

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.

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Response to Referee #2

General comment: The topic of this study fits the journal but the general conclusions are not new.

Response: In this study, we used a combination of bulk organic geochemical parameters (C/N ratio and $\delta^{13}\text{C}$) with carbohydrate biomarkers to define the organic matter source and to examine the transferring of TrOC in a highly dynamics estuarine system. 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 the 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 $\delta^{13}\text{C}$ which tends to deposit in the estuary and delta areas and the other one is characterized by highly degraded soil-derived material with higher $\delta^{13}\text{C}$ which can be transported farther off shore. As such, using end-members only with land plant $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$) 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 matter. 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 comment: Their two end-member model oversimplified OM cycle in a complicated environmental system.

Response: We agree that our model calculation is a first order estimation, which is subject to simplicity and uncertainties. Yet we believe that such estimation provides useful information to help understanding the system in terms of the terrestrial organic carbon contribution to the sediment. Moreover, the modeled mixing curves overall agreed well with the observations although we used a two end-member mixing model (Fig. 6 in the revised MS). We also noted that two end-member mixing model of this kind has been successfully applied in many river dominated estuaries such as Amazon river and estuary (Cai et al., 1988), Gulf of Mexico (Hedges and Parker, 1976) and the margin off Washington (Prahl et al., 1994) to characterize relative contributions of organic carbon from the terrestrial and marine sources.

Considering the complicated sources of the Pearl River estuary system, we chose surface sediments collected from the upper reach (fresh water part) of the estuary as the riverine end-member, which might represent the relatively long term compositional average of the potential riverine input (referred to as terrestrial organic matter, TrOC) to the ocean.

General comment: Some assumptions in the model have not been reasonably validated. For example, they assume that OM in the upper reach sediments is dominantly soil-derived. In fact, at station R01, OM from sewage source is much more important. If this is a true case, the data at station R01 should not be included to calculate mean parameters for the end-member. Second, they assume that all degradation of OM occurs before particle settling. In a shallow and dynamic environment, a lot of labile organic matter can sink to sediments and degraded in the sediments. Measurements of reactive organic compounds such as Chl-a for sediment samples can prove this point.

Response: We thank the comment from the reviewer and agree that sediments from R01 may be influenced by sewage. However, our $\delta^{13}\text{C}$ and C/N ratio of sediments ($-24.92 \pm 1.0\%$, 13.3 ± 1.4) collected from the upper reach was overall consistent well with that from the river bank soil ($24.1 \pm 1.0\%$, 12.5 ± 2.3 ; Yu et al., 2010), indicating that OM accumulated in this area was dominated by soil-derived material. We also agree that OM can be further decayed in sediments, and therefore we have revised our description in order to avoid misunderstanding. Considering the reviewer's suggestion, we have excluded the station R01 from the river end-member.

General comment: This study used carbohydrate compositions and specific indexes to assist identification of OM sources and microbial processes. However, both compositions and indexes seemed not to be exclusive: working for some samples but not for other samples. It may be helpful to set a new table to provide the meanings of these indexes and citation.

Response: We are not 100% sure about the issues the reviewer is referring to. We believe that our study does not have cases of significant discrepancy when using different carbohydrate compositions or specific indices, or between elemental composition/ stable isotopic composition

and carbohydrate composition. For example, the highest percentage abundance of ARA was observed at station E8-1 indicating that the dominant contribution of terrestrial carbohydrate. The highest GLU/RIB ratio and the lowest % (RIB + FUC) at this station also suggested that carbohydrate in this area was dominantly terrestrial sourced. This conclusion deduced from carbohydrate composition agrees well with the organic source derived from the bulk property of $\delta^{13}\text{C}$ and C/N ratios at this station. In contrast, the lowest percentage abundance of ARA was observed at station S5 in the outer shelf indicating that the carbohydrate at this station was dominantly marine sourced. Although this station did not contain the highest percentage of FUC, the lowest GLU/RIB ratio suggested that the carbohydrate was dominated by marine sources. Such a conclusion was further supported by the enrichment of $\delta^{13}\text{C}$ and the lower C/N ratio. Nevertheless, we have added a new table (Table 1 in the revised MS) with a summary of the carbohydrate composition and the relative abundance of neutral sugar being used as indicators of organic matter sources and diagenetic states.

