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.

Jianzhong Su¹, Minhan Dai^{1*}, Biyan He^{1, 2}, Lifang Wang¹, Jianping Gan³, Xianghui Guo¹, Huade Zhao¹ and Fengling Yu¹

¹State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen, China

²College of Food and Biological Engineering, Jimei University, Xiamen, China

³Department of Mathematics and Division of Environment, Hong Kong University of Science and Technology, Kowloon, Hong Kong, China

*Correspondence to: Minhan Dai (mdai@xmu.edu.cn)

Anonymous Referee #1

The paper by Su et al. deals with hypoxia and its causes in the Pearl River Estuary (PRE). Hypoxic events are a growing concern from human societies as they threat the environment and the resources on which coastal population lives. Furthermore, it strongly impacts the environment with a resilience time which is now largely unknown. Attribution of hypoxia to a type of organic matter mineralization has been seldom done, and is very interesting from a watershed manager point of view. It is the kind of effort that Su and his/her colleague have started, and for that reason their paper is of potential great interest. Indeed, they use DIC stable isotopic composition and a wealth of other data collected from two cruises in the Pearl River estuary and the adjacent coastal zone to estimate the contribution of terrestrial and marine organic matter to the decrease of oxygen in stratified bottom waters. The contribution is thus original as only a few attempts exist to quantify the source, e.g. in the South China Sea near Changjiang River, but the reading of the paper raises some fundamental issues which are poorly answered in the manuscript: was the perturbation of the typhoon small enough that it can be neglected (see page 4, line 17-18)? Is the proportion of 75-25% a robust estimate of the contribution of the marine and terrestrial pools? Can we quantify better the uncertainty? Overall the paper lacks precision in description of sampling for isotopes, position of sampling for DIC (surface or deep), arguments for endmembers determination which is crucial in estuaries with River plumes. It thus requires a deep reworking before it can be published.

[Response]: We are grateful that the reviewer valued our study. We also appreciate the critical and constructive comments, which have been fully considered in our revised MS. We will address these major concerns of the reviewer in our responses below.

Main comments:

MC1- Typhoon influence: after presenting the study period and the occurrence of a typhoon "Rammasun", the authors write on page 4, line 17-18 ". . . that this study represented a typical situation of the area in terms of terrestrial material discharge". Yet, the typhoon brought heavy rain (and I suppose waves) which increased the Pearl River discharge to 26000 m3/s (double of the monthly average in July of 15000 m3/s).

Later in the paper (page 8 line 8-18), the authors describe the changes of the bottom water composition at one station (A10, Fig. 5) which clearly show the changes in DIC, DIP, O2 and TSM concentration after the typhoon and until the end of the cruise. I think that the authors should reconsider the "typhoon" issue by saying that i) it has modified the system; ii) the system has restratified quickly due to large freshwater discharge iii) isotopic composition and DIC concentration before and long after the typhoon (1 week) may reflect the mineralization of OM (to be justified).

[Response]: The reviewer is correct. Typhoon "Rammasun" did increase riverine discharge and de-stratify the water column, which was however quickly re-established (Fig. 6). Following these suggestions from the reviewer, we have deleted the statement "that this study represented a typical situation of the area in terms of terrestrial material discharge". To further clarify the impact of the typhoon in terms of freshwater discharge, we have added daily river discharge measurements during 15-18 July, which were 19480, 26115, 22981 and 17540 m³ s⁻¹, respectively. Note that our sampling was interrupted during 17-18 July due to the typhoon. Excluding the discharge rate during these two days, the average freshwater discharge rate during our actual sampling period was 16369 m³ s⁻¹, which was slightly higher than the multi-year (2000-2011) monthly mean (15671 m³ s⁻¹). Please see P4 L4-7 and P5 L19-21.

The impact of the typhoon has been illustrated in Fig. 6 and presented in Sect. 3.4. Unfortunately, we only sampled $\delta^{13}C_{DIC}$ at Station A10 on 20 July, which does not allow us to compare $\delta^{13}C_{DIC}$ values before and after the typhoon. However, other parameters we measured, such as DIC, O₂ and DIP, accurately reflect the mineralization of OM. Related revisions have been made in the revised MS in P5 L21-23.



