Review of “The composition and flux of particulate and dissolved carbohydrates from the Rhˆone River into the Mediterranean Sea” by Panagiotopoulos et al.

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.

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. 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.

Method

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

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.

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. 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. 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.

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.

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
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
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.

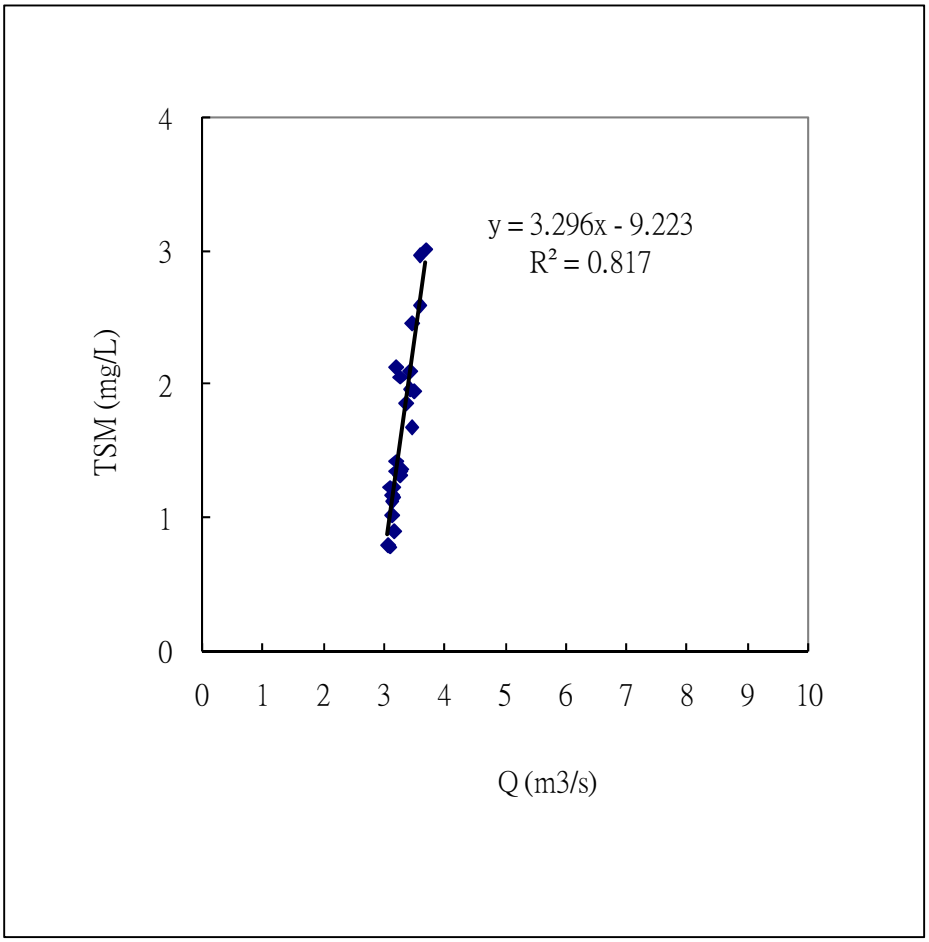

Fig. 1

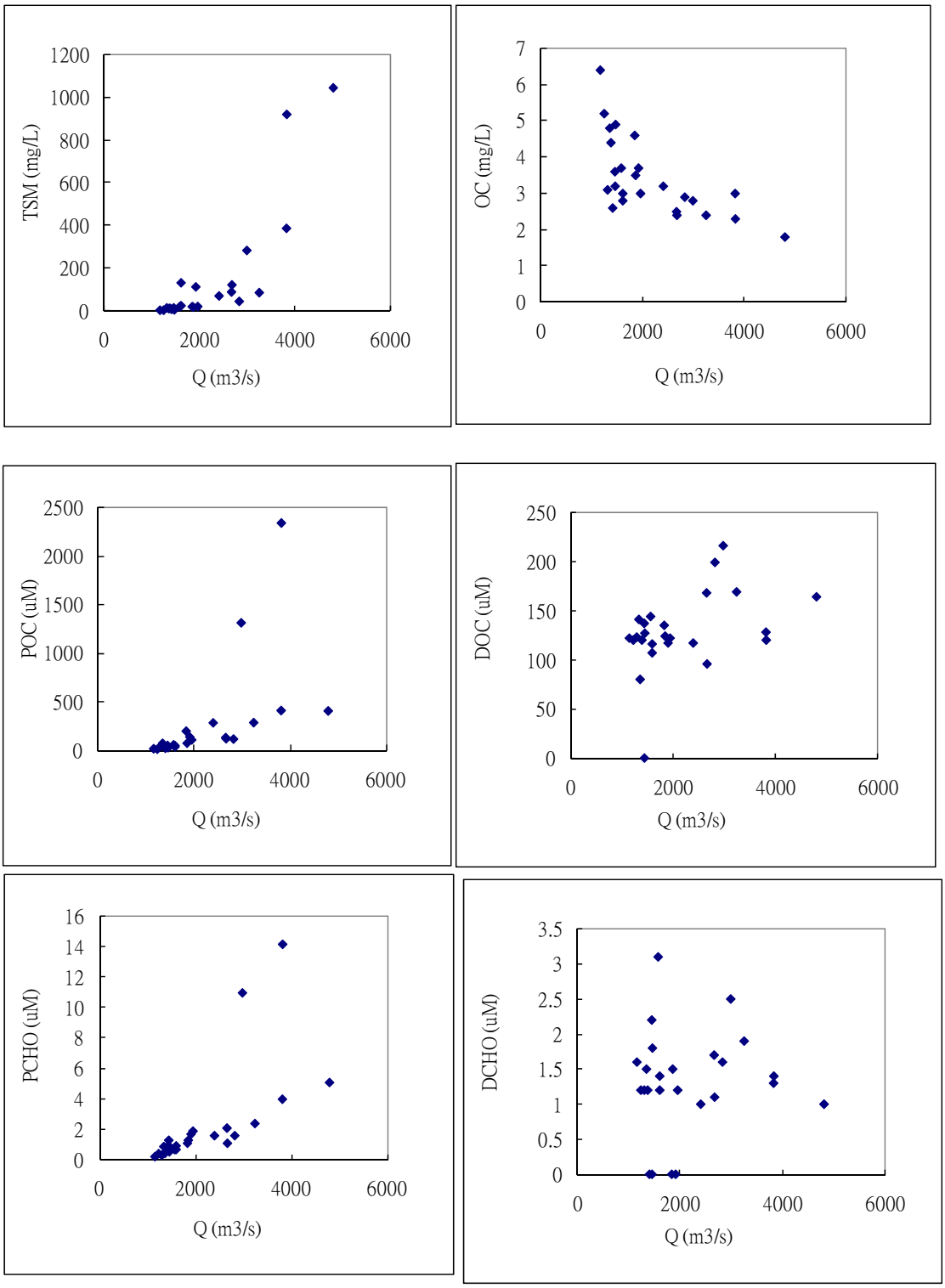
TSM (mg/L)
1200
1000
800
600
400
200
0
0
2000
4000
6000
Q (m3/s)
OC (mg/L)
7
6
5
4
3
2
1
0
0
2000
4000
6000
Q (m3/s)
POC (uM)
2500
2000
1500
1000
500
0
0
2000
4000
6000
Q (m3/s)
DOC (uM)
250
200
150
100
50
0
0
2000
4000
6000
Q (m3/s)
PCHO (uM)
16
14
12
10
8
6
4
2
0
0
2000
4000
6000
Q (m3/s)
DCHO (uM)
3.5
3
2.5
2
1.5
1
0.5
0
0
2000
4000
6000
Q (m3/s)

