Response to Editor's comments

Responses are *italicized*.
AR stands for authors' response

1. Main conclusions of the article are difficult to follow since there is repetition of results throughout the text, and there are results that are not considered in the discussion, deviating attention to main points of the article. Examples: a) Water temperature is shown but there is no discussion of it, b) idem with results on water column mixing, c) in page 263, "Bottom water salinity at most stations was nearly identical to SWS in January, slightly greater in May, moderately elevated in November, and much higher in August (Fig. S2)". There is no discussion of it in the text. If there is a meaning for this, then it needs to be quantitatively explained, not as currently written (slightly, much, etc.).

***AR:** We have re-organized the structure of the article to minimize the repetition of the results. a) water temperature has now been incorporated into the principal component analysis (PCA) for discussion (lines 453-461); b) & c) the effect of water column mixing/stratification on the vertical distribution of DOM has now been briefly discussed (lines 486-491); c) this sentence has been modified (lines 253-256).*

2. There is an excessive use of Supplementary tables and figures around relevant discussion and conclusions. Supplementary figures and tables are meant to back up tables and figures of the main text. A new version will require rethinking and reorganizing tables and figures accordingly.

***AR:** We have substantially reduced the supplementary tables and figures in the new version.*

3. Qualitative assessments should be avoided. such as saltier, less salty (Reviewer 3 suggests using well-known and accepted terminology by the estuarine community).

***AR:** The "head region" is now used to refer to the narrow low-salinity zone and "main estuary" to denote the saltier zone.*

4. Hypothesis. "… hypothesize that DOM in the PRE presents substantial seasonal variability in terms of both abundance and chemical composition and that the PRE is an important source of DOM to global oceans. "Chemical composition you are referring to is targeting a quantitatively minor fraction of DOC pool (in the order of 2%), therefore you cannot test that hypothesis for the entire pool using this approach.

***AR:** The hypothesis has been modified to "Given the large volume and seasonality of the freshwater discharge of the Pearl River, we hypothesize that the quantity of DOM and the quality of CDOM in the*

PRE present substantial seasonal variability and that the PRE is an important source of DOM to the global ocean".

5. What are units of DOC and CDOM fluxes in Table 6. Nowhere is mentioned how you estimated fluxes from absorbance data.

AR: *The units are already there: grams for DOC and* m^2 *for CDOM. The first 4 rows are for each season and the last row for one year. The equation and procedure for estimating the CDOM flux are already given in the original version (first paragraph of section 4.4).*

6. Keep in mind Short Comment:
" 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…."

AR: *Following the reviewer's comments, we have restructured and shortened the Introduction and Results sections.*

7. Section on Pearl River estuary is definitely too long, so it is background on DOM. Please choose the most relevant aspects.

AR: *Theses two sections have been restructured and shortened.*

8. "… [DOM], [CDOM], and [FDOM] stand for the abundances of…". Square brackets are used in chemistry to denote concentration and [CDOM] and [FDOM] are not; they could be considered proxies of concentration. Different things.

AR: *Now* $\langle CDOM\rangle$ *and* $\langle FDOM\rangle$ *are used to denote the proxies of CDOM and FDOM abundances.*

9. Use of non-standard acronym such as SWS only makes reading more difficult (It is used only 7 times in the text, all in one page).

AR: *This acronym has now been spelled out throughput the text.*

10. P, 286, P 409, etc.. Correlation and regression are not the same. In correlation there is no independent variable and coefficient of correlation (r) ranges from -1 to +1. In regression, there is X and Y, and coefficient of determination (R2) ranges from 0 to 1 (0 to 100%). Please check and revise accordingly

AR: *This has been checked and revised.*

11. Method. "Hansell's low carbon ([DOC]: 1–2 µmol L−1) and deep Florida Strait ([DOC]: 41–44 µmol L−1) reference waters "
What was the quantitatively results of this calibration?

AR: *The calibration results have been added to the revised version (lines 153-154)*

12. About the analytical uncertainty mentioned by Reviewer 2. #8. " … aCDOM at 330 nm (a330) was 2.19 m−1 (range: 1.19–4.37 m−1)…" corresponds to the range of values of a330 measured in the river during the August cruise. Analytical uncertainty on the other hand, deals with dispersion of values associated to a measure and, therefore samples has to be as similar as possible.

AR: *Now the uncertainty of measurements on 6 replicates of the same sample is reported. (lines 160-163).*

13. Lines 375-376. Please explain what you want to say here

AR: *This sentence does not exist anymore in the revised version.*

14. Lines 235-236 should be in methods

AR: *Now moved to the Methods (lines 225-227).*

Response to Reviewer 1

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The paper entitled "Distribution, seasonality, optical characteristics, and fluxes of dis- solved organic matter (DOM) in the Pearl River (Zhujiang) estuary, China" investigated seasonal and spatial variations of CDOM and FDOM characterized by absorption and fluorescence spectroscopy. Since I am an organic geochemist focusing on the organic carbon and nitrogen cycling mechanism in estuarine coastal zones and the role of microbes during the organic matter cycling, I am very familiar with the topic of this manuscript. This manuscript identified the compositional characteristics and sources of DOM. The main conclusion is that (i) microbial inputs and anthropogenic inputs are important sources of DOM in the freshwater end; (ii) small seasonal variations with respect to DOC and CDOM; and (iii) PR exports the lowest quantality of DOC among 30 large world rivers, although the size of PR watershed ranked the thirteenth largest in the world by area. Considering the anthropogenic activities can influence the quality and quantity of DOM in aquatic ecosystems and urbanization trends continue in response to human population growth, anthropogenic influences on DOM composition will likely become more widespread. Such human effects on DOM quality could have strong impacts on carbon cycles and need to be better understood. Therefore, this study provides a typical case study to approach the scientific questions mentioned above. However, some points need to be addressed as follows. Nevertheless, this work did provide interesting findings, and the data is reasonably strong to make the conclusions, and there I suggest a moderate revision needs to perform before the acceptance of this manuscript.

