SHIPBOARD UNDERWAY MEASUREMENTS OF PARTIAL PRESSURE OF CO_2 (pCO_2)

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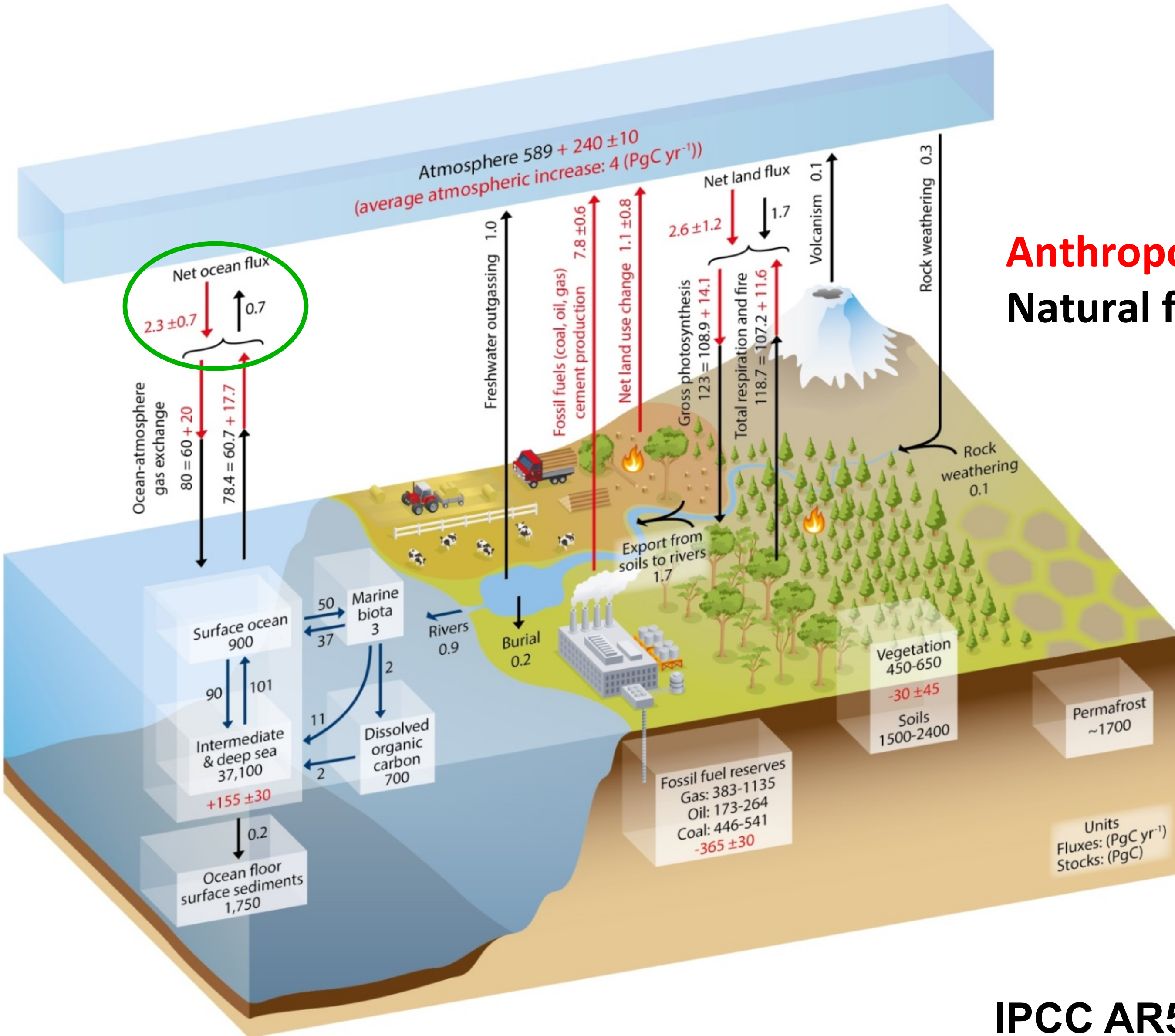
Overview

- Intro: marine carbon cycling and carbonate chemistry
- Principle of pCO_2 measurements based on non-dispersive infra-red (NDIR) detection
- Intro to General Oceanics pCO_2 system (underway or flow-through measurements)

