A review of carbonate chemistry and data quality objectives

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A review of carbonate chemistry and data quality objectives

Outline:
• Organism response to ocean acidification (OA)
• Review of carbonate chemistry
• Validating, uncertainty, and presenting data
Ocean acidification chemistry

\[ \text{CO}_2 \text{ (atmosphere)} \leftrightarrow \text{CO}_2 \text{ (seawater)} \]

\[ \text{CO}_2 \text{ (seawater)} + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \quad \text{Results in decreasing pH} \]

\[ \text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{HCO}_3^- \quad \text{Results } \text{CO}_3^{2-} \text{ decrease} \]
Calcium carbonate

2 main forms of CaCO$_3$ minerals: aragonite and calcite

Saturation state ($\Omega$) of these minerals:

$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}^*}$$

Supersaturation/precipitation ($\Omega>1$)
Equilibrium ($\Omega=1$)
Undersaturation/dissolution ($\Omega<1$)

Saturation state depends on T, P, S and differs among calcium carbonate minerals
Studies have shown $\Omega$, pH, and $pCO_2$ can affect species growth, survival, and behavior.
The carbonate system

4 measureable parameters (measure 2, calculate the rest)

1. dissolved inorganic carbon (DIC; also called total CO₂)
2. pCO₂
3. total alkalinity (TA)
4. pH

Each of these tell us something different about the basic processes operating in the ocean.

cdiac.ornl.gov/oceans

from: Andrew Dickson, OCB Ocean Acidification Short Course
www.whoi.edu/courses/OCB-OA/
DIC

DIC (or $T\text{CO}_2$, $T\text{C}$, or $C_T$) = [$\text{CO}_2$] + [$\text{HCO}_3^{-}$] + [$\text{CO}_3^{2-}$]

influenced by biology

T and P independent

surface distribution similar to nutrients

measured by acidifying sample, extracting $\text{CO}_2$ gas, and measuring via coulometry or infra-red

from: Chris Sabine, OCB Ocean Acidification Short Course
www.whoi.edu/courses/OCB-OA/
\[ p\text{CO}_2 = \frac{[\text{CO}_2]}{K} \]

mostly influenced by gas exchange

function of T and P

measured by equilibrating with gas phase and measuring via infra-red or gas chromatography

from: Sabine et al. 2004 and 2010
Total alkalinity

TA (or Talk, $A_T$, Alk) =

$[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] - [\text{H}^+]$

influenced by ocean physics (*can also be influenced by reef calcification)

surface distribution similar to salinity

T and P independent

measured via acidimetric titration

from: Chris Sabine, OCB Ocean Acidification Short Course
www.whoi.edu/courses/OCB-OA/
pH

\[ pH = -\log[H^+] \]

influenced by biology, gas exchange, and ocean physics

function of T and P

surface distribution similar to a combo of TA and DIC

measured via spectrophotometry or pH electrodes

from: Chris Sabine, OCB Ocean Acidification Short Course
www.whoi.edu/courses/OCB-OA/
4 measurable parameters:

each of the 4 measurable carbon parameters can tell us something different about the basic processes operating in the ocean.

GAS EXCHANGE

pCO₂
pH
DIC
TA

OCEAN PHYSICS
BIOLOGY

ARTICLES

Global phytoplankton decline over the past century
Daniel G. Boyce¹, Marlon R. Lewis² & Boris Worm³
SOPs: measurements and data reporting

cdiac.gov/oceans

www.epoca-project.eu
SOPs: measurements and data reporting

Best ways to learn SOPs:
• practice, practice, practice
• training workshops★
• utilize your OA network
• GOA-ON Pier2Peer

OceAn pH Research Integration and Collaboration in Africa - ApHRICA
SOPs: sampling

From: Andrew Dickson, SIO
SOPs: sampling

Core principles:

• Use a container impervious to CO₂ and H₂O (i.e., Pyrex) and make sure it is completely clean
• Fill slowly and from the bottom to prevent bubbles and exchange with the air
• Poison to prevent biological activity
• Leave 1% volume of headspace and seal completely
• Follow filtering SOPs if collecting water from biologically-productive regions with high biomass and heavy particle loads
### Data quality objectives