Figure 6. Profiles of (a) temperature, (b) salinity, (c) DO, (d) DIC, (e) DIP, (f) TSM and their evolution during repeated sampling at Station A10.

MC2- Calculation of the proportion of terrestrial versus marine OM mineralization in bottom water DIC: these calculations are made using a mixing model which is fine to me and well handled. However, due to

the difficulty in defining the endmembers (which is common in such models), I believe that the uncertainty on the final proportion (75% marine-25% terrestrial) is much larger than that reported. Furthermore, the arguments given for the endmember isotopic values are very weak: page 10 line 21-27 for 13CTerrPOC, and page 11 line 1-7 for 13C-MarinePOC. In this last case, the authors quote 4 papers with values between -21.2 and -20.5 permil and finally choose -19.4+-0.8 which is out of the previous range. It is known that defining this value in estuaries or near estuaries is very complex and cannot be done with a restricted number of data (Harmelin-Vivien et al., 2008, CSR. Yet, changing this value from -19.4 permil to -21 permil would decrease de proportion of Terrestrial OC from 25% to 10%. With the uncertainty on the predicted values used in the equation and the uncertainty on the endmembers, the final uncertainty is certainly much larger than the 10% reported. The authors should give better arguments for their choice of isotopic composition of the end members and provide a sound estimation of the error propagation throughout their mixing model. They should also revise their estimation of terrestrial fraction, and modulate the conclusions.

[Response]: Again, we appreciate the reviewer's comments, which are indeed critical to this study. We have thus made great efforts to go through every detail regarding the selection of end members and the estimation of uncertainty.

1. Selection of $\delta^{13}C_{terr}$ and $\delta^{13}C_{mar}$

We initially defined the end-member values of δ^{13} C by using a composite value of particulate organic carbon (POC) and surface sediment organic carbon, which was not strictly correct because sedimentary organic matter often contains larger terrestrial components while POC is composed of more freshly produced organic matter (Middelburg and Nieuwenhuize, 1998). In the revised MS, we adopted the endmember values of δ^{13} C from POC.

Here, for the terrestrial end-member ($\delta^{13}C_{terr}$), we adopted the average $\delta^{13}C$ value of POC sampled near the Humen Outlet (S<4), which represents the predominant source of riverine material entering the estuary (He et al., 2010b). The mean POC value, -28.3±0.7 ‰ (n=7), is very similar to the freshwater $\delta^{13}C_{POC}$ value of -28.7 ‰ reported by Yu et al. (2010), which reflected a terrigenous mixture of the C3 plant fragments and forest soils. For the marine end-member ($\delta^{13}C_{mar}$), we calculated the mean surface water $\delta^{13}C_{POC}$ value (-19.4±0.8 ‰, n=8) from stations with S > 26 where significant phytoplankton blooms were observed, as indicated by DO supersaturation (DO% > 125 %) and relatively high pH values (> 8.3) and POC contents (5.3±2.4 %). This value is similar, although slightly heavier than the marine end-member used by Chen et al. (2008), who measured a $\delta^{13}C$ value of -20.9 ‰ in tow-net phytoplankton samples from outer Lingdingyang Bay, in the same region as this study. Additionally, He et al. (2010a) reported a $\delta^{13}C$ value of -20.8±0.4 ‰ in phytoplankton collected from the northern South China Sea (He et al., 2010a). These values are consistent enough for us to compile and obtain use average $\delta^{13}C_{mar}$ value of -20.5±0.9 ‰. This value also agrees very well with the reported stable carbon isotopic signature of marine organic matter in other coastal regions. For example, mean isotopic values for phytoplankton were reported as -20.3±0.6 ‰ in

Narragansett Bay (Gearing et al., 1984), -20.3±0.9 ‰ in Auke Bay and Fritz Cove (Goering et al., 1990), and -20.1±0.8 ‰ in the Gulf of Lions (Harmelin-Vivien et al., 2008).

2. Error propagation (uncertainties)

As shown in the revised Fig. 8, the composite uncertainty for the average $\delta^{13}C_{OCx}$ value is 1.1 ‰, which is close to the uncertainty (1.0 ‰) reported by Wang et al. (2016).

