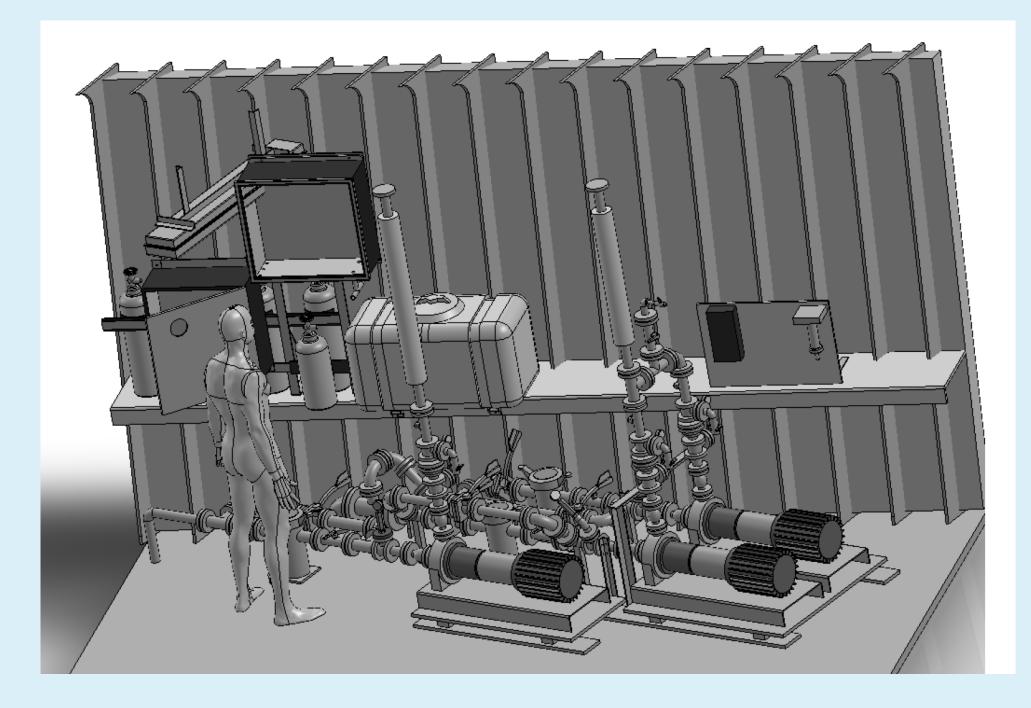
Denis Pierrot<sup>a,\*</sup>, Craig Neill<sup>b</sup>, Kevin Sullivan<sup>a</sup>, Robert Castle<sup>c</sup>, Rik Wanninkhof<sup>c</sup>, Heike Lüger <sup>a</sup>, Truls Johannessen<sup>b</sup>, Are Olsen<sup>b,d,e</sup>, Richard A. Feely<sup>f</sup>, Catherine E. Cosca<sup>f</sup>

#### • Target:

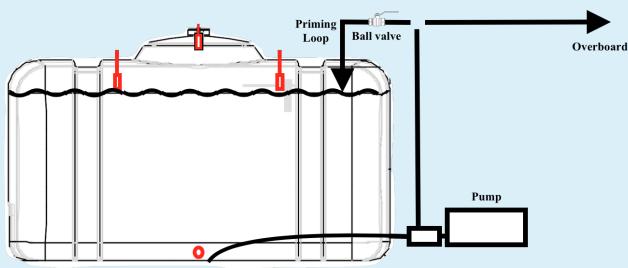
- Final test December 2019
- Operational early 2020



