PICES Annual Meeting, Oct. 16, 2013, Nanaimo, Canada

Multiple stressors in the coastal ocean

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Overview

- Ocean Acidification (OA): Another CO2 problem has emerged-yet coastal ocean more complex
- Coastal ecosystems under multiple forcings: temp rising + O₂ decline+ acidification within a similar time frame
- Need consider the hydrodynamics: e.g., Upwelling/Submarine Groundwater Discharge
- OA observation system & multidisciplinary researches essential and consider the multiple stressors at a system level

Outline

- Coastal Ocean Acidification
- Multiple stressors in the Coastal Ocean
- Concluding Remarks

Ocean Acidification: another CO₂ problem: increase in [H⁺] or drawdown of pH



From PMEL

pH = -log (H⁺) = -log $\gamma_{\rm H}$ {H⁺} CaCO₃ saturation state: $\Omega = [Ca^{2+}][CO_3^{2-}]/Ksp',$ $\Omega_a > 1 \sim$ supersaturated $\begin{array}{c} \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{H}^+ \\ \text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{HCO}_3^- \\ \hline \text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{2HCO}_3^- \end{array}$

When CO₂ invades sea water: • [HCO -lincreases

- [HCO₃⁻]increases
- [CO₃²⁻]decreases
- Ω decreases

 a small part of HCO₃⁻ formed dissociates into carbonates + H⁺ ("ocean acidification")

Calcification rate vs. Ω_{arag} in coral reef systems



Fig. 6. Ω_{arag} versus calcification rate for coral reef ecosystems (solid symbols) and coral mesocosms (open symbols). Lines are the linear least-squares best fit of the data. References for data are: Kaneohe Bay barrier reef data (black diamonds and solid line), this study; Eilat Reef, Red Sea (dark gray squares and solid line) (Silverman et al., 2007a, b); Rukan-sho, Japan (light gray triangles and solid line) (Ohde and van Woesik, 1999); Biosphere 2 (black circles and dashed line) (Langdon et al., 2000, 2003); Kaneohe Bay mesocosm, 2005 (light gray squares and dashed-dot line); Kaneohe Bay mesocosm, 2009 (dark gray triangles and dotted line) (Andersson et al., 2009).

Shamberger et al. (2011)

Why Coastal Ocean?



- A unique physicalbiogeochemical ecosystem links the land and the open ocean but vulnerable
- Boundary processes across the land-margin and margin-ocean are key drivers
- Characterized by complex circulations, abundant river/groundwater input, dynamic sediment boundary and high productivity: large gradients chemically and biologically

Why are some marginal seas sources of atmospheric CO₂?

Minhan Dai,¹ Zhimian Cao,¹ Xianghui Guo,¹ Weidong Zhai,¹ Zhiyu Liu,¹ Zhiqiang Yin,¹ Yanping Xu,¹ Jianping Gan,² Jianyu Hu,¹ and Chuanjun Du¹



An updated province –based global shelf air-sea CO₂ flux:



Dai et al., GRL, 2013

Coastal ocean mitigates more CO₂ than the open ocean





Figure 2. pH dynamics at 15 locations worldwide in 0-15 m water depth. All panels are plotted on the same vertical range of pH (total hydrogen ion scale). The ordinate axis was arbitrarily selected to encompass a 30-day period during each sensor deployment representative of each site during the deployment season. See Table 1 for details regarding sensor deployment. doi:10.1371/journal.pone.0028983.g002

pH dynamics in different marine systems



Figure 1. Map of pH sensor (SeaFET) deployment locations. See Table 1 for details regarding deployment locations. doi:10.1371/journal.pone.0028983.0001

Hofmann et al. (2011) High-Frequency Dynamics of Ocean pH: A Multi-Ecosystem Comparison. PLoS ONE 6(12): e28983. doi:10.1371/journal.pone.0028983

OA in coastal ocean more dramatic

A NE Pacific Coastal Site (Tatoosh Island, 2000-2008)



- Wootton et al., PNAS, 2008



doi:10.4319/lo.2011.56.5.0000

Neap Tide



Spring Tide

Jiang et al., L&O, 2011

Neap Tide

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Spring Tide

nwan Bay

China Mainland

MEL-SMMC CO2-A



Cases: main drivers of OA in coastal ocean

- Anthropogenic CO2
- Upwellings of low pH waters
- Respirations
- Ground water

Anthropogenic CO2-driven pH changes in the South China Basin

The South China Sea

(Station SEATS, 1998-2009)