  Setup, measurement cycle, maintenance
- Data quality and processing

PRESENT-DAY GLOBAL CARBON CYCLE



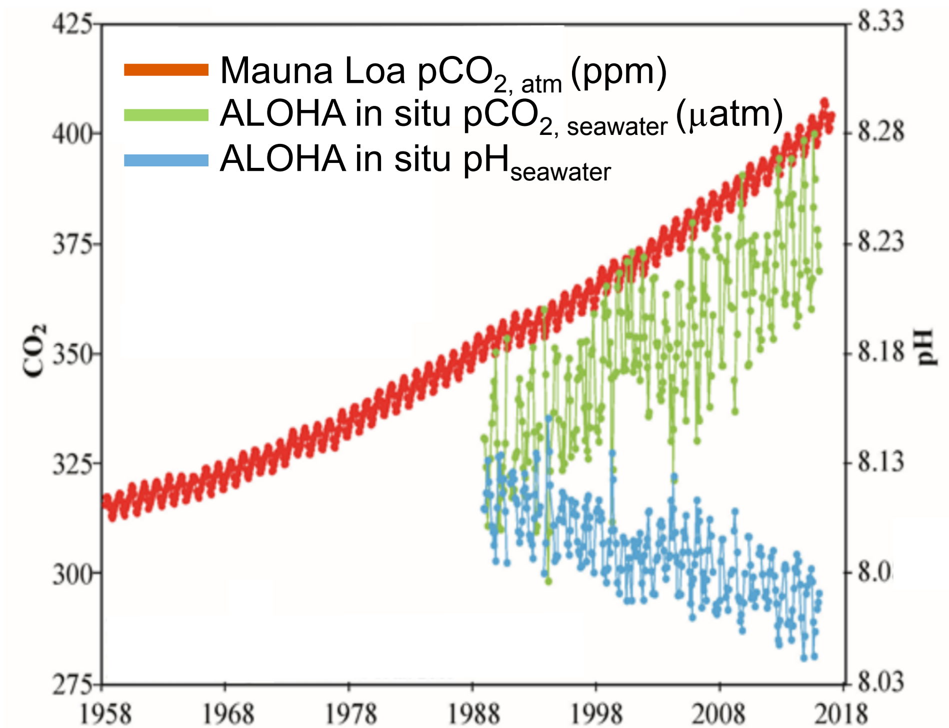
Anthropogenic fluxes in Red

Natural fluxes in Black

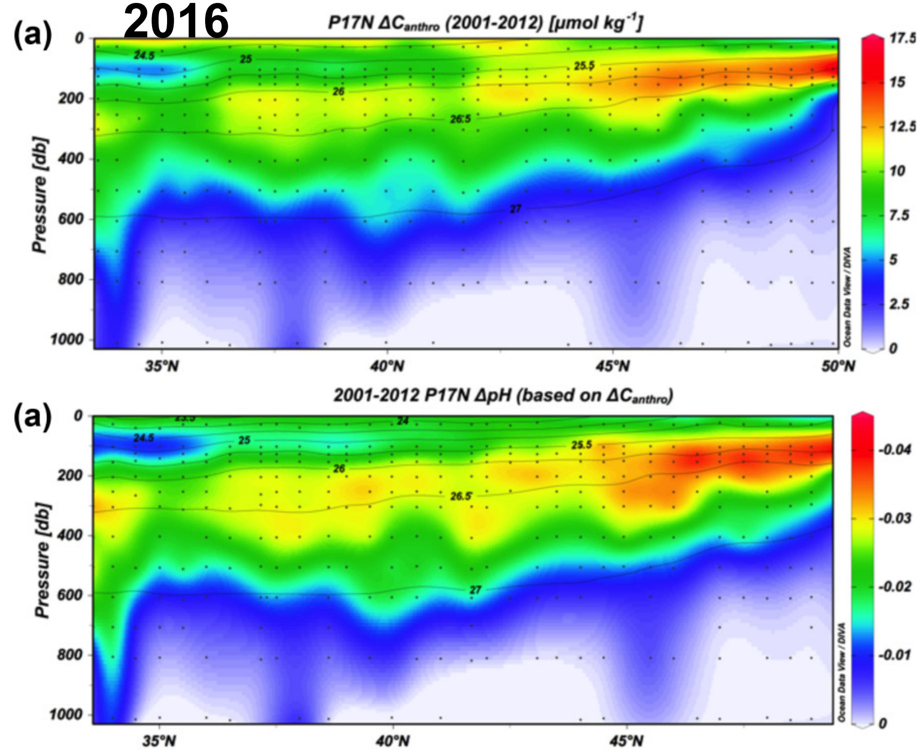
IPCC AR5

Increase of CO_2 and Ocean Acidification

Hawaii Time-Series

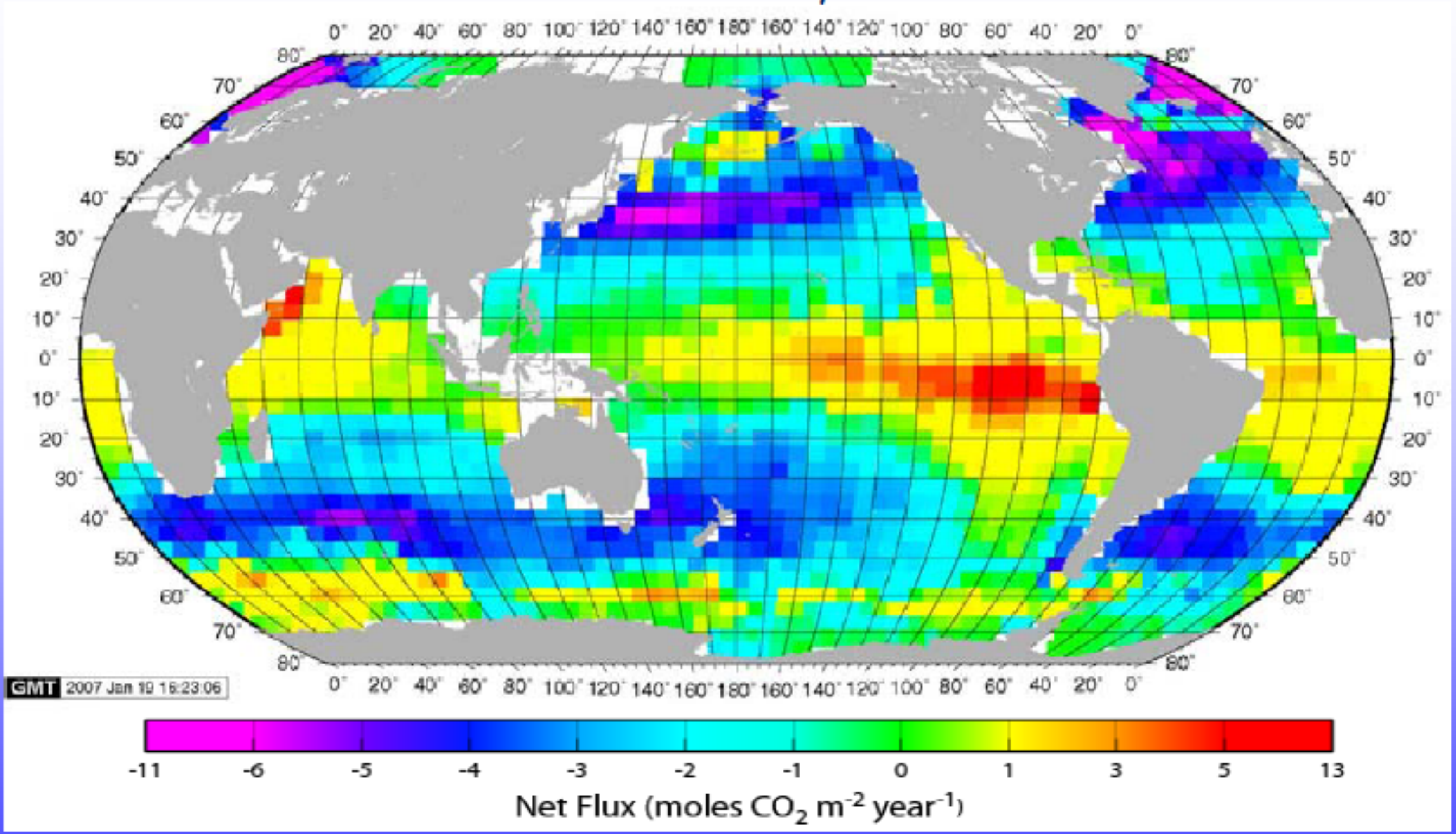


Northeast Pacific, Chu et al., 2016



OA rate: pH -0.001-0.003/yr; *pCO_2 +1-2µatm/yr*; DIC +1-2 µmol/kg /yr

Takahashi climatological annual mean air-sea CO_2 flux for reference year 2000



Based on ~3 million measurements since 1970 and NCEP/DOE/AMIP II reanalysis.

Global flux is 1.4 ±0.7 Pg C/yr

Takahashi et al., Deep Sea Res. II, 2009

Seawater Carbonate Chemistry
(Acid-base Chemistry in Seawater)

Acid-base chemistry in sea water

- Carbon dioxide equilibria

$$CO_2 + H_2O = H^+ + HCO_3^-$$
$$HCO_3^- = H^+ + CO_3^{2-}$$

- Boric acid equilibrium

$$B(OH)_3 + H_2O = H^+ + B(OH)_4^-$$

- Water dissociation

$$H_2O = H^+ + OH^-$$

Dickson lecture slides, OA Short Courses 2009

Analytical Parameters of the CO_2 system

1. pCO_2 or fCO_2: $pCO_2 = [CO_2^*]/K_0$

Dissolved $CO_2 + H_2CO_3$

Species concentrations *f*(t,S,p)

2. $pH = -\log[H^+]$

3. Total dissolved inorganic carbon (DIC, C_T, or TCO_2)

$= [CO_2^*] + [HCO_3^-] + [CO_3^{2-}]$ **Mass balance**

t,S,p Independent

4. Total alkalinity (TA or Alk)

$= [HCO_3^-]+2[CO_3^{2-}] + [B(OH)_4^-]+[\text{Org. Alk}]+[\text{other Alk}]+[OH^+] – [H^+]\ldots$

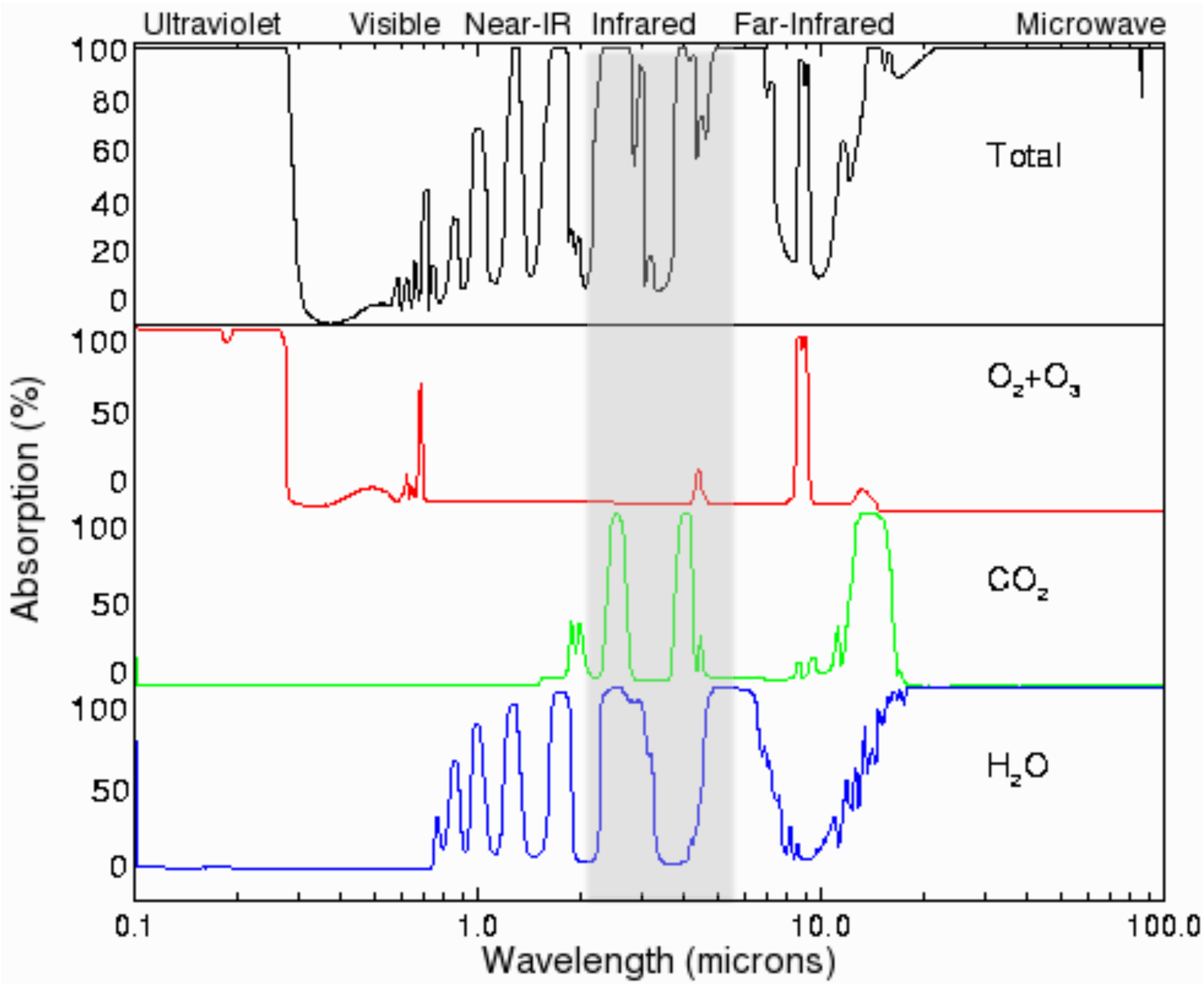
Charge balance

And you need two parameters to solve the CO_2 system

Woods Hole Oceanographic Institution

Non-dispersive infra-red (NDIR) CO_2 detection

Gaseous CO_2, oxygen, and water vapor absorption spectrum



Theory

A gas mixture (e.g. air) consisting of a suite of gasses (e.g. O_2, N_2, CO_2 …):