The fractional contribution of OC_{terr} and OC_{mar} to $\delta^{13}C_{OCx}$ is determined by $\delta^{13}C_{terr}$, $\delta^{13}C_{mar}$ and $\delta^{13}C_{OCx}$ values, and are calculated using the following equation:

$$f(\%) = \frac{\delta^{13} C_{mar} - \delta^{13} C_{OCx}}{\delta^{13} C_{mar} - \delta^{13} C_{terr}} \times 100$$
(9)

The composite uncertainty associated could be calculated by the following equation (Taylor, 1997; Han et al., 2012):

$$\varepsilon_{f(\%)} = \sqrt{\left(\frac{\partial(f)}{\partial(\delta^{13}C_{mar})} \times \delta([\delta^{13}C_{mar}])\right)^2 + \left(\frac{\partial(f)}{\partial(\delta^{13}C_{terr})} \times \delta([\delta^{13}C_{terr}])\right)^2 + \left(\frac{\partial(f)}{\partial(\delta^{13}C_{oCx})} \times \delta([\delta^{13}C_{oCx}])\right)^2 \times 100}$$

Using end-member values of -28.3 ± 0.7 ‰ and -20.5 ± 0.9 ‰ for $\delta^{13}C_{terr}$ and $\delta^{13}C_{mar}$, respectively, and the derived $\delta^{13}C_{OCx}$ value of -23.2 ± 1.1 ‰, as justified above, the fractional contribution of marine organic matter is 65 ± 16 %, while the terrestrial organic matter accounted for the remaining 35 ± 16 %. We have revised the MS accordingly as in P10 L21-22, P11 L4-26 and P13 L20-24.



Figure 8. Δ ($\delta^{13}C_{DIC} \times DIC$) vs. ΔDIC in the PRE. Samples were collected from subsurface water (> 5 m). The grey circles represent samples with AOU > 100 µmol kg⁻¹. Δ is the difference between the field-

observed and model-predicted values. Also shown is data from the CJE reported by Wang et al. (2016). The straight and dashed lines indicate linear regression lines of data from the PRE and CJE, respectively.

MC3- Lack of precision for isotopic data: In stratified estuaries, the positioning of the sampling in the water column is crucial as strong vertical gradients (Fig. 5) are common in estuaries. Yet, when describing the isotopic measurements (page 5, line 1), it is not clear which samples were analysed. Were all samples analyzed as for DIC and O2? If so, which sample values are reported in Fig. 4 for 13C-DIC and which are reported in Fig 6d and Fig. 7? How were they chosen? Are there only 9 samples of subsurface waters for 13C-DIC measurements (reported on Fig. 7)? Clearly a better description of these data would be welcome with more maps (surface-bottom).

[Response]: We appreciate the comments. We measured DIC and O_2 at all stations where depth profiles were sampled. We primarily measured $\delta^{13}C_{DIC}$ along Transect A and at depth in the low oxygen layers (28 stations and 84 layers in total), which are now shown in revised Figs. 2i (surface in Leg 1), 2l (surface in Leg 2), 3i (bottom in Leg 1), and 3l (bottom in Leg 2). The sampling locations where $\delta^{13}C_{DIC}$ was measured along Transect A are shown in the revised Fig. 4f for Leg 1 and Fig. 4l for Leg 2. Figure 5 (original Fig. 4) now shows all the $\delta^{13}C_{DIC}$ (n=84) data collected in July 2014 with the surface and subsurface data distinguished.

Following the reviewer's suggestion, Fig. 7d (original Fig. 6d) has now been revised and includes all the subsurface data used in our three end-member mixing model (i.e. points within the solid triangle in Fig. 7a). In Fig. 8 (original Fig. 7), the data used for the linear regressions includes all the points in the revised Fig. 7d.



Figure 2. Surface water distribution of temperature, salinity, DO, Chl-a, DIC and $\delta^{13}C_{DIC}$ during Leg 1 (a-c, g-i) and Leg 2 (d-f, j-l).



Figure 3. Bottom water distribution of temperature, salinity, DO, Chl-a, DIC and $\delta^{13}C_{DIC}$ during Leg 1 (ac, g–i) and Leg 2 (d–f, j–l). Note that the black lines in (c) and (f) indicate DO contours of 63 µM and 95 µM.



