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Interactive comment on “Diagenetic alterations of amino acids and organic matter in the upper Pearl River Estuary surface sediments” by J. Zhang et al.

J. Zhang et al.

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Dear Editor:

We are submitting the revision of the manuscript, titled “Diagenetic alterations of amino acids and organic matter in the upper Pearl River Estuary surface sediments” by J. Zhang, R. Zhang, Q. Wu, N. Xu. We greatly appreciate the reviewers’ comments and suggestions about the manuscript, which indeed assist us to improve the quality of the manuscript significantly. Carefully studying the comments and suggestions, we have made an extensive revision of the manuscript. The response to the reviewer’s

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comments was summarized as follows.

Referee 1: This manuscript presents a potentially interesting study. However, I do have some concerns about the study as well as the manuscript. These are my main comments: GENERAL COMMENTS -Size fractionation: Different sediment size fractions were analyzed. I am not sure whether one can compare size fractions of sediment with those in the water column (as done in the discussion). I can imagine that physical and chemical interactions working on sediment up to 8 cm deep result in different size fractions that those in the SPM in the water column. Moreover, how does freeze drying and sonication affect these size fractions? These points should at least be addressed. On a more basic level, I wonder about the usefulness of studying different size fractions within the sediment. The rationale behind this size fractionation should at least be explained.

Response (R): Basically, the objective to study the sediment size fractionation was to separate organic matter pools with different reactivities in different sediment particle size classes, a similar idea to the “size-reactivity model” originally derived from SPM in water columns (P4, L15-17). The diagenetic indicators of OM of the three size fractions support the idea of size fractionations to separate OM with different reactivities. Major differences in the diagenetic state were observed among the three size fractions of sediment OM based on amino acid compositions (P10, L8-11; Fig. 4). In our subsequent incubation studies on the sediment size fractions, direct evidence shows that CPOM is more reactive than FPOM. Nevertheless, our results in the estuary system may not be comparable with those in the Amazon system due to the different origins and compositions of OM in the two different systems, thus we have deleted the comparison in the discussion section in the revision. The effects of freeze-drying and sonication on the yields of three size fractions are related to factors such as sediment texture. The sediments in our study area are mostly sandy in texture. Therefore, the effects of freeze-drying and sonication should be minimum (P7, L12-14).

-A whole suite of amino acids was analyzed but the manuscript only deals with the

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D-AAs. The non-DAAAs actually provide a very useful diagenetic indicator, for example in the form of a degradation index (Dauwe et al. 1999) (as indicated in the introduction). Inclusion of these data would make the manuscript more complete and thereby stronger.

R: Done (P10, L8-11; Fig. 4).

-Those data that are presented are not fully exploited. In particular the bacterial contribution to total sediment OM (based on D-AA data) can be quantified further (see comment below) and should be combined with the non-DAA data.

R: Based on D-AA data, the bacterial contribution to total sediment OM can be quantified further. However, some of the concentrations of D-AAAs in the three sediment fractions were below the detection limits in our study (Table 4). We only presented the concentrations of total D-AAAs (sum of the four D-AAAs) (Table 4; Fig. 6) and the averages of each specific D-AA in the three fractions (Fig. 7). We did not calculate D/(D+L) values because of the large variation of the data. Overall, we just discussed the qualitative estimate of bacterial contribution to the total sediment OM.

-The discussion is rather descriptive and the main findings and conclusion are not (or only loosely) derived from data presented in this manuscript. Related to the previous: The discussion and conclusions appear to rely quite strongly on findings by others. In particular data from previous studies in the studied system (section 4.1, page 3332) and findings and conclusions from other studies (in particular Tremblay and Benner 2009).

R: We have revised the discussion section to make the main findings and conclusion be closely related to the data presented in this manuscript (P11-15).

-Referencing to other studies is rather focused on studies by Benner and co-workers (e.g. Tremblay and Benner 2009, Davis et al. 2009) that primarily focus on dissolved organic matter in the water column. These studies are certainly relevant but given that

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the present study concerns total organic matter in sediment, there should be more attention to studies on (D-)amino acid diagenesis in sediments (for example: Keil et al. 2000, Grutters 2002, Lomstein et al. 2006/2009, Vandewiele et al. 2009).

R: Based on the suggestion of the reviewer, we have revised the discussion section accordingly in the revised MS (P12, L14-24; P13, L2-25). Initially, we obtained the idea of sediment fractionation based on Benner and co-workers' work. As for organic matter in sediment, we have referenced and added the relevant information on the sediment studies (P12, L14-24; P13, L2-25).

SPECIFIC COMMENTS -Methods: I do not understand the choice of sampling locations. Sampled stations were all in the same part of the estuary within a relatively small area with similar characteristics (Table 1) and similar results. It would probably have been more informative/interesting to study a larger spatial scale (e.g. gradient from fresh water to the open sea).

R: The aim of this study was to assess the sources and diagenetic states of sediment OM of different size fractions through measurements of compositions and concentrations of sediment particulate and dissolved amino acids (P5, L6-9). The samples taken in our area presented a wide range of weight percent of different size fractions of sediments (P9, L13-15; Table 1). Furthermore, patterns of amino acid composition and bulk sediment parameters (i.e. C/N ratio) can be affected by both the sources and diagenetic processing of organic compounds. Therefore, sampling within a relatively small area can eliminate the influence of varying sources of organic matter because sediment organic matter originated identically within a relatively small area.

-Results: Section 3.2 and Table 4: "D-enantiomers . . . were measured in some samples". Does this mean that only a selection of samples was analyzed for D-AAAs or that concentrations were below detection limit in many samples? In the latter case, this should be indicated as such instead of presenting concentrations of 0.00 nmol mg C-1 in table 4 and text.

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R: This means that the concentrations of D-enantiomers were below detection limit in many samples, which was indicated in the text (P10, L18) and Table 4.

Discussion: -Structure is not very clear. Sections 4.1 and 4.2 appear to overlap (sources of OM). -It should be made more clear which results are derived from the present study and which are derived from other studies.

R: We have revised this part in the revision (P11, L9-P12, L6).

-As mentioned above, the bacterial contribution to OM is not quantified while this was done in previous (comparable) studies (e.g. Keil et al. 2000, Grutters et al. 2002, Lomstein et al. 2009, Vandewiele et al 2009).

R: Based on D-AA data, the bacterial contribution to total sediment OM can be quantified further. However, some of the concentrations of D-AAAs in the three sediment fractions were below the detection limits in our study (Table 4). We only presented the concentrations of total D-AAAs (sum of the four D-AAAs) (Table 4; Fig. 6) and the averages of each specific D-AA in the three fractions (Fig. 7). We did not calculate D/(D+L) values because of the large variation of the data. To make our study focused, we deleted this part in the revision.

-As mentioned above, the manuscript would be much stronger when non-DAA results are included (and compared with those for the D-AAAs, THAA yields, and C/N ratios).

R: The degradation index based on amino acid compositions were included in the revision and the data were compared with those for the D-AAAs, THAA yields, and C/N ratios (P10, L8-11; P13, L2-7; Fig. 4).

-Concluding remarks: As mentioned above, few of the findings and statements in this section appear to be based directly on the data presented in this manuscript.

R: We have revised this part in the revised MS (P15, L10-22).

We hope now that that manuscript is publishable in Biogeosciences. Thank you for

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your consideration on our manuscript. Best regards.

Sincerely yours,

Jiaying Zhang

CC: R. Zhang, Q. Wu, N. Xu

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