Multiple stressors in coastal ocean environments – rethinking the impact of ocean acidification

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Outline

• Introduction
• Examples of acidification and low $O_2$ events in coastal waters
• Responses of ocean $CO_2$ system to multiple stressors: based on first principles
• Possible impacts on organisms, ecosystem and biogeochemical processes
• Summary
Fig. 1. Schematic of human impacts on ocean biogeochemistry either directly via fluxes of material into the ocean (colored arrows) or indirectly via climate change and altered ocean circulation (black arrows). The gray arrows denote the interconnections among ocean biogeochemical dynamics. Note that many ocean processes are affected by multiple stressors, and the synergistic effects of human perturbations is a key area for further research.
Coastal ocean stressors—either directly or indirectly related to OA

- Temperature stress
  - Global warming; local extreme weather
- Salinity stress
  - Tidal cycle; reduced or increased freshwater input
- River end-member increase
- Nutrient stress
  - Fertilizer use (NO$_3$); sewage discharge (NH$_4$)
- (low) O$_2$ stress
- CO$_2$ (high and low) stress
- More frequent storm
- ...
Ocean acidification (in coastal waters?)

- Global ocean uptake of atm-CO$_2$ ($\Delta\text{pH} = -0.1$)
- Source water with a higher DIC/TA ratio advect onshore and mix with low S waters
- This water is further acidified by respiration
Examples of acidification and low $O_2$ events in coastal waters

- Major upwelling impacted waters
- Within and under eutrophic river plumes (warm waters)
- Low temp waters
- The Bering Sea and Arctic Ocean coastal waters
- Chesapeake Bay
- Baltic Sea
- Gulf of Mexico
- GOM
Acidification and low O$_2$ events in coastal waters--1.

At an eastern boundary current shelf

– dominated by upwelling of open ocean subsurface water with low temp, low [O$_2$], low pH, low Ω, and high pCO$_2$/DIC on to the shelf (Feely et al. 2008, Science)
Acidification and low $O_2$ events in coastal waters--2.

- In an upwelling dominated submerged estuary/bay (Puget Sound)

Feely et al. 2010, ECSS
Acidification and low O$_2$ events in coastal waters—3.

- High latitude waters
  (Eastern Bering Sea)

(Mathis et al. 2011; JGR)
4. St. Lawrence Estuary & Gulf

Mucci et al. (2011) Atm-Ocean
Acidification and low O$_2$ events in coastal waters—5.

- Eutrophication-hypoxia is not only a serious regional stressor, it is also a globally threat.

Spreading Dead Zones and Consequences for Marine Ecosystems
Robert J. Diaz, et al.
Science 321, 926 (2008);
DOI: 10.1126/science.1156401
Acidification and low $O_2$ events in coastal water--5.

- Gulf of Mexico hypoxic water

Cai et al. 2011
Nature Geoscience
Subsurface water pH and [O₂] relationship

Mississippi
- Apr 2006
- Jun 2006
- Sep 2006
- May 2007
- Jul 2007
- Aug 2007
- Aug 2008
- Jul 2009

hypoxic

O₂ (μmol/kg)

pHₚ
Subsurface water pH and $[O_2]$ relationship

$$\text{(CH}_2\text{O)}_{106}(\text{NH}_3)\text{H}_3\text{PO}_4 + 138 \ O_2 \rightarrow 106 \ CO_2 + 16 \ HNO_3 + H_3\text{PO}_4 + 122 \ H_2\text{O}$$

Cai et al. (2011)
How do anthropogenic CO$_2$ and CO$_2$ from respiration interact?

Enhanced ocean acidification!

Mississippi
- Apr 2006
- Jun 2006
- Sep 2006
- May 2007
- Jul 2007
- Aug 2007
- Aug 2008
- Jul 2009

Changjiang
- Jul 2007
- Jul 2008
- Aug 2009

Model (atm. CO$_2$)
- 280 ppm
- 385 ppm
- 800 ppm

How do anthropogenic CO$_2$ and CO$_2$ from respiration interact?
Respiratory CO$_2$-driven acidification is enhanced by anthropogenic CO$_2$.

Why?