Figure 4. Profiles of temperature, salinity, DO, Chl-a, DIC and $\delta^{13}C_{DIC}$ along Transect A during Leg 1 (a–f) and Leg 2 (g–l). Note that the black lines in (c) and (i) indicate DO contours of 63 µM and 95 µM.



Figure 5. Distribution of $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ with respect to salinity in the PRE. The up-facing and down-facing triangles denote surface and subsurface $\delta^{13}C_{DIC}$ data, respectively, from July 2014, while the open circles represent $\delta^{13}C_{POC}$ values in surface water from July 2015. Additionally, the plus signs and crosses show the $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ data, respectively, from the CJE in Wang et al. (2016).



Figure 7. (a) Potential temperature (θ) ($^{\circ}$ C) vs. salinity in the PRE and adjacent coastal waters (open circles) based on data collected during the July 2014 cruise. The three end-members are shown as different coloured symbols. The blue triangles represent data collected during the August 2011 cruise in the CJE (Wang et al., 2016); (b) Correlation between the field-observed Ca²⁺ (Ca²⁺_{obs}) and model-predicted Ca²⁺ (Ca²⁺_{pre}). The straight line denotes a linear regression line of both surface (square) and subsurface (diamond) data; (c), (d) Relationship between observed and model-predicted DIC and $\delta^{13}C_{DIC}$ values. The straight line represents a 1:1 reference line. Note that the grey dots in Fig. 7c identify data also in Fig. 7d; and (e) Correlation of Δ DIC vs. AOU for all subsurface water data. Δ DIC is the difference between the field-observed and model-predicted DIC and $\delta^{13}C_{DIC}$ values. The straight and dashed lines indicate linear regressions of data from the PRE and CJE, respectively.

Detailed comments:

Abstract: English should be checked by a native speaker

[Response]: We have had our revised MS proofread again by a native English speaker.

Page 1- line 13: "differently sourced" should be changed to "different sources of" [Response]: Accepted. We have changed "differently sourced" to "different sources of". Please see P1 L13.

Page 1- line 19: "hypoxias" is not used in the oceanographic literature. Use "hypoxic events" or "hypoxic zones" or just "hypoxia"

[Response]: Accepted. We have corrected "hypoxias" to "hypoxia" or "hypoxic zones" throughout the revised MS. Please see P1 L19.

Page 1- line 25: replace "marine sourced" by "from marine origin"

[Response]: Accepted. We have replaced "marine sourced" with "from marine origin" throughout the revised MS where appropriate. However, on P1 L25 we have changed this to "derived from marine sources," which fit better with the revised text.

Page 1- line 26: replace "terrestrially sourced" by "from the continent"

[Response]: Accepted. We have replaced "terrestrially sourced" by "from the continent" or "terrestrial" throughout the revised MS. Please see P1 L26.

Page 1- line 26:"eutrophication-stimulated marine sourced organic matter prevailed the oxygen consumption". Do the authors mean "marine organic matter stimulated by eutrophication dominated in the oxygen consumption"?

[Response]: The reviewer is right, and we have changed "eutrophication-stimulated marine sourced organic matter prevailed the oxygen consumption" to "marine organic matter stimulated by eutrophication dominated oxygen consumption". Please see P1 L27-28.

1. Introduction:

Page 2, line 5: Diaz and Rosenberg (2008) should be cited here. They showed in this paper that hypoxia was growing worldwide.

[Response]: Accepted. We have cited Diaz and Rosenberg (2008) here. Please see P2 L2-3.

Page 2, line 14:"restoration" rather than "restoring"

[Response]: This text has been significantly changed in the revised MS and the word "restoration" has been removed completely. Please see P2 L10-13.

2. Materials and Methods

Page 4, line 9: Fig. 1 is too small. You should mix leg 1 and leg 2 on the same map by superimposing crosses and circles, reduce the map of China and show the important stations (A8-A10). Indicate also Lindingyang Bay which is quoted in text

[Response]: Accepted. We have put both Legs 1 and 2 on one figure and inserted an inset map of China. We have marked Lingdingyang Bay in the revised Fig. 1.



Figure 1. Map of the Pearl River Estuary and adjacent coastal waters. The open circles denote the Leg 1 stations on 13–16 July 2014 and the crosses represent the Leg 2 stations on 19–27 July 2014. Note that the filled diamond is the location of Station A10.