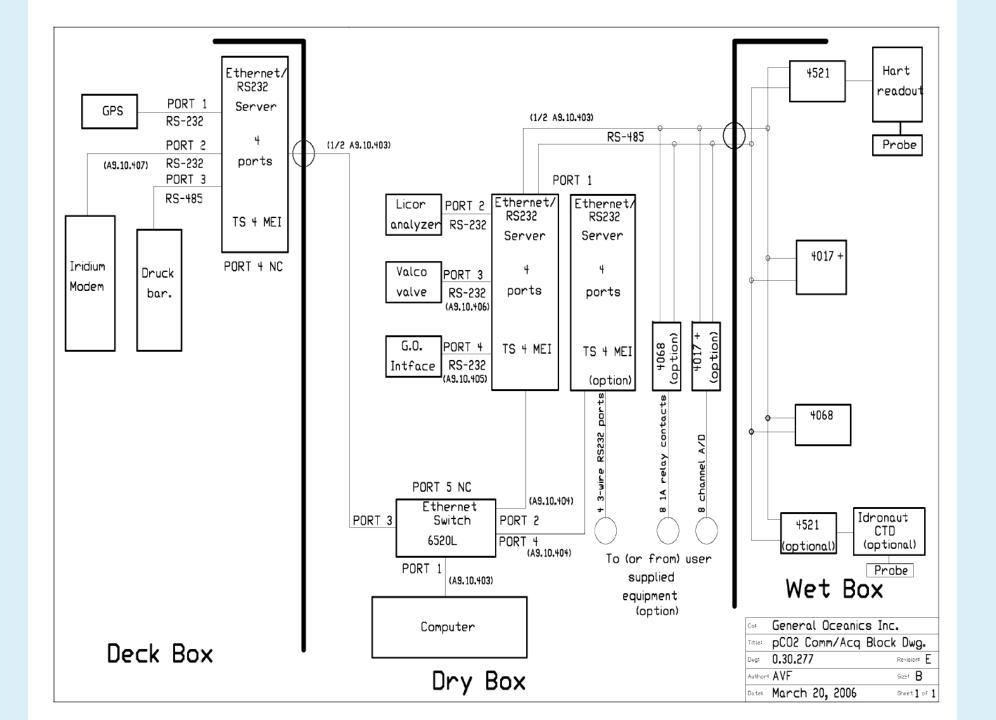




- Completed and tested February 2019
  - SS 316 plumbing of SW and FW
  - Drain tank system
  - New TSG mount and plumbing
  - Emergency e-actuated shut off valve
  - Gas standards and instrument calibrations





