Responses to Anonymous Reviewer #1

The authors collect dissolved inorganic carbon (DIC), total alkalinity (TAlk), and nutrients (NH4, NO2, NO3, PO4) in the Changjiang estuary, including the North Branch and the South Branch, during a 6-day cruise in spring. The purpose of this study is to evaluate the biogeochemical impact of North Branch saltwater spillover on the South Branch. The authors also try to couple the nitrogen dynamics with carbonate system to explain the carbonate system in this study area. The authors explain the relationship between seawater-introduced [CO32-] and respiration induced CO2 in Section 4.3. However, the major purpose seems still ambiguous in this study. The authors try to demonstrate this study as a method by coupling nitrogen and carbonate dynamics, but the assumptions (both physical and biogeochemical ones) are speculated and the result is ambiguous.

[Response] In the revised MS, we focus on explaining controls of estuarine CO_2 by coupling the nitrogen and carbonate dynamics. Seasonal data obtained in 2011 have been added so as to discuss seasonal and interannual variations.

This study lacks sufficient references in Discussion (less than 10 references in Discussion).

[Response] Earlier researchers rarely discuss the coupling between nitrogen and carbonate dynamics in estuaries. However, we have added more references in the modified MS so as to strengthen the discussion.

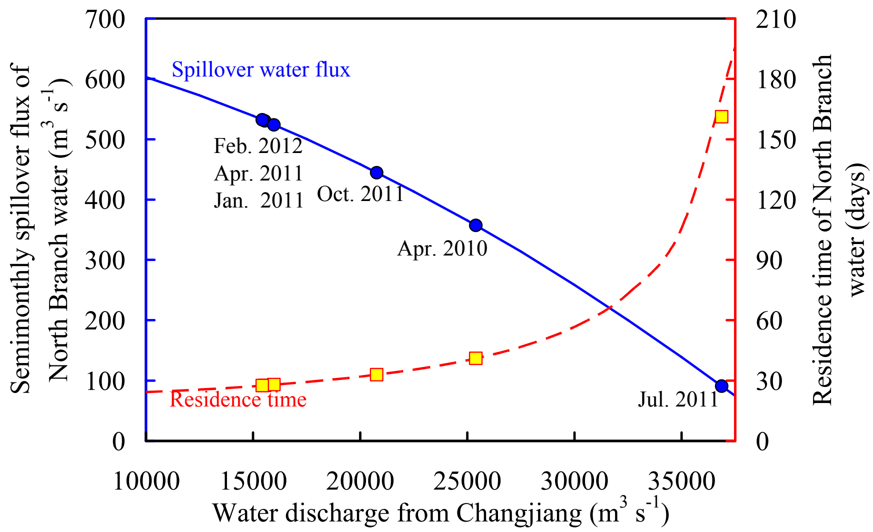
Finally, the mixing scheme should be reevaluated before further addressing the biogeochemical processes.

[Response] Following the reviewer #3's suggestion, we have separated conservative water mixing lines in the North Branch from those in the South Branch and/or the outer estuary.

Major comments:

(1) Physical assumptions. The assumption of mixing between river and sea endmembers is speculated. (1) While the purpose of this study is to evaluate the spillover water from the North Branch to the South Branch, this spillover source is not considered in the mixing model. (2) The seasonal variation of river end-member seems not considered though the authors have observed this in their previous study (Zhai et al., 2007). (3) The residence time in the North Branch is critical to the mixing model. If the residence time were low and do not allow additional in-situ biogeochemical processes, this model might be OK. If the residence time were long as the authors suggested and allowed in-situ biogeochemical process (such as organic matter decomposition, NH4 regeneration, and nitrification), these in-situ biogeochemical processes might generate an end-member in addition to the river and sea end-members. Finally, the tidal effect is mentioned but is not really taken into consideration. There are some references which have calculated and discussed the residence time in this study area. Please cite and discuss.

[Response] (1) In the revised MS, we focus on explaining controls of estuarine CO_2 by coupling chemical dynamics of the nitrogen and carbonate systems. (2) In the revised MS, seasonal data obtained in 2011 have been added so as to discuss seasonal and interannual variations. (3) The reviewer is right. In this study, however, the key is quantifying the additions and/or removals of biogenic elements via the North Branch biogeochemical processes. Therefore, we have assumed the two end-member mixing between the Changjiang freshwater and the East China Sea surface water to be the baseline conservative water mixing model of relevant elements. This is a reasonable simplification method in the study area. As for the South Branch, we would like to regard the North Branch intrusion as an external addition, rather than an end-member of steady state. (4) The tidal effect affects biogeochemical parameters mainly via hydrological movements in the estuary. It has been considered in those distribution graphs along salinity. (5) In the modified MS, we have discussed residence time with more details in the study area, following the reviewer's suggestion. For example, a quantified plot (see below) has been added based on the earlier modeling results (Wu et al., 2009).