Page 4, line 17-18: "suggesting that this study represented a typical situation of the area in terms of terrestrial material discharge". This part of the sentence should be removed, and be consistent with paragraph 3.4 (Reinstatement of hypoxic stations. . .). See major comment MC1

[Response]: Accepted and we have removed this sentence. Please also see our responses to MC1.

Page 5, line 1-4: which samples were measured for 13C-DIC? Please specify (See MC3) [Response]: Please see our response to MC3.

Page 5, line 16-26: The mixing model is described here, but not the final equations for DIC and 13C which are reported on page 10. I think that they should be all reported here for consistency.

[Response]: Accepted. We have added Eq. (4) and (5) to define the predicted values of DIC and $\delta^{13}C_{DIC}$. Please see P5 L13-14.

$$DIC_{\rm RI} \times F_{\rm RI} + DIC_{\rm SW} \times F_{\rm SW} + DIC_{\rm SUB} \times F_{\rm SUB} = DIC_{\rm pre}$$

$$\tag{4}$$

 $\frac{\delta^{I3}C_{\text{DICRI}} \times DIC_{\text{RI}} \times F_{\text{RI}} + \delta^{I3}C_{\text{DICSW}} \times DIC_{\text{SW}} \times F_{\text{SW}} + \delta^{I3}C_{\text{DICSUB}} \times DIC_{\text{SUB}} \times F_{\text{SUB}}}{DIC_{\text{pre}}} = \delta^{I3}C_{\text{DICpre}}$ (5)

3. Results

Page 6, line 7-8: rephrase "we noted that the survey . . .". No explanation is given why only the outside was covered during that first leg.

[Response]: Our sampling was interrupted during 17-18 July due to the typhoon. Thus, we only covered outer Lingdingyang Bay during Leg 1. We have rephrased "The interruption of Leg 1 due to the typhoon (July 17-18) led to a smaller survey area, covering only outside Lingdingyang Bay (traditionally regarded as the PRE), while Leg 2 covered Lingdingyang Bay from the Humen Outlet to the adjacent coastal sea". Please see P5 L23-26.

Page 6, line 10: Fig. 2 is much too small. There are too many data and type of data on this graph. You can either remove some data, cut bottom and surface in 2 different figures, or shift DIC in another graph. Two important things: the need to add 13C-DIC as it is the heart of this paper, use similar scales for all graphs of one type (e.g. O2) as this will allow easier and better reading of the graphs.

[Response]: Per the reviewer's suggestion, we have split the surface and bottom water data into two figures (Figs. 2 & 3). Also, we added $\delta^{13}C_{DIC}$ plots in both figures. We are now using similar scales for both surface and bottom data. Moreover, we added $\delta^{13}C_{DIC}$ plots and used similar scales for the profiles along Transect A in the revised Fig. 4. The related descriptions have been revised accordingly. Please see our response to MC3.

Page 6, line 14: "hypoxia lay more landward", I would say "central" more than landward.[Response]: Accepted. We have replaced "lay more landward" by "was located more centrally". Please seeP6 L11.

Page 6, line 16: "the bloom zone was more westward" I see it more "eastward" (to the right on the map) [Response]: By comparing the surface distributions of DO, Chl-a and pH during Leg 2, we have revised this to say "During Leg 2, there were three patches of high productivity, south of Huangmaohai, at the PRE entrance, and off Hong Kong. The central region of high productivity had the highest DO%, greater than 140% at Station A14, and was characterized by relatively high concentrations of Chl-a (7.8 μ g kg⁻¹) and low concentrations of DIC (1737.3 μ mol kg⁻¹)." Please see P6 L6-12.



Figure S1. The surface distribution of pH during Leg 2.

Page 6, line 19: "hypoxic zone was discovered southeast of Wanshan Islands" I see it more "southwest of the islands" (left side on map). Again, it is hard to see as the graphs are very small![Response]: The reviewer is right. We have corrected it as "southwest of the Wanshan Islands". Please see P6 L16-17.

