Response to Public Short Comment

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

SC stands for short comment from the scientific community
AR stands for authors' response

SC: Dissolved organic matter is an important component of the carbon cycle in aquatic systems and it exerts direct impact on the overall biogeochemical process in the ocean. DOM spectroscopy has emerged as a cost-effective and easy-to-measure technique for quantifying and, more recently, qualify the DOM content in the environment. The manuscript by Li and colleagues brings results on DOM amount (expressed by means of DOC and spectroscopic measurements), characterization (through EEM- PARAFAC), fluxes and seasonal variability for the Pearl River Estuary, China. The data set is robust and the methods applied align with current literature. Although the sampling grid remains the same for the different seasons, the seasonal averages presented in the MS might be biased by the spatial variability presented within the water masses spatial distribution within the region. Therefore, I suggest the authors to have lead the MS through a more "oceanographic point of view", i.e., by investigating the seasonal changes within the water masses presented within the region.

***AR:** We adopted the classical approaches for describing chemical variables in an estuary: property vs. distance and property vs. salinity. Salinity is an indication of mixing processes, while distance is more related to residence time and processing time. These two approaches are complementary. The seasonal averages presented in our MS are based on the "distance" approach, given that the coordinates of the sampling stations were the same for different seasons. These averages thus reflect the seasonality of the residence and processing times of the water masses in the estuary. On the other hand, the property vs. salinity plots provided information on how the mixing behavior of a variable of interest changed seasonally. As water masses in an estuary are primarily defined by salinity, the seasonal variability revealed by this approach is essentially water mass-based. A more complete picture of the seasonality of the variables is acquired by combining the results from the distance and salinity approaches. This is the rationale behind the scheme we employed to present our data.*

As our sampling stations were principally distributed along the main longitudinal axis of the estuary with little lateral coverage (as is true for many other estuarine studies), the data thus collected is insufficient to characterize the spatial distribution of water masses in the region, making the "oceanographic point of view" approach suggested by the reviewer difficult to implement.

SC: Although the manuscript is well written and reads easily, the way that sections are structure makes the manuscript repetitive when presenting and discussing results. I think it would become more concise and interesting if the authors focus on making a rearrangement of sections (by merging/condensing some of them) and on making a review through the text to avoid such repetitions. Additionally, the introduction is a bit too long and could be shortened by providing only information needed for interpretation of results from this study. Thus, to my judgment, the manuscript may be publishable after major reviews.

AR: *The rationale for presenting the data in two ways (i.e. property vs. distance and property vs. salinity) is given in the above response. By grouping the variables into the quantitative and qualitative categories, we structured the manuscript in a manner that substantially differs from the stepwise style (i.e. a sequential treatment of individual variables) taken by many publications of similar nature. Our approach minimized the repetition needed to delineate the similarities of many variables in each category while maximizing the difference between the quantitative and qualitative variables, which is a major finding of this study.*

We understand readers have different preferences for the way by which a paper is written. For example, Reviewer#2 thinks that this manuscript is well structured. Reviewers#1 and 2 do not provide comments on the structure, implying that they either have a favorable or at least do not have a major unfavorable opinion on this style. We believe the current structure well meets the need to clearly and concisely present the data obtained and thus decided not to make a major structural change. However, we did make an effort to further reduce any potential repetitive text.

The Introduction has now been condensed and re-organized (much of the description of the PRE is moved to the Methods as a separate subsection "Study area"). See response to RC1's comments 2&3 on the Introduction.

GENERAL COMMENTS:

SC: The abstract does not clearly illustrate the main findings obtained in the study.

AR: *We have shortened and rewritten the abstract to focus on the main findings.*

SC: The hypothesis presented in section 1.3 seem weak and vague, and could be sharper. Seasonal variability in DOM flux is already expected from an estuary with marked seasonal variability in freshwater export, as documented by the authors.

AR: *DOM flux is only one of the many DOM variables (both quantitative and qualitative) reported in this study. In fact, most other variables showed smaller spatial and seasonal variations than expected from this sizable estuary with an important seasonal fluctuation of freshwater discharge (see the Conclusions section). The fluxes of DOC and CDOM are also the lowest compared to other major world rivers, contrasting with the hypothesis. Therefore, we feel that the current working hypothesis is appropriate and strong enough. Although a "sharper" hypothesis may be more eye-catching and sensational, it may not necessarily help improve the science of this paper.*

SC: Sampling strategy: why was decided to collect the "deep water" sample near the bottom and not below the pycnocline? It can be affected by sediment resuspension, if there is any.