Relations among water discharge from Changjiang, spillover water flux from the North Branch, and Residence time of North Branch water. Modified from modeling results in Wu et al. (2009), based on the assumption that the bathymetry in the North Branch and thereby the tidal effects on water exchanges are changeless in recent several years.

Reference

Wu, H., Zhu, J.-R., Chen, B.-R., and Chen, Y.-Z.: Quantitative relationship of runoff and tide to saltwater spilling over from the North Branch in the Changjiang Estuary: A numerical study, Estuar. Coast. Shelf Sci., 69, 125–132, doi:10.1016/j.ecss.2006.04.009, 2006.

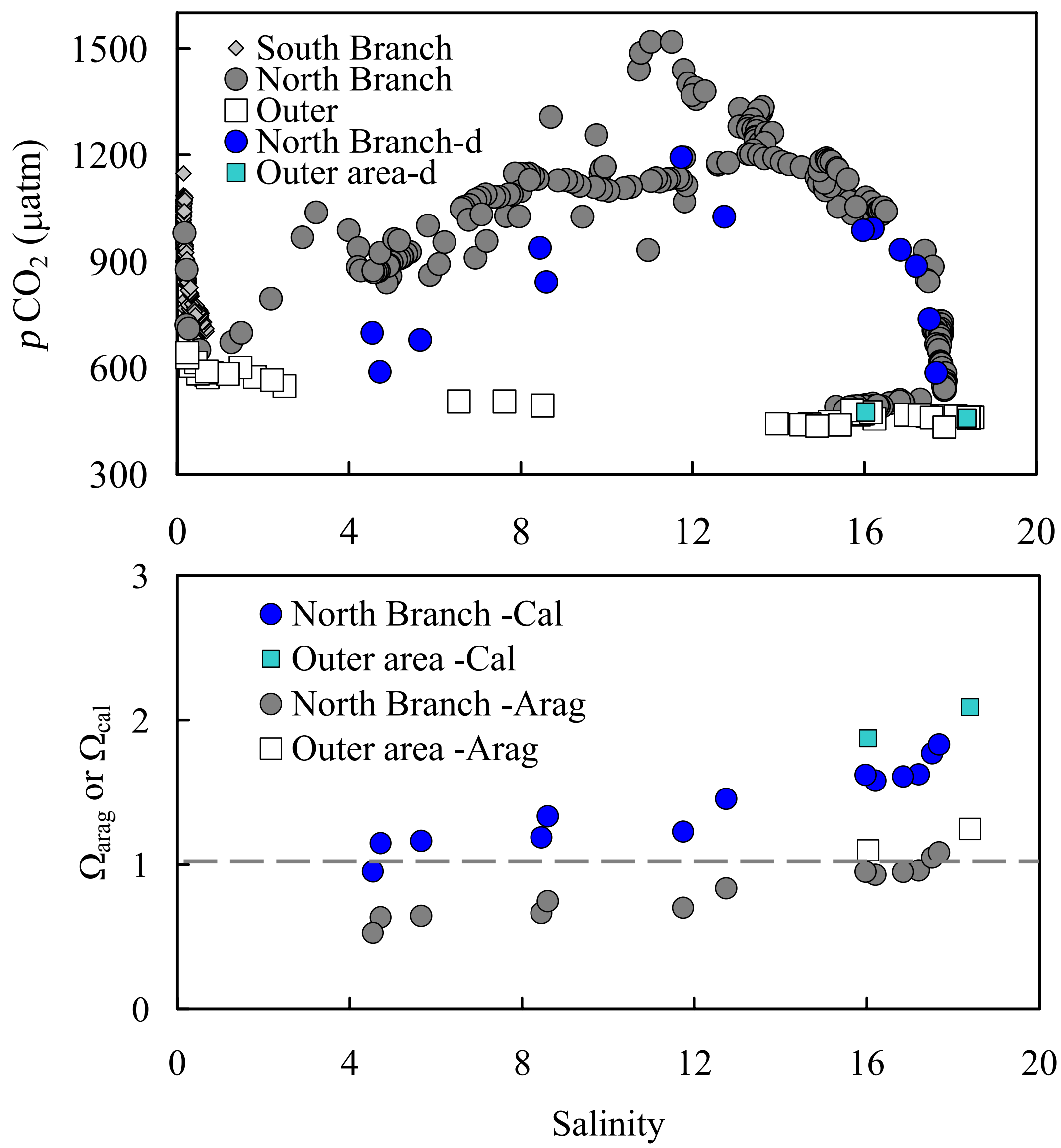
(2) Biogeochemical assumptions. The authors assumed nitrification and CaCO3 dissolution in the North Branch. But the final result does not match the ratio of any equations and they explain the ratio is proportional to varied processes. While there is no direct evidence to show CaCO3 dissolution and nitrification in addition to the ratios in Fig. 7, the result is speculated especially when the mixing scheme might be complicated as suggested in Comment 1.