General comments:

1. In terms of English, I suggest the writing should be improved further.

AR: *We did further language polishing.*

2. The description of "overview of DOM" is great. However, I realize that it is too general. I hope the authors could provide introduction related with their discussion or the questions that need to be solved (or knowledge gap). In addition, the transition from 1.1 to 1.2 seems not that smooth to me.

3. The chapter "1.2 The Pearl River estuary (PRE)" is too lengthy to describe the important focus and

question, and some of descriptions can be moved to “Site description”, otherwise part of the information seems duplicated. For instance, the authors spent 9 paragraphs to describe the PRE, and some of the information is not closely related with the results/discussions. This needs to be shortened and be questions oriented.

***AR:** Re comments 2&3. The introduction has now been restructured and shortened.*

4. The authors mentioned precipitation is an important factor affecting soil flushing, which may affect both DOM equality and quantity. It would be great if the author could incorporate some monthly or seasonal precipitation data to support their claims. In particular, the article indicated the terrigenous DOM is the main source of investigated areas, but it did not describe the influences of land runoff and rainfall on seasonal variations of DOM.

***AR:** The freshwater discharge to the PRE, which has already been described in the paper, is directly correlated to precipitation over its watershed and is a more direct indicator of the impact of precipitation (than precipitation itself) on the study area.*

Note that the article does not conclude that terrigenous DOM is the main source of DOM in the PRE. Instead, it underscores the microbial nature of this DOM pool and a potentially important contribution from river-borne DOM (line 462-471 in the original version).

5. In this manuscript the author suggested that the low DOC concentrations in PRE (especially the low salinity region) was affected by biological degradation (due to input of labile DOM) and low inputs due to the low forest cover. This is a good point! I suggest the author expand this description a little bit. For instance, (i) the addition of labile DOM may “prime” the degradation of terrestrial (relatively more recalcitrant) DOM; (ii) the author could specify the land use percentages of the PR watershed and compare it with the other large river-estuarine systems (such as the Amazon River). Some of the land use% data has been organized in Wagner et al. (2015), and I believe the land use% data is not that difficult to find for PR watershed; (iii) since the authors claim that the PRE is a super eutrophic system, it would be interesting at least present some nutrient data (from literatures) to further support their main findings.

***AR:** (i) The “priming” concept is a good suggestion. Nonetheless, our results indicate that this effect, if any, was minor, at least in May, August, and January. In the low-salinity section, the [DOC] after the rapid removal of the labile constituents (Fig. 3), except November, was in the same range as that of the* *background [DOC] reported for the Pearl River upstream of the Pearl River Delta (114-137 uM, line 122 and line 465-466 in the original version), demonstrating little "priming". Downstream of the upper reach, [DOC] either decreased (August and January) or remained roughly constant (May and November) with increasing salinity, again disproving a major DOC loss process caused by priming. We believe that the land-derived DOC in the Pearl River is either priming-resistant or the short residence times of freshwater in the PRE (a few days, line 496-498 in the original version) prevented a significant priming effect from occurring.*

In the revised manuscript, we have briefly discussed the potential role of the priming effect, particularly for November when the [DOC] at the downstream side of the low-salinity section was substantially lower than the land-derived background [DOC].

(ii) Sorry, we exhausted our resources but could not find the land use% data for the Pearl River region. The landscape information reported by Luo et al. (2002), which we cited, though in a more general nature, provides a similar support for the relevant discussion.

(iii) We thoroughly checked the manuscript and found that ***nowhere*** *does the article claim the PRE to be a super eutrophic system. The word "eutrophic" does not exist in this article.*

6. I really like the main findings in the manuscript, but these findings are not well reflected in the abstract. I suggest the author re-organize their abstracts and focusing on the main findings. Reporting numbers are great, but there seem to be too many. Keep the important ones would be good enough.

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

7. Considering the author spent a huge effort collecting all these samples, it would be very interesting to perform some statistical analysis such as the principal component analysis (PCA) to further confirm the major controls to the DOM variability across the whole dataset.

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 nitrate and silicate) 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 linked to the freshwater discharge rate, again consistent with our result (line 604-606 & Fig. S9 in the original version).*

We have added the plot to the main text (Fig. 9) and briefly discussed it in the revised manuscript (lines 453-461).

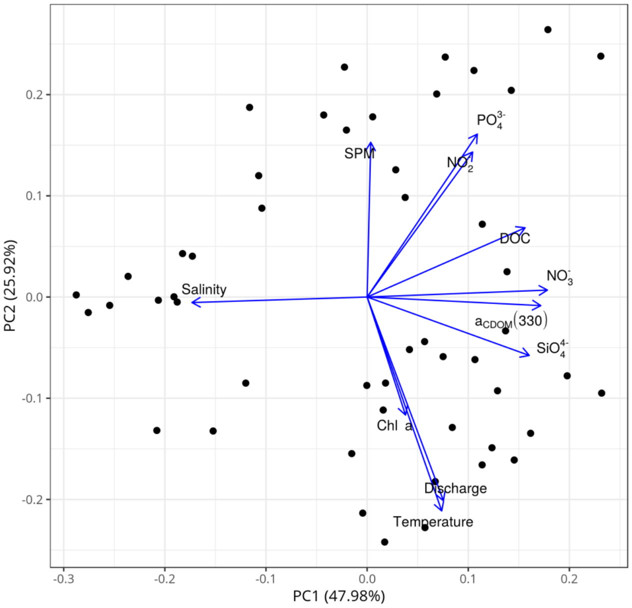

Figure: PCA analysis based on the all-season dataset. SPM: suspended particulate matter; PO_4^{3-}*: phosphate;* NO_2^-*: nitrite; DOC: dissolved organic carbon;* $a_{CDOM}(330)$*: CDOM absorption coefficient at 330 nm;* NO_3^-*: nitrate; Chla: chlorophyll a;* SiO_4^{4-}*: silicate; discharge: freshwater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

Specific comments:

1. There was no explanation about the inverse changes of BIX and HIX in Fig.7

AR: *This is self-evident according to the definitions of BIX and HIX (now in the Methods section): BIX denotes the relative contribution of fresh, microbial-derived FDOM, while HIX signifies the degree of humification, with old, humified FDOM having higher HIX values.*

Now a statement as follows has been added in the second last paragraph of section 3.5:

"BIX displayed a distribution roughly inverse to that of HIX (Fig. 7d), as can be inferred their definitions (Sect. 2.3)."

