Reply to referee 2 (Nicolas Savoye)

M. Higueras, P. Kerhervé, A. Sanchez-Vidal, A. Calafat, W. Ludwig, M. Verdoit-Jarraya, S. Heussner, and M. Canals
"Biogeochemical characterization of the riverine organic matter transferred to the NW Mediterranean Sea"

General overview

The manuscript of Higueras et al reports fluxes of total suspended matter (TSM) and of particulate organic carbon, along with stable isotope ratios of particulate organic matter (POM) in order to investigate its origin in eight rivers of the NW Mediterranean Sea. These eight rivers are one large river (the Rhône River) and six small coastal rivers.
The scientific goals of the ms (assessing "the quantity and quality of POM discharged into the NW Mediterranean Sea" "investigating their role in the transport of POM according to their watersheds and anthropogenic uses, as well as the occurrence of meteorological events") are of high interest in coastal biogeochemistry. In addition, the large spatial footprint highly increases the potential interest of the manuscript.
However, the present version of the ms suffers from few issues that necessitate the ms to be revised. Especially much information is missing in the methods, few bad interpretations and/or unneeded information have to be removed and/or corrected. At last, I think the interest of the ms could still increase by adding PN fluxes and comparing the studied systems with other systems.

Dear Dr. Savoye,

We thank you for your careful review of the manuscript and for your useful comments. We have considered all your recommendations and have included in the manuscript. Next, we provide detailed responses to your comments (in blue text).

Detailed main comments

PN fluxes
Why PN fluxes are not estimated in the same way as POC fluxes? There is a lack of literature regarding PN fluxes. The ms would participate in filling the gap. I encourage authors to perform these calculations and add the results in the manuscript.
Response: PN fluxes have been calculated and added in the table 3.

Comparison with other systems
POC and TSM fluxes calculated in the present ms are compared to other estimates from previous studies dedicated to the same systems. It would be very interested to compare POC and TSM fluxes estimated in the present ms to fluxes from other systems in order to state on how the studied systems range in a river typology. Many POC and/or fluxes were estimated in the literature (e.g. Schäfer et al., 2002; Polsenaere et al., 2013; see also papers from W. Ludwig and co-authors and references cited in Harmelin-Vivien et al, 2010).
Response: According to the review's suggestion, POC and TSM fluxes have been compared to fluxes from other systems.

Results *versus* discussion

Section Results, even if quite short, is almost an exhaustive description of all parameters for the two kinds of rivers (Rhône River versus coastal rivers) without really pointed out key results. In contrast, large paragraphs of section 4.1 (from page 13288 – line 20 to page 13289 – line 25) are more results than discussion and point out key results (especially the impact of storms to the different parameters). Thus, I suggest 1) rewording the section Results in the latter manner in order to drive the reader to what the discussion will be (this is valid for the whole section) and 2) removing the lines cited above from section Discussion and replace them by few summarizing sentences only.

Response: 1) The section Results has been reworded. 2) these lines have been removed from Discussion.

Riverine OM transferred to the NW Mediterranean Sea or to the NW Mediterranean estuaries?

It looks like, from section Methods, that sampling stations are upstream the estuaries.
Thus, because of the sampling design, the study is dedicated to the riverine OM that is transferred to the NW Mediterranean estuaries but not to the NW Mediterranean Sea.
However it could be assumed that what is transferred to the estuaries arrives to the sea if the processes that occur in estuaries (especially sedimentation and OM consumption / remineralisation) are negligible compared to transport. This may be valid forshort residence-time estuaries. However, I wonder if this assumption is valid for the Rhône estuary. Other studies dedicated to other estuaries have shown that the riverine organic matter can be deeply transformed or reworked prior its arriving in the seas/oceans (e.g. Fankignoule et al., 1998; Middelburg et al., 2007). This assumption should be stated and discussed.

