Response to Reviewer#3

We appreciate the reviewer's constructive comments. Our responses are *italicized*.

AR stands for authors' response

This work presents the seasonal distribution (May, Aug, Nov, and Jan 2015) of DOM (DOC concentrations, CDOM absorption and CDOM fluorescent components (from PARAFAC analysis) in Pearl River estuary (PRE), China. DOC concentrations and CDOM absorption and fluorescence properties (and their qualitative metrics) were examined in relation to salinity as well as to each other. In addition, fluxes of DOC and CDOM from the PRE to South China Sea were also estimated. Overall, results of this study provides new insights into the seasonal DOC and optical properties of CDOM in PRE. In comparison, most previous studies have mainly reported one or two field campaigns, while this study comprised a more seasonal study (four field campaigns).

However, the analysis of the data throughout involves simple correlation analysis and is descriptive with no rigorous analysis of field data (spatial analysis, precipitation, chlorophyll and turbidity measurements that were indicated in the text to have been measured). The additional analysis would support a better understanding of the sources and sinks related to the DOM in PRE.

AR: *All the discussion and conclusions are based on the quantitative analysis of the data. Our results have clearly demonstrated that physical mixing (i.e. salinity) is the predominant factor controlling the variability of DOM in the PRE (Figs. 3 and 4). We have now added a principal component analysis (PCA) on the all-season dataset to further strengthening the manuscript. The PCA includes variables in addition to salinity, such as water temperature, chl-a, nutrients, suspended particulate matter, and freshwater discharge rate. The DOM dynamics is represented by CDOM absorption at 330 nm (a_{330}) and DOC concentration. The first two axes of the PCA explained >74% of the variability in the dataset (see graph below). Using the first axis on the following graph, one can see that DOC and a_{330}, along with a bunch of other variables (e.g. nitrate, nitrite, silicate, chl-a), are strongly negatively correlated to salinity, which is a typical indication of a conservative mixing behavior. In contrast, DOC and a_{330} are only weakly (negatively) linked to the freshwater discharge rate, again consistent with our result (line 604-*

606 & Fig. S9 in the original version).

As the PCA does not bring much new information on the DOM dynamics, we have added the plot to the Supplemental Material (instead of the main text) and briefly discussed it (i.e. reinforcing the conclusion already reached) in the revised manuscript.

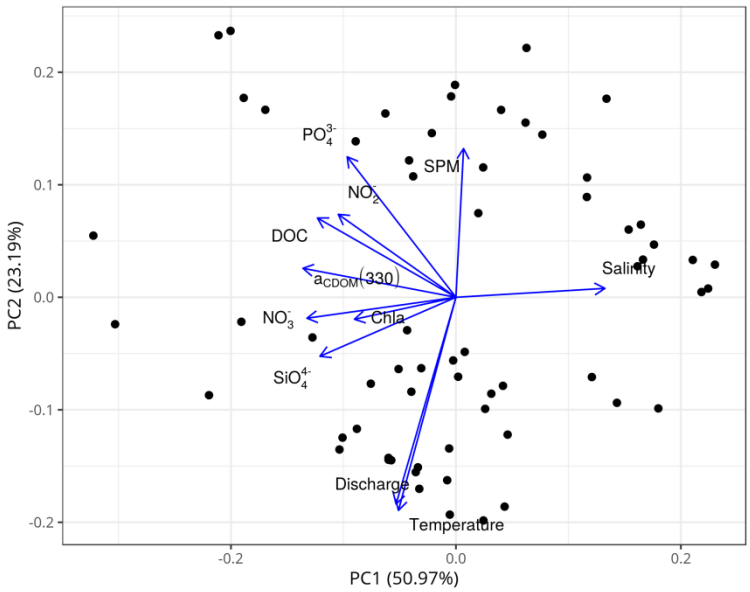

Figure: PCA analysis based on the all-season dataset. SPM: suspended particulate matter; PO_4^{3-}: phosphate; NO_2^-: nitrite; DOC: dissolved organic carbon; $a_{CDOM}(330)$: CDOM absorption coefficient at 330 nm; NO_3^-: nitrate; Chla: chlorophyll a; SiO_4^{4-}: silicate; discharge: freshwater discharge rate.