Page 6-line 21-22: "Hypoxia covered at least 800-900km2". Do the authors refer to stations with $\leq 2mg/l$ O2? They should provide the number of stations with DO<62 µmol/l (=2mg/l)

[Response]: Accepted. We have revised our estimate of the surface area of the hypoxic zone as well as the text. The section now reads "...our results suggest it covered an area of > 280 km² during Leg 1 and > 290 km² during Leg 2 according to the definition of hypoxia as DO < 2 mg L⁻¹ or 63 μ M, or an area of > 900 km² during Leg 1 and > 800 km² during Leg 2 assuming the threshold of the oxygen-deficit zone was < 3 mg L⁻¹ or 95 μ M (Rabalais et al., 2010; Zhao et al., 2017).". We have also added 63 μ M and 95 μ M DO contours to Figs. 3c, 3f, 4c and 4i. Please see P6 L20-24.

Page 7, line 12: Fig. 4 does not specify if the 13C-DIC is measured in surface or bottom Water [Response]: We now distinguish between surface and subsurface $\delta^{13}C_{DIC}$ data in the revised Fig. 5. Please see our response to MC3.

Page 7, line 19: replace "d13C through" by "large d13C decrease" [Response]: Accepted. We have replaced " $\delta^{13}C_{POC}$ trough" by "large $\delta^{13}C_{POC}$ decrease". Please see P7 L18

Page 7, line 19: remove "geologically", replace by "geographically" or by "this station" [Response]: Accepted. We have replaced "Geologically" by "Geographically". Please see P7 L19.

Page 7, line 21: Are sediments d13C as low as -35 permil? I do not see where this value can arise from.

[Response]: We are grateful that the reviewer spotted this specific data point. By examining the previous studies in the region (e.g., Hu et al., 2005; Ye et al., 2010; He et al., 2010), we judged that this data point may be erroneous and thus have deleted it in the revised MS. Please see revised Fig. 5 in the response to MC3.

Page 7, line 24: LT means Local time? If so please notify[Response]: Accepted. We have specified LT as Local Time. Please see P7 L24.

Page 8, line 6: "might be the trail". Does it mean "might reflect"? [Response]: Accepted. We have revised "might be the trail" to "might reflect". Please see P8 L2.

4. Discussion

Page 8, line 25: "when we chose S=34.6". In the Guo and Wong article, there are two depths of the profile which correspond to S=34.6: at 100 meters depth and at >1500 m. I suppose that the authors chose 100 meters which correspond to 2023 uM but they should specify.

[Response]: The reviewer is right. We have revised this to read "Here, by choosing S=34.6 as the offshore subsurface water salinity end-member, we obtained a DIC value of ~2023 μ mol kg⁻¹, similar to the value at ~100 m depth adopted by Guo and Wong (2015)." Please see P8 L22-25.

Page 8, line 26: "DIC of 2023 umol/kg" cite the ref, I think it is Guo and Wong (2015) [Response]: Thanks for the comment. Yes, it is Guo and Wong (2015).

Page 9, line 9-15: the authors explain well how they chose DIC endmember for river water/plume at S=10.8. But the way that 13C-DIC was calculated is not clear, it is all reported in the footnotes of Table 1. They should be exposed here more clearly, and the same approach should be taken for 13C as for DIC, which is not the case. Indeed, the 13C-plume endmember is calculated via simple mixing between freshwater and surface offshore water (footnote b of Table 1) which is not correct if biological uptake is active and differentiate between 12C and 13C. Please specify in text how the endmembers were calculated and justify your choices.

[Response]: The reviewer is correct. Since biological alteration may differentiate between ¹²C and ¹³C, we derived the plume-water ¹³C_{DIC} end-member value based on the conservative mixing curve of freshwater and seawater end-members, where little biological alteration occurred. We have moved the footnotes into the main text with more explanations. "The $\delta^{13}C_{DIC}$ value was 0.6±0.2 ‰ in the offshore surface seawater at S=~33.7, where nutrient (NO₃⁻⁺+NO₂⁻ and DIP) concentrations were close to their detection limits and DO was nearly saturated, indicating little biological activity. As DIC remained overall conservative when salinity was <10.8, the $\delta^{13}C_{DIC}$ value of -11.4±0.2 ‰ at S<0.4 is representative of the freshwater source. Assuming the plume water is a mixture of freshwater and offshore surface seawater, the initial plume end-

member of $\delta^{13}C_{DIC}$ at S=10.8 can be calculated via an isotopic mass balance (-7.0±0.8 ‰)". Please see P9 L9-15.

