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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.

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This manuscript investigated particulate and dissolved organic matters, including POC, DOC, dissolved and particulate monosaccharides (measured by the HPAEC method) in the Rhone River into the Mediterranean Sea. It is known that carbohydrates and some specific sugars, produced by phytoplankton and bacteria are important for organic matter transportation, degradation status of organic matter and trace element cycling etc. Nevertheless, little is known about the flux of particulate and dissolved monosaccharides from river to the ocean. Authors estimated the annual fluxes of total suspended matter (TSM), particulate organic carbon (POC), dissolved organic carbon

(DOC) and particulate monosaccharides (PCHO) based on the relations between water discharge and TSM, POC, DOC, PCHO etc. The data indeed showed significant seasonal variation (flood and non-flood conditions) in their samples indicating that extreme flood events play an important role on annual fluxes of TSM, POC, DOC and PCHO. During non-flood seasons, these parameters seem to be related to organism (phytoplankton and bacterial) activity or/and terrestrial influence. The authors did a good interpretation on their seasonal variations. However, the biggest weak portion of this manuscript is on the method which is used to estimate annual fluxes of TSM, POC, DOC, PCHO etc. Basically, the authors used log-log figures (e.g. water discharge vs. TSM Fig. 1) (same as previous authors) to calculate previous TSM, POC, DOC fluxes. It looks like that both r and p are very good when both parameters are changed to log scale. However, if one looks the detailed relations between water discharge and TSM, POC, etc., the relations are quite complicated (Fig. 2). As a consequence, some of the data will be significantly under- or over-estimated (see detailed comments below) if one uses the equations listed on lines 21-24 at page 11177. My major concerns are that the authors should carefully process their data and only estimate fluxes of TSM, POC etc. during the sampling period.

All of these comments were addressed and fluxes were calculated only for the sampling period. See below and in the revised MS.

The presented total sugar level is different from the reported data. This could be caused by different method like spectrophotometry or HPLC etc. The authors need to mention it in the text. Additionally, I also found that the manuscript is too long and need to be largely shortened. Overall, I suggest that the manuscript should be published after major modifications.

We do not understand here the comment of the reviewer. Which sugar data are different from the reported data? In our paper we compared our sugar results (obtained by HPLC) with those in literature and they were in good agreement. What kind of spectrophotometric data the reviewer refers to? We agree with the reviewer that the paper

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was quite long and we remediate it. In particular we have shorten the materials and methods section and we have deleted several paragraphs from the discussion section (5.3 section second and 4 paragraph; 5.4 section last paragraph; see also methods section).

The specific comments are as follows: Abstract The annual fluxes only need to be reported from 2007 o 2009 (or in 2008) because the log-log figure (Fig. 1) looks good visionally, while the relations between water discharge and other parameter are not so good (Fig. 2). As a result, the estimated previous fluxes contain large uncertainty or even data are questionable. DONE

Method In this section, I did not see where is OC% (called weight percentage of organic carbon, reported in Table 1) measured by. . ... DONE

P 11177, 4.1.3 Relations between.. and 4.1.4 Annual fluxes. . .. In these two sections, I suggested that the authors need to re-process it. The reasons are: (1) the increased TSM (same as POC, DOC etc.) did not linearly correlate with water discharge (as mentioned early, if the log-log figures look much better). One can use water discharge to estimate other parameters, if a linear relationship between two parameters (water discharge vs. TSM, POC, DOC etc) exists. The fact is that TSM discharge is not proportional to water discharge. For example, similar water discharge (3822 vs. 3817 m3/s) resulted in different TSM (920 mg/L vs. 388 mg/L). Same as POC, when the water discharge was 3822 m3/s, the POC conc. was 2334 uM. However, in another flood case, when the water discharge was 3817 m3/s, the POC conc. was 412 uM, approximately 5 times lower than 2334 uM.

Daily TSM measurements were available from 2007-2009 therefore TSM fluxes were calculated by multiplying TSM values with the corresponding flow rate (see page 12 lines 341-345 from the bottom in the revised MS). In such a way we do not need to establish a relationship between TSM and Q to estimate TSM fluxes. In the initial submitted MS the relationship between TSM and Q was established because we intended

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Discussion Paper

to extrapolate our results and provide fluxes for TSM from 2001-2010. For POC and PCHO fluxes estimation (for the sampling period 2007-2009) two linear relationships were established:

(POC)= 0.1154(Q)-112.99 (n=23; r=0.90) (1) (PCHO)= 0.0012 (Q)-1.0077 (n=23; r =0.94) (2)

These relationships were made after excluding 2 experimental points (20 May 2008 flood & 8 Sep 2008 flood) which we believe that they are not related to the dynamics of the system. Interestingly enough these events have extreme POC values (2334 -1311 μM C; the highest in the whole POC data set, see Table 1) which is also reflected to the PCHO-C pool. We do believe that our values are good however, they do not represent well the dynamics of the system. For example the 30 May 2008 (flood) event was related to artificial releases of water occurred in the Serre-Ponçon dam (located approximately 250 km in the north-east of the sampling station). This event can not be considered as representative of a flood (http://www.youtube.com/watch?v=CZQRynjJX4g). This information was acknowledged in the initial submitted MS. The second event (8 Sep. 2008) was due to an exceptional watershed overflow occurred 200 Km in the North. This info is also included in the MS.

Another case is on the relation between water discharge and DOC, for example, under flood conditions, the maximum DOC concentration was 216 uM (observed on 8 Sep. 2008) and water discharge was 2983 m3/s, while the water discharge on maximum flood was 4800 m3/s (observed on 7 Feb 2009) and DOC concentration was only 164 uM.

