Interactive Comment on "Tracing the origin of the oxygen-consuming organic matter in the hypoxic zone in a large eutrophic estuary: the lower reach of the Pearl River Estuary, China" by Su et al.

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Anonymous Referee #2

This paper determines the origin of the oxygen-consuming organic matter in the hypoxic zone of Pearl River Estuary, China. The approach is the same as that used for the Changjiang Estuary (ES&T 2016), utilizing C-13 value for the increased DIC in the hypoxic zone. I think that the approach is technically valid and provides useful information regarding the cause of hypoxia so as to make right policies for hypoxia remediation. However, authors do not show any advances in data analyses and interpretation, compared with the previous ES&T paper. Authors found that 73% of the oxygen-consuming organic matter is of marine source (the rest portion is terrestrial), which is different from the hypoxia in the Changjiang Estuary (100% marine organic matter contributions). Although authors do suggest some speculations for the cause of this difference, they do not go through thorough data analyses and interpretations about this issue. I suggest following trials to better interpret the data.

(1) Authors may compare all C-13 data for POC and DIC between the two estuaries together in the same plots, so that any systematic difference between the two estuaries can be examined.

[Response]: Thanks for the constructive comment. We have added data from the CJE reported by Wang et al. (2016) and expanded the comparison between the two systems. We see similarities between these two systems: a) As shown in Fig. 5 (original Fig. 4), there is little difference between $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ values in the marine end-member. b) In Fig. 7e, the amplitude of ΔDIC and AOU reveals a similar intensity of OM biodegradation, and the slope of ΔDIC vs. AOU (0.71 ± 0.03 vs. 0.65 ± 0.04) indicates a predominance of aerobic respiration in the two systems. c) As seen from Table 2, there is no significant difference in $\delta^{13}C$ surface sediment values within the hypoxic zone between the PRE and CJE. We also note important differences between these two systems: a) In Fig. 5, the $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ values of the freshwater end-members show some dissimilarity, with lighter values in the PRE (-11.4±0.2 ‰, -28.3±0.7 ‰) than in the CJE (-8.8 ‰, -24.4±0.2 ‰). b) Figure 7a indicates that the water temperature of the PRE is generally higher than in the CJE. For instance, the temperatures of surface and subsurface seawater end-

members in the PRE are 2-3 ℃ higher than in the CJE. c) From a spatial point of view, the distance from the river mouth to the hypoxic zone in the CJE is 2-3 times longer than in the PRE, possibly resulting in a longer travel time of OC_{terr}. Please see P12 L10-27.

Table 2. Comparison of $\delta^{13}C$ values in surface sediments within the hypoxic zone[a] between the PRE and CJE.

$\delta^{13}C$ (‰)	Mean±SD	Stations involved	References
		Pearl River Estuary	
-23.4 ~ -22.1	-22.9±0.5	A4, A5, C1-C4, D1	Hu et al. 2006
-23.2 ~ -22.3	-22.7±0.5	28, 29, 30	Zong et al. 2006
-23.6 ~ -21.5	-22.5±1.1	E8-1, E7A, S7-1, S7-2	He et al. 2010a
-[b]	-23.1±0.6	Clustering groups G6 and G7	Yu et al. 2010
Average	-22.8±0.6		
		Changjiang Estuary	
-22.9 ~ -20.9	-21.8±0.6	-[c]	Tan et al. 1991
-22.4 ~ -19.9	-21.2±1.0	32, 37, 38, 42, 48, 49, 54, 56, 64	Kao et al. 2003
-22.7 ~ -20.8	-22.0±0.8	H1-12, H2-10, H2-11, S1-2, S2-4	Xing et al. 2011
-23.5 ~ -20.4	-22.6±1.0	3, 12, 13, 20-25	Yao et al. 2014
Average	-21.9±1.0		

[a]In the PRE, the data is from similar sites to our present study, which is in the northeast (Leg 1) and southwest (Leg 2) of the Wanshan Islands. While in the CJE, the hypoxic zone is located around 30.0 °N–32.0 °N, 122.7 °E–123.2 °E, which is frequently reported in previous studies (Li et al., 2002; Zhu et al., 2011; Wang et al., 2016).

[b]The authors provide an average value of clustering groups instead of individual data from each site.

[c]In Fig. 7 of Tan et al. (1991), the sampling sites are shown without numbers.

