Interactive comment on "Sources and accumulation of organic carbon in the Pearl River Estuary surface sediment as indicated by elemental, stable carbon isotopic, and carbohydrate compositions" by B. He et al.

mdai@xmu.edu.cn

Response to Referee #1

General comment: This manuscript reports the results of a survey of the organic contents of sediments from the Pearl River Estuary. These are interpreted them in terms of organic matter source and, to some extent, organic matter accumulation. I feel that this manuscript, while containing good data, requires relatively substantial re-writing in order to ensure that a novel contribution to the literature is made. In particular it needs to be re-written to highlight any new findings, and to produce conclusions regarding the overall organic matter dynamics of the estuary in question. At present most data interpretation/discussion is focused on explaining individual features of the data, with little considerations of the wider implications of those features. I therefore do not recommend publication at present. My specific comments are outlined in the following section.

Response: We do appreciate this constructive comment from the review to improve our presentation with wider implications. As a matter of fact, this study does have important implications in the context of organic carbon biogeochemistry. We contend that characterizing organic matter to resolve their sources and/or fate in dynamic estuarine settings remains a grand challenge both in terms of methodology and science itself.

1) Although there have been abundant researches that have attempted to tackle such questions related to the sources and fate of organic matter in coastal environments (Berner, 1982; Goni et al., 1997; Gordon and Goni, 2004; Hedges et al., 1986; Hedges and Parker, 1976; Kuwae et al., 2007; Ramaswamy et al., 2008), our understand remains limited, and sometimes inconsistent. For example, Berner (1982）estimated that ~80% of the terrestrial organic carbon was buried in deltaic and shelf sediments while follow-up studies suggested a significant fraction of the terrestrial carbon may be transported to outer shelf and slope (de Haas et al., 2002; Goni et al., 1998; Prahl et al., 1994). Recent studies based on stable and radio carbon isotopes in combination with biomarkers revealed that the organic matter discharged into the Gulf of Mexico is of high heterogeneity (Goni et al., 1997; Gordon and Goni, 2003), which are composed of at least two groups of organic matter with contrasting source terms. One of them is of land plant origin characterized by lower $\delta^{13}C$ which tends to deposit in the estuary and delta areas and the other one is characterized by highly degraded soil-derived material with higher $\delta^{13}C$ which can be transported farther off shore. As such, using end-members only with land plant $\delta^{13}C$ could have underestimated the contribution of terrestrial input to the shelf systems. Gordon and Goni (2004) therefore called for a reassessment of the burial of terrestrial organic carbon in the ocean.

2) Bulk indices such as elemental stoichiometry and bulk isotopic composition have been widely adopted to characterize the source of organic matter, there have been, however, limited studies to our best knowledge, using a combination of these bulk properties with molecular biomarker techniques. Boschker et al.(1995) have applied such methodologies in Lake Gooimer. Marchand et al. (2005) applied a similar approach to study the sediment in a mangrove system. Relatively comprehensive studies using multiple markers have been in the Amazon system (Bernardes et al., 2004; Hedges et al., 1994). It must be pointed out that due to the complexity of the composition/source terms of organic matter and their biogeochemical evolvement undergone in

the estuarine environments, such multiple markers are important as each individual biomarker may be subject to limitations.

3) At the regional level, the present study examined carbohydrate composition at the molecular level in a dynamic estuarine system highly impacted by anthropogenic activities. We believe that our study for the first time used a combination of bulk property (C/N ratio and $\delta^{13}C$) with molecular biomarker techniques to examine the sources and accumulation of terrestrial organic carbon in this large subtropical estuary. The approach we adopted should have applicability to other large river estuarine systems for evaluation of the contribution of terrestrial organic carbon to sediment TOC, and to help understanding the biogeochemical cycle of terrestrial organic mater. The predominance of terrestrial originated organic matter in the sediment and their generally low accumulation efficiency is not surprising yet it may have important implications in light of heavy anthropogenic discharges into the Pearl River Estuary during the past thirty years.

The above notions and justifications have been emphasized in the introduction/conclusion and been discussed throughout the MS discussion.

General comments: At some points the text makes slightly unusual use of English, and this could lead to confusion. I suggest that it be edited once again by a native English speaker.

Response: We have the MS edited once again by Prof. John Hodgkiss.

General comment: The way the data is presented needs to be improved. Due to the spatial distribution of sampling sites, values of $\delta^{13}C$, C/N and aldose concentration and composition should be plotted on colour coded maps in order to make trends clear. At present this data is only given in tables. I would also suggest that figures 3 and 4 add little to the manuscript, and could be excluded.

