

All the suggestions and corrections of the Reviewer are now included in the revised manuscript (MS). As suggested by the Reviewer 1, we added supplementary data, more particularly CDOM data related to the Rhône River and photo irradiation experiment. We found that most of the reviewer comments were helpful and contribute to improve the quality of the paper.

Questions

1. *P. 5684, line 12. We're any other standards ran to calibrate the TOC analyser? Or was a 1 point calibration to the DAW done? Interesting about the LCW: I also find it much higher than my MilliQ!*

Answer: The calibration of the TOC analyzer was done on a daily basis by injecting 4 successive and increasing standard solutions prepared by diluting potassium hydrogen Phthalate “stock solution”. DAW allows us to check the quality of the running analyses. Concerning LCW carbon content there is a mistake, of course the DOC content of the LCW was 1 +/- 0.3 μM and not 10 +/- 3 μM . The typical blank value with MilliQ deionized water was 4-5 μMC . Correction was made in the revised MS

2. *P. 5687, line 9. I wonder how your CDOM absorbance results might change if you focused on lower wavelengths. For example, a₃₀₀ or a₂₈₀, which give a stronger signal than longer wavelengths. Did you do this analysis?*

Answer: Analysis of temporal evolution of normalized a_{CDOM} at 300 nm (red line) compared to the one at 350 nm (green line) at both depths studied exhibits similar general patterns (see Fig. 1), with maximum observed on 6 May 2008 for both a_{CDOM} . Whereas the most contrasted temporal evolution of normalized a_{CDOM} is observed at 350 nm compared to 300 nm because processes that drive CDOM dynamic in this area are more sensitive at 350 nm compared to 300 nm. Indeed, the photobleaching effect of CDOM causes a shift from larger molecular weight compounds absorbing at longer wavelengths to smaller ones absorbing at shorter wavelengths. This is why, on 23 Sept. 08, normalized $a_{\text{CDOM}}(350) < \text{normalized } a_{\text{CDOM}}(300)$. Mixing events may inject from the bottom into the surface humic-aged CDOM, i.e. C peak, which absorbs wavelengths between 320-360 nm. This is why, on 25 Nov. 08 and winter 08, normalized $a_{\text{CDOM}}(350) > \text{normalized } a_{\text{CDOM}}(300)$. Finally, during Rhone plume intrusion (6 May and 23 June 08) a complex mixtures of compounds (residual terrestrial CDOM, autochthonous CDOM, nutrients...) that certainly absorb in the whole UV spectral domain is suspected. Hence, during such events normalized a_{CDOM} could be (1) comparable at 300 and 350 nm as observed on 6 May 08 or (2) normalized $a_{\text{CDOM}}(350) > \text{normalized } a_{\text{CDOM}}(300)$ as observed on 23 June 08 (especially at 2 m depth) and probably also (3) normalized $a_{\text{CDOM}}(350) < \text{normalized } a_{\text{CDOM}}(300)$. All these statements were mainly dependant of time and hydrological context. Thus, with regards to this result, it appears that studied a_{CDOM} at 350 nm is more relevant than at 300 nm and is a good compromise for this study area.

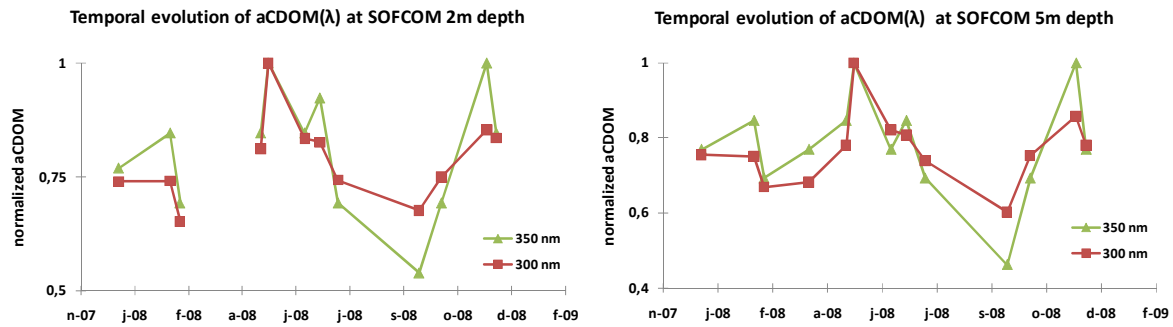


Fig. 1: Temporal evolution of normalized a_{CDOM} at 300 and 350 at SOFCOM station

3. P. 5688. Three points here:

1) the slope ratio method of Helms would be good to investigate in this environmental setting. Does this value (S_R) change between your 2 m and 5 m depths consistently with BIX or with photobleaching?