2. I suggest the author make it clear what is “the saltier zone” because this is a ambiguous description.

AR: *The saltier zone is indirectly defined between line 358 and 361 in the original version. It refers to the zone with salinity generally >5, where the reported DOM variables showed much slower changes with increasing salinity as compared to the rapid changes near the head of the estuary (i.e. the low-salinity zone). However, the salinity separating these two areas was at times slightly season- and/or variable-specific.*

Following relevant comments from reviewer 3 and the associate editor, we have now termed the low-salinity zone as the head region of the estuary and the saltier zone as the main estuary.

3. Considering there are way too many tables. I suggest move some of the tables (e.g., Table 1) to the supplementary information. The DOC (μmol L-1) needs to be moved to the second column.

AR: *Tables 1, 4, and 5 were moved to Supplemental Material. DOC was moved to the second column in Table 8.*

4. Would be wonderful if the author could point out the major metropolitan areas (or even land use patterns) in Figure 1 since it closely related with the major discussions in this manuscript.

AR: *As stated in our response to comment#5, we could not find the land use data for this region. The major cities are already labeled. The discussion does not require information on the metropolitan borderlines.*

5. When the authors describe each PARAFAC component, I suggest the author use DOM Open- fluor database to compare the components in this study with literature data. Murphy, K. R., Stedmon, C. A., Wenig, P., & Bro, R. (2014). OpenFluor–an online spectral library of auto-fluorescence by organic compounds in the environment. Analytical Methods, 6(3), 658-661.

AR: *This has now been done and added to the Methods section.*

6. R.U. should be defined in the abstract.

AR: *Thanks. Done.*

Response to Reviewer 2

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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 Introduction has been re-arranged and shortened. Details of the PRE are moved to a separate section (2.1. Site description) in the Methods.*

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:** This sentence does not exist anymore in the revised Introduction.*

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:** Now the uncertainty of measurements on 6 replicates of the same sample is reported. (lines 160-163).*

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 $S_{275\text{-}295}$ (lines 205-210).

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 and t-test have been conducted. The results indicate 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. The results of ANOVA and t-test are incorporated into the Results section.*

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 nitrate and silicate) 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 linked to the freshwater discharge rate, again consistent with our result (line 604-606 & Fig. S9 in the original version).*

We have added the plot to the main text (Fig. 9) and briefly discussed it in the revised manuscript (lines

453-461).

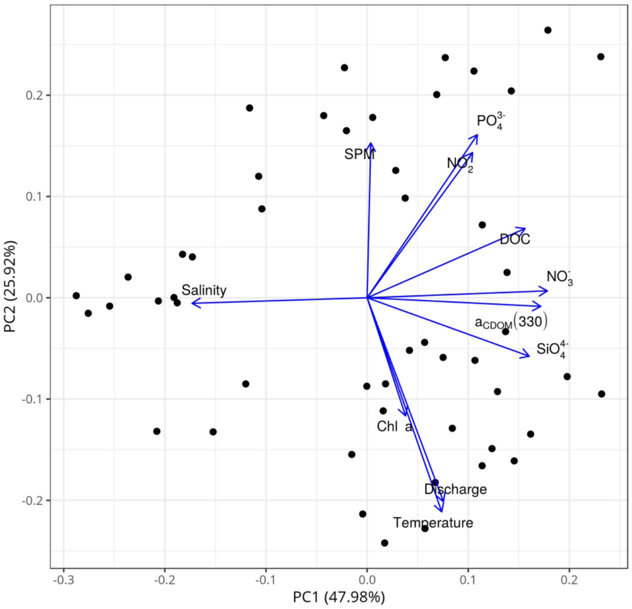

Figure: PCA analysis based on the all-season dataset. SPM: suspended particulate matter; PO_4^{3-}*: phosphate;* NO_2^-*: nitrite; DOC: dissolved organic carbon;* $a_{CDOM}(330)$*: CDOM absorption coefficient at 330 nm;* NO_3^-*: nitrate; Chla: chlorophyll a;* SiO_4^{4-}*: silicate; discharge: freshwater 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. A river-born component (from phytoplankton and/or bacterial activities) is added to this proposition (lines 568-570).*

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.

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.

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.

Response to Reviewer 3

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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 nitrate and silicate), 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 linked to the freshwater discharge rate, again consistent with our result (line 604-606 & Fig. S9 in the original version).*

We have added the plot to the main text (Fig. 9) and briefly discussed it in the revised manuscript (lines 453-461).

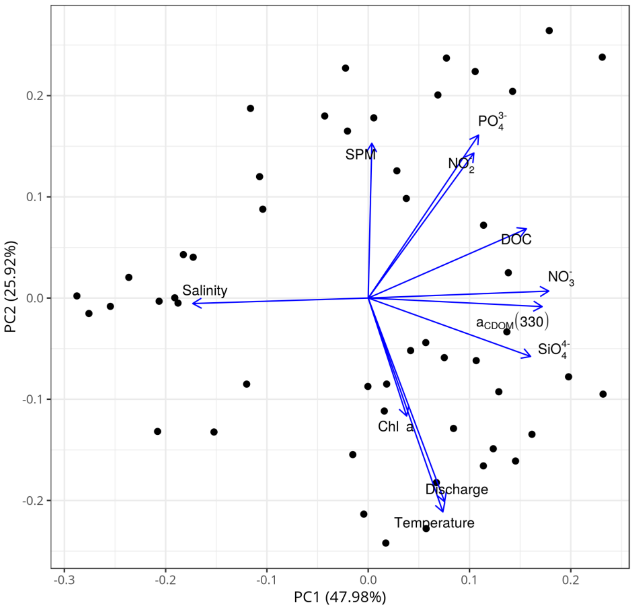

Figure: PCA analysis based on the all-season dataset. SPM: suspended particulate matter; PO_4^{3-}*: phosphate;* NO_2^-*: nitrite; DOC: dissolved organic carbon;* $a_{CDOM}(330)$*: CDOM absorption coefficient at 330 nm;* NO_3^-*: nitrate; Chla: chlorophyll a;* SiO_4^{4-}*: silicate; discharge: freshwater 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: *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 (including chlorophyll and SPM) 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: *The "head region" is now used to refer to the narrow low-salinity zone and "main estuary" to denote the saltier zone.*

