Measuring Ocean Acidification in Blue and Green Waters: *Capabilities and Challenges*

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Outline

1. Measurement Capabilities and Limitations
2. Lessons Learned from Internal Consistency Evaluations
3. Challenges in the Coastal Zone (heterogeneity and non-carbonate alkalinity)
4. Remedy for Monitoring-Challenges Created by High Spatial and Temporal Variability
5. Remedy for Problems Created by Total-Alkalinity Ambiguities

What CO_2 System Parameters Should Be Measured?

Characteristics of Current Measurements

Parameter	Precision	Calibration	Matrix Effects
DIC	± 1-2 μM	CRM	No
TA	± 2-4 μM	CRM	Yes
pH	± 0.0004-0.0010	Internal	No (?)
fCO_2	± 0.1%	Gas standards	No
$[CO_3^{2-}]$	± 2%	Internal	No (?)
Ω	Highly variable	No direct observation	Possibly

Selection of Measured Parameters

Choices should be made in view of measurement resolution

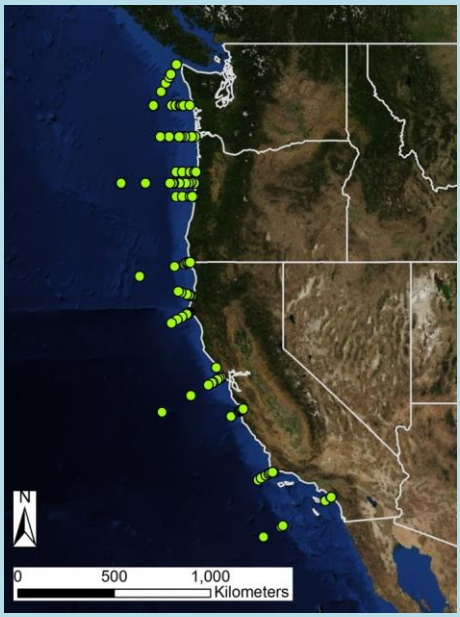
Parameter	Range	Precision	Range/Precision
pH	0.8	0.0004	2000
DIC (μmol/kg)	500	1	500
TA (μmol/kg)	220	2	110
pCO_2 (μatm)	1840	1	1840

J.-Z Zhang (2000) *Mar. Chem.* 70: 121-131

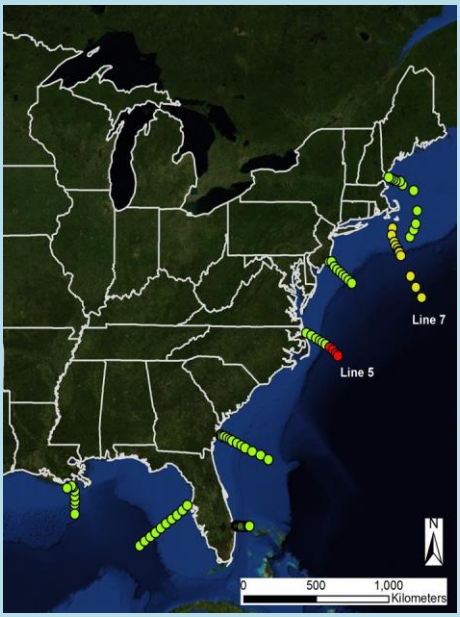
Lessons Learned From Redundant Measurements

