

Response to Referee #2's comments :

Thank you very much for your time and effort in reviewing our manuscript and providing valuable comments, which have greatly helped us in revising the manuscript. We have carefully read your comments and have revised the manuscript in accordance with your suggestions. Our responses to each comment are provided below.

(1) The present introduction is full of well known carbonate chemistry. I see saturation state is the central theme of the paper and thus authors should make efforts to define the fundamental questions related to saturation states under the stressors of anthropogenic CO₂ and nutrients loading, and how this study would address the issues.

The "Introduction" section has been largely revised. The following paragraphs were added to elucidate the importance of the study on the carbonate minerals saturation states under the stressors of anthropogenic CO₂ and nutrient loading in the East China Sea.

"Nevertheless, recent studies show that the coastal ocean is experiencing multiple environmental stressors that may act synergistically to exacerbate acidification (Doney, 2010). For instance, it has been suggested that eutrophication, rather than acidification induced by anthropogenic CO₂ uptake, may have dictated pH changes in coastal oceans (Borges and Gypens, 2010; Provoost et al., 2010). Recently, Cai et al. (2011) further showed that anthropogenic CO₂ invasion and eutrophication have acted in concert to lower the hypoxic bottom water pH and carbonate saturation state greatly on the continental shelf impacted by the nutrient-laden Mississippi River. They also found that the combined effect is greater than the simple addition of each, due to a synergism between respiratory and fossil fuel-derived CO₂, which reduces seawater buffering capacity. Furthermore, atmospheric nitrogen and sulfur deposition may also aggravate acidification in coastal waters (Doney et al., 2007). Therefore, the coastal ocean, which is subject to the strong influence of multiple environmental stressors, may represent one of the systems most vulnerable to the potential negative effects of ocean acidification. More importantly, because coastal oceans are some of the most productive marine ecosystems that sustain numerous commercially valuable fisheries, e.g. those for shellfish and crustaceans, it is critical to gain a better understanding on how multiple environmental stressors would affect acidification in the coastal ocean.

The subtropical East China Sea (ECS), located off the southeast coast of China, is one of the largest marginal seas in the northwest Pacific. The Changjiang (Yangtze River) is the longest river in Asia and the third longest in the world. It flows through densely populated areas with intensive agriculture and industrial activities, and then empties

into the northwestern part of the ECS with an enormous water discharge of $9 \times 10^{11} \text{ m}^3 \text{ yr}^{-1}$, which accounts for 90-95% of the total riverine input to the ECS (Chen et al., 2001). The materials carried by the Changjiang runoff thus greatly influence the marine environment of the ECS (Zhang et al., 2007). Due to the rapid development of industry and increased agricultural production associated with the growth of the Chinese population, the export of dissolved inorganic N from the Changjiang increased threefold between 1970 and 2003 (Yan et al., 2010). This is ten times faster than the increase of total global river export over the period 1970–2000 (35%; Seitzinger et al., 2010). Therefore, the ECS may represent one of the areas most impacted by worsening eutrophication worldwide over recent decades. Some recent studies have shown that the elevated nutrient discharge had led to some ecological consequences (e.g. harmful algal blooms and hypoxic events; Li et al., 2007), and might have altered biogeochemical cycles in the ECS (Chou et al., 2013). Nonetheless, how eutrophication would act together with anthropogenic CO_2 invasion to impact carbonate mineral saturation states in the ECS has not been investigated to date. In this study we first describe the seasonal variability of the seawater carbonate system over the ECS shelf in spring and summer of 2009, and then we investigate the role of riverine runoff on regulating carbonate mineral saturation states. Finally, future scenarios of the saturation states are explored in the context of the combined impact of eutrophication and augmentation of atmospheric CO_2 .”

Newly added references:

Chou, W.-C., Gong, G.-C., Cai, W.-J., and Tseng, C.-M.: Seasonality of CO_2 in coastal oceans altered by increasing anthropogenic nutrient delivery from large rivers: evidence from the Changjiang–East China Sea system, *Biogeosciences*, 10, 3889–3899, doi:10.5194/bg-10-3889-2013, 2013.

Doney, S. C.: The growing human footprint on coastal and open-ocean biogeochemistry, *Science*, 328, 1512–1516, doi: 10.1126/science.1185198, 2010.

