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Reply on RC1

Julia Gensel et al.

Author comment on "Origin, transport, and retention of fluvial sedimentary organic matter in South Africa's largest freshwater wetland, Mkhuze Wetland System" by Julia Gensel et al., Biogeosciences Discuss., https://doi.org/10.5194/bg-2021-172-AC1, 2021

Julia Gensel and colleagues have presented a paper that characterizes organic matter and its recent spatial distribution in the Mkhuze Wetland System and its catchment. Overall, the paper is sound, but there are some major issues to clarify, especially concerning the n-alkane data.

- We thank anonymous Reviewer #1 very much for her/his very valuable comments. These will certainly be helpful in improving the quality of the manuscript. We appreciate very much to get a view from the outside and thereby to reflect at which points we have not yet expressed ourselves clearly enough. In addition, we are very grateful for the reviewer's attention, even to the small details that we didn't even recognize anymore. We appreciate very much that she/he took the time to improve our work. Thank you very much for that! Below are the individual responses to each comment.

1. Overall, I suggest major minor revisions to this paper. Two broad comments I have: The separation in three end-member, i.e. aquatic (C_{25}), woody (C_{29}) and grassy (C_{33}) is not visible in the n-alkane pattern of modern plants presented in this study. Please clarify why these end-member were chosen, because the vegetation in the studied area likely shows a different pattern for aquatic and grassy vegetation while woody plants were not investigated.

- a) We thank the reviewer very much for this very valuable comment. We will revise section 4.1 in the discussion section to make it clearer why we used the respective *n*-alkanes for each identified cluster. Also, we will replace the word "endmember" with "marker compound".
- b) We fully agree that the *n*-alkane distribution patterns of the plants studied show dominances of *n*-alkanes that are inconsistent with those selected to represent the identified clusters. Briefly, our approach involves identifying specific groups of marker compounds, i.e., C_{23}/C_{25} and C_{33}/C_{35}, that are exclusive to certain plant types such as aquatic plants and grasses, respectively. These *n*-alkanes are not present (or only in negligible concentrations) in the other plant types studied and can therefore be used as marker compounds for the respective clusters. We selected one of the marker compounds in each case (the higher concentrated one across all samples) to represent the respective trends. The *n*-alkanes we selected to represent the cluster labeled "woody" were C_{29} and C_{31}. We absolutely agree that these *n*-alkanes are not produced

exclusively by woody plants but are found in almost all plants. We mention this limitation in line 347ff. For this reason, we will delete the term "woody" as a cluster name and instead explain that these particular *n*-alkanes are rather an integrated signal of all plants to avoid confusion. We will restrict the term "woody" to subsection 4.2.1.

2. Additionally, it is demonstrated that organic matter in lake surface sediments is dominated by local vegetation. I suggest a more clear statement there: What does this imply for paleoenvironmental and –hydrological studies at the end of the respective section and in the conclusions, where it is stated that this study is of great importance for future studies.

- We thank reviewer #1 very much for her/his comment. We will revise the relevant sections to provide a more concise and clear statement of implications for future paleoenvironmental studies.

Specific comments:

3. 3ff.: Please rephrase this sentence.

- We will.

4. 7f.: Please indicate which signal is present in the upstream area.

- We will add the information that the upper reaches have a much more degraded OM signature indicated by the R- and I-indices.

5. 9f.: […] higher dD values. Compared to what?

- We will rephrase the sentence to indicate that the comparison is with δD values from samples from upstream subareas.

6. 10ff.: I cannot follow these two sentences. First you state that lake surface sediments are dominated by local vegetation incorporating a local hydrological signal. Afterwards, you state that those sediments integrate hydrological conditions of the whole watershed. Please clarify these contradicting statements.

- We thank reviewer #1 for her/his comment. We will reword the sentences to better convey our main message to the reader. (Meaning that our study provides evidence that (paleo)environmental studies which assume watershed-integrated signals in sedimentary archives/surface sediments can be constrained under certain conditions.)

