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Interactive comment

Interactive comment on "Organic and inorganic carbon and their stable isotopes in surface sediments of the Yellow River Estuary" by Zhitong Yu et al.

Zhitong Yu et al.

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We appreciate the editor's precious time for handling our manuscript and the reviewers' time for reviewing the manuscript. We have thoroughly considered all the comments that are very helpful for improving the interpretations of our findings. We provide our detailed responses below.

Response to the Referees Anonymous Referee #2

1. In lower Yellow River and the Bohai Sea, large anthropogenic nutrient inputs caused the eutrophication in the Bohai Sea. For example, Yu et al (2013, Mar. Environ. Sci. 32,

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175–177) reported that the total Bohai Sea area with eutrophication status increased from 110 km2 in 1997 to 14080 km2 in 2010. Under this condition, the water and sediments contain significant amount of inorganic nitrogen that inevitably affects the C/N values. Based on method description of the manuscript, the authors did not separate organic and inorganic nitrogen. The C/N as a source indicator is valid only for organic carbon and organic nitrogen (C/N >15 for terrigenous plants and 4-10 for aquatic algae). If they did not pay attention to this point, the estimation of organic matter source based on the C/N is not proper and very likely to underestimate the contribution of terrigenous component, as the authors did in section 4.2 (line 243-248).

Response: While Yu et al., (2013) reported an increasing trend in eutrophication area from 1997 to 2010 in the Bohai Sea, the most heavily eutrophic water was mainly in these bays (Wang et al., 2015). According to the recent studies (Liu et al., 2015;Zhang et al., 2012), δ 15N values in the Yellow River mouth were 4-5‰ which were much different from the elevated δ 15N values (10-25‰ delivered from farm runoff and human sewage. These findings indicate that inorganic nitrogen should not be a concern. On the other hand, the approach using the TOC/TN ratio is a common method to quantify different sources of OC, which has been widely applied to study wetland and lake sediments (Meyers, 1997;Brodie et al., 2011;Kaushal and Binford, 1999), and offshore and marine sediments (Lamb et al., 2006;Rumolo et al., 2011). Nevertheless, we will conduct an uncertainty analysis to assess the potential underestimation of terrigenous component. Author's changes in manuscript: In our revision, we will add a section of uncertainty analysis by assuming different degrees of underestimation for the C/N ratio.

2. In the introduction part, the authors claimed that one of their objectives was to explore the underlying mechanisms that regulate the carbon burial in the Yellow River estuary. Unfortunately, I did not see much discussion about this topic. In fact, most of their statements are speculative. For example, from line 256 to 260, given a strong linear correlation between TIC and TOC (r = 0.97, p < 0.01), the authors concluded that the production of organic carbon influences on the formation of carbonate, and most

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TIC was from autogenic carbon in the Yellow River estuary. This conclusion is very surprising for me. How could it be like this just based on the correlation. A correlation does not mean cause and effect.

Response: We appreciate the reviewer's constructive comment. We have re-evaluated our analyses and interpretations, and intend to revise our discussion and interpretation regarding the underlying mechanisms responsible for the spatial distributions of TOC and TIC. Author's changes in manuscript: Our analysis shows a significantly negative relationship between δ 13Ccarb and TIC, indicating that higher level of TIC is a result of higher rate of biological production, which would lead to more negative δ 13Ccarb. Thus, TIC in the surface sediment of Yellow River Estuary is primarily from autogenic carbonate. Interestingly, there is also a significantly negative relationship between δ 13Ccarb and TOC, implying that higher level of TOC may also result from higher rate of biological production, thus TOC is primarily autochthonous.

3. Furthermore, in the semiarid region of China, such as Loess Plateau, soil contains a lot of inorganic carbon. Since Loess Plateau contributes 90% of the Yellow River's sediment load, the severe soil erosion at the Loess Plateau will bring large amounts of allochthonous organic carbon and inorganic carbon into the Yellow River as well as its estuary. Regarding the degradation of organic matter to produce CO2, the author did not explain at all which mechanism could convert organic matter derived CO2 into carbonate. I don't know either since the extremely turbidity in the Yellow River great restricts the algal growth.

Response: According to Wang et al. (2016), the Yellow River sediment load has decreased since the 1950s (see Figure 1 below). Thus, it is reasonable to assume that Loess's contribution is small. Our re-analyses lead to the following interpretations and conclusions: "Our analysis shows a significantly negative relationship between δ 13Ccarb and TIC, indicating that higher level of TIC is a result of higher rate of biological production, which would lead to more negative δ 13Ccarb. Thus, TIC in the surface sediment of Yellow River Estuary is primarily from autogenic carbonate. Interestingly,

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there is also a significantly negative relationship between δ 13Ccarb and TOC, implying that higher level of TOC may also result from higher rate of biological production, thus TOC is primarily autochthonous." Figure 1 The hydrologic regime of the Yellow River in recent decades (Wang et al., 2016)

Author's changes in manuscript: We will revise our discussion/interpretation /conclusion, and also make changes in other relevant sections (e.g., Abstract).

