Past and Present Trends in Ocean Carbon Uptake and Storage in the North Pacific

by

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This work would not be possible without the efforts of many scientists involved in the hydrographic survey cruises.
The atmospheric $CO_2$ growth rate is highly variable and increases with time.
Generally surface ocean CO$_2$ values track the atmospheric increase.

From Takahashi et al 2009
Models suggest that uptake efficiency will decrease in future.

Data from Jorge Sarmiento

- < 3x increase in 45 years for constant climate models
- 2x increase in 45 years for climate change models
Chemical Reactions of Carbonate Species in Seawater

**Atmospheric CO₂ partial pressure**
- Pre-Industrial
- Present Day
- 2xCO₂
- 3xCO₂
- 4xCO₂

**Surface Ocean CO₂**
- Total CO₂ (inorganic)
- pH

**Chemical Reactions**
- \( \text{CO}_2 \rightleftharpoons \text{H}_2 \text{CO}_3 \)
- \( \text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-} \)
- \( \text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \)
- \( \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \)

**Equilibrium Constants**
- \( K_1 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2\text{aq}]} \)
- \( K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} \)

**Calcification**
- \( \Omega_a = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{sp}} \)
- \( \Omega_a > 1 \sim \text{Supersaturated} \)

**Dissolution**
- \( \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \)
Revelle Factor

R. Revelle, H. E. Suess, Tellus 9, 18 (1957) 

\( \frac{\Delta fCO_2/\Delta DIC}{fCO_2/DIC} \)
Here we define six new buffer factors, each of which can be explicitly calculated:

\[
\gamma_{\text{DIC}} = \left( \frac{\partial \ln[\text{CO}_2]}{\partial \text{DIC}} \right)^{-1} = \text{DIC} - \frac{\text{Alk}_C^2}{S} \quad \text{equivalent to traditional Revelle Factor that can be used to determine the efficiency of the ocean sink as CO}_2 \text{ rises}
\]

\[
\gamma_{\text{Alk}} = \left( \frac{\partial \ln[\text{CO}_2]}{\partial \text{Alk}} \right)^{-1} = \frac{\text{Alk}_C^2 - \text{DIC} \times S}{\text{Alk}_C} \quad \text{similar to Revelle Factor but looks at the impact of changing alkalinity on CO}_2
\]

\[
\beta_{\text{Alk}} = \left( \frac{\partial \ln[\text{H}^+]}{\partial \text{Alk}} \right)^{-1} = \frac{\text{Alk}_C^2}{\text{DIC}} - S \quad \text{general buffer capacity – resistance of pH to addition of acid/base}
\]

\[
\text{Revelle Factor} = \frac{\text{DIC}}{\gamma_{\text{DIC}}}
\]

\[
\beta_{\text{DIC}} = \left( \frac{\partial \ln[\text{H}^+]}{\partial \text{DIC}} \right)^{-1} = \frac{\text{DIC} \times S - \text{Alk}_C^2}{\text{Alk}_C} \quad \text{in practice this is equivalent to } - \gamma_{\text{Alk}}
\]

\[
\omega_{\text{DIC}} = \left( \frac{\partial \ln \Omega}{\partial \text{DIC}} \right)^{-1} = \text{DIC} - \frac{\text{Alk}_C \times P}{[\text{HCO}_3^-]} \quad \text{a measure of the impact of DIC changes on saturation state}
\]

\[
\omega_{\text{Alk}} = \left( \frac{\partial \ln \Omega}{\partial \text{Alk}} \right)^{-1} = \text{Alk}_C - \frac{\text{DIC}[\text{HCO}_3^-]}{P} \quad \text{a measure of the impact of alkalinity changes on saturation state}
\]

\[
S = [\text{HCO}_3^-] + 4[\text{CO}_3^{2-}] + \frac{[\text{H}^+][\text{B(OH)}_4^-]}{K_{hb} + [\text{H}^+]} + [\text{H}^+] - [\text{OH}^-] \quad P = 2[\text{CO}_2] + [\text{HCO}_3^-]
\]
All Buffer Factors show a minimum where DIC = Alk

Buffer factors at Alk = 2.25 mM
\[
\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- \rightarrow \text{H}^+ \rightarrow \text{CO}_3^{2-}
\]
All Buffer Factors show a minimum where DIC=Alk

Buffer factors at Alk = 2.25 mM

As CO$_2$ 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

1994 Surface GLODAP data
fCO$_2$ ≤ atmospheric CO$_2$
Range is from the shallow slope, but as DIC increases the slope increases.
Preindustrial North Pacific ranges from 0.17-0.23 ($\Delta=0.06$)
Modern North Pacific ranges from 0.15-0.21 ($\Delta = .06$)
Modern North Pacific ranges from 0.13-0.19 (Δ=0.06)
Modern North Pacific ranges from 0.11-0.17 ($\Delta = 0.06$)
Higher buffer factor means larger DIC increase for the same amount of CO$_2$ rise.
Higher buffer factor means larger DIC increase for the same amount of $CO_2$ rise.
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2X $CO_2$

60% drop in uptake

Preindustrial

Modern
Higher buffer factor means larger DIC increase for the same amount of CO₂ rise.
Omega-DIC has much steeper slope than gamma-DIC
The more negative omega-DIC gets, the larger the drop in saturation state.
Preindustrial North Pacific ranges from -0.22-0.41 ($\Delta = .19$)
Modern North Pacific ranges from -0.20-0.37 ($\Delta = .17$)
2X CO$_2$ North Pacific ranges from -0.15-0.28 ($\Delta=.13$)

omega DIC x 2
$3 \times CO_2$ North Pacific ranges from -0.14-0.22 ($\Delta = 0.08$)
The more negative omega-DIC gets, the larger the drop in saturation state.
The more negative omega-DIC gets, the larger the drop in saturation state.

30% drop in $\Delta$ sat. state

Preindustrial

Modern

$\Delta \Omega_{\text{Aragonite}}$ for 10 $\mu$atm $fCO_2$ increase
The more negative omega-DIC gets, the larger the drop in saturation state.

65% drop in $\Delta$ sat. state
The more negative omega-DIC gets, the larger the drop in saturation state.
As we move to higher CO₂ levels, the spatial gradients get smaller.
Conclusions

1) Buffer factors are a useful way to examine how ocean carbon chemistry will change as a result of rising $CO_2$.

2) The buffer capacity of the surface ocean will decrease until $DIC=ALK$, then will increase again sharply as $CO_2$ continues to rise.

3) The average uptake efficiency of the ocean will drop by 75% from preindustrial conditions to 3x $CO_2$.

4) The saturation state of the waters is more sensitive to change than either pH or DIC.

5) The decrease in uptake efficiency, however, will result in an 80% decrease in the SS change for a given increase in $CO_2$ between the preindustrial and the 3x $CO_2$ world.