AR: *One of the purposes of this study was to determine if there was a significant sedimentary impact on DOM in the water column. The consistent property–salinity patterns (Figures 3 and 4) and lack of relationship with suspended particle concentration (Line 512 in the original version) suggest that this effect was minor. Note that the effect of sediment resuspension could reach the depths just below the pycnocline, given the overall shallow water depths of the PRE (mostly <10 m, Table 1 in the original version)*

SC: Have the authors looked at the CDOM absorption spectral slope and slope ratio? It could provide more insights into the photochemical reactions along the estuarine mixing.

AR: *The spectral slope and slope ratio ($S_{275\text{-}295}$, $S_{350\text{-}400}$ 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 $S_{275-295}$.

SC: The authors could also try to use multivariate analysis (e.g., PCA) to analyze the variability between the campaigns (i.e., over time) and to elucidate what are the main drivers on DOM variability within the region.

AR: *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). Here we performed a principal component analysis (PCA) on the all-season dataset that 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. 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.

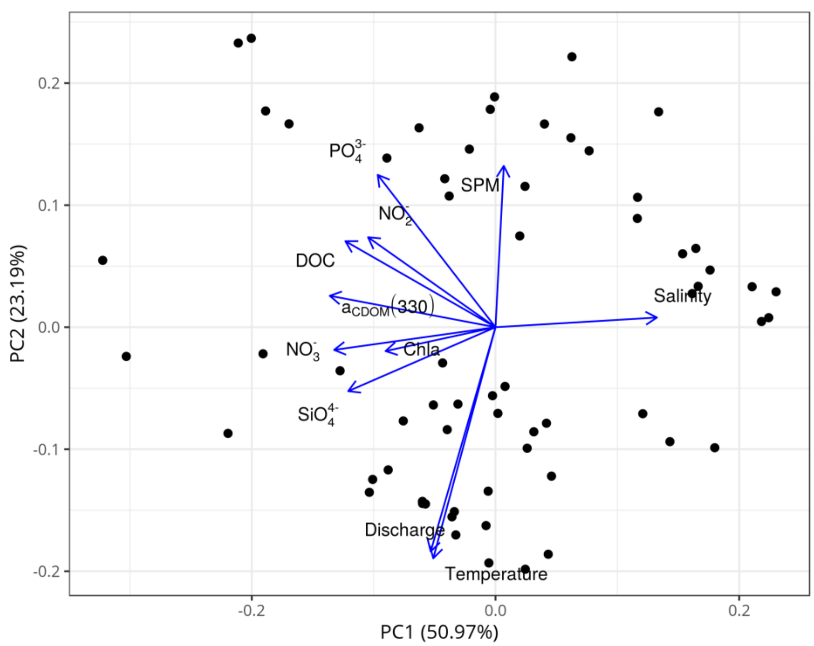

Figure: PCA analysis based on the all-season dataset. SPM: suspended particulate matter; PO_4^{3-}: phosphate; NO_2^-: nitrite; DOC: dissolved organic carbon; $a_{CDOM}(330)$: CDOM absorption coefficient at 330 nm; NO_3^-: nitrate; Chla: chlorophyll a; SiO_4^{4-}: silicate; discharge: freshwater discharge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

SC: I suggest the authors to compare their PARAFAC-derived components spectra with the OpenFluor database (https://openfluor.lablicate.com/). This would benefit the comparison established with other studies along the MS.

AR: *This has now been done and a table is added to the Supplemental Material to show the results of comparison.*

SC: With respect to the sources of DOM to region, especially the pollution-derived DOM, they could be more stressed along the MS. It is not totally clear how the findings of this study support that.

AR: *Pollution-derived DOM is a dominant source of DOM in the upper reach of the PRE, generally upstream of Humen. Note that this is* ***not*** *a finding of our study, rather a conclusion of* *previous studies (as clearly stated in the Introduction, line 120-130 in the original version). Some previous studies (e.g. Lin et al., 2007; He et al., 2010) conducted sampling much farther upstream into the Guangzhou Channel, where the capital of the Guangdong Province is located. The concentration of DOC in that channel could reach as high as 500 uM, which is ~4 times the background DOC (119 uM) in the Pearl River upstream of the Pearl River Delta (He, 2010). This observation, combined with the enormous amount of industrial and domestic waste discharged into the PRE ($5.8*10^9$ tons/year) across its deltaic region, led these authors to concluding that the highly enriched DOC in the upper reach of the estuary mostly originates form sewage effluents. The pollution-derived DOC is, however, very labile and much of it is consumed by bacteria in the low-salinity zone of the estuary (He, 2010, He et al., 2010). Our data provided two lines of evidence to support the pollution argument for our sampling seasons: 1) a rapid drawdown of DOC and CDOM in the upper reach, which is consistent with the labile character of pollution-derived DOM as elucidated in the previous studies; 2) the protein-rich character of this DOM pool as revealed by the fluorescence-based metrics (BIX and %(C1+C5)). These two points are elaborated in the relevant context (section 4.1).*

SC: Section 4.5 establishes comparisons among global DOM studies but I expected the discussion to bring some conclusions on the reason for such differences rather than just comparing them.