Response: We have added a color coded map to show the spatial distribution of TOC, $\delta^{13}C$, C/N and total neutral sugar yields (new Fig. 4). We also plotted the relative abundance of individual neutral sugar in our new Fig. 5, which better shows their spatial trends. Note that we deleted the original Fig.3 following the reviewer's suggestion. Considering that Fig. 4 (in the original version) is necessary for discussion of the sediment organic carbon mixing between terrestrial and marine end-members, we kept this figure and re-arranged as Fig. 6.

General comment: It would be best if study sites could be numbered/named in a more logical way (for example with prefixes to indicate which region each is in such as estuary, inner shelf, outer shelf), so that the reader does not have to continually refer back to the site map.

Response: Accepted. We re-named the sampling stations with prefix R- for the river section, E- for the estuary (Lingdingyang Bay), and S- for the shelf.

Comment: Page 2891 line 6. Please add a statement to the abstract highlighting the importance and wider implications of the study (e.g. impact on our understanding of the fate of terrestrial OM in estuaries), and the novel contribution which it makes.

Response: Accepted. We added a statement to show the contribution of our study as follows:
"This study demonstrated that the combination of the bulk organic matter properties, isotopic composition and molecular-level carbohydrate compositions can be an efficient way to track down the source and fate of organic matter in highly dynamic estuarine and coastal systems. The predominance of terrestrial originated organic matter in the sediment and their generally low

accumulation efficiency is not surprising yet it may have important implications in light of heavy anthropogenic discharges into the Pearl River Estuary during the past thirty years."

Comment: line 8. I think it is rather strong to say that the fate of terrestrial organic matter in the ocean is the key to understanding the global C cycle. Perhaps 'an important key' would be more accurate.

Response: Accepted.

Comment: Line 17. Where you use the term 'ocean' here do you include the estuary? Please clarify.

Response: Yes, "ocean" here was meant in a broad sense to the oceanic region inclusive of estuaries.

Comment: Line 25. The phrase 'in internal heterogeneity source identification' is unclear. Please re-phrase.

Response: We changed the phrase "in internal heterogeneity source identification" to "in the identification of multiple sources".

Page 2892
Comment: Line 14. I suggest that the word 'recently' be deleted, as many of the studies referred to are more than 10 years old.

Response: Accepted.

Comment: Line 22. Please give specific examples of how carbohydrates have been used previously to provide insight into the biogeochemical cycling of OM.

Response: We have provided an example in the revised MS.

Comment: Line 26. Please give references to support your statement regarding the fate of particles discharged by the Pearl River.

Response: We have added a reference.

Comment: Line 26. 'It is thus vital: : :.' To 'shelf system of the SCS.'I suggest that this should be re-framed to say that an understanding of the fate of terrestrial OM in the Pearl River will be applicable to other estuarine systems. This will provide a stronger justification for the study.

Response: Accepted. We have emphasized wider implications of this study in a much broader context. Also see our response above.

Comment: Line 7. State which biochemical classes have been studied previously.

Response: We have stated the biochemical classes, such as lipids and fatty acids in the revised MS.

Comment: Page 2894.Line 5. The sampling programme was not accomplished during a single season; therefore the authors need to include a justification as to why they do not think that

seasonal processes will have affected their results.

Response: Our ^{210}Pb profiles (see below) in sediment cores from selected sites in the Pearl River estuary showed relatively well mixed surface sediments over the top 10 cm (equivalent to ~5-10 years of sedimentation), likely resulting from bio-perturbation and/or sediment re-suspension. Our study thus is examining an average scenario during the past 5-10 years prior to the sampling dates with no intention to resolve the seasonal variability.

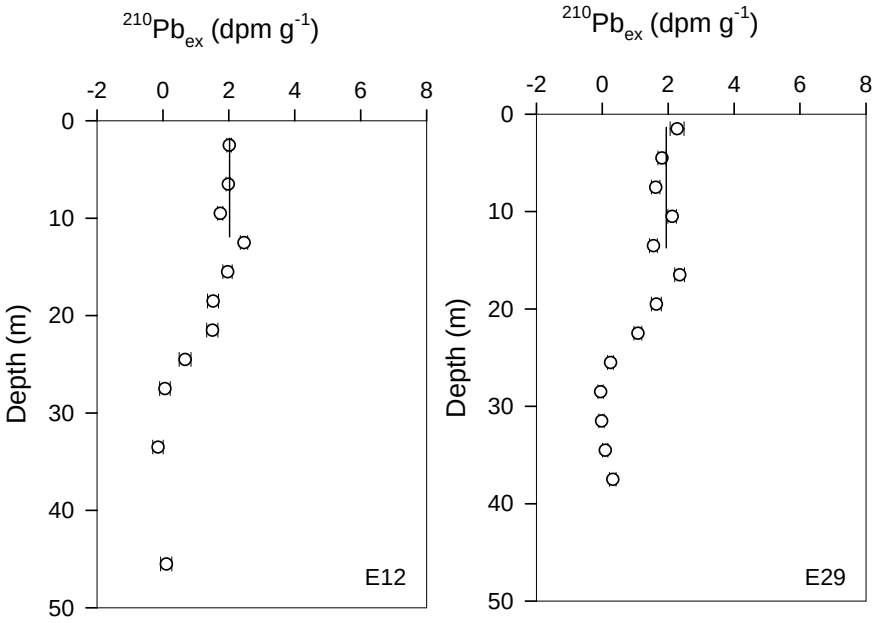

Fig. 1 Excess ^{210}Pb activity versus sediment depth in Lingdingyang Bay. Vertical line shows the surface mixed layer.