[Response] In the modified MS, we add dissolved calcium data obtained in April and July 2011 so as to present the direct evidence of $CaCO_3$ dissolution. As for the nitrification, this is evidenced by our nitrite data of as high as 8 to 18 μmol/kg.

What is omega saturation status?

[Response] In such high-$p$$CO_2$ estuarine areas, usually the $CaCO_3$ saturation states are low. To evaluate the possible calculation bias from organic alkalinity, we firstly calculate aquatic $p$$CO_2$ using our DIC and TAlk data (also using our phosphate and silicate data). And then we compare them with field-measured $p$$CO_2$ data. The results (upper figure) are exciting. In relatively high-salinity (>16) areas, the calculated $p$$CO_2$ is highly consistent with the field measurements, suggesting that both calculation and measurement are reliable. In relatively low-salinity (<13) areas, the measured $p$$CO_2$ data are always higher than calculated values, suggesting that the real pH is likely lower than the calculated values. Therefore, in the low-salinity (<13) areas, the real $CaCO_3$ saturation states should be lower than those calculated values.

The lower plot shows that, calculated $CaCO_3$ saturation states for aragonite are mostly lower than saturated level in the North Branch, while the North Branch $CaCO_3$ saturation states for calcite are also at critical values of 0.9 to 1.8. If considering the above-mentioned uncertainties during calculation, the hypothesis that $CaCO_3$ dissolution occurs in the North Branch is sound.



A comparison between calculated and field-measured pCO_2 values (upper), and the calculated $CaCO_3$ saturation states (lower) against salinity in the study area in April 2010

What is the proportion of CaCO3 in PIC (Fig. A1) and how much CaCO3 dissolution can result in the delta DIC in Fig. 6e.

[Response] As for the proportion of $CaCO_3$ in PIC, sorry, I don't know it exactly. According to a study conducted in August 1998 (Chen et al., 2001), based on the X-ray powder diffraction method, the major components of suspended particulate and sediment matters in the Changjiang Estuary are identified as α-Quartz [SiO_2], Illite [$(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$], Chlorite [$(Mg_{2.6}Fe_{2.2}Al_{1.2})Si_{2.8}Al_{1.2}O_{10}(OH)$], Montmorillonite [$Ca_{0.24}Na_{0.01}Mg_{0.36}Fe_{0.02}Al_{1.75}Si_{3.87}O_{10}(OH)_{21.078}H_2O$], Albite [$NaAlSi_3O_8$], Microcline [$KAlSi_3O_8$], Kaolinite [$Al_2Si_2O_5(OH)_4$], and Calcite [$CaCO_3$]. Therefore, it is likely truth that most of PIC observed in this study should be $CaCO_3$.

As for the amount of $CaCO_3$ dissolution, we can make an estimation via our original Reaction (R8), i.e., $(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 118O_2 + 88CaCO_{3(s)} \rightarrow 16CO_2 + 88Ca^{2+} + 178HCO_3^- + 10NH_4^+ + 6NO_3^- + HPO_4^{2-} + 22H_2O$. To sustain the observed ΔDIC of ~750 μmol/kg (Fig. 6e), we need the $CaCO_3$ dissolution of $750/(16+178)\times88 = 340$ μmol/kg. This value is comparable to the observed PIC concentrations (250 to 300 μmol/L, Fig. A1c) in April 2010 in the North Branch.

In the modified MS, these discussions have been added.

Reference

Chen, Q.-M., Qiu, Y.-Q., Chen, B.-L., and Chen, J.-Y.: The phase analysis of the suspended sediments and depositions in Changjiang Estuary by the X-ray Powder Diffraction method, J. East China Normal Univ. (Nat. Sci.), (1), 77–83, 2001 (in Chinese with English abstract).

If the PIC changes (300 to 150) in Fig. A1 were CaCO3 dissolution, how this amount will affect delta DIC in Fig. 6e. If PIC also affected by mixing, CaCO3 dissolution might be less important than expected as the authors.

[Response] No, our PIC data is just the background to support the hypothesis of $CaCO_3$ dissolution. The estuarine transportation of particulate matters is much different from that of dissolved matters.

