Biogeosciences Discuss., 8, C3022–C3029, 2011
www.biogeosciences-discuss.net/8/C3022/2011/

Biogeosciences Discussions

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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Received and published: 12 September 2011

September 10, 2011

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

comments was summarized as follows.

Referee #2 General comments: This manuscript describes amino acid composition in different size fractions of sediments from an estuary in the Pearl River. Three different size fractions were studied for C and N conc., and ratios, total hydrolysable and D amino acids. Whereas the idea of looking into different size fractions is a good one, I have my doubts that the fractions that were chosen are relevant for the amino acid investigation that was done. This is a very crucial point and please see my comments below concerning this topic. Furthermore I think that the discussion does not really discuss the samples that were investigated but focuses on studies that were done by others and therefore rather represents a literature review.

R: The objective to study the sediment size fractionation was to separate organic matter pools with different reactivities in different sediment particle size classes (P4, L14-17). The diagenetic indicators of OM of the three size fractions support the idea of size fractionations to separate OM with different reactivities. We have revised the discussion section to make the main ïňĄndings and conclusion be closely related to the data presented in this manuscript (P11-15).

Methods: I do not understand the sampling strategy, why were samples taken in this round shaped area of the estuary? Wouldn't it be much better to take a transect from the river towards the open sea? For me the samples do not look very different from each other when looking at O2 and chlorophyll for instance. Maybe make clear why the samples were chosen using Table 1.

R: The aim of our study was to investigate the diagenetic state of organic matter among different sediment size fractions (P4, L14-17). The samples taken in our area presented a wide range of weight percent of different size fractions of sediments (CPOM, 7.28% to 75.92%; FPOM, 23.58% to 87.54%) (P9, L13-15; Table 1). On the other hand, 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.

I have some concerns that the treatment of the samples has an effect on the size fractions, as sediment aggregates probably get destroyed by freezing, grinding and/or sonication. When then afterwards the samples were dispersed how original is the sample in respect to grain size (after grinding)? This is a major point! There is also no real overlap of the description of the "Sediment fractionation" paragraph and Figure 2 explaining how the fractions were reached. What was done exactly, what are the grain sizes of the resulting fractions named CPOM, FPOM, UDOM? I think it would have been much more appropriate to separate the fractions and especially the UDOM fraction from the original fresh sample (before freeze drying and grinding). Maybe it would have even been more useful to compare amino acid concentrations of the pore water with the amino acid concentrations of the solid phase. It is necessary to include error estimations on the different methods used.

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 and sediment aggregates were merely formed. Therefore, the effects of freeze-drying and sonication were minimum (P7, L13). Besides, we gently ground the sediments to homogenize them (P6, L20-22). Thus, the processing has minor effect on the size distribution of sediment OM. We have clearly defined the sediment fractions in 2.3 (P7, L2-13) and modified Fig. 2 accordingly in the revision.

Another issue is the use of the 0-8 cm sediment fraction instead of concentrating on single sediment depths (or only the surface sediment) since as stated sedimentation rate is very distinct between samples (a factor of 10). This makes the 0-8 cm very different in age and probably ongoing degradation and difficult to compare.

R: The sediments were well mixed over the top 8 cm in our study area, likely resulting

from bio-perturbation and/or sediment re-suspension. Although the sediments may vary among sampling sites, the present study mainly aimed to investigate amino acids composition and diagenetic stage of OM among the three sediment sizes (P4, L14-17).

- Results: The description of the results rather concentrates on the THAA and the DAA. It could be also of interest to look at the concentrations of other amino acids. Especially, the concentration pattern of the nonprotein amino acids Orn, -Ala, -Aba and -Aba which were analyzed could indicate organic matter degradation as they are diagenetic in origin. Is there an increase in the concentrations of these amino acids along the river or with decreasing sediment fraction size? Also the calculation of the degradation index based on amino acids by Dauwe et al. (1999) could give insights into the degradation of the organic matter in the sediments. Muramic acid data might also be used to estimate the contribution of bacteria to the organic matter. One would also include D/L ratios into the study. All this data seems to be available and need to be used. This might lead then to a valuable contribution.

R: The degradation index based on amino acids by Dauwe et al. (1999) has been given in Fig. 4 in the revision. The degradation index decreased with increasing sediment size. However, there was no obvious trend in the concentrations of the non-protein amino acids with decreasing sediment fraction size. The labile nature of muramic acid made it unsuitable to be used to estimate the contribution of bacteria to the organic matter. We did not show D/L ratios in our study because the D/L ratio values varied much among samples and sediment fractions, and some DAAs concentrations were below detection limits (Table 4).