Internal Consistency and Saturation State Measurements

W1108C Cruise Track

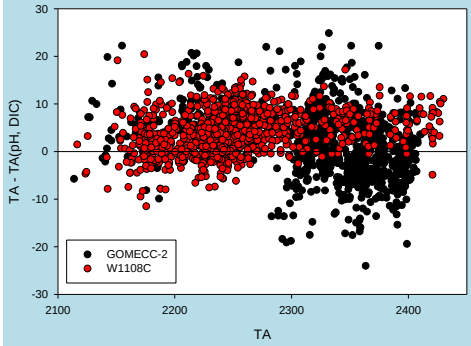


GOMECC-2 Cruise Track

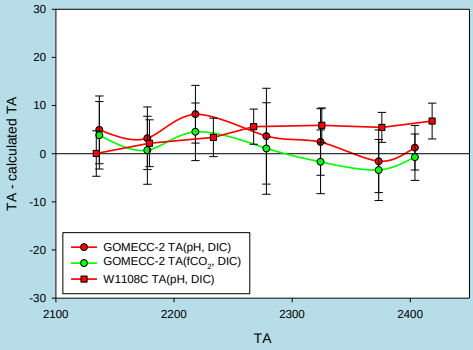


b

TA Residuals

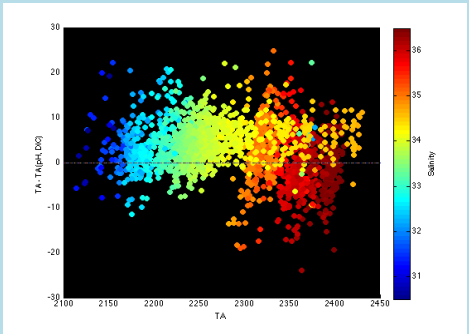


Binned TA Residuals

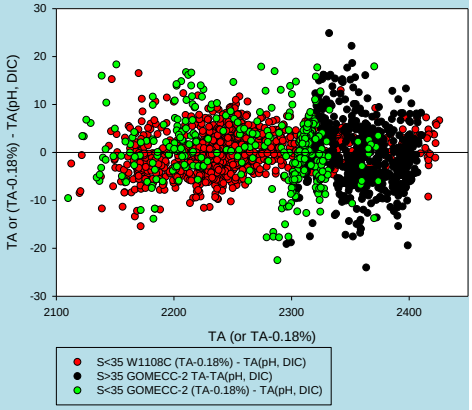


Patsavas et al. (2014)

TA Residuals (the salinity effect)

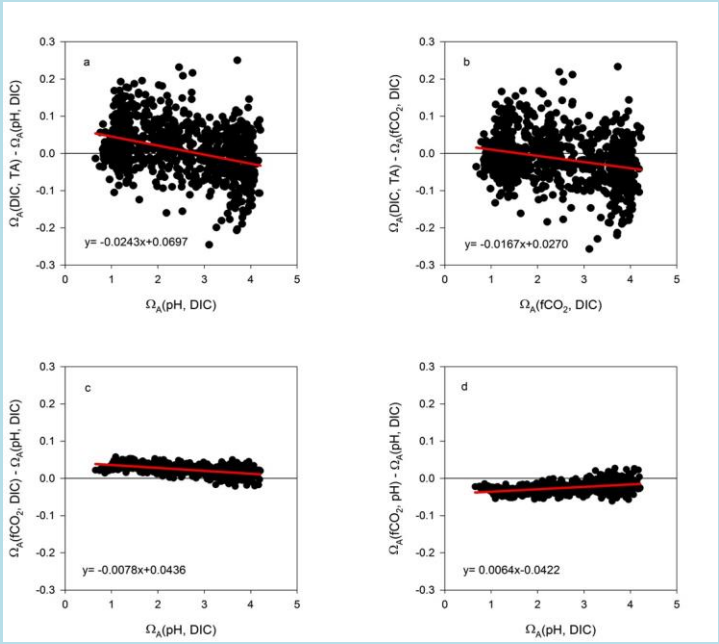


TA "corrected" for Organic Bases



Patsavas et al. (2014)

GOMECC-2 Saturation State Residuals



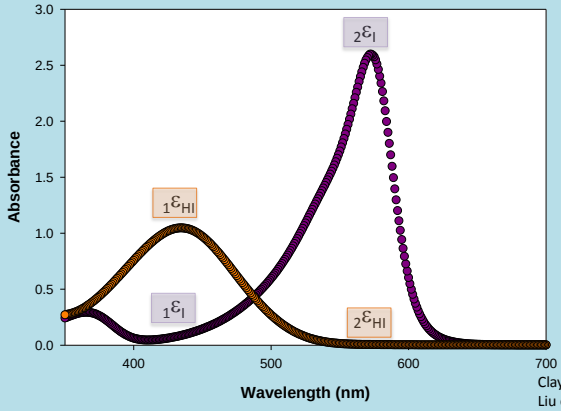
Coastal Zone Challenges (A)

