

Interactive comment on “The composition and flux of particulate and dissolved carbohydrates from the Rhône River into the Mediterranean Sea” by C. Panagiotopoulos et al.

C. Panagiotopoulos et al.

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General comments In the manuscript entitled “The composition and flux of particulate and dissolved carbohydrates from the Rhône River into the Mediterranean Sea”, Panagiotopoulos et al. used measurements of DOC, POC, TSM and particulate and dissolved carbohydrates for the Rhône River obtained monthly for the period 2007-2009. The measurements were used to calculate corresponding fluxes to the Mediterranean Sea. The composition of particulate and dissolved carbohydrates was also investigated in order to provide insights on the origin of carbohydrates in the Rhône River and on the diagenetic state of POM and DOM. Overall, the manuscript is written in proper En-

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glish and presents novel data worthy and appropriate for publication in BGD. However, I think some changes need to be made about the overall organization of the paper. I also think the current version of the manuscript is too long and convoluted to effectively convey the most interesting aspects of this research.

Yes, it is true that the MS is long and we considerably reduce the text (We have deleted 5.3 section second and 4 paragraph; 5.4 section last paragraph; Fig.2. We also shortened the material and methods section, we recalculate the flux of OM according to reviewer#2 suggestions). However, we need specific guidance from the reviewer for further modifications.

The main arguments are not presented as clearly as they should be. In my view, the organization of the “Results” and “Discussion” needs to be adjusted. Part of the “Results” reads like a “Discussion” and vice-versa.

We agree in part with this point, however the main objective of our paper was to discuss the OM fluxes along with carbohydrates as well as to evaluate the diagenetic status of OM based on its carbohydrate composition. For this reason in the results section we indicated that our POC, DOC values are similar to previous studies (the same holds for carbohydrates) because we did not want to get into that in the discussion section which is trivial information and does not advance the ideas that we would like to develop. In the discussion section based on PCA we look for changes in the carbohydrate composition during flood and low water events, estimated carbohydrate fluxes for labile and refractory organic matter and finally we assessed the origins of OM based on the carbohydrate composition. All of this information was carefully discussed using the appropriate literature.

Technically, figures and tables should not be referenced to in the Discussion. I suggest that the authors present the results shown in figures and tables in the “Results” section only, following the order in which the figures and tables are presented. In the discussion, the results are used to support the arguments made in the discussion and are put in

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the perspective of other works.

We are not sure to understand the point of this argument. How can we discuss our results without referring to the figures? Besides, some important outcomes of the discussion are better presented in Figures. For example Fig.6a that shows the dependence of mannose with the flow rate is an outcome of our discussion (the same holds for Figs 2, 3; 6b). Is it possible to present this Fig. in the result section ? Again we need specific guidance from the reviewer to improve our MS for those points.

The manuscript also presents an overwhelming number of citations. In my view, these could be cut down a bit because this is not a review paper. The Methods also, tend to be lengthy and overly detailed and could be written more concisely. I think the manuscript needs be written more concisely and be properly organized.

We agree with the reviewer that the paper contains an overwhelming amount of references and consequently we deleted 20 references. It is true that the method section is long however, all given information is important especially for the separation/detection of other classes of sugars such as uronic acids (use of gradient conditions). We considerably decrease the text by deleting several sentences from the 3.2.2; 3.2.3 and 3.2.4 paragraphs.

Specific comments Tables: The tables are nice, clearly presented and very informative. However, I was wondering why the tables are not numbered followed the order in which they are presented in the results. Figure 4 should be Figure 2.

We do not understand the comment of the reviewer. Tables are numbered in the order that they are presented in the results (Paragraph 4.1.1: Table 1; Paragraph 4.12: Table2 and Tables 1 &3; Paragraph 4.14: Table 4).

Figures: I question the need for figure 1 since this information is already presented in Table 1. A map of the Rhone river + sampling site showing a time-series of river discharge could be a nice replacement.