Answer: According to Reviewer's comment, we determined S_R (Helms et al. 2008) at 2 and 5 m depths (see Fig.2) and examined whether the values change between these two depths consistently with BIX or photobleaching (when it was possible, i.e., on 9 and 23 June 08, 10 July 08, 23 September 08, 25 November 08 and 4 December 08). Before presenting the results, we want to underline that the denominator (i.e. $S_{350-400}$) of S_R was similar at both depths excepted on 25 November 08, where $S_{350-400}(2m) > S_{350-400}(5m)$ and on 4 December 08 where $S_{350-400}(2m) < S_{350-400}(5m)$.

- 9 June: $S_R(2m) > S_R(5m)$ and $BIX(2m) > BIX(5m) \Rightarrow$ consistent with BIX.
- 23 June: $S_R(2m) > S_R(5m)$ and $BIX(2m) > BIX(5m) \Rightarrow$ consistent with BIX.
- 10 July: $S_R(2m) > S_R(5m)$ and $BIX(2m) < BIX(5m) \Rightarrow$ consistent with photobleaching.
- 23 September : $S_R(2m) > S_R(5m)$ and $BIX(2m) < BIX(5m) \Rightarrow$ consistent with photobleaching.
- 25 November: $S_R(2m) < S_R(5m)$ because $S_{350-400}(2m) > S_{350-400}(5m)$ and $BIX(2m) > BIX(5m) \Rightarrow$ consistent with mixing
- 4 December: $S_R(2m) > S_R(5m)$ because $S_{350-400}(2m) < S_{350-400}(5m)$ and $BIX(2m) < BIX(5m) \Rightarrow$ consistent with mixing.

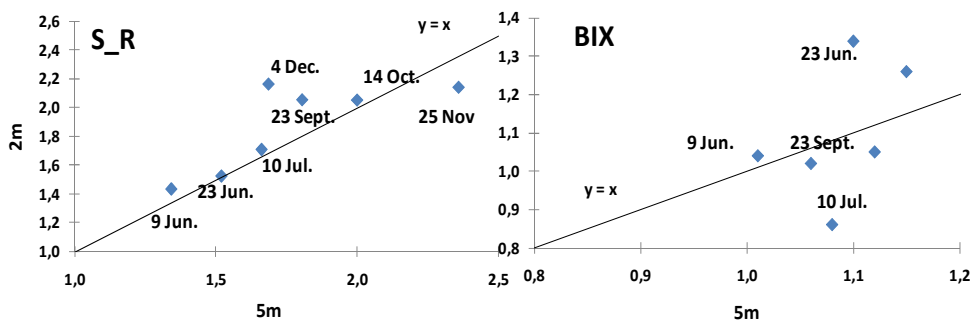


Fig. 2: $S_R(2m)$ versus $S_R(5m)$ on left panel, $BIX(2m)$ versus $BIX(5m)$ on right panel.

The slope ratio method of Helms is in good agreement with our results and does not change the interpretation of our results, so we decided to not include this method in the revised MS.

2) *Your mixing analysis is interesting, but your interpretation is potentially flawed. For example, a statistical evaluation of the outliers above and below the mixing line (i.e., adding or removing CDOM) (just a model error estimate will do) would strengthen the argument. Also, was a linear fit to the data modeled (linear regression), or did you calculate a mixing line between end-members? It appears that you performed a linear regression fit and used that model as the mixing model. That method should produce some error estimate on slope and intercept.*