Provoost, P., van Heuven, S., Soetaert, K., Laane, R. W. P. M., and Middelburg, J. J.: Seasonal and long-term changes in pH in the Dutch coastal zone, *Biogeosciences*, 7, 3869–3878, doi:10.5194/bg-7-3869-3878, 2010.

(2) P5562, L7-8: Here, $[\text{Ca}^{2+}]$ is calculated by salinity according to Riley and Tongudai (1967). I suspect that Ca^{2+} may not be that conservative in the present complex system in particular in the bottom water where dissolution of CaCO_3 may well occur. This could significantly change your calculations of the saturation state.

We agree that dissolution of calcium carbonate in the bottom water may cause non-conservative variation of Ca^{2+} concentration ($[\text{Ca}^{2+}]$), but we don't think that this dissolution would significantly change the calculation of the saturation state. In a

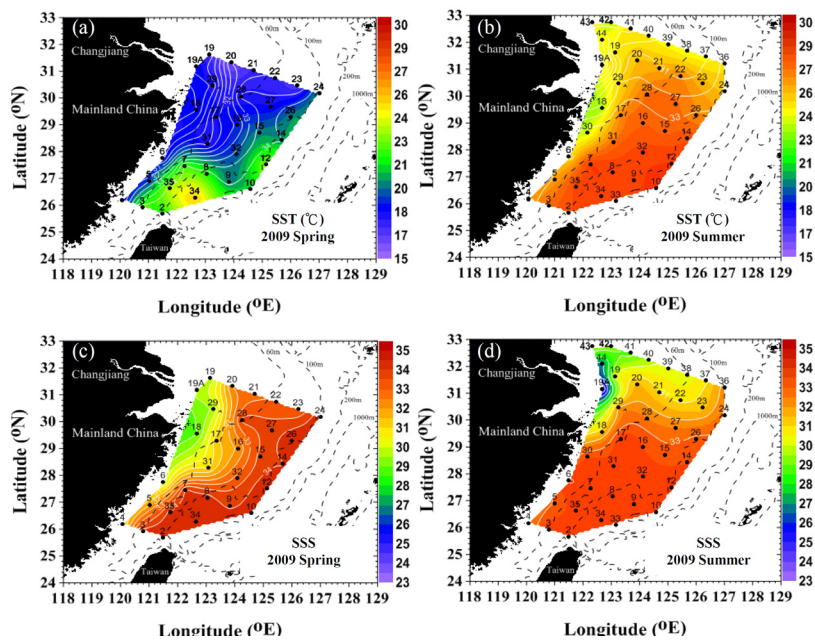
recent study, Cross et al. (2013) estimated that shallow-water CaCO_3 mineral dissolution caused TA concentrations to increase by as much as $36 \mu\text{mol kgSW}^{-1}$ on the Bering Sea (BS) shelf (corresponding to a $[\text{Ca}^{2+}]$ increase of $18 \mu\text{mol kgSW}^{-1}$). The addition of the released Ca^{2+} from CaCO_3 dissolution can increase $[\text{Ca}^{2+}]$ of seawater by only 0.175%, providing that the original $[\text{Ca}^{2+}]$ is about $10280 \mu\text{mol kgSW}^{-1}$ at salinity=35. Since the saturation levels of carbonate minerals in the bottom water on the ECS shelf are apparently higher than that on the BS shelf (note that currently the bottom water on the ECS shelf remains supersaturated with respect to aragonite, while the bottom water on the BS shelf is already undersaturated), we can expect that the potential impact of CaCO_3 dissolution on $[\text{Ca}^{2+}]$ variation would be even less significant on the ECS shelf compared with the BS shelf. Therefore, even if dissolution of calcium carbonate occurs in the bottom water on ECS shelf, we don't think it would significantly change our calculations of the saturation states.

Reference:

Cross, J. N., Mathis, J. T., Bates, N. R., Byrne, R. H.: Conservative and non-conservative variations of total alkalinity on the southeastern Bering Sea shelf, *Mar. Chem.*, 154, 87–99, doi:10.1016/j.marchem.2013.05.012, 2013.

(3) P5562, the results section: authors did not at all present the basic hydrology of the region during their sampling, which is clearly problematic if they are to examine the complicated hydrochemistry and the carbonate chemistry therein.

