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Interactive comment on “The stoichiometric ratio during biological removal of inorganic carbon and nutrient in the Mississippi River plume and adjacent continental shelf” by W.-J. Huang et al.

W.-J. Huang et al.

wcai@uga.edu

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Thanks for your comments. We appreciate the chance to respond. Therefore, we would like to emphasize that this study is focused on DIC uptake and nutrient removal. We are not checking the Redfield ratio in organic matter itself. We are checking “if the DIC uptake and nutrient removal stoichiometry to be the Redfield ratios”, which has been used in large-river-plume biogeochemical models but lacks evidence to support.

In the following paragraphs, we will reply to each comment one by one.

1. General comments Using changes in the DIC and TA pools to track nutrient removals in the plume seems like an interesting and innovative way to check on whether Redfield

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ratios exist in this plume (as uptake). The better term for this is to use TN and TP, rather than portions of the DIN and DiP pool. After all, the authors are examining the TC pool, not part of the DIC pool (e.g., fatty acids, or whatever).

Reply: In this study, we focused on examining the stoichiometry of biological CO₂ uptake and nutrient removal during a river-ocean mixing process. We focused on whether it is appropriate for the ecological models to treat the stoichiometry of DIC uptake and nutrients removal as the Redfield ratios to estimate the biogeochemical processes in a larger river plume. Our objective were not to consider the Redfield ratio itself nor organic matter. However, if we were examining Redfield ratios itself, we would collect phytoplankton and measure the C/N/P/Si stoichiometry of them. Besides, using TN, TP and TC to calculate the stoichiometry would generate a similar result as the conclusion of Frigstad et al., 2011 (Biogeosciences, 8, 2917–2933). But we are not examining the Redfield ratio itself nor examine the stoichiometry of organic matters. It has frequently been assumed that the CO₂ uptake and nutrient removal appropriately represents the Redfield ratios in many models. As phytoplankton converts inorganic carbon and nutrients to organic matters, using DIC uptake and nutrient removal is the way to examine this assumption as that has not been examined in larger river plumes before. Additionally, we avoid using this kind of description in this study: “whether Redfield ratios exist in this plume (as uptake)”, because such description has already mixed these two concepts (i.e. “stoichiometry of DIC uptake and nutrient removals” and “the original definition of Redfield ratios”) together and is easy to confuse ourselves and also readers.

2. individual scientific questions/issues ("specific comments")

2.a near shore sources: There is a gradient of speculation to firm conclusion regarding the estuarine sources of silicate. I.e.: Abstract line 15: near shore source of silicate are attributed to marshes as potential sources of Si 3.7 line12: we: : ‘speculate’ 3.7 line 21 “may also reflect a preferentially high source term for Si from the marsh.” 4. line 9 “inputs from marshes were contributing factors” This string of logic is inconsistent and

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inappropriate. It can be speculative, but not a conclusion.

Reply: The reviewer 2 has considered three inconsistent sentences: 1) Abstract, line15; 2) Sect. 3.7, Page 15, line 12 and 21; and 3) Sect. 4, P16, line 9. We will modify the text as you have suggested to improve consistency. We would like to point out that only part of the data is influenced by this extra source of data. Since we didn't specifically design our survey to find out this source, we became less conclusive. However, we believe our conclusion on this marsh derived Si is reasonable based on circumstantial evidence and literature reports. To reduce speculation, we have revised our abstract (page 2, line 14-17) to "Lower C/Si and N/Si ratios in one nearshore area were attributed to a preference removal of nitrogen, likely from the nearby marsh surrounded bay. When net biological uptake was separated from river-ocean mixing and this preference removal was removed, stoichiometric ratios of C/N/Si were similar to the Redfield ratios, thus supporting the applicability of the Redfield-type C/N/Si ratios as a principle in river-plume biogeochemical models." Additionally, we will delete the speculated sentence in conclusion (page16, Line7-8).