Total pressure vs. partial pressure

$$P = \sum p_i$$

Individual gas mole fraction x_i

$$1 = \frac{\sum p_i}{P} = \sum x_i$$

$$P_e = P \sum a_i x_i$$

$$= P(1 + \quad = T\psi_i f_i\left(\frac{\alpha_i}{\psi_i P}\right) \;) \quad = P\psi_i$$

Effective pressure (P_e): Weighted sum of partial pressure

$$x_i = \frac{p_i}{P} \quad = T\psi_i f_i\left(\frac{\alpha_i}{\psi_i P}\right)$$

Partial pressure of gas *i* is related to its absorbance α_i

NDIR detection: Measure xCO_2

Early design

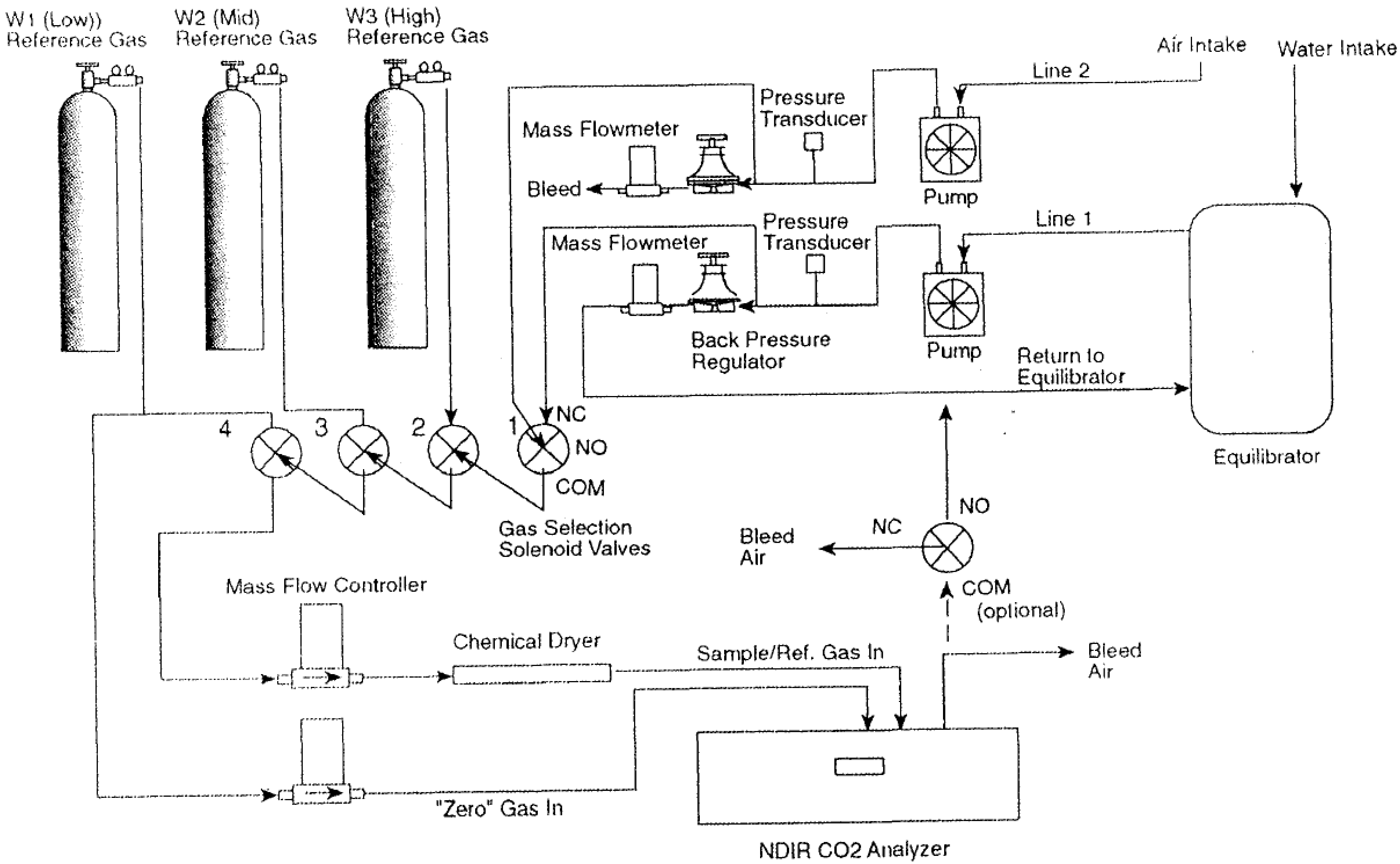
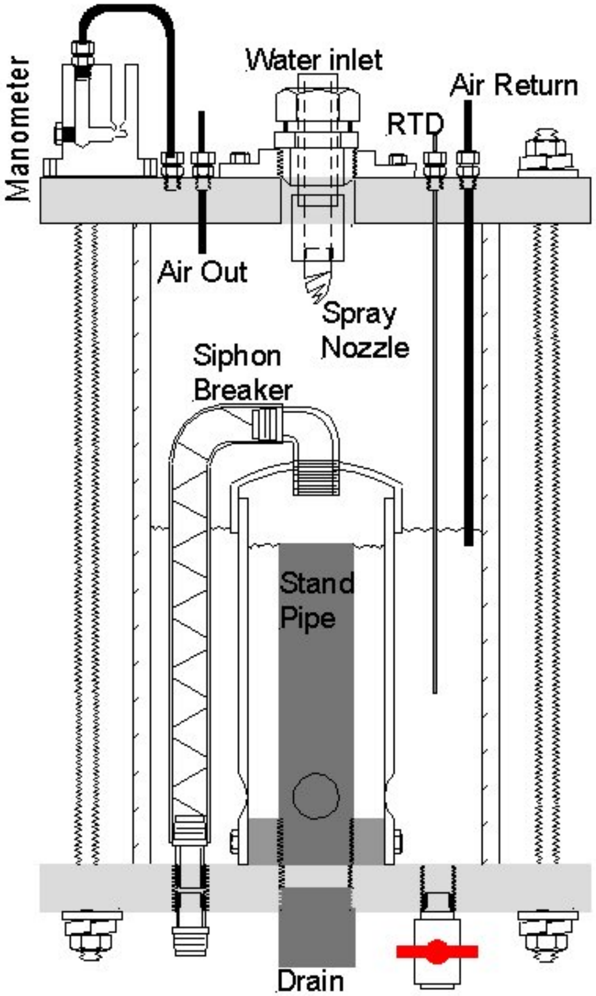


Fig. 1. Schematic of the plumbing of the underway system. For the three-way gas solenoid valves *NC* stands for normally closed, *NO* for normally open, and *COM* for common.

Woods Hole Oceanographic Institution

Wanninkhof and Thoning, 1993

Early design: CO_2 equilibrator



Courtesy by Taro Takahashi's group at LDEO Columbia U.

