

Acidification in estuarine and coastal ocean waters

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SOCAN Ocean Acidification Webinar

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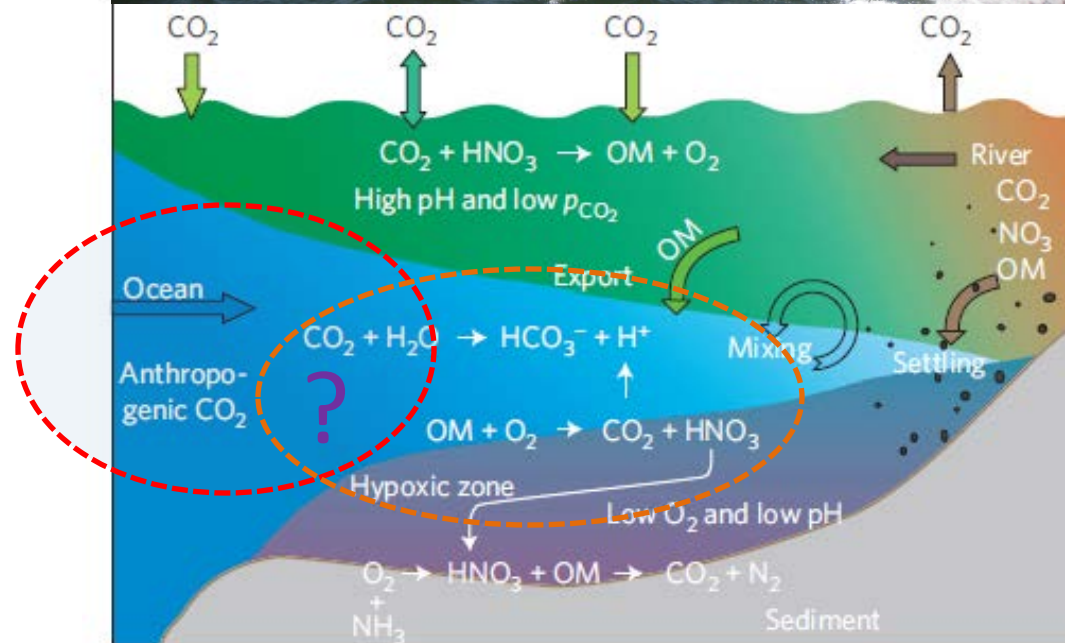
Outline

- Introduction
- Examples of acidification and low O₂ events in coastal waters
- Responses of ocean & estuarine CO₂ system to multiple stressors: based on first principles
- Summary
- Recent results from the Delaware and Chesapeake Bays (if time permits)

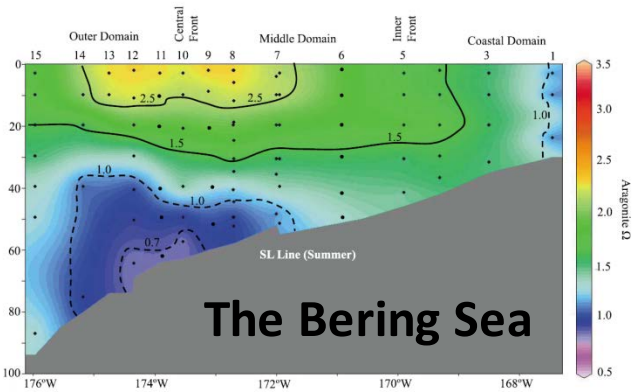
Ocean acidification (in coastal waters?)

- 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 (or anth- CO_2 can be taken up locally)
- This water is further acidified by respiration

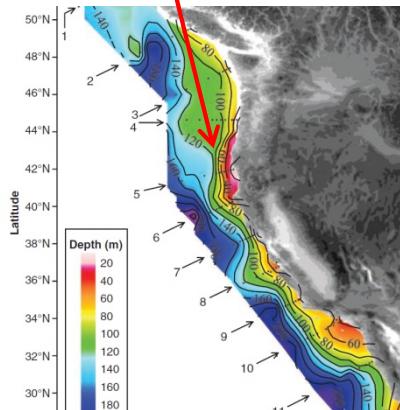
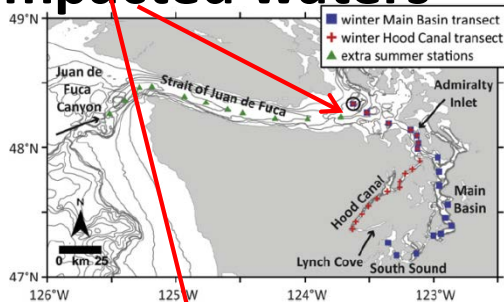
How do they interact?



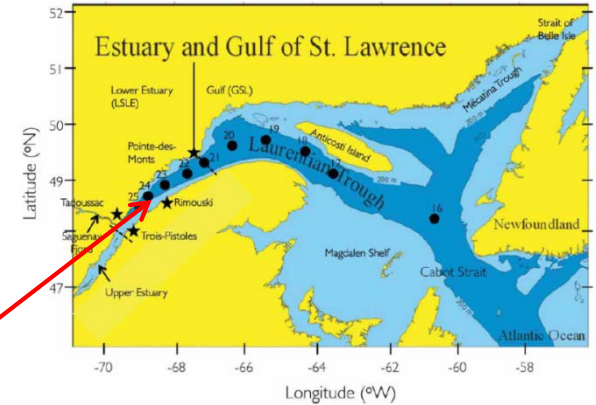
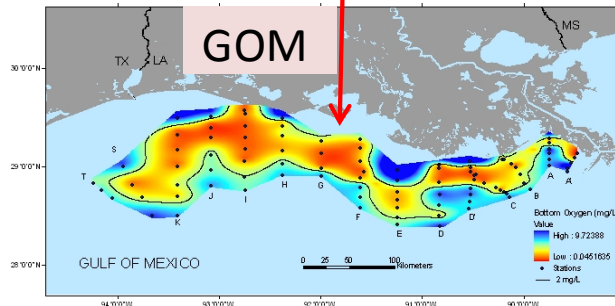
Examples of acidification and low O₂ events in coastal waters



Major upwelling impacted waters

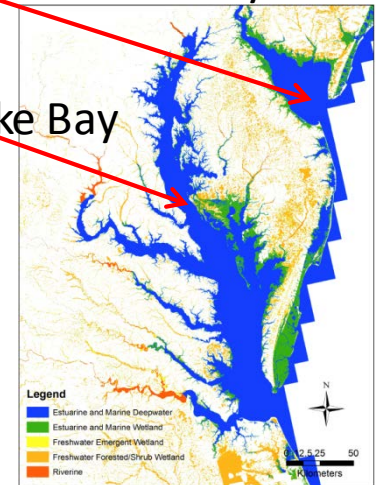


Within and under eutrophic river plumes



Delaware Bay

Chesapeake Bay

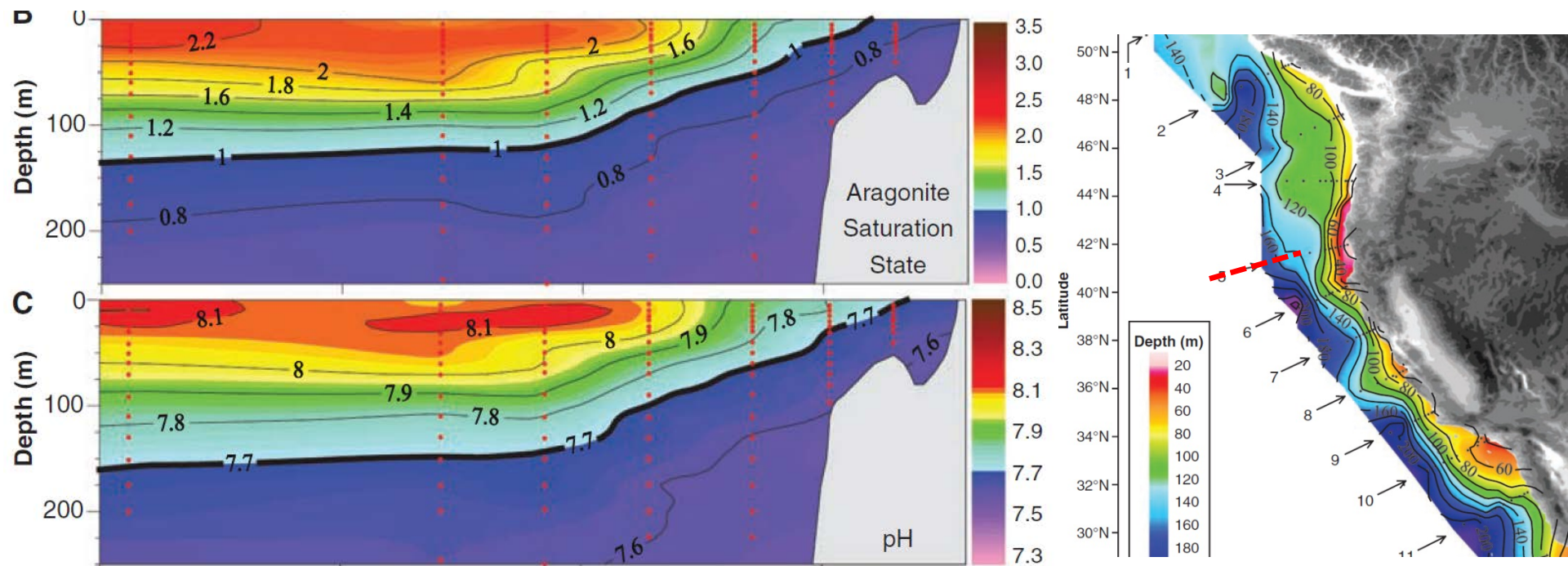


SAB

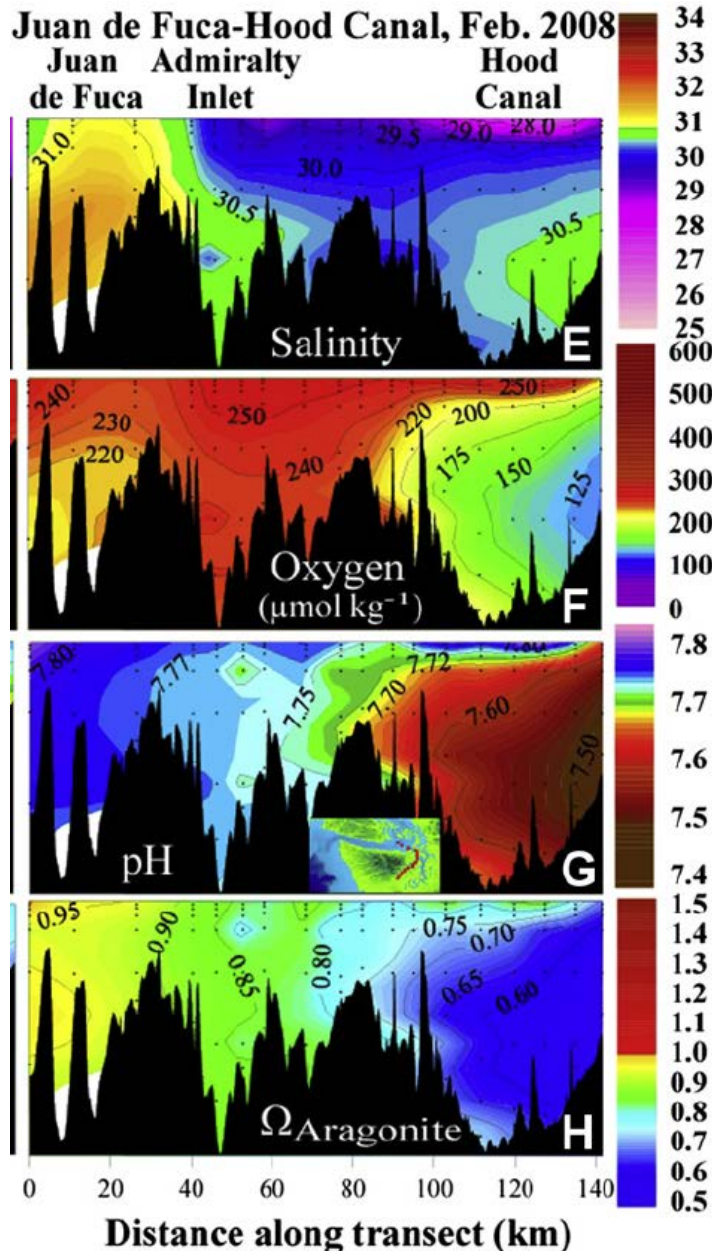
Acidification and low O₂ events in coastal waters--1.

At an eastern boundary current shelf

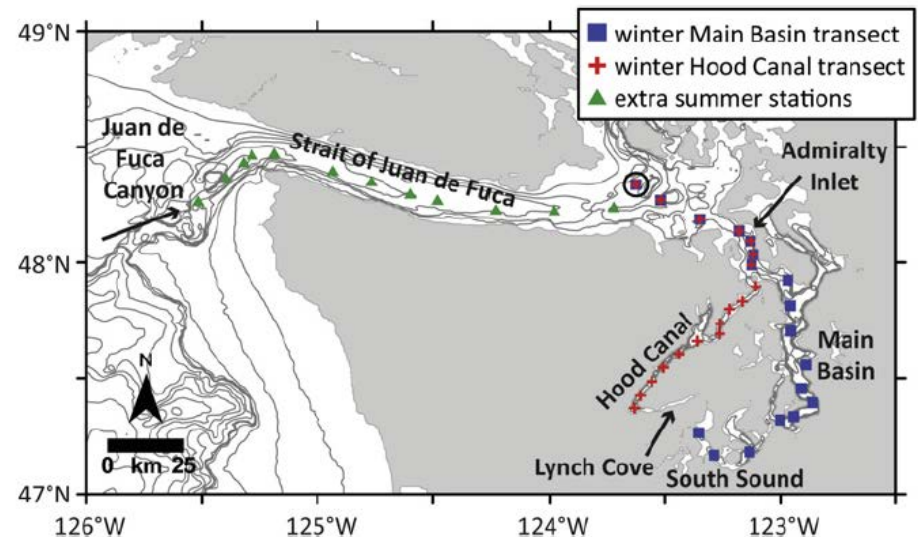
- dominated by upwelling of open ocean subsurface water with **low temp**, **low [O₂]**, **low pH**, **low Ω** , and **high $p\text{CO}_2/\text{DIC}$** on to the shelf (Feely et al. 2008, Science)



Acidification and low O₂ events in coastal waters--2.