Response: As the Mediterranean Sea is a microtidal sea, mouths of Mediterranean rivers are called deltas and not estuaries. In these deltas, the seawater may enter in rivers along the bottom up to several 10 km upstream the mouth. All the studies performed on sediment inputs from these rivers have always considered their marine prodeltas as the main locations where riverine particle are sedimenting (e.g Rhône river: Lansard et al., 2007 SotTE, Cathalot et al., 2013 GCA, Po River: Miserocchi et al. 2007 CSR; Ebro river: Puig et al. 2001 Marine Geology).Thus, all the studies that estimated river fluxes (e.g TSM and POC) assumed that this material is discharged into the Mediterranean Sea (i.e for the Rhône river and Têt river: Cauwet et al., 1990, Sempéré et al., 2000; Garcia-Esteves, 2005; Ludwig 2003). Moreover, the Rhône station as the Têt station have been designed to monitor the river inputs into the Mediterranean Sea Ocean Observing System on Environment (MOOSE).
Precisions added in Sampling strategy and Discussion.

Methods

Much information is missing in the methods:

- Indicate, for each river, if the sampling station is located upstream, within or downstream the estuary (it looks like all stations are upstream).

Response: The locations of stations have been chosen in order to guaranty the collect of freshwaters without saltwater intrusions. Further information on the sampling locations have been added in the subsection Sampling strategy.

- Indicate how long the water samples were stored at 5°C and darkness before the filtration.

Response: Added in the subsection Sampling strategy.

- GF/F filters and their analysis: what was the diameter? Indicate if a single filter

was analyzed for all parameters (TSM, POC, PN, C and N stable isotopes). If yes, was the filter punched? Were blank filters performed? If yes, were they taken into account for data correction? For what parameters? How?
Response: Corrected according to the review's suggestion.

- Were LECO CN 2000 and GVI Isoprime connected for the isotopic analyses? If not which EA was connected to this IRMS?
Reponse: Precisions have been added in the subsection Analytical method.

- What kind of internal standards were used to calibrate the IRMSs? Against what reference material the internal standards were calibrated?
Reponse: Precisions have been added in the subsection Analytical method.

- Were the two IRMS inter-calibrated (e.g. by analyzing aliquots of different samples) in order to ensure they give the same results?
Response: As both laboratories were using the same IAEA reference materials, no inter-calibrations have been performed between both EA-IR/MS systems. However, $\delta^{13}C$ intercalibrations have been successfully performed on Rhone suspended materials between both EA-IR/MS systems from the CEFREM (Univ. Perpignan) and the LSCE (Gif-sur-Yvette) (see Cathalot et al., 2013, Geochim. Cosmochim. Acta 118, 33-55).

- Add a paragraph explaining how coefficients a and b were estimated for the regressions that appear in Table 2 and Figures 6-8.
Response: Coefficients a and b are regression coefficients. These coefficients have been estimated with EXCEL software with the power functions: $TSM=a \cdot Q^b$, $\%POC=a \cdot TSM^b$ and $\%PN=a \cdot TSM^b$. We respect this suggestion, but after discussion with co-authors, we consider that is not pertinent add a paragraph explaining how coefficients has been estimated. Moreover, the first reviewer did not suggest to add this paragraph.

Also indicate that only significant regressions (p-value < 0.05) were considered.
Response: Added according to the review's suggestion

Principal Component Analysis (section 3, last paragraph; section 4.2, last paragraph, Fig. 5) It is very welcome to use multivariate analysis for investigating the environmental forcing to core parameters or processes and I deeply encourage authors to perform this kind of analysis. However, in the present study, the PCA is erroneously described and interpreted, the way it is performed is not optimal, and finally, it is not needed in this case.

Analytical method: it looks like data were scaled prior to carrying out the PCA. This should be stated.
Response: Precisions have been added in the subsection Analytical method (a centred and standardized PCA was realized so as to homogenize variances of the various variables).

Also, it should be more informative for the reader to know in this section what the objective of this analysis is.
Response: Precisions relative to the aims of the method have been added in the subsection Analytical method: The aim of this ordination method is to represent the data along a reduced

number of orthogonal axes, constructed in such a way that they represent, in decreasing order, the main trends of the data.