We have added a new figure to the revised manuscript to show the basic hydrology during the sampling period (please see the figure in the next page). Also, the following paragraph was added to the revised “Results” section 3.1 to describe the distributions of temperature and salinity: *“The distributions of sea surface temperature (SST) and salinity (SSS) in spring and summer 2009 on the ECS shelf are shown in Fig. 2. SST varied from 15.8 to 25.3°C and 23.3 to 29.6°C in spring and summer, respectively (Fig. 2a, b). Waters with relatively higher SST were generally confined to the southeastern part of the study area, whereas waters with relatively lower SST were mainly found in the northern and western parts. SSS ranged from 27.9 to 34.5 in spring, and from 23.8 to 34.1 in summer (Fig. 2c, d). The higher SSS values were observed in the southeastern part of the study area for both seasons. The lower SSS values occurred mainly in the inner shelf along the coast of China in spring, and in the northwestern part of the study area in summer.”*



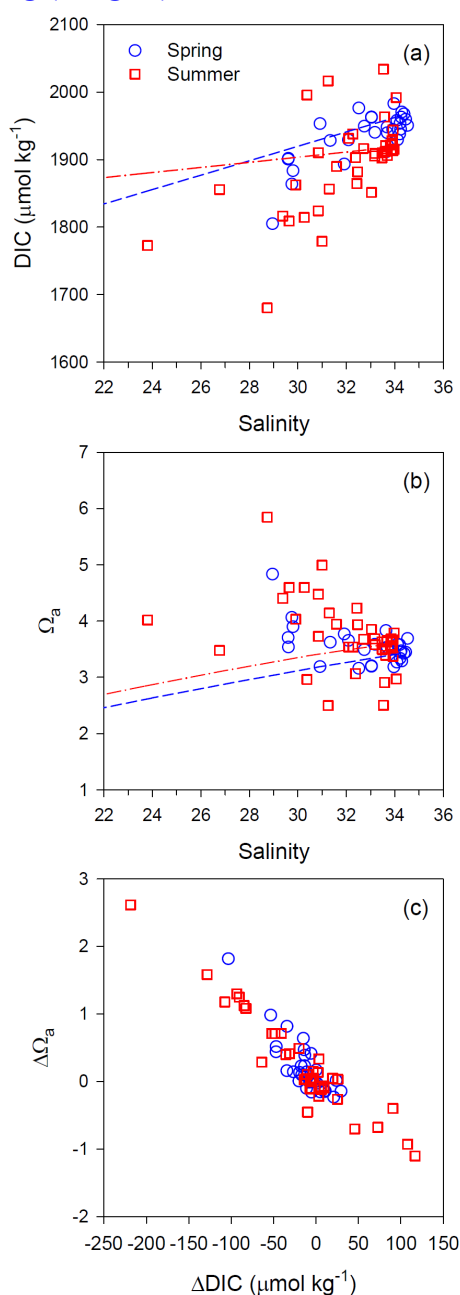
(4) P5566, L10-& Fig 5: here the mixing processes between different water masses are critically important (if not the foundation of this study) to further evaluate the changes in carbonate parameters caused by biological processes, e.g., Δ DIC & Δ . Both the freshwater end-member for the Changjiang runoff and the seawater end-member are subject to large temporal variations, which should be very carefully justified and the implications of such variability to their conclusion should be quantitatively assessed. By the way, how does the TA-S curve look like? Did the authors assume TA is conservative here? If the authors cannot lay a concrete foundation of these mixing processes, the main conclusion of the study would be unfounded. Similar concerns also go to p5571 for the scenario analysis. I also have troubles with the future trend of DO declining rate being assumed to be 0.72 $\mu\text{mol}/\text{yr}$ in the bottom water. I did not check back into Ning et al. (2011) but such extrapolation could be very misleading because so far it is very difficult to even define the changes in areas of the hypoxic zones at inter-annual time scale.

(i) We have reanalyzed the relationships of DIC and Ω_a vs. salinity by considering the seasonal variations in both freshwater and seawater end-members. The new end-members for freshwater and seawater in spring and summer and their sources are given in the table in the next page. Based on the new relationships, the deviations of the measured DIC and Ω_a in spring and summer from their corresponding seasonal theoretical mixing values (Δ DIC and Δ Ω_a) were re-calculated. As shown in the figure in the next page, the re-calculated result also shows a strongly negative correlation between Δ DIC and Δ Ω_a in both spring ($r = -0.85$, $p < 0.05$) and summer ($r = -0.95$, $p < 0.05$), further lending support to that biological processes may play a dominant role on regulating Ω_a variability on the ECS shelf, in particular during the summertime.