Comparison of various underway pCO_2 systems

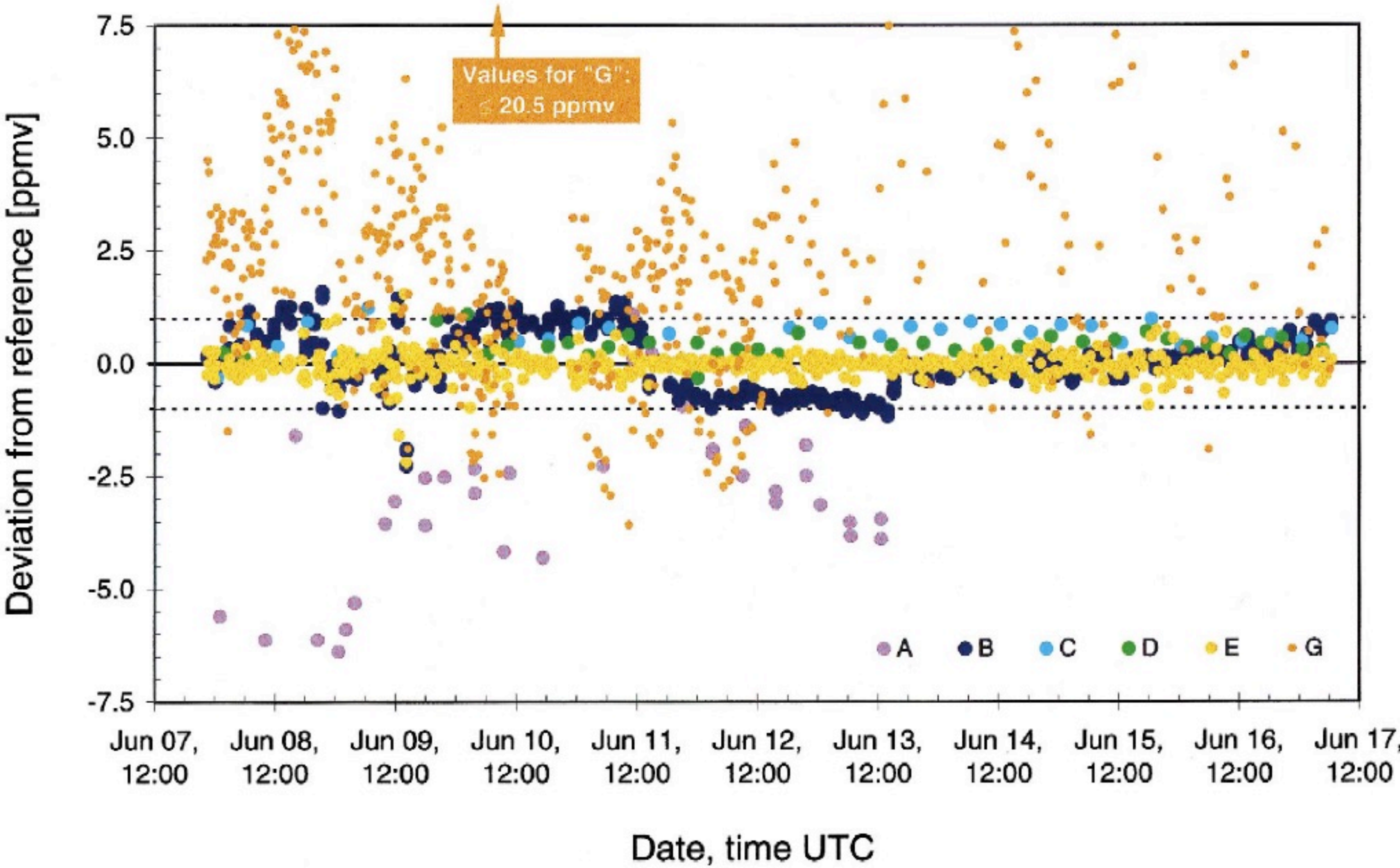
Table 1
Summary of main features of the underway fCO_2 systems "A" through "G" which participated in the exercise

	"A"	"B"	"C"	"D"	"E"	"F"	"G"
Equilibrator							
Design	Shower head	Bubbler	Shower head	Thin film[a]	Showerhead	Bubbler	Showerhead
Total volume	1000 ml	1400 ml	13.1 l	119 ml	11.0 l	36 ml	1200 ml
Water volume	500 ml	1000 ml	2.3 l	21 ml	10.0 l	18 ml	~ 75 ml
Air volume	500 ml	400 ml	10.8 l	98 ml	1.0 l	18 ml	500 ml
Water flow rate	4–6 l min^{-1}	2.0 l min^{-1}	8.0 l min^{-1}	2.0 l min^{-1}	10–15 l min^{-1}	0 l min^{-1}[b]	1.2 l min^{-1}
Air flow rate	0.2 l min^{-1}	0.8 l min^{-1}	0.5 l min^{-1}	1.0 l min^{-1}	0.5 l min^{-1}	0.17 l min^{-1}	0.18 l min^{-1}
Vented?	Yes	Yes	Yes	No[c]	Yes	No	Yes
Time constant[d]	2–3 min	75 s	3–5 min	2–3 min	60–90 s	n/a	Unknown
Mean temperature difference[e]	0.30 ± 0.05	0.30 ± 0.04	0.24 ± 0.02	0.39 ± 0.12	0.17 ± 0.03	0.32 ± 0.03	0.56 ± 0.09
CO_2 measurement							
Method	NDIR	NDIR	NDIR	NDIR	NDIR	NDIR	NDIR
Wet/dry?	Wet	Wet	Dry	Dry	Dry	Dry	Wet
Analyzer calibration							
Number of standard gases	2	2	2	2	4	2[f]	2
Zero gas?	No	Yes	No	No	No	Yes	No
Measurement cycle							
Calibration frequency	6–8 h	6 h	6 h	4–6 h	1.5 h	15 min	2 h
Air measurement frequency	6–8 h	1 h	6 h	4–6 h	0.5 h	n/a	7 min
Interrogation interval	6 s	6 s	1 s	10 s	0.1 s	15 min	0.33 s
Averaging interval	(1[g]) 3 min	1 min	4 min	5 min	1 min	n/a	1 s
Reporting interval	(1[g]) 3 min	1 min	4 min	5 min	~ 13 min	20 min	~ 8 min
Data points per average	10; 30	10	240	33	600	1	3

[a] Film thickness approximately 0.75 mm.
[b] Semi-continuous technique.
[c] Vented only every 20 min.
[d] This is the overall time constant of the system (not the time constant of equilibration).
[e] Mean difference between equilibrator temperature and in situ temperature based on corrected temperature readings (Section 2.3.2).
[f] Standard gas generator was initially calibrated using all six calibration gases; linearity checks are carried out for every sample with only two calibration gases.
[g] Until June 9, 0230 UTC.

(Kortzinger et al., 2000)

Inter-comparison of underway pCO_2 systems



Kortzinger et al. 2000, Marine Chemistry

Schematic of the pCO_2 monitoring system

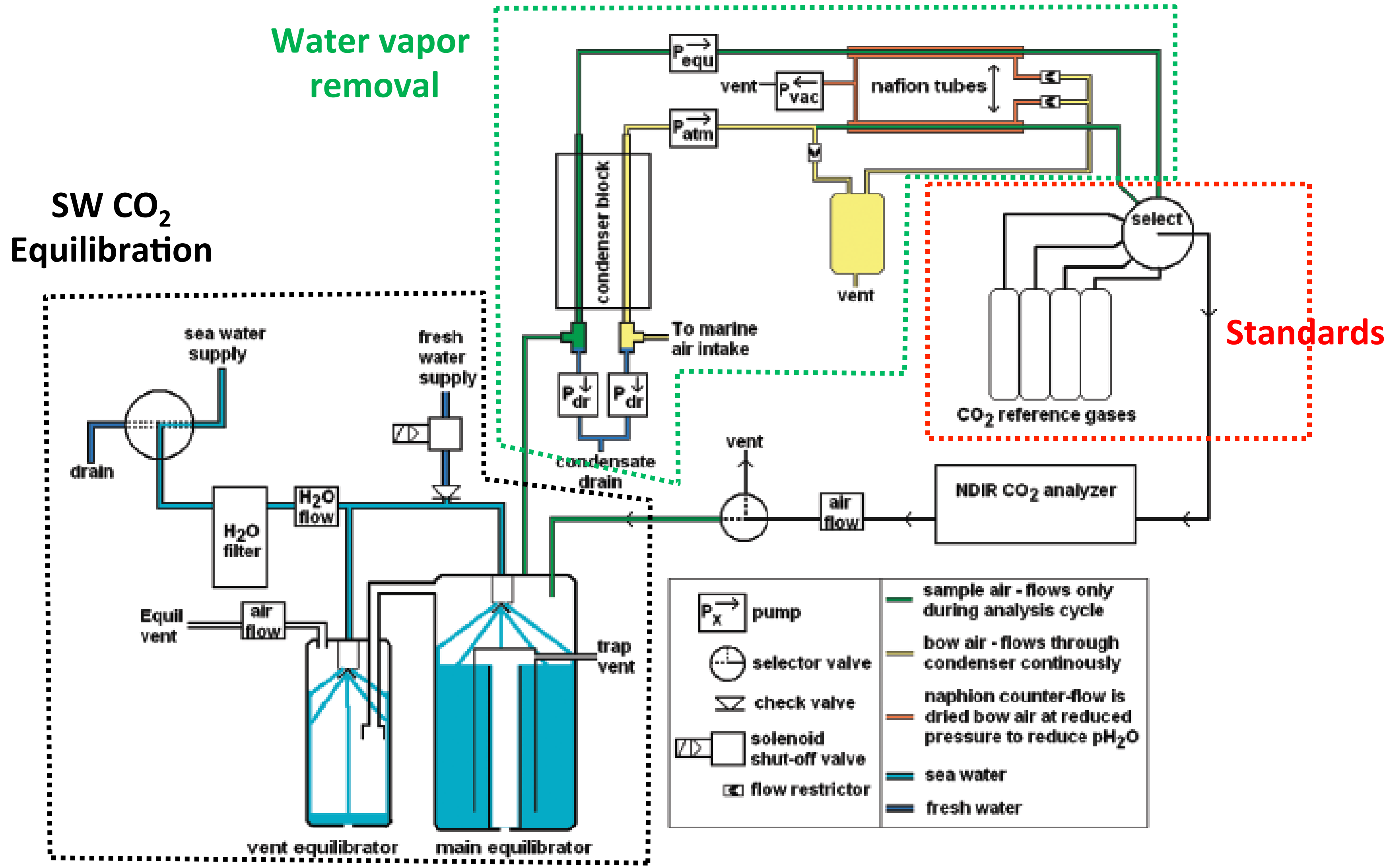


Figure 1. Schematic of a typical pCO_2 monitoring system, reprinted with permission from Neill et. al., (2007).

