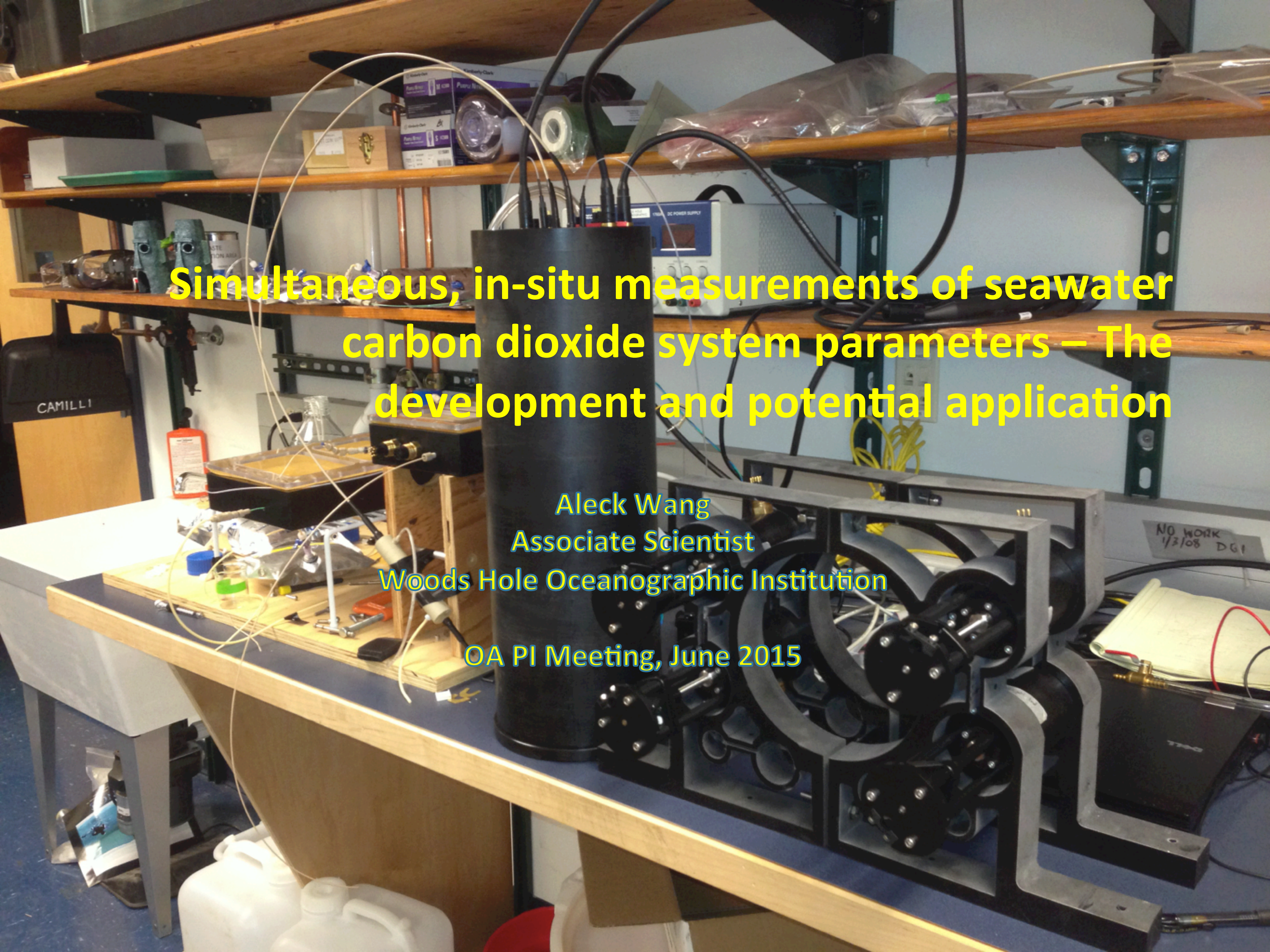

Simultaneous, in-situ measurements of seawater carbon dioxide system parameters – The development and potential application

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Woods Hole Oceanographic Institution

OA PI Meeting, June 2015

Accknowledgement

Funding: NIST, NSF, WHOI Green Tech Award

Collaborator:
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Gareth Lawson, WHOI

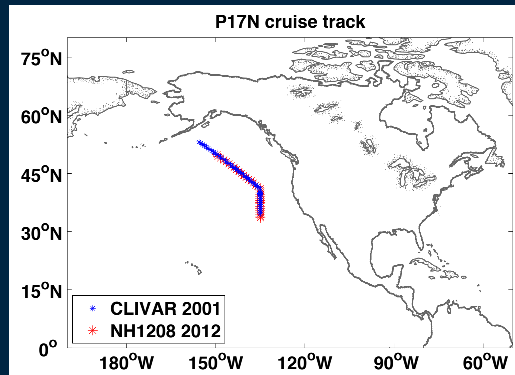
Development Team:

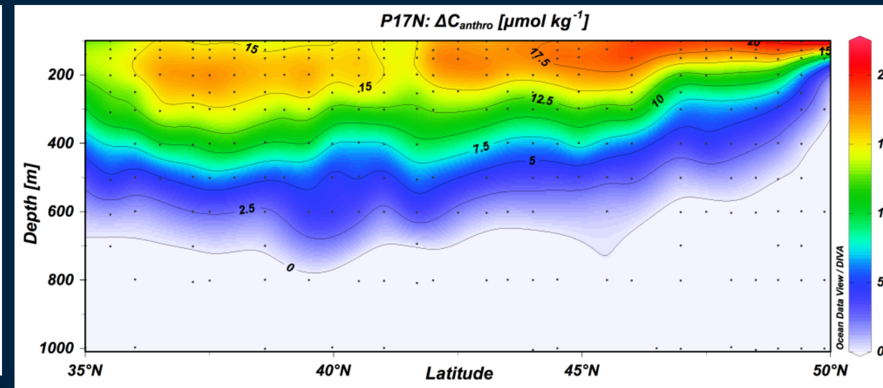
Engineers: Fritz Sonnichsen, Al Bradley, Tom Lanagan, Terry Hammar, Kevin Manganini, Norm Farr

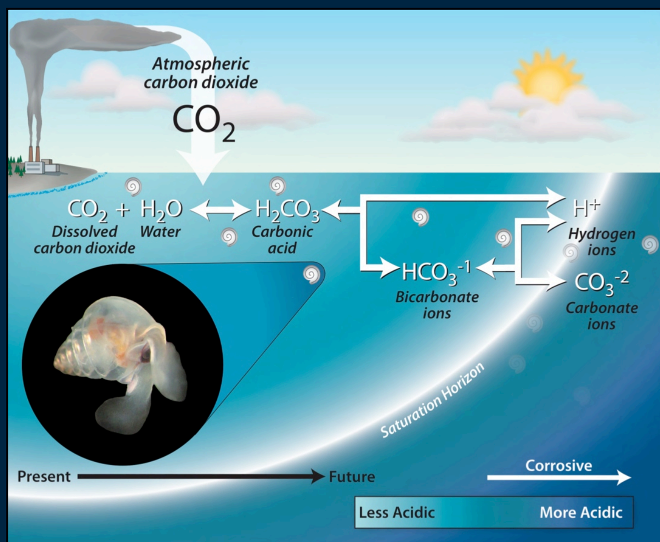
Chemists: Katherine Hoering, Sophie Chu, Jacinta Edebeli,, Lenna Quackenbush

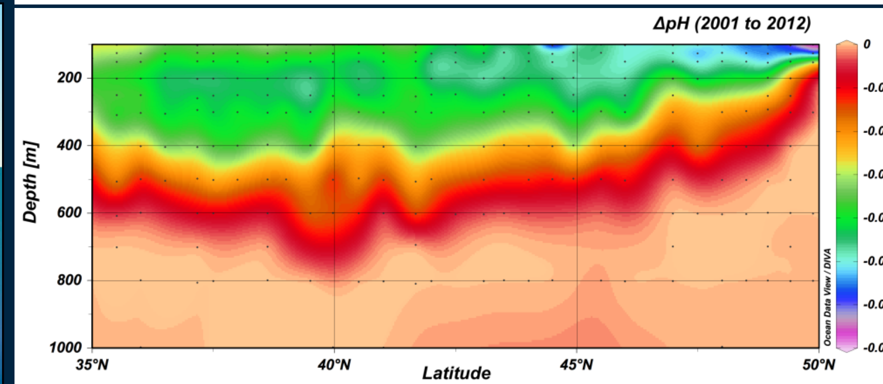
CO_2 Invasion and Ocean Acidification (OA)