Page 9, line 18-21: "we chose Ca2+ as a conservative tracer. . .". Again, the endmembers for this element are not described in text, but in table 1 (footnote c). It is said that Ca2+ values of the endmembers were calculated by correlation with Salinity. So, I wonder if the correlation between prediction and observation for Ca2+ of Fig 6b is a test of the accuracy of the mixing model, because the mixing model is calibrated by T and S (line 16) and mostly S for surface waters, and Ca2+ is also calculated from S. . . Furthermore, it is not specified if the data points for Ca2+ refer to surface or subsurface water. Specify and remove argument if circular.

[Response]: We apologize for the confusion. We only derived end-member values of the plume and surface seawater using the Ca-salinity relationship, and our Ca²⁺ data collected during the 2014 cruise was only for the purpose of validating our three end-member mixing model. In the revised version, the Ca²⁺ values of the plume and surface seawater end-member were derived independently from a conservative mixing calculation (Ca²⁺ vs. S) based on a 3 years of surface data during the summer (August 2012, July 2014 and July 2015). As shown in Fig. S2, we obtained mean values of $3670\pm16 \mu mol kg^{-1}$ at S=10.8 as the plume end-member and $9776\pm132 \mu mol kg^{-1}$ at S=33.7 as the offshore surface seawater end-member. The subsurface Ca²⁺ end-member was chosen from the measured value at S=~34.6 during the 2014 cruise. In the revised Fig. 7b (original Fig. 6d), all of the Ca²⁺ data from both surface and subsurface waters (shown with distinguished symbols) are plotted to compare with model-predicted Ca²⁺ values. These values agree well, which strongly supports our model predictions. Please see revised Fig. 7b in the response to MC3.



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

Page 10, line 21 to page 11 line 7: see my main comment (MC2) above on endmembers and uncertainty. The authors should justify their choice better, when the range is large as for terrestrial OM (-28.7 to -24.9 permil) and the choice is made to stick to one end of the range based on a few measurements. The situation is even worse for the offshore surface water POC where the chosen value (-19.4 permil) is out of the range reported by the authors (see above). Furthermore, it is very difficult to assess pure plankton signature by surface water sampling as POM in estuaries or offshore is a mixture of marine POM and terrestrial POM (Harmelin-Vivien et al. 2008, CSR). The choice of this endmember is thus questionable and should be better justified.

[Response]: Please see our response to MC2 regarding the selection of $\delta^{13}C_{terr}$ and $\delta^{13}C_{mar}$ end-member values.

Page 12: one possibility for the difference between the Changjiang and the Pear River could also be the presence of the megacity of Guangzhou and its fresh anthropic OM discharge into the river. As the typhoon washed away some of the material deposited in the river conduit, it could have led to more labile matter in the estuary.

[Response]: We very much agree with this comment. We have added it to the discussion of the bioavailability of OC_{terr} in Sect.4.3 as "Moreover, the increased precipitation and runoff during the typhoon may have mobilized additional fresh anthropogenic OM from surrounding megacities (e.g. Guangzhou, Shenzhen and Zhuhai) deposited in the river channel, which could lead to more labile OC_{terr} in the PRE". Please see P13 L6-9.

5. Conclusion

Page 13, line 8-12: the authors should report a possible range for the share of terrestrial OM mineralization based on uncertainties in endmembers (between 10-25%) instead of the values reported here 27%.

[Response]: Accepted. We have revised it as "...we demonstrated that the organic matter decomposed via aerobic respiration in the stratified subsurface waters of the lower PRE and adjacent coastal waters was predominantly OC_{mar} (49-81 %, mean 65 %), with a significant portion of OC_{terr} also decomposed (19-51 %, mean 35 %)." Please see P13 L20-24.

Figures and Tables (see also comments in text above):

Fig. 6: The calculation of the "biological effect" on DIC and 13C-DIC is based on subsurface values. These values should be visible (dark dots?) on graph to identify the data used for deriving the signature of mineralized OM (on Fig. 7)

[Response]: Accepted. Please refer to our response to MC3. Also, we have identified the data in revised Figs. 7c (grey dots) that corresponds to the data in Fig. 7d.

