Review of

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"

Comments to authors

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.

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.

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).

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.

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 for short 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.

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).
- Indicate how long the water samples were stored at 5°C and darkness before the filtration.
- 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?
- Were LECO CN 2000 and GVI Isoprime connected for the isotopic analyses? If not which EA was connected to this IRMS?
- What kind of internal standards were used to calibrate the IRMSs? Against what reference material the internal standards were calibrated?
- Were the two IRMS inter-calibrated (e.g. by analyzing aliquots of different samples) in order to ensure they give the same results?
- Add a paragraph explaining how coefficients a and b were estimated for the regressions that appear in Table 2 and Figures 6-8. Also indicate that only significant regressions (p-value < 0.05) were considered.

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. Also, it should be more informative for the reader to know in this section what the objective of this analysis is. 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 $\delta^{13}C$).

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. This looks in contradiction with the data interpretation that appears in section 4.2 and that is illustrated on figures 3 and 4. 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 Fluvia 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.

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). 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.

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.

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.

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".

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.

Introduction: page 13280, lines 7-15

The details regarding long-term changes are not needed in the Introduction. I suggest removing them.

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?

Introduction: page 13281, lines 13-21

No need to deeply detail the values for each studied years. The overall values would be enough.

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.

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.

Delta notation: equation and figures

Use the new IUPAC notation (Coplen, 2011).

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.

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.

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 13C-depleted 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.

Discussion: page 13295, line 7

This is not correct for "spring (Tordera River)". Reword the sentence.

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.

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.

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’.

Abstract and conclusion

These sections have to be reworded depending of the above comments.

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.

Results: page 13286, line 3

Replace ‘the’ with ‘most’ in ‘in the coastal rivers’ since this is not valid for all the rivers.

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).

Results: page 13286, line 16

Replace ‘an’ with ‘a’ in ‘an fast increase’.

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.

Discussion: page 13290, line 1-2

Cite a more appropriate ref than Liquete, 2008.

Discussion: page 13291, line 25

I guess authors mean Figs 7 and 8.

Discussion: page 13293, line 5

I suggest adding “and anthropogenic inputs” at the end of the sentence.

Discussion: page 13293, line 7

I suggest replacing “the presence of anthropogenic inputs” with “land use”.

Discussion: page 13293, line 22

Add “of” between ‘source’ and ‘organic’.

Discussion: page 13294, line 22

Replace “Dissolved atmospheric CO_2” with “Dissolved inorganic carbon from atmospheric CO_2 origin”.

Discussion: page 13295, line 10

Add “even in winter” at the end of the sentence.

Discussion: page 13295, line 10-13

It looks like this is valid in winter only. If yes, state it.

Discussion: page 13295, line 15

Replace “whereas” with “and”.

Discussion: page 13295, line 16

Replace “mainly” with “likely” or cite a ref.

Fig. 2

Indicate in the caption what curve corresponds to what parameter.

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.

Chanton, J.P. and Lewis, F.G., 1999. Plankton and dissolved inorganic carbon isotopic composition in a river-dominated estuary: Apalachicola Bay, Florida. Estuaries, 22(3A), 575-583.

Coplen, 2011. Guidelines and recommended terms for expression of stable isotope-ratio and gas-ratio measurement results. Rapid Communications in Mass Spectrometry, 25, 2538–2560.

Frankignoulle, M., G. Abril, A. Borges, I. Boruge, C. Canon, B. Delille, E. Libert, J.M. Théate, 1998. Carbon dioxide emission from European estuaries. Science, 282, 434-436.

Middelburg, J.J., P.M.J. Herman, 2007. Organic matter processing in tidal estuaries. Marine Chemistry, 106, 127–147.

Polsenaere, P., N. Savoye, H. Etcheber, M. Canton, D. Poirier, S. Bouillon and G. Abril., 2013. Export and degassing of terrestrial carbon through watercourses draining a temperate podsolized catchment. Aquatic Sciences, 75(2), 299-319.

Savoye, N, V David, F Morisseau, H Etcheber, G Abril, I Billy, K Charlier, G Oggian, H Derriennic, B Sautour, 2012. Origin and composition of particulate organic matter in a macrotidal turbid estuary: The Gironde Estuary, France. Estuarine, Coastal and Shelf Science 108 (2012) 16-28.

Schäfer, J., Blanc, G., Lapaquellerie, Y., Maillet, N., Maneux, E., Etcheber, H., 2002. Ten-year-observation of the Gironde fluvial system: fluxes of suspended matter, particulate organic carbon and cadmium. Marine Chemistry 79, 229-242.