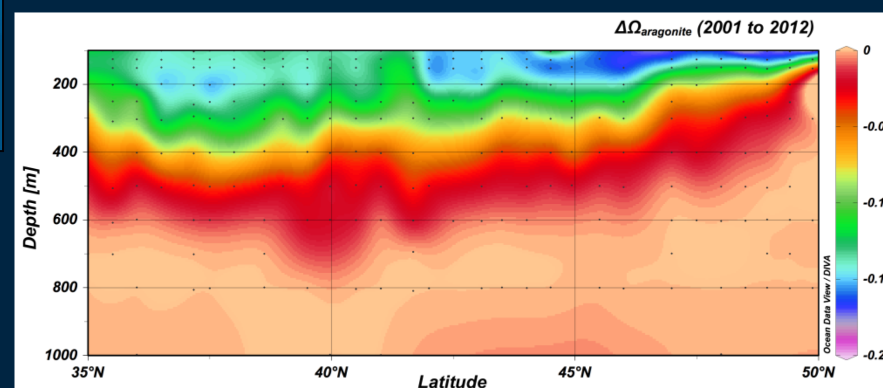
What is the signal we want to detect?









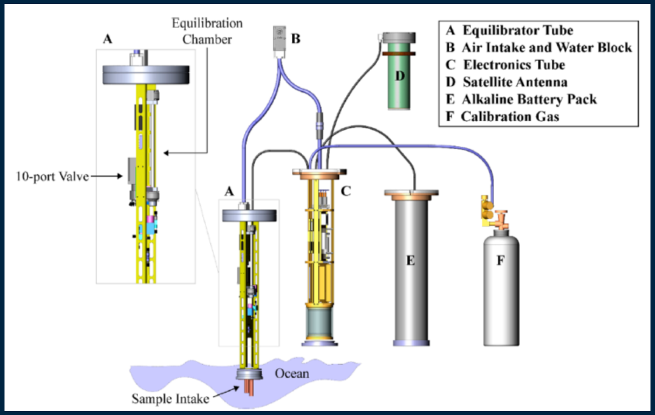


- ✓ **OA is a relatively small signal in terms of what we can measure**
- ✓ **Cost to do this transect over two cruises: >$3M**

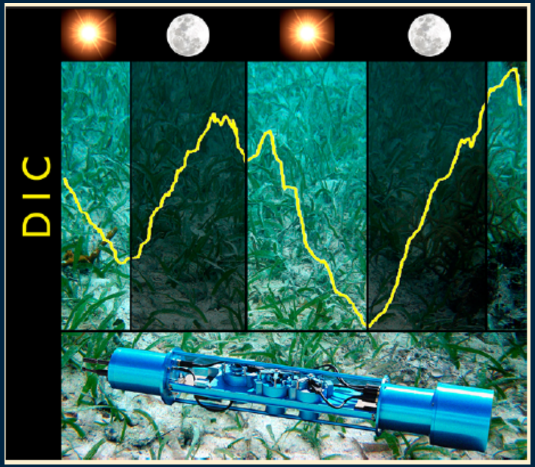
Chu, Wang, Lawson in prep

New In-situ DIC and TA Sensors

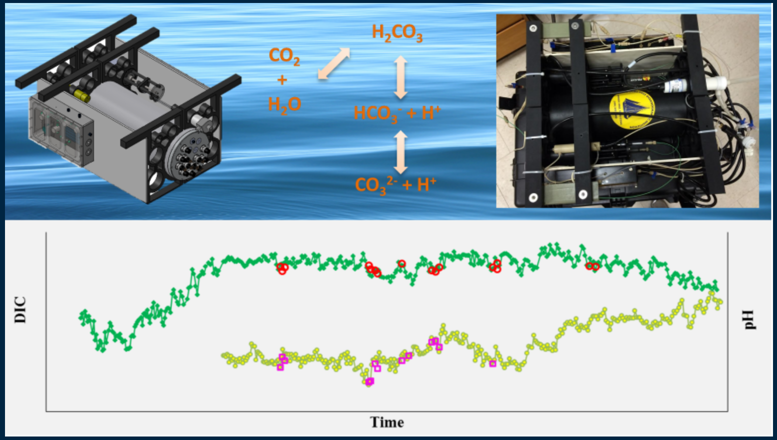
Robotic Analyzer for the TCO_2 System (RATS). Sayles et al (2009, DSR), recent pH addition by W. Martin and D. McCorkle.



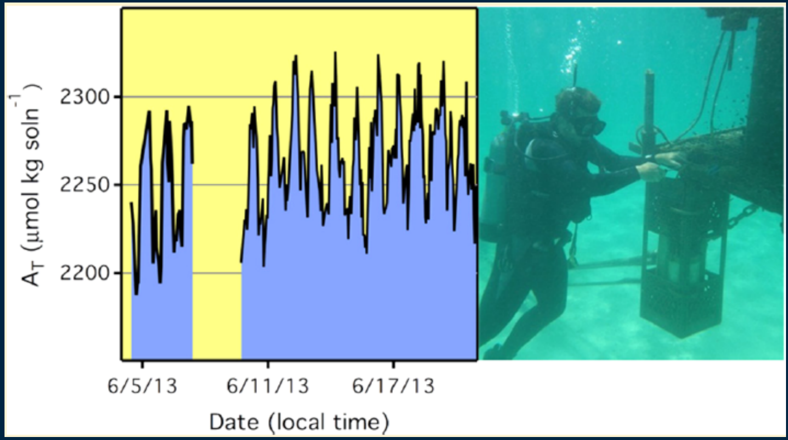
Moored Autonomous DIC (MADIC). Fassbender et al. 2015, ES&T.



Spectrophotometric Elemental Analysis System - DIC (SEAS-DIC). Liu et al. 2013, ES&T.

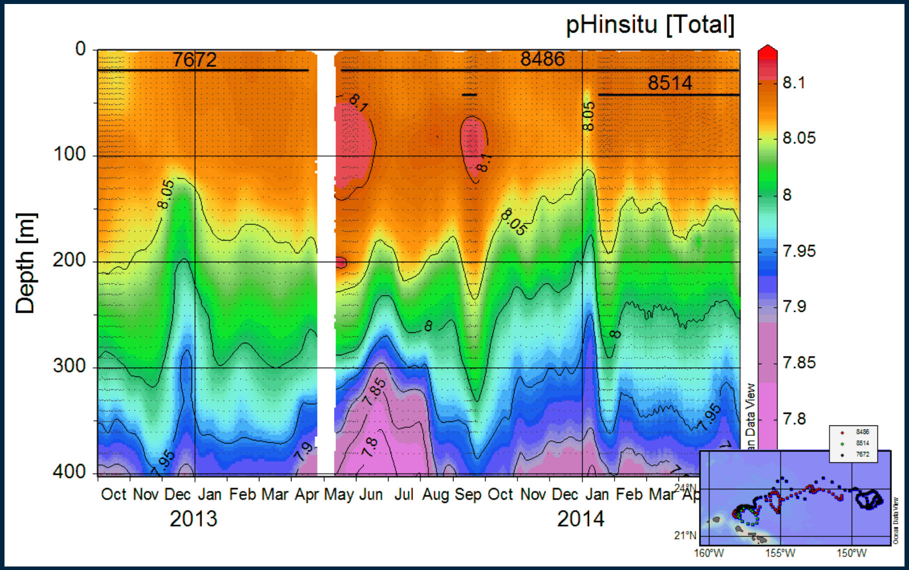


Channelized Optical System (CHANOS) for DIC and pH. Wang et al. 2015, ES&T.



