Response to Reviewer#2

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

AR stands for authors' response

This paper deals with the seasonal variability, spatial distribution, transformation processes and fluxes of dissolved organic matter (DOM) in the Pearl River estuary (PRE) in China. DOM is investigated through dissolved organic carbon (DOC), chromophoric (CDOM) and fluorescent (FDOM) dissolved organic matter. Overall, this work provides relevant results and good quality data concerning the dynamics and fluxes of DOM in the PRE. The manuscript is well structured, quite well written, and is obviously within the scope of Biogeosciences. Therefore, I recommend the paper to be published in Biogeosciences after "moderate" revisions. Below my comments:

1. Title. The part "optical characteristics" could be removed from the title.

AR: *"optical characteristics" was removed.*

2. Although English is not bad, the manuscript could benefit from corrections of an English native speaker.

AR: *The language has been further polished.*

3. The abstract has to be substantially improved. It does not reflect at all the relevance of the study. For instance, the following part: "The seasonality of average DOM abun- dance varied as follows: DOC: May (156 μmol L−1) > January (114 μmol L−1) ~ August (112 μmol L−1) > November (86 μmol L−1); CDOM absorption at 330 nm: Au- gust (1.76 m−1) > November (1.39 m−1) ~ January (1.30 m−1); FDOM expressed as the sum of the maximum fluorescence intensities of all FDOM components: November (1.77 R.U.) > August (1.54 R.U.) ~ January (1.49 27 R.U.). Average DOM abundance in surface water was higher than in bottom water, their difference being marginal (0.1– 10%) for DOC in all seasons and for CDOM and FDOM in November and January, and moderate (16–21%) for CDOM and FDOM in August" did not deserve to be included in the abstract.

AR: *We reorganized the abstract by emphasizing the major findings and reducing numbers.*

4. Introduction. Subtitles ("1.1 Overview of DOM", "1.2 The Pear River estuary", "1.3 Hypothesis and objectives") should be removed. Usually there is no subtitle in the introduction. The first part concerning DOM is OK but the second one (PRE) is too long and too detailed. Most of these details should go in the "2 Methods" part, in a "2.1 Study area" section, which currently does not exist by the way. Only information about PRE that is useful for highlighting the problematic and hypothesis is necessary in the Introduction.

AR: *The description of the PRE in the Introduction section was condensed and the details were moved to a new section "2.1 Study area" in the Methods. Please see our detailed response to Reviewer#1's General Comments 2&3.*

5. Introduction. The sentence: "The biogeochemical and optical significance of DOM depends on both its abundance and quality (i.e. chemical composition), with the latter strongly linked to its origin of formation" is not clear. Please re-phrase.

AR: *Now rephrased to "The significance of DOM-driven biogeochemical and optical processes depends on DOM's abundance and quality (i.e. chemical composition), with the latter strongly linked to the source of DOM*"

6. Sample collection. I guess the number of samples collected at each season for DOM analyses is not mentioned. This should be mentioned here.

AR: *Stating the number of samples does not provide extra essential information, since the numbers of sampling stations and depths are already reported.*

7. The subtitle "2.2 Sample analysis" should be replaced by "2.2. DOM "analysis"

AR: *Changed to "DOM analysis".*

8. DOM analyses. "The analytical uncertainty of aCDOM measurement was assessed by analyzing six pairs of duplicate samples collected from the August cruise. Average aCDOM at 330 nm (a330) was 2.19 m−1 (range: 1.19–4.37 m−1); the average difference in each pair was 0.07 ± 0.05 m−1, or 3.0% ± 1.4%." This method for assessing the analytical uncertainty (precision?) is not clear to me. Why using six pairs of duplicates? I would have used six replicates (of the same sample). The values "0.07 ± 0.05 m−1, or 3.0% ± 1.4%" is not pertinent.

AR: *Analyzing replicates of the same sample excludes the uncertainty associated with the fact that the uncertainty, particularly the relative uncertainty, changes with a_{CDOM}. As shown in the article (Fig. 3), a_{CDOM} in the PRE decreased substantially from the head to the mouth of the estuary. An uncertainty determined from "the same sample" thus cannot represent the entire PRE. In this respect, the uncertainty obtained from our approach is more realistic, since the samples for this assessment essentially covered the entire estuary. In fact, we also determined the uncertainty using 6 replicates of one sample (a_{330}: 4.37 m^{-1}), arriving at a standard deviation of 0.06 m^{-1} or 1.3%, which, not surprisingly, is lower than that determined with the multi-sample approach.*

Note that our approach is not new. It has been adopted by previous studies for measuring other chemical variables (e.g. Zafiriou et al., 2008; Xie et al., 2009).

9. DOM analyses. CDOM spectral slope in the range 300-500 nm (S300-500 in nm-1) is reported in the supplementary material (Table S1) but is not really discussed in the manuscript. Also, in addition to S300-500 I would recommend the determination and examination of S275-295, proposed by Helms et al. (2008) and largely used yet. It could bring significant information about CDOM molecular weight and transformation processes.

AR: *The purpose of providing the $S_{300\text{-}500}$ in the Supplemental Material, as stated in the manuscript, is to facilitate the reader to compare results from different studies.*

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); 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 $S_{275\text{-}295}$ and MW.

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

10. DOM analyses. HIX, BIX and E2/E3 should be defined in this section and not in the results section.

AR: *Revised according to the reviewer's suggestion.*

11. Results. The number of Tables is quite high. I recommend adding some in the supplementary material: Tables 1, 2, 4, 5.