AR: *We are a bit confused by this comment. Section 4.5 clearly indicates that two factors mainly contribute to the lowest DOM abundance and flux in the PRE: 1) the deficiency of organic matter in soil of the Pearl River's watershed having almost no forest; 2) the rapid microbial consumption of pollution-derived DOM in the upper estuary. These two factors are once again emphasized in the Conclusions section. Moreover, the main portion of section 4.5 is discussion instead of "just comparison".*

SPECIFIC COMMENTS:

SC: L75-79: authors could give more background on anthropogenic/pollution-derived DOM, given that it is a DOM source for the region, as pointed out in this study.

AR: *This point is actually brought up on two other occasions in the Introduction about the PRE (line 122-125; line 145-148 in the original version). We believe the background information for this point is sufficient, particularly considering that the Introduction is already long and needs to be shortened.*

SC: L115-119: Please present values (ranges) for the variables. How much does the phytoplankton biomass vary within the seasons?

AR: *The ranges were added.*

SC: L124-125: Are there only those two studies supporting this affirmation? No study published in English?

AR: *After re-searching the literature, we found one more paper (He et al., 2010, published in English) for supporting this argument. This reference has now been added.*

SC: L306-307: what do the authors mean by "freshwater input from this river appeared to have little influence on [DOC]" ?

AR: *Sta. M01, 02 and 03 were distributed along a transect across the three outlets of the East River (i.e. upper, middle, and lower outlets, Fig. 1). However, the [DOC]s at these three stations in May were nearly constant, suggesting that the freshwater input from the East River did not significantly affect the [DOC]. This further implies that [DOC] in the East River in May was roughly equal to that in the North River, which is the larger freshwater source of the upper reach of the PRE (~2 times that of the East River, line 95-98 in the Introduction).*

SC: L500-503: Missing references.

AR: *Thanks. The missing reference (He, 2010) was added.*

SC: L522-526: I found the explanation for different mixing behavior weak and should be discussed more in deep.

AR: *The observation needs to be explained: In the saltier zone, [DOC] remained rather constant while [CDOM] (in terms of a_{330}) decreased linearly with increasing salinity in November; in*

August and January, [CDOM] decreased much faster than [DOC] with increasing salinity.

Our explanation: 1) CDOM was only a minor component of the entire DOM pool (so that the change in [CDOM] had little impact on [DOC]); 2) the marine endmember was less colored (i.e. lower a_{CDOM}*) than the freshwater endmember (so that [CDOM] decreased with increasing salinity); 3) the difference between the marine and freshwater DOC endmembers was much smaller than that for CDOM (so that the salinity-based gradient for [DOC] was much smaller than that for [CDOM]). A combination of points 2 and 3 leads to a smaller [DOC]-normalized* a_{CDOM} *for the marine endmember than that for the freshwater endmember (which is what we presented in the manuscript).*

We are confident that our explanation is sound. To make our explanation clearer, these three points have now been stated separately (instead of combining points 2 and 3).

SC: L527-535: this paragraph/discussion could be deepened in the sense to explain the reasons for such variations.

AR: *This paragraph is actually a summary of section 4.2. The deeper discussion is presented in the preceding paragraphs. Moreover, the lack of sampling within the main freshwater outlets (e.g. Hengmen, Jiaomen, Hongqimen) downstream of Humen prevents us from further discussing the potential impact of different freshwater masses.*

SC: L538-547: Why does it only have good correlations for summer and winter? What happens with the correlations during the other seasons? Additionally, was the DOC- aCDOM correlation significant and strong? I ask that, because that correlation does not hold true for several environments.