For nitrogen dynamics, there is no direct evident to support the words from Line 24 Page 6420 to Line 2 Page 6421. The equations are correct but do not mean this study area is only dominated by these processes.

[Response] If no nitrification, how to explain our nitrite data of as high as 8 to 18 μmol/kg? The North Branch is far away from any sewage outlet. We don't think there are any other point sources to support the observed signals.

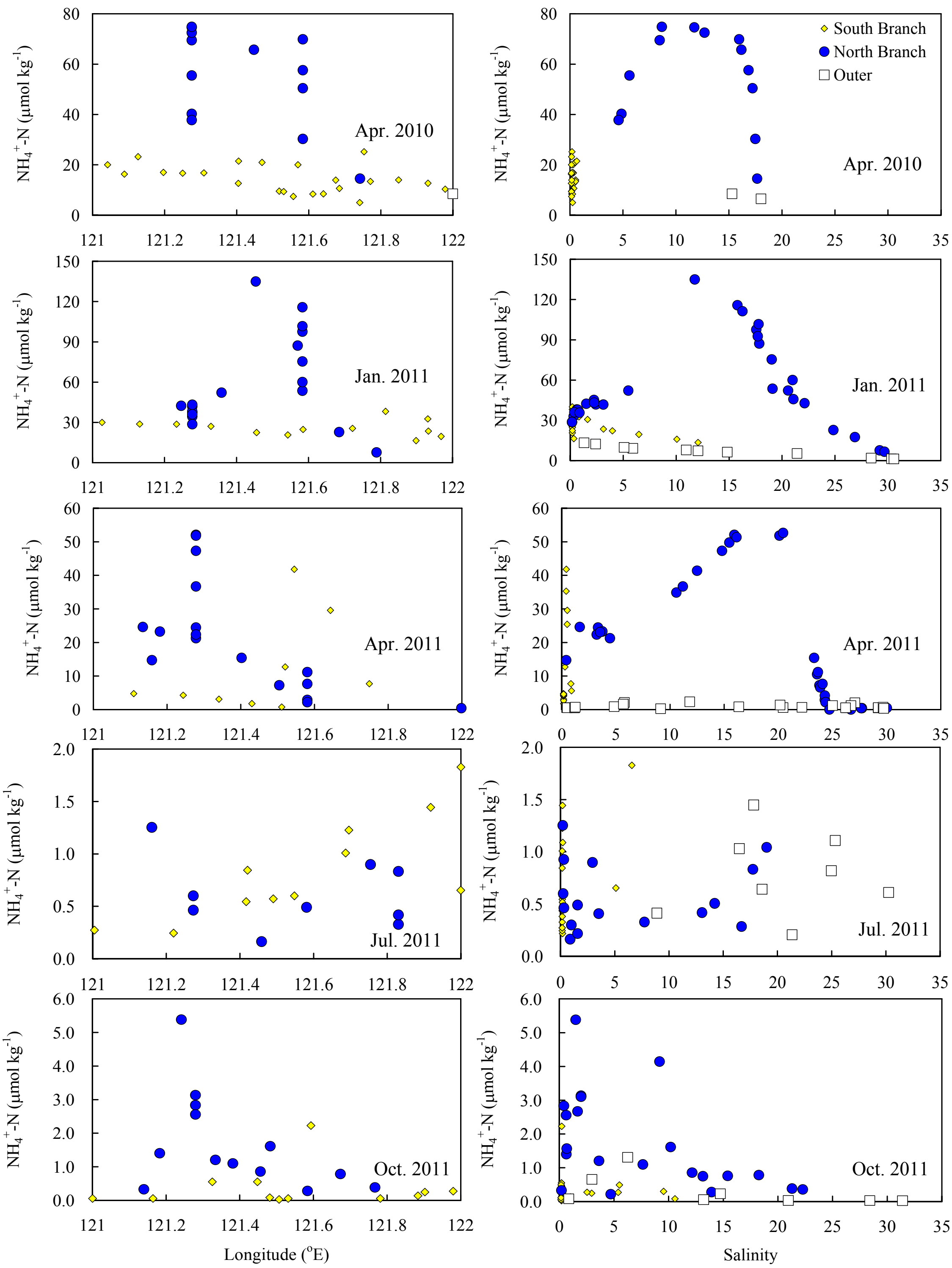
What is the role of NH4 regeneration in Fig. 7c as the residence time in the North Branch is long? How the ratio in Fig. 7c can be affected by NH4 regeneration?