7. 27: The Mkhuze Wetland System, […], is […].

- We will edit the sentence as suggested.

8. 53ff.: Move this paragraph to line 23-28 to discuss risks and benefits of wetlands in one paragraph.

- We will act as suggested and are very grateful for this suggestion.

9. 60: I suggest a short section introducing to n-alkanes and their compound-specific (CS) $d^{13}C$ and dD isotopic composition including their interpretation. Here you could introduce why you choose C_{25}, C_{29}, C_{33} and you can refer to recent studies analyzing CS $d^{13}C$ and CS *dD in topsoils (e.g. Carr et al., 2014, org. geochem., Herrmann et al., 2016, QSR, 2017, org. geochem., Strobel et al. 2020, STOTEN).*

- We will proceed as suggested. We will include a section on our general approach, including an introduction to each method and the rationale for its use. We will also reference CSIA in topsoils, as proposed.

10. 69: Please avoid one-sentence paragraphs in the whole manuscript.

- We will.

11. 71ff.: It seems like a word is missing?

- We thank the reviewer for her/his awareness and will add the missing word.

12. 73: Can you please characterize the river a bit more in detail, e.g. as episodic/periodic/… river system?

- We will provide the requested information.

13. 110: Please provide a reference for this numbers and also for % precip. in the next line.

- We will.

14. 119ff.: Please provide references for all these information.

- We will.

15. 131: Can you please provide information about the potential natural vegetation in your studied area?

- To the best of our knowledge, the vegetation cover shown in Figure 3 (left subfigure) is the oldest available information on the vegetation of the system, which is also consistent with typical wetland vegetation. Therefore, we are unable to provide any additional information.

16. 229ff.: Repetition of "Here" at the beginning of the sentence, please modify.

- We will do that, and we thank reviewer #1 again for her/his attention.

17. 270ff.: Is there a table to which you can refer, that the reader can follow this numbers? If not, please provide or add these data to table 1.

- We will add a table with the requested information.

18. 290ff.: Can you please refer to a figure? Figure 8?

- For both wetland grasses, the reference to the respective sub-figure of Figure 8 is already given after the common name in parentheses.

19. 321ff.: Please check if a minus is missing prior to the dD values.

- It is definitely missing and we will add it. We are very grateful for the reviewer's attention.

20. 339ff.: In figure 8A, B both show a distinct (C_{27}) C_{29} dominance. Please clarify.

- This is absolutely correct. Despite the predominant presence of (C_{27}) or C_{29}*n*-alkanes, both species have elevated relative concentrations of the medium-chain *n*-alkanes C_{23} and C_{25}, which is not the case in the other plant species. Thus, the presence of these medium-chain *n*-alkanes makes aquatic plants distinguishable from the others, allowing these specific alkanes to serve as marker compounds. As indicated in response "b" to comment #1, we will make this point more clearly in a revised version.

21. 345ff.: Okay, and how can you distinguish the two woody and grassy end-member when modern grassy plant samples in your study show distinct contribution of C_{29} (figure 8C, E, F)?

- We distinguish the grass plant samples based on the presence of the identified marker compounds C_{33} in combination with C_{35}, which have elevated concentrations only in grass plants, while other plants have no or negligible relative concentrations of these very long-chain *n*-alkanes. As mentioned earlier, we will clarify our approach and replace the word "end-member" with "marker compound" to avoid confusion. We will also avoid the term "woody" because the C_{29} alkane represents an integrated signal from all plants, as all plants contribute to the long-chain alkanes in comparable relative concentrations. We will retain the term "woody" only in subsection 4.2.1. to explain that elevated measured concentrations are most likely due to woody vegetation, which is much more prevalent in the upper reaches of the Mkhuze River compared to the other sub-areas.

22. 353ff.: When there are differences in photosynthetic pathway, what does this mean for the dD signal? Does the photosynthetic pathway has an influence on this signal – see e.g. Sachse et al., 2012. If the abundance of C4 vegetation in the studied area changed during the past, what does this mean for the interpretation of dD in sedimentary record?