1. **High temporal variability**
   (→ need for high-frequency measurements)
2. **High spatial variability**
   (→ need for measurements on broad spatial scales)

Response:
Multiple-parameter autonomous instrumentation (e.g., MICA)

Principles of Spectrophotometric Measurements: pH, fCO_2, DIC, TA

$$\mathrm{pH_T} = -\log\left(K_2^T e_2\right) + \log\left(\frac{R - e_1}{1 - R\frac{e_3}{e_2}}\right)$$



$$H_2I \overset{K_1}{\leftrightarrow} HI^- \overset{K_2}{\leftrightarrow} I^{2-}$$

$$K_2^T = \frac{[I^{2-}][H^+]_T}{[HI^-]}$$

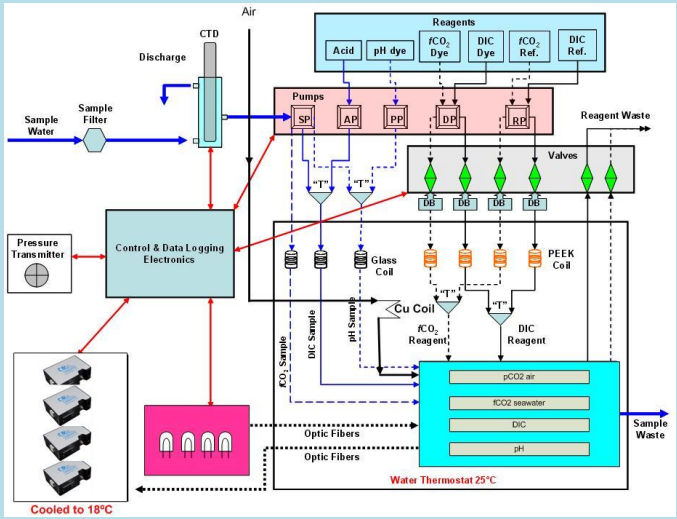
$$e_1 = \frac{{}_2\varepsilon_{HI}}{{}_1\varepsilon_{HI}}, e_2 = \frac{{}_2\varepsilon_I}{{}_1\varepsilon_{HI}}, e_3 = \frac{{}_1\varepsilon_I}{{}_1\varepsilon_{HI}}$$

Clayton and Byrne (1993) *Mar. Chem,* **40**(10): 2115-2129
Liu et al. (2011) *Environ. Sci. Technol,* **45**(11): 4862-4868

MICA Measurements of Marine CO_2 System

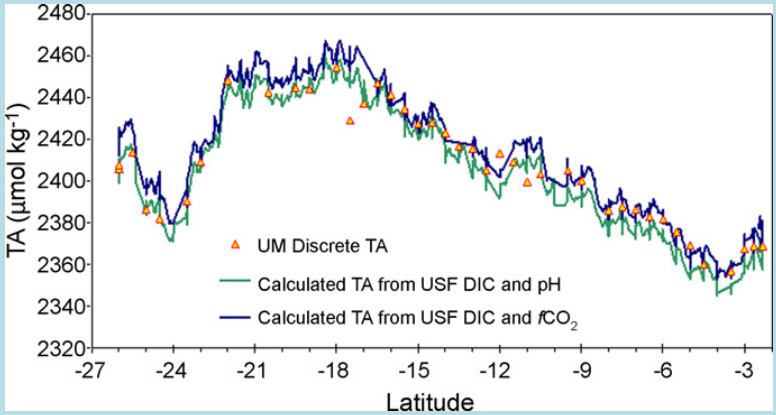
Spectrophotometric Measurements

- fCO_2
- DIC
- pH
- (TA)