(2) When I look at both data sets from the two estuaries, the difference in the contribution of marine organic matter for the two estuaries is within the uncertainties of this approach. Depending on how to omit the outlier in the relationship (Fig. 7 vs. Fig. 6 of ES&T), the proportion of marine organic matter varies significantly. The ES&T paper shows a large scattering for the slope (if hypoxic zone is collected separately) but reduced the error by including the subsurface layer data which is not reasonable. Therefore, I am not convinced with the argument that the sources of organic matter in the hypoxic zone of the two estuaries are different.

[Response]: We appreciate this critical comment from the reviewer.

a) After carefully re-examining all of the end-members and their error propagations, we have derived a $\delta^{13}C_{OCx}$ value of -23.2±1.1 ‰. For more details please see our response to MC2 from reviewer #1. This value of -23.2±1.1 ‰ is statistically different from the marine-derived OM, which has an isotopic composition of -20.5±0.9 ‰. Therefore, OM than that derived from marine sources must have been contributing to the DO consumption in the PRE hypoxic zone.

b) As clearly depicted in comment (1), the PRE has higher water temperatures, relatively lighter isotopic compositions of DIC and POC, and shorter travel times of OC_{terr} than the CJE, which has implications for microbial activity and the bioavailability of OC_{terr} and OC_{mar}. Combined with the dissimilarity of bacterial community structures in the PRE and CJE, the aforementioned factors can explain the observed differences in the relative distribution of terrestrial and marine OM contributing to oxygen consumption in these two systems. Please see our more detailed description in Sect. 4.3.

(3) I think that most of the oxidation happens in the surface sediment layer. In order to determine the reason for the difference between the two esturaries, authors should show surface sediment C-13 data (any difference between the two estuaries?). Otherwise present any difference in the characteristics of organic matter (C3/C4 plants vs. marine OM) in surface sediments.

[Response]: Although the sediment oxygen demand might be significant, the present study suggests that the oxidation happens mostly in the water column, which is quite similar to observations of CJE hypoxia. Jinwen Liu has demonstrated that the community respiration rate in the subsurface water of the CJE could nearly account for the entire decrease in oxygen after the passing of the typhoon (Liu, 2014). In addition, Wang et al. (2010) claims that water column respiration plays a greater role than sediment respiration in contributing to the establishment of hypoxia in the CJE, and that sinking POC derived from diatom blooms dominate this oxygen depletion in the water column (Wang et al., 2017). In both cases, the decline in oxygen happened after the typhoon passed and resuspended sediment concentrations in bottom waters returned to pre-typhoon levels (Wang et al., 2016). We cannot distinguish between the contribution of resuspended sediment vs. sinking POC to oxygen depletion, because both of these isotopic signals would have been reflected in oxidation product (DIC) and the derived $\delta^{13}C$ value of the remineralized OC ($\delta^{13}C_{OCx}$).

As seen from Table 2, there is no significant difference of $\delta^{13}C$ surface sediment values within the hypoxic zones of the PRE and CJE.

In the PRE, Yu et al. (2010) showed that the $\delta^{13}C$ value of surface sediments in the estuary increases from -25.0 ‰ at the freshwater-dominated reaches to -21.0 ‰ at the marine-dominated mouth, suggesting a weakening of terrestrial/freshwater (C3 plants detritus and soil) inputs and a strengthening of marine contribution to sediments seaward. Agricultural inputs (enhanced fertilization and an increase in the proportion of C4 plants such sugarcane) and anthropogenic inputs (crude oil and PAHs, PCBs and organochrolinate pesticides) would elevate the organic $\delta^{13}C$ of the sediment. In the CJE, Li et al. (2014) also concludes that the distribution pattern of $\delta^{13}C$ showed a general trend of enrichment seaward and

southward from the CJE. While the depleted $\delta^{13}C$ values were largely attributed to terrestrial inputs of lignin-rich C3 vascular plant debris coupled with coarse sediments, the enriched values were primarily thought to be derived from marine phytoplankton in the relict sands of deeper waters.

(4) Authors state that "We chose the concentrations of Ca2+ as a conservative tracer to validate our model prediction, and the model values were in good accordance with the field-observed values..". In order to choose a conservative tracer, authors may use another conservative element instead of Ca which is not necessarily conservative in the coastal system. I think that Ca should be used to examine the effect of CaCO3 in this system, proving that no addition or removal of DIC associated with CaCO3. This result suggests that the DIC change in the hypoxia is solely owing to the organic matter dissolution.