Answer: We agree with this comment and effectively in the first version of the MS we performed a linear regression fit and used it as the mixing model, keeping in mind that this method should produce some error estimate on slope and intercept. Thus, to strengthen the apparent conservative behavior of $a_{\text{CDOM}}(350)$ with salinity and to avoid introducing potential biases, we have performed (following Reviewer's suggestion) a linear regression with all the data available at 2 m depth (i.e. 13 values from SOFCOM station completed by 2 values acquired close to Rhone estuary in the Rhone River plume) by using a model. We can noticed the similarity of the equation of the model ($a_{\text{CDOM}}(350) = -0.029 \text{ salinity} + 1.199$, $n=15$, $R^2=0.96$) with the one determined before ($a_{\text{CDOM}}(350) = -0.028 \text{ salinity} + 1.201$, $n=6$, $R^2=0.98$). We have thus improved Fig. 3 (see above, Fig. 3. of the revised MS) with the result of this more rigorous method to establish the mixing line. In addition, the confidence interval at 95% was also plotted on the figure to show which data are significantly above and below the mixing line.

Fig. 3. of the revised MS

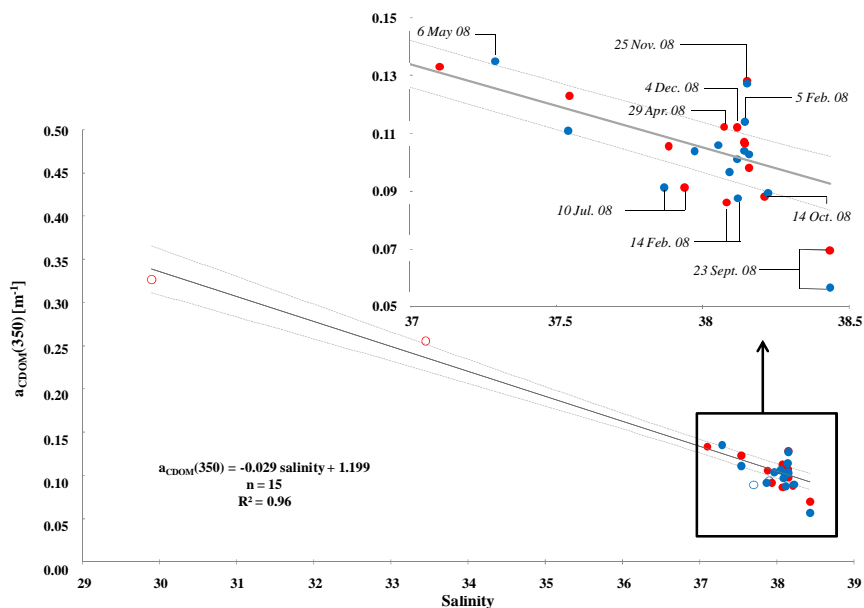


Fig. 3. Relationship between salinity and CDOM absorption at 350 nm (in m^{-1}) acquired at SOFCOM station at 2 m (red circle, $n = 13$) and 5 m (blue circle, $n = 14$) depths. Data from

Rhône plume acquired in May 08 during CHACCRA cruise at 2 m (red open circle, n = 2) and 5 m (blue open circle, n = 2) were also plotted. The mixing line (black line) with its confidence interval at 95% (dashed line) was established using all SOFCOM station data at 2 m depth (n=13) plus Rhône estuary stations (CHACCRA cruise data) at 2 m depth as well (n = 2).

3) A mixing model of the S values (following Stedmon's work; see 2003 paper in *Estuarine Coastal and Shelf Sci.*) would also be insightful here.

Answer: Results of a mixing model of the S values is presented in Fig. 4. It clearly appears that our data set is not well adapted because it is dominated in volume by autochthonous CDOM compared to allochthonous CDOM. Acquired additional data along a salinity gradient will certainly provide insightful results. Nevertheless the Fig. 4 shows the clear impact of the Rhône River plume at 2 m depth compared at 5 m depth.

So we decided to not include this method in the revised MS.