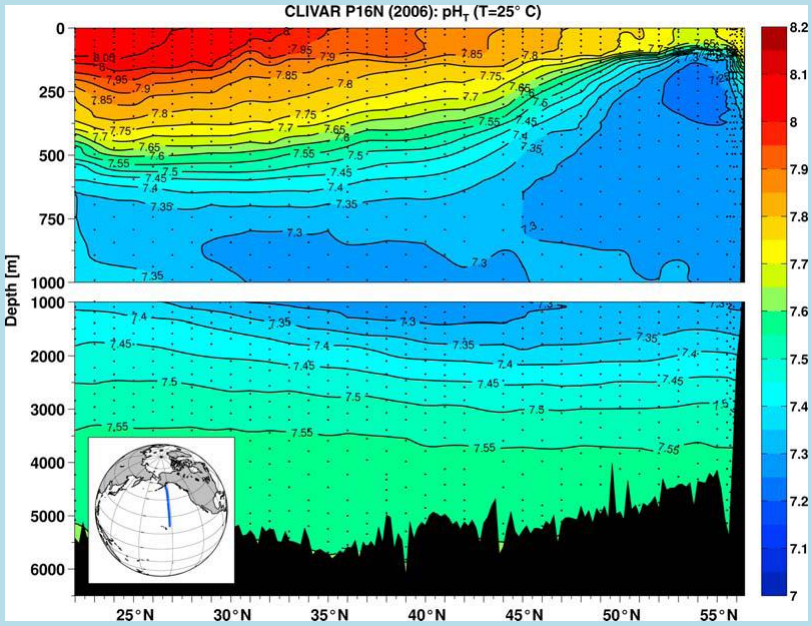


Wang et al. (2007) *Anal. Chim. Acta*, **596**: 23-36

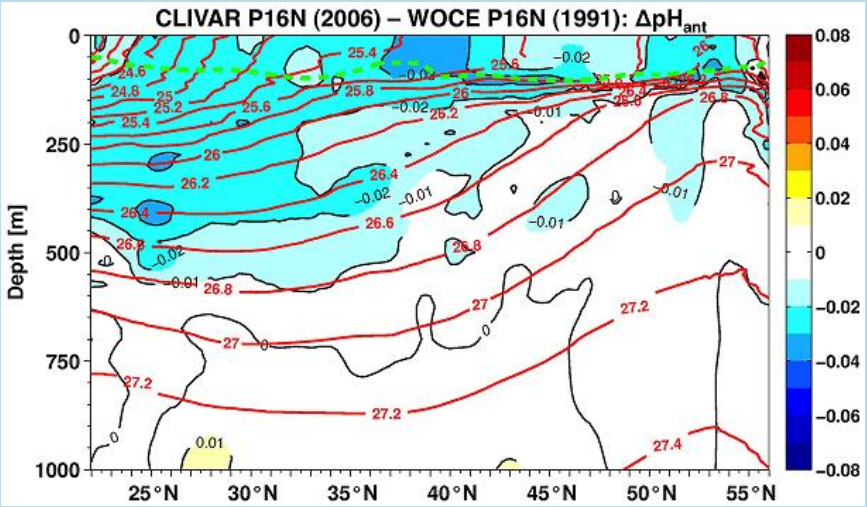
Measured and Calculated TA
(DIC-fCO_2 and DIC-pH)



Wang et al. (2007) *Anal. Chim. Acta*, **596**: 23-36



Byrne et al. (2010) *GRL* **37**: L02601



Anthropogenic pH change in the North Pacific Ocean

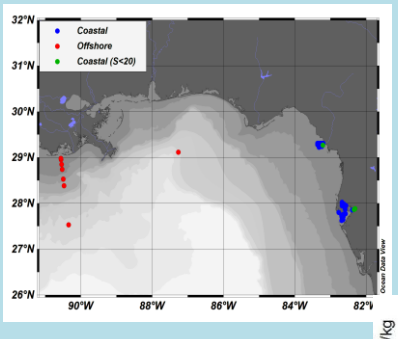
Byrne et al. (2010) *GRL* **37**: L02601

Coastal Zone Challenges (B)

Large non-carbonate alkalinity contributions to TA imply that TA cannot be rigorously interpreted in CO_2 system calculations