<table>
<thead>
<tr>
<th><strong>“Climate”</strong> uncertainty</th>
<th><strong>“Weather”</strong> uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Omega$: 1%</td>
<td>$\Omega$: 10%</td>
</tr>
<tr>
<td>pH: 0.003</td>
<td>pH: 0.02</td>
</tr>
<tr>
<td>TA and DIC: 2 $\mu$mol kg$^{-1}$</td>
<td>TA and DIC: 10 $\mu$mol kg$^{-1}$</td>
</tr>
<tr>
<td>$pCO_2$: 0.5%</td>
<td>$pCO_2$: 2.5%</td>
</tr>
</tbody>
</table>

**Box 2. MEASUREMENT QUALITY GOALS FOR GOA-ON**

**“Climate”**
- Defined as measurements of quality sufficient to assess long term trends with a defined level of confidence
- With respect to ocean acidification, this is to support detection of the long-term anthropogenically-driven changes in hydrographic conditions and carbon chemistry over multi-decadal timescales

**“Weather”**
- Defined as measurements of quality sufficient to identify relative spatial patterns and short-term variation
- With respect to ocean acidification, this is to support mechanistic interpretation of the ecosystem response to and impact on local, immediate OA dynamics

*from GAO-ON Requirements and Governance Plan, 2014*
What are your data quality objectives?

Depends on your research questions.

from: Pelejero et al. 2010
Assessing data quality

Box 1. MEASUREMENT UNCERTAINTY AND GOA-ON

A key goal for any observing network is to ensure that the measurements made are of appropriate quality for their intended purpose, and that they are comparable one with another— even though such measurements are made at different times, in different places, and in many cases by different instruments, maintained by different groups. It is thus as important to communicate the uncertainty related to a specific measurement, as it is to report the measurement itself. Without knowing the uncertainty, it is impossible for the users of the result to know what confidence can be placed in it; it is also impossible to assess the comparability of different measurements of the same parameter (de Bièvre & Günzler, 2003).

The term uncertainty (of measurement) has a particular technical meaning (ISO, 1993; Ellison & Williams 2012). It is a parameter associated with the result of a measurement that permits a statement of the dispersion (interval) of reasonable values of the quantity measured, together with a statement of the confidence that the (true) value lies within the stated interval. It is important not to confuse the terms error and uncertainty. Error refers to the difference between a measured value and the true value of a specific quantity being measured. Whenever possible we try to correct for any known errors; for example, by applying calibration corrections. But any error whose value we do not know is a source of uncertainty.
Tools for assessing uncertainty

- Compare your measured values to certified reference materials (CRMs) with known values
- Participate in inter-lab comparisons

*from Bockmon and Dickson, 2013*
Tools for assessing uncertainty

- Compare your measured values to certified reference materials (CRMs) with known values
- Participate in inter-lab comparisons
- “Over-constrain” or predict carbon parameters and compare measured to calculated
Tools for assessing uncertainty

• Compare your measured values to certified reference materials (CRMs) with known values
• Participate in inter-lab comparisons
• “Over-constrain” or predict carbon parameters and compare measured to calculated
• Test effect of SOPs
e.g., filtering vs not filtering
• Test measurement bias between analysts
• Compare measurements to independent datasets or model output
Examples of assessing uncertainty

Table 2. Estimates of the likely uncertainty contributions to measurement accuracy and repeatability from various sources. Uncertainties are expressed as standard deviations here and, unless otherwise noted, in the text.