Predicted anthropogenic CO2 induced pH decrease-0.0019 yr⁻¹

Surface pH decreasing: -0.002 yr⁻¹ pH(25°C; cal.) 8.16 (e) 8.12 8.08 8.04 $= -0.002x (yr^{-1}) + 8.1018 R^{2} = 0.0677$ p=0.110 8.00 8.16 $y = -0.0026x (yr^{-1}) + 8.1204$ pH(25°C) 8.12 $R^2 = 0.0244$ 8.08 n= 0 549 8.04 8.00 $\varphi R^2 = 0.0171$ chl. a(µg/L) $y = -0.0006x (yr^{-1}) +$ p=0.469 0.6 0.2036 0.4 (g) 0.2 0.0 1998 9992000200120022003200420052006200720082009

- Arthur Chen, MEBC-SCS Conference Abstract, 2010 http://mebcscs.marine.nsysu.edu.tw/images/Text/Abstract_Chen.pdf



*Air p*CO₂ 2 μatm yr⁻¹ At TAlk=2200 μmol kg⁻¹; Temp=29.0 °C; S=33.5; PO₄=0.01 μM; Si(OH)₄=2 μM

Examples: OA in coastal ocean

- Anthropogenic CO2
- Upwellings of low pH waters
- Respirations
- Ground water

Aragonite Saturation Depth ($\Omega_{arag} = 1.0$) in the Global Oceans



- Feely et al., 2004

Coastal Upwelling System Western NP vs. Eastern NP Case I: Continental shelf off the Oregon-California border (Upwelling in the Eastern NP)

Evidence for Upwelling of Corrosive "Acidified" Water onto the Continental Shelf

Richard A. Feely,^{1*} Christopher L. Sabine,¹ J. Martin Hernandez-Ayon,² Debby Ianson,³ Burke Hales⁴

13 JUNE 2008 VOL 320 SCIENCE www.sciencemag.org

Distribution of the depths of the undersaturated water (Ω_{arag} < 1.0; pH < 7.75) on the continental shelf of western North America.



Due to the upwelling process, the corrosive water reaches all the way to the surface in the inshore waters near the Oregon-California border.

- Feely et al., 2008



 Upwelling from depths of 150 to 200 m onto the shelf; First observation of surface undersaturated waters with respect to aragonite (in open ocean surface waters until 2050); ~30 µmol kg⁻¹ of anthropogenic CO₂ lowered Ω_{arag} by ~0.2 units.

- Feely et al., 2008

Case II: The Northern South China Sea (NSCS) Shelf (Upwelling in the Western NP)

Dynamics of the carbonate system in a large continental shelf system under the influence of both a river plume and coastal upwelling

Zhimian Cao,¹ Minhan Dai,¹ Nan Zheng,¹ Deli Wang,¹ Qian Li,¹ Weidong Zhai,¹ Feifei Meng,¹ and Jianping Gan²

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 116, G02010, doi:10.1029/2010JG001596, 2011

Field work-2008 summer Leg 1 (Transects 1-7; Jun 30 - Jul 8) Leg 2 (Transects 5-2; Jul 9 - Jul 12)





Upwelling Centers (UC): Low Temperature High DIC Low Ω_{arag} UC 2 > UC 1

Surface Ω_{arag} values:
 2.3 ~ 3.9
 Lowest 2.3 in UC 2
 Oversaturation state

Upwelled waters were transported northward from the position of UC 2 to the position of UC 1 [Gan et al., 2009].

Ω_{arag} in the upwelling



Lowest values in UC 1 and UC 2 were largely imprints of upwelled subsurface waters enriched with both anthropogenic CO₂ and respired CO₂;

During the northward transport of the upwelled water, however, Ω_{arag} increased whereas fCO_2 decreased with increasing Δ DIC. The consistent biological production gradually consumed CO₂ and raised [CO₃], resulting in the increasing Ω_{arag} pattern in the upwelled water.

Behaviors of DIC, TAlk and Ca²⁺ in the upwelled water



No significant impact of the upwelling on the net community calcification!

Summary for the NSCS upwelling

• Upwelling delivered low Ω_{arag} waters onto the shelf, but Ω_{arag} values are still > 1.0;

- Enhanced OC production during the upwelling further increased Ω_{arag} ;
- The patterns of Ω_{arag} are largely controlled by water circulation and biological activities at present;
- Oversaturation for now.