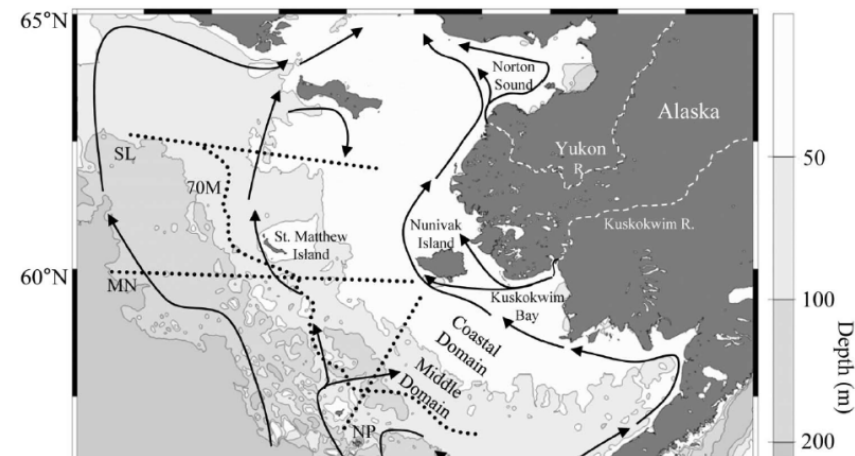
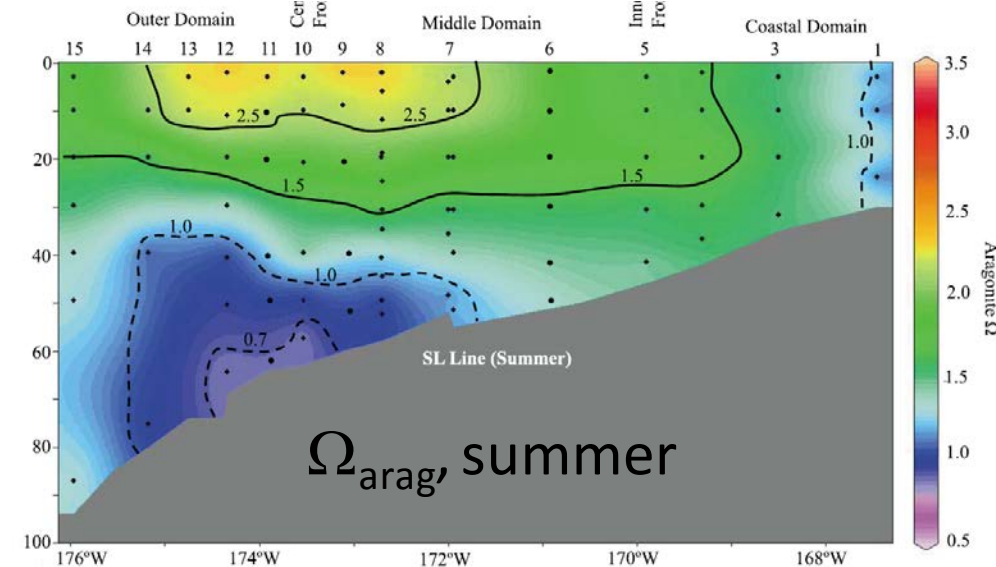
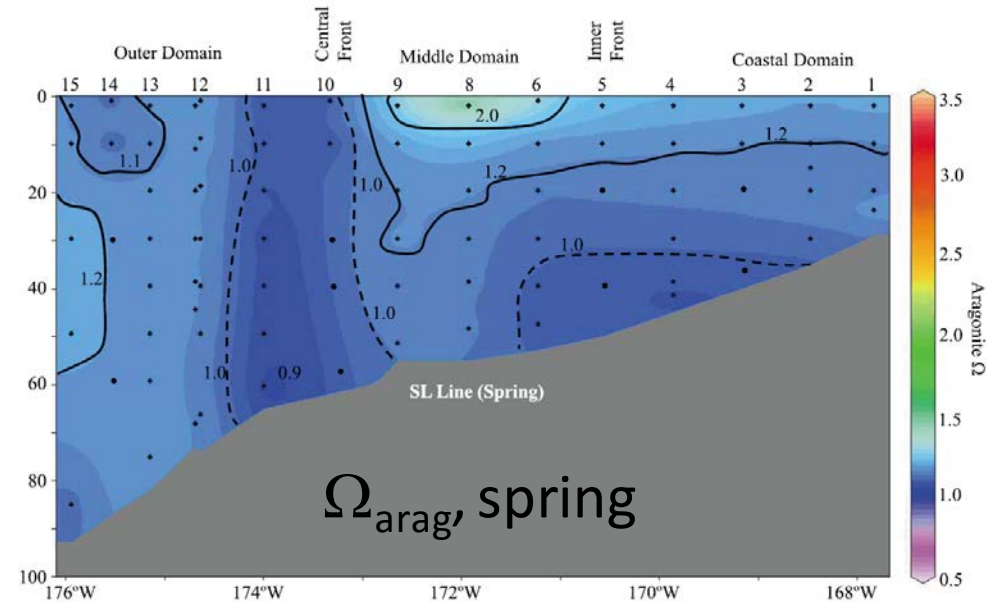
- In an upwelling dominated submerged estuary/bay (Puget Sound)



Feely et al. 2010, ECSS

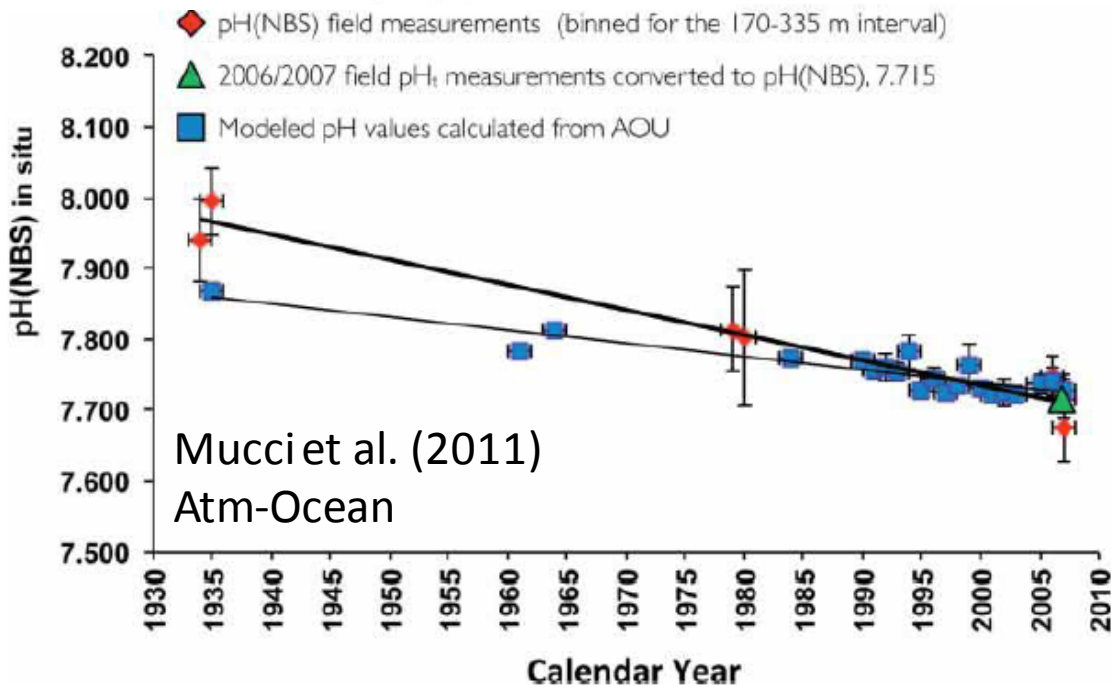
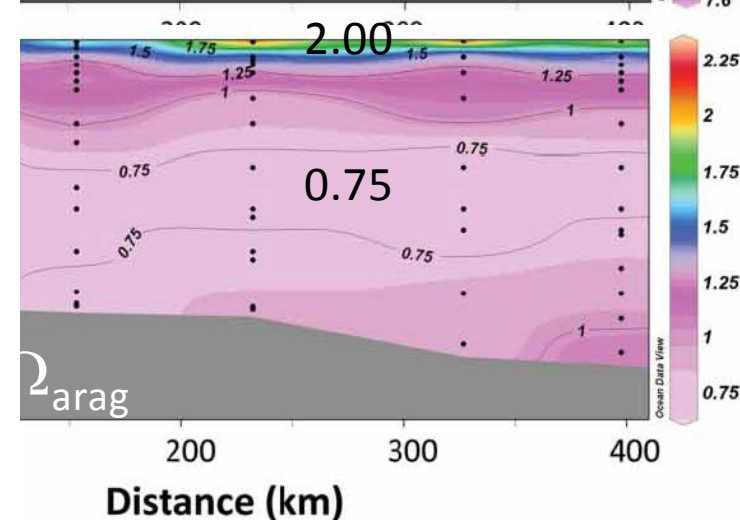
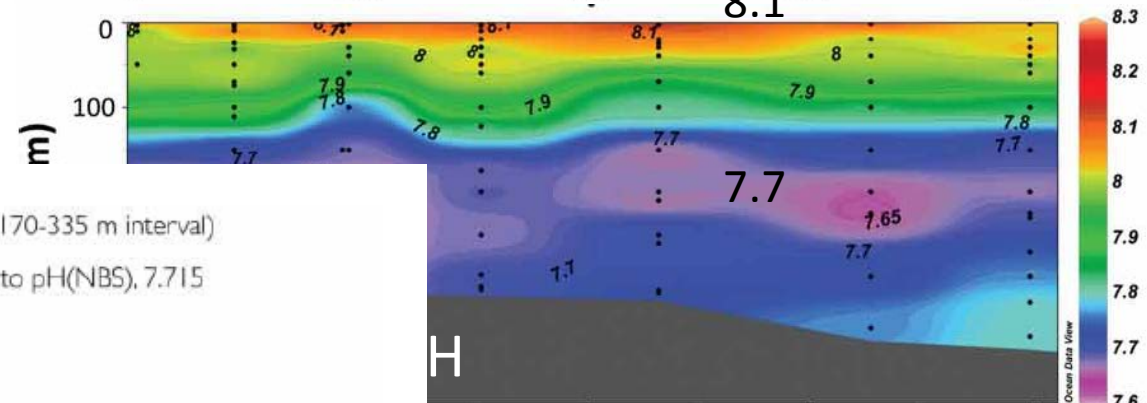
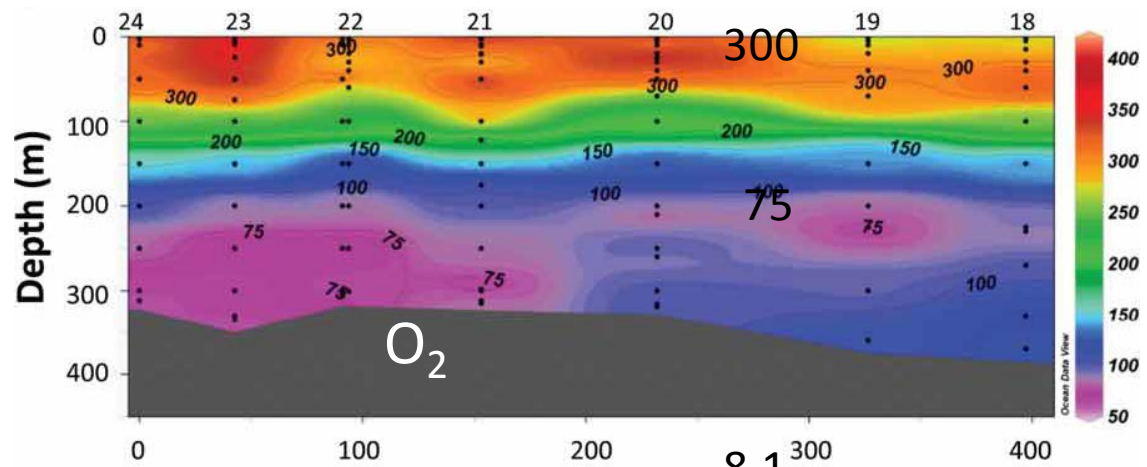
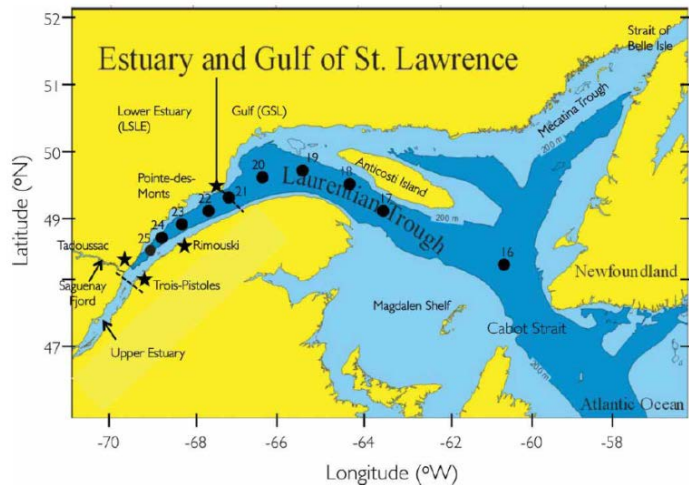
Acidification and low O₂ events in coastal waters—3.