Fig. 2

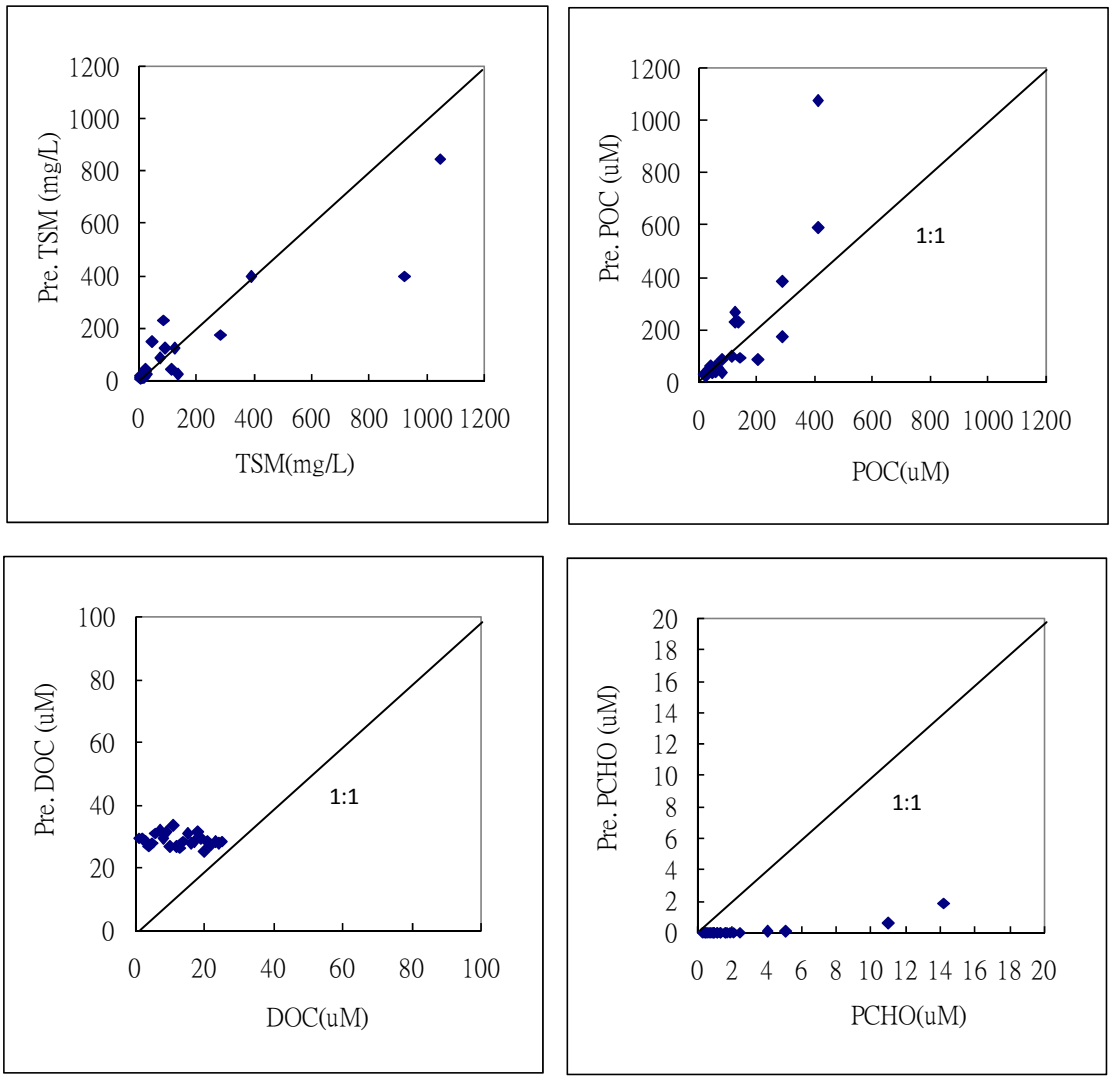
Pre. TSM (mg/L)
TSM(mg/L)
Pre. POC (uM)
POC(uM)
1:1
Pre. DOC (uM)
DOC(uM)
1:1
Pre. PCHO (uM)
PCHO(uM)
1:1

Fig. 3