**Biogeosciences
Discussions**

Interactive
Comment

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.

christos.panagiotopoulos@univmed.fr

Received and published: 3 April 2012

General comments Carbohydrates of both particulate and dissolved forms in the Rhone River which flows into the Mediterranean Sea were investigated in regard to their origin, diagenetic status and flux. Overall the manuscript appears to be written well. The data quality is likely high and the discussion is also appropriate. As mentioned by authors, there seem to be not so much previous studies on carbohydrates dynamics in river systems. However, the present study, against these studies, hasn't made special progresses in the research approach and techniques. And basically the conclusion obtained here is just to confirm the previous findings. Therefore it is strongly expected

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

that more unique and creative points of the present techniques and/or knowledge could be emphasized.

We believe that our paper provides new results on fluxes especially for the carbohydrate component in the Rhône River compared to the bulk of the organic matter and its relevant importance to the Mediterranean Sea. This point was acknowledged in the introduction, discussion and the conclusion of the paper. In addition for the first time we analyzed uronic acids and we showed that galacturonic acid which was previously missed by HPLC may provide important information about the origin of the carbohydrates. We believe that this information from a perspective point of view is very interesting for the readers. We agree with the reviewer that our foundings in the origins and the degradation status of carbohydrates did not revolutionized the terrestrial biogeochemistry of sugars however, we believe that they were appropriately discussed and confirmed/or advanced previous ideas.

In addition, there are some doubtful points as specified below. Especially the estimation of flux and the discussion about categorizing POC and DOC into labile and refractory fractions should be described more carefully.

We addressed most of the comments of the reviewer as best as we could and fluxes were calculated only for the sampled period according to reviewer #2 suggestions (see below).

It is also recommended that background data such as temperature, conductivity, chlorophyll and nutrients could be added (If they are not available in this study, related literatures could be cited).

The sampling station at Arles is among those routinely studied by the French community (Sempéré et al. 2000; Pont et al. 2002; Ollivier et al. 2010; Sicre et al. 2008, Eyrolle et al. submitted etc) and therefore background data information about temperature conductivity and nutrients can be easily found. We do not believe that all of this information is necessary to understand the biogeochemistry of sugars and

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

besides this will make the paper much heavier. Additional info can also be found at http://www.com.univ-mrs.fr/spip.php?rubrique49. The only parameter that we do not have any values during the sampling period is the chlorophyll but this was acknowledged in the paper and we cited previous work (Harmelin et al. 2010).

Specific comments 1. P.1172, L.10: The present filtration method missed part of dissolved (colloidal) fraction in the size range between 0.2-0.7 um. Why was the sequential filtration through a 0.2 um membrane after a GF/F filter used ? Is the missing fraction completely negligible?

We agree with this comment. The fact that we filtered through 0.7 μm and then 0.2μm was to avoid problems with the filtration (blinding) because our samples were quite charged in POM and therefore the filtration was not easy to carry out. We are aware that we missed with this procedure the 0.2-0.7 μm colloidal fraction, however previous studies in Rhône Estuary (salinity 0) indicated that the 0.01-0.7μm represented about 15% of the DOC (Sempéré et al. 1993). Therefore by performing a rough estimation the colloidal fraction within the size range 0.2-0.7μm would not represent more than 5% of DOC. Interestingly, other studies showed that most of colloidal fraction lies in <0.2μm fraction (McKenzie River; Whitehouse, 1989).

Sempere, R., Charriere, B., Cauwet, G., (1993) Importance of organic colloids in estuarine waters and continental margin. Annales de L'institut Oceanographique, 69, 167-171. Whitehouse, B., Macdonald, R.W., Iseki, K., Yunker, M.B., and McLaughlin, F.A.1989 Organic carbon and colloids in the Mackenzie River and Beaufort Sea. Marine chemistry 26, 371-378.

2. P.11172, L.18: Doesn't $CaCO_3$ degenerate partly under high temperature (450 C) into CaO ? The reaction $CaCO_3(s)$ $CaO(s)$ +$CO_2(g)$ occurs in high temperatures >800 °C. Above 550°C $CaCO_3$ begins to outgas CO_2 into the air. As the temperature of the combustion is set at 450°C it is unlikely that CaO is formed, therefore we believe that we do not produce CaO during this procedure.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

3. P.11178, L.4: Why didn't only DCHO load correlate with Q. As far as we estimate from the uniform relation between POM and DOM that is shown in Fig.6., DCHO might have indicated the same relation as PCHO. We recalculated DOC and DCHO according to reviewer#2 suggestions. Annual fluxes of DOC and DCHO were obtained by multiplying average DOC/DCHO values (Table1 & Table 3) with the daily water discharge.

4. P.11178, L.14: The intention of this correction should be explained in further detail. This point was deleted.

5. P.11180, L.10: The method for estimating LPOC should be explained in further detail. We believe that this information is already given in the paper since we refer to the papers of Meybeck, 1982 and Ittekkot, 1988. These authors indicated that : 0-15 mg/L TSM LPOC makes up 35.2% of POC 15-50mg/L TSM LPOC makes up 46.6% of POC 50-150 mg/L TSM LPOC makes up 22.1% of POC 150-500 mg/L TSM LPOC makes up 11.8% of POC Etc...... As it can be seen most of LPOC lies between 0-50mg/L TSM concentrations. We believe that in the discussion section we do not need to repeat this information which can be easily found in these papers. However, we agree with the reviewer that a minimum info must be given and we did so in the figure 3 legend.

6. P.11181, L.25: It is no surprise that the LDOC estimated from multiplying DOC by DCHO/DOC ratio correlated with DCHO. LDOC should be estimated only using the ratio of LDOC/DOC ratio (15%) in the literatures.