- Discussion: My major point here is that data that was produced and shown or to a great extent not shown (there were 21 AA analyzed but only the D-AA are shown and the other combined to THAA) is hardly used to make a story here in the discussion. Please use all the data that seems to be available (see recommendations below). What it is so far is a description of work from other people and the outcome of their work. However, the link to the studied samples here is not made. A main part of the

discussion bases on data from other studies about particulate matter in ocean water and the Amazon River and not on other sediment studies. It is very difficult to compare water sample fractions like done in Hedges et al. with the sediments investigated here. Also the fractions used in the Hedges study are different from the ones presented here (if I understood the grain size fractions correctly). I would suggest to the authors to go very thoroughly through their data, if samples are still available use a surface sediment sample and a deeper sampler (same age, depending on the sediment rate) and compare the THAA composition and concentration, use various degradation indices (DI, non -protein AA, D/L ratios etc.), and compare this to studies that used sediments instead of water column work. It would be really good if it is possible to include some samples towards the open ocean.

R: Our study is mainly focused on diagenetic stage of OM among different sizes (P4, L14-17). Additional information on deeper sediment amino acid compositions may provide some useful information on sediment OM diagenetic alterations in the studied area, which seems out of scope of this study. We have analyzed all our data and the data on amino acid based DI was added into the revised MS (P10, L8-11; Fig. 4). The data on non-protein amino acids and DAA/LAA did not show a clear trend. We have deleted the comparison statement on water column samples and added the relevant sediment studies (P12, L13-15; P12, L15-18; P12, L21-22; P13, L2-7; P13, L20-22). We have revised the sample fractionation part and given a definite size interval of each fraction in the revised MS (P7, L2; P7, L4-5; P7, L9).

Specific comments: - Sampling: As the sedimentation rate varies in the system between 0.42-4.26 cm a-1, it might be interesting to have more detailed information about the sedimentation rates of the single sampling sites. How strongly is the system affected by tidal dynamics? Can the timing of the sampling explain differences in the water samples properties?

R: The sedimentation rate data was from Zhang et al. (2002), in which the variability of the data probably attributed to natural disturbance due to flood or storm tide, and

human activity such as land reclamation (P18, L33-P19, L1). Since we do not have available data of each specific sampling site, we only use the average data in the revised MS.

- Methods: Was deionized water used for the sieving procedure?

R: Yes.

p. 3334 line 4 I do not understand the sentence “the low abundance of muramic acid. . .” how can a low abundance indicate a significant contribution?

R: The occurrence of muramic acid (a biomarker unique in bacterial peptidoglycan) in the UDOM fraction in our study confirmed the contribution of bacterial DOM to this sediment fraction (10.2-178 nmol muramic acid mg C-1 in the UDOM samples). (P12, L1-4).

Figure 2: This figure is not clear and describes the fractionation business different from the text in the method section.

R: We have revised the figure in the revision (Fig. 2).

Figure 6: Why is D-Asp in the FPOM so low, i.e. lower than in UDOM, any explanation?

R: The low concentration of D-Asp in FPOM may be due to different diagenetic pathways of D-Asp in the three sediment size fractions from other DAAs (P15, L2-3).

Figure 7: I think this figure does not add new knowledge but is only representing nitrogen to occur in amino acids which is naturally true.

R: We have deleted this part in the revised MS.

- Table 2 lines 4 to 7 are redundant.

R: We have deleted the redundant information in Table 2.

- There are some misspellings: e.g. p. 3325 line 11: Lomestein -> Lomstein,

R: Done (P3, L22).

p. 3325line 18:dissolved,

R: Done (P4, L3).

p. 3325 line 20: aminobytyric -> aminobutyric.

R: Done (P4, L5).

- p. 3328 line 10 should read “sediment accumulation” instead of sediment flux

R: To be clear, we have deleted this sentence.

- p.3328 line 15, reference for 78% is missing

R: Done (P6, L5).

- p. 3329 line 26, “which included” must be replaced by “to which were added”

R: Done (P9, L5-6).

- p. 3331 line 20 should read “were found in..”

R: Done (P10, L21).

-p. 3331 line 22 should read “both” instead of “either” (?)

R: Done (P10, L23).

- p. 3333 line 5 “were other sources”

R: We deleted this sentence to make our discussion more focused.

- p. 3333 line 23 delete “recently”

R: We deleted this sentence to make our discussion more focused.

- p. 3337 line 8, diversified -> diverse

R: We deleted this sentence to make our discussion more focused.

-p. 3337 line 24 should read “to accurate quantify bacterial: : :”

R: We deleted this sentence to make our discussion more focused.

- p. 3338 line 14 “that” should be deleted.

R: We deleted this sentence to make our discussion more focused.

- Fig. 2: TOC and Total N do not occur in the figure and can be deleted in the caption. The line starting between 63-μm sieving and <63μm going to the right is irritating.

R: We have deleted TOC and total N in the caption and revised Fig.2 in the revision.

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

Interactive comment on Biogeosciences Discuss., 8, 3323, 2011.