General comment: This study also used an average sedimentation rate and entire surface area of the Lingdingyang Bay to calculate accumulation rates of sediments and sedimentary OM by assuming homogeneous settling process. Actually, export of POM from the river to the bay is very season-dependent and sedimentation rates varied largely (from 0.4 to 9.1 cm/yr at different sites) in the bay. It may be better to estimate a range of flux based on low and high parameters and discuss the potential causes for the variations.

Response: We used the spatially weighted average accumulation rate rather than assuming homogenous settling processes to calculate the accumulation flux. We agree that the sedimentation rate may largely vary depending upon the hydrodynamics of sedimentation environment. Considering that the sedimentation rate had a relatively narrow range of 0.4-3.8 cm yr⁻¹ with the exception of 9.1 cm yr⁻¹ confined to a very small area, we reasoned that the surface area weighted average accumulation rate should be reasonable.

Specific comment: P2890-L4-5: “stable carbon isotopic ($\delta^{13}\text{C}$)” should be “bulk stable isotopic ($\delta^{13}\text{C}$ TOC)” while “molecular-level analyses” should be more specific like “carbohydrate composition analyses”.

Response: Accepted. We have specified the expression

Specific comment: P2890-L5-7: Since TOC in station R01 sediment (4% higher than those in other sites) contains a large fraction (>70%) of OM from anthropogenic input (with a much higher C/N ratio), it should not be included to estimate average end-member parameters in the upper reach. On the other hand, data at R01 may be used to estimate parameters of anthropogenic OM end member if the natural terrestrial OM end member parameters are known from data in the upper reach stations.

Response: The reviewer is right. $\delta^{13}\text{C}$ in three sewage POM samples we took in 2008 from the upper reach of the Pearl River estuary were $-24.42 \pm 2.16\text{‰}$. This bulk organic carbon isotope composition did not show significant difference from the sediment at station R01 with a $\delta^{13}\text{C}$ value of -24.89‰ . However, the sewage samples had significantly different C/N ratios (6.1 ± 0.4) from the sediment at R01 (C/N=22.4). So the high percentage (4%) of organic carbon content at station R01 may not be simply attributable to anthropogenic inputs. Anyway, we have excluded R01 from the river end-member as the reviewer suggested.

Specific comment: P2890-L11-14: TCHO varied in a small range while TOC varied in a large

rage in the estuarine and shelf sediments, so TCHO did not follow TOC.

Response: The yields of TCHO presented in our paper are the organic carbon normalized yields rather than absolute values.

Specific comment: P2890-L14-18: What does mean if a significant amount of carbohydrates were not neutral aldoses? Actually, TSN/TCHO ratios in these samples varied from 18% to 80%, which implies different microbial activities at different sites?

Response: A probable reason is that carbohydrates determined by the PSA method (TCHO) include neutral monosaccharides and their methyl derivatives including uronic acids (Dubois et al., 1956). Moreover, the differences may also be due to structural changes of individual aldoses incorporated into refractory DOC molecules that can still be characterized by the PAS method but not by the GC method (Khodse et al., 2008). Therefore, TSN/TCHO ratios may imply that OM has undergone different transformation processes.

Specific comment: P2890-L21-26: The first sentence should be deleted because it repeats the following sentence.

Response: Accepted.

Specific comment: P2891-L3: “burial efficiency of OM” generally refers the ratio between the flux at the sediment interface ($x = 0$) and the downward flux into non-diagenetic zone (deep sediment). In this paper, it just compares the relative fluxes of total particles and OM into the surface sediment. Thus, it may be more appropriate to use “flux ratio” or “relative accumulation rates” between particles and OM.

Response: We changed “burial efficiency of OM” to “relative accumulation efficiency” in the revised MS.

Specific comment: P2891-L23: “ $\delta^{13}\text{C}$ ” should be “bulk $\delta^{13}\text{C}$ of TOC”.

Response: Accepted.

Specific comment: P2892-L5: “in polysaccharide forms” changes to “in polymer structures”.

Response: Accepted.

Specific comment: P2892-L20-22: “insights of the organic matter biogeochemical cycle” needs more specific means such as “microbial activity” and others?

Response: We have specified the statement in the revised SM.

Specific comment: P2893-L23-24: “sedimentation types” changes to “sediment types” and “the hydrodynamics of sedimentation environment” changes to “the hydrodynamics in the area”.

Response: Accepted.

