Ocean Acidification and other Climate Change Implications

A deeper look at the effects of growing CO$_2$ and climate change on the ocean

OCN 623 – Chemical Oceanography
19 April 2018

Reading: Libes, Chapter 25
At the completion of today’s section, students should be able to:

1. Know the basic definition of Revelle Factor and how it will change with rising CO₂

2. Describe the impact of rising CO₂ on calcifying organisms

3. List some of the concerns for OA on marine ecosystems

4. Understand how IPCC views risk for climate change and OA
Carbon Inventories of Reservoirs that Naturally Exchange Carbon on Time Scales of Decades to Centuries

- Oceans contain ~90% of carbon in this 4 component system
- Anthropogenic component is difficult to detect in the ocean

Average stocks for 2000-2009

- Ocean: 38,155 PgC
- Soil: ~2000 PgC
- Plants: ~550 PgC
- Atmosphere: 829 PgC

Ocean $C_{\text{Ant}} = 0.4\%$ (Ocean $C_{\text{ant}} < 1.5\%$ of upper 1000 m)

Preind. Atmos. $C_{\text{Ant}}$ = 71%

$C_{\text{Ant}} = 29\%$ (Ocean Cant < 1.5% of upper 1000 m)
**Ocean Carbon Chemistry Review**

\[ \text{CO}_2(gas) \]

\[ \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \]

**Carbonic acid**

\[ \text{H}_3\text{CO}_2 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \]

**Bicarbonate**

\[ \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \]

**Carbonate**

\[ \text{pCO}_2 = \text{xCO}_2 \cdot \text{P} \]

\[ \text{TCO}_2 = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \]

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

\[ \text{pH} = -\log\{\text{H}^+\} \]

\[ \text{CO}_2 + \text{CO}_3^{2-} \rightleftharpoons 2 \text{HCO}_3^- \]
Ocean Carbon Chemistry Review

$\text{CO}_2(\text{gas})$

$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$

Carbonic acid

$\text{H}_3\text{CO}_2 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$

Bicarbonate

$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$

Carbonate

$\text{CO}_2 + \text{CO}_3^{2-} \rightleftharpoons 2 \text{HCO}_3^-$

$280 \mu\text{atm}$

$560 \mu\text{atm}$

$8 \mu\text{mol kg}^{-1}$

$15 \mu\text{mol kg}^{-1}$

$1617 \mu\text{mol kg}^{-1}$

$1850 \mu\text{mol kg}^{-1}$

$268 \mu\text{mol kg}^{-1}$

$176 \mu\text{mol kg}^{-1}$

$1893 \mu\text{mol kg}^{-1}$

$2040 \mu\text{mol kg}^{-1}$

$100\% \Delta p\text{CO}_2 \rightarrow 8\% \Delta \text{TCO}_2$

Taken from Feely et al. (2001)
Global Distribution of Surface Revelle Factor

R. Revelle, H., E. Suess, Tellus 9, 18 (1957)
Egleston et al. (GBC, 2010) define six new buffer factors, each of which can be explicitly calculated:

\[ \gamma_{DIC} = \left( \frac{\partial \ln[CO_2]}{\partial DIC} \right)^{-1} = DIC - \frac{Alk_C^2}{S} \]

\[ \gamma_{Alk} = \left( \frac{\partial \ln[CO_2]}{\partial Alk} \right)^{-1} = \frac{Alk_C^2 - DIC \times S}{Alk_C} \]

\[ \beta_{Alk} = \left( \frac{\partial \ln[H^+]}{\partial Alk} \right)^{-1} = \frac{Alk_C^2}{DIC} - S \]

\[ \beta_{DIC} = \left( \frac{\partial \ln[H^+]}{\partial DIC} \right)^{-1} = \frac{DIC \times S - Alk_C^2}{Alk_C} \]

\[ \omega_{DIC} = \left( \frac{\partial \ln[OH^-]}{\partial DIC} \right)^{-1} = DIC - \frac{Alk_C \times P}{[HCO_3^-]} \]

\[ \omega_{Alk} = \left( \frac{\partial \ln[OH^-]}{\partial Alk} \right)^{-1} = Alk_C - \frac{DIC[HCO_3^-]}{P} \]

\[ S = [HCO_3^-] + 4[CO_3^{2-}] + \frac{[H^+][B(OH)^-]}{K_{hb} + [H^+]} + [H^+] - [OH^-] \]

\[ P = 2[CO_2] + [HCO_3^-] \]
All Buffer Factors show a minimum where DIC=Alk

As CO₂ increases, North Pacific subtropical gyre waters are approaching the buffer minimum.
Higher buffer factor means larger DIC increase for the same amount of CO$_2$ rise.
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75% drop in uptake.
CO₂ is an acid gas so the addition of 26 million tonnes of carbon dioxide to the ocean every day is acidifying the seawater...we call this process “ocean acidification”

Phenol Red is a pH sensitive Dye

Q: How would the color change if someone breathed into water with Phenol Red dye in it?