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: *There are several points to support 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 the 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 ($S_{275\text{-}295}$, $S_{350\text{-}400}$ 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 $S_{275\text{-}295}$ and MW.

We have explicitly stated in the revised manuscript that E_2/E_3 serves similar functions to those of $S_{275\text{-}295}$ (lines 205-210).

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 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 is 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 in part 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 main estuary (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 494-497 in the original version; 2) the competition of light absorption by particles (water in the PRE is turbid); and 3) self-shading due to 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 causes 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).*

References: X. Lei, J. pan, A. T. Devlin. 2018. Mixing behavior of chromophoric dissolved organic matter in the Pearl River Estuary in sprig. Continental Shelf Research, 154, 46-54.

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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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technology, 40(24), 7771-7777.

Response to Public Short Comment

Responses are *italicized.*
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:** Following the reviewer's comments, we have restructured and shortened the Introduction and Results sections.*

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.*

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 and now the PCA* *analysis as well) suggest that this effect was minor. Note that the effect of sediment resuspension, if any, 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* $S_{275\text{-}295}$ *and MW.*

We have explicitly stated in the revised manuscript that E_2/E_3 *serves similar functions to those of* $S_{275\text{-}295}$ *(lines 205-210).*

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 nitrate and silicate) 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 linked to the freshwater discharge rate, again consistent with our result (line 604-606 & Fig. S9 in the original version).*

We have added the plot to the main text (Fig. 9) and briefly discussed it in the revised manuscript (lines 453-461).

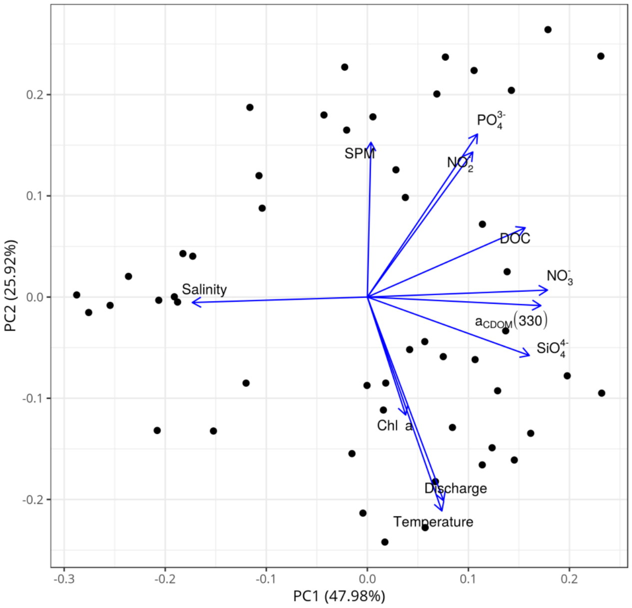

Figure: PCA analysis based on the all-season dataset. SPM: suspended particulate matter; PO_4^{3-}: phosphate; NO_2^-: nitrite; DOC: dissolved organic carbon; $a_{CDOM}(330)$: CDOM absorption coefficient at 330 nm; NO_3^-: nitrate; Chla: chlorophyll a; SiO_4^{4-}: silicate; discharge: freshwater discharge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

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*** *our finding, 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 Introduction is greatly shortened and this kind of non-essential information is not provided in the revised version in part because different papers reported widely different values and in part because we conducted a PCA that includes the chl-a values from our cruises.*

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).*

The revised manuscript does not contain this content anymore in order to restructure and condense the Results section.

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 believe that our explanation is sound. These points are made clearer in the revised version.

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.*

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Distribution, seasonality, and fluxes of dissolved organic matter (DOM) in the Pearl River (Zhujiang) estuary, China

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Abstract

Dissolved organic carbon (DOC) concentration in the Pearl River estuary (PRE) of China was measured in May, August, and October 2015 and January 2016. Chromophoric and fluorescent dissolved organic matter (CDOM and FDOM) in the latter three seasons were characterized by absorption and fluorescence spectroscopy. CDOM and FDOM exhibited negligible seasonal variations, while DOC displayed a significant seasonality with the average concentration being highest in May (156 µmol L^{-1}), lowest in November (87 µmol L^{-1}), and comparable between January (118 µmol L^{-1}) and August (112 µmol L^{-1}). Although DOC, CDOM, and FDOM in surface water were generally higher than in bottom water, the difference between the two layers was statistically insignificant. DOC showed little cross-estuary variations in all seasons, while CDOM and FDOM in January were higher on the west side of the estuary than on the east side. All three variables showed rapid drawdowns in the head region of the estuary (salinity <5); their dynamics in the main estuary were primarily controlled by conservative mixing, leading to linearly declining or relatively constant (for DOC in May and November only) contents with increasing salinity. The decrease of FDOM with salinity was 5–35% faster than that of CDOM, which in turn was 2–3 times quicker than that of DOC. Salinity and CDOM absorption coefficients could serve as indicators of DOC in August and January. Freshwater endmembers in all seasons mainly contained fresh, protein-rich DOM of microbial origin, a large part of it being likely pollution-derived. Protein-like materials were preferentially consumed in the low-salinity zone but the dominance of the protein signature was maintained throughout the estuary. Exports of DOC and CDOM (in terms of the absorption coefficient at 330 nm) into the South China Sea were estimated as 195 × 10^{9} g and 266 × 10^{9} m^{2} for the PRE, and 362 × 10^{9} g and 493 × 10^{9} m^{2} for the entire Pearl River Delta. The PRE presents the lowest concentrations and export fluxes of DOC and CDOM among the world major estuaries. DOM delivered from the PRE is, however, protein-rich and thus may enhance heterotroph in the adjacent coastal waters. Overall, the PRE manifests lower

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abundances and smaller spatiotemporal variabilities of DOM than expected for a sizable estuary with a marked seasonality of river runoff due supposedly to the poorly forested watershed of the Pearl River, the rapid degradation of the pollution-derived DOM in the upper reach, and the short residence time of freshwater.