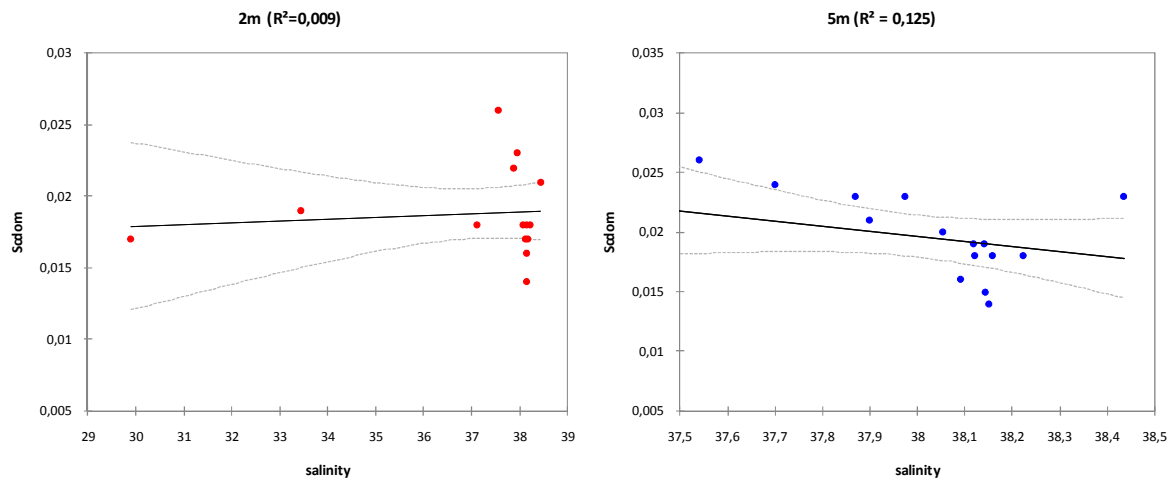


Fig. 4: Mixing model of S values at 2 m (left panel) and 5 m (right panel) depth

4. P. 5690. *The discussion on CDOM flu vs CDOM abs is interesting, but doesn't this just prove the greater sensitivity of fluorescence vs absorbance? This is what I got from the data: in low CDOM environments, flu will elucidate changes and processes that abs will not, simply because of the greater sensitivity. The argument made by the data (and partly by the text) is that the system is truly non-conservative even if CDOM absorption coefficients and TOC exhibit conservative behavior.*

Answer: Yes, we completely agree with Reviewer 3 comment. So, in the conclusion section this sentence was added in the revised MS: "In such oligotrophic environment, it appears that fluorescence analyses gather more pertinent information on CDOM composition and dynamics than absorbance analyses."

5. P. 5690, line 3: *change 'homologue' to a more appropriate word.*

Answer: In reply to the comment 21 of the Reviewer 2 the sentence containing this word was already modified for a better understanding. And the word ‘homologue’ was removed. And now the sentence in the revised MS is: “This result indicates that fluorescent CDOM character in the surface is mainly driven by processes other than water mixing and thus highlights the dissimilar trends in CDOM absorption and fluorescence properties.”

6. P. 5690, line 18: *‘the purest material’; I don’t understand what this means. Please clarify your usage of this phrase.*

Answer: Yes, using the word ‘purest’ is not appropriate here since we do not know the chemical composition of the fluorescent peak. Thus to clarify our explanations here, and in the rest of the revised MS, we deleted the words ‘pure’ or ‘purest’ and replaced them by other terms to describe the relative degree of complexity of the fluorescent compounds mixture that shaped the different fluorescent peaks. Moreover, accordingly to the Reviewer 2 general comment 3, the “purity” paragraph was rephrased in the revised MS.

7. P. 5691, line 10. *Is the Rhone River CDOM conservative or highly photodegraded in this system?*

Answer: At this stage, we have few data points along a salinity gradient from which it appears that Rhone River CDOM seems to be conservative. But fluorescence analyses underlined the change in CDOM composition suggesting that terrestrial CDOM, photobleached and diluted, is progressively replaced by autochthonous fluorescent material. So we believe that Rhone River CDOM has only an apparent conservative behavior in this system.

8. P. 5692, line 20-25. *Do you have any evidence that C peak may be at all autochthonous? Is it a feature that can migrate into the EEM with biodegradation of phytoplankton DOM (re: Coble 1998; Parlanti et al. 2000)?*

Answer: We agree with the Reviewer comment. It is true that we have only attributed to the peak C a terrestrial origin, and it is quite restrictive. However, we have stipulated both origin for the peak C. Indeed, autochthonous marine DOM through successive condensation reaction and structural rearrangements stages may also produced humic-like components (M and C peaks). That is why upward mixing could inject humic-like autochthonous CDOM in surface waters, as expected on 25 November 2008. We agree that it a continuum may exist between labile towards refractory DOM which could be illustrated by the different fluorescent peaks. As observed by Coble (1998), there is an increase in fluorescence intensity of C and M peaks with depth.

