

***Interactive comment on “Short term variability of dissolved lipid classes during summer to autumn transition in the Ligurian sea (NW Mediterranean)” by M. Goutx et al.***

**Anonymous Referee #2**

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General comments

This work assesses the short time dynamics (variation in concentration and composition) of different dissolved lipid classes, in order to get out information on the role of physical and biological forcing on lipids concentration and distribution in the surface and mesopelagic layers of the Ligurian Sea, during a transition period from the summer oligotrophy to autumn. The paper provides the first data set on total lipid concentrations and lipid class composition in DOM from surface to the mesopelagic layer in the open Ligurian Sea. These data are novel and relevant, but the authors have to stress better their importance, taking also into account that lipids represents only a very low percent-

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age of DOM. The data set is very large and the results support the interpretation and conclusion of the authors, but the text need some revisions. The structure could be improved and there are a number of sentences and concepts that should be clarified (see specific comments). The conclusion should better underline which is the contribution of this paper to advances in DOM characterization, in particular the authors should better evidence which information the distribution of the different lipid classes, observed in this study, can give on DOM origin and degradation. I recommend a careful check of the abbreviations, (they are many and there is often a little confusion) and of the units of measurement, for example the lipids concentration is expressed sometimes as  $\mu\text{g C L}^{-1}$ , other times as  $\mu\text{g L}^{-1}$ , both in the text and in the captions. I also recommend a general improvement of the English.

Below I report a list of specific and technical observations.

#### Abstract

Pag. 29 lines 9-10. "Lipid class composition provided valuable information on the origin of DOM, and the changes that occurred during the period investigated." Which information lipid can give on the origin of DOM? What does the second part of this sentence mean?

#### Introduction

Pag. 30 lines 2-3. The sentence "primary production by photosynthetic microorganisms is a major source of DOM" should be corrected. In the surface layer many are the mechanisms of DOM production, and the importance of one with respect to the other has not been assessed. This sentence should be rewritten, indicating that phytoplankton may be one of the most important source of DOM, or that primary production define the upper limit to DOM production because photosynthesis is the first step to transform inorganic carbon into organic material, but DOM can be produced at each step of the food web.

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Pag. 30 lines 5-6. "primarily composed of proteins, carbohydrates and lipids." Proteins, carbohydrates and lipids are the major constituent only of the fraction of DOM characterized at molecular level. This fraction represents about the 10% of DOM surface pool and a lower percentage of deep DOM (Benner, 2002).

Pag. 30 lines 6-9. "Understanding the dynamics of these biomolecules, their resistance to remineralization and their transformation to more complex and refractory substances is essential to predict the response of biogeochemical cycles to climatic changes." I suggest to correct this sentence underlining that these biomolecules can give information only about a very low percentage of DOM, as the authors report in the following sentence.

Pag. 31 line 24. Correct the sentence:" The analytical TLC/FID technic on an "Iatroscan" apparatus..."

Pag. 32 line 10. Why did you collect samples until 1000 m depth and not until the bottom? In this area, an increase in DOM concentration should be present close to the bottom, due to deep water formation; so it could be very interesting to have information on the occurrence of different lipids classes also in the deep waters, where DOM may be less degraded than in the intermediate layer. I think you should explain the choice to collect samples only until 1000 m.

Pag. 32 lines 11-15. "Our overall objective...Mediterranean" I think you should clarify that your interest is mainly in the surface and mesopelagic layers.

#### Material and methods

Pag. 32 lines 20-21. What does "dynamics of the biological system" mean? To which parameters are you referring?

Pag. 33 lines 1-3. "Additional 0-150 m surface profiles at C1", which kind of profiles were measured? CTD profiles? Or did you take samples for lipid analysis? Which was the frequency of this sampling? Did you perform the more frequent sampling only

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during C1 cycle?

Pag. 34 lines 7-8. I suggest to indicate the sum of all lipid compound classes except hydrocarbons with the sigle: TLd-HC, as in the supplement table.

Pag. 34 line 12. Why did you use two precombusted glass fiber filters?

Pag. 34 line 18. The concentration of the reference water for DOC analysis is in micromole per litre. In addition you should also indicate the batch you used, because the range of DOC concentration changes in the different batches.

Pag. 34 lines 22-23. You indicate as biogeochemical parameters only CDOM and pigments, I think you should include also nutrients, DOC and oxygen. In addition, you use CDOM data in your paper, so I think you should report how you measured it, in the material and methods section. (Excitation emission matrix? Fluorescence emission spectra? Absorption spectra? Which wavelength did you use?)