<table>
<thead>
<tr>
<th>Source</th>
<th>Estimated uncertainty</th>
<th>Resulting pH inaccuracy</th>
<th>Estimated imprecision</th>
<th>Resulting pH repeatability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncertainties in properties used in the pH calculation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperatures</td>
<td>0.3°C</td>
<td>0.001</td>
<td>0.05°C</td>
<td>0.00015</td>
</tr>
<tr>
<td>Salinities</td>
<td>0.002</td>
<td>0</td>
<td>0.002</td>
<td>0</td>
</tr>
<tr>
<td>Absorbances</td>
<td>see text</td>
<td>0.002</td>
<td>0.00031</td>
<td>0.00033</td>
</tr>
<tr>
<td>Uncertainties in adjustments</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baseline</td>
<td>see text</td>
<td>0.00017</td>
<td>see text</td>
<td>0.0001</td>
</tr>
<tr>
<td>Dye perturbation</td>
<td>see text</td>
<td>0.0012</td>
<td>see text</td>
<td>0.00012</td>
</tr>
<tr>
<td>Dye impurity corr.</td>
<td>see text</td>
<td>0.003</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>HgCl₂ addition</td>
<td>0.02%</td>
<td>0.00005</td>
<td>0.002%</td>
<td>0.00003</td>
</tr>
<tr>
<td>Sample storage</td>
<td>&lt;4 h</td>
<td>0.00006</td>
<td>1.7 h</td>
<td>0.00004</td>
</tr>
<tr>
<td>Deuterium lamp</td>
<td>1 exposure</td>
<td>0.00007</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Constants used</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH formula</td>
<td>—</td>
<td>0.004</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Overall</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Combined</td>
<td>—</td>
<td>0.0055</td>
<td>—</td>
<td>0.00041</td>
</tr>
</tbody>
</table>

from Carter et al. 2013
Examples of assessing uncertainty

Table 5. Descriptive statistics of $\Delta$ (MAPCO$_2$ measurement – comparison measurement). The MAPCO$_2$ measurements (both pre- and post-offset if applied during data QC) are compared to biweekly GLOBALVIEW-CO$_2$ MBL values from the latitude nearest to average buoy location, single discrete measurements made within 10 km and 1.5 h, and averaged underway pCO$_2$ measurements made within 10 km and 10 min of the MAPCO$_2$ system measurement. Standard error is the standard error of the mean, and confidence intervals illustrate that with a 95% probability the actual population mean = sample mean ± confidence interval.

<table>
<thead>
<tr>
<th>MAPCO$_2$ air xCO$_2$ (dry) comparison to MBL$^a$ air (µmol mol$^{-1}$)</th>
<th>$n$</th>
<th>Mean</th>
<th>Standard error</th>
<th>Standard deviation</th>
<th>Confidence interval (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data prior to QC (estimate of MAPCO$_2$ system in situ accuracy)</td>
<td>1823</td>
<td>-1.5</td>
<td>0.1</td>
<td>2.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Finalized data (estimate of finalized MAPCO$_2$ data accuracy)</td>
<td>1823</td>
<td>-0.3</td>
<td>&lt; 0.1</td>
<td>1.7</td>
<td>0.1</td>
</tr>
</tbody>
</table>

| MAPCO$_2$ seawater pCO$_2$ comparison to calculated pCO$_2$ (µatm) from discrete DIC, TA | | | | |
| WHOTS vs. HOTS$^b$ | 7 | 0.1 | 1.4 | 3.7 | 3.4 |
| BTM vs. BATS$^c$ | 9 | 1.3 | 1.9 | 5.6 | 4.3 |
| Papa vs. Station Pd | 10 | -0.4 | 2.0 | 6.2 | 4.5 |

| MAPCO$_2$ seawater pCO$_2$ comparison to underway pCO$_2$ (µatm) | | | | |
| BTM vs. Atlantic Explorer$^e$ | 76 | 1.8 | 0.5 | 4.8 | 1.1 |
| TAO125W vs. Ka'imimoana$^f$ | 16 | -3.3 | 3.8 | 15.2 | 8.1 |
| TAO140W vs. Ka'imimoana$^f$ | 13 | 2.1 | 2.3 | 8.3 | 5.0 |

from Sutton et al. 2014
Summary

• Ocean acidification is not just a change in ocean pH; organisms may be impacted by changes in pH, $p\text{CO}_2$, $\Omega$, and...

• Each of the 4 measurable carbon parameters can tell us something different about the basic processes operating in the ocean

• Best ways to learn SOPs:
  • practice, practice, practice
  • training workshops
  • utilize your OA network
  • GOA-ON Pier2Peer program

• Understanding and reporting measurement uncertainty is just as important as the measurement itself
Discussion time!