Biogeosciences Discuss., 12, C2541–C2544, 2015
www.biogeosciences-discuss.net/12/C2541/2015/

Biogeosciences
Discussions
Open Access

Interactive comment on "Coupling the chemical dynamics of carbonate and dissolved inorganic nitrogen systems in the eutrophic and turbid inner Changjiang (Yangtze River) Estuary" *by* W.-D. Zhai and X.-L. Yan

Anonymous Referee #1

Received and published: 2 June 2015

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. This study lacks sufficient references in Discussion (less than 10 references in Discussion). Finally, the mixing scheme should be reevaluated before further addressing the biogeochemical processes.

Major comments:

(1) Physical assumptions. The assumption of mixing between river and sea end-members 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.

(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. What is omega saturation status? What is the proportion of CaCO3 in PIC (Fig. A1) and how much CaCO3 dissolution can result in the delta DIC in Fig. 6e. 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, $CaCO_3$ dissolution might be less important than expected as the authors. 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. What is the role of NH_4 regeneration in Fig. 7c as the residence time in the North Branch is long? How the ratio in Fig. 7c can be affected by NH_4 regeneration? 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? Is there any point source in the North Branch to increase delta NH_4? The increase of delta NH_4 and other species in Fig. 6 are mentioned. But why these delta C in Fig.6 decrease after salinity 16 (except delta NO_3.)

Those equations in 4.2 should have their references. How many delta DIC in the South Branch is induced/reduced by spilled water from North Branch?

(3) For discussion 4.3. It is good that the authors present the idea in Section 4.3 that seawater-introduced [CO_3^{2-}] was mostly titrated by respiration-induced CO_2, and transferred into HCO_3^- 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 CO_2 were potentially titrated by CO_3^{2-} (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 CO_2 was removed?

(4) For Discussion 4.4, the authors suggest that pCO_2 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 NH_4, NO_3, and pH values.

(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 $CaCO_3$ formation is not considered in the South Branch?

Minor comment:

1) The authors suggest that the spillover water has salinity 15 and can increased the salinity and reduce the pCO_2 in the South Branch (Fig. 3n). It is not clear on Fig. 3n, do you mean Fig. A2d?

2) The authors said "Although 80 to 85% if estuarine CO_2 . . ." 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.

Interactive comment on Biogeosciences Discuss., 12, 6405, 2015.