4. In line 241, the authors suggested that TOC was mainly autochthonous in surface sediments of the Yellow River estuary based on C/N (6.3) and δ 13C (-23.35% whereas in the southern shallow bay, up to 60.8% of TOC was from soil source give slightly more negative δ 13C (-23.91% and higher C/N (8.8). Here the author used 10.8 as the terrigenous end member value for C/N based on the soils collected from the river mouth. As I mentioned above, the major sediment load in the Yellow River is not from the soils around the estuary, but from the Loess Plateau in the middle to lower River. Second, there is no much difference in δ 13C between the estuary (-23.35% and southern bay (-23.91% so they should have similar organic matter sources. In the northern China marginal seas, C/N ratio is not as reliable as δ 13C give the interference of inorganic nitrogen and selected degradation of N-containing organic matter.

Response: We appreciate the reviewer's constructive comment. In our earlier responses, "inorganic nitrogen should not be a concern", and "Loess's contribution is small". Our re-evaluation based on the significantly negative relationship between $\delta 13 C carb$ and TOC suggests that TOC is primarily autochthonous. However, our approach using the two-end-member mixing model may introduce bias or uncertainty due to the choice of end member value for soil C/N ratio. For example, our recent study shows a wide range of soil C/N ratio in the lower Yellow River Basin, with a mean value of $\sim\!\!10$ (Shi et al., 2017). We will carry out an uncertainty analysis to address this issue. Author's changes in manuscript: We will revise the discussion/interpretation and add a section uncertainty analysis.

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Discussion paper



Brodie, C. R., Leng, M. J., Casford, J. S. L., Kendrick, C. P., Lloyd, J. M., Yongqiang, Z., and Bird, M. I.: Evidence for bias in C and N concentrations and δ 13C composition of terrestrial and aquatic organic materials due to pre-analysis acid preparation methods, Chemical Geology, 282, 67-83, http://dx.doi.org/10.1016/j.chemgeo.2011.01.007, 2011. Kaushal, S., and Binford, M.: Relationship between C:N ratios of lake sediments, organic matter sources, and historical deforestation in Lake Pleasant, Massachusetts, USA, J Paleolimnol, 22, 439-442, 1999. Lamb, A. L., Wilson, G. P., and Leng, M. J.: A review of coastal palaeoclimate and relative sea-level reconstructions using δ 13C and C/N ratios in organic material, Earth-Science Reviews, 75, 29-57, http://dx.doi.org/10.1016/j.earscirev.2005.10.003, 2006. Liu, D., Li, X., Emeis, K.-C., Wang, Y., and Richard, P.: Distribution and sources of organic matter in surface sediments of Bohai Sea near the Yellow River Estuary, China, Estuarine, Coastal and Shelf Science, 165, 128-136, https://doi.org/10.1016/j.ecss.2015.09.007, 2015. Meyers, P. A.: Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. Organic Geochemistry, 27, 213-250. http://dx.doi.org/10.1016/S0146-6380(97)00049-1, 1997. Rumolo, P., Barra, M., Gherardi, S., Marsella, E., and Sprovieri, M.: Stable isotopes and C/N ratios in marine sediments as a tool for discriminating anthropogenic impact, Journal of Environmental Monitoring, 13, 3399-3408, 2011. Wang, R., Tang, J., Huang, G., Chen, Y., Tian, C., Pan, X., Luo, Y., Li, J., and Zhang, G.: Provenance of organic matter in estuarine and marine surface sediments around the Bohai Sea, Oceanologia et Limnologia Sinica, 46, 497-507, 2015. Wang, S., Fu, B., Piao, S., Lü, Y., Ciais, P., Feng, X., and Wang, Y.: Reduced sediment transport in the Yellow River due to anthropogenic changes, Nature Geoscience, 9, 38-41, 2016. Zhang, D., Yang, W., and Zhao, J.: Tracing nitrate sources of the Yellow River and its tributaries with nitrogen isotope, Journal of Ecology & Rural Environment, 28, 622-627, 2012.

Please also note the supplement to this comment: https://www.biogeosciences-discuss.net/bg-2017-353/bg-2017-353-AC2-

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Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-353, 2017.

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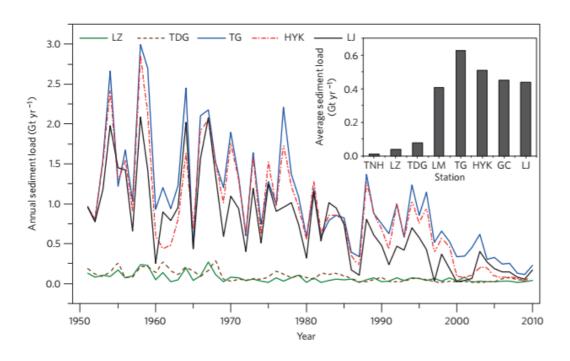
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 $\textbf{Fig. 1.} \ \textbf{The hydrologic regime of the Yellow River in recent decades}$

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