

## ***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.**

jjayingzhang2008@yahoo.com

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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 #3 The study presented in this manuscript does not provide any substantially new concepts, ideas or methods. The title of the manuscript sounds promising; however, the announced topic is not really addressed. Most of the discussion is based on carbon and nitrogen concentrations and ratios (see comments below) and concentrations and yields of D-amino acids. Diagenetic alteration of other amino acids is not included, although data are available. Surface sediments in this study include the upper 8 cm of sediment, irrespective of sedimentation rate, sediment mixing, and thus sediment age (diagenetic stage). The potentially interesting approach of size fractionation is most likely biased by the sample preparation. Large parts of the discussion and respective conclusions are based on unpublished data and data from previous or related studies.

R: To address our objective more clearly, we included the data on the composition of 21 protein amino acids in the revised manuscript (P10, L8-11; Fig. 4). Considering the effects of sedimentation rate and sediment mixing, we took totally 13 sediment samples from a wide range of sediment ages to investigate the applicability of diagenetic indicators based on amino acids. More specific details on the size fractionation approach were presented in the revised manuscript (P7, L1-11; Fig. 2). The discussion and conclusion sections were revised accordingly (P11-15). Overall, we believe that our study provides the new ideas about the diagenetic index for sediment OM size fractions based on the amino acid data (21 protein amino acids and D-amino acids) in the Pearl River Estuary in South China.

SPECIFIC COMMENTS - Introduction: The introduction is very general and includes aspects that are not addressed in the presented study, e.g. diagenetic indicators based on the composition of THAA. There are very few places linked to the present study, e.g. "few studies are available on the diagenetic state of sediment OM of different sizes, especially in estuarine sediments" and "the bacterial contributions to sediment OM of different size fractions and the respective diagenetic status are still poorly understood".

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The authors should elaborate more carefully on these aspects, which are meant to be the key aspects of the manuscript. Why is it interesting/relevant to know? What should we expect? What is the research question/hypothesis behind? The last paragraph sounds promising. If data on THAA composition were included, the study would have the potential to address these questions.

R: The data on THAA composition (21 amino acids) were included (P10, L8-11; Fig. 4), and the content of protein amino acid-based diagenetic indicators was added in the revised MS (P10, L8-11). The key aspect of our study is to investigate the sources and diagenetic states of sediment OM size fractions. We intended to explore several diagenetic indicators based on amino acid compositions and bulk parameters of sediment fractions. Since diagenetic indicators could indicate the diagenetic history of OM, we can establish the relationship of sediment size and diagenetic stage of OM according to the “size-reactivity continuum”.

- Materials and methods: 2.1. Site description: The site description is very detailed, but it is not explained why this site was chosen for this study and the discussion never refers to any of the information given here. The authors should check section 2.1 and Table 1 for relevant information.

R: The aim of our study was to investigate the diagenetic state of organic matter among different sediment size fractions (P5, L6-9). The samples taken in the site presented a wide range of weight percent of different size fractions of sediments. The data on the weight percent of the 13 sediment samples were included in the revised Table 1. The discussion referred the relevant information (P11, L7-9).

-There is a reference missing page 3327, line 14-17.

R: Done (P6, L5).

2.2. Sediment sampling and sample processing: Water column samples are mentioned but not included in the following manuscript. Sample processing might bias sediment

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fractions (see below).

R: To be concise, we have deleted the data on water column samples in Table 1.

2.3. Sediment fractionation: I have major concerns regarding the processing and fractionation of the sediments samples. Samples were freeze-dried and homogenized in an agate mortar (gives a fine powder), and afterwards dispersed by sonication. After fractionation CPOM and FPOM were oven-dried. This procedure should have an effect on the size distribution of OM in the sediments. The authors definitely have to address this point and assess a possible bias. It would be interesting to know the yields of the individual fractions and how they vary for the investigated samples. This could also be compared to untreated sediment. The description in 2.3. does not match the scheme in Fig. 2 (e.g. filtration steps). The sediment fractions should be defined more exactly.

R: The effect of freeze-drying on the yields of three size fractions is affected by factors such as sediment texture. The sediments in our study area are mostly sandy in texture. Thus, the effect of freeze-drying was minimum (P7, L13). Besides, we gently grounded the sediments to homogenize them (P6, L20-21). The oven temperature for sediment fraction drying was set less than 40 °C, at which the OM content and composition were not significantly affected. Therefore, the processing had minor effect on the size distribution of sediment OM. The yields of the individual size fractions of sediments are shown in the revised Table 1 in the revision. The total yields of the three fractions were compared to untreated sediments, and the standard deviation is within 5%. We have clearly defined the sediment fractions in 2.3 (P7, L2; P7, L4-9) and modified Fig. 2 accordingly.

2.4. Elemental analysis: The information is not sufficient to reproduce the analysis. How much material was used for the analysis? What was the precision and the detection limit? How many replicates were analyzed and what was the deviation? The concentrations reported in the manuscript are quite low and display strong variations. Total N includes inorganic and organic N. Is there any information on the fraction of

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inorganic N? Since large parts of the discussion are based on C/N-ratios and N-yields of amino acids, this aspect should be elaborated and discussed carefully. There is a reference missing page 3328, line 20.

R: We measured the concentrations of inorganic N and found that the fraction of inorganic N was less than 3.3% of total N for all the samples. One replicate was used for the elemental analysis. The information on the amount of material used (P7, L17-25), and the precision were provided in section 2.4 (P7, L17-25). The missed reference was added in 2.4 in the revision (P7, L23).