Comment: Line 9. The reference to results in Table 1 belongs in the results section.

Response: Accepted.

Comment: Line 18. Please state the size in mm of a 60-mesh sieve.

Response: Stated as “250 μm” in size.

Comment: Line 20. 1N HCl is fairly weak acid to use for de-carbonation of sediments prior to C/N analysis. The authors should justify the choice of acid, and provide evidence that it did achieve complete de-carbonation.

Response: We thank the reviewer for the comment. We soaked our sediment samples in 1N HCl solution for 24 h to de-carbonate according to Prahl et al. (1994). We have compared the different de-carbonation methods showing that the soaking method gave almost identical C/N ratios (10.7±0.5, n=10) as the de-carbonation method by concentrated HCl fume for 24 h (9.7±1.0, n=10). We have added these comparison results in the revised MS.

Comment: Page 2895.Line 1. 'The precision was no more than 0.2 ‰'. This phrasing is confusing. Do you mean the standard deviation was <0.2 ‰? How many replicates was this based on? Please clarify.

Response: Yes. The standard deviation of carbon isotope determination for both a working standard (reagent grade histidine) and replicate samples over a two-year period of the instrument runs was better than 0.2 ‰.

Comment: Line 5. When you state your choice of sugar extraction and analysis method, please refer the reader to the later section where you justify your choice.

Respones: Accepted.

Comment: Page 2896.Line 25. 'identified using its relative retention time' Please state what the retention time was relative to (i.e. the internal standard?).

Response: We have stated that the retention time is "relative to the internal standard adonitol".

Comment: Page 2897. Line 5. Did this hydrolysis use the same conditions as described previously? Please state.

Response: Yes. The hydrolysis conditions used here are the same as described in section 2.4.1. We have added this information in the revised MS.

Comment: Line 14. Do you mean that you checked your C/N and isotopic procedure by analyzing Pacific samples for which you already knew these values? It is not clear from this section exactly what you did. It is also not clear why you consider it important that the Pacific samples had a $\delta^{13}C$ close to marine OM and a C/N ration in line with Redfield. Please clarify.

Response: Yes. Pacific samples were used as our working reference material for quality control on a daily basis during the sample preparation and analysis because the Pacific sediments have been reported to have very uniform C/N ratios and organic carbon isotopic composition, identical to the typical values of marine phytoplankton (e.g., Goering et al., 1990).

Comment: Line 24. Is this a RSD of sugar concentrations or of spike recovery? Please clarify, and if the latter, please add the former.

Response: This RSD is for spike recovery. We have added the RSD for the sugars analysis in the revised MS.

Comment: Lines 16-20. This information belongs in the results section.

Response: Taken.

Comment: Page 2898. Line 25. I would suggest that the difference between the two hydrolysis techniques is likely to be largest where there is the largest amount of cellulose present, i.e. where terrestrial OM is most dominant. I therefore think that the authors should re-do this comparison using three samples, covering the full upstream-downstream range of the study. I feel that this is the only way to justify the hydrolysis methods used, and this to show that the aldose data are of good quality.

Response: The reviewer brought up a right issue. We agreed that TFA hydrolysis might give significant lower yields of glucose if the sample contain large amount of α-cellulose. Given that TFA hydrolysis has been compared with concentrated sulfuric acid hydrolysis in hydrolyzing refractory carbohydrate (containing a large amount of α-cellulose) in soil samples (Amelung et al., 1996), as well as hydrolyzing labile carbohydrate in marine dissolved organic matter (Aluwihare et al., 1997), we only compared these two hydrolysis methods using an inner-shelf sample (from station S7-1) for the purpose of confirmation. Our own results have shown consistent outcomes with prior researches, i.e., TFA hydrolysis gives comparable or higher yields of all sugars except for glucose. As such, we are confident that our hydrolysis method using TFA was in order. Given the potential uncertainty of our glucose data, we excluded glucose in attempting to characterize the sources and diagenesis of organic matter. This statement has been added in the revised MS.

Comment: Page 2899. I suggest that this section should be called 'Results and interpretation' References to Table 1 are required at several points through this page.