- a) Yes, the photosynthetic pathway most likely has an impact on the δD of the *n* -alkanes, as summarized in the review by Sachse et al., 2012. With respect to our study, the δD becomes important when discussing its highly enriched values in the lake area (Figure 9 and subsection 4.2.4). The differences in δD in the lake area are not due to a higher contribution from C4 plants, such as grasses. The data show that both the relative contribution of marker *n*-alkanes and their respective $\delta^{13}C$ isotopic compositions are comparable with the upstream subareas, suggesting a similar or even the same vegetation community (see 455ff). Since the contributing vegetation does not differ, the difference in δD values must be due to hydrological reasons (differences in source water, evapotranspiration, etc.). We will add a sentence to clarify.
- b) For sedimentary records, vegetation change must be taken into account when interpreting the δD of plant wax-derived *n*-alkanes. Since we have not presented any sedimentary records, this answer remains speculative, but we agree with the statement of Sachse et al. that changes in vegetation cover most likely result in changes in sediment δD. If it is possible to track changes in vegetation cover through other proxies (e.g., relative alkane contribution, *n*-alkane-$\delta^{13}C$), we believe it should still be possible to attribute changes in δD to environmental/climate controls.

23. 358ff.: This section is more or less a data description, and a discussion of the data is very limited. I suggest to provide a statement if your findings match the expected environmental conditions in each sub-environment.

- These paragraphs were intended to provide an introduction and explanation of the approach for the following subsections as they apply to all four. However, we agree that the placement was confusing and will move this information to the newly planned "Approach" section.

24. 378: Would the odd-over-even predominance (OEP) of the n-alkanes may also provide useful information concerning the state of degradation?

- No, the observed OEP values do not provide useful additional information, except that the analyzed *n*-alkanes can be used as conservative tracers since no contamination or extremely advanced degradation processes can be observed.

25. 379ff.: Closing bracket is missing. Does this approach really work out at your study site? I agree that this approach is widely applied and I also noticed your statement in lines 332-339, but does this really work in your setting? The data are great, but could you may make this vegetation statement a little more cautious?

- a) We add the closing parenthesis (thank you for your attention even on these minor details).
- b) We are convinced that the approach works in our environment, but we fully agree that in addition to the mentioned statement in line 332-339, we should reword the sentence to tone it down. In general, we believe that such approaches should be used with caution in any case.

26. 387: Please see comments above (C_{29} vs C_{33}). Additionally, I suggest to provide a figure showing the n-alkane patterns in each sub-environment.

- a) Please refer to the answers to the comments above.
- b) Unfortunately, because the subareas gradually merge into each other rather than being sharply separated (e.g., the contributing vegetation in floodplain, swamp, and lake areas is quite similar), a visual representation of the *n*-alkane patterns of the subareas is not helpful. The overall similarity would mask the much finer differences, making it difficult for the reader to see and understand our results and interpretations. It would simply weaken our argument, as the human eye would instinctively assume that they all look almost the same, rather than recognizing the differences that exist. Therefore, we chose to present the data as boxplots for direct comparison of individual subsections. The boxplot also have the advantage that some statistical information is directly apparent to the reader, such as the median, the dispersion of the data set, etc.

27. 394: Please provide a short paragraph in the introduction how the isotopic signals are interpreted at your site for both d13C (C3/CAM/C4) and dD (amount/source/continentality…). Recent calibration studies provide a nice overview for South Africa. Are there any plants using CAM-metabolism in your studied area?

- a) We will provide this information in the new section where we will summarize information about our general approach.
- b) The presence of CAM plants in the region is not mentioned in any of the previous reports and was not observed during the field trip.

28. 413: Please provide a figure showing the n-alkane patterns in each sub-environment, as mentioned above.

- See answer "b" to comment #27.

29. 426: Can I see this sub-deviation in any plot?

