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Biogeosciences Discussions

Interactive comment on "Fluorescence and absorption properties of chromophoric dissolved organic matter (CDOM) in coastal surface waters of the Northwestern Mediterranean Sea (Bay of Marseilles, France)" *by* J. Para et al.

Anonymous Referee #2

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The study reports on a time series of measurements of the optical properties of dissolved organic matter in the Northwestern Mediterranean. Both absorption and fluorescence measurements are used to characterise and trace the mixing of allochthonous material supplied by the River Rhône (to the west) and the effects of local production in surface waters and mixing. The results show that absorption data does reveal an influence of the river as far East as their marine station. However, the fluorescence data does not agree and the changes occurring largely result from in situ production and destruction (photooxidative). The work has limited impact for the broader international

readership but is apparently the first of its kind for the region revealing the ocean-blue-water type characteristics of these coastal waters and the occasional influence of the Rhône plume. The study and the findings are constrained by a very limited dataset with only surface water samples. To improve the work a more in depth analysis of how the characteristics changed across the gradient sampled could be made. For example by including a comparison of how the relationship between fluorescence and absorption changed, and also the relationship to TOC (I presume POC is small, but a comment on this should be included in the paper). I urge the authors to revise the paper.

General points. 1. How valid it is to include data from excitation wavelengths below 240 nm. What were the absorption values at these wavelengths? I am guessing that they might be quite high at times depending on the nitrate concentrations (especially in association with mixing events). This might make it necessary to correct the data for inner filter effects. 2. For the majority of the sampling dates it would seem that the surface 5 m was mixed and that the 2 and 5 m samples were basically replicates. Maybe you could just report the averages instead of always referring to. 3. I don't agree with the "purity" paragraph with regards to discussing the shapes of the emission spectra in Figure 6. We know that the fluorescence signal is (to some extent and with some assumptions) the sum of different fluorescence signals present. Why not look at these samples in another way. For example by subtracting the normalised spectra from each other. Wouldn't this reveal the fluorescence spectrum of the additional material that is present? Finally, it is not clear to me why these samples were specifically chosen. It seems that they represent contrasting hydrological conditions but this should be stated more clearly and maybe labelled on the figures as e.g. "Rhone intrusion", "well mixed" etc. . .. 4. The comparison of their data to the Determann et al results on the excitation and emission characteristics of the remains of bacteria and algae cultures is interesting although a little difficult to follow due to the figure being a unclear. There is a lot of data plotted on the same graphs. Again a different labelling of the graphs might make it easier to follow. They also have to be cautious with over interpreting the results. They may fit with the expected seasonal succession in phytoplankton and bacteria, but there

is still a large difference between the conditions that Determann et al measured and these samples. And as no bacteria data was collected they cannot really be sure what the after chlorophyll peak effect is. Maybe there are some other studies from the region where bacterial counts have been done which can help with this extrapolation?

Specific comments

âĂć p.5677. Line 7. Delete “with”. âĂć P5678. Line 6. The Coble and Nelson references are not appropriate here. There are other works that have looked at these processes specifically. âĂć P5678. Line 7. Opsahls paper states 0.7-2.4 %. âĂć P5678. Line 9 rephrase “changing local bacterial carbon demand”. Don’t you mean something along the lines that bacteria acquire some of their carbon from terrestrial DOM. Or supplement their carbon demand with terrestrial C. âĂć Paragraph starting on Line 20 p 5678. Does not read well and should be re-phrased. I don’t agree with EEMs now being a standard approach. The community is still trying to work out what the signals represent and how to standardize the methods used. âĂć Line 7-10. P5679. How does this compare with what you say earlier about Opsahl and Benners 1997 where terrestrial DOC can represent up to 2.4 % in the Atlantic? âĂć Line 19. P5679. Replace “showed” with shown. âĂć Line 20. “depends”. âĂć Line 7. P5680. Delete “for the first time”. âĂć Line 9. 5680. “dynamics in the Northwestern Med. . .”. âĂć Line 13. P5682. This reference 2004 is incorrect. The Blough & Del Vecchio book chapter in Hansell&Carlson DOM book (2002), reviewed these fitting techniques. so you could reference this or the original work, also cited in the chapter. âĂć Lin 13-14. P5682. “. . .Here, SCDOM was determined by applying a non- linear fit of log-linearized absorption data in the spectral range 350–500 nm (R2>0.99). . ..” I don’t understand this. It sounds line the log of the absorption spectra was modeled with a nonlinear fit. Either a nonlinear fit was used on the original data, fitting the exponential to the spectrum, or a linear regression was applied to the log transformed absorption data. Can you explain? âĂć Line 15-29 p. 5683. Why aren’t exactly the same wavelengths as suggested by the two studies by Zsolnay et al and Huguet et al for the indicies?

The wavelengths seem to have been shifted a little for your study. How does this effect the results? I understand why you use ex 255 instead of 254 nm, for example for the HIX, but why haven’t you used the integrals of the two emission regions? âĂć Mehtods section: You have forgotten to mention how you measured chlorophyll. âĂć Line 8. P 5686. Replace “reformation” with re-establishment. âĂć Line 20. P5686. Chl is more an indicator of phytoplankton biomass than primary productivity. âĂć Line 4. P5687. Delete “indeed”. âĂć CDOM absorption results. In the paragraph at the bottom of p5688 you start by mentioning that CDOM behaves conservatively, and then towards the end of the paragraph start discussing the production of CDOM. This seems conflicting. Another point to consider is, how far does a data value have to deviate from the regression line to be considered as significantly different? And. . . âĂć Line 5689. Line 22. I can not see the T peak in the EEM from 23 of September. I can see it labelled but can not see the peak. âĂć Line 2-3. P5690. Aren’t these two statements one and the same. âĂć Line 4- P5690 and rest of the paragraph. You should not use the words purity or pure when discussing the fluorescence peaks. It implies that we know chemically what it is and this we do not. âĂć Line 5-9. P5692. Have you considered the fact that the presence of tryptophan can quench the fluorescence of tyrosine (See lLakowicz2006, Fluorescence book) âĂć Please refrain from referring to the fluorescence peaks as fluorophores. We have no idea what they are, or if they are single fluorophores that are responsible. âĂć BIX and HIX data should be presented as part of the Results section and then discussed in the Discussion. As is the reader is introduced to them as part of the discussion.

Tables. Suggestion: Drop table 1 as the information it provides is basically apparent in the other tables. Could also consider combining tables 2 and 3 (i.e. adding a columns with the fluorescence data. Space for this can be made in table 2 by dropping the error information (+/-) for the irradiance data.

Interactive comment on Biogeosciences Discuss., 7, 5675, 2010.