[Response] The so-called ammonia regeneration (ammonification) is associated with respiration and/or remineralization of biogenic organic matters, which had been expressed by our first reaction:

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 106O_2 \rightarrow 92CO_2 + 16NH_4^+ + 14HCO_3^- + HPO_4^{2-} + 92H_2O \quad \text{(R1)}$$

In this study, we divide the classic Redfield respiration function into two steps, including the organic matter decomposition with a release of ammonia (i.e., ammonification) and the following ammonia oxidation (Abril and Frankignoulle, 2001; Brewer et al., 2014). This is because the latter reaction is usually slower than the organic matter decomposition. Also this hypothesis has been evidenced by our ammonia data obtained during multiple cruises. See below figures.

Therefore, the original Fig. 7c is controlled by the ammonia oxidation reaction, instead of the organic matter decomposition (i.e., ammonification or ammonia regeneration). Based on our data, we have suggested that the ammonia oxidation reaction may only transform a part of respiration-induced DIN additions into NO_2^--N and/or NO_3^--N. This ratio depends on environmental conditions such as water temperature. Therefore it is different in each survey. During our April 2010 cruise, this ratio is 37%.



Ammonia versus longitude and salinity in the study area during different cruise.

Reference

Abril, G. and Frankignoulle, M.: Nitrogen–Alkalinity interactions in the highly polluted Scheldt basin (Belgium), Wat. Res., 35, 844–850, 2001.

Brewer, P.G., Hofmann, A.F., Peltzer, E.T. and Ussler, W.: Evaluating microbial chemical choices: The ocean chemistry basis for the competition between use of O_2 or NO_3^- as an electron acceptor, Deep-Sea Res. Pt. I, 87, 35–42, 2014.

The authors suggest that organic matter decomposition is the major source of delta DIC. What kind of organic matter is expected? Terrestrial organic matter or in-situ born organic matter?

[Response] In a parallel study of ours, Guo et al. (2014) analyze fluorescent components of DOM in the area. They suggest multiple sources of the North Branch organic matters. During the wet season (July 2011), much freshwater flows into the North Branch due to the high water discharge from the Changjiang River, accompanied by the input of terrestrial-derived particulate matter with age. In dry seasons (April 2011), however, most organic matters in the North Branch are protein-like, suggesting the in situ sources of organic matters. The latter is consistent with our data implied bacterial activities over there.

Reference

Guo, W.-D., Yang, L.-Y., Zhai, W.-D., Chen, W.-Z., Osburn, C. L., Huang, X., and Li, Y.: Runoff-mediated seasonal oscillation in the dynamics of dissolved organic matter in different branches of a large bifurcated estuary—The Changjiang Estuary, J. Geophys. Res. Biogeosciences, 119, 776–793, doi:10.1002/2013JG002540, 2014.

Is there any point source in the North Branch to increase delta NH4?

[Response] No, we don't find any significant point source of ammonia in the North Branch. Below are ammonia distributions during our five mapping cruises. The changeful peak of ammonia excludes any fixed source of pollutant.

The increase of delta NH4 and other species in Fig. 6 are mentioned. But why these delta C in Fig.6 decrease after salinity 16 (except delta NO3.)

[Response] The North Branch also exchanges water with the outer area. The latter has the high salinity of seawater. Therefore, both the freshwater end and the seawater end have relatively short residence times, as compared with the central water with mid-salinity. The central water also has more organic matters to be decomposed than the high-salinity waters. So, we can expect the highest biogeochemical signals are located in the central water of the North Branch.

Those equations in 4.2 should have their references.

[Response] In the modified MS, those references have been added following Abril and Frankignoulle (2001) and Brewer et al. (2014).

Reference

Abril, G. and Frankignoulle, M.: Nitrogen–Alkalinity interactions in the highly polluted Scheldt basin (Belgium), Wat. Res., 35, 844–850, 2001.

Brewer, P.G., Hofmann, A.F., Peltzer, E.T. and Ussler, W.: Evaluating microbial chemical choices: The ocean chemistry basis for the competition between use of O_2 or NO_3^- as an electron acceptor, Deep-Sea Res. Pt. I, 87, 35–42, 2014.

How many delta DIC in the South Branch is induced/reduced by spilled water from North Branch?

[Response] In the North Branch, the average ΔDIC is ~400 μmol/kg (Fig. 6e). Therefore, based on the steady-state estimation of the North Branch spillover water flux (Table 2), the spilled water delivers ΔDIC of 400 × 214 / 1000 = 85.6 mol/s from the North Branch to the South Branch. This is a minor contribution as compared with the Changjiang transport of DIC and the North Branch spillover flux of DIC (Table 2). This is because the ΔDIC is much lower than bulk DIC values in the North Branch.

