General Oceanics
Underway pCO$_2$

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Outline

• Oceanographic Data Facility
• Underway pCO$_2$ 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$_2$ 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$_2$ 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$_2$ systems (2003?)
- Fully automated measurements with option of stand alone operation
  - Particularly useful on ships of opportunity
- NOAA/AOML installation guides and support
Figure 1. Schematic overview of the full installation of an autonomous underway $pCO_2$ system.
General Oceanics

- Three main components:
  - Wet Box – Seawater gas exchange
  - Dry Box – CO₂ 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 Wanninkhof, AOML
- Kevin Sullivan, RSMAS
- Peter Quesada, General Oceanics
- Craig Neill, CSIRO
UCSD Installations
R/V Sally Ride

• Target:
  • Final test December 2019
  • Operational early 2020
UCSD Installations
R/V Sally Ride

• 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
UCSD Installations
R/V Sally Ride

- 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 CO₂ measurements

- Intake temperature - dry dock 2021
  - Requires pipefitter and custom probe mount
UCSD Installations
R/V Sally Ride

• 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, ΔT (intake to equilibrator) < 1° C
    • Ex: If ΔT = 1° C, then 16.8 μatm correction with uncertainty of 0.8 μatm pCO₂
    • General instrument uncertainty ~1 μatm, so total in this scenario ~2 μatm
    • Remember, overall accuracy needed to 2 μatm pCO₂

• Barometric Pressure - accuracy 2 mbar
• At least 3 non-zero WMO traceable standards
Surface Ocean CO₂ Atlas (SOCAT)

- International repository for pCO₂ 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 for QC software
  - http://access.pmel.noaa.gov/SOCAT

**SOCAT Quality Control Cookbook**
-For SOCAT version 7-

Seven SOP criteria:
1. The data are based on xCO$_2$ analysis, not fCO$_2$ calculated from other carbon parameters, such as pH, alkalinity or dissolved inorganic carbon;
2. Continuous CO$_2$ measurements have been made, not discrete CO$_2$ measurements;
3. The detection is based on an equilibrator system and is measured by infrared analysis, or gas chromatography or cavity ring-down spectroscopy;
4. 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$_2$;
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.
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 $f_{CO_2}$ (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 $f_{CO_2}$.
  - 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 $\Delta f\text{CO}_2$ arising from uncertainty in the temperature ($T_{\text{equil}}$) and pressure ($P_{\text{equil}}$) of equilibration, respectively. For equilibrator-based systems, the uncertainty in the \textit{in situ} and measurement temperatures and the measurement pressure needs to be evaluated in order to assess the overall accuracy of $f\text{CO}_2$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{The impact of uncertainties in temperature and pressure on $f\text{CO}_2$ (from Wanninkhof et al., 2013).}
\end{figure}