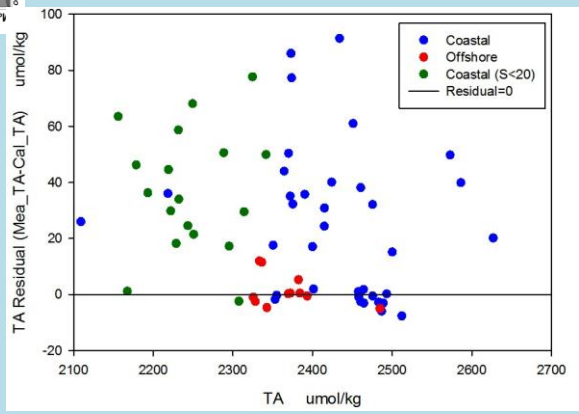
Response:
In Situ Instrumentation

Sample locations



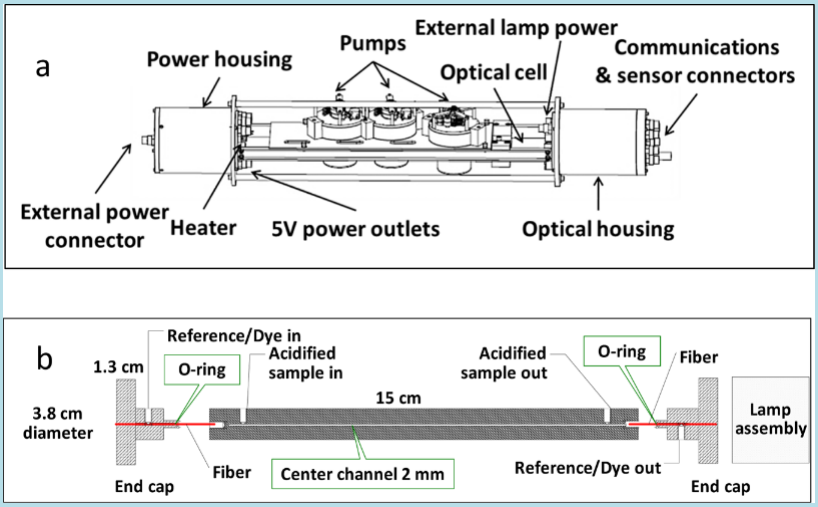
TA Residuals

Yang et al. (2014)

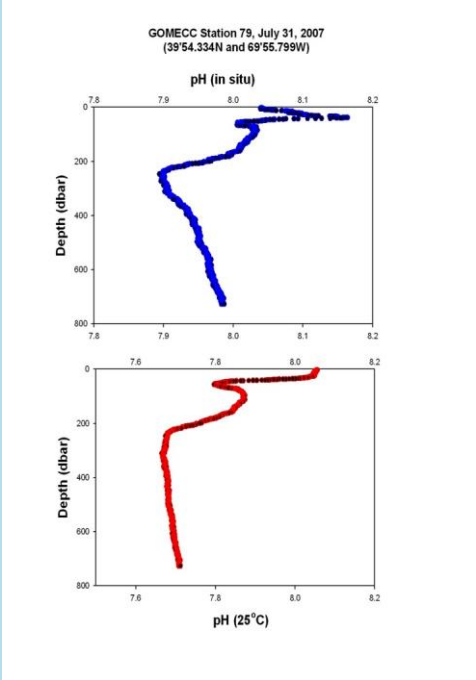


Calculation of Parameters at In Situ Conditions

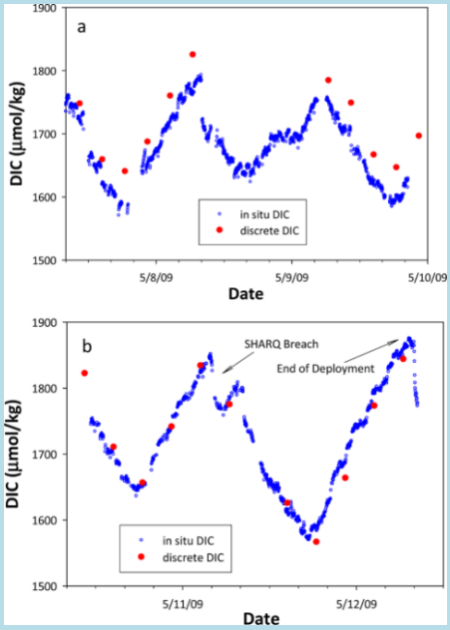
Shipboard Measurements		**Calculated Pair**		**In Situ Parameters**
DIC + TA	→	TA(measured) + DIC(measured) upper bound	→	fCO_2, pH, $[CO_3^{2-}]_T$
DIC + [pH (25°C) or pCO_2 (20°C)]	→	TA(calculated) + DIC(measured) lower bound	→	fCO_2, pH, $[CO_3^{2-}]_T$