General Oceanics pCO_2 system

Figure 4. Picture of the Wet box

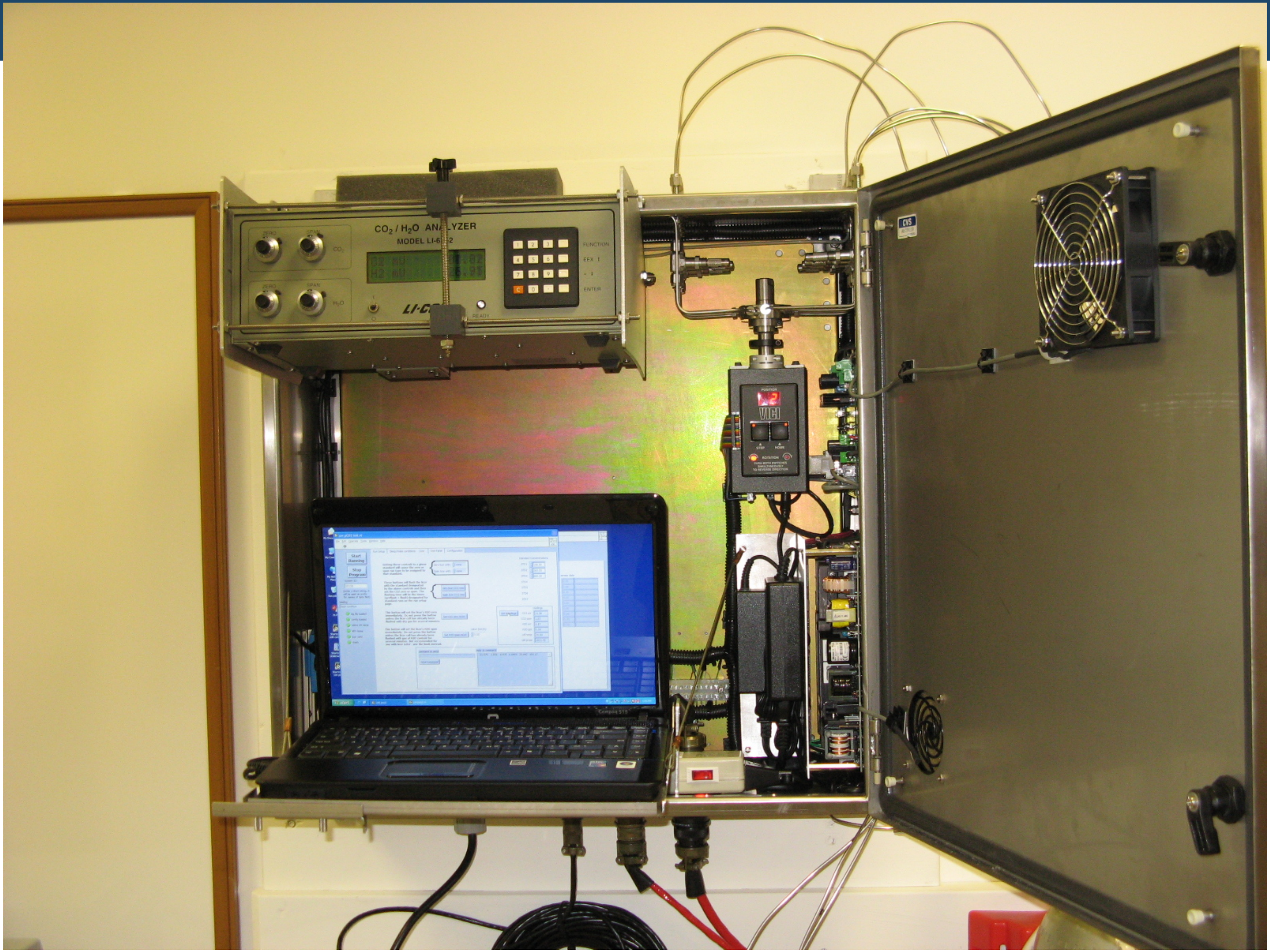
Wet box

Figure 1. Picture of the Dry Box

Dry box


RECONNECT TO PRESSURE
RECONNECT TO WATER TRAP


FLUKE
ADAM
EVSCO
ELLIPTIC VALVES
CAUTION
STATS
HOLD
SETUP
ENTER
NEXT
RECONNECT TO PRESSURE TRANSDUCER


CO2 / H2O ANALYZER
MODEL LI-6262
VICI

Schematic of LI-7000 Optical System

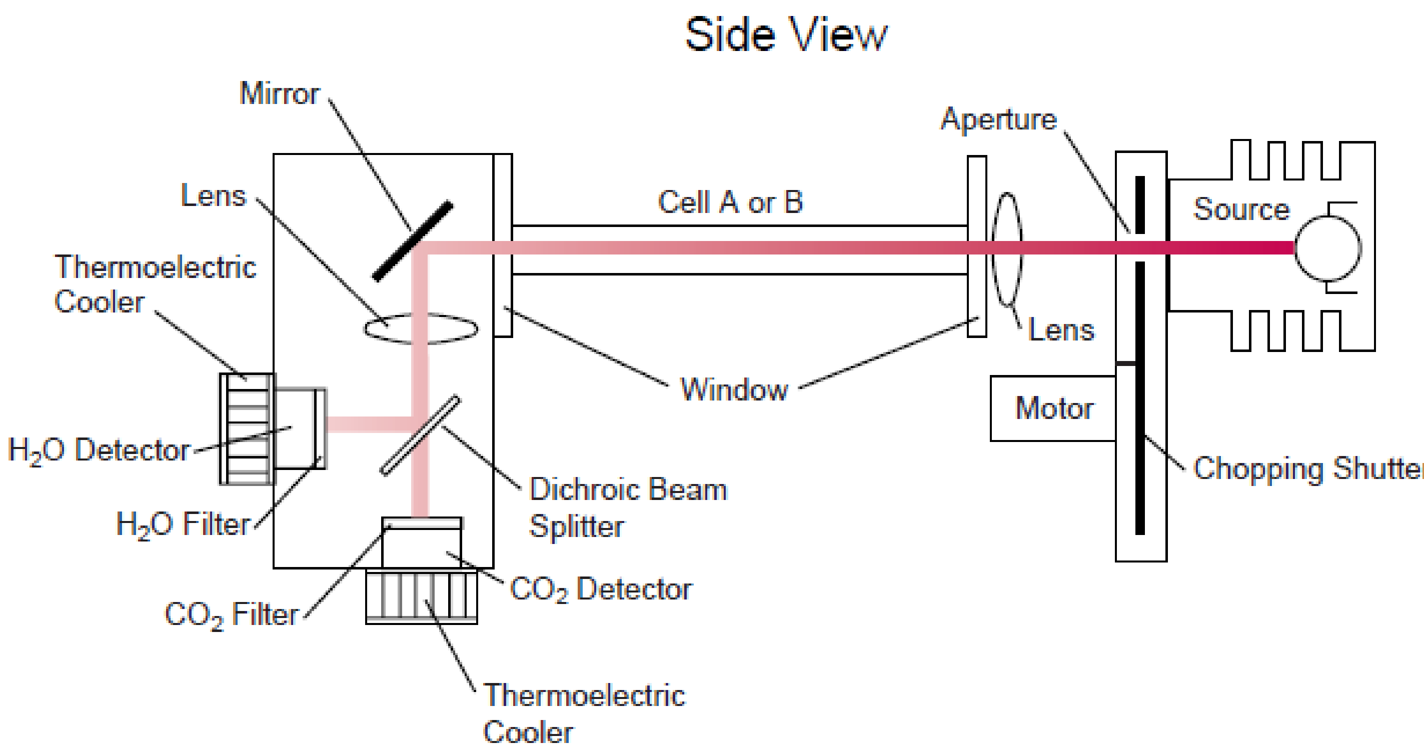
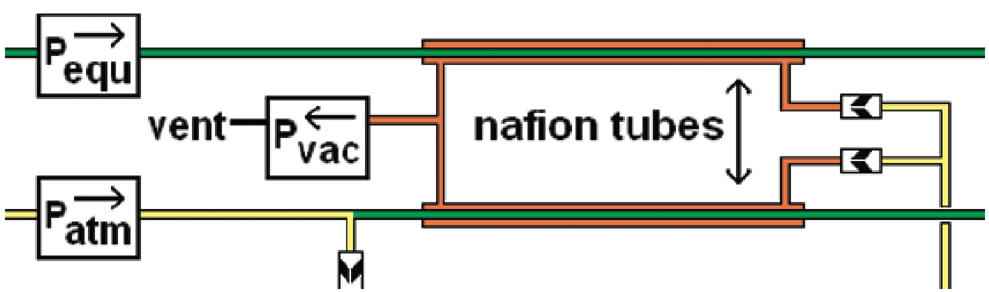


Figure 1-1. Schematic of LI-7000 optical path.