2.b The Liu et al. 2011 paper is based on only 24 h data and the measured TSS concentrations were several times higher than those in Das et al. 2011. In contrast, Das et al. 2011 (Environmental Research Letters 6: 025001) used many years of monthly samples to conclude that the carbon export was minor. You really have to wonder about using a one-time sampling with very different numbers to use for an extrapolation to estimate export (of Si) of something they did not measure.

Reply: Thank you for pointing out to us the Das et al. paper. We will cite Das et al. 2011 and Das et al. 2010 as references in 3.7, line 17 and also in page 4, line 25. Besides, we believe that you mean "Li et al. 2011" instead of "Liu et al. 2011" in this comment. However, we did not estimate the export of Si at all in this paper. We merely used high Si (and low NO₃) inside the bay to support our explanation of the high Si/N ratio for a small part of the data that cannot be explained by our approach (river-ocean mixing plus biological removal).

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2.c How much of the change in nitrate and carbon can be attributed to sinking particles? The hypoxia in bottom waters is driven by this amount. Dagg and Breed (2003) estimate that the amount of Carbon sinking to the bottom layers equals the amount produced in the surface waters (Table 1; J. Mar. System. 43: 133-152). Surely this sedimentation rate affects the distribution of carbon in the plume, contributes to the sag at 10-20 psu, and occurs at the edge of the buoyancy plume (which is where the turbulence of diatoms diminishes, hence their sinking rate). In addition, this salinity range is where microzooplankton grazing is at its maximum (Liu and Dagg 2003 Mar. Ecol. Prog. Ser. 258: 31-42)

Reply: The premise of our approach is that all changes in nitrate and DIC are caused by (1) river-ocean mixing and (2) net biological removal, which is exported as sinking particles or as DOC (though we also discussed local impacts by the bay). We used salinity and TA to determine the mixing component and then constrain the biological component by examining differences between the observations and the mixing model. Assuming plume DOC production is not significant (which is not always true), then the Δ DIC (i.e. the difference between observed and the predicted by mixing alone) we constrained can be attributed all to sinking or export of POC. However, we do not feel the need to draw this conclusion in our paper as our primary focus was to examine the ratio of DIC and nutrient removal. The Dagg and Breed paper will be cited in Section 3.5 where it is more relevant. We will also include a statement that from our DIC mass balance and removal rate research, we have reached the same conclusion as Dagg and Breed. We also intend to present our results with more recent data in another paper.

2.d There is more than nitrate involved. I suppose that nitrite is a very small portion of the DIN pool, but NH_4 is also there and can be recycled within the DIN pool. Relying on nitrate alone seems risky without data to show it is a meaningless contributor to the N uptake rates.

Reply: We don't have NH_4 data for these two cruises. But we have data from five

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cruises showing that NH_4 concentrations were on the same scale as nitrite concentrations and were only 1-3% of nitrate in the Mississippi River channel. Therefore, NH_4 from the Mississippi River can be neglected in this model. Thanks for your remind. We will add this point in the text. Furthermore, in a biological-physical model (Green et al. 2008), riverine NO_3 was the main driven nitrogen source and while NH_4 concentration from the Mississippi River was neglected. NH_4 was considered recycling among phytoplankton, zooplankton, and bacteria, but its relationship to the physical mixing can be neglected. Therefore, we would like to focus on nutrient removal in relation to mixing processes, although NH_4 recycling is certainly on important as a biological cycling intermediate.

2.e Re: 3.6, line 20-30 makes a distinction between the northeast and northwestern part of the sampling area. These are quite different areas, in that the northeast zone has suspended sediments, different clay-nitrate exchange capacities, and very different light conditions.

Reply: Thanks your comment. Such information will be useful for examining biological uptake rates and we will include this information where it is appropriate. However, as previous noted, our focus was to examine the DIC uptake and nutrient removal stoichiometry.