Context

• Corrosive waters with Ω < 1.0 may be possible on most of wide shelves including the NSCS shelf!

 How the calcifying organisms, including many species of shellfish of economic importance to coastal regions, deal with this intermittent exposure of corrosive waters?



China is the largest mariculture country, contributing to 68.81% of the total global yields (FAO, 2006);

Shellfish is the most important composition.

Production of shell fish in 2008 was ~ 10 MT

Aragonite Saturation Depth ($\Omega_{arag} = 1.0$) in the Global Oceans



Source Water Depth	~150 m	~150 m
Source Water pH	~7.95	< 7.75
Source Water Ωarag	~1.9	< 1.0
Aragonite Saturation Depth	~500 m in the Western NP	100-300 m in the Eastern NP

The contrasting scenarios between the two cases are related to the different "acidity" of source waters of upwelling.

Examples: OA in coastal ocean

- Anthropogenic CO2
- Upwellings of low pH waters
- Respirations/nutrification
- Ground water



Respiration + Nitrification induced pH drawdown in the Pearl River Aerobic respiration $(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138$ $O_2 + 18 HCO_3^- \rightarrow 124 CO_2 +$ $140 H_2O + 16 NO_3^- + HPO_4^{2-}$

Nitrification

NH4⁺ + 1.89 O2 + 1.98 HCO₃⁻ → 0.984 NO₃⁻ + 0.016 C₅H₇O₂N +1.90 CO₂ + 2.93 H₂O

Fig. 10. A mechanistic explanation of the effect of nitrification on the formation of pH minimum (A) and *p*CO₂ maximum (B) during the dry season. For the dry season simulation, the solid black lines are the result of conservative mixing among the three end-members; the gray solid lines (same symbols as in Fig. 8) represent those with the effect of nitrification in dry season as explained in the text; the black and gray "*" symbols represent February 2004 and January 2005 data, respectively. For the wet season simulation, only conservative mixing (dashed gray lines) is presented since nitrification is not significant in the mixing zone.

Fig A from Zhang Cao Fig B from Guo et al., 2008, CSR

Coastal acidification in summer bottom oxygen-depleted waters in northwestern-northern Bohai Sea from June to August in 2011

ZHAI WeiDong^{1,2*}, ZHAO HuaDe^{1,2}, ZHENG Nan¹ & XU Yi² Chin Sci Bull, 2012, 57: 1062–1068, doi: 10.1007/s11434-011-4949-2



Examples: OA in coastal ocean

- Anthropogenic CO2
- Upwellings of low pH waters
- Respirations
- Ground water

Acidification in Hainan Coral Reef

Low pH in Sanya fringing reef system



Coastal ocean has large natural variability due to changes in physical and biological conditions and various anthropogenic impacts including:

River Plume

High TA Input pH ↑ Low TA Input pH ↓

Eutrophication $CO_2 \downarrow pH \uparrow OA pH \downarrow$

Photosynthesis $CO_2 \downarrow pH \uparrow$ Respiration $CO_2 \uparrow pH \downarrow$

Upwelling + OM Respiration $CO_2 \uparrow pH \downarrow$ Coastal Upwelling High $CO_2 pH \downarrow$

Basics about coastal OA

- OA in coastal ocean? pH change in coastal ocean may be more complex, driven by anthropogenic CO₂, riverine/groundwater input (eutrophication & respiration) and water circulation (upwelling of low pH/DO waters), and other biogeochemical reactions under low/no DO.
- Physical dynamics must be considered.
- OA observation is essential to set the stage of OA in coastal ocean
- Coastal ocean is particularly facing multiple stressors

Outline

- Coastal Ocean Acidification
- Multiple stressors in the Coastal Ocean
- Concluding Remarks

Multiple stressors in marine ecosystems



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.

Doney et al., 2010

Multiple forcings & responses: offset? Amplifying?

– Eutrophication-hypoxia + OA +temp?

-SGD + upwelling +....

Multiple stressors: case 1

Enhanced OA by hypoxia and effect of temp?