- High latitude waters (Eastern Bering Sea)



(Mathis et al. 2011; JGR)

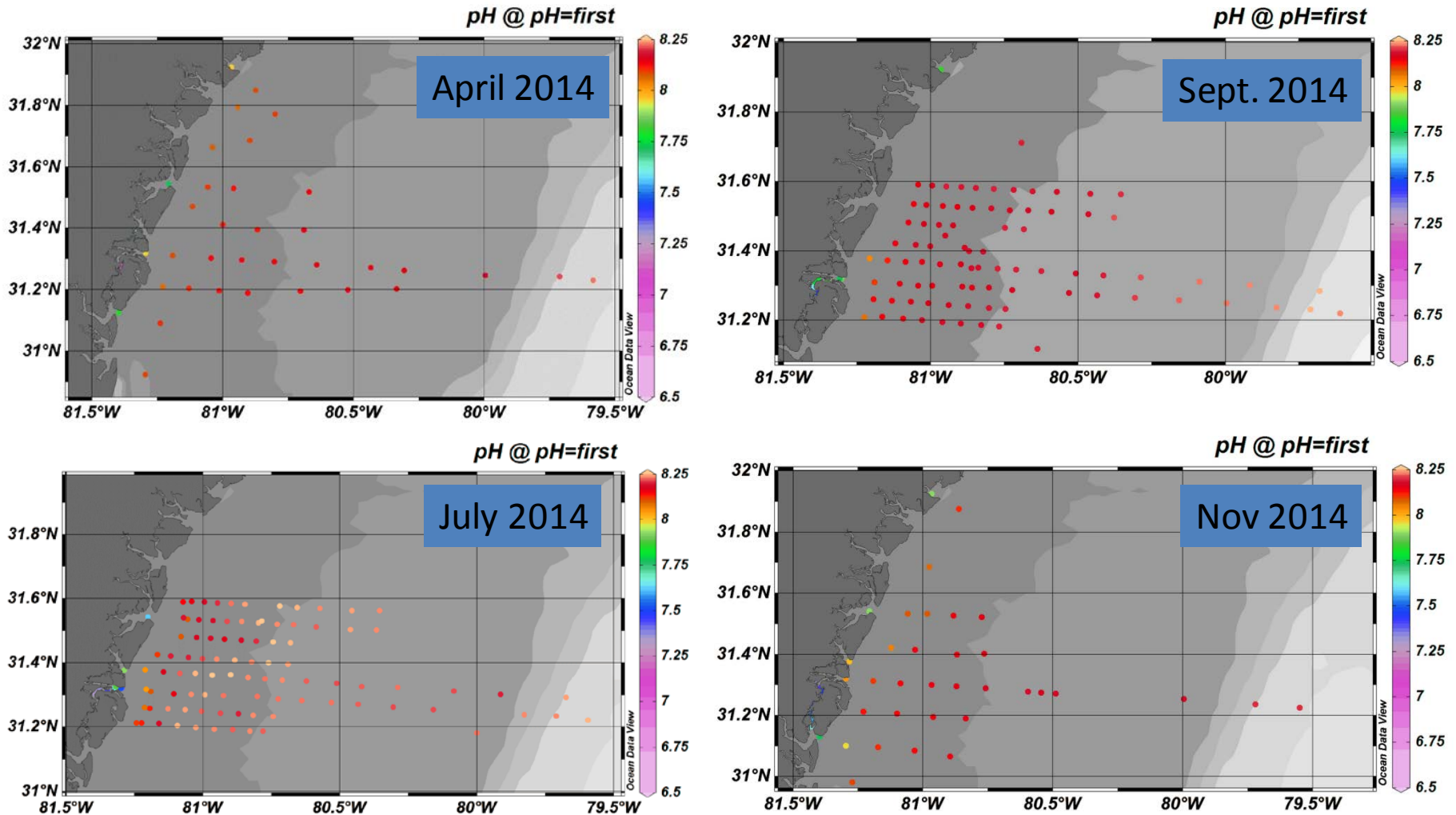
4. St. Lawrence Estuary & Gulf



5. South Atlantic Bight

- Jiang, L.-Q., **Cai, W.-J.**, Feely, R., Wang, A. Y., X. Guo, Gledhill, D. K., Hu, X., Arzayus, F., Chen, F., Hartmann, J., and Zhang, L. 2010. Carbonate mineral saturation states along the U.S. east coast. *Limnology and Oceanography*, 55(6), 2010, 2424-2432, DOI: 10.4319/llo.2010.55.6.2424.
- Wang, Z. A., Wanninkhof, R., **Cai, W.-J.**, Byrne, R.H., Hu, X., Peng, T.-H., Huang, W.J. The marine inorganic carbon system along the Gulf of Mexico and Atlantic coasts of the United States: Insights from a transregional coastal carbon study. 2013. *Limnology and Oceanography* 58 (1): 325-342.

2014 survey of pH (SAB estuaries & shelf)

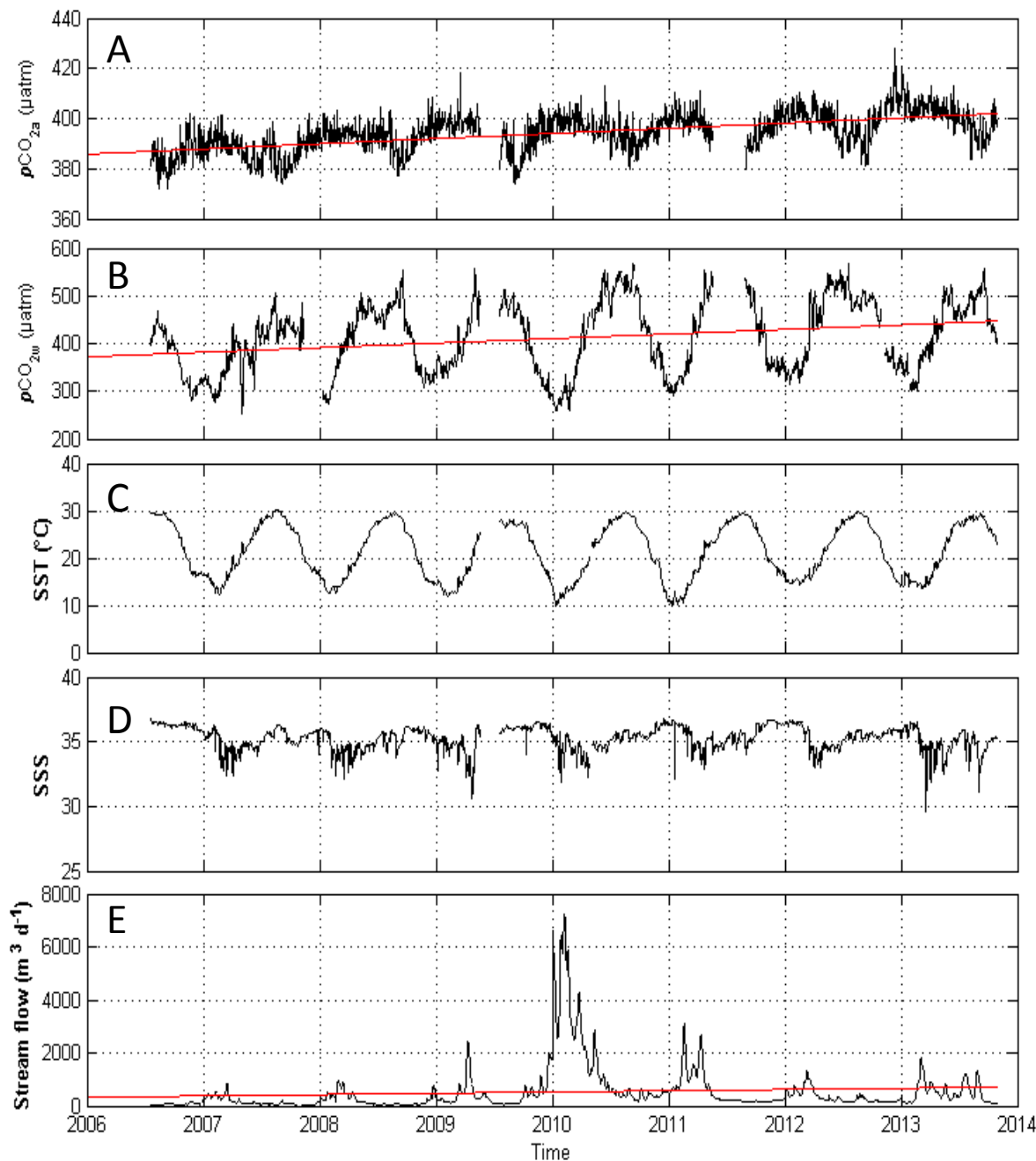


1) decomposition of marsh-exported OM, 2) acidity of humic substance, 3) low buffer capacity

What have we
learned from OA
mooring at the
Gray's Reef site?

$p\text{CO}_{2,w}$ increases at
10 $\mu\text{atm/yr}$,
meaning rapid pH
pH decrease

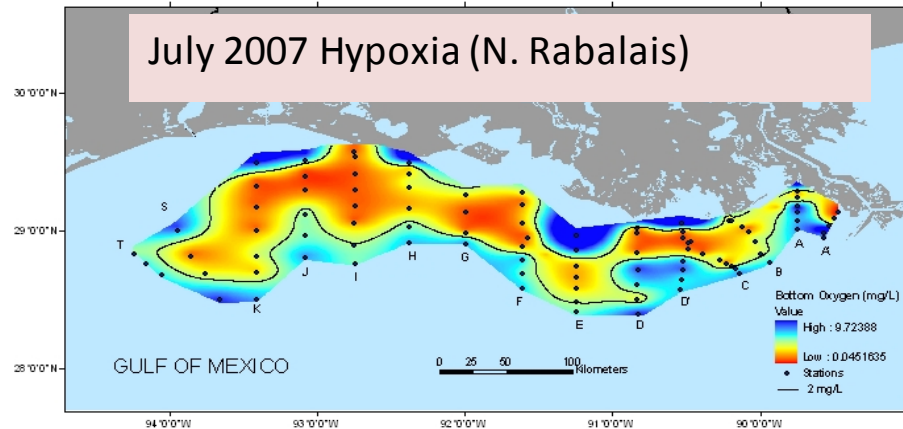
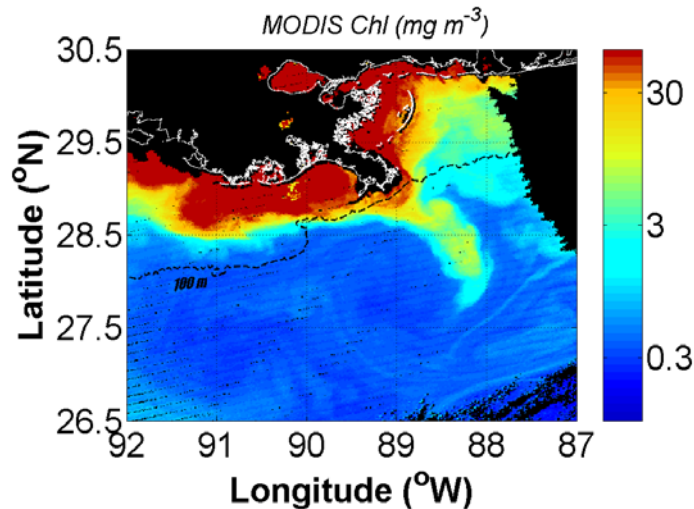
Time series of variables
with slopes of the
linear least squares fit
from deseasonalized
data (red line); from
the top: $p\text{CO}_{2a}$, $p\text{CO}_{2w}$,
SST, SSS, and Altamaha
River stream flow.



Acidification and low O₂ events in coastal waters—6.