- We will change the sentence accordingly, since the partial deviations mentioned are no longer shown in the figures submitted.

30. 430: Please highlight these cluster in the respective figure.

- We will do as suggested.

31. 435: Please refer to the respective figure(s).

- We will do as suggested.

32. 442f.: What is the base of this argumentation? Please introduce to the site-specific dD interpretation earlier.

- a) We will modify the sentence to indicate that although the δD indicates slightly wetter growing conditions for the contributing plants, the *n*-alkanes cannot be derived exclusively from local vegetation because the extent is only moderate and shows more of a mixture of deposition of upstream transported material and, in addition, a slight overprinting with local sources.
- b) For the structure, we would like to maintain the order in which the bulk parameters (Rock-Eval interpretation of degradation and classic bulk parameters) are discussed first, then the relative concentration of *n*-alkanes, the *n*-alkane carbon isotope composition, and finally the *n*-alkane hydrogen isotope composition in each subsection (upper reach to delta and lake).

33. 453: One sentence paragraph which is a result and no discussion. Please modify.

- We will make sure that no one-sentence paragraph occurs in a revised manuscript. Therefore, we will include this information (and, moreover, repetitions) of results in the previous Rock-Eval interpretation, which is simply confirmed by the reference to the input of fresh material.

34. 465: […] which use the lake's water as dominant water source? How about the effects of lake water evaporation, salinity to the dD and $d^{13}C$ signal, and emergent/submerged plants contributing to the C_{25} to C_{33}n-alkane pool?

- a) We will include salinity in the characteristics of the lake. It is well known that the lake is subject to high rates of evaporation, which in turn increases salinity (in extreme periods, the lake can reach three times the salinity of the ocean). This process leads to isotopically enriched lake water. Indeed, this process is the main argument that leads us to conclude that although the vegetation type contributing to the lake surface sediments is very similar in terms of relative alkane concentration and carbon isotope composition compared to the upstream swamp, the corresponding offset in δD is actually a consequence of the contributing plants using the lake water as a water source.
- b) Evaporation can also affect the carbon isotopic composition of alkanes. C_3 plants, for example, are likely to adjust the opening time of their stomata during "water stress" to limit water loss through transpiration. This could affect the isotopic composition of plant *n*-alkanes, which should be reflected in more enriched $\delta^{13}C$ values. Comparing the $\delta^{13}C$ values of the alkanes in the lake area with those in the swamp area (wetland), there is a slight enrichment, which is not statistically significant, but could be explained by the "water stress" of the plants.
- c) One of the most important plant species in both the upstream swamp area and the lake area is the emerged wetland plant Phragmites australis, which is probably the main producer of medium-chain alkanes. In the lake area, submerged aquatic plants were neither mentioned in previous studies nor observed during the field campaign. The characteristics of the lake (salinity, strong winds, turbidity) are probably not particularly favorable for these plant species.

35. 489: Please highlight these clusters in the respective figure. For example, use colored/shaded circles in the background of the data points

- We will do as suggested.

36. 496: Does this statement implies that organic (bio)markers in the wetland are of local origin and thus reflect local eco-hydrological conditions instead of an integrated signal including the wetlands catchment? Please clarify, because it is an essential finding of your study and of great importance for future studies at the site.

- No, therefore we will clarify. In all areas except the (delta)/lake area, the characteristics of transported hinterland signals predominate, although in the floodplain and somewhat more pronounced in the swamp sub-area, a slight overprinting by local signals can be observed. The original statement is therefore intended to imply that the organic (bio)markers in the lake area are local in origin and thus reflect local ecohydrologic conditions rather than an integrated signal encompassing the river catchment.

37. 517: Remove space before comma.

- We will.

38. 535: A trap for local organic material – see comment above.

- See answer to comment #37.

39. 549: Isn't this also the case at your site now – see comments above? Please clarify.

- See answer to comment #37.