2.5. Amino acid analysis: Is there co-precipitation of amino acids during neutralization of the hydrolysate? Reference missing page 3329, line 8. What is the procedural blank of the method, including the two filtration steps? What filters were used (resistant to 6 N HCl)? Individual amino acids were analyzed – where are the data?

R: We did not observed significant co-precipitation of amino acids during neutralization of the hydrolysate. The missed reference was added in the revision (P8, L11). The procedural blank of the method included the two filtration steps. We used Whatman GF/F filters, which are resistant to 6 N HCl (P8, L7; P8, L9). We have provided the data related to amino acid composition in the three fractions in Fig. 3 in the revised MS (P10, L8-11; Fig. 4).

- Results: The results part is extensively descriptive; there are far too many details, e.g. page 3330, line 26 to page 3331, line 21. All the data are given in tables 3 and 4. The authors should highlight the most important findings and trends, rather than repeating all the numbers given in the tables. Concentrations and yields of 0.00 are below the detection limit or just  $<0.01$ ?

R: This part has been rewritten to highlight the most important findings and trends. Concentrations and yields of 0.00 are below the detection limit (P10, L18; Table 4).

- Discussion: The discussion (and results) is restricted to the size fractions. Intersite

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differences are not discussed at all. What was the rationale for sampling different sites?

R: The objective of sampling different sites in our study area was to obtain sediment size fractions from a variety of yields of sediment fractions in different sampling sites. The yields of sediment size fractions were summarized in Table 1. However, we did not find any significant correlations between amino acid-based parameters with the yields of three sediment size fractions.

4.1. Sources of CPOM, FPOM and UDOM: The first part of this section describes findings and interpretations of previous studies without linking them to the present study. In the second part, there is a clear statement that CPOM is mainly composed of “soil sand-associated terrestrial OM and floated vascular plant fragments” (page 3333, line 10). However, it is not clear how this conclusion was reached or whether it was taken from literature (in the latter case, a reference has to be included). There is a back and forth of arguments, partly from literature, partly referring to data of the present study. Same holds for the discussion of FPOM and UDOM sources. A key conclusion (“contribution of bacterial DOM to UDOM”) is based on unpublished data (muramic acid). Large parts of the source discussion are based on C/N-ratios. It is very likely that N is not entirely organic – this has to be considered when evaluating the ratios.

R: We deleted the first part of the discussion section related to the findings and interpretations of previous studies. The statement of CPOM source was reached from our data (P11, L9-21). We included the muramic acid data in the revised MS (P12, L3-4). The inorganic nitrogen content just accounted for less than 3.3% of the total nitrogen in the three sediment fractions. Thus, the C/N ratios can be a reliable parameter when discussing the organic matter source for the sediment fractions.

4.2. Diagenetic trends for sediment OM of different size classes: The first part of this section summarizes and extends the information given in the introduction. There is no discussion included in these 16 lines. The remaining section is rather descriptive. Findings of earlier studies are not well linked to the present study. Conclusions are rare

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and poorly supported by unambiguous data. The “size-reactivity continuum” model is mentioned but not explained and not well linked to the present study. It should clearly be stated that the applied diagenetic indicators are well-established in organic matter research and not the novel outcome of the present study (e.g. page 3337, lines 3-5).

R: Based on the suggestions of the reviewer, we have revised this part. The “size-reactivity continuum” model was explained and linked to the present study (P14, L8-11).

4.3. Qualitative bacterial contribution to sediment OM of different sizes: I cannot follow the argumentation, neither the conclusions reached in this section. What is the message?

R: We have deleted this part in the revision to make our MS more focused.

- Concluding remarks The conclusions are not well constrained with data and discussion (see comments above).

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

- Tables: 1: Most of the data presented in table 1 are not relevant for the study and not included in site description or discussion.

R: We have deleted the irrelevant data in Table 1 and added the data of weight percentages of three sediment fractions in the revised Table 1.

2: Why is this gradient table shown? The authors should give the reference for the original method and describe important modifications in the text.

R: The gradient of the method was designed by us.

3: I wonder how many decimals can be justified for the different parameters.

R: We kept different decimals (or significant digits) for the different parameters.

4: See comment above: - Figures: 1: It would be helpful for readers to have an idea

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about the location in China, e.g. where is the ocean?

R: Done (Fig. 1).

2: The scheme contains information that is not mentioned in the text. The figure caption mentions TOC and Total N, which are not in the scheme.

R: We have revised the figure caption and Fig. 2 in the revised MS.

3-6: It is more appropriate to show the data range as average and standard deviation (or even as box and whisker plot). Bars do not show the minimum values.

R: We have revised the Figs. 3-6 as suggested by the reviewer.

6: Standard deviation should be included.

R: Done (Fig. 7).

7: See comments above: N might partly be inorganic. The regression in 7a is mostly determined by 3 data points with high total N concentrations, almost 100 mg N per 100mg C (obvious inorganic contribution). And I do not see the value of the figures. All axes are normalized to 100 mg C. The more N in the sediments, the more N in THAA. Is this the message here?

R: We have measured the contents of inorganic N in the three sediment fractions. In Fig. 7, all axes are normalized to 100 mg C. The figure demonstrated that the more N in the sediments, the more N in THAA. To make our study focused, we have deleted this figure.

We hope now that that manuscript is publishable in Biogeosciences. Thank you for your consideration on our manuscript. Best regards.

Sincerely yours,

Jiaying Zhang

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

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