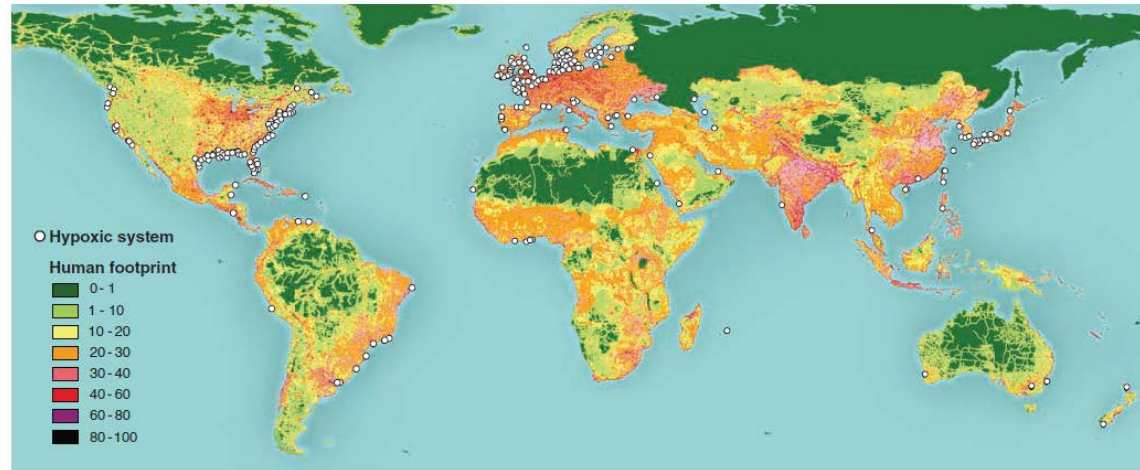
- Eutrophication-hypoxia is not only a serious local/regional stressor, it is also

MR/GOM



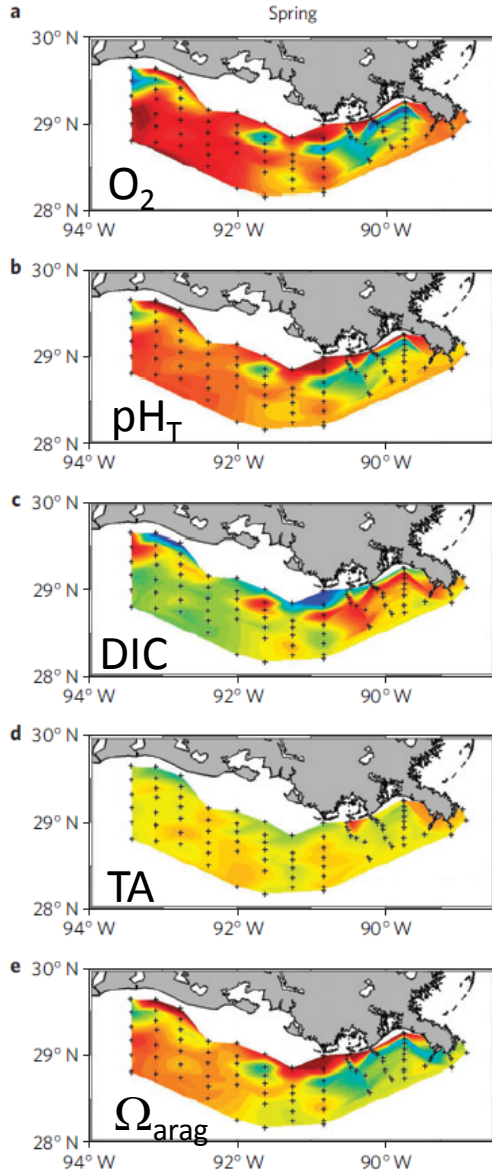
a globally threat.

Spreading Dead Zones and Consequences for Marine Ecosystems
Robert J. Diaz, *et al.*
Science **321**, 926 (2008);
DOI: 10.1126/science.1156401

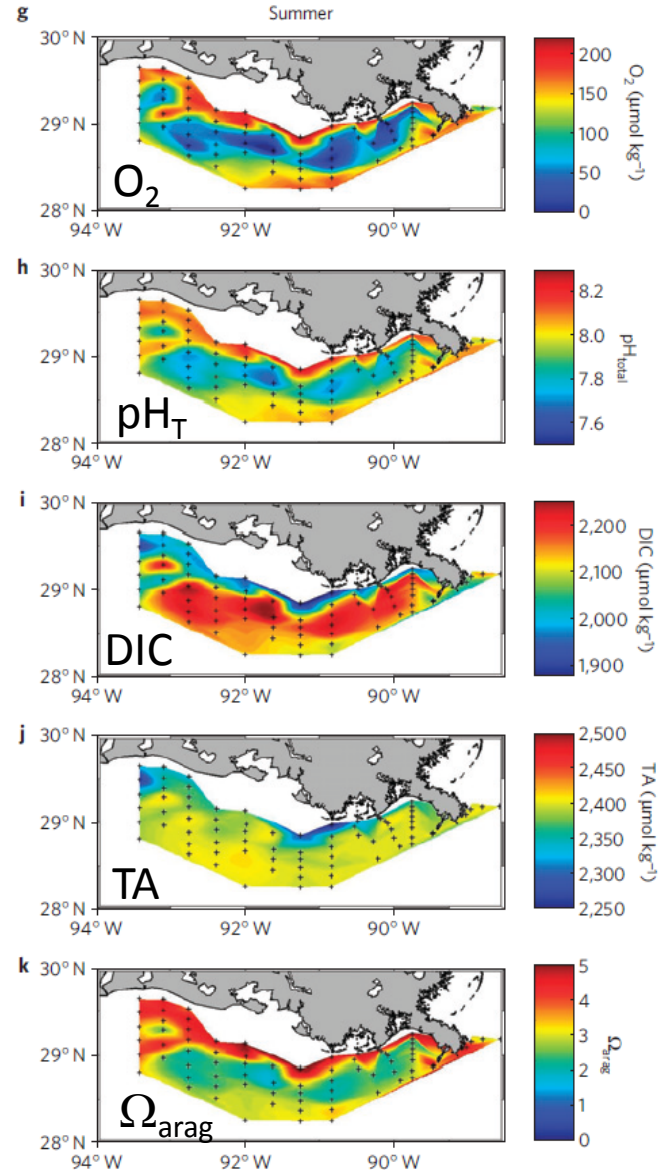


Acidification and low O₂ events in coastal water--5.

April/May 2007



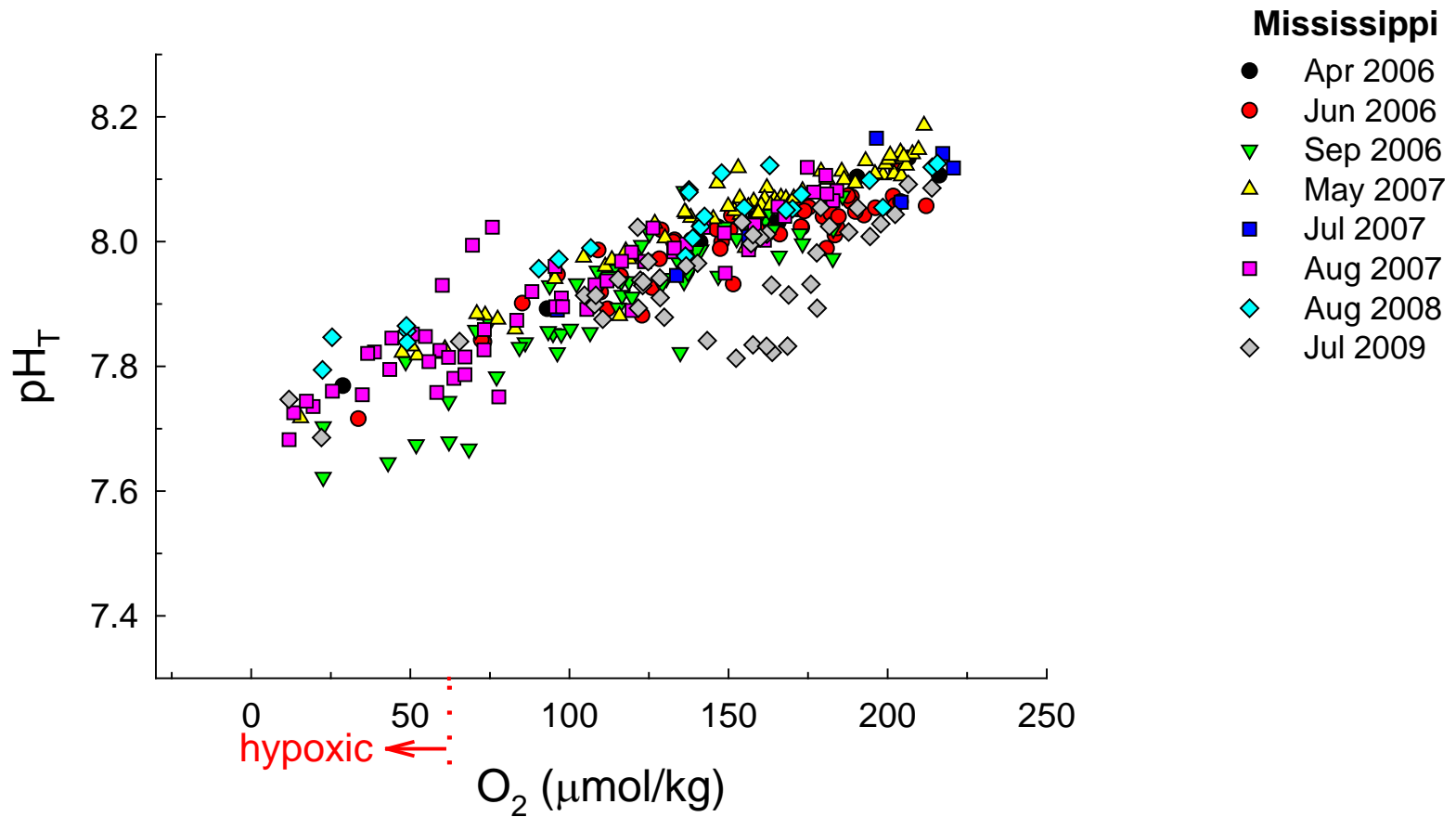
August 2007



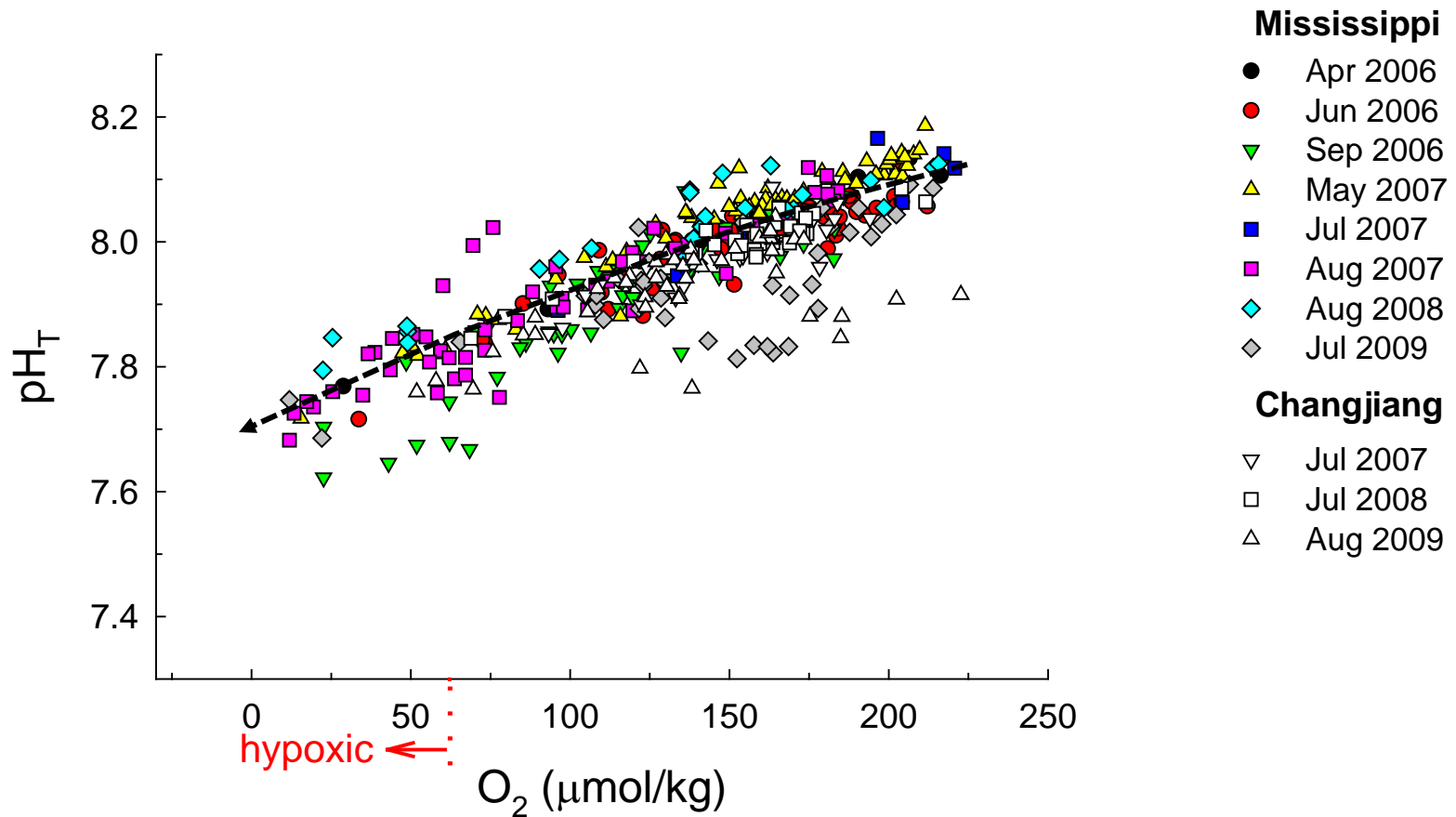
- Gulf of Mexico hypoxic water

Cai et al. 2011
Nature Geoscience

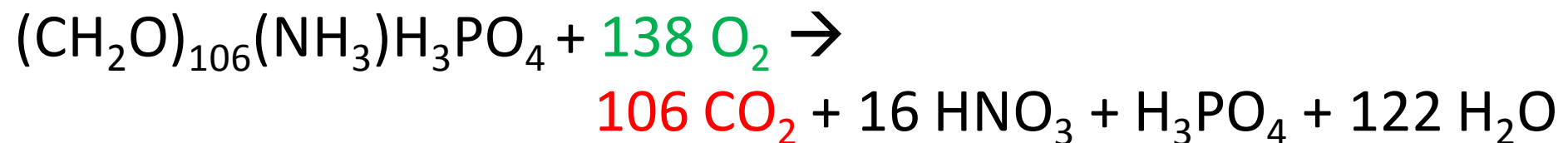
Subsurface water pH and [O₂] relationship