Mississippi
- Apr 2006
- Jun 2006
- Sep 2006
- May 2007
- Jul 2007
- Aug 2007
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Changjiang
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Model (atm. CO$_2$)
- 280 ppm
- 385 ppm
- 800 ppm

OA'$_{P-I-P}$ = -0.16
OA'$_{P-F}$ = -0.27
OA$_{P-I-P}$ = -0.11
OA$_{P-F}$ = -0.27
OA = -0.40
Resp$_{P}$ = -0.47
Resp$_{P-I}$ = -0.29
Resp$_{P-F}$ = -0.34
Resp$_{P-I-P}$ = -0.34
pH$_T$ = 7.74

Respiratory CO$_2$-driven acidification is enhanced by anthropogenic CO$_2$.

Why?
Weakening of buffer capacity in CO$_2$-enriched waters

Cai et al. (2011)
Nature Geoscience
Impact on carbonate saturation state

- with the same hypoxia level, by year 2100, large areas of GOM will be driven to under-saturation with respect to aragonite!
Responses of ocean CO$_2$ system to multiple stresses: from first principles

- Salinity
- Temperature
- River-Ocean mixing
- Metabolic CO$_2$ consumption and release
- N cycle (NO$_3$ and NH$_4$)
- More frequent storm
- ...

A simple model
--examining the impact of respiration on pH, $pCO_2$ and $\Omega$
under various conditions (T, S, ...)

• Initial partial pressure ($pCO_2$ and $pO_2$) is set by the atmosphere

• Alk is known
  – River end-member = 1.0 mmol/kg
  – Ocean end-member = 2.3 mmol/kg

• Bottom water is no longer in contact with the atmosphere

• Metabolic processes follows the Redfield CN ratio...

$\text{(CH}_2\text{O})_{106}\text{(NH}_3\text{)}\text{H}_3\text{PO}_4 + 138\text{O}_2 \rightarrow$

$106\text{CO}_2 + 16\text{HNO}_3 + \text{H}_3\text{PO}_4 + 122\text{H}_2\text{O}$
Effects of T & S on respiratory-driven CO$_2$ acidification (over a complete consumption of O$_2$)

- The greatest increases in [CO$_2$] (13-fold) and decreases in pH (~1.1) occur at the lowest S and T.
- At higher S & T, less increase in Rel.[CO$_2$] and decrease in pH (0.25–0.77 at S=36).
- [CO$_3^{2-}$] decreases by 12-fold (low S & T) and 1.6-fold (high T &S).

Why there is such a big difference between low ST and high ST?

(Sunda and Cai, ES&T, under review)
Effects of T & S on respiratory driven CO₂ acidification (over a complete consumption of O₂)

• Due to higher solubility of O₂ in colder and less saline waters?
  - A 2.3-fold increased in O₂ solubility increase the resp-CO₂ release
  - But the effect is small due to a higher (2.9X) initial [CO₂] & lower initial pH at lower T and S (ΔpH from 1.07 to 1.10).

(Sunda and Cai, ES&T, under review)
Effects of T & S on respiratory driven CO$_2$ acidification (over a complete consumption of O$_2$)

- The different initial [CO$_3^{2-}$] is responsible for the very different sensitivity to salinity and temp
  - Higher TA at high sal (2.4 mM vs. ~1.2 mM)
  - Mainly, a change in dissociation constants

(Sunda and Cai, ES&T, under review)
Will increasing Atm-$P_{\text{CO}_2}$ amplify or suppress respiratory-$\text{CO}_2$ acidification ($\Delta p\text{H}_R$)?

- For high T & S waters (GOM), amplify
- For low T (arctic waters), at the max. point, start to suppress
- Initial $[\text{CO}_3^{2-}]$ is the key

(Sunda and Cai, ES&T, under review)
What is so magic about this point of max-$\Delta$\text{pH}_R? 

- Where the system has minimum buffering capacity
- A point where DIC = TA or $[\text{CO}_2] = [\text{CO}_3^{2-}] + \text{B(OH)}^-$
  
$$[\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + \text{B(OH)}^-$$
How can a storm make bottom waters even more acidic?
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Possible impacts on the marine nitrogen cycle

Hutchins et al. 2009, Oceanography
Enhanced denitrification?

\[ N^* = [\text{NO}_3^-]_{\text{obs}} - 16/106^* \Delta \text{DIC} \]

Cai unpublished data

\[ \text{RI} = \log(pO_2/pCO_2) \]

(Brewer & Piltzer 2009)
Summary

• Respiration often plays a more important role in acidifying coastal bottom waters today, but

• Anthropogenic CO$_2$ uptake from the atmosphere will play an increasingly important role in acidifying coastal bottom waters.