## Results

Pag. 35 General hydrological conditions. To understand this paragraph we have to look at the figures reported by Andersen et al. 2008. The graphs in Andersen et al. 2008 paper, are limited to the layer 0-150 m, whereas your data arrive until 1000 m. In order to understand the relationship between physical forcing and lipids distribution, you should better describe hydrological condition observed below 150 m too. For example you could report potential temperature, salinity and dissolved oxygen vertical distribution from the surface to the bottom, in order to identify the different water masses occurring during the cruise in the study area. Did you observe the occurrence of the Levantine intermediate water? At which depth? Did you find lower lipids concentrations, or different lipids classes in the core of this old water?

Pag. 35 Lines 20-22. "We observed a strong water column stratification partially disrupted at the end of the cruise, low nutrients stocks and successive meteorological events." The last part of this sentence is not clear for me. What does the expression

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"successive meteorological events" mean? Where nutrients data are visible? They are not reported in the Andersen paper!

Pag. 36 lines 8-11. What is the meaning of the intrusion of low salinity water masses? Are they coming from the land? Clarify why you are interested in them.

Pag. 36 lines 20-21. "...but with hydrological and nutrient resources (N/P) similar to summer oligotrophic conditions (Andersen et al., this issue#(1))." Nutrients data are not reported neither in this paper nor in the Andersen et al. paper.

Pag. 36 line 23. "TLd concentrations varied from 5.3 to 48.5  $\mu\text{g C L}^{-1}$  (0.4 to 4  $\mu\text{M}$ )". Why is the colour bar range (10-40  $\mu\text{g C L}^{-1}$ , figure 2) different from the range reported in the text? You should use the same word and/or abbreviation to indicate all lipid compound classes except hydrocarbons, in the paper. In the caption of figure 2 you wrote "total biogenic lipids", in the caption of figure 3 "Total dissolved lipids (HC not included)", in the text "Total dissolved lipids TLd", this create a little confusion for the reader.

Pag. 36 line 25. "The highest values were found in the 0-150 m surface layer (Fig. 2). The concentration gradient with depth was more pronounced during Leg 1, with values  $<18 \mu\text{g C L}^{-1}$  below 100 m, than during Leg 2 when concentrations below the surface layer were up to 40  $\mu\text{g L}^{-1}$  (Fig. 2)." I suggest to rewrite this sentence, in fact the highest TLd-HC values are visible in fig. 2 in the upper 50 m of the water column (with the exception of the data collected the 19/09 and the 4/10). The depth at which you found TLd-HC concentrations up to 40  $\mu\text{g C L}^{-1}$  during Leg 2 should be indicated. A C is missing after 40  $\mu\text{g}$ .

Pag. 37 lines 3-5. What it is visible in figure 3 is not in agreement with the sentence "The day/night pattern of TLd profiles was not significant throughout the period investigated although lower concentrations at night than during the day were observed during Leg 2 (Fig. 3)". The observation that lower concentrations were observed at night than during the day is not true for all the depths. In the Leg 2 below 500 m values are higher

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during the night than during the day. In addition, I suggest to report a zoom of the first 150 m of these graphs, in order to better investigate the day/night pattern at surface in which I guess a trend should be visible. In the figure 3 you should indicate Leg 1 and Leg 2.

Pag. 37 lines 8-10. "almost homogeneous values down to a minimum concentration at 1000 m depth ( $39.8 \pm 0.7 \mu\text{M}$ ) and no apparent difference between days and 10 night (Fig. 4)". Control this sentence, the verb is missing!

Pag. 37 lines 14-15. "The only significant re-increase of DOC ( $+20 \mu\text{g L}^{-1}$ ) at depth (700 m) was noticeable later at the end of Leg 2 (12 October)".  $20 \mu\text{g C L}^{-1}$  correspond to  $1.67 \mu\text{M}$ , this value is lower than analytical precision of DOC measurement ( $2 \mu\text{M}$ ), I don't think this is a significant increase of DOC.

Pag. 37 line 23-24. "Daily variations of TLD contribution to DOC were not significant." Where these data are visible?

Pag.38 lines 1. Why did you define in the text "chloroplast lipids" and you call them phytodetritus in the caption of fig.6? I think that it is less confusing if you use the same word.

Pag. 38 lines 4-6. "Except hydrocarbons, the glycolipids (monogalactosyldiglycerides) were the major lipid class, followed by pigments, monoglycerides and non nitrogen containing phospholipids (phosphoglycerides)." Looking at table 2, it seems that the major lipid class after glycolipids (25.09%) and pigments (13.58%) are the free aliphatic alcohols (12.34%), the monoglycerides (11.84 %) and free fatty acids (11.38%), then the phospholipids (3.71%). Why don't take into account free fatty acids and free aliphatic alcohols?