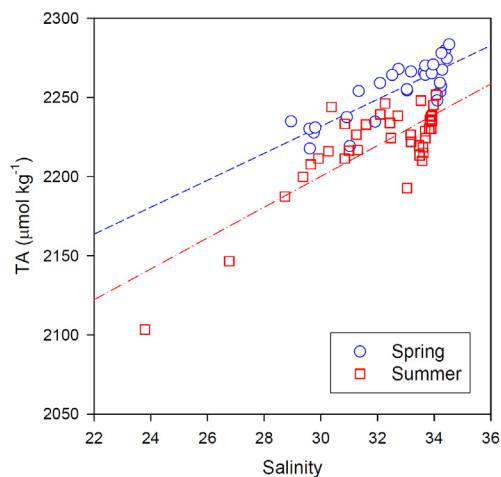
	Freshwater end-member			Seawater end-member		
	TA	DIC	Source	TA	DIC	Source
Spring	1600	1600	Zhai et al. (2007)	2277	1965	The average values at stations 10, 12, and 14 during the spring cruise.
Summer	1790	1790	Zhai et al. (2007)	2231	1918	The average values at stations 10, 12, and 14 during the summer cruise.

Reference:

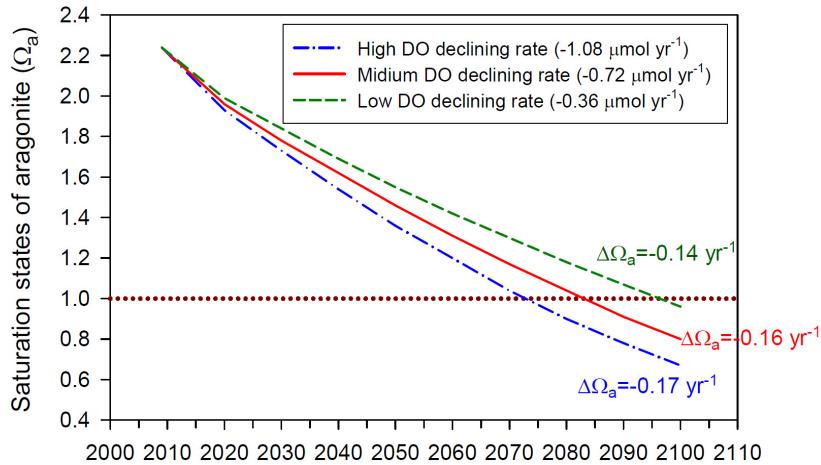
Zhai, W., Dai, M., and Guo, X.: Carbonate system and CO₂ degassing fluxes in the inner estuary of Changjiang (Yangtze) River, China, *Mar. Chem.*, 107, 342-356, 2007.



(ii) The TA vs. salinity plot for surface waters is given below. As shown, strongly positive correlation between TA and salinity can be found in both spring ($r=0.83$, $p<0.05$) and summer ($r=0.80$, $p<0.05$), suggesting that TA is generally conservative on the East China Sea shelf during the study period.