Response: Although we agree that this section can also be called 'Results and interpretation', we would keep the typical journal style as it is.

Comment: Lines 10-15. It is not clear what information is gained by producing a regression of TN against TOC, apart from an averaged C/N ratio. I suggest that instead the C/N ratio for each sample should be calculated, and then plotted on a colour-coded map. This will highlight changes in C/N, and this in OM source, across the study site.

Response: The linear regression showed that TOC and TN in the sediments collected from the upper reach of the estuary were highly correlated, indicating a same origin of TOC and TN. The intercept of the regression line was ~ 0, suggesting that most of the nitrogen measured by our method was related to sedimentary organic carbon and probably in the organic form (Hedges et al., 1986). The slope of the regression line indicated a best-fit atomic C/N ratio of 12.7, consist with the C/N ratio of the soil TOC (8-14), suggesting that most of the TOC in the upper reach of the Pearl River Estuary was attributable to soil derived organic matter. We added this statement in the revised MS.
We accepted the suggestion and plotted the C/N ratio of sediments collected from Lingdingyang Bay and SCS shelf on a colour-coded map in revised MS.

Comment: Line 24. What would the $\delta^{13}C$ of sewage input have been, and why do you think that it did not have a measurable influence? Please also state the evidence/reasoning on which you base your conclusion that selected degradation is responsible for the dominant presence of terrestrial OM in the sediments.

Response: $\delta^{13}C$ in three sewage POM samples we took in 2008 from the upper reach of the Pearl River estuary were -24.42 ± 2.16‰. This organic carbon isotopic composition did not show significant difference from the sediments collected in the upper reach of the estuary with a $\delta^{13}C$ value of 24.91±0.94. However, the sewage samples had significantly different C/N ratios (6.1 ± 0.4) from those in the sediment (14.4±3.5). Difference was also obvious when comparing the sewage and planktonic material. The latter has a much negative isotopic composition (-31.23‰ to -25.83‰) as compared to the sewage although the C/N ratios (6.5 to 8.4) of the planktonic material were not much different from the sewage material. Taken together, the preserved sedimentary OM we observed in the upper reach did not show significant contribution from sewage discharge or on site biomass. In contrast in the water column, sources characterization of

suspended POM in the upper reach showed a significant contribution from phytoplankton biomass and sewage (our unpublished data). This portion of POM therefore must have been degraded in the water column or in the early stage of the sedimentation.

Considering the reviewer's suggestion, we have added our data of $\delta^{13}C$ and C/N ratios in the sewage samples and have revised the MS accordingly.

Comment: Lines 26-27. Please provide references for the high Chl-a and low oxygen concentrations which you mention. Also state whether they exist in the water column or in the sediment.

Response: We have added a reference (He et al., 2010) in the revised MS. Note that oxygen depletion and high Chl-a co-existed in the water column.

Comment: Page 2900. Line 1. Please explain why the presence of Chl-a and an oxygen depletion should lead to/imply a rapid removal of labile OM. I would have thought that the opposite would apply, and that these features would suggest enhanced preservation of labile OM (such as Chl-a) in low oxygen conditions.

Response: High Chl-a (>20 μg L^{-1}) in water column indicated a significant biomass contribution to POM, while oxygen depletion in this well mixed area suggested high rates of organic matter respiration (Dai et al., 2006). At the same time, our results did not show that sediment organic matter contained significant phytoplankton signals (see above response). It is therefore suggestible that labile OM derived from phytoplankton should have been degraded in the water column and/or at the sediment-water interface.

Comment: Line 19. Please give examples of the TNS yield values found in previous studies, rather than just stating that your values are in line with previous studies.

Response: We have provided examples in the revised MS.

Comment: Line 20. Please add a figure giving a graphical representation of the average sugar composition of different types of sample. The information is very difficult to assimilate when it is only given in the text.

Response: We have added a figure (Fig. 5 in the revised MS) to show the spatial distribution of neutral sugar composition. We also calculated the average sugar composition in two different zones (Table 3).

Comment: Line 22. From 'As compared to plant: : :' onward, this is discussion type material, and it could therefore be moved.

Response: Accepted. We have put this paragraph to the *Discussion* section in the revised MS.

Comment: Page 2901. Section 3.3 and onwards. I suggest that the following sections be re-structured, so that there is no separation of riverine and estuarine sediments. I would describe the bulk characteristics for all samples, then move onto the carbohydrates for all samples. This will facilitate an understanding of how things change in a continuous way from the river out to the shelf. Any division of the system into sections is slightly arbitrary, and stand in the way of a whole-system understanding.

Response: We accepted the reviewer's suggestion and re-structured these sections in the revised MS.

Comment: Line 15. Please state which 7 stations are being described here.

Response: We added information.