1 Introduction

River runoff is an important contribution of dissolved organic matter (DOM) to the ocean (Raymond and Spencer, 2015). DOM in river water originates from soil leaching (terrigenous DOM, or tDOM) and in situ microbial production. Terrigenous DOM, abounding with lignin phenols (Opsahl and Benner, 1997), differs substantially from microbial-derived DOM, richer in proteins (Martínez-Pérez et al., 2017; Brogi et al., 2018), in optical property and biological and photochemical lability (Hansen et al., 2016; Sulzberger and Arey, 2016). The loads of terrigenous and microbial DOM and their proportions in river water rely on many factors, among which precipitation is a key player. High precipitations mobilize more terrigenous DOM from soil into rivers compared to drier conditions (Fichot et al., 2014; Li et al., 2015). Moreover, the residence time of river water during high-flow seasons is shorter, tending to decrease autochthonous DOM production (Taylor et al., 2003). During its transit through estuaries, riverine DOM may be subject to physical (e.g. flocculation and coagulation, Asmala et al., 2014), biological (e.g. microbial uptake, Benner and Kaiser, 2011), and photochemical (Del Vecchio and Blough, 2002) removals, thereby reducing its abundance and modifying its chemical and optical properties before reaching the ocean. Conversely, biological production in estuaries can add organic matter to the riverine DOM pool (Bianchi et al., 2004; Fellman et al., 2010; Benner and Kaiser, 2011; Deutsch et al., 2012). In highly populated areas, industrial and residential wastes can also be a significant contribution of DOM to river systems (Baker, 2001; Guo et al., 2014). Pollution not only directly brings anthropogenic DOM but also carries nutrients that enhance biological DOM production.

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The Pearl River estuary (PRE), located in the highly urbanized and industrialized Pearl River Delta, is a subtropical embayment receiving large freshwater discharge with marked seasonal fluctuations (Sect. 2.1) and an annual input of 5.8 x 10^9 tons of industrial and domestic sewage (Lu et al., 2009). A number of studies in the PRE have determined the concentrations of DOC ([DOC]) and/or the proxy of chromophoric abundance (⟨CDOM⟩) in terms of absorption coefficients and fluorescence intensities (e.g. Dai et al., 2000; Callahan et al., 2004; Chen et al., 2004; Hong et al., 2005; He, 2010; Lei et al., 2018; Ye et al., 2018). These studies show no consistent seasonality and estuarine mixing behavior of [DOC] and ⟨CDOM⟩ and no correlation between the two variables except one occasion for the mid-salinity (5–20) section of the estuary (Callahan et al., 2004).

The lack of seasonality and consistent estuarine mixing behavior of [DOC] and ⟨CDOM⟩ suggests complex processes controlling their transport, production, and loss in the PRE; it could, however, also result in part from the difference in spatiotemporal coverage of the stations sampled by different studies. As previous DOC and CDOM data were collected over a span of 18 and 15 years, respectively, the possibility of interannual variability cannot be ruled out. In addition, none of the past DOC studies save that of Ye et al. (2018) surveyed all four seasons and many of them chose two different months to represent the wet and dry seasons, though [DOC] and its mixing behavior may change on smaller time scales. The more limited number of CDOM absorption surveys only sampled a single season with no winter visits. Concerning the spatial coverage, studies often differ in the distribution of sampling stations (e.g. Hong et al., 2005 vs. Lei et al., 2018) and many did not cover the upper reach of the estuary (e.g. Chen et al., 2003; Chen et al., 2004; Wang et al., 2014; Lei et al., 2018).

Compared with the quantitative information on DOC and CDOM, much less is known about the seasonality and mixing behavior of their qualitative aspects. He et al. (2010) examined the DOC compositions (monosaccharides vs. polysaccharides and dissolved free amino acids vs. dissolved combined amino acids) along a longitudinal salinity-gradient transect in the PRE. Hong et al. (2005)

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Deleted: Mountainous and hilly landscapes dominate the drainage basin of the Pearl River with almost no forests (Luo et al., 2002), leading to relatively low dissolved organic carbon concentrations ([DOC]) (117–132 µmol L^{-1}) upstream of the Pearl River Delta (Shi et al., 2016). On the other hand, the Pearl River Delta, a highly urbanized and industrialized region, delivers 5.8×10^9 tons of industrial and domestic sewage per year into the PRE (Lu et al., 2009), which is considered the principal source of DOC in the upper reach of the PRE (Lin, 2007; He, 2010; He et al., 2010).

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Finally, only a few studies have estimated the DOC export flux from the Pearl River to the South China Sea (Lin, 2007; Ni et al., 2008; He et al., 2010), often with limited seasonal coverage. The estimate made by Lin (2007) is almost two times that by Ni et al. (2008). No estimates of CDOM export have been made for the PRE.