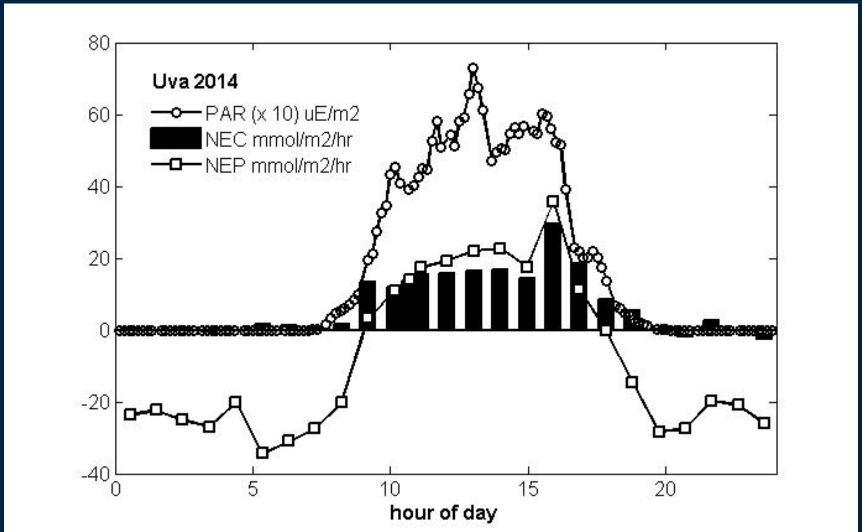
Submersible Autonomous Moored Instrument for alkalinity (SAMI-alk). Spaulding et al. 2014, ES&T

Deep-Sea DuraFET pH



http://www.mbari.org/chemsensor/teamdurafet/

Net Ecosystem Productivity and Net Ecosystem Calcification



From W. McGillis

Carbon Sensor Development to Address Two Challenges

Challenge 1:

- Requirement: Need to measure two of the four CO_2 parameters to fully define the CO_2 system; Which pair to choose makes difference

Analytical Errors (Best Practice)

Table 8. Estimates of the Analytical Precision and Accuracy of Measurements of pH, TA, TCO_2, and pCO_2

analysis	precision	accuracy	ref
pH (spectrophotometric)	±0.0004	±0.002	42
TA (potentiometric)	±1 μmol kg^{-1}	±3 μmol kg^{-1}	29
TCO_2 (coulometric)	±1 μmol kg^{-1}	±2 μmol kg^{-1}	96
f_{CO_2} (infrared)	±0.5 μatm	±2 μatm	97

Calculation Errors

Table 9. Estimated Probable Errors in the Calculated Parameters of the Carbonate System Using Various Input Measurements

input	pH	TA (μmol kg^{-1})	TCO_2 (μmol kg^{-1})	f_{CO_2} (μatm)
pH−TA			±3.8	±2.1
pH−TCO_2		±2.7		±1.8
pH−f_{CO_2}		±21	±18	
f_{CO_2}−TCO_2	±0.0025	±3.4		
f_{CO_2}−TA	±0.0026		±3.2	
TA−TCO_2	±0.0062			±5.7

Problem: only pH and pCO_2 sensors are readily available, but DIC and TA sensors is much less mature

Millero 2007

Carbon Sensor Development

Challenge 2:

- Except pH, all other measurements have long response times (many minutes) → long measurement cycles → Not ideal for mobile platforms (AUV, ROV, gliders etc.) and highly dynamic environments (e.g. coastal oceans, estuaries)

  DIC, pCO_2/fCO_2 methods: 5-15 minutes (CO_2 equilibrating or extracting processes)

  TA method: ~10 minutes (titration)

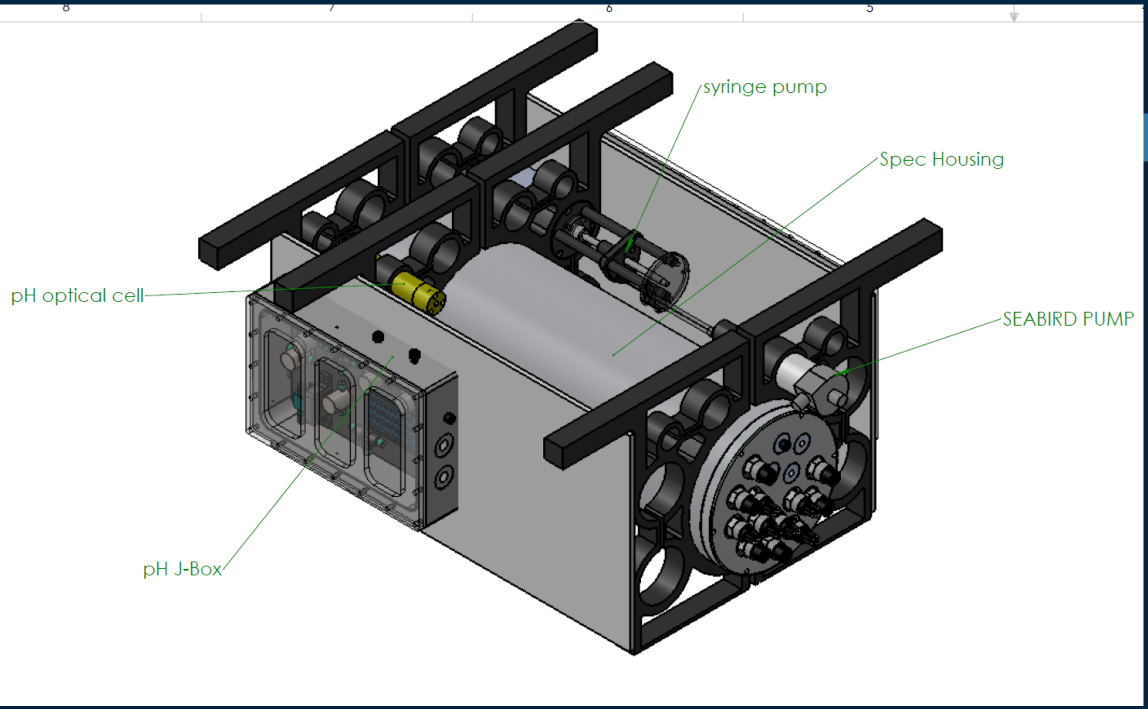
Development Strategy: using spectrophotometric methods

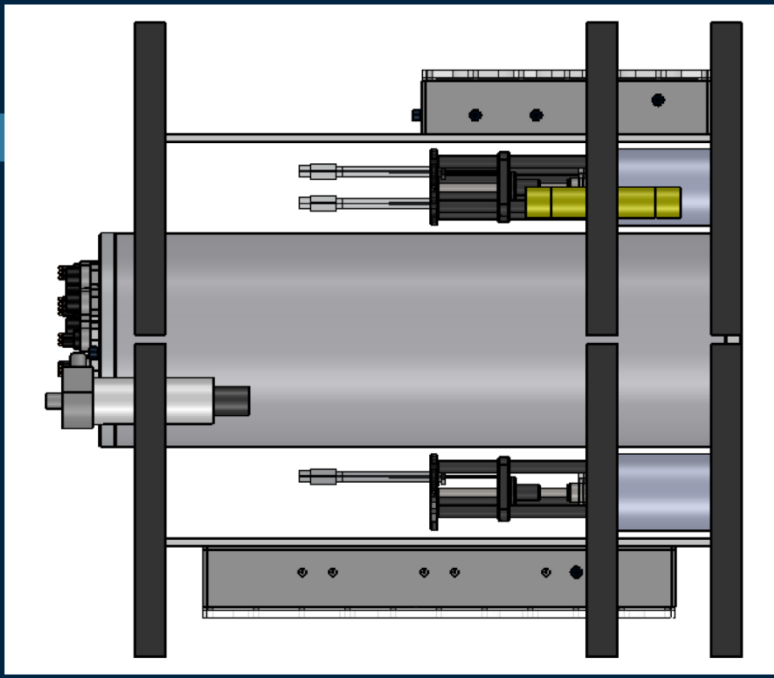
- ✓ Simultaneous measurements of pH and DIC
- ✓ High-frequency, flow-through measurements

Advantages:

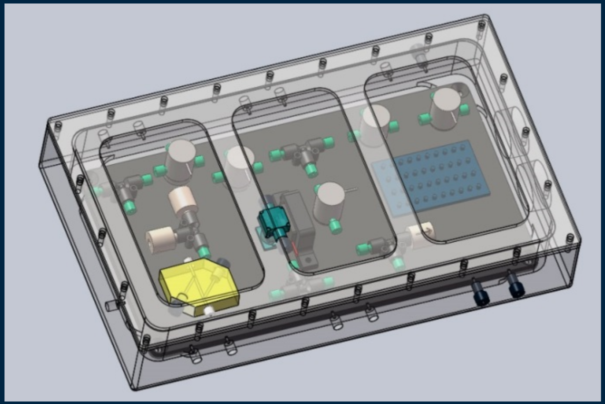
- ✓ Fully resolve the CO_2 system, with good calculation accuracy
- ✓ Sensitive
- ✓ Similar spectrophotometric principles (spec pH), modular
- ✓ Direct measurements of water, deep deployments