Q2: Would fresh water and seawater react the same way?
\[
\begin{align*}
\text{CO}_2^{(aq)} + \text{H}_2\text{O} + \text{CO}_3^{2-} & \rightleftharpoons 2\text{HCO}_3^- \\
\text{CO}_2^{(aq)} + \text{H}_2\text{O} & \rightleftharpoons \text{HCO}_3^- + \text{H}^+
\end{align*}
\]
Rising Ocean CO$_2$ = Decreasing Oceanic pH

CO$_2$ Time Series in the North Pacific

NOAA PMEL Carbon Program: [www.pmel.noaa.gov/co2/](http://www.pmel.noaa.gov/co2/)
Mauna Loa data from NOAA ESRL
ALOHA data adapted from Dore et al. 2009

• For the last 20 Million years the pH of the ocean has remained relatively stable between approximately 8.1 and 8.2

• The uptake of anthropogenic CO₂ has lowered ocean pH by 0.1, representing a 28% increase in acidity over the last 200 years.

• The estimated drop in pH by the end of the century is not only larger than seen over the last 20 million years, but is also at least 100 times faster than in the past.

Ocean Acidification: Historical Perspective

Turley et al., 2006
Ocean Acidification: Fundamental Chemistry

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^- \]

- More than 99% of the H\(^+\) formed consume CO\(_3^{2-}\) to form HCO\(_3^-\) making it more difficult for organisms to form their shells.
Ocean Acidification: Fundamental Chemistry

\[ Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \]

Calcification Index

Saturation State

\[ \Omega_{phase} = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp,phase}} \]

- \( \Omega > 1 \) \( \rightarrow \) \( CaCO_3 \) stable
- \( \Omega = 1 \) \( \rightarrow \) equilibrium
- \( \Omega < 1 \) \( \rightarrow \) \( CaCO_3 \) dissolves
Corals show a strong response to high CO$_2$/ low saturation state

Shamberger (2011)
Surface Water Aragonite Saturation States in Preindustrial Times

Distribution of saturation states in reef locations

Cao and Caldeira, 2008

Corrosive $\Omega_{\text{Aragonite}}$ Optimal
Cao and Caldeira, 2008

Surface Water
Aragonite
Saturation
States Circa
2000

Distribution of saturation states in reef locations

Cao and Caldeira, 2008
Surface Water
Aragonite
Saturation States Possible by 2100 or Earlier

Distribution of saturation states in reef locations

Cao and Caldeira, 2008
The Great Barrier Reef has seen a 50% reduction in coral cover over the last three decades.
Shellfish are a big business along the US West Coast.
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Commercial oyster Industry is $100M/yr in Pacific NW (3000 Jobs)

But starting in 2005 there was no natural recruitment of oysters in WA state for a decade in part due to ocean acidification…

Oysters in deep trouble: Is Pacific Ocean's chemistry killing sea life?

By Craig Welch
Seattle Times environment reporter

WILLAPA BAY, Pacific County â€”

The collapse began rather unspectacularly.

In 2005, when most of the millions of Pacific oysters in this tree-lined estuary failed to reproduce, Washington's shellfish growers largely shrugged it off.

Oysters' failure to reproduce will lead workers like Northern Oyster Co.'s Gildardo Mendoza to collect far more of their product from a state "oyster preserve" in Willapa Bay. Pacific oysters haven't successfully reproduced in the wild since 2004.
Seawater conditions linked to low recruitment

By turning off the water flow when the water showed low pH values, the hatcheries had their best year since the collapse saving the industry ~$35M in 2010.

Figure courtesy of Alan Barton
Distribution of Societally Important Calcium Carbonate Species
Concern for Marine Organisms and Ecosystems

- Reduced calcification rates
- Increased photosynthesis and nitrogen fixation
- Reduced growth, production and life span of adults, juveniles & larvae
- Reduced tolerance to other environmental fluctuations
- Significant shift in key nutrient and trace element speciation

Changes to:
- Fitness and survival
- Species biogeography
- Key biogeochemical cycles
- Food webs

Reduced:
- Sound Absorption
- Homing Ability
- Recruitment and Settlement

Concern for Marine Organisms and Ecosystems
How does IPCC evaluate how things might change in the future?

The IPCC has been associated with four generations of emission scenarios:


Source: Peters et al. 2012a; CDIAC Data; Global Carbon Project 2013
In the lead up to the IPCC’s Sixth Assessment Report new scenarios have been developed to more systematically explore key uncertainties in future socioeconomic developments.

Five Shared Socioeconomic Pathways (SSPs) have been developed to explore challenges to adaptation and mitigation. Shared Policy Assumptions (SPAs) are used to achieve target forcing levels (W/m²).

Source: Riahi et al. 2016; IIASA SSP Database; Global Carbon Budget 2016
Assessing Risk in AR5
key risks are those relevant to article 2, UNFCCC
“dangerous anthropogenic interference with the climate system”

PRINCIPLES

Risk Level with Current Adaptation

Risk Level with High Adaptation

Potential for Additional Adaptation to Reduce Risk

Risk Level with Current Adaptation

Present
Near Term (2030-2040)
Long Term (2080-2100)

Very Low
Med
Very High

4°C
2°C
Where do we go from here?

Atmospheric CO₂
Rate of CO₂ Rise (ppm/100y)

Global Temperature
Rate of Temp. rise (°C/100y)

Maximum Last 420,000 y
Last 100 y
Next 100 y (B1)
Next 100 y (A2)

Maximum Last 420,000 y
Last 100 y
Next 100 y (B1)
Next 100 y (A2)

Rates of Change are Important

Hoegh-Guldberg et al. 2007, Science