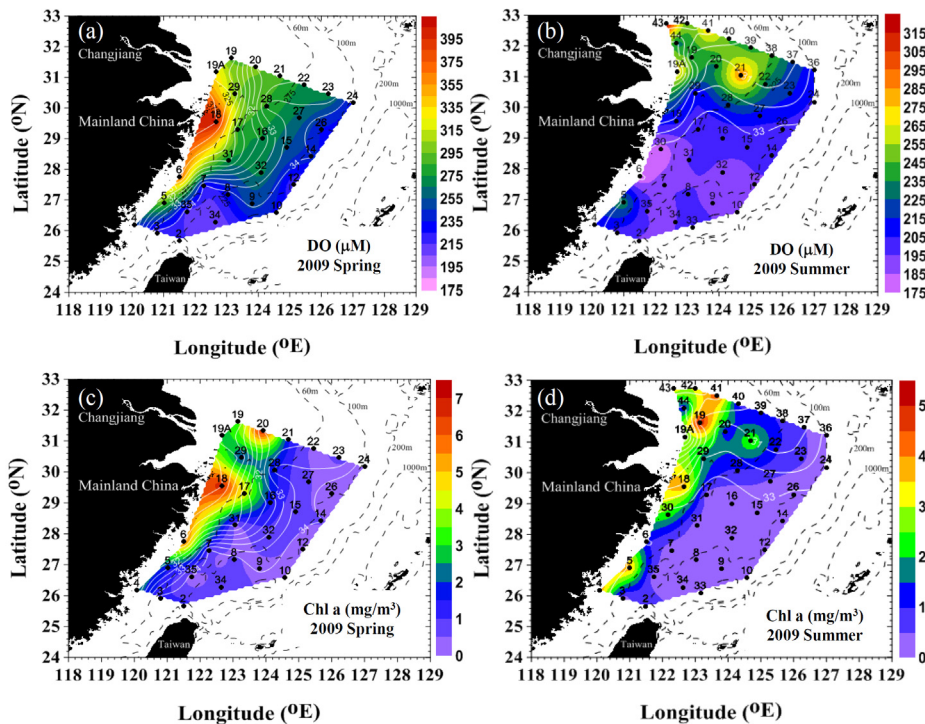


(iii) We agree that our projection is subject to the uncertainty in predicting the future DO declining trend. In order to quantify the potential error arising from such an uncertainty, we reprocess the projections with three different DO declining scenarios, i.e. high, medium, and low rates. The DO decreasing rate reported by Ning et al. (2010) is chosen to represent the medium condition ($-0.72 \mu\text{mol yr}^{-1}$), because to our best knowledge it is the only available long-term DO data set on the ECS shelf. The high and low DO declining rates are defined as 50% higher and lower than the medium value, respectively. As shown in the figure in the next page, the re-projected result demonstrates that the average decreasing rate of Ω_a between 2009 and 2100 is -0.14 , -0.16 , and -0.17 yr^{-1} with low, medium, and high DO declining rate, respectively. In other words, an increase of 300% in the presumed DO declining rate (-0.36 to $-1.08 \mu\text{mol yr}^{-1}$) would cause a corresponding increase in the projected Ω_a decreasing rate by 21% (-0.14 to -0.17 yr^{-1}). We have noted this uncertainty as follows in the revised manuscript: “It is noteworthy that the uncertainty in the presumed DO declining rate may cause a minor error in the projected decreasing rate of Ω_a (e.g. an increase of 300% in the presumed DO declining rate (-0.36 to $-1.08 \mu\text{mol yr}^{-1}$) may cause a corresponding increase in the projected Ω_a declining rate by 21% (-0.14 to -0.17 yr^{-1})).”



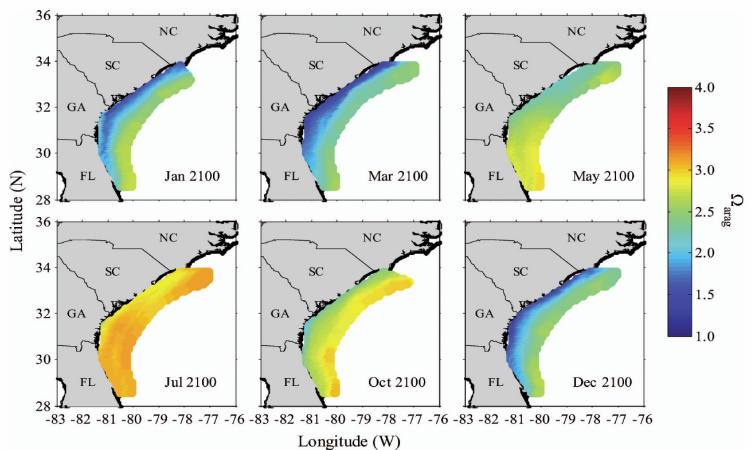
(5) P5566, L5-7: please show Chl-a and DO data to support your conclusion.

The distributions of DO and Chl *a* in spring and summer 2009 are shown in the figures below. The higher DO and Chl *a* values were commonly found along the coast of mainland China in spring (a, c) and in the northwestern part of the study area in summer (b, d). This distribution pattern generally corresponds to the seasonal dispersion of the Changjiang Diluted Water, thus supporting our conclusion that the elevated biological production fueled by the nutrient discharge from the Changjiang runoff is the main driving force to form the highest Ω_a values in the freshwater-impacted area.



(6) P5567, L20-24, the assumptions of the projections: (1) the assumption of air-sea equilibrium may be overall OK at longer time scales. But here the authors are projecting both summer and spring, or, at seasonal time scale without appropriate justification of the assumption. It is well known that air-sea CO₂ exchange takes long time depending on the mixed layer depth, wind stress and chemical buffer in the seawater. (2) constant TA may not be valid in the context of rising air CO₂, in particular when the authors are looking at changes at seasonal time scale. (3) Based on what, the authors would assume a SST rise of 2 degree C at air CO₂=723 ppmv. Note that 2 degree C is a very high rise for the ocean.