Channelized Optical System (CHANOS) for Simultaneous, In-situ Measurements of Seawater DIC and pH



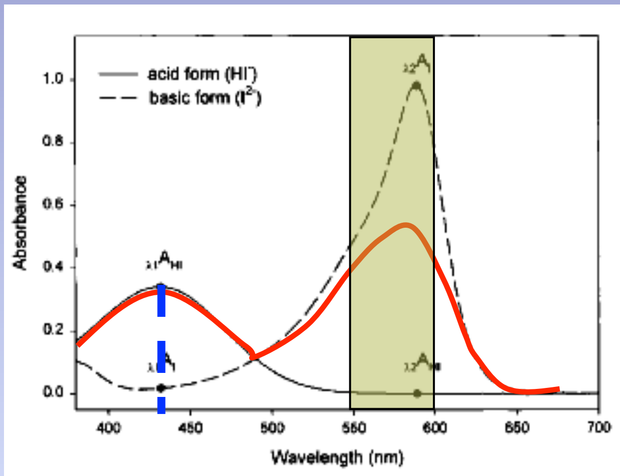


- ❑ Syringe Pumps: precise reagent delivery, small reagent consumption; not continuous (time-series)
- ❑ Two oil filled J-boxes for two channels
  - Fluid handling sub-system
  - ✓Pressure compensated
  - ✓Protection
  - ✓Independent channels



40 × 20 cm

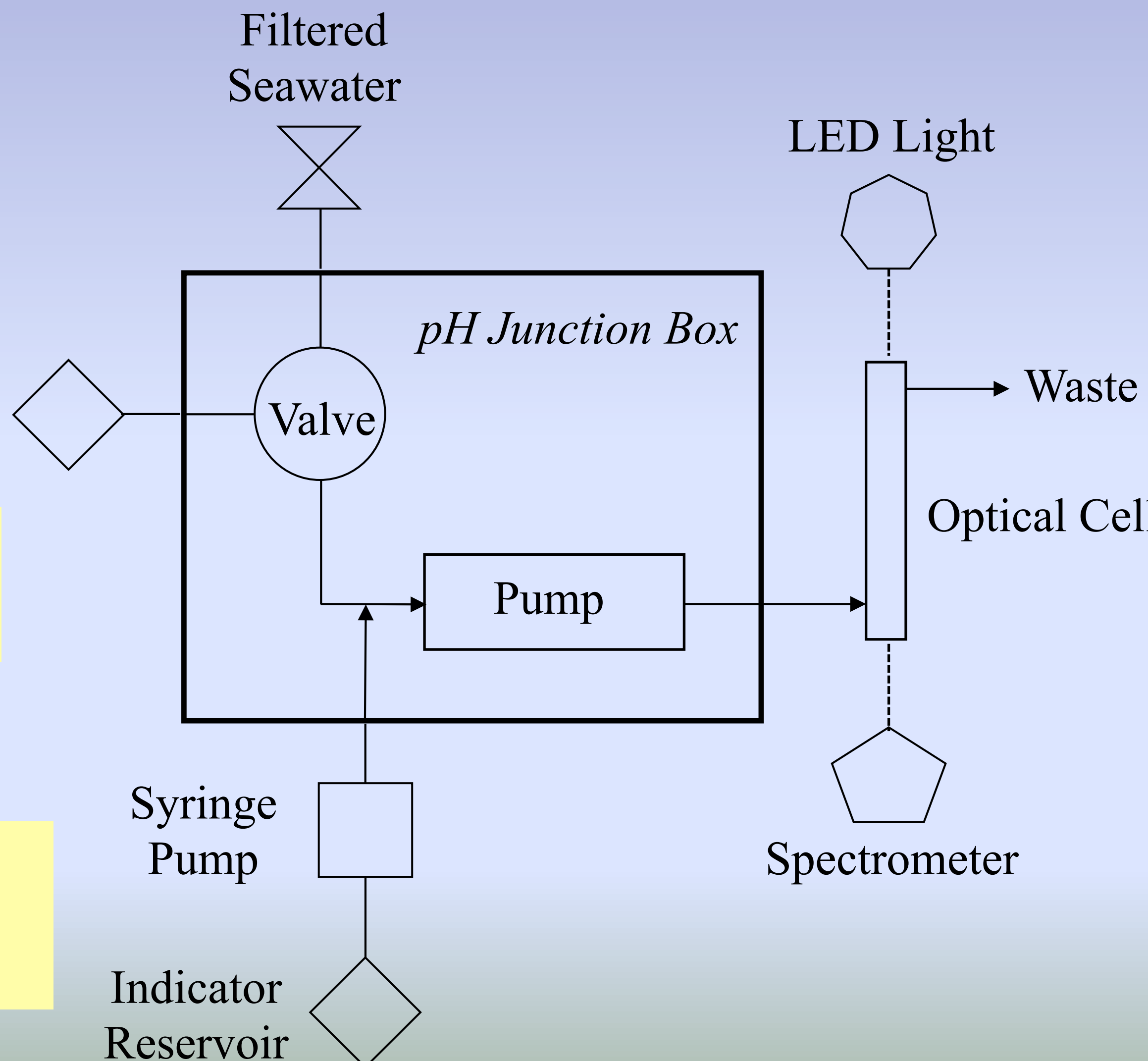
pH channel schematic (Flow-through method)



$$\mathrm{pH} = \mathrm{pK_{II}} + \log \frac{[\mathrm{I^{2-}}]}{[\mathrm{HI^-}]}$$

$$\mathrm{pH} = \mathrm{pK_{II}} + \log \frac{\mathrm{R} - e_1}{e_2 - \mathrm{R}e_3}$$

$R = {}_{\lambda 2}A_I / {}_{\lambda 1}A_{HI}$ (measured)
e_1, e_2, e_3: molar absorbance ratios
K_{II}: dissociation constant



Typical Principle of DIC Measurements for In-situ Sensors

CO_2 exchange / equilibrium **(~5 - 10 minutes)**

Acidified Water Sample
(carbonate species → dissolved CO_2)