Given the large volume and seasonality of the freshwater discharge of the Pearl River, we hypothesize that the quantity of DOM and the quality of CDOM in the PRE present substantial seasonal variability and that the PRE is an important source of DOM to the global ocean. To test this hypothesis, the present study sampled the same locations in different seasons within a 12-month period, with the objectives of 1) evaluating the seasonality and estuarine mixing behavior of DOC and CDOM in the PRE; 2) improving the estimate of DOC export to the South China Sea; 3) providing a first assessment of seaward export of CDOM from the PRE. Results from this study further increase our understanding of DOM cycling in human-impacted estuarine waters and their contribution to the oceanic DOC and CDOM budgets.

2 Methods

2.1 Site description

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Ranked the 13th largest river in the world in terms of freshwater volume discharge (Zhang et al., 2008), the Pearl River delivers 285 × 10^9 m^3 of freshwater annually to the South China Sea, with 70% to 80% of this discharge occurring in the wet season (April–September) and only 20–30% in the dry season (October–March) (Wei and Wu, 2014). The Pearl River is composed of three main tributaries, the West, North, and East Rivers (Fig. 1), with the West River contributing 73% of the total freshwater discharge, the North River 14%, and the East River 8% (Wei and Wu, 2014). In the delta area, the three tributaries continuously bifurcate to form a complex water network that is connected to the South China Sea via three estuaries: Lingdingyang, Modaomen, and Huangmaohai. Lingdingyang, the principal estuary of the Pearl River, is commonly referred to as the Pearl River estuary (PRE hereafter) and is the study area of this work. The PRE receives 50–55% of the Pearl River's total freshwater flow from four major water outlets, namely Humen, Jiaomen, Hongqimen, and Hengmen (Mikhailov et al., 2006), with Humen providing 35% of the freshwater input, followed by Jiaomen (33%), Hengmen (20%), and Hongqimen (12%) (Kot and Hu, 1995).

The PRE covers an area of ~2000 km^2 and has an average depth of 4.8 m, with a topography featured with shoals of <2 m deep and channels of >5 m deep (Fig. 1) (Dong et al., 2004; Wai et al., 2004). Turbidity maxima may occur at different sections of the estuary, depending on hydrological conditions (Zhao, 1990; Wai et al., 2004). Tides in the PRE are irregular and semi-diurnal, with a mean tidal range of 0.86–1.7 m (Zhao, 1990). Phytoplankton blooms develop only on local scales, usually in the mid-estuary during the dry season and in the lower part of the estuary during the wet season (Lu and Gan, 2015).

2.2 Sample collection

The sampling area covered the entire PRE, stretching from ~30 km upstream of Humen to the outer limit of the estuary (Fig. 1). Ten stations (M01–M10) were distributed across the main longitudinal axis

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of the estuary, together with two shorter along-estuary transects, each having four stations on the east (E01–E04) and west (W01–W04) sides. The coordinates of the stations alongside other sampling information are shown in Table S1. Water samples were collected in duplicate from the surface (~1 m) and near the bottom (1–2 m above the seabed) using a 5-L plexiglass sampler between 8–12 May, 7–11 August, and 16–19 November 2015 and 10–14 January 2016 for [DOC] measurement and in the last three seasons for CDOM analysis. The samples were filtered through 0.2-μm polyethersulfone (PES) filters (Pall Life Sciences) under low vacuum and the filtrates were transferred into 20-mL (DOC) and 100-mL (CDOM) clear-glass bottles with Teflon-lined screw caps. DOC samples were acidified to pH ~2 with 2 N HCl (Reagent grade, Merck). All samples were stored in the dark at 4°C until being analyzed in a land-based laboratory within two weeks after water collection. Prior to use, the glass filtration apparatus and the sample storage bottles were acid-cleaned and combusted at 450°C for 4 h, and the PES filters were thoroughly rinsed with Milli-Q water and sample water. Water temperature and salinity were determined with a SBE-25 conductivity-temperature-depth (CTD) profiler.

2.3 DOM analysis

[DOC] for each subsample was determined in triplicate using a Shimadzu TOC-L$_{CPH}$ analyzer calibrated with potassium hydrogen phthalate, with the coefficient of variation < 2%. The performance of the analyzer was checked, at intervals of 10 consecutive sample analyses, against Hansell's low carbon ([DOC]: 1–2 μmol L^{-1}) and deep Florida Strait ([DOC]: 41–44 μmol L^{-1}) reference waters; the measured [DOC]s for the reference waters were 2.36 ± 0.06 μmol L^{-1} and 43.6 ± 1.5 μmol L^{-1}.

CDOM absorbance spectra were scanned from 800 nm to 200 nm at 1-nm intervals with a Shimadzu UV-2550 dual beam spectrophotometer fitted with 10-cm quartz cells and referenced to Nanopure water. The samples were allowed to warm up to room temperature in darkness before analysis. A baseline correction was made by subtracting the mean absorbance value over 683–687 nm from all

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spectral values (Babin et al., 2003). The Napierian absorption coefficient, a_{CDOM} (m^{-1}), was calculated as 2.303 times the absorbance divided by the light pathlength of the cell in meters (0.1 m). The analytical uncertainty of a_{CDOM} measurement was assessed by analyzing six replicates of the sample collected at Sta. M01 from the August cruise, arriving at a standard deviation of 0.06 m^{-1} or 1.3% at 330 nm with the mean a_{CDOM} at 330 nm (a_{330}) being 4.37 m^{-1}. In this study we choose a_{330} as an indicator of the CDOM abundance, given that this variable has been frequently used for this surrogate role (e.g. Osburn et al., 2009; Gareis et al., 2010; Mann et al., 2012; Song et al., 2017) and that the wavelength of 330 nm is where many aquatic CDOM photoreactions, including photobleaching, exhibit maximum rates in surface water under solar radiation (e.g. Vähätalo et al., 2000; Osburn et al., 2001; Zhang et al., 2006; White et al., 2010; Xie et al., 2012a). CDOM absorption coefficients at other commonly used wavelengths and the spectral slope coefficient between 300 nm and 500 nm are presented in Table S2.