(3) For discussion 4.3. It is good that the authors present the idea in Section 4.3 that seawater-introduced [CO32-] was mostly titrated by respiration-induced CO2, and transferred into HCO3- ions. However, this part is not the purpose of this study. The presentation is unclear. Please list all the calculations as equations. The authors suggest 40% of estuarine CO2 were potentially titrated by CO32- (Line 24, Page 6422), but said 50 to 60% at Line 25 Page 6423. Which one is correct? What is the uncertainty, especially when comment 1 is considered? How much proportion of delta DIN is used in Line 4, Page 6423 if only 60% if respiration-induced free CO2 was removed?

[Response] At the beginning of Section 4.3, we have suggested that only 60% of respiration induced free CO_2 was removed via $CaCO_3$ dissolution, based on the ratio of ΔTAlk to ΔDIN of 6.56, which accounts for ~60% of the necessary ratio of 11.125 (corresponding to the respiration induced free CO_2 being removed by $CaCO_3$ dissolution). Furthermore, we have suggested that the other 40% of the estuarine CO_2 products have been titrated 50 to 60% by CO_3^{2-} ion supplied by the seawater end-member (Fig. 8a). Therefore, 60% + 40% * 0.5 = 80%. As for the rest of 10 to 15% of the estuarine CO_2 products, they are free CO_2. In the modified MS, we have clarified the unclear wordings.

(4) For Discussion 4.4, the authors suggest that pCO2 decrease (and salinity increase) is due to spillover water from the North Branch. Then what is the role of tidal mixing in the South Branch? The suggestion that North Branch contained activate nitrifies is highly speculated. Tidal effects and potential sewage export could change NH4, NO3, and pH values.

[Response] Changjiang is the world's fourth largest river, by virtue of its huge water discharge. Even in dry seasons, the water discharge is usually more than 10000 m^3/s. Tidal effects on large river estuaries are different from those in small river estuaries. Along the South Branch, the salinity front is located around the estuarine mouth. Most areas of the South Branch are occupied by unpolluted freshwater. Usually we don't need to consider salty water in the South Branch (Zhai et al., 2007), except for the spillover water from the North Branch. Over there the largest sewage source is the Huangpujiang River, of which the water discharge is only ~350 m^3/s, having very limited impacts on the South Branch water chemistry (Zhai et al., 2007). Furthermore, all of sewage inputs in the study area have high $p$$CO_2$, inconsistent with our observation.

Reference

Zhai, W.-D., Dai, M.-H., and Guo, X.-H.: Carbonate system and CO_2 degassing fluxes in the inner estuary of Changjiang (Yangtze) River, China, Mar. Chem., 107, 342–356, doi:10.1016/j.marchem.2007.02.011, 2007.

(5) The discussion for the South Branch is not as much as the North Branch. Fig. 5 and Fig. 7 are dominated by data in the North Branch and the data in the South Branch is hard to follow. Is photosynthesis important in the South Branch since delta DIC is negative? Why CaCO3 formation is not considered in the South Branch?

[Response] In the South Branch, the residence time is only 7 days based on the evolution of the North Branch intrusion water induced salinity peak. This time scale is insufficient for remarkable $CaCO_3$ formation. According to our earlier research (Zhai et al., 2007, Marine Chemistry, 107, 342–356), the South Branch is a heterotrophic system. Although chlorophyll has been detected at 0.98 to 2.54 mg m^{-3}, photosynthesis is not important in the South Branch mainly due to its turbid environment. This opinion is also evidenced by our DO saturation (lower than 100%) and pCO_2 (higher than the air-equilibrium level) data.

Minor comment:

1) The authors suggest that the spillover water has salinity 15 and can increased the salinity and reduce the pCO2 in the South Branch (Fig. 3n). It is not clear on Fig. 3n, do you mean Fig. A2d?

[Response] The North Branch water has a mean salinity of 15, based on our April 2010 cruise. The spillover water should have a salinity of much lower than 15 since it has been diluted via water mixing with Changjiang freshwater.

As for the statements that the spillover water increase the salinity and reduce the pCO_2 in the South Branch, the readers can see them via original Fig. 3a and Fig. 3n. Fig. A2d also helps. Our 7-Apr data show the period without the influence of spillover waters (Fig. 3a). The associated South Branch pCO_2 is as high as ~1000 µatm (Fig. 3n). In contrast, at the salinity peaks during our 3-April and 6-April surveys, the South Branch pCO_2 is only 700 to 760 µatm (Fig. A2d). In the modified MS, the unclear wordings have been reorganized.

2) The authors said “Although 80 to 85% if estuarine CO2 : : :” at Line 23, Page 6423. It is unclear where does this number “80 to 85%” come from? “. What is the rest of 10 to 15 %? Line 23 to 25 are also confusing.