Indicator, base, or CO_2 free air

$f(CO_2)_{ex}$

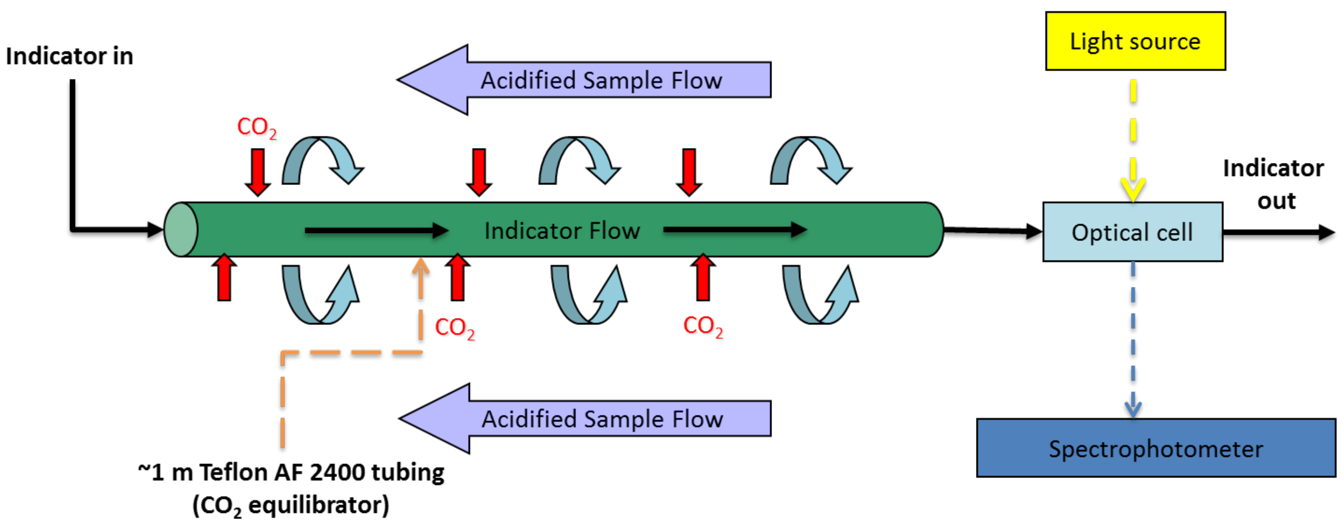
$f(CO_2)_i$

$f(CO_2)_{ex} = f(CO_2)_i$

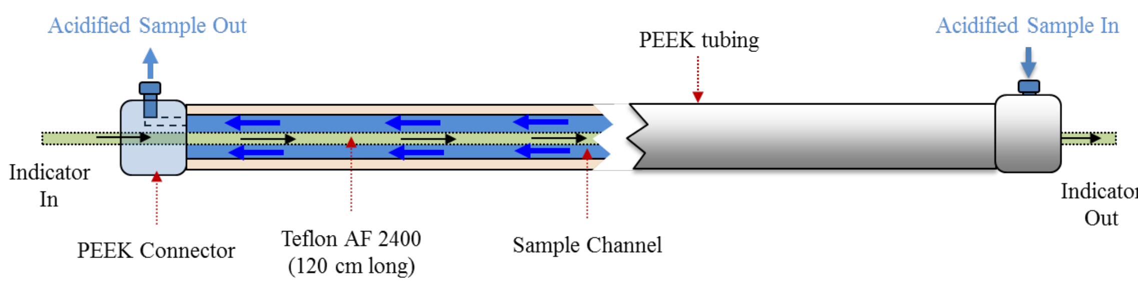
Spectrophotometric
Conductimetric
Or Infrared detection

Membrane: e.g. silicone, Teflon AF, PTFE

High-frequency spectrophotometric DIC (pCO_2) measurement:



(Wang et al. 2013, ES&T)



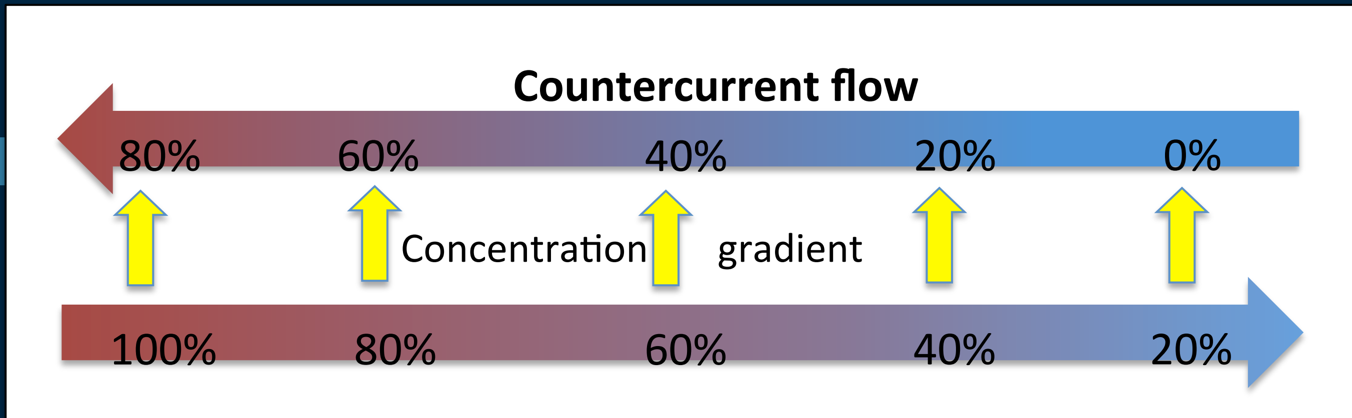
$$\log\left(p \times \frac{[\mathrm{DIC}]}{(K_0)_a}\right) = B(t) - \log(K_0)_i - \log\left(\frac{R - e_1}{1 - Re_3 / e_2}\right),$$

$\log(p \times fCO_2)_a$ $\qquad$ $\log(fCO_2)_i$

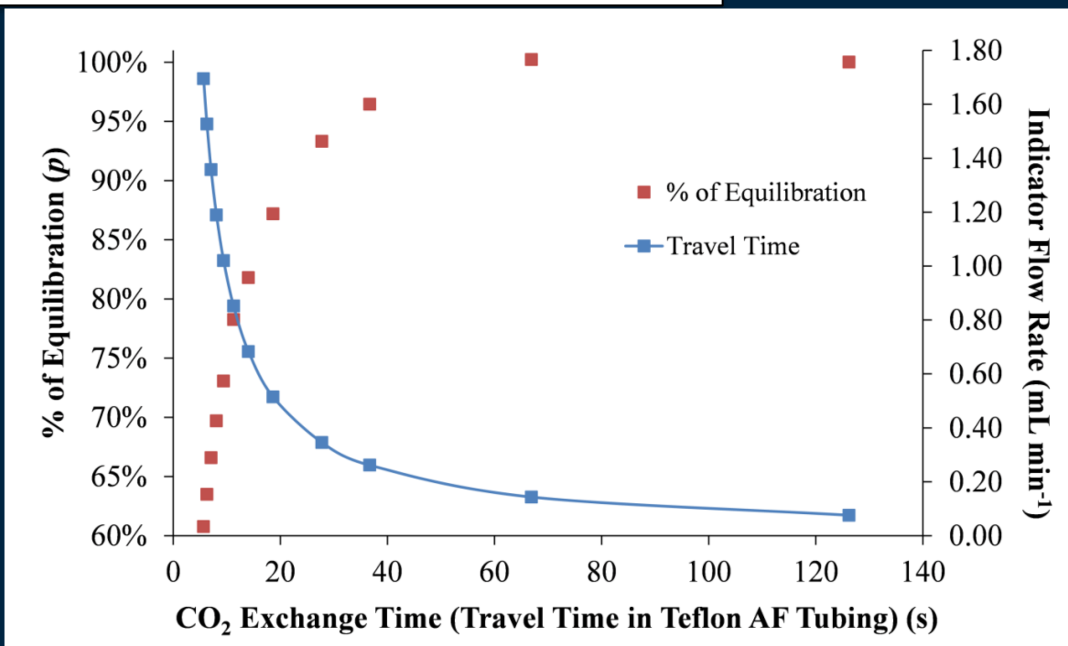
Calibration variables
p – percentage equilibration
B(t) – constant

(Modified from Byrne et al. 2002)