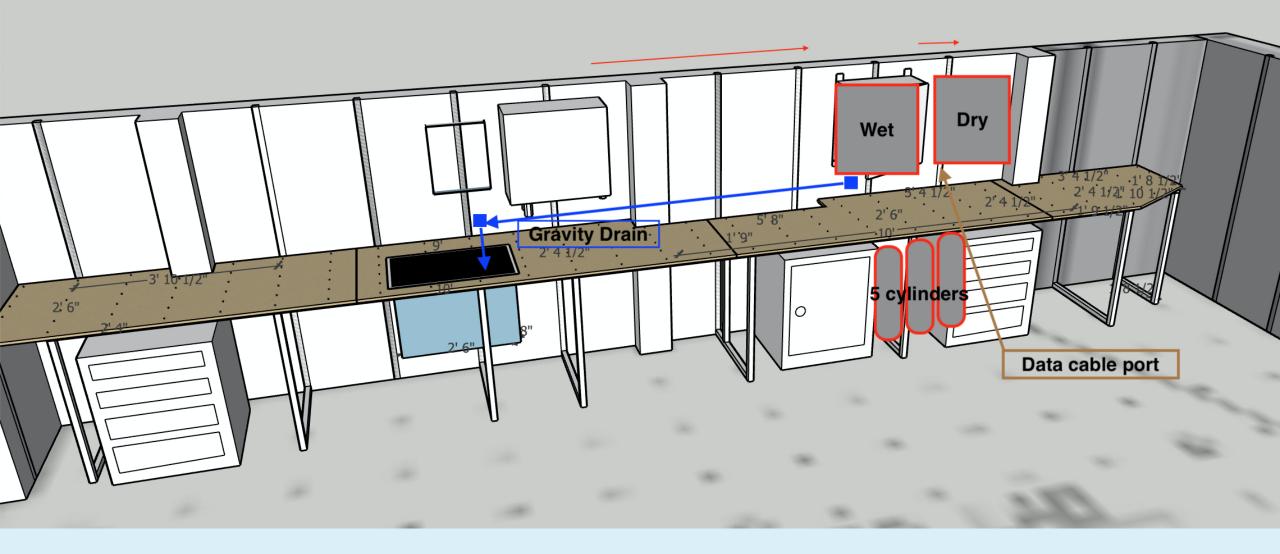


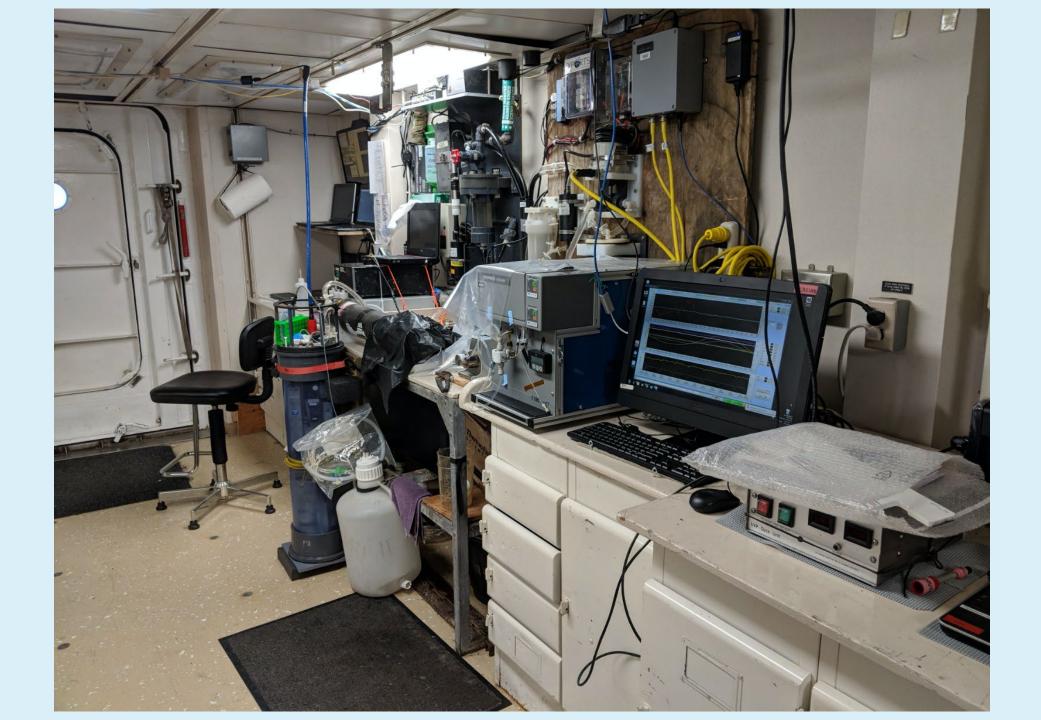
- Integration with our network
  - GO ethernet switch routed into network drop (transceiver room)
  - Virtual machine instead of laptop
    - Local remote access for maintenance and QC
  - UDP protocol for inputs
    - GPS, barometric pressure, intake temperature, and TSG
    - Labview updates?
    - GO will accommodate custom communication settings
- FW backflush of plumbing between wet box and underway SW pump
  - Manual ball valves
  - Each port stop?
  - Bleach annually? Test biofouling in plumbing with CO<sub>2</sub> measurements
- Intake temperature dry dock 2021
  - Requires pipefitter and custom probe mount

- Heavy vibrations in bow thruster room (bow slap)
  - Dampers on frame and box mounts
  - Are dampers enough?
  - Shortened instrument life or leaks?
- Limit intake temp change
  - Heat exchange SSW pump and bow thruster
  - Insulate plumbing
  - High flow rates with bypass valve
- TSG and GO flow rates displayed in MET
- GO equilibrator temp displayed side by side with TSG
- Discrete sampling valve near wet box

#### UCSD Installations R/V Revelle

- Target:
  - Install and test early 2020
  - Operational mid 2020
- Network integration will follow Sally Ride template
- Intake temperature
  - SBE 38
  - Inline installation does not require dry dock
- QC procedure
  - Precedent set by Sally Ride
  - Likely involve a group of interested PIs (ie: Todd Martz)
  - New funding?