Specific comment: P2893-L25: “the eastern parts” changes to “the eastern side”.

Response: Accepted.

Specific comment: P2894-L2-3: What does mean “clayed silt”? Clay and silt have different sizes.

Response: Sorry for the mistake. We replaced it by “Clayey silt”.

Specific comment: P2894-L5-15: “Surface sediment samples” What depth (0-1cm? 0-2cm? 0-5cm?) is for these surface samples? Because grab sampler will fold the sediments, how can the surface samples be collected as the box samples? More details are needed for sampling procedure.

Response: Grab samplers were used to collect surface sediments in the higher deposition rate area ($> 2 \text{ cm yr}^{-1}$). The sampling depth was ~0-10 cm, representing ~5 year’s average sedimentation. Box sampler was used to collect sediment samples in the lower deposition rate area. Samples from top 3-5 cm, representing ~5 year’s average sedimentation, were used as surface samples. We have added this information in the revised MS.

Specific comment: P2894-L24: “The CO₂ was purified” How?

Response: The CO₂ was purified by cryogenic traps in a vacuum line and collected in sealed 6-mm glass tubes. We have added this information in the revised MS.

Specific comment: P2896-L24-25: Was identification made by comparing peak retention times of samples and the standard mixture?

Response: Monosaccharide was identified by comparing peak relative retention time (relative to internal standard adonitol) of the samples with that of the standard mixture.

Specific comment: P2899-L8-12: If TOC and TN (from anthropogenic input) at station R01 sediment were not correlated as equation (1), why the C/N ratio was used to estimate an average parameter of end member for TrOM in the upper reach (as in Table 1)?

Response: R01 has been excluded from the river end-member in the revised MS.

Specific comment: P2899-L13-21: It needs to be clarified what difference between “soil derived OM” and “OM derived from land plants and undergone extensive biotransformation and/or biodegradation before deposition”. What does mean “organic matter demineralization”?

Response: Sorry for the confusion. We meant that soil OM was ultimately derived from land plants and have undergone extensive biotransformation and/or biodegradation. We have revised our description for clarity. Note that “demineralization” should be “remineralization”, which we have corrected in the revised MS.

Specific comment: P2899-L21-P2900-L6: The argument here is conflicting: high Chl-a concentration (in surface sediments?) coupled with permanent oxygen depletion does not support selected degradation of autochthonous OM. $\delta^{13}\text{C}$ of phytoplankton varies with season and a large deposit of phytoplankton generally occurs after bloom. If sewage-derived POM (C/N > 20) and planktonic deposit (C/N=7) are all significant, the C/N ratio in the sediments can be balanced to the measured values. More evidence (e.g., biomarkers and compound-specific isotopic compositions) is needed to clarify this point.

Response: High Chl-a ($>20 \mu\text{g L}^{-1}$) in water column indicated significant biomass contribution to

SPOM. Oxygen depletion in this well mixed area suggested high organic matter respiration (Dai et al., 2006). The C/N ratios of three sewage POM samples we took in 2008 from the upper reach of the Pearl River estuary was 6.1 ± 0.4 . The C/N ratio of the planktonic material collected from the upper reach of the Pearl River Estuary was 6.5-8.5. Therefore the mixture of sewage POM with planktonic material could not give the value of the C/N ratios of 13.3 ± 1.4 in the sediments. The preserved sediments OM we observed in the upper reach did not have shown significant contribution from planktonic POM or sewage POM. This portion of POM therefore must have been degraded in the water column or in the early stage of the sedimentation.

In addition, our incubation experiments showed that the highest bacterial respiration rate was $5.8 \mu\text{mol O}_2 \text{ L}^{-1} \text{ h}^{-1}$ (He et al., 2010), and the POC consumption rate was $1.7 \mu\text{mol C L}^{-1} \text{ h}^{-1}$ in water column (our unpublished data), strongly suggesting that OM was undergone significant degradation in this area. We have modified our description and added this information.

We fully agreed that $\delta^{13}\text{C}$ of phytoplankton may vary with seasons and a large deposit of phytoplankton generally occurs after bloom. However, in the upper reach of the Pearl River Estuary, high Chl-a occurred year-round, and either $\delta^{13}\text{C}$ or C/N has shown substantial seasonal variations based on our observations.

We have added the above justification in the revised MS.