I find that the manuscript needs further improvements and the authors should address some major concerns/suggestions before the paper can be accepted for publication.

Major comments/suggestions: 1) There are various major sources of freshwater to the PRE. Previous studies have also indicated spatial differences in the surface and bottom properties in CDOM optical properties (absorption coefficients and spectral slope; e.g., Lei et al. 2018). Furthermore, seasonal analysis of DOC (Ye et al. 2018) indicated strong seasonality in DOC with substantial removal of DOC in the salinity range 5-22. I think a more comprehensive

analysis using all the available data (e.g., chlorophyll, turbidity, etc) including spatial distribution plots (surface and bottom) would greatly help in supporting the conclusions of this study.

AR: *The spatial plots are already provided (Figs S1, S2, and S4-S7 in the Supplemental Material) and discussed in the main text. Our conclusions are based on an analysis of not only quantitative variables ([DOC], a_{CDOM}, and 5 FDOM components) but also a large number of qualitative variables (E_2/E_3, BIX, HIX, and the percentages of FDOM components). The more comprehensive data analysis using PCA shown above further strengthens the conclusions already reached in our article.*

The difference between the studies the reviewer mentioned and ours may be caused by different spatiotemporal coverage of water sampling and potentially large interannual variability of the DOM dynamics in the PRE, as already suggested in the original manuscript (line 131-141; line 548-553 in the original version). In the revised manuscript, we reinforced this point by including the very recent reference suggested by the reviewer (i.e. Ye et al., 2018; the paper by Lei et al. (2018) was already cited). Note that the potential interannual variability further complicates the generalization of the DOM dynamics and biogeochemical cycling in the PRE.

2) Throughout this study the authors describe the data collected in the main estuary as the saltier zone as opposed to fresh water zone. I think a more traditional separation of the zones (e.g., Cai et al. 2004; upstream region, estuary, outer estuary) would be more appropriate and could better support the results of this study.

AR: *We disagree. Our data clearly show that essentially all DOM variables showed distinctly different behaviors between the low-salinity and the saltier zones (as defined in the manuscript), while in each of the two zones these variables exhibited consistent patterns. Hence, it is logical to split the estuary based on this characteristic. The way one chooses to divide the estuary depends on how well it facilitates data presentation and interpretation not on if it follows previous models.*

3) The absorption coefficient at 330 nm used in this study has not generally been used and therefore not easily comparable to other studies. Although Table S1 includes some of these wavelengths, it would help if the authors replace the absorption at 330 nm with another

commonly used wavelength. Also the spectral slope between 275-295 nm is now generally used to assess CDOM properties and should be included in the analysis.

AR: *We disagree with the reviewer on the use of the wavelength of 330 nm for a_{CDOM}. First, the wavelength at or close to 330 nm is where the majority of aquatic CDOM photoreactions (including photobleaching) exhibits the maximum rates in surface waters under solar radiation (e.g. Vähätalo et al., 2000; Zhang et al., 2006; Osburn et al., 2009; Xie et al., 2009, 2012; White et al., 2010; Song et al., 2013; Hong et al., 2014; Qi et al., 2018). The wavelength of 330 nm is, therefore, is linked to an important process controlling the cycling of CDOM in natural waters. This point has now been explicitly stated in the revised manuscript. Second, $a_{CDOM}(330)$ has been used as an indicator of CDOM content by many labs including those well recognized labs (e.g. Brisco and Ziegler, 2004; White et al., 2008; Osburn et al., 2009; Xie et al., 2009; Gareis et al., 2010; Mann et al., 2012; Song et al., 2017; Qi et al., 2018). Third, there is no consensus on which wavelength is best to serves as a proxy of CDOM content. A limited review of the literature shows at least 13 wavelengths (254, 300, 320, 325, 330, 350, 355, 375, 380, 400, 412, 420, and 440 nm) have been adopted for this purpose. Finally, in case the reader is interested in other wavelengths, we have provided absorption coefficients at 6 other wavelengths across the UV and visible regimes that are commonly seen as well in the literature (Table S1 in the Supplemental Material). Furthermore, we also published the spectral slope between 300 and 500 nm (again in Table S1), so that the reader can retrieve the absorption coefficient at any wavelength between 300 and 500 nm interval. We believe we have done our best to accommodate the different needs of the scientific community.*