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Fluorescence excitation-emission-matrices (EEMs) were acquired using a Hitachi F-4600 fluorescence spectrophotometer fitted with a 1-cm quartz cuvette to characterize the FDOM composition (Coble, 1996; Boehme et al., 2004). Again, samples were warmed up to room temperature before analysis. Emission spectra were scanned from 230 nm to 600 nm at 2-nm intervals over excitation wavelengths between 200 nm and 450 nm at 5-nm increments. Raman scattering was removed by subtracting Nanopure water EEMs that were scanned on the same day as those for the samples. The spectral fluorescence intensities were normalized to Raman Units (R.U.) following the Raman Scatter Peak correction reported by Lawaetz and Stedmon (2009). Potential inner-filtering effects were corrected using the obtained absorbance spectra (Ohno, 2002), even though self-shading should be insignificant since the absorption coefficient at 254 nm (a_{254}) was less than 15 m^{-1} for all samples.

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PARAFAC analysis was performed to decompose the EEMs into a set of underlying fluorescent components (Bro, 1997; Stedmon et al., 2003; Stedmon and Bro, 2008). The analysis was fed with 117

EEMs from all three seasons sampled for CDOM (Sect. 2.1). To reduce the dominance of high fluorescence intensity signals, the EEMs were first scaled to a unit of variance within the sample mode to construct the calibration model (Bro, 1997). PARAFAC models from 2 to 7 components with constraints of non-negativity in all modes were successively conducted with MATLAB (version 2008b; MathWorks 2008) using DOM Fluorescence Toolbox (DOM Fluor version 1.6) and validated using residual and split-half analyses as described by Stedmon and Bro (2008). The parameters obtained from the PARAFAC model were used to calculate an approximate abundance of each component, expressed as F_{max} in Raman units (R.U.), which corresponds to the maximum fluorescence intensity for a particular sample. Based on analysis of triplicate samples from Sta. M01, M08, and M10, the uncertainty of F_{max} for each modeled component was <2%.

PARAFAC modeling identified five distinct FDOM components (C1-C5, Fig. 2), which explained 99.75% of the variance and thus adequately modeled the different FDOM profiles in the dataset. Based on a comparison with the OpenFluor database (https://openfluor.lablicate.com/), particularly with the PARAFAC spectra published by several well-recognized groups (e.g. Stedmon et al., 2003; Cory and McKnight, 2005; Yamashita and Jaffé, 2008; Murphy et al., 2008; Santín et al., 2009; Massicotte and Frenette, 2011), components 1 (C1) and 5 (C5) were assigned as tyrosine-like and tryptophan-like fluorophores, components 2 (C2), 3 (C3) and 4 (C4) as humic-like DOM fractions, respectively. As C1 is highly correlated with C5 (r = 0.997) and C2 with C3 (r = 0.990) and C4, (r = 0.993), the sum of the F_{max} values of C1 and C5 (C_p hereafter) and of those of C2, C3, and C4 (C_h hereafter) will be used as proxies of the abundances of the protein-like and humic-like fractions, respectively.

To characterize the quality of DOM, the E_2/E_3 quotient, biological index (BIX), and humic index (HIX) were calculated from the measured absorbance and fluorescence spectra. E_2/E_3, defined as the ratio of a_{250} to a_{365}, serves as a proxy for the average molecular weight (MW) and aromaticity of CDOM, with lower values indicating higher MW and higher aromaticity (Peuravuori and Pihlaja, 1997; Lou and Xie, 2006; Li and Hur, 2017). E_2/E_3 responds quantitatively to CDOM photobleaching (Lou

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and Xie, 2006) and its proxy function is similar to that of the later developed absorption spectral slope coefficient between 275 nm and 295 nm (Helms et al., 2008). BIX, the ratio of fluorescence intensity at 380 nm to that at 430 nm with excitation at 310 nm, indicates the relative contribution of fresh, autochthonous DOM; higher BIX values signify higher contributions of freshly produced FDOM of microbial origin (McKnight et al., 2001). HIX, the ratio of the fluorescence intensity integrated over 435–480 nm to that over 300–345 nm with excitation at 254 nm, is a surrogate of the extent of FDOM humification (Ohno, 2002). BIX values of >0.8 indicate fresh, microbially derived DOM, while values of <0.6 signify little autochthonous material (Huguet et al., 2009). Fresh DOM derived from plant biomass usually displays HIX values of <5, whereas soil-derived DOM has values between 10 and 30 (Birdwell and Engel, 2010; Sazawa et al., 2011). In addition, the percentages of C_p (%C_p hereafter) and C_h (%C_h hereafter) in the sum of C1-C5 will serve to represent the proportions of protein-like and humic-like components in the total FDOM pool.

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2.4 Miscellaneous aspects

Analysis of statistical significance (α = 0.05) was performed using one-way ANOVA (analysis of variance) and Student’s t-test in Microsoft Excel 2010. For the benefit of conciseness, this statistic approach will not be re-described when presenting and discussing the results.

The monthly-averaged freshwater discharge rates of the Pearl River for the sampling months were obtained from the Ministry of Water Resources of the People’s Republic of China (available online at http://www.mwr.gov.cn/zwzc/hygb/sqnb).

For brevity of presenting and discussing data, seasons for a property, where applicable, are added as a superscript to the symbol or abbreviation denoting that property. For example, $[DOC]^{Aug}$ stands for [DOC] in August. Names of the PARAFAC-modeled FDOM components signify their F_{max} as well. Symbols and abbreviations are used as both singular and plural forms.

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3 Results

3.1 Hydrological settings

The discharge rates to the PRE were estimated as 8.9 × 10^3 m^3 s^{-1} in May, 5.7 × 10^3 m^3 s^{-1} in August, 6.7 × 10^3 m^3 s^{-1} in November, and 5.0 × 10^3 m^3 s^{-1} in January based on that the PRE receives 54% of the total discharge from the Pearl River (Mikhailov et al., 2006). The discharge was 15% lower in August than in November due to an atypically dry weather in summer. Higher-than-normal discharge rates occurred in November and January due to above-average precipitations.