(i) We understand that using the equilibrium approach to project future changes in carbonate chemistry may be subject to the uncertainty in the status of air-sea equilibrium. For the surface water being under-saturated with respect to CO₂ (generally corresponding to the highly productive areas such as the CDW area), the equilibrium approach may over-estimate the decrease of carbonate saturation states. Unfortunately, to our knowledge, the only approach that can provide a projection by accounting for air-sea CO₂ disequilibrium is based-on global-scale ocean models (Orr, 2011), which is apparently beyond the scope of the present study. Therefore, the equilibrium approach is conventionally adopted by the non-modelers to conduct a first-order estimation on the future change of carbonate chemistry. For instance, Jiang et al. (2010) used the same approach to predict surface water $\Omega_{\text{aragonite}}$ by the year 2100 at a monthly time scale in the South Atlantic Bight (please see the figure below). In order to remind readers of the indigenous uncertainty in the equilibrium approach, we have added the following paragraph to the revised manuscript: “As a result, under the assumption of air-sea equilibrium, the projected Ω_a decrease between the present day and the year 2100 would be larger for waters with a higher chemical potential for atmospheric CO₂ sequestration (corresponding to the larger reciprocal of the Revelle factor in Fig. 7b), suggesting that the projected Ω_a decline in the highly productive CDW area may represent a high-end estimate.”



From Jiang et al. (2010)
Figure 7

Fig. 7. Predicted surface water aragonite saturation state in the SAB coast by the year 2100.

References:

Jiang, L.-Q., Cai, W.-J., Feely, R. A., Wang, Y., Guo, X., Gledhill, D. K., Hu, X., Arzayus, F., Chen, F., Hartmann, J., and Zhang, L.: Carbonate mineral saturation states along the U.S. East Coast, *Limnol. Oceanogr.*, 55, 2424–2432, 2010.

Orr, J. C.: Recent and future changes in ocean carbonate chemistry, in: *Ocean acidification*, Gattuso, J.-P and Hansson, L. (Eds.), Oxford University Press, New York, 41–66, 2011.

(ii) It is well known that TA of seawater CANNOT be changed by air-sea CO₂ exchange. Orr (2011) clearly points out that “*the equilibrium approach computes future surface ocean pH and [CO₃²⁻] using basic thermodynamic equilibrium equations while varying CO₂ and holding constant another carbonate system variable, typically TA.*”. In fact, this basic assumption is not only applied in computing the changes of pH and carbonate mineral saturation states due to anthropogenic CO₂ invasion (e.g. Bates et al., 2009; Mathis et al., 2011), but also has been extensively used to quantify anthropogenic CO₂ concentration in the ocean in earlier studies (e.g. Brewer, 1978; Chen and Millero, 1979; Sabine et al., 2004). Therefore, we strongly believe that the assumption that TAs remain unchanged with the rising air CO₂ should be valid.

References:

Bates, N. R., Mathis, J. T., and Cooper, L. W.: Ocean acidification and biologically induced seasonality of carbonate mineral saturation states in the Arctic Ocean, *J. Geophys. Res.*, 114, C11007, doi:10.1029/2008JC004862, 2009.

Brewer, P. G.: Direct measurement of the oceanic CO₂ increase, *Geophys. Res. Lett.*, 5, 997-1000, 1978.

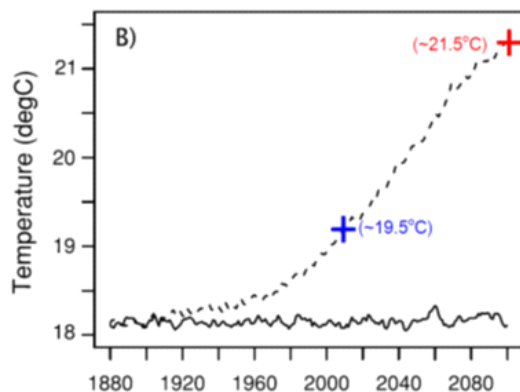
Chen, C. T. A., Millero, F. J.: Gradual increase of oceanic CO₂, *Nature*, 277, 205–206, 1979.