• There is a strong enhancement of acidification in CO$_2$-enriched waters, and such effects vary greatly with salinity and temperature, with a greater effect in low T and S water (decreasing) and a smaller effect in high T and S water (increasing).

• Storm on pH and N cycle...
### Ocean Stress Guide

What the ocean will experience this century without urgent and substantial reduction in greenhouse gas emissions.

| Stressor      | Causes                                                                 | Result                                                                 | Direct effects                                                                 | Impacts                                                                 | Feedback to climate |
|---------------|------------------------------------------------------------------------|                                                                      |                                                                                 |                                                                         |                    |
| **Warming**   | Increasing greenhouse gas emissions to the atmosphere                  | Temperature increase, particularly in near-surface waters            | Decreased carbon dioxide solubility                                             | Stress to organism physiology, including coral bleaching                | Reduced ocean uptake of carbon dioxide due to solubility effect        |
|               |                                                                        | Less ocean mixing due to increased stratification                    | Increased speed of chemical and biological processes                        | Extensive migration of species                                           | Increased oxygen consumption, carbon dioxide production and decrease in oxygen transfer to the deep ocean |
|               |                                                                        | Increased run-off and sea-ice melt will also contribute to stratification in Arctic waters | Reduced natural nutrient re-supply in more stratified waters                 | More rapid turnover of organic matter                                   | Potential decrease in the export of carbon to the ocean’s interior     |
|               |                                                                        |                                                                      |                                                                                 | Nutrient stress for phytoplankton, particularly in warm waters            | Decreasing productivity except in the Arctic                            |
| **Acidification** | Increasing atmospheric carbon dioxide emissions                      | Unprecedented rapid change to ocean carbonate chemistry               | Reduced calcification, growth and reproduction rates in many species        | Impeded shell or skeletal growth and physiological stress in many species, including juvenile stages | Reduced ocean uptake of carbon dioxide due to chemical effects         |
|               | Coastal nutrient enrichment, methane hydrates and acid gases from industrial emissions may also contribute locally | Much of the ocean will become corrosive to shellfish animals and corals, with effects starting in the Arctic by 2020 | Changes to the carbon and nitrogen composition of organic material          | Change to biodiversity and ecosystems, and the goods and services they provide | Changes to the export of carbon to the ocean’s interior                |
|               |                                                                        |                                                                      |                                                                                 | Cold and upwelling waters currently supporting key fisheries and aquaculture likely to be especially vulnerable | Higher oxygen use throughout the water column due to changing composition of organic material |
| **Deoxygenation** | Reduced oxygen solubility due to warming                               | Less oxygen available for respiration especially in productive regions, and in the ocean interior | Reduced growth and activity of zooplankton, fish and other oxygen-using organisms | Stress to oxygen-using organisms                                        | Enhanced production of the two greenhouse gases methane and nitrous oxide |
|               | Decreased oxygen supply to the ocean interior due to less mixing       |                                                                      |                                                                                 | Risk of species loss in low oxygen areas                                  |                                                                      |
|               | Nutrient rich land run-off stimulating oxygen removal locally           |                                                                      |                                                                                 | Shift to low oxygen-tolerant organisms, especially microorganisms and loss of ecosystem services in these areas |                                                                      |
| **All three together** | Increasing greenhouse gas emissions, especially carbon dioxide, to the atmosphere | More frequent occurrence of waters that will not only be warmer but also have higher acidity and less oxygen content | Damage to organism physiology, energy balance, shell formation: e.g. coral reef degradation | Ocean acidification can reduce organisms’ thermal tolerance, increasing the impact of warming | Major change to ocean physics, chemistry and ecosystems              |
|               | Few studies                                                             |                                                                      |                                                                                 | Combined effects further increase risk to food security and industries depending on healthy and productive marine ecosystems | Risk of multiple positive feedbacks to atmosphere, increasing the rate of future climate change |