"Recommended to service annually or regularly"
-- Users can change chemicals and clean the optical path

Water vapor in NDIR CO_2 detection

- Both water vapor (WV) and CO_2 absorb light in the IR range: WV interfere CO_2 detection
- Solution: **Remove water vapor**
  - Condenser (cooling) and drain
  - Nafion tubes: dry air exchange with sample gas



  - Desiccants before detector: Soda lime or Magnesium perchloride (need to change regularly)

Setup

- **Physical connection**
  - Underway water: >2 L/min consistent flow, uncontaminated sample water (clean pipes regularly)
  - Gas standards (3+): Carbon Dioxide (CO_2) WMO Scale (https://www.esrl.noaa.gov/gmd/ccl/co2_scale.html)
  - Uncontaminated atmospheric air sample line
  - Tap/freshwater (for backflash CO_2 equilibrator)
  - GO system dry box and wet box
  - Deck unit (GPS, Air pressure, Iridium communication) (optional)

GO pCO_2 system: Physical connection

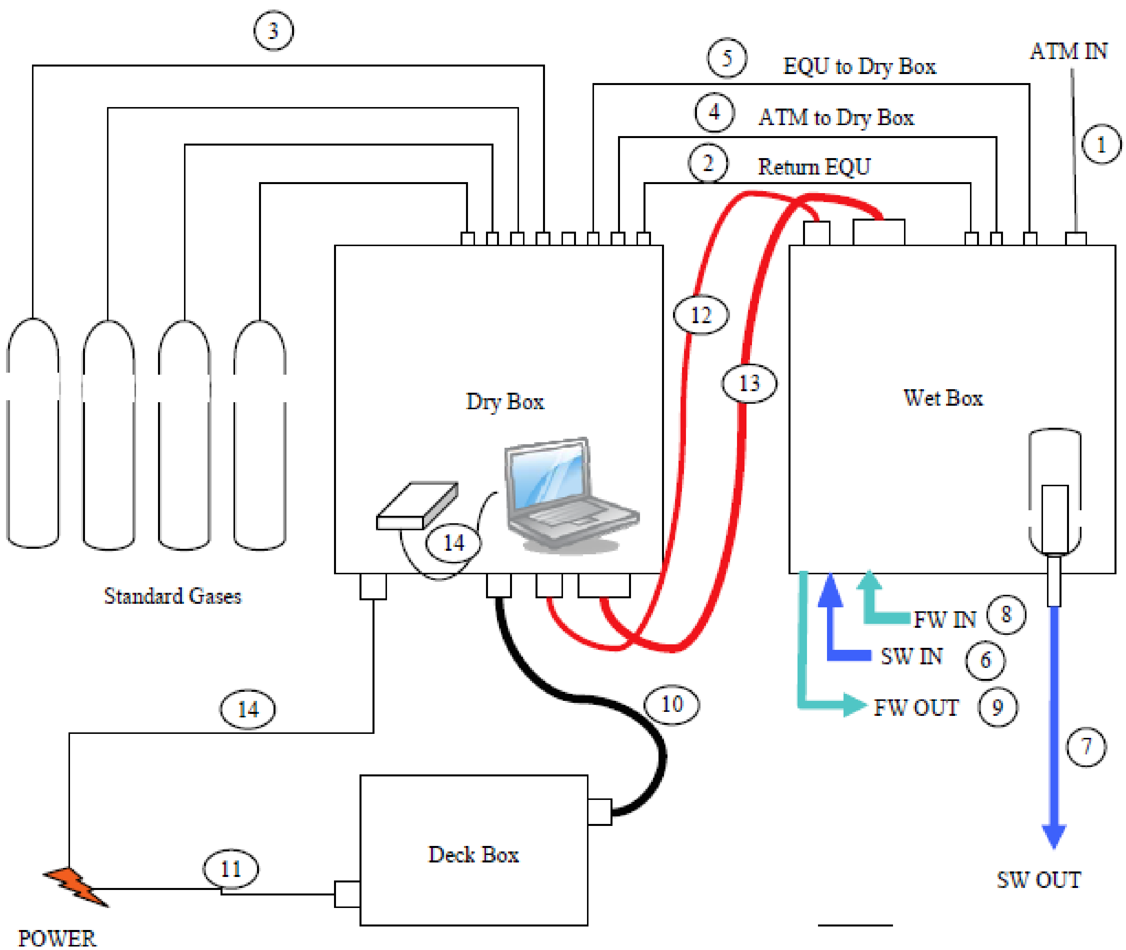
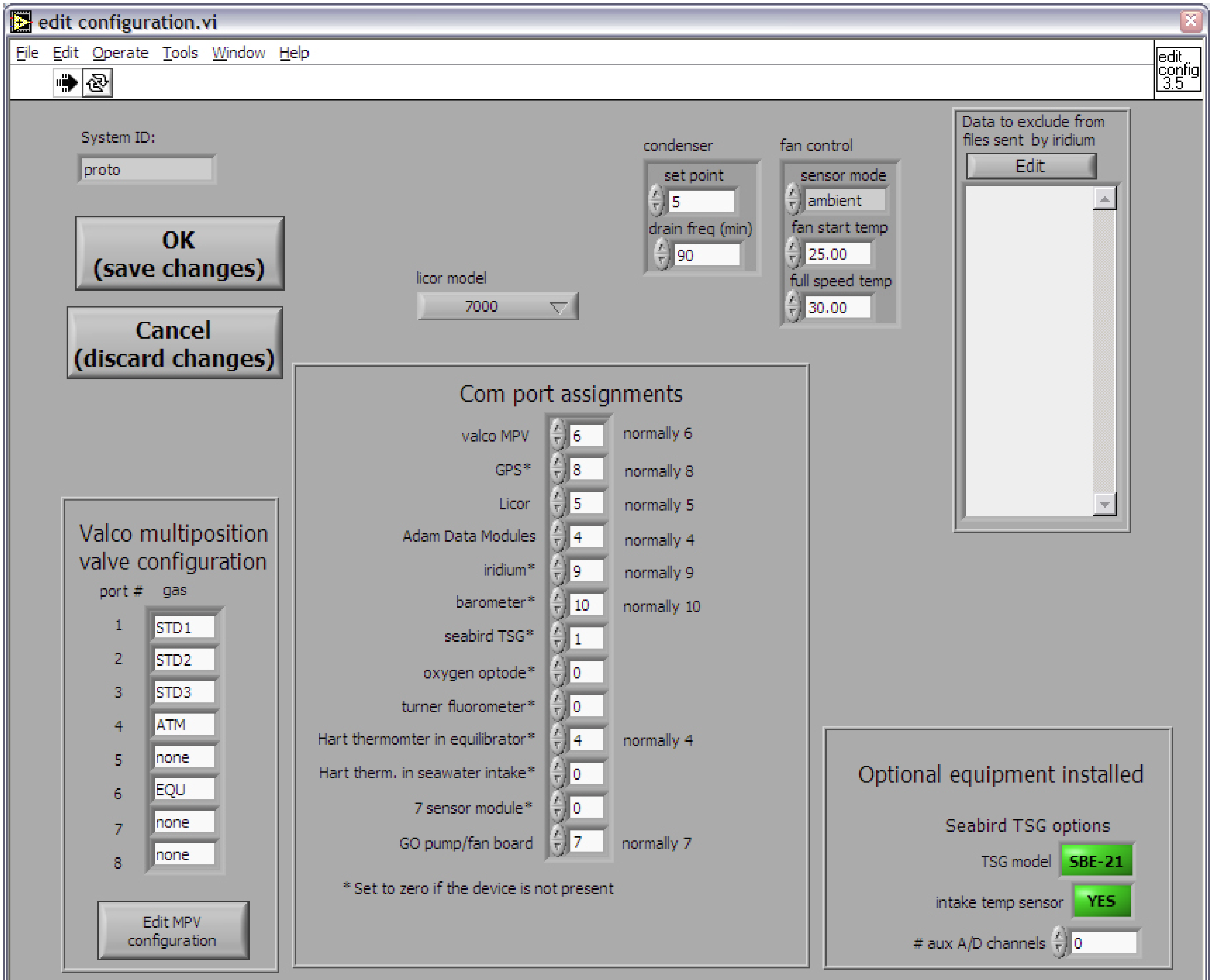