Advantages of Countercurrent flow

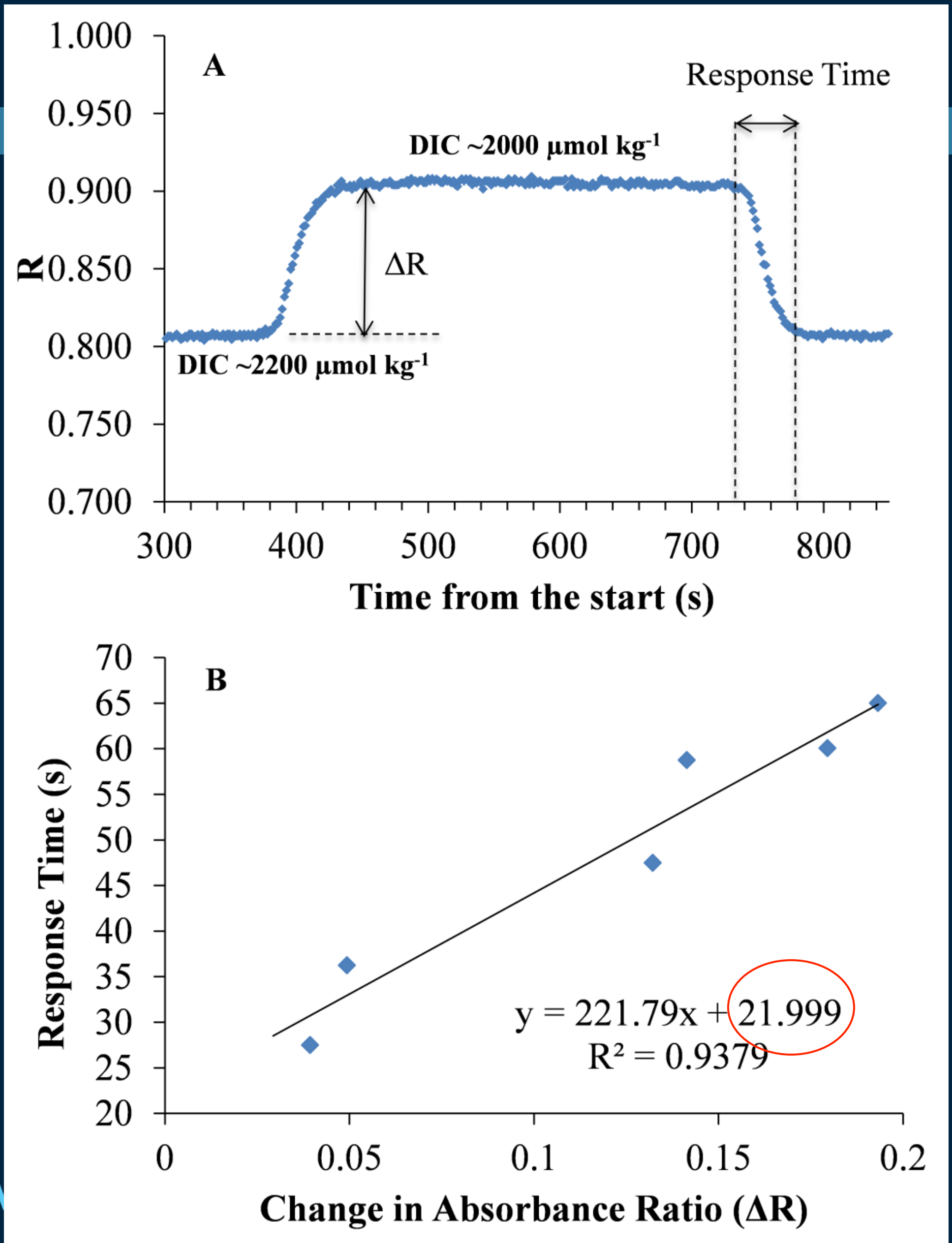


- ✓ Improve diffusion efficiency
- ✓ Partial to full CO_2 equilibrium on the fly
- ✓ Allow flow-through measurements and continuous recording
- ✓ Avoid using Teflon AF as optical cell (sometimes not stable)



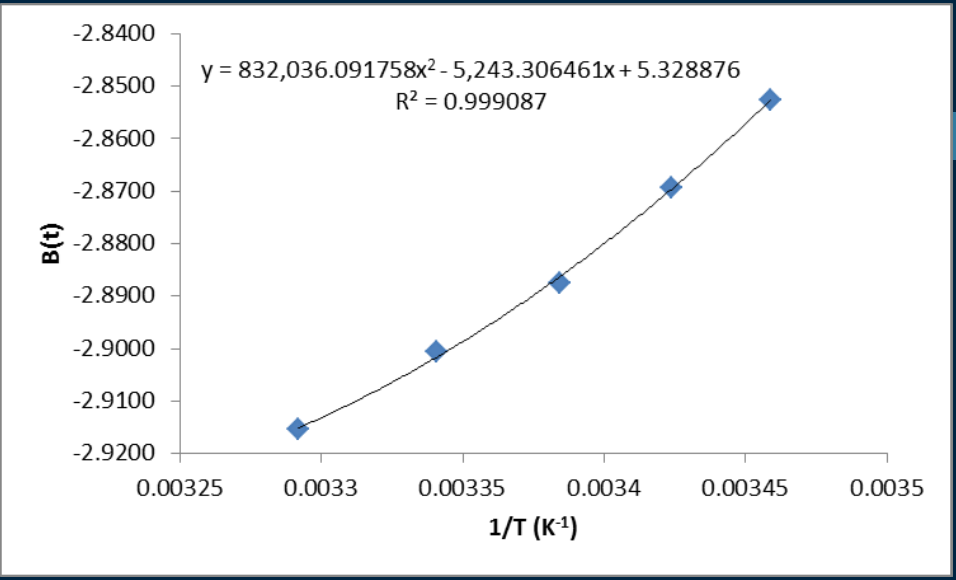
Full equilibrium: ~70s

Under partial equilibration, response time is much faster

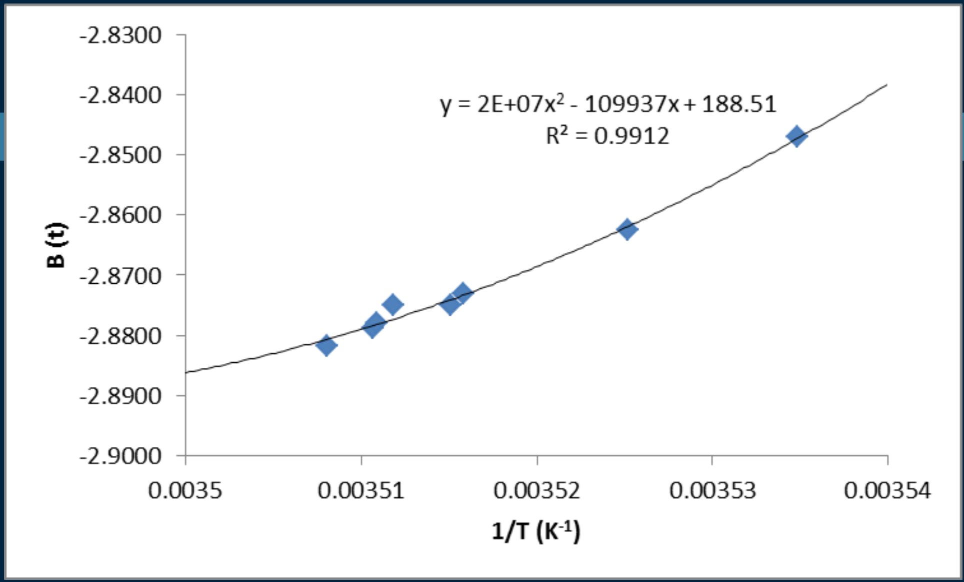


Intercept time ~22s → flushing time
Response time <22s upper limit,
Near continuous

CHANOS DIC calibration on temperature effect



Lab Calibration

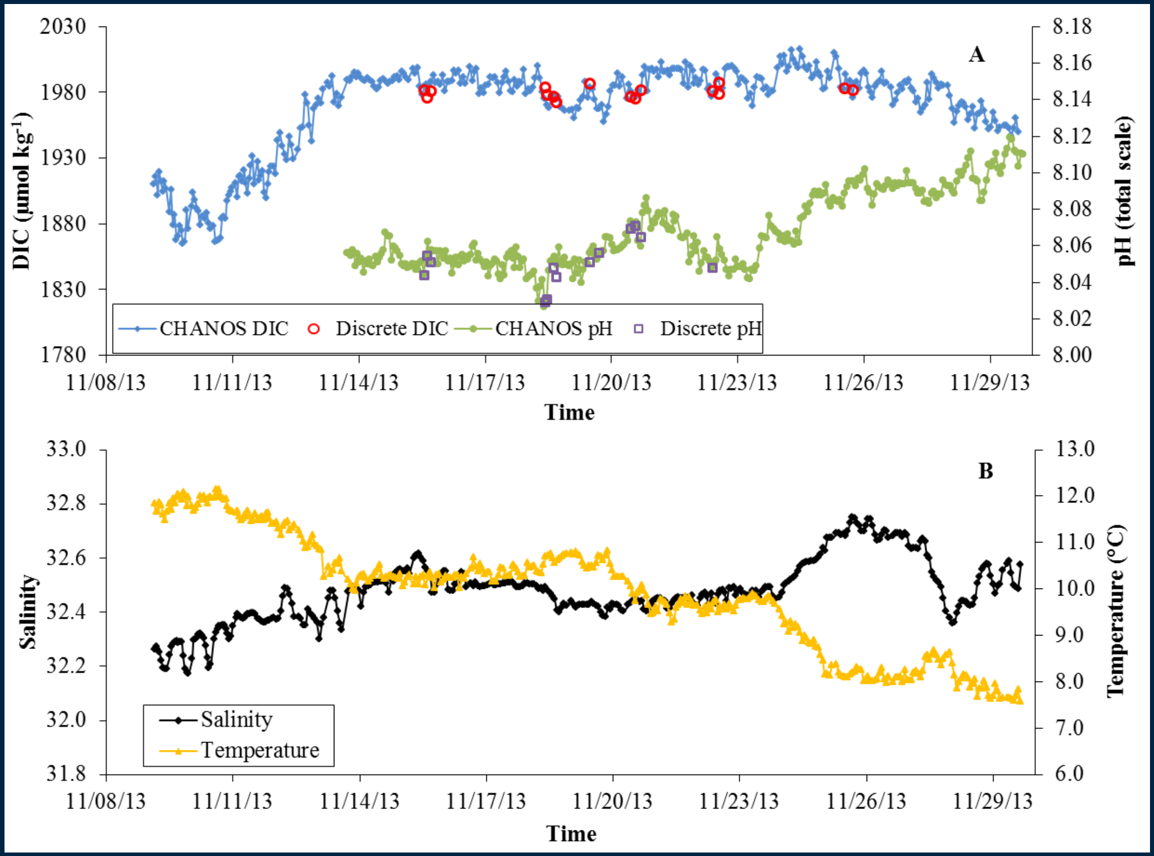


In-situ Calibration

In-situ calibration using Certified Reference Materials (CRMs):