Liu et al. (2013) *Environ. Sci. Technol,* **47**: 11106-11114



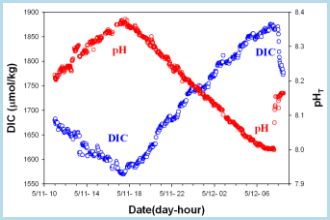
Byrne et al. (2010)
Proceedings of Ocean Obs' 09

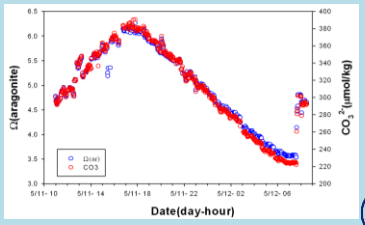


Liu et al. (2013) *ES&T* **47**: 11106-11114

SEAS: in situ DIC and pH instrumentation

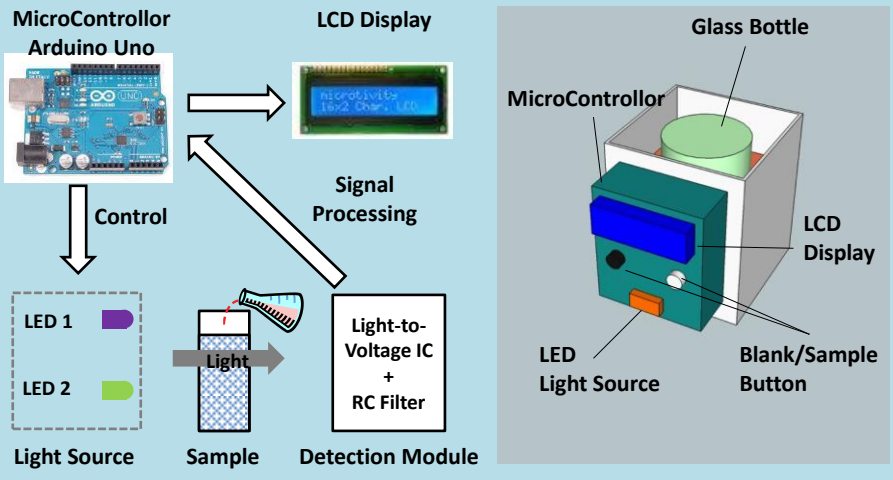
- Modular
  - Spectrometer
  - Three two-channel pumps
  - Internal or external lamp options
  - Configurable optical cell
  - Data collection from up to four peripheral sensors (e.g., CTD, fluorometer, transmissometer, second SEAS instrument)
  - Battery or externally powered
  - Heater option
- Sampling rate (pH = 1 Hz, DIC = 1 per minute)
- Ambient-temperature pH and DIC measurements
- Rated to 1000 m depth
- Configurable for carbon system, nutrient, or trace metal analysis





