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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Precision</th>
<th>Calibration</th>
<th>Matrix Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIC</td>
<td>$\pm$ 1-2 $\mu$M</td>
<td>CRM</td>
<td>No</td>
</tr>
<tr>
<td>TA</td>
<td>$\pm$ 2-4 $\mu$M</td>
<td>CRM</td>
<td>Yes</td>
</tr>
<tr>
<td>pH</td>
<td>$\pm$ 0.0004-0.0010</td>
<td>Internal</td>
<td>No (?)</td>
</tr>
<tr>
<td>fCO$_2$</td>
<td>$\pm$ 0.1%</td>
<td>Gas standards</td>
<td>No</td>
</tr>
<tr>
<td>[CO$_2$]</td>
<td>$\pm$ 2%</td>
<td>Internal</td>
<td>No (?)</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Highly variable</td>
<td>No direct observation</td>
<td>Possibly</td>
</tr>
</tbody>
</table>

### Selection of Measured Parameters

Choices should be made in view of measurement resolution

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Precision</th>
<th>Range/Precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>0.8</td>
<td>0.0004</td>
<td>2000</td>
</tr>
<tr>
<td>DIC ($\mu$mol/kg)</td>
<td>500</td>
<td>1</td>
<td>500</td>
</tr>
<tr>
<td>TA ($\mu$mol/kg)</td>
<td>220</td>
<td>2</td>
<td>110</td>
</tr>
<tr>
<td>pCO$_2$ ($\mu$atm)</td>
<td>1840</td>
<td>1</td>
<td>1840</td>
</tr>
</tbody>
</table>

Lessons Learned From Redundant Measurements

Internal Consistency and Saturation State Measurements

W1108C Cruise Track  GOMECC-2 Cruise Track
TA Residuals (the salinity effect)

TA “corrected” for Organic Bases

Patsavas et al. (2014)
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, $f$CO$_2$, DIC, TA

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

$$H_2I \leftrightarrow HI^- \leftrightarrow I^{2-}$$

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

$$e_1 = \frac{2E_{HI}}{1E_{HI}}, e_2 = \frac{2E_I}{1E_{HI}}, e_3 = \frac{1E_I}{1E_{HI}}$$


**MICA Measurements of Marine CO$_2$ System**

Spectrophotometric Measurements
- $f$CO$_2$
- DIC
- pH
- (TA)

**Measured and Calculated TA**

**(DIC-fCO$_2$ and DIC-pH)**

![Graph depicting TA (µmol kg$^{-1}$) against Latitude](image)

- ▲ UM Discrete TA
- Green line: Calculated TA from USF DIC and pH
- Blue line: Calculated TA from USF DIC and fCO$_2$


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![Map and Depth Profile of CLIVAR P16N](image)

*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 CO₂ system calculations

Response:
In Situ Instrumentation
Sample locations

**TA Residuals**
Yang et al. (2014)

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### Calculation of Parameters at In Situ Conditions

**Shipboard Measurements**
- DIC + TA
- DIC + pH (25°C) or pCO₂ (20°C)

**Calculated Pair**
- TA(measured) + DIC(measured) → TA(calculated) + DIC(measured)

**In Situ Parameters**
- $fCO_2$, pH, [CO₃²⁻]ₜ

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<th>In Situ Parameters</th>
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<td>$fCO_2$, pH, [CO₃²⁻]ₜ</td>
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Byrne et al. (2010) *Proceedings of Ocean Obs’09*
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. (2013) *ES&T* 47: 11106-11114
Photometry

Photometer Characteristics


Perspectives on Future Sensor Development

• In situ measurements of compatible parameters are urgently needed (DIC-pH or DIC-fCO2)

• 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

\[-\log[\text{CO}_3^{2-}]_T = \log\left(\frac{c_{\text{CO}_3}R_1}{e_2}\right) + \log\left(\frac{R - e_1}{1 - R\frac{e_3}{e_2}}\right)\]

Carbonate ion concentration profiles: calculated or measured spectrophotometrically