Comment: Line 25. 'A probable reason which may explain this difference: : :' The difference highlighted here is not surprising, and I don't think that comparing the bulk carbohydrates and GC methods is sensible or useful. It is sufficient simply to state that they give different values, and to state the well-established reasons for that. I am not convinced that there are any conclusions to be drawn from the difference between methods, as they are not considered comparable.

Response: We accepted the suggestion and have substantially shortened the related texts.

Comment: Page 2902.Line 13. Please place this description of the weight percentage monosaccharide composition much earlier in the section, and include in a figure as suggested earlier.

Response: Accepted.

Comment: Page 2903. Line 15. Please justify why sediments from the northwest Pacific were used to represent the marine end-member. For example, how do you know that they were purely marine? How can you show that the Pacific sediments were in any way relevant to your site, given that they were probably generated by different phytoplankton communities, sinking depths, water masses and water column chemistry? Local phytoplankton should have been used for this purpose, and I think it is highly questionable whether sedimentary organic matter from another site entirely is a valid candidate for defining the marine end-member.

Response: We have taken the suggestion and used local net phytoplankton from the northern South China Sea as the marine end-member and revised the MS accordingly.

Comment: Line 19. Here you need to be able to refer to maps of C/N and $\delta^{13}C$ of your study site.

Response: Accepted.

Comment: Line 28. Please state in detail what Zhang et al found, so that the reader can see for themselves whether your results are consistent with theirs.

Response: We added the results of Zhang et al. (2009) in the revised MS.

Comment: Page 2904. Line 1. I don't see why it would be expected that the Pearl River Estuary and the Amazon delta would be in any way similar. I think you need to explain why they might show similar proportions of terrestrial OM in their sediments, and perhaps make more of the fact that they do (i.e. does this make your results applicable on a regional or global scale?).

Response: We did not intend to draw a general conclusion per the proportions of terrestrial OM in their sediments and thus we deleted the sentence that may have misled.

Comment: Line 10. Sentence starting ‘So carbohydrate composition: : :’ Please explain the reasoning behind and justify this statement. I would have though that the opposite were true. If there are reactive and un-reactive fractions of OM then the carbohydrate composition would depend on degradation state (i.e. which of those fractions is still present).
Amazon

Response: Carbohydrates are classified into storage and structural polymers. The former is typically very labile, and they could even be removed completely in the water column. Therefore it is very likely that only the refractory structural carbohydrate was buried in sediments. Having said so, the left over carbohydrates should be able to be buried in the sediments and their composition would depend on the degradation state. We have modified the text according to this comment from the reviewer.

Comment: Line 18. Please state in the text which samples/sites were put into each group.

Response: Accepted.

Comment: Line 23. You should not use the term ‘very significant’ when describing the results of a statistical test. The test simply tells you whether a trend is significant or not. The reader can make any further judgments of their own based on the P value.

Response: These are statistical terms for t-test. $P<0.1$ means not significant, $P<0.05$ means significant, and $P<0.01$ means very significant. Nevertheless, we took the advice of the reviewer and have modified the text.

Comment: Line 26. Sentence starting ‘Our results support: : :’ This is not a very new or interesting conclusion and need not be included. You should concentrate on highlighting the new conclusions that your data support.

Response: Accepted.

Comment: Page 2905. Lines 1-7. This section essentially says that galactose may come from almost anywhere. I would suggest that if this section is to be useful you should use it to state where you think the galactose is from and why.

Response: We have taken the suggestion. This section has been modified as “Considering GAL was elevated in the inner shelf (stations S7 and S6A-1) where primary productivity was much higher (3000 - 4300 mg C m^{-2} d^{-1}) as compared to that of the Pearl River Estuary (<100 mg C m^{-2} d^{-1}) (Yin et al., 2004). Phytoplankton seemed to be the main source of this monosaccharide.”

Comment: Line 7. The sentence starting ‘The mixed sources: : :’ appears only to say that the sediments have been analysed for other biochemical classes, which is not a particularly relevant thing to say here. Perhaps you could include more detail of the findings of the studies you reference, and state how they match with your findings.

Response: We have deleted this sentence.

Comment: Line 11. It would be helpful to know what the trend was from estuary out onto the shelf.

Response: We have shown the pattern of these sugars in the revised MS.

Comment: Line 11. ‘Such high: : :’, to ‘outer shelf sediments’ on line 17. Having given all this information, please clarify exactly what conclusion it leads you to in relation to your own data.

Response: This section has been re-written following the suggestions of the reviewer.

Comment: Line 29. Please state the concentrations found and the field areas studied in the previous studies which you reference.

Response: Accepted. We have given the detail information which we referred to.

Comment: Page 2906.Line 5. You also need to discuss whether this difference between your study and others could have been due to different hydrolysis methods.

Response: We have justified the influence of different hydrolysis methods on the carbohydrate compositions in the revised MS.