It looks like the idea is to investigate if Q and TSM are forcing parameters (= drivers) for the core parameters (%PN, %POC, $\delta_{15}N$ and $\delta_{13}C$).
Response: In PCA, the analysis is unconstrained, and so are the results. Simple (unconstrained) ordination analyses one data matrix and reveals its major structure in a graph constructed from a reduced set of orthogonal axes. It is therefore a passive form of analysis, and the user interprets the ordination results *a posteriori*.

Results and discussion: the two groups of parameters (Q and TSM on the one hand, %PN, %POC, $\delta_{15}N$ and $\delta_{13}C$ on the other hand) are orthogonally projected. Contrarily to authors interpretation, this means that these two groups of parameters are independent, i.e. that there is no statistical link between these groups, i.e. that Q and TSM does not drive the core parameters.
Response: This remark is erroneous: regarding the active variables, those that were significant (according to test values) on the first axis were: Q, TSM and $\delta_{13}C$ on the one hand, and %PN, %POC, and $\delta_{15}N$ on the other hand. This structure doesn't means that there is no statistical link between these groups. It means that both groups are negatively correlated and within a same group variables are positively correlated each others. Therefore, a sentence was added in the result section in order to help the reader to interpret the results.
For instance, on the first axis, POC, PN and $\delta^{15}N$ are positively correlated between them but are negatively correlated to Q, TSM and δ13C.

This looks in contradiction with the data interpretation that appears in section 4.2 and that is illustrated on figures 3 and 4.
Response: The above precisions indicate that results of the PCA are not in contradiction with figures 3 and 4 and section 4.2.

In fact, I guess that a statistical link may appear if PCAs would have been performed for each single river. Indeed core parameters do not respond in a similar manner to Q and TSM depending on the river, i.e. depending on the river hydrological regime. For instance during drought periods $\delta_{13}C$ is low in the Hérault and Aude river but high in the Fluvià river, whereas $\delta_{13}C$ is constantly high in the Orb river, whatever the Q conditions. This precludes any statistical relationship between Q and $\delta_{13}C$ at the scale of the 8 rivers.
Response: The objective of the performed PCA was to summarize the main trends and relationships between variables for the eight rivers simultaneously and not for each river independently that helps identify what are the rivers that share the same characteristics. As explained, even at the scale of the 8 rivers and without constraint, a link appears between forcing and core parameters (and also, a positive correlation between Q, TSM and $\delta_{13}C$).

A better way to perform PCA in order to look at environmental parameters as drivers for core parameters is to consider these environmental parameters as 'supplementary variables' (e.g. Berto et al., in press).
Response: In our case, this option is not possible because it is not possible to make a PCA with only two active variables.

Another option would be to perform a redundancy analysis (e.g. Savoye et al., 2012). However, I am sure that the message delivered by these analyses would still be that Q and TSM does not drive the core parameters at the scale of the 8 rivers.

Response: We preferred used an unconstrained ordination analyses rather than a constrained method such as RDA. In the unconstrained ordination analyses, the ordination procedure itself is not influenced by external variables; these may be only considered after the computation of the ordination. One lets the data matrix express the relationships among objects and variables without constraint. This is an exploratory, descriptive approach.

Figure 5: authors cannot superpose the correlation circle and the factorial plan since at least (it is not the only reason) the units are not the same. This would lead to misinterpret the results.
Response: Indeed, while the correlation circle and point cloud may not be superposed in theory; in practice, the use of a biplot (i.e. a plot showing two types of results, here the sites and the variables) is very common and accepted. The SPAD software display optimally (by scaling) objects and variables together in a PCA biplot thus minimizing the risk of misinterpretation. Please refer to Legendre and Legendre (1998, Numerical Ecology) for a complete account.

Finally: I suggest removing the PCA from the ms since it is not useful and it may add confusion to the reading of the ms. The discussion can stand without this PCA.
Response: We believe that the ACP has an interest because it allows to summarize the relationships between all the variables considered simultaneously, which was not shown in the other figures or analysis. This is why we would like to keep this analysis, especially since the first reviewer did not suggest to remove or modify this part.