Hypoxia in the East China Sea off the Changjiang (Yangtze River) Estuary





DO< 2 mg/L, ~10000 – 20000 km² Taiwan: ~32,260 km²

(Zhu et al., 2011)

Enhanced warming over the global subtropical western boundary currents

Lixin Wu¹*, Wenju Cai², Liping Zhang¹, Hisashi Nakamura³, Axel Timmermann⁴, Terry Joyce⁵, Michael J. McPhaden⁶, Michael Alexander⁷, Bo Qiu⁴, Martin Visbeck⁸, Ping Chang⁹ and Benjamin Giese⁹

SST anomaly of global ocean in 20th century



The enhanced warming over the global subtropical western boundary currents in the 20th century might be attributable to the poleward shift of their mid-latitude extensions and/or intensification in their strength.

Enhanced OA by respiration in hypoxic zone off the Changjiang estuary



All data points with S > 31 and depth > 10 m are selected.

Survey in Aug. 2011

The offshore water: S = 33.2716 T = 26.7065 P = 10.471 dbar DO = 208.31 µmol/kg DIC = 1937.25 µmol/kg

TA = 2227.98 μ mol/kg NO₃+NO₂ = 0 μ mol/kg Silicate = 0 μ mol/kg Phosphate = 0 μ mol/kg $pCO_{2_Calculted}$ = 420 μ atm

Model 1: S, T, P, and Nutrients Constant



Considering the slight TA change during respiration by TA:O=-17/138; DIC:DO=106/138 BC: Buffering Capacity; PI: preindustrial pCO_2 (280 ppm); P: present pCO_2 (420 ppm); F: future pCO_2 (year 2100, 800 ppm)

Model 2: S, P, Nutrients Constant, T Changes



Consider the slight TA change during respiration by TA:O=-17/138; DIC:O=106/138Consider the temperature change but no effect of temperature on respiration $T_{preindustry}$: T-076°C $T_{year 2100}$: T+4°C

Model 1 vs 2: Higher temperature buffers the effect of ocean acidification



The values beside the "/" come from the model 1 (left) and model 2 (right)

Considering the effect of temperature on respiration



Because the effect of temperature on CR, pH will drop 0.21 unit ($Resp_F$ -Resp_) in the future than at present

Reminder

Subsurface enhancement of oxygen consumption and/or ocean acidification will depend on the seasonal hydrodynamics (if transport to the open ocean)

Multiple stressors: case 2

Coastal Coral system under the impact of groundwater, upwelling and anthropogenic CO2?

Acidification in Coral Reef Environment



Acidification in Hainan Coral Reef

Low pH in Sanya fringing reef system



Tidal-driven Submarine Groundwater Discharge (SGD) in Sanya fringing reef





Upwelling in Sanya Coral Reef

SY station is located at the edge of coral reef ecosystem.

Average depth of SY station: 14m



Contribution of SGD to acidification

Large diurnal changes of pH and pCO_2 in spring tide when SGD was significant: up to 70% of the changes.

The aragonite saturation decreased to 1.77 during low tide of spring tide, a potential threat to coral reef systems.



Threats to coral reef around Hainan

Coral reefs in Hainan waters account for more than 98% of the total area of that in China (Wu et al., 2012).



Current and Future Scenarios



In 2100

- air *p*CO₂=750 μatm
- pH=7.6~7.8
- CaCO₃
 saturation
 down to
 1.62~2.06.

Multiple stresses to coastal coral reefs



Multiple stresses to coastal coral reefs: future changes?



Gordian Knot?



Figure 1| A Gordian Knot made up of differing thematic information, indicating the wide range of research issues associated with the study of the response of biota to changing oceanic conditions.

from Boyd, 2013, Nature Climate Change, 3, 530-533

Summary

- Coastal ecosystem are clearly under multiple stressors
 - Hypoxic zones
 - Coral reef systems
- The ecosystem responses/feedbacks to multiple stressors are complex.

Concluding remarks

- Penetration of CO2 in the coastal ocean has emerged
- The geochemistry of acidification is based on very well defined knowledge – yet coastal ocean more complex
- Coastal ecosystems under multiple forcings: temp rising + O2 decline+ acidification within a similar time frame
- Need consider the hydrodynamics: e.g., Upwelling/SGD
- OA observation system & multidisciplinary researches essential

Thank you for your audience!

CHOICE-C: Carbon Cycling in China Seas - budget, controls and ocean acidification

A national program funded by Ministry of Science and Technology through National Basic Research Program of China (973 Program) & a SOLAS endorsed program

Jan 2009-Aug 2013

Funding sources: NSF-China, MOST