Comment: Line 10. Why does station 8-1 have the highest percentage of ara and xyl? What does it mean, and what point are you trying to make here? Be careful to spell out all your conclusions for the reader. If you just supply them with the evidence and expect them to work out the conclusion for themselves they may get it wrong!

Response: The highest percentage abundance of ARA and XYL at station E8-1 was likely due to the high contribution of terrestrial organic matter input to this area. It might also be caused by the selective degradation of hexose leading to the elevation of the remnant sugar abundance. Considering the reviewer’s comments, we have revised the manuscript. We have discussed the carbohydrate composition at this area in a more detailed fashion along with the data of C/N and $\delta^{13}C$ to support the conclusion from the sugar data.

Comment: Line 26. Do you mean extracellular polysaccharides here? It would help avoid confusion if you use the more standard term.

Respose: Accoding to Aluwihare et al. (1997), Man is enriched in the high molecular weight fraction of the dissolve organic matter derived from marine diatom incubations. We have rephrased the sentence for clarity.

Comment: Page 2907. Line 6. ‘We excluded GLU: : :’ Excluded glucose from what? Why mention it if it has been excluded? In any case, the variation in response to environmental conditions and diagenetic status which you use to exclude glucose is the very thing you are studying; therefore it seems sensible not to exclude it.

Response: We only excluded the GLU data from the hexoses/deoxysugar ratio (GAL+MAN+GLU/FUC+RHA), an indicator to distinguish fresh/labile and refractory organic matter, because our TFA hydrolysis could have potentially underestimated the GLU as mentioned in the above response. Moreover, a fraction of GLU such as storage polymers is extremely labile and thus is subject to dynamic changes in the environment. Therefore, we used GAL+MAN/FUC+RHA, instead of GAL+MAN+GLU/FUC+RHA as the indicator to characterize the diagenesis of organic matter.

Comment: Line 8. This ratio should be plotted in a figure, not just included in a table.

Response: Accepted. We have plotted the ratios of GAL+MAN/FUC+RHA in our new Fig. 9 in the revised MS.

Comment: Line 12. What were the galactose and mannose trends at the rest of the stations? If you have this data plotted it makes it easier to justify focusing in on interesting trends/stations.

Response: Galactose tended to increase seaward, and mannose showed almost uniform distribution at the rest stations. We have added carbohydrate composition plot as suggested before, and revised the MS accordingly.

Comment: Line 13. ‘: : :might be associated with the selective degradation of these two monosaccharides.’ You need to elaborate on this point. What are the implications for sediment supply and decay dynamics? Where is there more or less decay, and which type of OM (terrestrial or marine) is decaying?

Response: We have taken the suggestion and have rewritten this section in the revised MS.

Comment: Line 16. Please explain more fully what you mean by ‘structural features’.

Response: ‘Structural features’ means “the molecular structure of sugar”.

Comment: Line 21. ‘The sources of this highly degraded organic matter were unclear’. Surely you can suggest something based on your C/N, isotopes and sugars?

Response: We have further discussed the sources of this highly degraded organic matter based on C/N ratios, $\delta^{13}C$ and sugar composition.

Comment: Line 24. You need to supply evidence and reasoning to support the suggestion that some OM is coming from Disneyland.

Response: First of all, we did not mean to suggest that the OM was from Disneyland. The highly degraded terrestrial organic matter observed at station E8-1 near Dayushan Island might come from the erosion of the deeper (“old”) sediment from Dayushan Island due to the especially rapid development of this area at the end of the last century, including construction of Hong Kong International Airport and Tsing Ma Bridge as well as the Hong Kong Disneyland. We have modified the text to try to minimize potential confusions.

Comment: Page 2908. Line 1. ‘leading to coarse suspended accumulation: : :’. Please clarify this statement, do you mean that there is deposition of coarse sediment in this area?

Yes, only the coarse sediment is deposited in this area due to the relatively strong currents in the east part of the estuary.

Comment: Line 5. I suggest that figure 5 adds little. You can delete it and simply describe the useful features in the text.

Response: We believe that Fig. 5 is useful to understand the carbohydrate composition reflected in both TrOC rich and TrOC poor sediments and thus we have kept it (re-arranged as Fig. 7) in the revised MS.

Comment: Line 9 and below. You imply here that there is ^{210}Pb data presented in this paper, which there isn't (nothing about it in the methods, no table or figure of data). Please give the correct reference to this data.

Response: We have provided references to the sedimentation rates we adopted.

Comment: Equation 4. Presumably this is applied separately to each site. Please clarify. Why do you calculate this parameter? It does not seem to be used anywhere else in the manuscript. Consider excluding, or clarify why the calculation is useful.