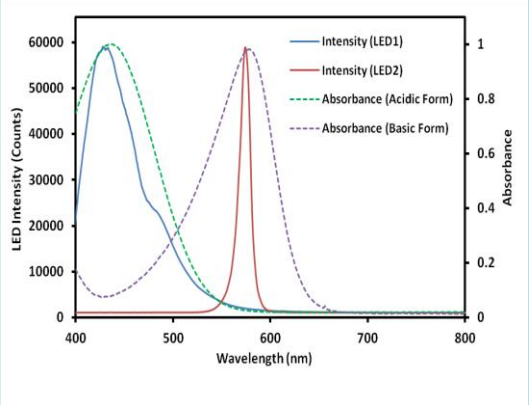
Liu et al. unpublished

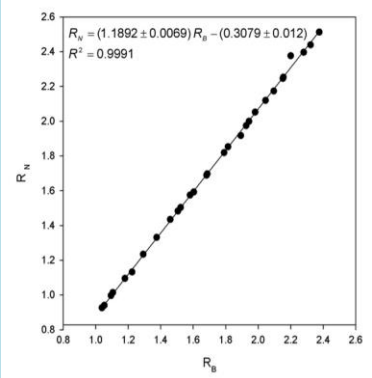
Photometry



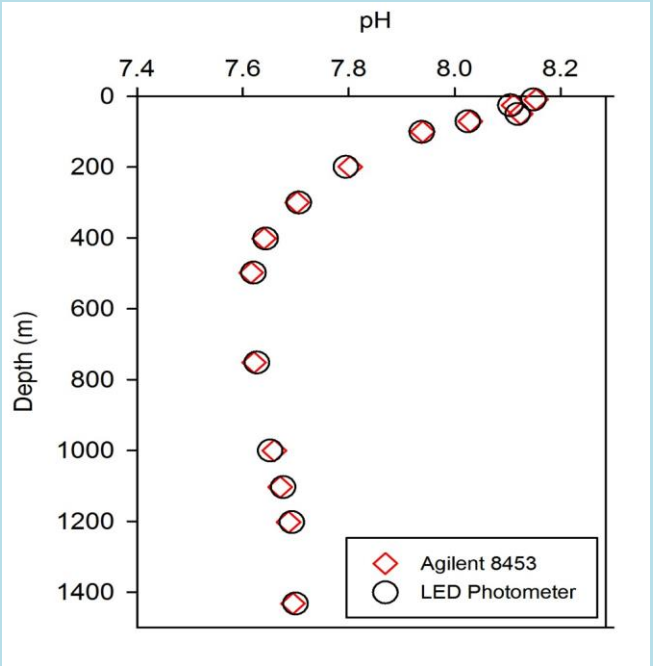
Yang et al. (2014) *Mar. Chem.* 160: 75-81

Photometer Characteristics





Yang et al. (2014) *Mar. Chem.* 160: 75-81



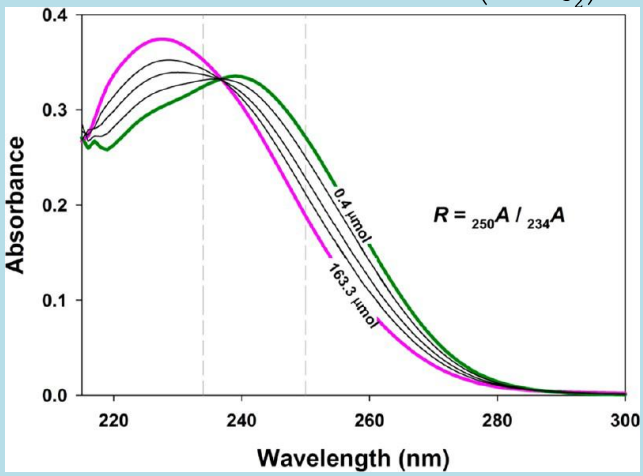
Yang et al. (2014) *Mar. Chem.* 160: 75-81

Perspectives on Future Sensor Development

- In situ measurements of compatible parameters are urgently needed (DIC-pH or DIC-*f*CO2)
- Over-determination (measurement of ≥3 parameters) is an important means of assessing sensor and measurement quality
- High-frequency measurements are required in coastal regions where variability is high
- Sensors with poorer precision but high measurement frequency may be suitable for many coastal regions

Carbonate Ion Measurement Characteristics

$$-\log[CO_3^{2-}]_T = \log\left(\frac{{}^{CO_3}\beta_1}{e_2}\right) + \log\left(\frac{R - e_1}{1 - R\frac{e_3}{e_2}}\right)$$



Easley et al. (2012) *Environ. Sci. Technol.* 47: 1468-1477

Carbonate ion concentration profiles: calculated or measured spectrophotometrically