Subsurface water pH and [O₂] relationship

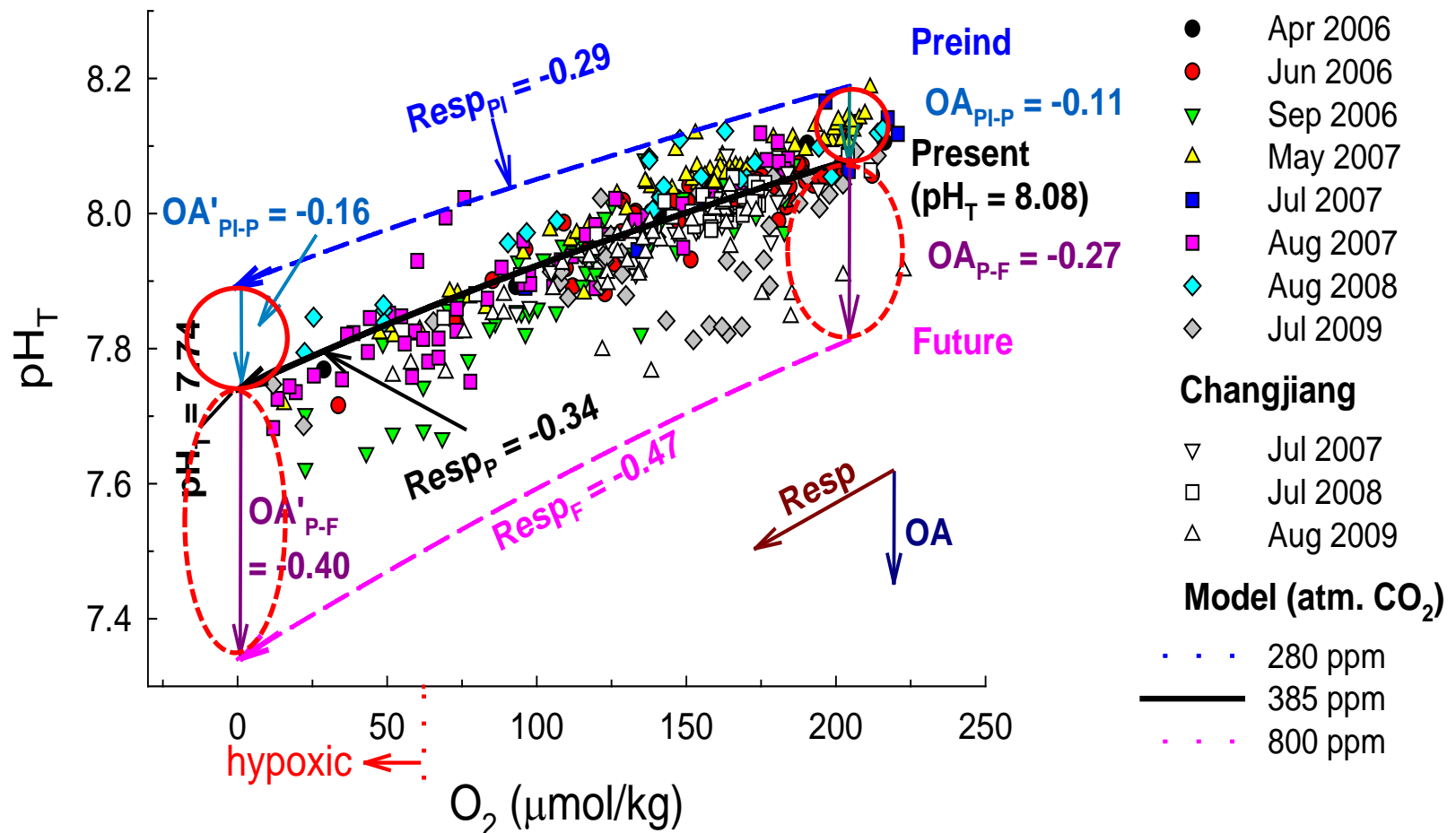


Cai et al. (2011)



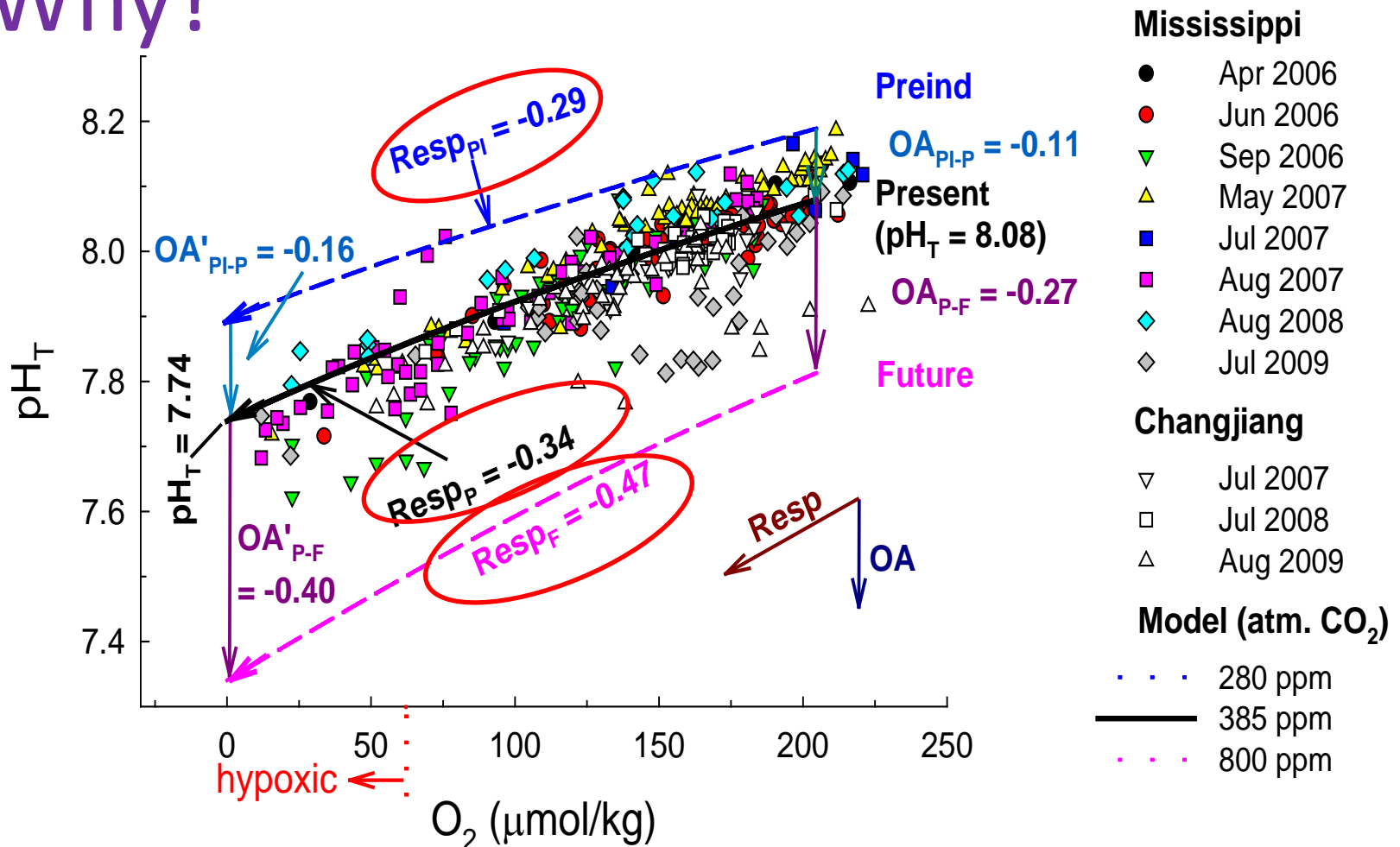
How do anthropogenic CO₂ and CO₂ from respiration interact?

Enhanced ocean acidification!

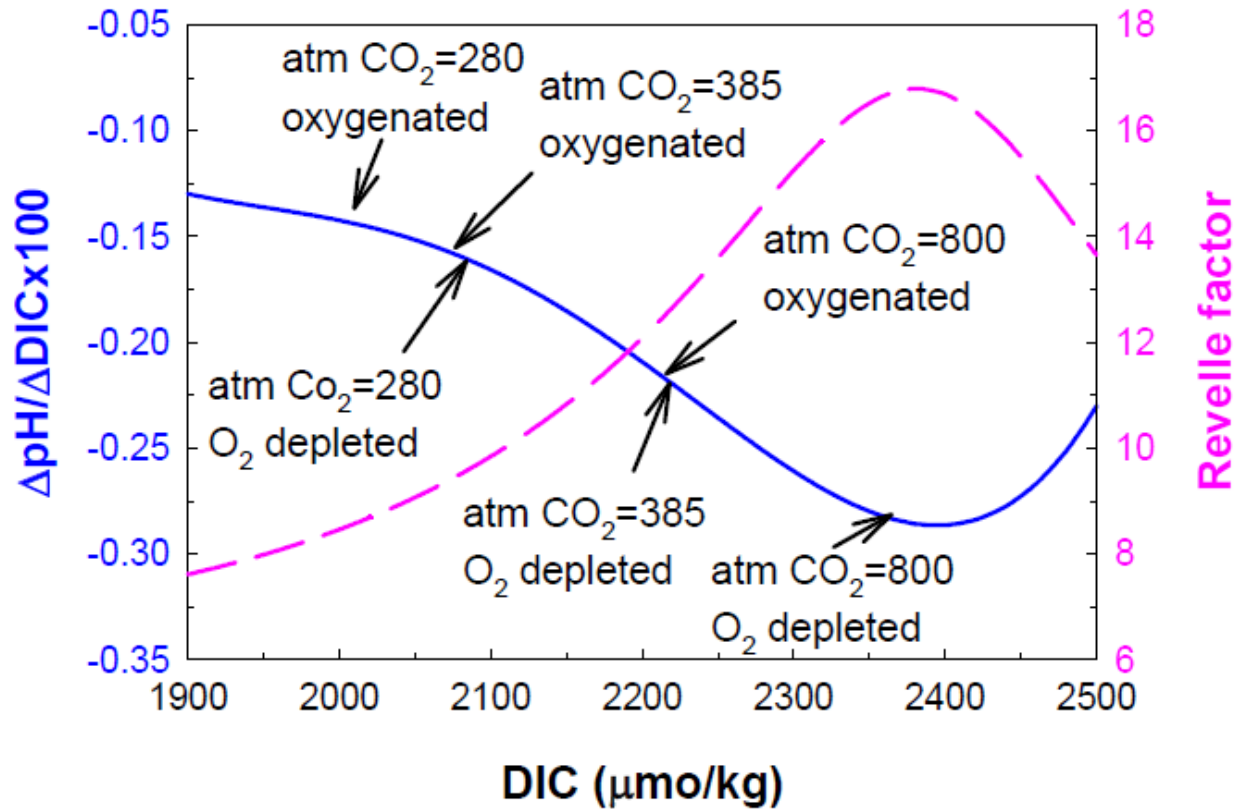


Respiratory CO₂-driven acidification is **enhanced** by anthropogenic CO₂

Why?



Weakening of buffer capacity in CO₂-enriched waters



Cai et al. (2011)
Nature Geoscience

Responses of ocean CO₂ system to multiple stresses: from first principles

- Salinity
- Temperature
- River-Ocean mixing
- Metabolic CO₂ consumption and release
- N cycle (NO₃ and NH₄)
- More frequent storm
- ...