[Response] At the beginning of Section 4.3, we have suggested that only 60% of respiration induced free CO_2 was removed via $CaCO_3$ dissolution, based on the ratio of ΔTAlk to ΔDIN of 6.56, which accounts for ~60% of the necessary ratio of 11.125 (corresponding to the respiration induced free CO_2 being removed by $CaCO_3$ dissolution). Furthermore, we have suggested that the other 40% of the estuarine CO_2 products have been titrated 50 to 60% by CO_3^{2-} ion supplied by the seawater end-member (Fig. 8a). Therefore, 60% + 40% * 0.5 = 80%. As for the rest of 10 to 15% of the estuarine CO_2 products, they are free CO_2. In the modified MS, we have clarified the unclear wordings.

Responses to Anonymous Reviewer #2

In this study, based on the in-situ data (T/S, nutrient, carbonate, etc.) the authors present the surface water condition in two branches of the Yangtze River estuary during one cruise shortly after a spring tide. The author made a estimation of the residency time in the two branches, concluded the influence from the North Branch to the South Branch is minor, and proposed several key chemical processes in the North Branch (decomposition, nitrification: : :). While the importance of understanding a eutrophic, human impacted estuary is beyond question, surface condition, with very limited temporal and spatial coverage, is hard to support the speculated mechanism of the key chemical processes in the estuary.

[Response] In the revised MS, we have added seasonal observations in 2011 so as to discuss seasonal and interannual variations. Also water depth samples collected during our 2011 surveys are included.

The author tried to conclude the influence from North Branch water spillover on the South Branch, yet it will be hard to prove this based on data from one cruise with very limited spatial and temporal coverage.

[Response] In the revised MS, we focus on explaining controls of estuarine CO_2 by coupling the nitrogen and carbonate dynamics. Seasonal dataset obtained in 2011 has been added so as to discuss seasonal and interannual variations.

The paper lacks a detailed background of the dynamics of the Yangtze estuary. I agree with reviewer #1 that a lack of the analysis of tidal components together with other physical conditions makes the residence time calculation ungrounded.

[Response] The hydrological dynamics of this estuary has been described in many western literatures, such as the numerical results presented by Wu et al. (2009). In the modified MS, we have discussed residence time with more details in the study area. Also see the response to reviewer #1's comments.

Reference

Wu, H., Zhu, J.-R., Chen, B.-R., and Chen, Y.-Z.: Quantitative relationship of runoff and tide to saltwater spilling over from the North Branch in the Changjiang Estuary: A numerical study, Estuar. Coast. Shelf Sci., 69, 125–132, doi:10.1016/j.ecss.2006.04.009, 2006..

In the abstract, the author stated that there are high salinity and residency time in the north branch, but what is the "unusual condition" (low salinity?) for the south branch and while this low salinity, if so, should be introduced by high salinity north branch water?

[Response] In the modified MS, the unclear wordings are reorganized.

A lack of a detailed map hurts this manuscripts a lot during my reading. I did not see a detailed mapping of the estuary system throughout the manuscript, which is very hard for readers that are not familiar with local conditions.

[Response] In the modified MS, we have added the detailed maps accordingly. We thank the reviewer for reminding us.

The authors imply that they want to provide a method/procedure for quantify such estuary water exchange process, which is good, but how will their method be applicable to other large river estuary systems? Is this spillover water problem also common in other systems? In the conclusion the author mentioned briefly that "this study demonstrated a procedure to : : :", but I could not see how their method could be applied to other system so far.

[Response] No, the spillover from the North Branch is a local phenomenon. However, the coupled dynamics of nutrients and carbonate system should be applicable in many estuaries and coastal lagoon systems with similarly eutrophic and turbid backgrounds. In the modified MS, we have reorganized the unclear wordings.

Responses to Anonymous Reviewer #3

This manuscript is generally written clearly and provides a fairly detailed analysis of linked carbonate and DIN systems over a brief time-period. One strength of this manuscript is that it outlines a method that could potentially be used to quantify DIN interactions with the carbonate system using a data set gathered during an intensive 6 day sampling. Studies of eutrophic estuaries are valuable in understanding carbonate system dynamics where respiration rates and rates of nitrogen cycling are extremely high. It is a disadvantage that the manuscript is based on such a limited time-period, as a seasonal study would be much more compelling. If the focus of the paper is indeed to highlight a method, as opposed to doing a comprehensive study, this point needs to be highlighted. The main conclusion the authors seem to draw is that the spillover effect on the South Branch is small - this is not very interesting or unexpected, so a compelling reason for this paper that describes such a limited time-window is needed. The manuscript could also benefit from an improvement in the language, where the abstract and multiple sections of the paper are sometimes difficult to understand.