Specific comment: P2900-L19-P2901-L4: Higher % of FUC in the sediment samples did not rule out the potential OM input from phytoplankton. Relatively higher ratios of (FUC+RHA)/(ARA+XYL) indicate strong bacterial activity, implying that OM has also extensively degraded in surface sediments but this paper assumes that degradation occurs only in water (before deposition of OM into sediments).

Response: We suggested that high % of FUC and RHA was associated with bacterial contribution, with however no exclusion of the contribution from phytoplankton. We agreed that OM may also be degraded in surface sediments. This section has been revised accordingly.

Specific comment: P2901-L17-19: Although TOC varies significantly from estuary to shelf, TCHO fractions in these sediment samples are almost constant. What is implication?

Response: TCHO presented in our paper are the organic carbon normalized yields (mg TCHO/100mg OC). Almost constant yields of TCHO indicated that TCHO was a constant fraction of TOC.

Specific comment: P2901-L22-25: The percentages of TNS in TCHO pool varied from 18 to 80 (in station 30), not 51%.

Response: The reviewer is right that the percentages of TNS in TCHO pool varied from 18 to 80%. We meant to point out that most of our measurements showed a TNS/TCHO range of 18-51%. We made this correction however in the revised MS.

Specific comment: P2902-L17-22: What are Liu et al.' modeling results and how can be compared to those from this study?

Response: What Liu et al. (2007) used was also a two end-member model as this study did.

Specific comment: P2903-L16-26: Parameters (especially C/N) for riverine OM should be corrected. Since R01 sediment receives OM from sewage source (distinctly different from other sites), the data should not be included to estimate an average value. In fact, C/N ratios in 7 upper reach stations (not R01) varied in a smaller range (13.3 ± 1.3). Therefore, all f_t (fraction of

terrestrial OM) values need to recalculate.

Response: We have excluded R01 from the river end-member. The mixing curve and the fraction of terrestrial OM (f_t) have been recalculated in the revised MS.

Specific comment: P2904-L10-12: If microbial activity is strong in surface sediments, more neutral sugars will be produced. What is the consequence for carbohydrate composition?

Response: We believe that bacteria may be an important consumer rather than a producer of neutral sugars. If microbial activity is strong in surface sediments, more neutral sugars will be consumed. The residual carbohydrate should be more refractory.

Specific comment: P2905-L1-7: Since GAL is produced by both terrestrial plant and marine phytoplankton, how can the significantly higher % in TrOC-poor sediments than in TrOC-rich sediments be explained (occurrence of phytoplankton bloom)?

Response: Phytoplankton contains more abundant GLA than terrestrial plants do.

Specific comment: P2905-L10-19: Since both ARA and XYL are abundant in terrestrial plants, why only ARA showed significantly higher % in TrOC-rich sediments (Fig. 5)? Is the correlation between ARA and GLU/RIB better than that between (ARA + XYL) and GLU/RIB?

Response: That XYL was not enhanced in the TrOC-rich sediments may be explained by the presence of a balance among various biological sources without any one being dominant. XYL is the second most abundant sugar in terrestrial plants as constituents of arabinoxylan and arabino-glucuronoxylan (Cowie and Hedges, 1984; Guggenberger et al., 1994; Ogier et al., 2001). Relatively high XYL (10-23%) was also observed in the cell lysate organic matter from phytoplankton *E. huxleyi* (Biersmith and Benner, 1998). The lack of specific signatures could also be due to the biodegradation of land-derived XYL during the transport of organic matter through the estuary. Opsahl and Benner (1999), in a study of carbohydrate composition of different degraded vascular plant tissues, demonstrated that there was a ‘selective loss’ of glucose and xylose with time. Arnosti (2000) investigated the potential hydrolysis of structurally distinct polysaccharides by extracellular enzymes in bottom water and surface sediment. He found that the hydrolysis of xylan was much higher than that of arabinogalactan. This might be the reason why ARA can be preserved better than XYL in sediments.

Note that the correlation between ARA and GLU/RIB is indeed better than that between (ARA + XYL) and GLU/RIB.

Specific comment: P2905-L29-P2906-L8: If RHA is abundant in bacteria, fungi, and phytoplankton not in terrestrial plant, then the higher proportion in the upper reach sediments suggests an extensive bacterial activity while in shelf sediments, the higher proportion may indicate both bacterial activity and phytoplankton input. Is it right?