2.f Is the TN, TP pools conservatively mixed? If not, then you have to assume that there is a loss term (e.g., grazing, sinking particles, etc). which affects the interpretation of the mixing diagrams. I am pretty sure that these are not conservative – why else is there a hypoxic zone in the bottom?

Reply: We were unclear as to the point the reviewer is trying to make in this comment. As we explained in previous responses, our approach did not rely on TN and TP. Instead, we used the dissolved concentrations of DIC, NO_3 and PO_4 and the loss terms of these materials to that predicted by mixing alone represent the “non-conservative” biological uptake terms. The reviewer is correct that TN and TP are not conservative,

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as is true for the dissolved components.

2.g The authors might compare the Si export of Struyl et al. on an area basis and the amount of Si in the river. How large is the theoretical export from the estuary compared to the river flowing past the estuary mouth?

Reply: This would be an excellent suggestion if we decide to give the Si export of coastal marsh/bay a full treatment. In the several versions we did before submission, we had also entertained this idea. But eventually we decided to reduce the local Si export issue to the minimum as we felt we didn't have enough solid evidence to estimate the Si export from the Barataria. So we noted this in Section 3.7 (i.e. "the extensive intertidal marsh needs further investigation"). Instead of the concentration itself, we have emphasized patterns in the Si/N ratio. While we do not feel that this information should be included in this paper, we still calculate it here as you requested. Struyl and Conley (2009) showed that DSi export from the upper 30cm of sediment of freshwater marshes in Belgian was 30 to 60 g m⁻² yr⁻¹. The area of Barataria Bay is 4783 km². Therefore, 30 g m⁻² yr⁻¹ x 4783 km² = 1.2 x 10¹⁰ g month⁻¹. USGS showed that Mississippi River had 6.2mg L⁻¹ as SiO₂ and the river discharge of June 2003 was 173000 m³s⁻¹. Therefore, the Si export from the Mississippi River was 16.7 x 10¹⁰ g month⁻¹. The estimated Si export from Barataria Bay is thus about 7 to 14% of export from the Mississippi River. In addition, we can also calculate the export by another method. In the upper Barataria Bay, Ren et. al. 2009 (Estuaries and coasts) measured 22 to 137 μM which is about the same concentration as the water from the Mississippi River. Since the concentrations are similar, the Si flux can be determined by the water flux. The tidal flux at the passes of Barataria Bay was ±10000 m³s⁻¹, which is 6% of the Mississippi River flow (173000 m³s⁻¹). As a result, these two methods for estimating marsh export of Si both showed the export from the Barataria Bay is ~<10% of the Mississippi River. However, this HSiLN area is confined to the northeastern Louisiana Bight not spread over the Louisiana shelf and all the export from the Barataria Bay towards to the northern Louisiana Bight. The clockwise eddy on the Louisiana Bight could force this

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export to the northeastern Louisiana Bight, while the Mississippi River would possibly flow to a much larger area, the northern Gulf of Mexico. Therefore, the proportion of these two water sources on the Louisiana Bight needs further investigations. Even if our assumptions were correct (i.e. this HSiLN waters were from the Barataria Bay), our findings still support that the export from the Barataria Bay was limited to the north-eastern Louisiana Bight as Fig. 4e, 5e and was less important to the hypoxia over the northern Gulf of Mexico. That means we agree with Das' et. al., 2011 conclusion that DOC export from Barataria Bay was minor by comparing to the Mississippi River as a source for the northern Gulf of Mexico. In order to make ourselves clear, we would modify the words in page15 line 25 to “provided that limited areas near marshes and bays are excluded from the analysis.”

3. compact listing of purely technical corrections at the very end ("technical corrections": typing errors, etc.). none, not that its perfect, but because it is fairly loose throughout and changes are needed, per comments above

Reply: Thanks. We will consider each comment and make changes in the manuscripts.

Interactive comment on Biogeosciences Discuss., 9, 1557, 2012.

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