40. 565. Generally, I agree with the conclusions, but doesn't the results demonstrate that the lake sediments are dominated by local organic matter representing very local ecohydrological condition instead of the lakes catchment. This absolutely limits the usage of dD and $d^{13}C$ as paleoecological markers because local effects might overprint the environmental signal, which is a very important finding for future records – although it might be unexpected.

- a) We are in complete agreement!
- b) In interpreting $\delta^{13}C$ and δD in sediment records derived from downstream areas of such "traps," we would expect to observe the change from an integrated signal to a locally received signal (if the "trap" formed within the sampled time period). This is the reason that the interpretation of sediment records used for paleoecological reconstruction should take into account the geomorphological setting of the sampling area.

Figures:

40. Figure 2: The grey shaded area is very hard to identify. Numbers at the precipitation and evaporation isolines are also very hard to read, please enlarge them.

- We will adjust the figure as suggested.

41. Figure 3: Please place the figure to the section where it is mentioned in the text. Are there any more recent data than 1996, which is already 25 years ago? Or is this landcover/-usage still present? It seems very important for your study to have the most recent land-cover map for comparison with your data and correct interpretations and implications for future paleo-studies.

- a) We will.
- b) To the best of our knowledge, this is the most current information on vegetation cover. Data availability for the region is rather sparse.

42. Figure 4: Overall, this figure provides a very nice overview of the analyses you did.However, I suggest to remove all the lab-steps, e.g. lipid extraction, and provide a little more details in the respective text and therefore reduce the size of the figure. Just keep the sample (e.g. plant samples [g]), used machines (e.g. GC-FID) and results (e.g. quantity n-alkanes).

- We will remove the figure and give the information as plain text.

43. Figure 5: Please name the figures in the text first and show them thereafter (Please check for all figures and tables)

- We will.

44. Figure 8: Why is CS $d^{13}C$ of C_{23} and C_{35} distinctly more positive compared to the other chain-length? Is there an amount-dependency in the IrMS? Please check to note if you did an amount and/or drift correction of your data for both $d^{13}C$ and dD. Additionally, none of the aquatic plant samples show a C_{25}-dominance, which is used as aquatic end-member later, but a distinct C_{29}-dominance which is interpreted as woody end-member later. Moreover, except for 8F, none of the grasses shows a C_{33}-dominance, which is used as grassy end-member in the following. Please clarify these issue, because it is very important for your manuscript.

- There is no amount dependency in the IrMS observable. A specific intra-laboratory cut-off threshold has been established, and only large enough peaks are integrated. Therefore, we are confident that the more positive values of alkanes C_{23} and C_{33} (for Nymphaceae, Figure 8A) and C_{35} (for Vossia cuspidate, Figure 8E) are real. The isotopic composition of *n*-alkane C_{35} (for Cynodon dactylon, Figure 8F) shows no such trend toward higher enriched values compared to the other alkanes, supporting that these values are not artifacts because they were all measured by the same person during the same time period and processed by the same person.

45. Figure 9: How can C_{25} be the aquatic end-member when your plants show a (C_{27}) C_{29} predominance? The same applies for C_{29} and C_{33} for woody and grassy vegetation, respectively. Is there a local study showing that C_{29} is a woody end-member in ZA? There are respective end-member based on you modern aquatic and grassy plant samples, but they are ignored in this figure. Overall, I have to note that the presentation of the data is very nice! However, please consider valid end-member.

- We will replace the word "end member" with "marker compound" as mentioned in previous answers. In short, the identification of certain alkanes and their use as indicators of certain plant types is based on the exclusive occurrence of certain *n* -alkanes in certain plants, while they are not found in others.

46. Figure 10: I really like this figure! Maybe also indicate the pastures, which distinctly contribute to the C4 signal in the floodplains.

- We are pleased to read this, and we will emphasize the already present sugar cane plants as we have to agree they are not recognizable as such yet. Most likely we will add a fence to indicate an agricultural field.

Tables:

47. Table 1: I suggest to move this table to the Results section.

- We agree.