AR: *Tables, 1, 4, and 5 were moved to the Supplemental Material.*

12. Results. Besides salinity, are ancillary parameters available for this sampling (i.e., dissolved oxygen, nutrients, chlorophyll,...) that could help the interpretation of the DOM dynamics?

AR: *No oxygen data is available. Other ancillary data were collected by other groups and we cannot explicitly publish them. However, we have now performed a principal component analysis (PCA) that includes nutrients, chlorophyll a, suspended particulate matter, etc. to further help interpret the DOM dynamics. Please see response to comment 14 below.*

13. Results. I find there is a lack of use of statistical analyses. For example, ANOVA, t test, Mann Whithney test,... (depending on the normal distribution or not of samples) could be applied to determine statistical differences in the DOM concentrations between seasons, surface/bottom,....

AR: *ANOVA has now been conducted. The result indicates that 1) there were no significant bottom-surface differences in both DOC and a_{330}; 2) DOC presented small but significant seasonal variability, while a_{330} lacked significant seasonal difference, which further strengthens our conclusion that the spatial and temporal variability of DOM in the saltier zone of the PRE is smaller than expected for a sizable estuary with a marked seasonality of river runoff. This result was added to the end of section 3.2 in the Results.*

14. Moreover, instead of separate a priori the samples by seasons and looking at differences between these seasons (that do not necessarily represent/reflect different hydrological or

meteorological events which have occurred during the sampling period), it could be also interesting to apply multi-way statistical methods (principal component analysis, hierarchical ascendant classification,...) on all samples regardless of their sampling period. This could lead to different clustering of samples and underline particular processes affecting DOM dynamics, such as the impact of the mixing between marine and river waters, the impact of precipitation/runoff/river flow rate (ex: discrimination between samples collected in dry period and samples collected wet period), which could be obviously independent from seasons.

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.

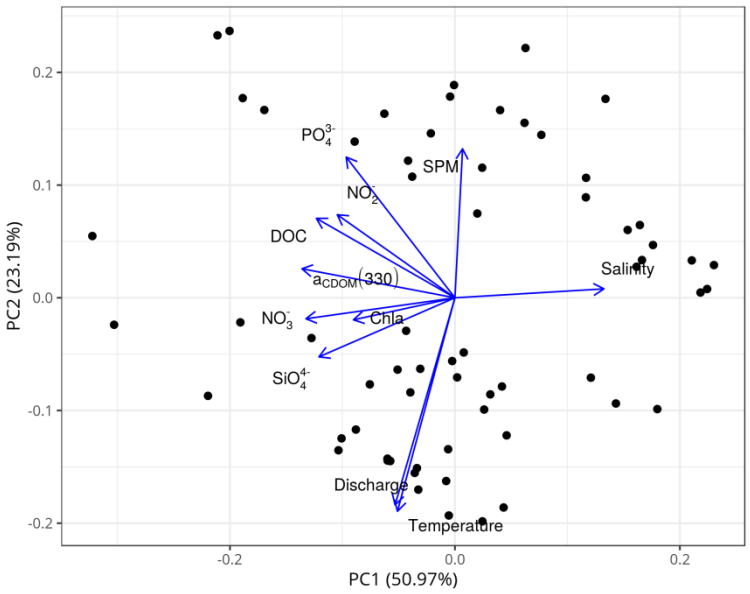

Figure: PCA analysis based on the all-season dataset. SPM: suspended particulate matter; PO_4^{3-}: phosphate; NO_2^-: nitrite; DOC: dissolved organic carbon; $a_{CDOM}(330)$: CDOM absorption coefficient at 330 nm; NO_3^-: nitrate; Chla: chlorophyll a; SiO_4^{4-}: silicate; discharge: freshwater discharge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

15. Discussion. Lines 600-614: "[DOC] and [CDOM] in the PRE are the lowest among the major world rivers..." This is indeed intriguing. Why DOC and CDOM contents are so low in the PRE. In this part, the authors should also include the assumption of a DOM loss by bacterial degradation and photochemistry.

AR: *We have demonstrated that bacterial uptake and photodegradation led to only minor losses of DOM in the saltier zone (usually at salinity >5) of the PRE due largely to the short residence time of freshwater in the estuary and the completion for light absorption by other optical constituents in the case photodegradation (line 492-509 in the original version). The manuscript proposed two main factors to explain the low DOM in the PRE: the poorly forested watershed and rapid bacterial DOM consumption in the upper reach of the estuary (salinity <5) (line 600-604).*

16. Discussion. Line 604: "The lack of correspondence between [DOC]* and a330* and the freshwater discharge rate (Fig. S9) suggests that [DOM] in the PRE be controlled by both soil leaching and pollution input". Here could be also added the hypothesis of in situ autochthonous

DOM production from phytoplankton activities, which are generally not negligible in rivers.

AR: *Good idea. This proposition was added.*

References cited in this response:

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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.

Xie, H., Bélanger, S., Demers, S., Vincent, W.F. and Papakyriakou, T.N., 2009. Photobiogeochemical cycling of carbon monoxide in the southeastern Beaufort Sea in spring and autumn. Limnology and Oceanography, 54(1), 234-249.

Zafiriou, O.C., Xie, H., Nelson, N.B., Najjar, R.G. and Wang, W., 2008. Diel carbon monoxide cycling in the upper Sargasso Sea near Bermuda at the onset of spring and in midsummer. Limnology and Oceanography, 53(2), 835-850.