Figure 28. System Connections Diagram

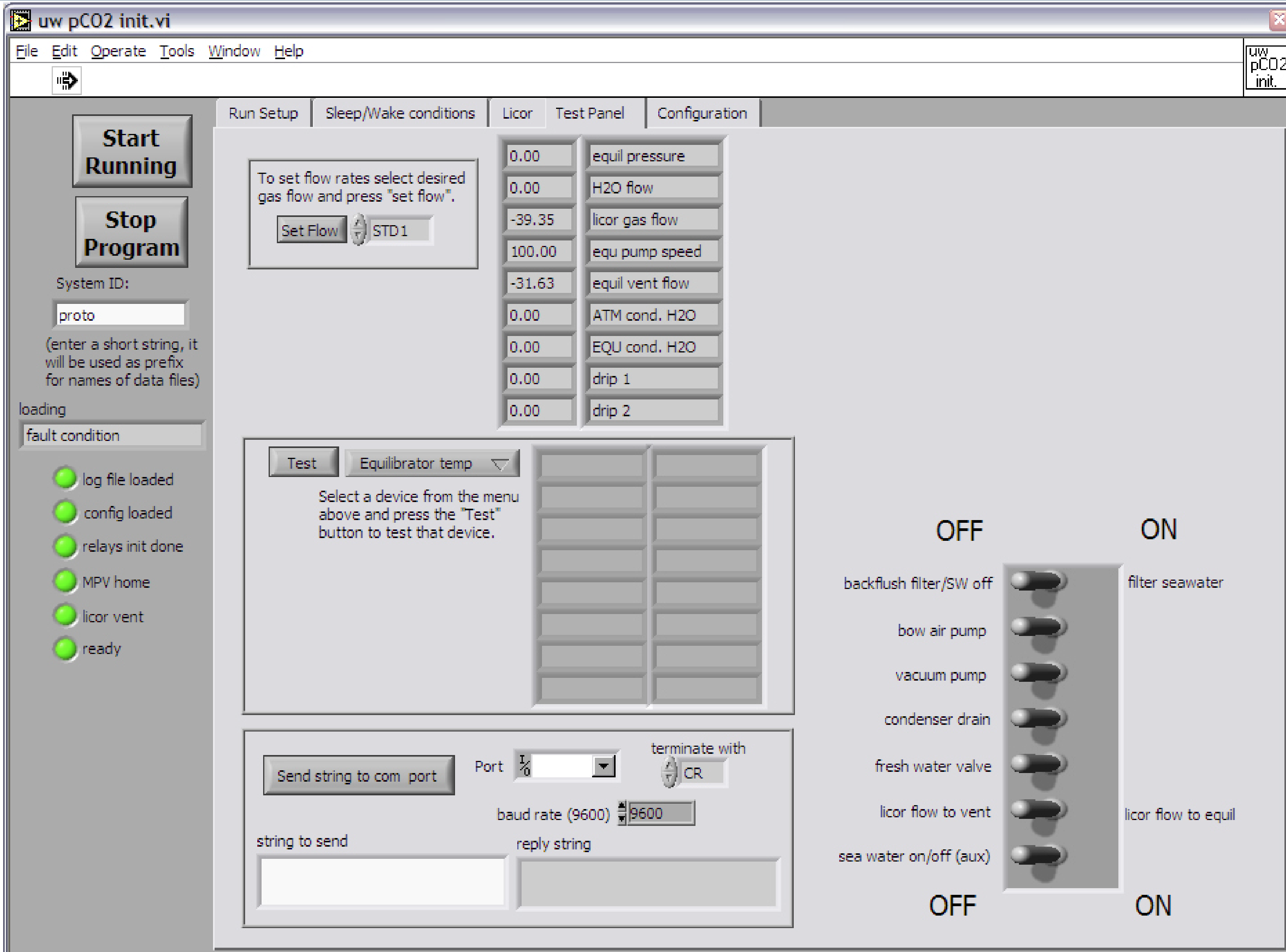
Setup continued…

- Software setup
  - Configuration file: sample SW/Air/Gas STDs ports and others
  - Running sequence: measurement cycle
    - Calibration every a few hours with at least 3 STD CO_2 gases (usually 3+)
    - Air measurements (usually hourly for a few mins)
      Note: Air xCO_2/pCO_2 vary little
    - SW measurements (usually once per min hourly)
    - Repeat Air + SW cycles for a few hours
    - Repeat: calibration and Air+SW cycles

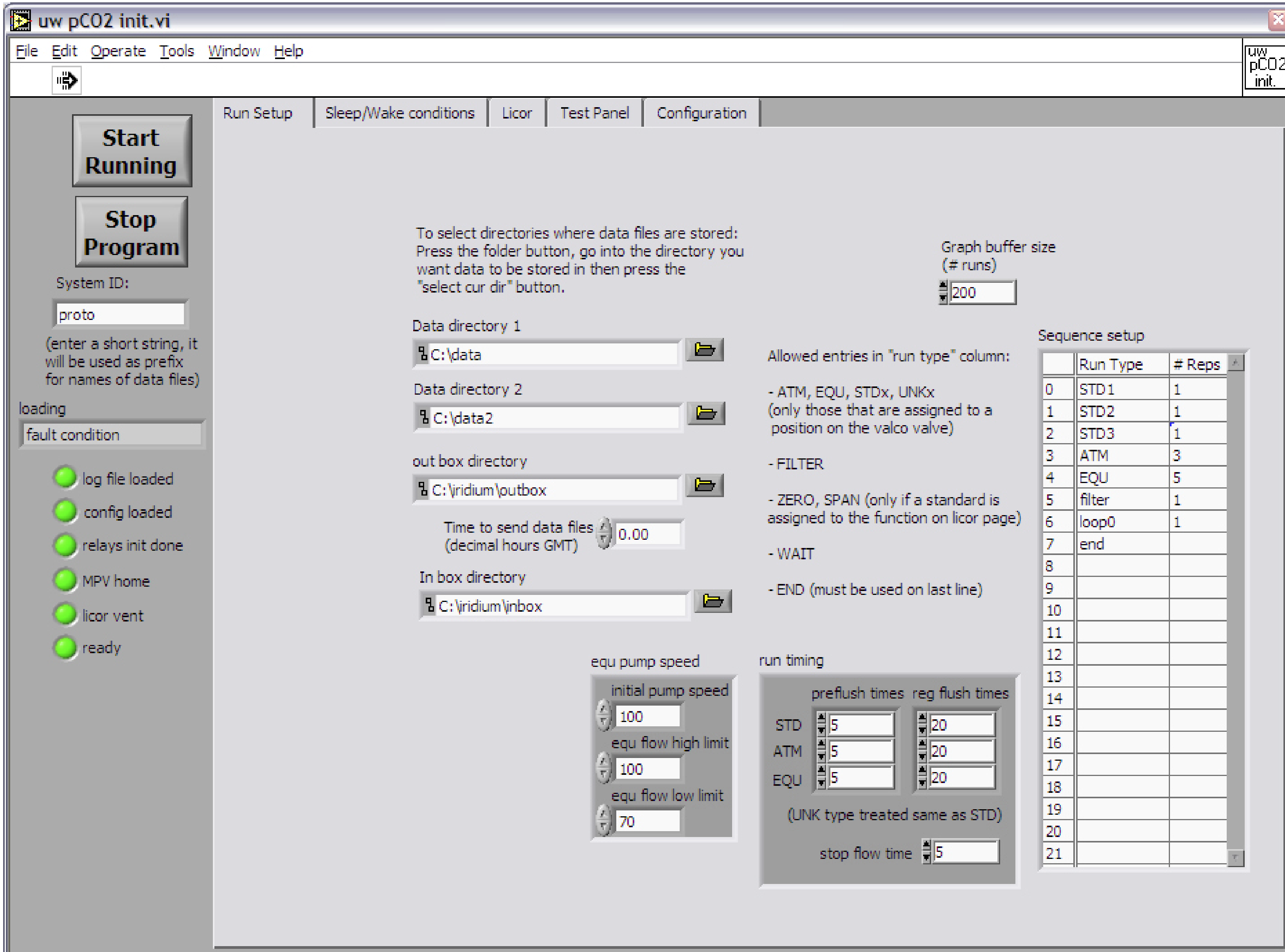
Edit Configuration.exe



Test flow rates (SW, Air, CO_2 STDs) - Important



Run setup


uw pCO2 init.vi
File Edit Operate Tools Window Help
uw pCO2 init.
Start Running
Stop Program
System ID:
proto
(enter a short string, it will be used as prefix for names of data files)
loading
fault condition
log file loaded
config loaded
relays init done
MPV home
licor vent
ready
Run Setup
Sleep/Wake conditions
Licor
Test Panel
Configuration
To select directories where data files are stored: Press the folder button, go into the directory you want data to be stored in then press the "select cur dir" button.
Data directory 1
C:\data
Data directory 2
C:\data2
out box directory
C:\iridium\outbox
Time to send data files (decimal hours GMT)
0.00
In box directory
C:\iridium\inbox
Graph buffer size (# runs)
200
Allowed entries in "run type" column:
- ATM, EQU, STDx, UNKx (only those that are assigned to a position on the valco valve)
- FILTER
- ZERO, SPAN (only if a standard is assigned to the function on licor page)
- WAIT
- END (must be used on last line)
Sequence setup
Run Type
Reps
0 STD1 1
1 STD2 1
2 STD3 1
3 ATM 3
4 EQU 5
5 filter 1
6 loop0 1
7 end
8
9
10
11
12
13
14
15
16
17
18
19
20
21
equ pump speed
initial pump speed
100
equ flow high limit
100
equ flow low limit
70
run timing
preflush times
reg flush times
STD 5 20
ATM 5 20
EQU 5 20
(UNK type treated same as STD)
stop flow time
5