Other comments

Title
Authors should add 'particulate' in the ms title since the ms deals with particulate organic matter and not dissolved organic matter. Thus, the title would be "Biogeochemical characterization of the riverine particulate organic matter transferred to the NW Mediterranean Sea".
Response: Precisions have been added in the title

Snowmelt *versus* storms
Since snowmelt events have similar impacts than storm events on the studied parameters, I suggest pointing out the former as much as the latter in sections Results and Discussions as well as in figure 2.
Response: Corrected in figure 2, in the section Results and Discussion (§4.1)

Introduction: page 13280, lines 7-15
The details regarding long-term changes are not needed in the Introduction. I suggest removing them.
Response: We respect this suggestion, but after discussion with co-authors, we consider this description on pressures (climatic and human uses) affecting the coastal rivers as pertinent to better understand the actual functioning of coastal rivers. These rivers are suffering of a long-term decrease of water flows and of an OM-enrichment (eutrophication) during low water stages. Moreover, as the first reviewer did not suggest to remove or modify this part, we would like to keep it.

Introduction: page 13280, line 27 and followings

Author should clearly explain why one needs to "assess the origin and nature of the organic matter discharged by Mediterranean rivers to the continental shelf for understanding the carbon and nitrogen cycling". In other words, what would change in the C and N cycling if the nature of POM would change?
Response: Added according to the review's suggestion.

Introduction: page 13281, lines 13-21
No need to deeply detail the values for each studied years. The overall values would be enough.
Response: Corrected according to the review's suggestion.

Study area: page 13282, first paragraph
Indicate that the Rhône river also receives water from the Central Massif, either one would not understand why "The third rainstorm […] (that) triggered intense rainfall in the Central Massif […] increased Q values […] in the Rhône" if the Rhône river is introduced as of Alps origin only.
Response: Corrected according to the review's suggestion.

Study area: page 13282, other paragraphs
I think river characteristics given in these paragraphs would better be placed in a dedicated table. The text should only give the main gradients among and the main differences between the rivers. This would rend the reading nicer.
Response: River characteristics have been placed in a table (table 1) and the text has been reworded.

Delta notation: equation and figures
Use the new IUPAC notation (Coplen, 2011).
Response: Corrected according to the review's suggestion.

Discussion: page 13291, lines 18-19
"Rhône River, the low water stages do not produce stagnant waters that enhance the primary production as in coastal rivers". Is this a statement from the literature? If yes, cite a ref. If no, this should be argued.
Response: Though the Rhone River is characterized by short water residence time (fast flowing rivers), we prefer to delete the sentence about the stagnant waters and to focus our explanation on the relative low freshwater phytoplankton production owing to the high turbidity. All this discussion on residence time, turbidity and freshwater phytoplankton biomass has been previously reported in Harmelin-Vivien et al. (2010)

Discussion: page 13293, line 18
In freshwater systems, phytoplankton $\delta_{13}C$ can be even more negative (see Savoye et al., 2012, and references therein). Authors' data set better match such low values.
Response: Corrected according to the review's suggestion.

Discussion: from page 13294 line 20 to page 13295 line 4
These lines dedicated to DIC origin and isotopic values in river systems are partly erroneous (e.g. rock dissolution is not cited as a source of DIC) and in fact not needed. I suggest replacing these lines with few sentences explaining that DIC $\delta_{13}C$ is highly 13Cdepleted in river systems compared to marine systems and that consequently $\delta_{13}C$ of riverine

phytoplankton is highly 13C-depleted in river systems compared to marine systems (e.g.Chanton and Lewis, 1999), with values even more negative than C3-plants.
Response: We agree that the long explanation on DIC were far to be exhaustive and therefore not pertinent. Thus, as suggested, we replaced these lines with a single sentence.

Discussion: page 13295, line 7
This is not correct for "spring (Tordera River)". Reword the sentence.
Response: Reworded according to the review's suggestion.

Discussion: page 13296, lines 13-14
What is written regarding high $\delta_{15}N$ and nitrification in lines 3-12 is correct. However, this is valid when phytoplankton dominates the POM. For instance, this process may explain the concomitant decrease in $\delta_{13}C$ (that may reflect the increase in phytoplankton dominance within the POM) with the increase in $\delta_{15}N$ in the Aude river in late summer - early fall. Since such temporal variation does not clearly appear in the Têt, Ter and Tordera rivers and since one have no idea of the dominance of phytoplankton in these rivers, the last sentence of the paragraph (lines 13-14) do not stand. It should be reworded or at least "may" have to be added before "reflects". The dedicated lines of the abstract and of the conclusion have to be similarly reworded.
Response: Corrected according to the review's suggestion.