Fig. 8: The "pseudo-equations" on top and bottom HNO3+DIC \rightarrow OM+O2 and OM+O2 \rightarrow HNO3+DIC should be removed as they are not consistent nor balanced, and replaced by Primary Production (on top) and oxic mineralization (at the bottom). The graph inserted in the Figure is not readable, please consider removing.

[Response]: Accepted. We have changed the previous equations to balanced equations of primary production and oxic mineralization. Also, the small inserted graph has been removed.



Figure 9. A conceptual diagram illustrating the source partitioning of oxygen-consuming organic matter $(OC_{mar} \text{ vs. } OC_{terr})$ within the hypoxic zone in the lower PRE and the adjacent coastal area. See Sect. 5 for explanations.

Table 1: most text in notes should go in text as explanation and justification of endmember calculation.

[Response]: Accepted. We have moved our notes on the selection of $\delta^{13}C_{DIC}$ values in the plume endmember into the text. Please see P22.

References:

Gearing, J. N., Gearing, P. J., Rudnick, D. T., Requejo, A. G., and Hutchins, M. J.: Isotopic variability of organic carbon in a phytoplankton-based, temperate estuary, Geochim. Cosmochim. Acta, 48, 1089-1098, doi:10.1016/0016-7037(84)90199-6, 1984.

Goering, J., Alexander, V., and Haubenstock, N.: Seasonal variability of stable carbon and nitrogen isotope ratios of organisms in a North Pacific Bay, Estuar. Coast. Shelf Sci., 30, 239-260, doi:10.1016/0272-7714(90)90050-2, 1990.

Han, A., Dai, M., Kao, S.-J., Gan, J., Li, Q., Wang, L., Zhai, W., and Wang, L.: Nutrient dynamics and biological consumption in a large continental shelf system under the influence of both a river plume and coastal upwelling, Limnol. Oceanogr., 57, 486-502, doi:10.4319/lo.2012.57.2.0486, 2012.

Harmelin-Vivien, M., Loizeau, V., Mellon, C., Beker, B., Arlhac, D., Bodiguel, X., Ferraton, F., Hermand, R., Philippon, X., and Salen-Picard, C.: Comparison of C and N stable isotope ratios between surface

particulate organic matter and microphytoplankton in the Gulf of Lions (NW Mediterranean), Cont. Shelf Res., 28, 1911-1919, 2008.

He, B., Dai, M., Huang, W., Liu, Q., Chen, H., and Xu, L.: Sources and accumulation of organic carbon in the Pearl River Estuary surface sediment as indicated by elemental, stable carbon isotopic, and carbohydrate compositions, Biogeosciences, 7, 3343-3362, doi:10.5194/bg-7-3343-2010, 2010a.

He, B., Dai, M., Zhai, W., Wang, L., Wang, K., Chen, J., Lin, J., Han, A., and Xu, Y.: Distribution, degradation and dynamics of dissolved organic carbon and its major compound classes in the Pearl River estuary, China, Mar. Chem., 119, 52-64, doi:10.1016/j.marchem.2009.12.006, 2010b.

Middelburg, J. J. and Nieuwenhuize, J.: Carbon and nitrogen stable isotopes in suspended matter and sediments from the Schelde Estuary, Mar. Chem., 60, 217-225, doi:10.1016/S0304-4203(97)00104-7, 1998.

Rabalais, N. N., D áz, R. J., Levin, L. A., Turner, R. E., Gilbert, D., and Zhang, J.: Dynamics and distribution of natural and human-caused hypoxia, Biogeosciences, 7, 585-619, doi:10.5194/bg-7-585-2010, 2010.

Taylor, J. R.: Introduction to error analysis, the Study of Uncertainties in Physical Measurements, 2nd Edition, University Science Books, New York, 1997.

Zhao, H.-D., Kao, S.-J., Zhai, W.-D., Zang, K.-P., Zheng, N., Xu, X.-M., Huo, C., and Wang, J.-Y.: Effects of stratification, organic matter remineralization and bathymetry on summertime oxygen distribution in the Bohai Sea, China, Cont. Shelf Res., 134, 15-25, doi:10.1016/j.csr.2016.12.004, 2017.