Thus, we have replaced the sentences:

- P. 5692, line 20-25 “Concerning CDOM fluorescence properties..... within surface fluorescent CDOM pool” by “Concerning CDOM fluorescence properties, our study showed the dominance of recent autochthonous compounds (peak T, BIX >1) and

extremely low values of humic substances (peaks C and M, HIX \approx 1) within surface fluorescent CDOM pool.”

- p 5692, line 27- p5693, line 3: “ The origins of peaks T and M.....deeper ocean water (Coble et al., 1998)” by “The origins of peaks T and M have been attributed to planktonic activity (Determann et al., 1998; Mykkestad, 2000; Nieto-Cid et al., 2006; Romera-Castillo et al., 2010) while the origin of peak C is known to be terrestrial and thus came from freshwater inputs (Sierra et al., 1997; 2005; Komada et al., 2002). However, peak C which is relatively abundant in deep waters could also originate from the humification of marine DOM and thus may reach surface waters during upward mixing events (Coble et al., 1998; Parlanti et al., 2000).”

9. *P. 5693, line 16. Should this really be that surprising? Isn't the Rhone River a very small influence here? The Arles station data show that the Rhone is low in TOC and CDOM (compared to other rivers).*

Answer: Yes at first we were surprised by the lack of terrestrial signature from the Rhone River in the Bay of Marseilles during plume intrusion. Indeed DOC values found in the Rhône River are relatively high and range from 100 to 400 μ M depending of the river regime (Sempéré et al., 2000) and 50% of the DOC pool absorb light (data not shown). The a_{CDOM} and DOC values are in the low range of those observed in the majority of World river waters (Chen et al., 2004). Rhone River water photo-irradiation experiment included in the revised MS showed a strong loss (60%) of a_{CDOM} after an irradiation time corresponding to 7 days under natural irradiation. Therefore, the lack of terrestrial signature during plume intrusion in Marseille's Bay is probably due to a combination of several processes: photobleaching, flocculation at low salinity and dilution.

10. *P. 5696, line 5. I think that most tryptophan isn't found as free protein, but rather as residue or bound to something else. That might also complicate your interpretation and your spectral analysis.*

Answer: Currently, there is no consensus concerning the origin of protein-like fluorescence in seawater, whether it is entirely from free amino acids in the DOM pool, or partially from amino acids bound in proteins/peptides or organism cell walls. EEM of standard free dissolved tryptophan displays both peaks: T1 (Ex/Em: 220-225/355-360 nm) and T2 (Ex/Em: 275-280/355-360 nm) (Determann et al., 1998; Mayer et al., 1999; Tedetti et al., 2010). Consequently, the tryptophan-like materials emission spectra observed in our samples were blue shifted compared to the corresponding standard. This could suggest that the tryptophan-like fluorescent materials present in the surface waters of Marseilles would be bound in proteins/peptides rather than being free amino acids (Lakowicz, 2006). Moreover, according to Lakowicz (2006) and Mayer et al. (1999) tyrosine fluorescence is quenched by tryptophan in folded proteins. This implies that the tryptophan observed at SOFCOM station is probably bounded in proteins rather than in free dissolved form.

11. P. 5695, line 28. Please clarify ‘CDOM exhibited... spectral slope (table 2)’; I don’t understand this at all.

Answer: In the revised MS, we replaced the sentence: “At the beginning of summer (23/06/2008 sample) during an important surface extent of the Rhône River plume in the Bay of Marseilles, CDOM exhibited an absorption coefficient in the upper range with the highest spectral slope (Table. 2), comparable to those generally observed in open ocean (Blough and Del Vecchio, 2002)” by “At the beginning of summer (23/06/2008 sample) during an important surface extent of the Rhône River plume in the Bay of Marseilles, CDOM showed a high absorption coefficient along with the highest spectral slope (Table 2) underlining the biological origin of CDOM.”

References

Chen, Z., Li, Y., and Pana, J.: Distributions of colored dissolved organic matter and dissolved organic carbon in the Pearl River Estuary, China. *Cont. Shelf Res.*, 24, 1845–1856, 2004

Lakowicz, J.R.: *Principles of fluorescence spectroscopy*. 3rd edition Springer Science; New York: 2006. pp. 158–204.