The spectral slope and slope ratio ($S_{275-295}$, $S_{350-400}$ and S_R) were also investigated and they showed similar patterns to those of E_2/E_3. E_2/E_3 was chosen, because 1) it exhibited larger variations than the spectral slopes and slope ratio; 2) it has been used as a valid proxy of molecular weight for a much longer history (De Haan, 1983; Peuravuori and Pihlaja, 1997) than the spectral slope and slope ratio, particularly for fresh and brackish waters (including estuarine waters); 3) it is very sensitive to and quantitatively responds to photobleaching (Lou and Xie, 2006; Qi et al., 2018) and biogeochemical processing; 4) a quantitative and validated relationship between E_2/E_3 and the molecular weight (MW) of CDOM is available (Lou and Xie, 2006; Qi et al., 2018), so that this relationship can be used to estimate the MW of CDOM for the

present study (line 439-443 in the original manuscript). Note that such a broadly applicable relationship has not been established between $S_{275-295}$ and MW.

We have explicitly stated in the revised manuscript that E_2/E_3 serves similar functions to those of $S_{275-295}$.

4) CDOM generally is a good optical proxy for DOC, especially in estuaries. Also, CDOM undergoes rapid photobleaching in the estuaries or the coastal waters. It may not be useful include estimates of CDOM fluxes at 330 mn from the estuary to the SCS, especially since the wavelength used is so unique to this study.

AR: *For the wavelength issue, we think we have chosen an appropriate wavelength to represent CDOM content and photobleaching and (see our response to RC3's comment 3).*

Even if CDOM degrades rapidly in estuaries and coastal waters (often that's not true, see below), it does not necessarily imply that the export of CDOM to the ocean is not important. If the remaining component of CDOM exported to the ocean, albeit small in amount, is bio- and photo-resistant, it can accumulate in open oceans. This why the oceanographic community has put tremendous efforts in identifying and quantifying potential terrigenous DOM (the main part of it could be CDOM) in open oceans (Opsahl and Benner, 1997; Cauwet, 2002; Raymond et al., 2007; Bianchi and Allison, 2009; Dai et al., 2012; Wang et al., 2012; Raymond and Spencer, 2015). This issue is fundamental for understanding the global carbon cycle! This is partly why (other aspects involve ocean optics) scientists have started making efforts to evaluate the land-to-ocean CDOM fluxes (e.g. Stedmon et al., 2011; Spencer et al., 2013; Aarnos et al., 2018).

Concerning the specific case of the PRE, our data clearly indicate that CDOM behaved essentially conservatively in the saltier zone (i.e. ca. salinity >5), implying that photobleaching was insignificant. We also made a direct estimate of the amount of CDOM that could be removed by photobleaching in the PRE; it was at most 7% (line 487-507 in the original version), supporting the inference from the conservative CDOM vs. salinity plots. This not surprising, given that 1) the residence time of freshwater (and thus CDOM as well) in the PRE is very short (a few days, line 494-497in the original version; 2) the competition of light absorption by particles (water in the PRE is turbid); and 3) self-shading due to sufficiently high CDOM and

particle abundances in the PRE.

In general, estuaries and strongly runoff-impacted coastal waters are not prone to having efficient CDOM photobleaching due to at least the three reasons stated above. Efficient photobleaching usually takes place in waters on the outer shelf (e.g. shelf break) where CDOM has been sufficiently spread out and the majority of the particles have settled down to the seafloor (so that self-shading is diminished).

5) It may be useful to look at meteorological data (e.g., wind field) to see if mixing played a role in reducing the variability in DOM surface and bottom properties.

AR: *It is the salinity and temperature structures (Figs. S1 and S2), not the meteorological information, that directly indicate the degree of water column mixing. We used the salinity and temperature data to discuss the surface and bottom variability on each relevant occasion.*

Minor comments: -No indication of how salinity was measured -Methods section could describe the study site rather than in the Introduction.

AR: *It is already there (see line 182-183 in the original version).*

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AR: *Thanks for providing these two references. Lei et al (2018) was already cited in the original manuscript. Ye et al (2018) has now been added.*

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