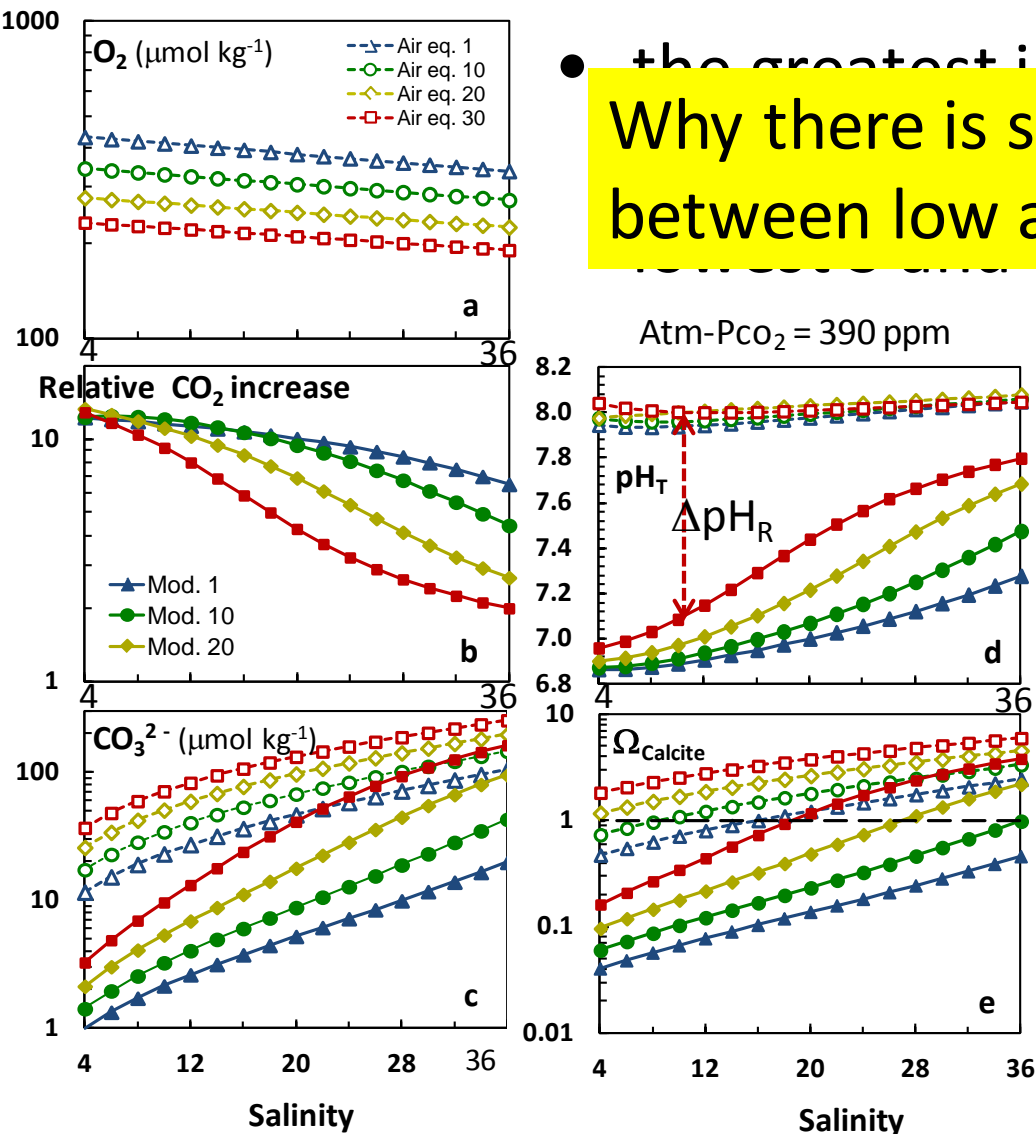
A simple model (model I)

--examining the impact of **respiration** on pH, $p\text{CO}_2$ and Ω under various conditions (T, S, ...)

- Initial partial pressure ($p\text{CO}_2$ and $p\text{O}_2$) is set by the atmosphere
- **Alk is known**
 - River end-member = 1.0 mmol/kg
 - Ocean end-member = 2.3 mmol/kg
- Metabolic processes follows the Redfield CN ratio...
$$(\text{CH}_2\text{O})_{106}(\text{NH}_3)\text{H}_3\text{PO}_4 + 138\text{O}_2 \rightarrow$$
$$106\text{CO}_2 + 16\text{HNO}_3 + \text{H}_3\text{PO}_4 + 122\text{H}_2\text{O}$$



Effects of T & S on respiratory-driven CO₂ acidification (over a complete consumption of O₂)



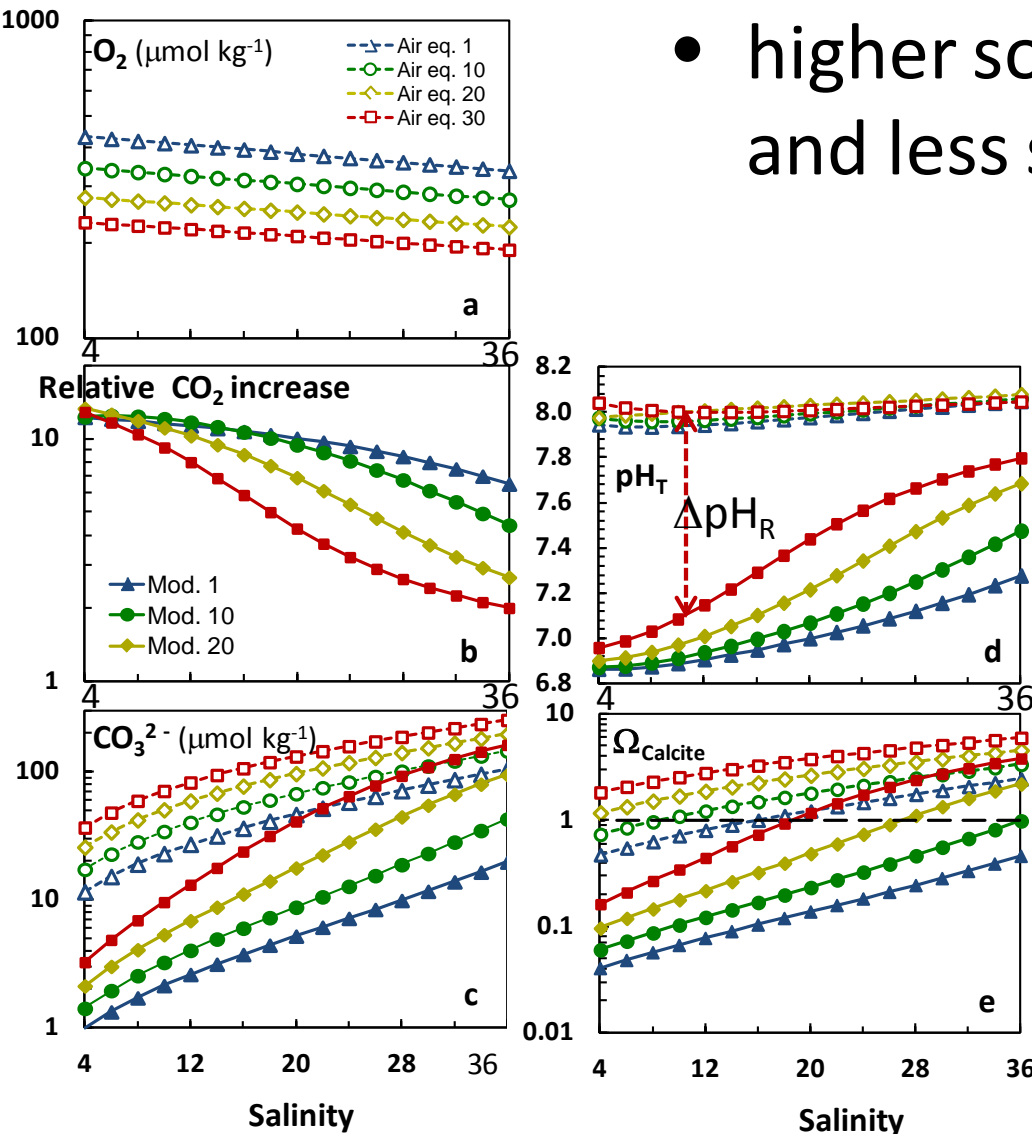
Why there is such a big difference between low and high S & T?

- at higher S & T, less increase in Rel.[CO₂] and decrease in pH (0.25–0.77 at S=36)
- [CO₃²⁻] decreases by 12-fold (low S & T) and 1.6-fold (high T & S)

(Sunda and Cai, ES&T, 2012)

Effects of T & S on respiratory driven CO₂ acidification (over a complete consumption of O₂)

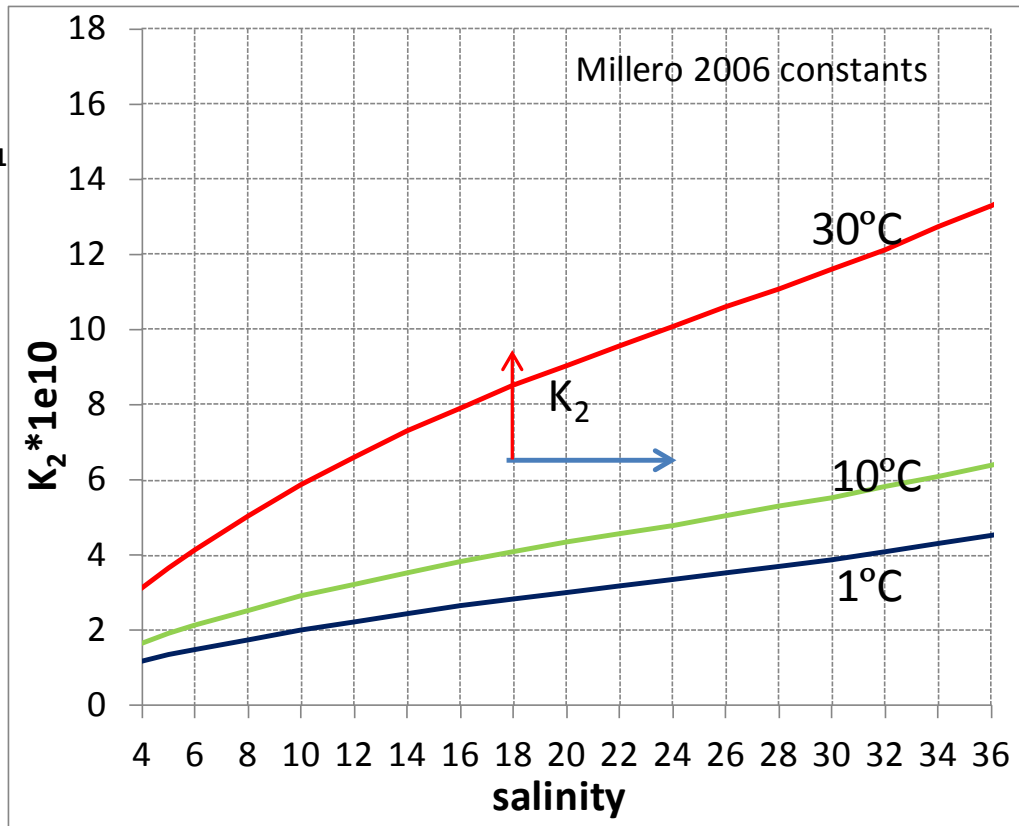
- higher solubility of gases in colder and less saline waters.



- 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).

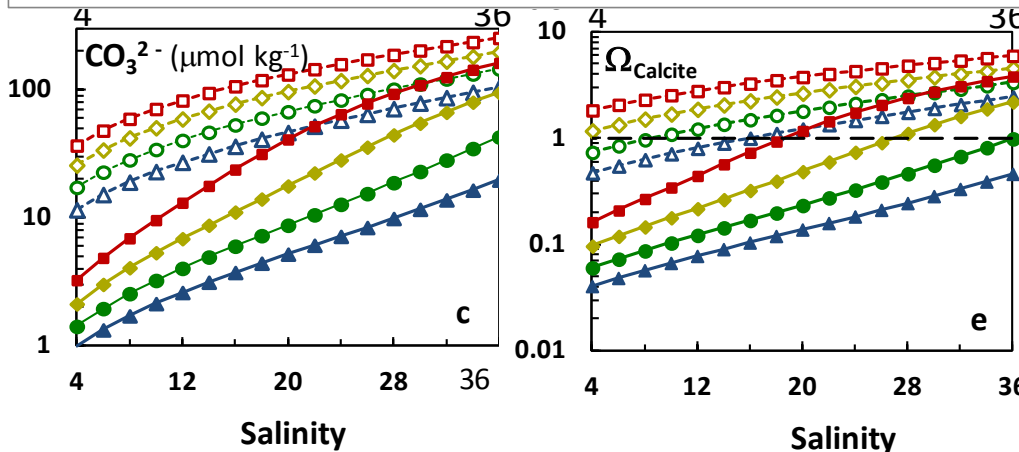
(Sunda and Cai, ES&T, 2012)

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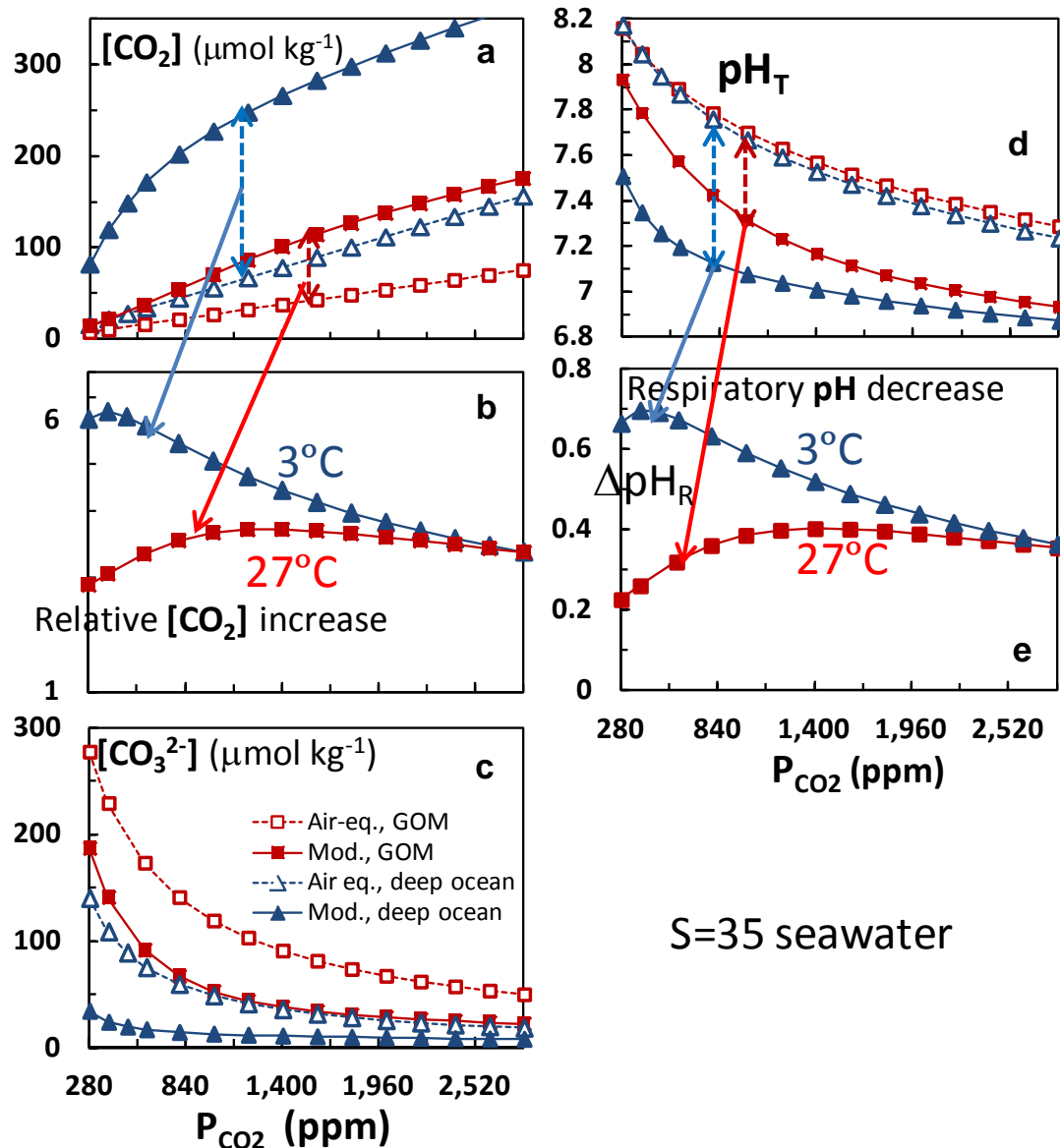
- The different initial $[\text{CO}_3^{2-}]$ is responsible for the very different sensitivity to salinity and temp

- Higher TA at high sal (2.4 mM vs. ~1.2 mM)
- Mainly, a change in dissociation constants (or greater CO_3^{2-})



(Sunda and Cai, ES&T, 2012)

Will increasing $\text{Atm-}P_{\text{CO}_2}$ amplify or suppress respiratory- CO_2 acidification (ΔpH_R)?