Response: Equation 4 was used to calculate sediment accumulation flux. As compared to the sediment inputs from the river we can calculate the sediment accumulation efficiency. This is an important data set to justify organic matter dynamics in the estuary.

Comment: Lines 18 and 19. Please give units for all terms.

Response: Accepted.

Comment: Equation 6. I'm not qualified to check whether this is correct. However, I can say that it is not clear why this calculation was done, and that needs explaining. I suggest that it be excluded, as results from it do not seem to be used elsewhere in the manuscript.

Response: Equation 6 is an error propagation formula. We accepted the suggestion and have deleted the equation because it is commonly used in any error propagation calculation.

Comment: Page 2909 Line 1. How did you calculate the average that you mention? I presume that it was spatially weighted. You need to acknowledge that this is an extremely approximate calculation, and consider whether it really has any use.

Response: Yes, it was the spatially weighted average.
We are aware that this is a first order estimate. However, we believe that such estimation provides valuable information to help understanding terrestrial organic matter accumulation and cycling in the estuarine and continental shelf. The uncertainties of this calculation have been justified in the revised MS.

Comment: Line 4. When you refer to an average for Lindinyang Bay, please list which stations are considered to be in that sub-region of your study area.

Response: Stations E7A, E8-1, E8-2, E12, E14, E18, E15, E21, E30, and E29 were in Lindingyang Bay. The sub-regions and their corresponding stations were shown in Table 1 in the revised MS.

Comment: Line 7. I don't see the use of the bulk sediment accumulation rate that you give. It is based on data that is not presented here, and it does not illuminate organic matter dynamics, therefore it should not be presented as a result of this study, which is how it looks at the moment.

Response: Our intention to present the bulk sediment accumulation rate was to examine the accumulation efficiency of organic matter in the study area. Based on the bulk sediment accumulation rate, we calculated that the bulk sediment accumulation efficiency was ~70% in Lingdingyang Bay, which was significantly higher than TrOC accumulation efficiency in the same area. This indicates that TrOC had undergone significant degradation or transformation.

However, we are aware that such estimation is again subject to uncertainties, which have been clearly stated in the revised MS.

Comment: Line 8. Be very careful about what you mean by organic matter accumulation. You seem to be assuming that all of the OM present in the surface sediment which you measured remains in the sediment over time. This is very unlikely to be the case, and most of it (up to 90%) will decay in the sediment over time. Therefore you cannot say that all this OM is being buried in the sediment in the long term.

Response: We appreciate that organic matter can be further decayed in the sediment in a longer time scale. We used "the relative accumulation" instead of "burial" in the revised MS to avoid misunderstanding.

Comment: Line 12. You mention the flood season. When is that? This detail needs to be included in the methods section. You also need to discuss the implications of the seasonal event on the fact that you sampled in a number of different seasons.

Response: Two flood seasons were August, 2001 and August, 2008.
We presented particle organic content (%POC) from the lower Pearl River sampled in four seasons (1.09 ± 0.29% in summer, 2.19 ± 0.12% in spring, 2.00 ± 0.46% in autumn, and 4.69 ± 1.51% in winter (our unpublished data)), and we used %POC of 1.09 ± 0.29% as the low limit to estimate TrOC input to Lingdingyang Bay in the revised MS. We are aware that the suspended particulate substances tend to contain higher %POC in the dry season in the Pearl River. Percentage of POC based on flood seasons might only result a slightly underestimation of TrOC inputs to the bay. We have discussed this uncertainty in the revised MS.

Comment: Line 27. What do you mean by replacement? Please clarify.

Response: We replaced the word "replacement" by "transformation" in the revised MS.

Comment: Table 1. I suggest that most of this data should also be presented in graphical form.

Response: Accepted. Also please see the response above.

Comment: Table 2. I would prefer this data to be presented as a bar graph with error bars, allowing an easier visual assessment of whether the two hydrolysis techniques were comparable or not. In addition, weight percentages should be compared as well as absolute concentrations.

Response: We have now presented the data as a bar graph with error bars. We also compared the weight percentage data.

Comment: Table 3. The key to the different sugar abbreviations should be in the caption to Table 2. I suggest plotting the data in this table as well.

Response: Accepted.

Comment: Figure 1. This needs to be bigger and clearer, with clear labelling of which sites are concluded in the different sub-sets such as inner shelf, outer shelf, river and estuary.

Response: We have modified this figure.

Comment: Figure 7. I don't think this plot should be included, as it presents data that was not part of this study (not included in methods). If it stays it should be made into a colour coded contour map.

Response: Accepted. We have deleted this figure.

References:

Aluwihare, L.I., Repeta, D.J. and Chen, R.F., 1997. A major biopolymeric component to dissolved organic carbon in surface sea water. Nature, 387(6629): 166-169.