Pag. 38 lines 18 and 20. I don't find PL between the abbreviation in table 2. What does it mean? Does it indicate phospholipids?

Pag. 38 line 27. "During Leg 1, TG integrated values were higher in the 0-150 m

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surface waters than in the 150-1000 m mesopelagic layer, whereas an opposite pattern prevailed during Leg 2 that is TG integrated values in the mesopelagic layer were much higher than TG integrated values in surface layer (Fig. 8, upper panel). During Leg 2, night concentrations were higher than day concentrations in the mesopelagic layer." This sentence should be rewritten more carefully, in fact TG night integrated values were always lower at surface (0-150 m) than in mesopelagic layer, if we exclude integrated night value observed at 278 day. An opposite trend was observed for the integrated day values, they were always higher at surface than in the mesopelagic layer.

Pag. 39 lines 6-8. "Finally, the hydrocarbon pool varied in the range 0.9-21.9  $\mu\text{g C L}^{-1}$  amounting 6.3–1.8%, on average, of the total lipids (Table 2). An increase of concentrations at 400-800m depth occurred in 6-8 October (Fig. 7, lower panel)." I suggest to shift this sentence at page 38 line 22. Otherwise you should move figure 7b after figure 8.

Pag. 39 line 11. As I wrote above, you didn't define CDOM. You have to explain how you determined it in the material and methods section.

Pag. 41 line 3. Probably figure 9 and 10 are reversed. You should refer to figure 10, not 9!

Pag. 41 lines 9-10. "...or exported to depth by other means than the mixing of water masses." Which mechanisms are you thinking about?

Pag. 41 line 12. What does "photosintetically-produced DOM" mean? Does it mean DOM produced by phytoplankton during photosynthesis?

Pag. 41 line 19. I didn't find Morris et al., 1983 in the references

Pag. 41 lines 19-22. "In these studies, only intracellular TG concentrations were related to Chl-a, which supported the conclusion by the authors that nitrogen availability was the major factor driving lipid content in particles at the time of phytoplankton blooms;"

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I don't understand this sentence, why the observation that intracellular TG concentrations were related to Chl-a indicates that nitrogen availability was the major factor driving lipid content in the particles, at the time of phytoplankton bloom?

Pag. 42 lines 11-21. Where are these relationships?

Pag. 43 lines 6-7. Where are these relationships?

Pag. 44 line 13. What does "microbiological production" mean? Bacterial lipid consumption or lipids release by microorganisms?

Pag. 44 line 27. I suggest to report the abbreviation HC in this line after hydrocarbons, it is simpler to understand the following sentences for the reader.

Pag. 45 line 11. I suggest to report the abbreviation PL in this line after phospholipid, it is simpler for the reader to understand the following sentences

Pag. 45 11-13 Where is it visible this significant re-increase of DOC at depth?

Pag. 45 line 27 What is BB?

Pag. 46 lines 6-10. "It also supports the conclusion of Bendtsen et al. (2002) about the Greenland Sea, that deep sea labile DOC may only be explained by a DOC released from the sinking flux of POC. Dissolution of POM would led to formation of colloids known to preferentially shelter phospholipids (Liu et al., 1998)." Are POC concentrations observed at this depth enough to explain this hypothesis?

Pag. 46 line 12. Why did you use a low salinity index, instead of salinity? Which is the advantage of this index?

Pag. 46 line 19. You should refer to figure 9 not 10

Pag. 47 line 7. Define PAH

Pag. 47 line. Define HC

Pag. 47 lines 9-10. Do you have any idea to explain this surprising finding?

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## Table

Table 1. You indicate the layer 0-1000 m as water column, whereas the depth of the station is higher than 2000 m (fig. 1)

Table 2. You indicate the layer 0-1000 m as water column in this table too. The concentrations are in  $\mu\text{g C L}^{-1}$ ?

Table 3 It is not readable, use a bigger character!

## Figure

Figure 3. The X scale of the first graph should be the same of the other ones. What does the dotted line indicate?

Figure 4. Should the symbols be different for each cast?

Figure 6. What indicate the number above each graph? How can I discriminate night and day data? Are the night data indicate with a grey square? Put this information in the caption.

Figure 8 Substitute "Jours Julien" with "Julian days". Indicate the first and second leg in the figure, or in the caption

Figure 9 and 10 are inverted

Figure 10. What does LT-HC mean? Use the same abbreviation reported in the text!

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