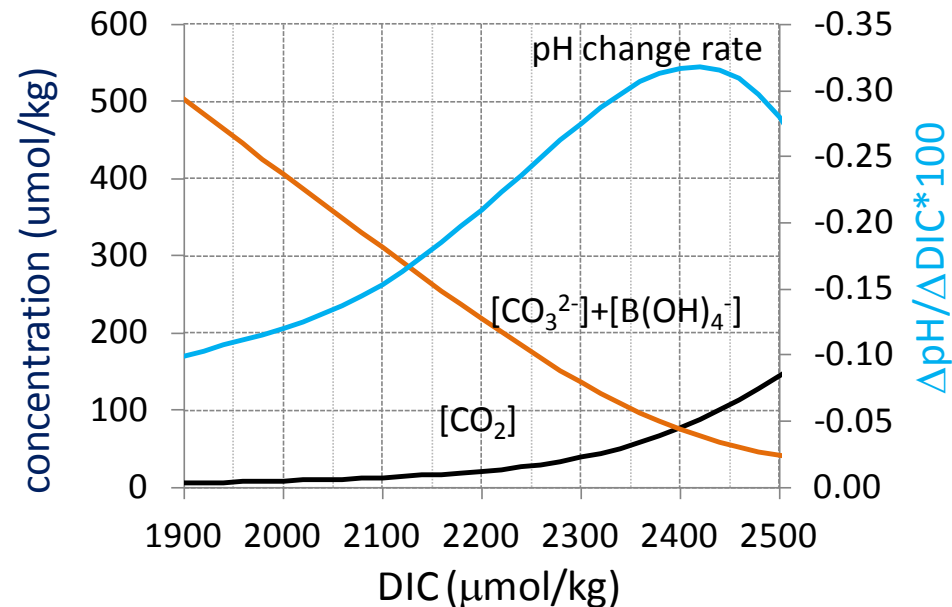
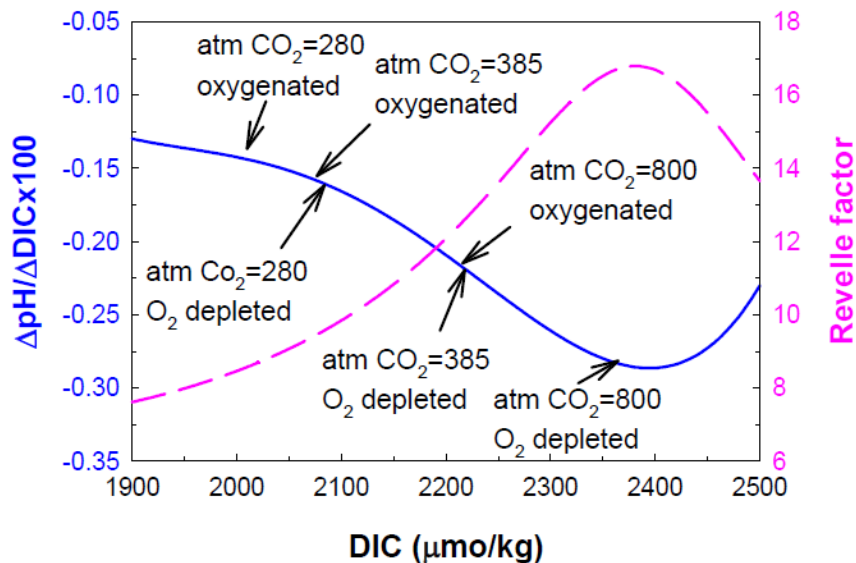


- For high T & S waters (GOM), amplify
- For low T (arctic waters & OMZ), at the max. point, start to suppress
- Initial $[\text{CO}_3^{2-}]$ is the key

(Sunda and Cai, ES&T, 2012)

What is so magic about this point of $\max-\Delta\text{pH}_R$?

- Where the system has minimum buffering capacity
- A point where $\text{DIC} = \text{TA}$ or
- $[\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + \text{B(OH)}^-$
- or $[\text{CO}_2] = [\text{CO}_3^{2-}] + \text{B(OH)}^-$



Modification of model I (model II)

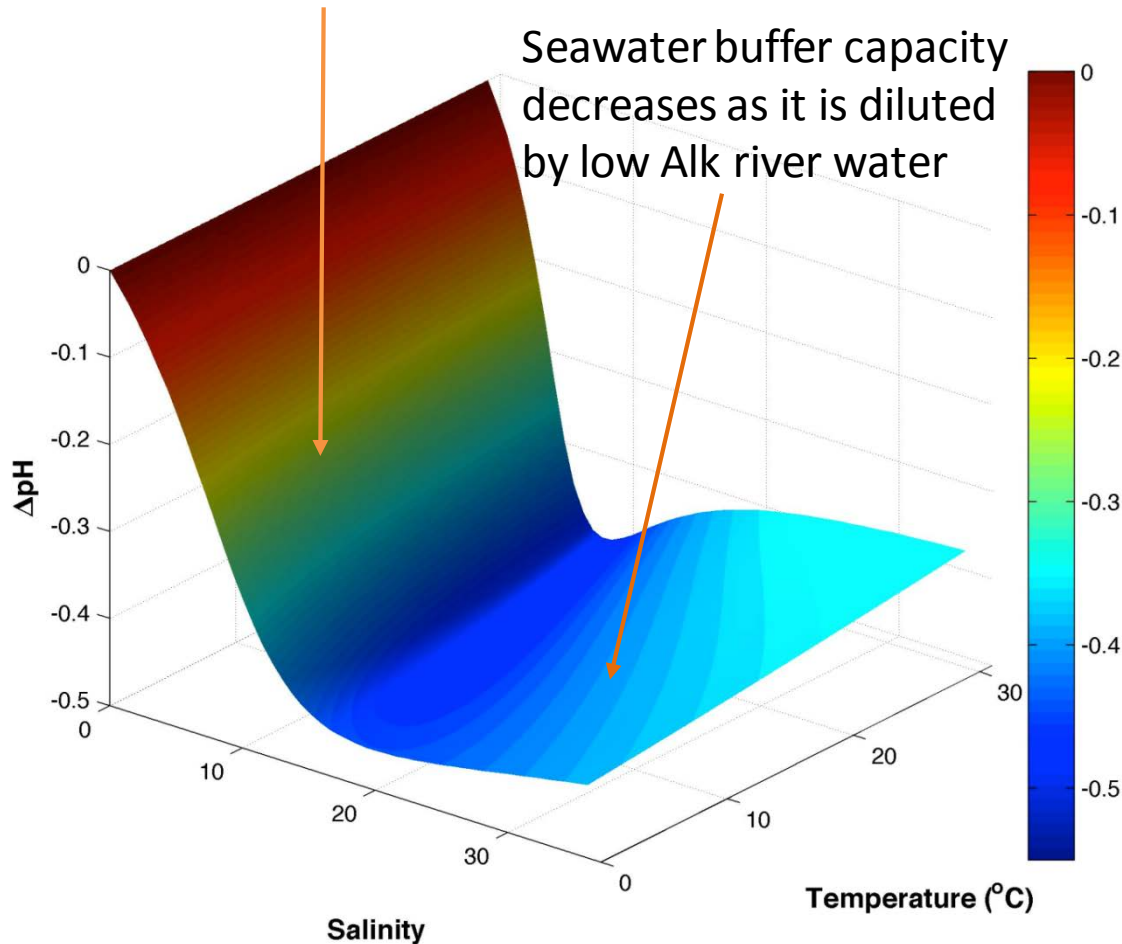
OA signal is only brought into an estuary via mixing of already acidified source seawater

- Either because of high $p\text{CO}_2$ in estuarine water
- Or estuarine $p\text{CO}_2$ is low but water residence time is too short to have a significant accumulation.

Estuarine maximum acidification zone (EMAZ)

Amount of anth-CO₂ decreases
as salinity approaches zero

Seawater buffer capacity
decreases as it is diluted
by low Alk river water



Courtesy of Xinping Hu, TAMU-CC

- pH difference between preindustrial era ($\text{CO}_2 = 280$ ppm) and future ($\text{CO}_2 = 800$ ppm) in an **simulated estuarine water across salinity and temperature gradients. Altamaha River (TA/DIC) was used as the river endmember, and the seawater endmember TA was calculated using salinity 36 and alkalinity-salinity relationship of Atlantic surface water in Millero and DIC was calculated using TA at the two CO_2 levels.**

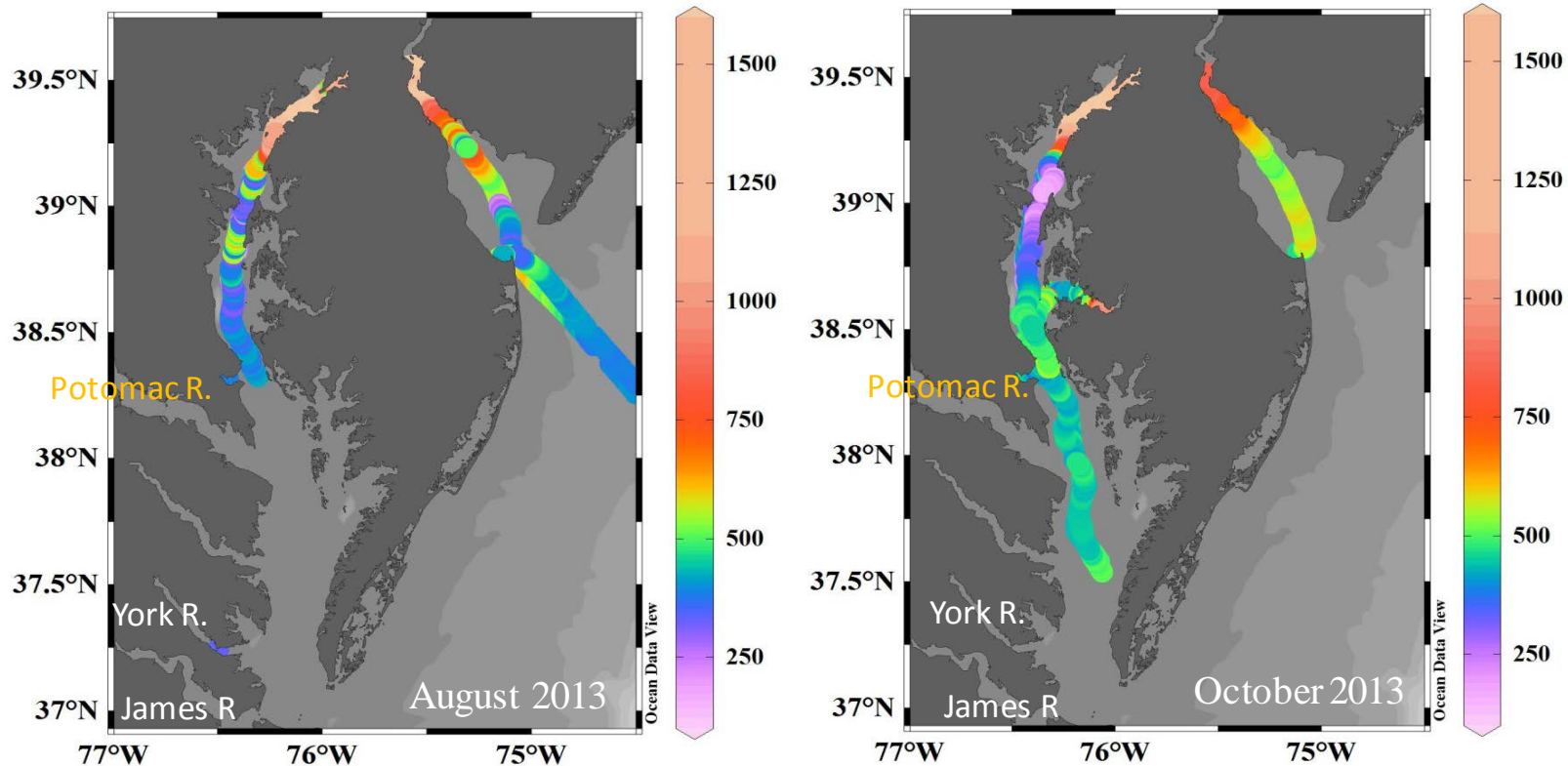
Summary

- Respiration often plays a more important role in acidifying coastal bottom waters today, but
- Anthropogenic CO₂ uptake from the atmosphere will play an increasingly important role in acidifying coastal bottom waters.
- There is a strong enhancement of acidification in CO₂-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).
- There exists an Estuarine Maximum Acidification Zone. How do we verify it?