Mathis, J. T., Cross, J. N., and Bates, N. R.: The role of ocean acidification in systemic carbonate mineral suppression in the Bering Sea, *Geophys. Res. Lett.*, 38, L19602, doi:10.1029/2011GL048884, 2011b.

Orr, J. C.: Recent and future changes in ocean carbonate chemistry, in: *Ocean acidification*, Gattuso, J.-P and Hansson, L. (Eds.), Oxford University Press, New York, 41–66, 2011.

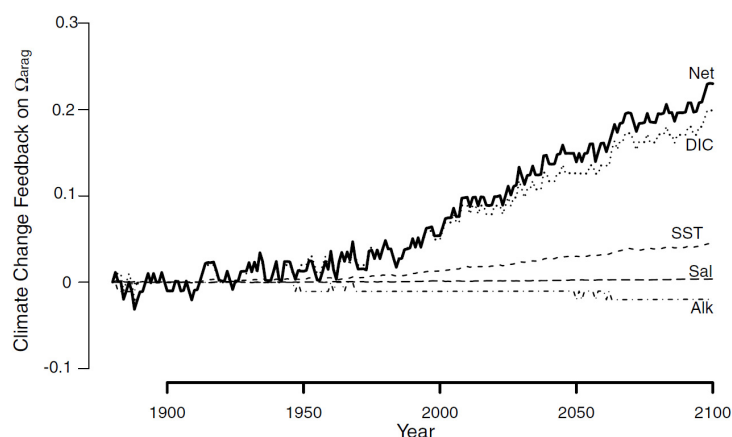
Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., Wannikhof, R., Wong, C. S., Wallace, D. W. R., Tilbrook, B., Millero, F. J., Peng, T.-H., Kozyr, A., Ono, T., Rios, A. F.: The oceanic sink for anthropogenic CO₂, *Science*, 305, 367-371, 2004.

(iii) The assumption of a SST rise of 2°C from the year 2009 to 2100 was after Mcneil and Matear (2007), in which they used a coupled atmosphere-ice-ocean carbon cycle model developed by the Commonwealth Scientific Industrial Research Organization to project the change of average sea surface temperature from the year 1880 to 2100 with climate change (please see the figure below).



From Mcneil and Matear (2007) Fig. 2B

Furthermore, in the same study, Mcneil and Matear also suggested that future projections of surface ocean acidification only need to consider future atmospheric CO₂ levels, not climate change induced modifications in the ocean, e.g. SST rising (please see the figure below). Therefore, we believe that SST rise of 2°C is a reasonable assumption and that the uncertainty in future SST prediction would not significantly change our projection. We have added Mcneil and Matear (2007) to the reference list.



From Mcneil and Matear (2007) Fig. 3

Reference:

Mcneil, B. I., and Matear, R. J.: Climate change feedbacks on future oceanic acidification, *Tellus*, 59B, 191–198, 2007.

(7) P5572, L14: Considering the DO consumption will add additional DIC to $\Delta\text{DIC}_{\text{ac}}$, you should also take account the change in TA given the high biological productivity in the surface and high respiration in the bottom water.

We have re-projected the future change of Ω_a in the bottom water by adding the effect of TA changes due to DO consumption. The re-projected result shows that negligence of TA changes would cause the predication of Ω_a to be slightly under-estimated with a maximum underestimation of 0.04 by the year 2100, which accounts for only about 3% of the total predicted Ω_a change (~ 1.44 ; please see the figure below). Note that the TA change rate in the above re-projection is estimated by the DO declining rate ($0.72 \mu\text{mol yr}^{-1}$; Ning et al, 2011) with a coefficient of 0.119 after Feely et al. (2002):

$$\Delta\text{TA} = 0.119 \times \Delta\text{DO}$$

Reference

Feely, R. A., Sabine, C. L., Lee, K., Millero, F. L., Lamb, M. F., Greeley, D., Bullister, J. L., Key, R. M., Peng, T. H., Kozyr, A., Ono, T., Wong, C.S.: In situ calcium carbonate dissolution in the Pacific Ocean, *Global Biogeochemical Cycles*, 16, doi:10.1029/2002GB001866, 2002.

Ning, X., Lin, C., Su, J., Liu, C., Hao, Q., and Le, F.: Long-term changes of dissolved oxygen, hypoxia, and the responses of the ecosystems in the East China Sea from 1975 to 1995, *J. Oceanogr.*, 67, 59–75, doi:10.1007/s10872-011-0006-7, 2011.