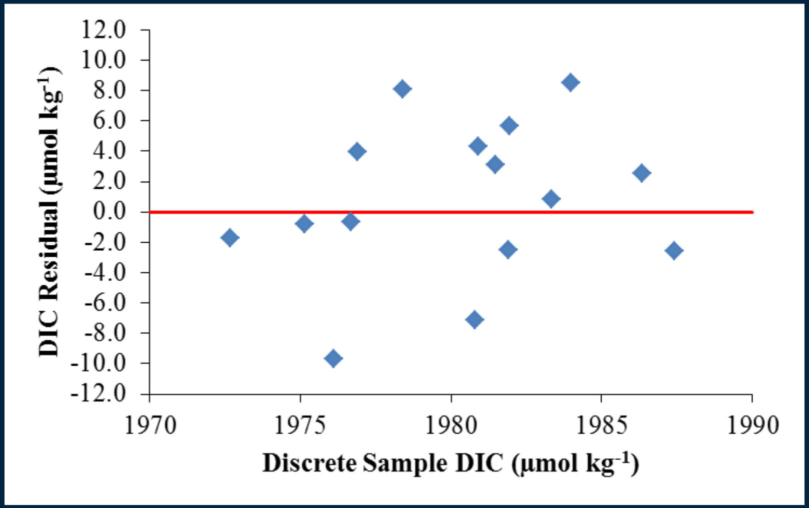
- ✓ **Reduce lab calibration that may be different from the field**
- ✓ **Ensure measurement quality**
- ✓ **Evaluate in-situ accuracy**
- × **Make the system complex**

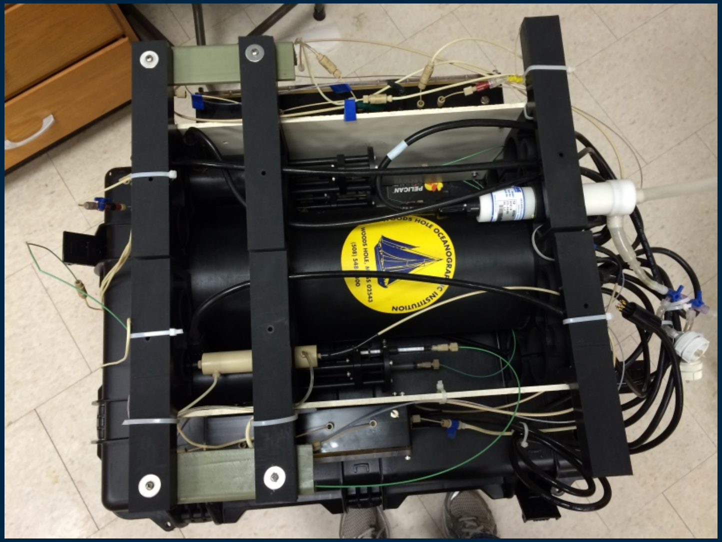
CHANOS In-situ Testing at the WHOI Dock

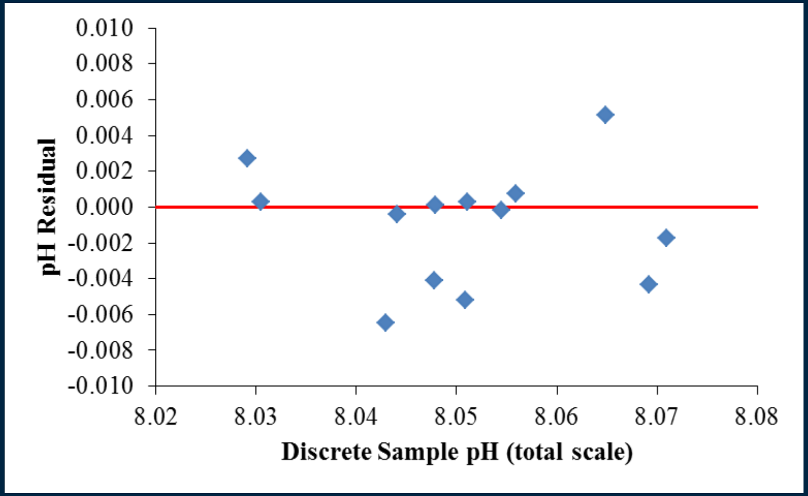


- ✓ Total ~2 months, 1st month functionality, 2nd month measurements
- ✓ Placed in a pelican case for antifouling
- ✓ Copper mesh filtering
- ✓ Co-deployed with CTD
- ✓ Discrete bottle sampling for DIC and pH

Data Comparison, Precision, and Accuracy







Sensor vs. bottle (1σ difference):

DIC: 0.8±5.2 µmol/kg for DIC and

pH -0.001±0.003

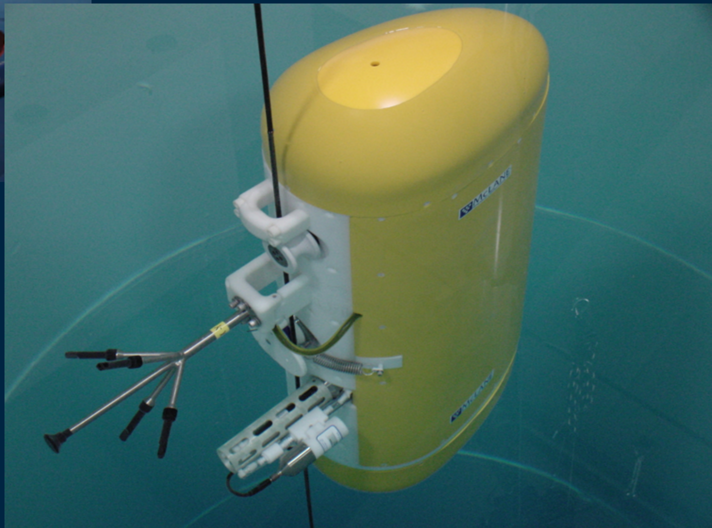
Summary and Comparison of CHANOS Measurements

	RATS	SEAS-DIC	MADIC	SAMI-alk	CHANOS
Parameters measured	DIC and pH	DIC	DIC	Alk	DIC and pH
Principle	Conductometric DIC; Spectrophotometric pH	Spectrophotometric	Infrared	Tracer based spectrophotometric	Both spectrophotometric
Measurement cycle time	Hourly	Preparation and equilibration ~9 min, measurement every minute afterwards for 50 min; repeat	~12 min	~12 min	Preparation 2-6 min, flow-through measurements every ~12s for ~6-8 min afterwards; repeat
Precision	±2.7 μmol kg^{-1}; pH ±0.001?	±2 μmol kg^{-1}	±5.0 μmol kg^{-1}	±4.7 μmol kg^{-1}	DIC ±2.5 μmol kg^{-1} pH ±0.0010
Accuracy (in situ)	±3.6 μmol kg^{-1}; pH ±0.003?	±2 μmol kg^{-1}	±6 – 7 μmol kg^{-1}	−2.2 ± 13.1 μmol kg^{-1}	DIC ±5.2 μmol kg^{-1} pH ±0.0024
Reported deployment time	8 weeks	~8 days	~8.5 months	~1 month	3 weeks
Calibration / quality control	Lab and in situ calibration with CRM	Lab calibration with CRM	Lab and in situ calibration with CO_2 gas	Lab and in situ calibration with CRM	Lab and in situ calibration with CRM
Deployment mode	Time-series	Time-series	Time-series	Time-series	Time-series

