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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* Jianzhong Su et al.

Anonymous Referee #1

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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

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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.

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).

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 13C-TerrPOC, 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.

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). See detailed comments below.

Detailed comments:

Abstract: English should be checked by a native speaker

Page 1- line 13: “differently sourced” should be changed to “different sources of”

Page 1- line 19: “hypoxias” is not used in the oceanographic literature. Use “hypoxic

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events” or “hypoxic zones” or just “hypoxia”

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

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

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”?

1. Introduction:

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

Page 2, line 14:”restoration” rather than “restoring”

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

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

Page 5, line 1-4: which samples were measured for 13C-DIC? Please specify (See 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.

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.

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.

Page 6, line 14: “hypoxia lay more landward”, I would say “central” more than landward.

Page 6, line 16: “the bloom zone was more westward” I see it more “eastward” (to the right on the map)

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!

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

Page 7, line 12: Fig. 4 does not specify if the 13C-DIC is measured in surface or bottom water

Page 7, line 19: replace “d13C through” by “large d13C decrease”

Page 7, line 19: remove “geologically”, replace by “geographically” or by “this station“

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

Page 7, line 24: LT means Local time? If so please notify

Page 8, line 6: “might be the trail”. Does it mean “might reflect”?

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.

Page 8, line 26: “DIC of 2023 umol/kg” cite the ref, I think 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.

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.

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.

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.

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%.

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)

Fig. 8: The "pseudo-equations" on top and bottom HNO3+DIC→OM+O2 and OM+O2 →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.

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

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