This is an interesting comment. Previous studies based on carbohydrate and amino acid measurement showed that LDOC constitutes 10-30% of the total DOC (with a mean of 15%) indicating that carbohydrates constitute the major fraction of labile DOC (Spitzy and Ittekkot, 1991; Volk et al. 1997). In our paper we had the unique opportunity to measure the carbohydrate component of DOC and therefore it is seems to us appropriate to calculate LDOC based on our carbohydrate measurements. The above

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

literature is cited in our text. We are aware that our LDOC fluxes are likely underestimated because we have not measured the amino acid component but this point was explained in text.

7. P.11182, L.23: POC was measured with a CN analyzer. In this case, the data of C:N ratio of POM is generally available. If so, C:N data should be included in discussion. If not, why ?

We agree with comment, but we have not measured N in this study. Our main objective was to follow the carbon and the carbohydrate fluxes. Note that carbohydrates do not contain nitrogen (except amino sugars which are generally a small portion of total carbohydrates) and therefore we have not look at nitrogen. Yes we agree that this was a missed opportunity.

8. P.11184, L.19: It should be clarified if cellulose could be hydrolyzed with the method used in this study.

In our study we performed the hydrolysis of samples in two steps (page 8, lines 206-211). (a) 12M H_2SO_4 for 2h at room temperature and then (b) dilution to 1.2 M and hydrolysis for 3 h at 100°C. This procedure is commonly used for environmental terrestrial samples resulting maximum yield of sugars and especially for glucose pointing to an effective depolymerization of cellulose (Cowie and Hedges, 1984, Mopper, 1977; see also review by Panagiotopoulos and Wurl, 2009). In contrast mild hydrolysis conditions may not depolymerize completely the cellulose and are generally used in aquatic samples where the amount of cellulose is relative small. We believe that all of this info is outside the scope of this paper and additional info can be easily found in literature cited in text (see review by Panagiotopoulos and Sempéré 2005 Limno. Oceanogr. Methods, Cowie and Hedges, 1984, Mopper, 1977; Panagiotopoulos and Wurl 2009).

9. P.11184, L.25: It should be clarified why fructose was not detected. It was not truly existing or due to any analytical problem ?

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

We agree with this comment and we have deleted this paragraph regarding the fructose which may confuse the readers. As a matter of fact very few studies in terrestrial or aquatic environments reported fructose concentrations, because this monosaccharide is generally destroyed during acid hydrolysis. In our study we did not detect fructose.

10. P.11186, L.25: The unit "uMC" should be removed from the equations. The multiplying symbol "X" should be added to the equation. The correlation among the other sugars should be presented.

DONE

11. P.11186, L.11: For "Fig.5C" read "Fig.5b"

DONE

12. P.11188, L.11-18: This paragraph should be moved to the next section "5.5".

In this paragraph we intended to explain other possible reasons for the low abundances of xylose found in DOM and not assess the diagenetic status of sugars as we did in next section. Therefore we believe that this paragraph is justified in this section.

13. P.11188, L.19- : This description needs some evidences such as chromatograms of LC. Otherwise, it is better to remove the whole of this paragraph.

We agree with this comment and we deleted this paragraph from the MS

14. P.11192, L.10-13: Importance of the glucose flux should be discussed in further detail with comparing to something (such as other substances flux).

We agree with this comment and in the revised version we compared the flux of glucose with the fluxes of total nitrogen, phosphorus, and silicate (see page 23, lines 664-670). Unfortunately we did not found any relevant work in this specific sampling station dealing with the fluxes of other organic compounds (i.e amino acids) to compare different organic species. If the reviewer has a paper in mind we will happy to included in a next revised version.

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

15. Relative abundance (%) of individual sugar was calculated relative to total amount of sugars, but sometimes it was calculated on a glucose-free basis. In the latter case, it should be confirmed that glucose % is not significantly changed. And it should be clarified why the calculation on a glucose-free basis is useful.

Glucose is the dominant sugar in highly degraded material as well as in fresh and labile DOM and generally accounts > 30% of the total sugars. Due to its high abundance it tends to force parallel trends in the relative proportions of the other less abundant sugars. For this reason most of the compositional parameters presented in this study were calculated on glucose free-basis. This approach has been used by John Hedges (Cowie and Hedges, 1984; Geochim. Cosmochimica Acta 1984) and then by many others (D'Souza and Bhosle, 2000; Panagiotopoulos and Sempéré, 2005; Khodse et al. 2007; Hedges et al. 1994 etc). Some of these papers are cited in our article. We believe that there is no need to explain why this calculation is made such a way since the info can be easily found in these papers. Note that the original paper Cowie and Hedges, 1984 is cited in our article.

16. The term "carbohydrate" and "sugar (or monosaccharide)" should be chosen appropriately.

We agree with this comment and we went through the text and made the appropriate corrections For some specific carbohydrates we can not use the term deoxy-carbohydrates these compounds are referred in literature as deoxy sugars. As such we keep this term all over the text.

17. Fig.1: A few bars of POC and PCHO indicating extreme high values should be replaced by a broken bar and the vertical axis should be also splited.

DONE

18. The lower panel in Fig.2 could be deleted because it is repeated in Fig.1.

We completely deleted the Figure 2 from the MS.

19. Fig.3&4: It should be explained in the caption how to estimate LPOC.

See above

20. Fig.6: What is the dotted line drawn in the graph?

The dotted line in Fig. 6 corresponds to a DOC/POC ratio of 1. As it was explained in the text (page 17, last paragraph) low water events are characterized by DOC/POC and DCHO/PCHO ratios higher than 1 while during flood events the opposite trend in observed. We believe that this dotted line makes our statement easier to readers to understand this result.

Interactive comment on Biogeosciences Discuss., 8, 11165, 2011.