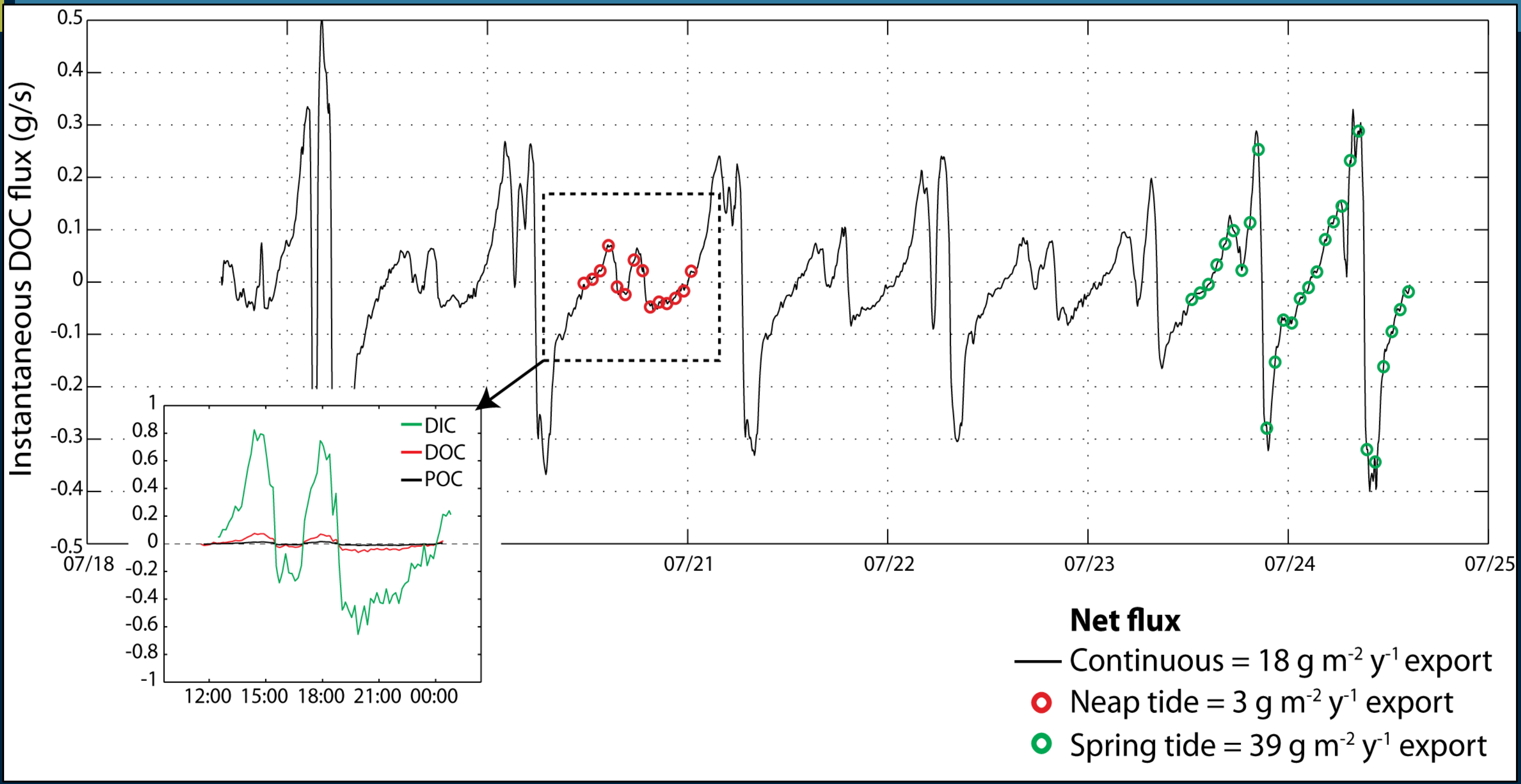
Under Development

- A continuous in-situ DIC sensor for mobile platforms (e.g. AUVs, ROVs, CTD cast).

Go mobile!

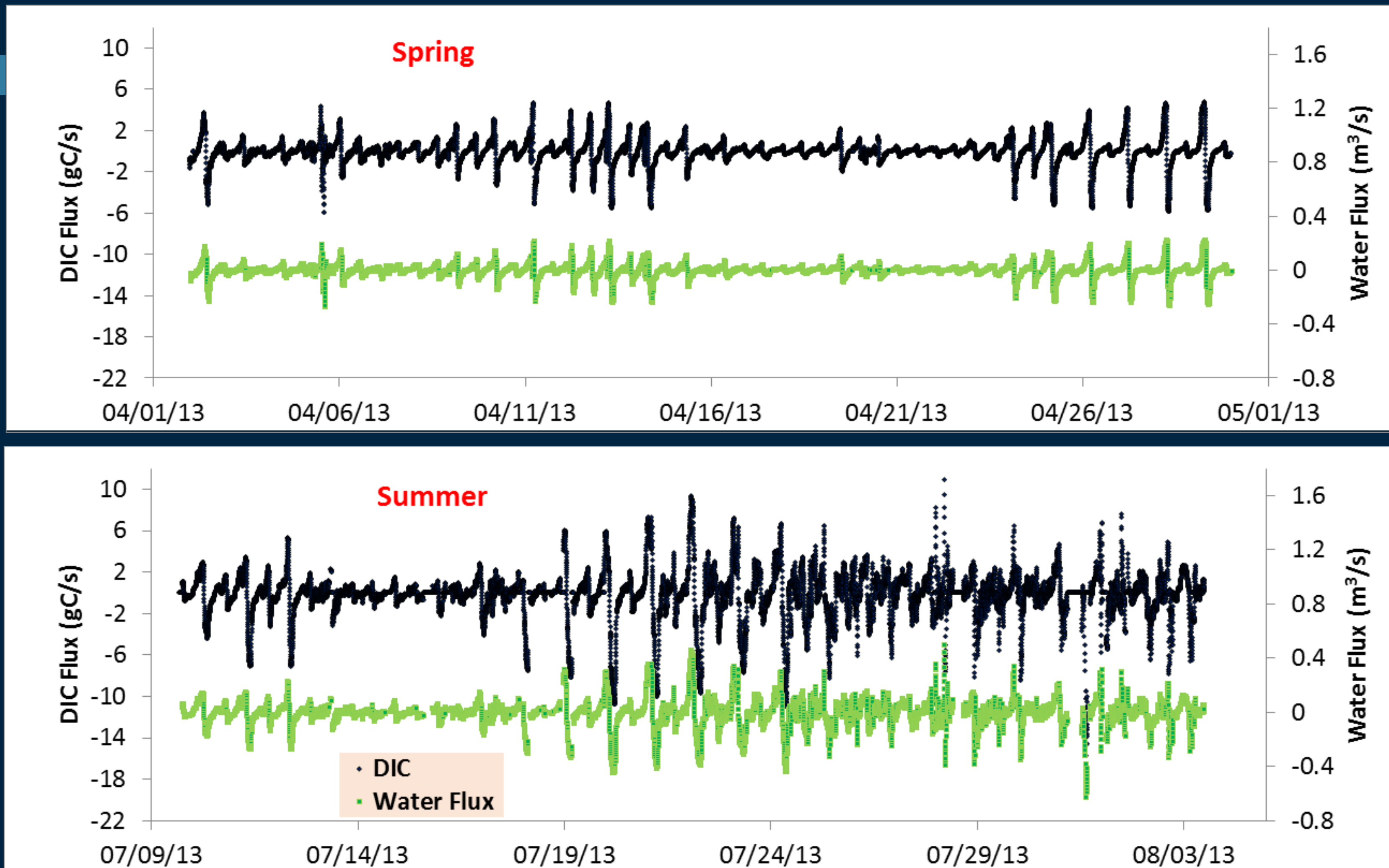


The need for high-resolution measurements
New project: Quantify highly variable DIC flux exported from intertidal salt marsh systems



Variability: daily tidal cycles, spring-neat tides, seasonal, episodic events

Variabilities of DIC Flux from Salt Marshes



Thanks for your attention