AR: *In spring and fall, [DOC] in the saltier zone was relatively constant and consequently not correlated with salinity as opposed to the case in summer and winter.* a_{CDOM}*, however, showed negative correlations with salinity in all three sampling seasons (summer, fall, and winter). This distribution pattern is already described in section 3.4 and discussed in section 4.2, and thus not repeated in section 4.3. Instead, we referred the reader to Fig. 3 for understanding the relevant context.*

Yes, the DOC-a_{CDOM} is significant and strong ($p<0.0001$, now added to the text). Although this kind of correlation may not hold universally, many marine environments, include estuaries and coastal waters, do exhibit such correlations, e.g. the Middle Atlantic Bight (Del Vecchio and Blough, 2004), Yukon River (Spencer et al., 2009), Yangtze River estuary (Guo et al., 2014), and the Baltic coastal sea (Harvey et al., 2015).

SC: L556-580: authors could deepen the discussion regarding the fluxes.

AR: *More discussion about the fluxes is provided in section 4.5.*

SC: L615-623: what could the authors point out as the reason for such differences?

AR: *This is because the [DOC] and [CDOM] in the PRE are the lowest among the world major rivers. Line 600-6004 in the original version has already speculated on two factors causing this phenomenon: the poorly forested watershed of the Pearl River and the rapid degradation of sewage-derived DOM.*

SC: Figure 1: It would be interesting to have two panel composing this figure: one with the sampling sites and another with the city names and also the main circulation patterns.

AR: *As the circulation pattern changes with season, which needs four panels to do it. Moreover, the distributional pattern of the sampling stations (an along-estuary transect without much cross-estuary coverage) does not allow us to adequately characterize the circulation patterns during our sampling periods. Hence, adding a circulation pattern panel may not significantly improve the presentation and interpretation of the data.*

SC: Figs 3, 4, 5 and 8: please present the curve fits and stats.

AR: *Lines in Figure 5 denote the conservative mixing lines, not the data fits. The curve fits and statistics are already presented in Table 4 for Figures 3 and 4 and in Table 5 for Figure 8 in the original manuscript.*

References cited in this response:

De Haan, H., 1983. Use of ultraviolet spectroscopy, gel filtration, pyrolysis/mass spectrometry and numbers of benzoate metabolizing bacteria in the study of humification and degradation of aquatic organic matter. In: Christman, R.F., Gjessing, E.T. (Eds.), Aquatic and Terrestrial Humic Materials. Ann Arbor Science, Michigan, pp. 165–182.

Del Vecchio, R. and Blough, N.V., 2004. Spatial and seasonal distribution of chromophoric dissolved organic matter and dissolved organic carbon in the Middle Atlantic Bight. Marine Chemistry, 89(1-4), 169-187.

Guo, W., Yang, L., Zhai, W., Chen, W., Osburn, C.L., Huang, X. and Li, Y., 2014. Runoff‐mediated seasonal oscillation in the dynamics of dissolved organic matter in different branches of a large bifurcated estuary—The Changjiang Estuary. Journal of Geophysical Research: Biogeosciences, 119(5), 776-793.

Harvey, E.T., Kratzer, S. and Andersson, A., 2015. Relationships between colored dissolved organic matter and dissolved organic carbon in different coastal gradients of the Baltic Sea. Ambio, 44(3), 392-401.

He, B., Dai, M., Zhai, W., Wang, L., Wang, K., Chen, J., Lin, J., Hua, A., and Xu, Y.: Distribution, degradation and dynamics of dissolved organic carbon and its major compound classes in the pearl river estuary, China, Mar. Chem., 119, 52–64, 2010.

He, B.: Organic Matter in the Pearl River Estuary: its Composition, Source, Distribution, Bioactivity and their Linkage to Oxygen Depletion (Ph.D. Dissertation), Xiamen university, 2010 (In Chinese).

Lin, J.: On the behavior and flux of Dissolved Organic Carbon in two large Chinese estuaries-Changjiang and Zhujiang (Master Dissertation), Xiamen university, 2007 (In Chinese).

Lou, T., Xie, H., 2006. Photochemical alteration of the molecular weight of dissolved organic matter. Chemosphere 65, 2333–2342.

Peuravuori, J., Pihlaja, K., 1997. Molecular size distribution and spectroscopic properties of aquatic humic substances. Anal. Chim. Acta 337, 133–149.

Qi, L., Xie, H., Gagné, J.P., Chaillou, G., Massicotte, P. and Yang, G.P., 2018. Photoreactivities of two distinct dissolved organic matter pools in groundwater of a subarctic island. Marine Chemistry, 202, 97-120.

Spencer, R.G., Aiken, G.R., Butler, K.D., Dornblaser, M.M., Striegl, R.G. and Hernes, P.J., 2009. Utilizing chromophoric dissolved organic matter measurements to derive export and reactivity of dissolved organic carbon exported to the Arctic Ocean: A case study of the Yukon River, Alaska. Geophysical Research Letters, 36(6).