Response: Yes. Note that RHA may not be abundant in phytoplankton (Cowie and Hedges, 1984; Biersmith and Bennerr, 1998).

Specific comment: P2906-L8-13: Although at station 8-1, carbohydrate composition (the highest % of ARA and XYL and the lowest % of RIB, MAN, FUC and GAL) and bulk property ($\delta^{13}\text{C}$ and C/N) are consistent for the dominant input of terrestrial OM, at station 5, they are inconsistent.

Response: At station 5, the lowest ARA+XYL% was coupled with the highest percentage of RIB and the lowest ratio of GLU/RIB, indicating that carbohydrate in this area was dominated by marine sources. This is also consistent with what the bulk property has suggested.

Specific comment: P2906-L22-25: If GLU and GAL are similarly abundant as cellular storage products and easily degraded, why are their distributions from estuarine to shelf sediments different (GLU – decreasing while GAL – increasing)?

Response: The reviewer is right that both GLU and GAL can be cellular storage products but they can also be cellular structure polymers. More importantly, as structural polymers, typically refractory and thus readily preserved in sediments, GLU is typically found in vascular plants, while GAL usually occurs in marine phytoplankton. Such fractionation will certainly result in their different trends in abundance from estuaries to shelf sediments.

Specific comment: P2908-L6-13: The highest sedimentation rate (9.11 cm/yr at station A3, central site of the bay) was not mentioned and what is the water depth at this site and how can this extremely high sedimentation rate occur?

Response: This high sedimentation rate was reported for a shallow area near an island, the Inner Lingding Island, a known area with highest sedimentation rates (Chen et al., 1992).

Specific comment: P2909-L24-28: No data or calculations show that accumulation efficiency of TrOC declines seaward. Low accumulation efficiency of TrOC is not only caused by degradation, but also due to a large export to shelf (preferentially compared to particles?).

Response: The Pearl River estuary is composed of three sub-estuaries, namely, Lingdingyang, Modaomen and Huangmaohai, all of which have sediment inputs into the shelf region of the South China Sea (SCS). Until now, we are unable to constrain the sediment fluxes from Modaomen or Huangmaohai and therefore we did not calculate the accumulation efficiency on the SCS shelf. Nevertheless, given that the shelf region has significantly lower sedimentary TOC and TrOC, and much lower sedimentation rates as compared to the estuary, we attributed that the low accumulation efficiency within the estuary is primarily due to degradation therein. As a matter of fact, assuming that all of the shelf sediment were from Lingdingyang Bay, a first order estimation would suggest only ~20% of the sediment from the river discharge would have been escaped from the estuary zone. Such an estimation with grand uncertainties is however not included in the MS.

Specific comment: P2910-L10-12: The TNS yields and the relative abundances did not suggest that degradation occurred only before settling.

Response: Accepted. We have modified.

Specific comment: Table 1: What are water depths at these sites? Mean parameters of samples from the upper reach should not include the data at station R01.

Response: We have added water depth information in Table 2. We have excluded R01 from the mean parameters calculation in the revised MS following the suggestion from the reviewer.

Specific comment: Table 2 is not necessary. One sentence may be enough to explain this point.

Response: The content in Table 2 has been presented in a format of a figure (our new Fig. 3) as

suggested by referee 1#.

Specific comment: Table 3: The meanings of various ratios such as (GAL+MAN)/FUC+RHA), FUC+RHA/(XYL+ARA), and GLU/RIB should be provided here.

Response: Accepted. We provided the information in the revised MS.

Specific comment: Fig. 1: It may be better to use different symbols to indicate sampling sites at different time.

Response: Accepted.

Specific comment: Fig. 2: What are meanings of numbers followed with compound names?

Response: They are sugar isomers. For example, glucose has two isomers, namely α - glucose and β -glucose. The isomer with short retention time was named as GLU1, and the other one was named as GLU2.

Specific comment: Fig. 4: The ranges of end members should be changed if the data at station R01 are not included. Where is the source for marine end-member data (published)?

Response: We have taken the suggestion and excluded the data from station R01 from the river end-member. Accordingly we have recalculated the ranges of end members. Phytoplankton collected from northern South China Sea was used as a marine end-member.

Specific comment: Fig. 5: Mark with (*) on the bars to indicate whether the differences are statistically significant.

Response: Accepted.

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