Yes we agree with the point; however we believe that these differences of DOC concentrations are most likely associated with the sampling (the same holds for the other parameters). Our measurements represent a snapshot during a flood event. If the measurement takes place at the beginning of the flood DOC values are likely to be high, while if it occurs at the end of the flood DOC values are much lower than the

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beginning of the flood. We agree with the reviewer that a more extensive sampling during the flood event is necessary to monitor the changes on TSM, POC and DOC parameters and provide accurate annual fluxes. However this is not always possible because it is not easy to predict a flood event and secondly the duration of a flood may be quite short and therefore completely miss it. In this paper we tried to interpretate our current results as best we could aiming to provide for the time carbohydrate fluxes for the Rhône River.

It is pronounced that good linear relations between water discharge and TSM (POC or DOC) did not exist. The authors should know that the fluxes of TSM, POC (or DOC) during flood events contribute more than 60∼70% of bulk TSM, POC (or DOC). In other words, the maximum uncertainty of annual fluxes is from flood events because the water discharge (concentrations of TSM and POC) is significantly higher than that during non-flood seasons. (2) the authors have all water discharge data, but only have a few TSM, POC, DOC data as compared to discharge data. As I mentioned above, fluxes of TSM, POC are dominated by the flood events. The concentration of TSM, POC and DOC data need to be intensively monitored at least during the flood event.

We agree with all of these comments and we processed our data with great attention to estimate annual fluxes.

I think some papers reported similar TSM or POC fluxes affected by extreme atmospheric events either in riverine system (Huh et al., 2009 in Marine Geology) or marine environment (Hung et al., 2010 in Biogeosciences; Hung and Gong, 2011 in Oceanography). These reports all emphasize that typhoons (or called hurricanes) can contribute significantly to TSM, carbon export fluxes. Therefore, I strongly suggest that the authors should focus on the effect of extreme atmospheric events on carbon (and other compounds) fluxes.

We agree with this comment that TSM and POC are affected by extreme events nevertheless these kind of events (typhoons) are not observed in the Rhône River and

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therefore such a comparison seems pointless to us. In the original submitted MS we clearly indicated that the Rhône River exhibits two periods of peak discharge: a spring peak related to snowmelt in the Alpine and Massif Central watersheds and a fall peak related to storm events originating from humid air masses over the Mediterranean Sea. These events control mostly the flood episodes that occur in the sampling station. Which extreme atmospheric events has in mind the reviewer?

Finally about the annual flux, I used the equations listed at page. 11177 to calculate the concentrations of TSM, POC, PCHO, and DOC (see the Fig. 3). Here I defined the calculated TSM as predicted (Pre.) TSM, same as POC, DOC and PCHO. I found that it exists a significant difference between predicted TSM and measured TSM (Fig. 3). These figures (Fig. 3) clearly demonstrate that the log-log relations are not a good approach to estimate annual TSM, POC etc. flux since the predicted data are significantly biased.

We used the equations (1) & (2) see above and we calculated the predicted and the estimated POC and PCHO. The bold line represents 1:1 slope.(See attached Figure)

The slopes for both parameters (POC, PCHO) are close to 1 which indicates that the above can be used to estimate POC and PCHO fluxes for the sampling period 2007-2009. Because DOC and DCHO did not correlate with the water discharge, the average value obtained for DOC and DCHO during the sampling period (see Table 1 and Table 3) was multiplied with the corresponding flow rate to estimate the annual flux.

P. 11180, the authors compared their LPOC data to others. . . I can not follow the same clasificantions and estimated labile POC fluxes. based on a specific range (0-15, 15-50, 50-150 mg/L, etc.), Unclear

In the figure 3 legend we gave more explanations how LPOC were estimated. Basically previous studies (Meybeck,1982; Ittekkot , 1988) 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

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11.8% of POC Etc. . .. . . As it can be seen most of LPOC lies between 0-50mg/L TSM concentrations.

Conclusions P11192, 4th paragraph needs to be re-worked using new results or just emphasize the contribution of extreme atmospheric events (flood) on TSM, carbon, etc. fluxes. Because of global warming, extreme

We used the new results calculated from the linear relationships and we provided fluxes only for the sampling period.

Table 4 As mentioned above, these estimated values were based on the log-log relations which may have large variations. I suggest it needs to be re-calcuated.

All parameters were recalculated according to reviewer#2 suggestions and the results are now provided in Table 4.

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

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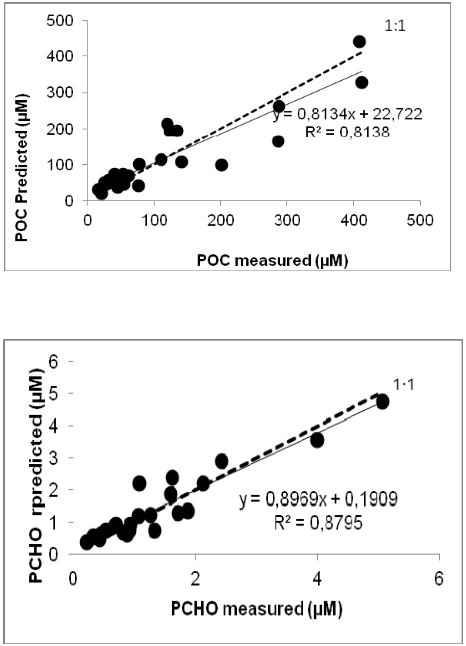

Fig. 1. Figure predicted/measured values for POC and PCHO