Amelung, W., Cheshire, M.V. and Guggenberger, G., 1996. Determination of neutral and acidic sugars in soil by capillary gas-liquid chromatography after trifluoroacetic acid hydrolysis. Soil Biology and Biochemistry, 28(12): 1631-1639.

Bernardes, M.C. et al., 2004. Riverine Organic Matter Composition as a Function of Land Use Changes, Southwest Amazon. Ecological Applications, Supplement, 14(4): S263-S279.

Berner, R.A., 1982. Burial of organic carbon and pyrite sulfur in the modern ocean: its geochemical and environmental significance. American Journal of Science, 282: 451-473.

Boschker, H.T.S., Dekkers, R.P. and Cappenberg, T.E., 1995. Sources of organic carbon in the littoral of lake Gooimeer as indicated by stable carbon isotope and carbohydrate composition. Biogeochemistry, 29: 89-105.

Dai, M. et al., 2006. Oxygen depletion in the upper reach of the Pearl River Estuary during a winter drought. Marine Chemistry, 102(1-2): 159-169.

de Haas, H., van Weering, T.C.E. and de Stigter, H., 2002. Organic carbon in shelf seas: sinks or sources, processes, and products. Continental Shelf Research, 22: 691-717.

Goering, J., Alexander, V. and Haubenstock, N., 1990. Seasonal variability of stable carbon and nitrogen isotope ratios of organisms in a North Pacific bay. Estuarine Coastal And Shelf Science, 30(3): 239-260.

Goni, M.A., Ruttenberg, K.C. and Eglinton, T.I., 1997. Sources and contribution of terrigenous organic carbon to surface sediments in the Gulf of Mexico. Nature, 389: 275-278.

Goni, M.A., Ruttenberg, K.C. and Eglinton, T.I., 1998. A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico. Geochimica et Cosmochimica Acta, 62(18): 3055-3075.

Gordon, E.S. and Goni, M.A., 2003. Sources and distribution of terrigenous organic matter delivered by the Atchafalaya River to sediments in the northern Gulf of Mexico. Geochimica et Cosmochimica Acta, 67: 2359-2375.

Gordon, E.S. and Goni, M.A., 2004. Controls on the distribution and accumulation of terrigenous organic matter in sediments from the Mississippi and Atchafalaya river margin. Marine Chemistry, 92(1-4): 331-352.

He, B. et al., 2010. Distribution, degradation and dynamics of dissolved organic carbon and its major compound classes in the Pearl River estuary, China. Marine Chemistry, 119: 52-64.

Hedges, J.I. et al., 1986. Compositions and Fluxes of Particulate Organic Material in the Amazon River. Limnology and Oceanography, 31(4): 717-738.

Hedges, J.I. et al., 1994. Origins and processing of organic matter in the Amazon River as Indicated by carbohydrates and amino acids. Limnology and Oceanography, 39(4): 743-761.

Hedges, J.I. and Parker, P.L., 1976. Land-derived organic matter in surface sediments from the Gulf of Mexico. Geochimica et Cosmochimca Acta, 40: 1019-1029.

Hu, J., Peng, P., Jia, G., Mai, B. and Zhang, G., 2006. Distribution and sources of organic carbon, nitrogen and their isotopes in sediments of the subtropical Pearl River estuary and adjacent shelf, Southern China. Marine Chemistry, 98(2-4): 274-285.

Kuwae, M. et al., 2007. Spatial distribution of organic and sulfur geochemical parameters of oxic to anoxic surface sediments in Beppu Bay in southwest Japan. Coastal and Shelf Science, 72(1-2): 348-358.

Marchand, C., Disnar, J.R., Lallier-Verges, E. and Lottier, N., 2005. Early diagenesis of carbohydrates and lignin in mangrove sediments subject to variable redox conditions (French Guiana). Geochimica et Cosmochimica Acta, 69(1): 131-142.

Prahl, F.G., Ertel, J.R., Goni, M.A., Sparrow, M.A. and Eversmeyer, B., 1994. Terrestrial organic carbon

contributions to sediments on the Washington margin. Geochimica et Cosmochimica Acta, 58: 3035-3035.
Ramaswamy, V. et al., 2008. Distribution and sources of organic carbon, nitrogen and their isotopic signatures in sediments from the Ayeyarwady (Irrawaddy) continental shelf, northern Andaman Sea. Marine Chemistry, 111(3-4): 137-150.
Yin, K.D., Lin, Z.F. and Ke, Z.Y., 2004. Temporal and spatial distribution of dissolved oxygen in the Pearl River Estuary and adjacent coastal waters. Continental Shelf Research, 24(16): 1935-1948.
Zhang, L. et al., 2009. The sources and accumulation rate of sedimentary organic matter in the Pearl River Estuary and adjacent coastal area, Southern China. Estuarine, Coastal and Shelf Science, 85(2): 190-196.