Recommended running sequence

- In the "Edit Configuration.exe" program
  - Condenser set point: 5 °C
  - Condenser drain frequency: 60 to 90 minutes
  - Fan start temperature: 25 °C
  - Fan full speed temperature: 30 °C
- In the "Run Setup" tab of the main program
  - Equilibrator flow high limit: 100 ml/min
  - Equilibrator flow low limit: 70 ml/min
  -
  - Preflush times (for all types): 180 seconds
  - Reg flush times (for all types): 60 seconds
  - Stop flow time : 10 seconds
- Sequence Setup

0	ZERO	1
1	SPAN	1
2	STD1	3
3	STD2	3
4	STD3	3
5	STD4	3
6	ATM	5
7	EQU	100
8	LOOP2	4
9	FILTER	1
10	STD1	3
11	STD2	3
12	STD3	3
13	STD4	3
14	END	

Timings for this sequence:

Zero/Span - Filter	every 10.0 hours
Standards	every 2.5 hours
ATM	every 2.5 hours
EQU	runs for 2.5 hours

Zero and Span: Internal calibration function

- **What and Why Zero and Span?**

Zero gas: CO_2 free gas (air)

Span gas: Highest CO_2 STD

***Important: Span gas should cover the range of xCO_2/pCO_2 to be measured**

Coast: <100 ppm -- tens of thousands ppm

Open ocean: <100 ppm -- 1000 ppm

*Zero/Span: **To determine the coefficients of the calibration function (non-linear)** for the LICOR analyzer to calculate xCO_2 values*

***But Zero/Span calibration is less accurate**

CO_2 STDs gases: More accurate calibration

- **Why measure WMO STDs between two Zero/Span calibrations?**
  IR detector drifts over time

To calibrate more accurately with drift correction between two STDs calibration

Drift correction: linear drift between two STD runs at t_0 & at t_1 (y: STD CO_2 true values; x: LICOR display values)

STDs calibration curve at t_0: $y = a_0+b_0x$

STDs calibration curve at t_1: $y = a_1+b_1x$

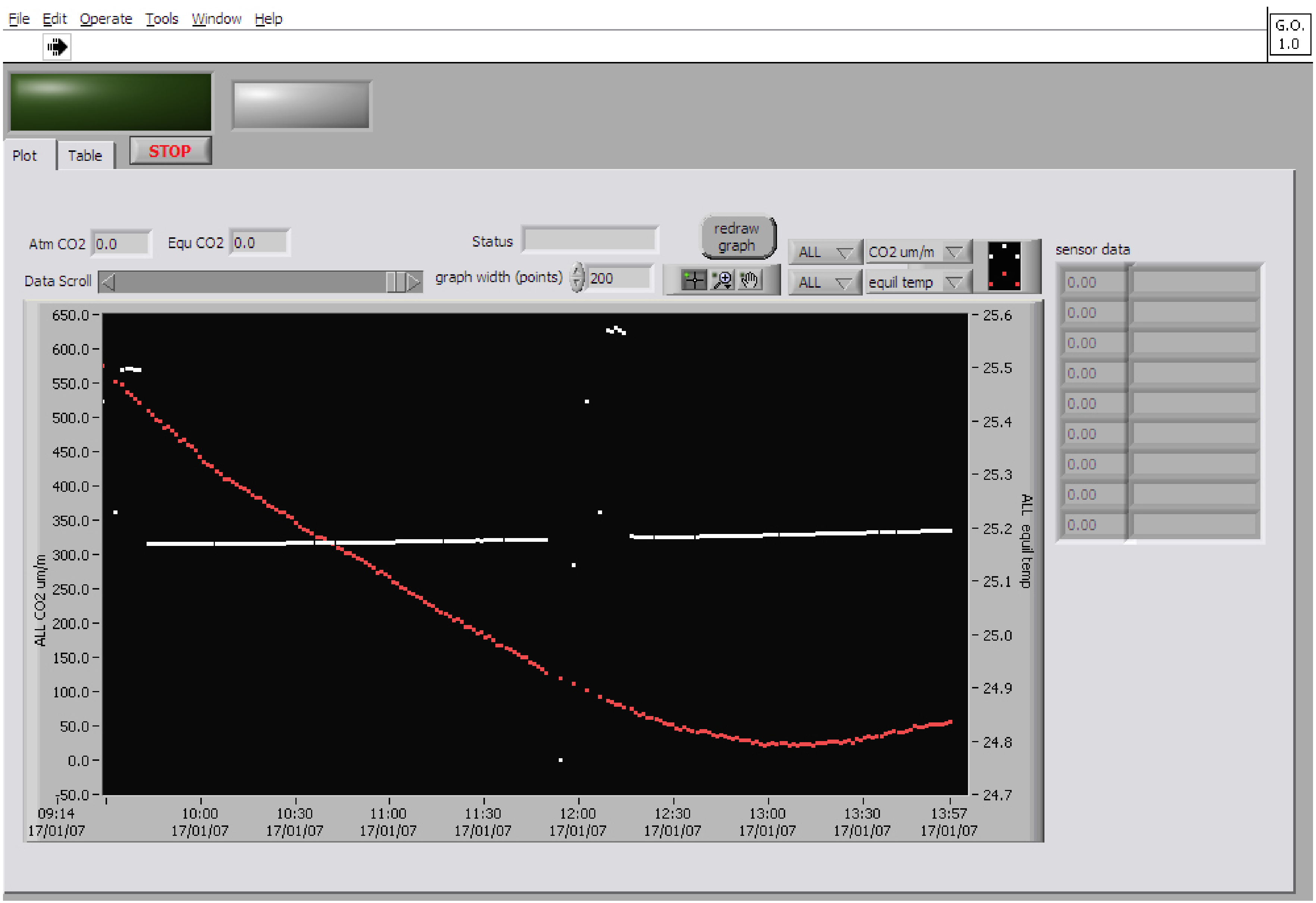
STDs calibration curve at t (between t_0 and t_1)

$$a_t = a_0+(t-t_0)/(t_1-t_0)*(a_1-a_0)$$

$$b_t = b_0+(t-t_0)/(t_1-t_0)*(b_1-b_0)$$

$y = a_t + b_t x$ *or* ***Refit a linear STD curve***

Running display



Data processing

- From dry xCO_2 to dry pCO_2 (if needed)

$$p(\mathrm{CO_2})_{T_\mathrm{E},\mathrm{dry}} = x(\mathrm{CO_2}) \cdot P_\mathrm{eq}$$

- Correction of water vapor

$$p(\mathrm{CO_2})_{T_\mathrm{E},\mathrm{wet}} = x(\mathrm{CO_2})\left[P_\mathrm{eq} - VP(\mathrm{H_2O})\right]$$

- Convert to CO_2 fugacity (fCO_2)

$$f(\mathrm{CO_2})_{T_\mathrm{E}} = p(\mathrm{CO_2})_{T_\mathrm{E},\mathrm{wet}} \cdot \exp\left[\frac{\left(B(\mathrm{CO_2})_{T_\mathrm{E}} + 2\cdot\delta(\mathrm{CO_2})_{T_\mathrm{E}}\right)p_\mathrm{atm}}{R \cdot T_\mathrm{E}}\right]$$

- Correction of temperature

$$f(\mathrm{CO_2})_{T_\mathrm{S},\mathrm{wet}} = f(\mathrm{CO_2})_{T_\mathrm{E},\mathrm{wet}} \cdot \exp\left[0.0423(T_\mathrm{S} - T_\mathrm{E})\right]$$

Necessary for CO_2 flux calculation

Data quality

- Flow rates should be in the normal ranges:

  SW flow rate

  air sample flow rate

  STDs flow rates…

- Stability of STDs

- Repeatability of samples

  -- Can use air sample measurements as a cue

Maintenance

- Follow recommended replacement schedule
- Check leaks of gases regularly
- Clean underway pipeline regularly (no respiration)
- Equilibrator and water filter cleaning (freshwater backflush regularly)
- Air sampling, avoid contamination (away from smokes, rain/water clog etc.)
- Data backup regularly

Reference sources

- Dickson, A. G., C. L. Sabine, and J. R. Christian. 2007. Guide to best practices for ocean CO_2 measurements. North Pacific Marine Science Organization. https://www.nodc.noaa.gov/ocads/oceans/Handbook_2007.html

- GO pCO_2 system manual
- LICOR 7000 CO_2 Analyzer manual

Thank you