[Response] In the revised MS, we focus on explaining controls of estuarine CO_2 by coupling the nitrogen and carbonate dynamics. Seasonal dataset obtained in 2011 has been added so as to discuss seasonal and interannual variations.

Specific Comments:

(1) Abstract, Line 17: the wording “CO2 productions were quantified by: : :” is difficult to understand. What is meant by this?

[Response] In the modified MS, the unclear wording has been changed into “CO_2 productions were determined by…”.

(2) Page 6408, Line 16: “Quantificationally” is not a word in the English language.

[Response] Deleted.

(3) Page 6409, Line 1: I think the word “solid” used here should be the more conventional “suspended solids”

[Response] Changed accordingly.

(4) Page 6415, Line 6: Here and in other parts of the manuscript, the language “presumably influenced by sewage” or something like it is used. Is there a major sewage treatment plant discharging into this region? If so, this should be stated clearly. Is there any information about what this plant discharges to the river (e.g., water, nutrients, carbon)?

[Response] Sorry, we don’t know the details on the sewage outlets. We know them since we can smell the sewages over there during many surveys. According to Chai et al. (2006), four major sewage outlets are located along the southern coast of the South Branch and discharge 84.5 m^3 s^{-1} of industrial and domestic sewage from Shanghai City in late 1990s. They have briefly discussed the local impacts on nutrients in the Changjiang Estuary. In the modified MS, we have added the relevant information. However, this is not crucial for this study.

Refersnce

Chai, C., Yu, Z.-M., Song, X.-X., and Cao, X.-H.: The status and characteristics of eutrophication in the Yangtze River (Changjiang) Estuary and the adjacent East China Sea, China, Hydrobiologia, 563, 313–328, doi:10.1007/s10750-006-0021-7, 2006.

(5) Page 6416, Line 1: In this sentence, the system is referred to as the "Changjiang estuary" when specifically talking about the data, and it is confusing because up until this point, only the three study zones are referenced. Why the change? It would be clearer if you specifically stated the study regions that contribute to the conservative mixing lines.

[Response] The reviewer is right. In this study, we have divided Changjiang Estuary into three parts, i.e., North Branch (salty), South Branch (mainly occupied by freshwater), and the outer area (open to seawaters). In the modified MS, we separate conservative water mixing lines in the North Branch from those in the South Branch and/or the outer estuary.

(6) In Figure 4 (and elsewhere), it appears that data from the south branch are used in the mixing diagrams. This seems odd, as apparently the south branch only exchanges with the other study regions in a limited way under spring tides and the overall exchange is small.

[Response] The reviewer is right. It is especially true in July 2011, when the spillover flux was forbidden due to the large water discharge from Changjiang. In this month, the North and South Branches were absolutely isolated by Chongming Island. In the other surveys, however, the two branches not only share the same end-members (of freshwater and seawater), but also exchange with each others via the spillover flux. Therefore, the two braches show similar conservative water mixing lines during most surveys. In the modified MS, we separate conservative water mixing lines in the North Branch from those in the South Branch and/or the outer estuary.

(7) Page 6418, Line 17: Equation 14 has two unknown values (Qs and Qn), but the text does not describe how both values are computed using the equation – please add this.

[Response] Both equations (13) and (14) have the two unknown Q_S and Q_N. They are simultaneous equations. Therefore, we can resolve the two simultaneous equations based on simple algebraic methods. In the modified MS, this issue has been clarified.

(8) In addition to the comment above, QN, the spillover flux was quite small relative to the other water inputs and elevated the South branch salinity to 0.2 to 0.67, but from what base value? Zero? This suggests a relatively small impact of the spillover fluxes.

[Response] Yes. Q_N has relatively minor impacts on nutrients and carbonate system in the South Branch. The background salinity of the South Branch is from 0.14 to 0.17. In the Modified MS, the purpose focuses on maintaining mechanisms of estuarine CO_2 degassing fluxes.

(9) In the absence of a map, I am having difficulty envisioning the dynamics of this system, especially the location and size of the exchange area between the North and South branch – a better, more resolved map would help.

[Response] Done. See the response to reviewer #2's comments.

(10) The limitation of this study, as it only involves data over relatively brief period, is highlighted by the fact that the study period occurred during a relatively dry period (Figure 2). Would this method work under much higher flow conditions, where residence time is much shorter? Some discussion would be helpful here.

[Response] In the modified MS, we include seasonal observations in 2011 so as to discuss seasonal and interannual variations. Since 2011 is a dry year for Changjiang, the July 2011 represents the longest residence time for the North Branch water. See the first figure in the response to reviewer #1's comments.