[Response]: It is true that other elements, like $\delta^{18}O$, can be used as alternative conservative tracers to observe the physical mixing of different water masses in coastal regions. However, in our case, Ca^{2+} was a good choice as a conservative tracer given that $CaCO_3$ precipitation or dissolution was not significant, as judged by the strong linear relationship between surface water Ca^{2+} and salinity (Fig. S2), and the oversaturation state of aragonite (Ω_{arag}=2.6±0.7) in subsurface waters. We used a version of CO2Sys_2.1 to derive Ω_{arag} from DIC and TA. DIC data is shown in Fig. 7c. The constants K1, K2 from Cai and Wang (1998) and KHSO4 from Dickson (1990) are adopted in the Ω_{arag} calculations.

As the slope of ΔDIC vs. AOU in the subsurface water was 0.71±0.03, approximating classic Redfield stoichiometry (i.e., 106/138=0.77), we concluded that no addition of DIC was attributed to $CaCO_3$, and the DIC change in hypoxic zone was due solely to organic matter remineralization.

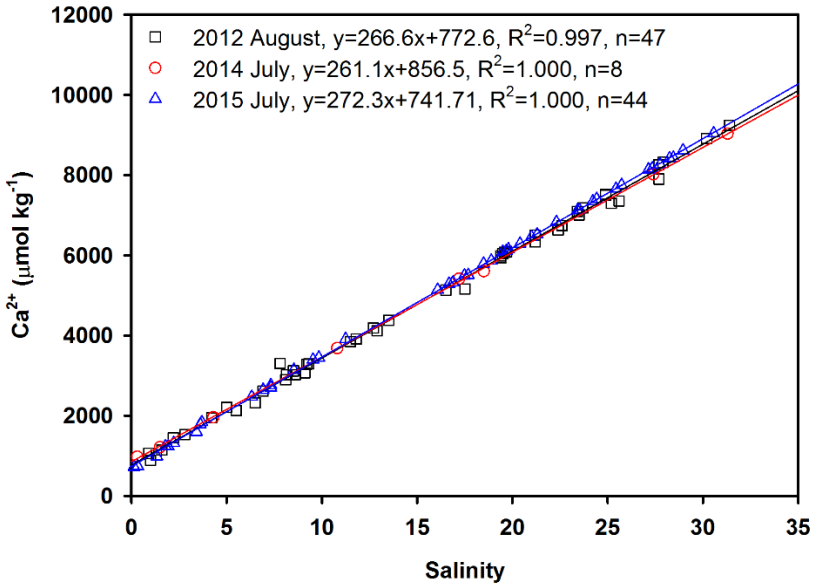

Figure S2. Historical surface Ca^{2+} data plotted against salinity in the PRE during the summer.

(5) Although the contribution is relatively small, authors should account for the contribution of DOC in this system.

[Response]: The reviewer brought up an important issue. Though it remains to be further explored, we contend that the contribution from DOC in consuming oxygen in the hypoxic zone should be minor as the reviewer expected. In the lower PRE (S>20), the DOC versus salinity showed an almost linear distribution, indicating conservative mixing and therefore minor oxidation of DOC (He et al., 2010). As shown in Wang et al. (2016), $\delta^{13}C_{DOC}$ is not generally significantly different from $\delta^{13}C_{POC}$ in most systems. Additionally, the oxidation of DOC in the lower PRE would only affect the estimates of non-conservative DIC mixing, rather than our estimates of the relative contributions of OC_{terr} or OC_{mar} to the oxygen-consuming OM pool. Thus, we did not account for the contribution of DOC to oxygen consumption.

Minor comments

- Authors do not use correct significant figures for DO and DIC (i.e., 153.1 umol/kg for DO and 1900.7 umol/kg for DIC). Otherwise, do you measure such accurate numbers?

[Response]: Thanks for the comment. The precision of DO measurement is ±1 μmol/kg. The precision is ± 2 μmol/kg for DIC measurements. We kept one decimal place for DO/DIC and use this data to plot the horizontal distributions in revised Figs. 2 & 3 and profiles along Transect A in revised Fig. 4.

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