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We agree with the reviewer comment that Figure 1 repeats a part of the results presented in Table1. However, we believe that the info is better presented in Figure while Table 1 includes additional information regarding OC% of particles, TSM (mg/ml), DOC/POC ratios etc. We believe that all of this info must be provided to the reader, especially if someone wants to look deeper in our results. In the revised we improved the quality of the Fig.1 according to the reviewer#3 suggestions. As the reviewer indicated previously our paper contains an overwhelming amount of information and needs to be shortened. An extra figure with the sampling location (total 7 figures) will make the paper heavier. We do not believe that such figure is necessary because the information about the location can be easily found in previous research articles (e.g. Sempéré et al. (2000), Olivier et al. (2010); Para et al. (2010)). All of these papers are cited in our article. In addition we sampled in only one station (Arles gauging station) and not in different areas within the Rhône River and therefore a map with only one sample point does not seem justified. If nevertheless the reviewer feels that this info is of great importance we can include it in a future version. Please also note that Fig. 2 was deleted

1) The sampling station is located about 50 km inshore, before the Rhone river actually flows through the Camargue region. Potential interaction between the river and the very productive marsh could potentially alter the estimated fluxes, especially during flood events. Is there any evidence that concentrations are not significantly different between Arles and the mouth of the Rhône River? Does the River interact much with the marsh (is the river levied?) (readers may not be familiar with this area). It would good to add some comments about this. If no evidence is available, then this problem should be clearly acknowledged.

This is an interesting comment. The gauging station in Arles is located in the Grand Rhône which does not cross the Carmargue Area (only the petit Rhone goes through this area) and therefore the fluxes measured at Arles are nearly the same to those at the mouth of river. This info was now included to the MS (page 6 line 140-141 from the

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top).

2) I understand that the PCA is used here primarily to look at changes in the carbohydrate composition of DOM and was performed using the concentrations of carbohydrates in POM and DOM. Most of the variance in the data set is carried by PC1, which simply reflects the change in the overall concentrations of carbohydrates (as is indicated by loadings approximating the value 1 in fig. 5). I would suggest doing the PCA on the relative abundance of carbohydrates (mol %) such that the principal components are indicative of changes in composition and not concentration. This is an interesting comment.

We performed again the PCA with the relative abundances of sugars and the result was completely different from that obtained with absolute values (concentrations). This is because we introduce a relation between the variables (sugars) due to the normalization. Glucose which is the most abundant sugar influenced the proportions of the other compounds. This approach using the proportions of sugars overtime provides different type of information. In our study our objective was to differentiate flood and non-flood events in terms of their carbohydrate composition. If one looks at Table No2 there are a lot of similarities in relative abundances of sugars between floods and low discharge periods (example: 21 May 2007 and 22 Oct2008 (flood); 17 Jan 2008 and 7 Feb 2009 (flood) etc) and therefore it is better to discriminate these events using absolute concentrations. Indeed the PCA showed that during flood events sugars have a unique composition compared to the low discharge periods (Fig. 4a). We believe therefore that this way is most appropriate to compare these contrasted events in the Rhône River.

3) The authors often use the correlation coefficient r to refer to the goodness of fit between linearly related variables. The authors should report the coefficient of determination instead (R^2).

We agree with this comment and we corrected in all Figures (2,3, 5 and 6) by giving

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the R^2 .

4) In section 2 (Study area and sampling): I think a map highlighting the river and its tributaries, the Camargue delta and the sampling site would provide a useful addition to this description of the study area.

See above

5) In section 3 (Methods): I did not see a method for TSM and for %OC. A one or two-line description would suffice.

DONE (see page 6 lines 152-161; methods section)

6) Please add a sentence or two describing the factor of Ferguson (1987) used to improve the estimated fluxes.

We have deleted the factor of Ferguson since annual fluxes were calculated using linear relationships and not log/log relationships (reviewer #2, comments). We also deleted the associated reference from the literature section.

7) I think the relationship $\text{Log (DOC)} = 0.23\text{log(Q)} + 1.34$ has a R^2 of about 0.19. Please justify the use of this relationship instead of using an average concentration of DOC to estimate the flux.

In the revised version DOC annual fluxes were calculated by multiplying an average DOC concentration with Q (reviewer#2 comments)

Technical corrections In some equation, the author used the napierian log (ln) (line 15, p11176) and sometimes the simple term (log) (line 21, p 11177). Does "log" refer to the log of base 10 here? Please, check for consistency.

We agree with this comment and we corrected as follows: $\text{OC\%} = -0.012\text{log(TSM)} + 0.054$ ($r^2 = \dots$) (see page 11 line 296 from the top)

Page 11184, Line 13: Change Orinico to Orinoco

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DONE

Page 11186, Line 20: the word “spectrum” should be replaced by “plot”

DONE

Page 11186, Line 26: replace “more than the half” by “more than half”

DONE

Last paragraph of section 4.1.4: The word “primarily” is not adequate because the ratio PCHO-C/DCHO-C is about 60%/40%.

We agree with this comment and we replace the word “primarily” with “mainly”

In section 5.6, the annual TOC input to the Gulf of Lions is to represent 1% of the standing stock of TOC. It is the said to be 2% in the Conclusions.

We agree with comment and we corrected in the conclusion 1%

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