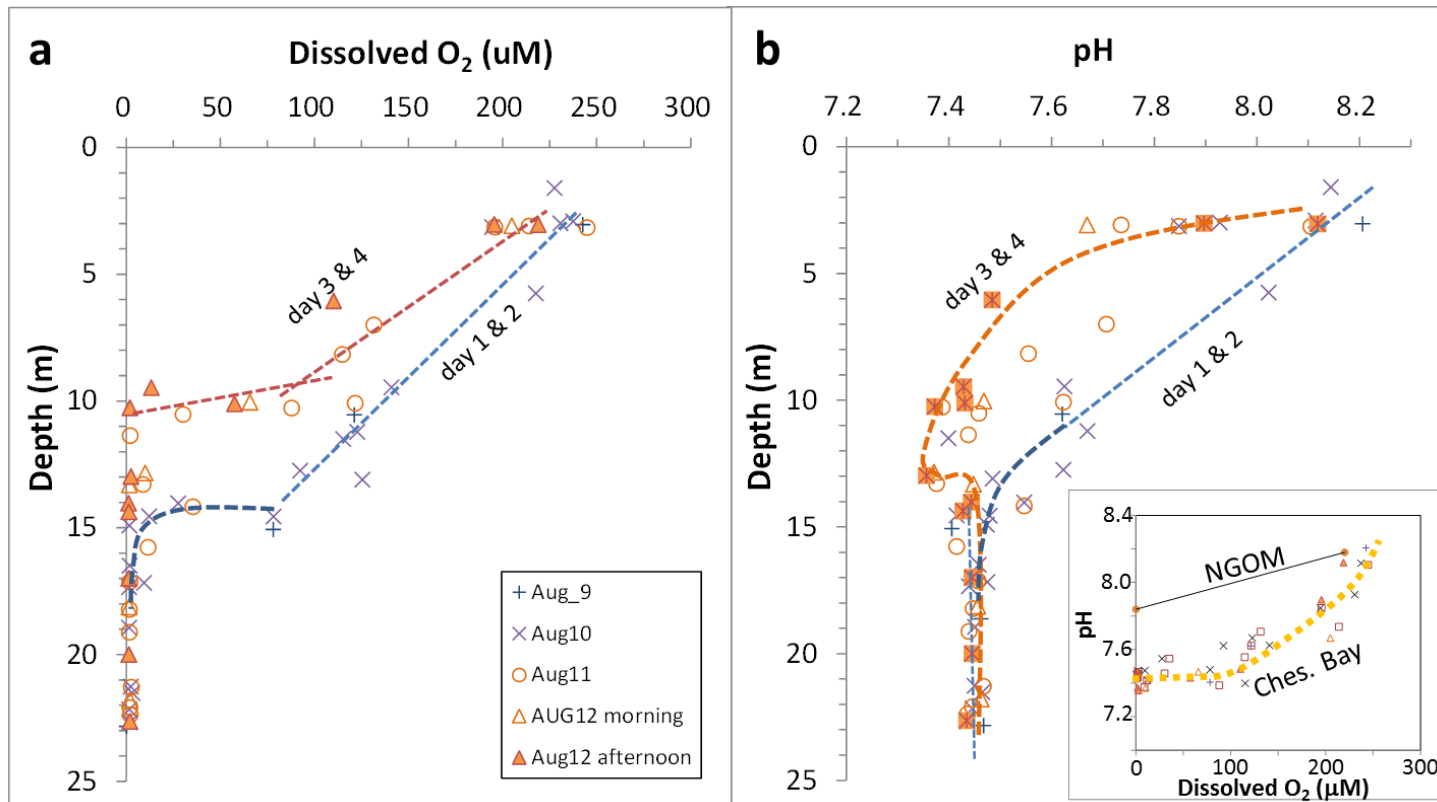
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$p\text{CO}_2$ in Chesapeake Bay



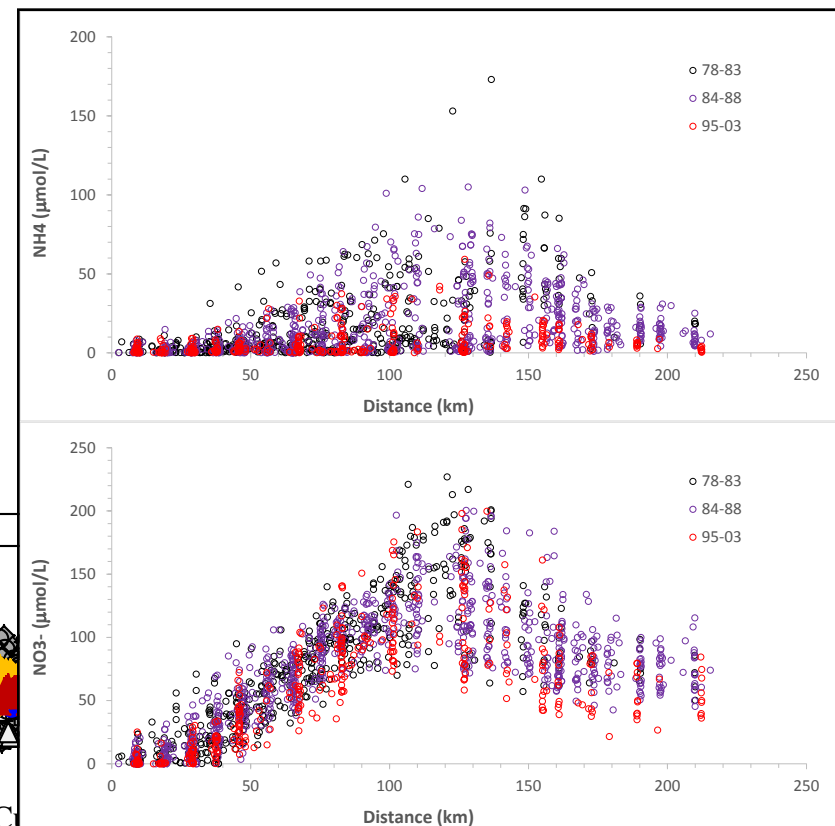
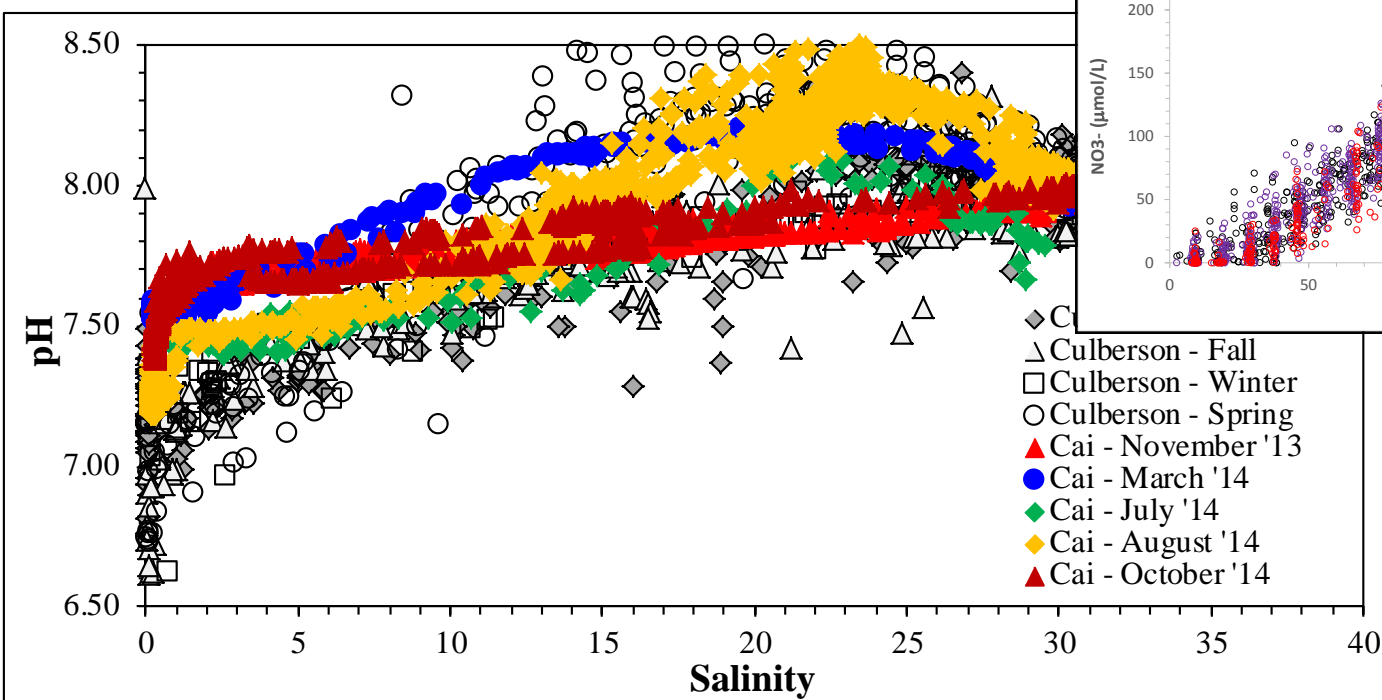
Near Bay Bridge 8/9 -12, 2013



- There is a pH minimum at the depth where DO approaches zero
 - day 1 [H₂S]=2-5 uM,
 - day 4, [H₂S]=30-40 uM
- pH-DO relationship is very different from that in the GOM.

Historical data from and recent changes in the Delaware Estuary

Lower $[\text{NH}_4^+]$ from pollution may explain the recent pH change



- Thank you!

Q & A

Q: In the plot showing the mooring time series off Georgia, the strong freshwater runoff in 2006 (?) didn't have any corresponding changes in SSS, PH etc... Why?

A: You are correct that direct responses in SSS and pCO₂ were weak during one peak flow time (early 2010). Probably there are two reasons. 1) there is a general but significant correlation between SSS and river discharge with a time delay from river discharge to mooring response (about 45 days from our data analysis); 2) but the plume pattern is irregular and specifically it is not clear how the 2010 peak affected the mooring. Nonetheless, for all summer data, we found a significant SSS decrease during time over the mooring period, correlating well with pCO₂ increase.

Q: To what degree can photosynthesis enhanced by eutrophication seasonally offset respiration effects

A: In a bathtub scenario (no OM input and export) and give enough time, the two signals should cancel each other. But even in that case, there is a time delay between respiration and photosynthesis. A couple of years ago, I reviewed a paper reporting O₂ & pH from Scott Nixon's famous "aquatic incubation ecosystem" which is vertically mixed (the paper is published). One can see that pH signal persisted long time after O₂ signal disappeared following the photosynthesis and respiration signal. The response time scale for CO₂/pH is much longer than that of that of O₂ (biological and gas exchange). In natural systems, the two signals are also spatially separated and cannot completely cancel each other. I'd say they make a system going to two extremes, part of the system (surface or upper stream) goes to a very high pH and the other part (bottom or downstream) goes to a very low pH.

Q & A

Q: Will full citations of all the work cited be available?

A: I provided most of them. Emil me if you have a specific target.

Q: Have you studied OA in any of the SAB estuaries?

A: We studied pH and the CO₂ system in several SAB estuaries since 1990s. We just didn't call it estuarine OA then. We are doing more now.

Q: With respect to humic TA in Georgia estuaries, do you see that signal in the rivers as well, or just in estuaries? I ask because many rivers are considered to be carbonate alkalinity dominates.

A: Yes in rivers, in particular in low carbonate black water coastal plain rivers in the southeast.

Q & A

Q: What are your thoughts on how we might verify the EMAZ?

A: Overall, there are two approaches. One is to model field data and the other is to design lab control experiments. This has to be done over a few estuaries or estuarine conditions that has different river TAlk values.

Q: How do propose that enhancing coastal habitats may impact the Estuarine maximum zone?

A: I am not sure if I understand the question. If the habitat ecosystem function/biogeochemical processes modifies DIC and TAlk, then, it would.

Q: Do you think results from investigating estuarine ocean acidification could have an influence on marine policy?

A: I hope so.

Q & A

Q: Given the substantial variability in run-off characteristics and physics between estuaries (locations), do you think we'll need to establish monitoring across the South East, or do you think key sites will be able to provide enough insight across sites?

A: Realistically we probably can only do a few key sites plus some across-site synthesis. For multiple sites, maybe it is better to collect samples and send them to one analytical lab to analyze, which will apply the same standard and QC to all analysis.

Q: If buffering capacity increases with salinity. Does that mean on the West Coast do we not need to worry as much about acidification in our reverse estuaries?

A: No, I never said buffer capacity increases simply with salinity. In most estuarine mixing examples this is true because the high salinity represents mixing of a low buffer capacity river water with a high buffer capacity ocean water. In the west coast, that “high salinity ocean water” happen to have low buffer capacity (has high DIC there) subsurface ocean water.