# Mandatory Hardware

- Intake Temperature
  - closest to opening to sea surface as possible
  - Accuracy 0.05° C required
  - Ideally,  $\Delta T$  (intake to equilibrator) < 1° C
    - Ex: If  $\Delta T = 1^{\circ} C$ , then 16.8 µatm correction with uncertainty of 0.8 µatm pCO<sub>2</sub>
    - General instrument uncertainty ~1  $\mu atm$ , so total in this scenario ~2  $\mu atm$
    - Remember, overall accuracy needed to 2 μatm pCO<sub>2</sub>
- Barometric Pressure accuracy 2 mbar
- At least 3 non-zero WMO traceable standards

# Surface Ocean CO<sub>2</sub> Atlas (SOCAT)

- International repository for pCO<sub>2</sub> data (>100 contributors)
- 'Cookbook' for data QC flag and SOP criteria
  - QC flags A + B (uncertainty 2 μatm), C + D (5 μatm), E (10 μatm)
  - 7 SOP criteria for flags A + B
- PMEL live access server fo QC software
  - http://access.pmel.noaa.gov/SOCAT

SOCAT Quality Control Cookbook -For SOCAT version 7-

Siv Lauvset, Kim Currie, Nicolas Metzl, Shin-ichiro Nakaoka, Dorothee Bakker, Kevin Sullivan, Adrienne Sutton, Kevin O'Brien, Are Olsen QC flag A + B Seven SOP criteria:

- 1. The data are based on *x*CO<sub>2</sub> analysis, not *f*CO<sub>2</sub> calculated from other carbon parameters, such as pH, alkalinity or dissolved inorganic carbon;
- 2. Continuous CO<sub>2</sub> measurements have been made, not discrete CO<sub>2</sub> measurements;
- 3. The detection is based on an equilibrator system and is measured by infrared analysis, or gas chromatography or cavity ring-down spectroscopy;
- The calibration has included at least two non-zero gas standards, traceable to World Meteorological Organisation (WMO) standards, which bracket the observed range in xCO<sub>2</sub>;
- 5. The equilibrator temperature has been measured to within 0.05 °C accuracy;
- 6. The intake seawater temperature has been measured to within 0.05 °C accuracy;
- 7. The absolute equilibrator pressure has been measured to within 2 hPa accuracy. Note that many equilibrator-based instruments only have a differential sensor in the equilibrator itself, and an external pressure sensor (often the LiCor pressure sensor) is used to estimate the absolute pressure (i.e., abs\_equ\_pressure = diff\_equ\_pressure + abs\_lab\_pressure). If this is the case then the absolute equilibrator pressure is a sum of two sensors so the accuracy of both (alternatively the combined accuracy of both) must be documented.

In addition, warming between in situ and measurement should be <1 °C as explained above.

QC flag C + D

For an accuracy estimate of better than 5 µatm (C or D) the criteria differ depending on type of instrumentation:

- Shipboard NDIR, gas chromatographs and CRDS systems must have:
  - Two calibration gases, one of which can be a zero gas. The non-zero gas should span nearly the entire range observed in fCO<sub>2</sub> (i.e. the observations cannot be >20% outside the certified standard gas value).
  - Both temperatures must be measured to within 0.2 °C accuracy, and absolute equilibrator pressure has been measured to within 5 hPa accuracy.
  - The warming between in situ and measurement should be <3°C.
  - In addition, all other SOP as given above are fulfilled and properly documented in the metadata.
- Alternative sensors need to have:
  - Daily or more frequent *in situ* (i.e. when the instrument is operating in its natural environment) calibration with at least two calibration gases, one of which can be a zero gas. The non-zero gas must span the range observed in *f*CO<sub>2</sub>.
  - A clear and detailed description of the calibration (including the frequency of it) needs to be provided in the metadata.

# Questions?



Figure 1 (from Wanninkhof et al., 2013) below shows isopleths of uncertainty in calculated  $fCO_2$  ( $\Delta fCO_2$ ) arising from uncertainty in the temperature ( $T_{equil}$ ) and pressure ( $P_{equil}$ ) of equilibration, respectively. For equilibrator-based systems, the uncertainty in the *in situ* and measurement temperatures and the measurement pressure needs to be evaluated in order to assess the overall accuracy of  $fCO_2$ .