Table 1
I think a figure similar to Fig 9 but illustrating all parameters should be more informative than Table 1. I suggest replacing this table with such a figure. In addition it would remove the redundancy between Table 1 and Fig 9.
Response: We found that data in Table 2 (before table 1) are pertinent data that can be used in further studies as most of them have been measured for the first time. Moreover, the first reviewer requested more calculations (Q-weighted means) in this table.

Table 2
There is no need to add parameters 'a' and 'b' as two dedicated column since these parameters already appear in the column 'equation'. Thus, I suggest removing columns 'a' and 'b'.
Response: Removed in table 3 (before table 3) according to the review's suggestion.

Abstract and conclusion
These sections have to be reworded depending of the above comments.
Response: Reworded according to the review's suggestion.

Technical corrections
Introduction: page 13281, lines 21-24
Replace 'show' with 'suggest' since the message of the sentence is not demonstrated, or cite ref(s) if it is.
Response: Corrected according to the review's suggestion

Results: page 13286, line 3
Replace 'the' with 'most' in 'in the coastal rivers' since this is not valid for all the rivers.
Response: Corrected according to the review's suggestion

Results: page 13286, line 8
Replace ‘relatively constant’ with ‘less variable’ since the water discharge is still variable (there is more than a factor of ten between minimum and maximum).
Response: Corrected according to the review's suggestion

Results: page 13286, line 16
Replace ‘an’ with ‘a’ in ‘an fast increase’.
Response: Corrected according to the review's suggestion

Discussion: page 13288, title of section 4.1
Replace ‘terrestrial’ with ‘river’ or ‘continental’ since, as it is discussed in section 4.2 river POM is of both terrestrial and phytoplanktonic origin.
Response: Corrected according to the review's suggestion

Discussion: page 13290, line 1-2
Cite a more appropriate ref than Liquete, 2008.
Response: Corrected according to the review's suggestion

Discussion: page 13291, line 25
I guess authors mean Figs 7 and 8.
Response: Corrected according to the review's suggestion

Discussion: page 13293, line 5
I suggest adding “and anthropogenic inputs” at the end of the sentence.
Response: Corrected according to the review's suggestion

Discussion: page 13293, line 7
I suggest replacing “the presence of anthropogenic inputs” with “land use”.
Response: Corrected according to the review's suggestion

Discussion: page 13293, line 22
Add “of” between ‘source’ and ‘organic’.
Response: Corrected according to the review's suggestion

Discussion: page 13294, line 22
Replace “Dissolved atmospheric CO_2” with “Dissolved inorganic carbon from atmospheric CO_2 origin”.
Response: Corrected according to the review's suggestion

Discussion: page 13295, line 10
Add “even in winter” at the end of the sentence.
Response: Corrected according to the review's suggestion

Discussion: page 13295, line 10-13
It looks like this is valid in winter only. If yes, state it.
Response: No, because the snowmelt occurs in spring (April-May 2009).

Discussion: page 13295, line 15

Replace “whereas” with “and”.
Response: Corrected according to the review's suggestion

Discussion: page 13295, line 16
Replace “mainly” with “likely” or cite a ref.
Response: Corrected according to the review's suggestion

Fig. 2
Indicate in the caption what curve corresponds to what parameter.
Response: Corrected according to the review's suggestion

Additional references

Berto D., F. Rampazzo, S. Noventa, F. Cacciatore, M.Gabellini, F. Bernardi Aubry, A. Girolimetto, R. Boscolo Brusà, in press. Stable carbon and nitrogen isotope ratios as tools to evaluate the nature of particulate organic matter in the Venice lagoon. Estuarine, Coastal and Shelf Science.

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observation of the Gironde fluvial system: fluxes of suspended matter, particulate