Surface water temperature ranged from 25.6-28.5 °C (mean: 27.2 °C) in May, 28.2-31.0 °C (mean: 30.0 °C) in August, 23.6-26.3 °C (mean: 25.2 °C) in November, and 17.2-19.7 °C (mean: 18.8 °C) in January. Temperature decreased seaward in August, whereas a reverse trend was seen in the other sampling seasons. Bottom temperature was lower than surface temperature on average by 1.6 % (range: 0–11.9%), 3.7% (range: 3–14%), and 0.9% (range: 0.08–2.5%) in May, August, November, respectively, with the difference generally increasing seaward. In January, there was essentially no difference between the surface and bottom (mean: 0.5%, range: 0-1.5%). Mean water temperature, with surface and bottom combined, was higher on the west transect than on the east one in May (27.7 °C vs. 27.0 °C) and August (30.1 °C vs. 28.7 °C) but the opposite was observed in November (25.6 °C vs. 16.0 °C) and January (18.4 °C vs. 19.1 °C).

Surface water salinity ranged from 0.2–30.3 (mean: 9.7) in May, 0.2–20.6 (mean: 8.0) in August, 0.2–26.9 (mean: 8.3) in November, and 0.2–32.6 (mean: 17.0) in January (Fig. 3a). Surface salinity increased seaward, with a mean gradient much lower in the upper estuary (Sta. M01 to M05; 0.01-0.15/km) than in the lower estuary (downstream of Sta. M05; 0.17-0.28/km). Mean bottom salinity in the upper estuary was higher than surface salinity by 52.6% in May, 100.4% in August, 129.2% in November, and 23.1% in January, while in the lower estuary by 23.0%, 69.0%, 63.1%, and 3.9%, respectively. Salinity, both at surface and bottom, was consistently lower on the west side than on the

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east side (Fig. 4a), in line with the observation that freshwater in the PRE tends to flow along the west side while coastal saline water intrudes landward along the east channel (Dong et al., 2004). The mean west–east difference follows a seasonal trend of January (14.7 vs. 26.3) > August (8.6 vs. 16.5) > November (10.2 vs. 16.4) > May (11.8 vs. 15.6).

Based on the salinity distribution, the water column was stratified in the upper estuary during all four seasons and in the lower estuary in seasons other than winter when the water column was essentially well mixed. The stratification in the lower estuary was strongest in summer. Substantial cross-estuary salinity gradients persisted throughout the year.

3.2 Distribution of DOM

Figure 3b-j depicts the spatial (upper vs. lower estuary and surface vs. bottom) and seasonal distributions of the mean values of the measured DOM variables. The mean values of all quantitative variables ([DOC], a_{330}, C_p, and C_h), with the surface and bottom data pooled together, were substantially higher in the upper estuary than in the lower estuary across all sampling seasons (Fig. 3b-e). The differences between the two areas were smaller for [DOC] (20-38%) than those for a_{330} (51-65%), C_p (47-70%), and C_h (37-64%). Neither the upper estuary nor the lower estuary and none of the sampling seasons exhibited significant surface–bottom differences in terms of the mean values of the quantitative variables, although the surface values at individual stations were often somewhat higher (1.2-26.5%) than the bottom ones, particularly in seasons other than winter (Fig. 3b-e).

The estuary-wide mean [DOC], with surface and bottom combined, followed the seasonality of May (156 ± 45 μmol L^{-1}) > January (118 ± 37 μmol L^{-1}) > August (112 ± 21 μmol L^{-1}) > November (87 ± 14 μmol L^{-1}). The differences were significant among all seasons save for that between January and August. No significant seasonal variations were observed for the mean a_{330} (August: 1.76 ± 0.88 m^{-1}; November: 1.39 ± 0.70 m^{-1}; January: 1.33 ± 1.02 m^{-1}) and mean C_p (August: 0.81 ± 0.46 R.U.;

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November: 1.16 ± 0.60 R.U.; January: 1.00 ± 0.81 R.U.). The mean C_h was significantly higher in August (0.73 ± 0.29 R.U.) than in January (0.49 ± 0.34 R.U.) but presented no significant differences between August and November (0.61 ± 0.23 R.U.) and between November and January.

Compared with the quantitative variables, the qualitative metrics showed much smaller along-estuary (upper vs. lower estuary) differences that were statistically insignificant irrespective of seasons (Fig. 3f-i), except that E_2/E_3 was marginally higher in the lower estuary than in the upper estuary (Fig. 3h). The mean values of the qualitative metrics for the surface were essentially identical to those for the bottom (Fig. 3f-j), excluding HIX for the upper estuary in November (Fig. 3j). HIX and %C_h were significantly higher in August than in November and January while %C_p displayed an opposite pattern; no significant seasonal variations were observed on all other occasions (Fig. 3f-j).

Cross-estuary differences in the quantitative variables were insignificant with the exception of [DOC] in May (24% higher on the east transect) and a_{330}, C_p, and C_h in January (56%, 44%, and 74% higher on the west transect, respectively) (Fig. 4b-e). Among the qualitative metrics, HIX and %C_h were consistently higher on the west transect than on the east one, while BIX and %C_p manifested a reversed trend (Fig. 4f,g,I,j). Yet significant differences were only identified for HIX in all three seasons and E_2/E_3 in January (Fig. 4h).

Across all sampling seasons and the entire estuary, %C_p was close to or >50% (mean: 61.1% ± 7.4%), except the west transect in August (Fig. 4f). BIX was mostly >1 with a mean of 1.10 ± 0.10, while HIX was <2.4 and averaged 1.13 ± 0.32.

3.3 Relationships between DOM variables and salinity

Surface and bottom data for each variable in each season form a consistent property–salinity pattern (data not shown) and are thus treated as a single dataset. All quantitative variables displayed sharp decreases at salinity <~5 but remained rather constant ([DOC] in May and November) or declined

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linearly (all other cases) at higher salinities (Figs. 5 and 6). Hereafter, the upper part of the estuary showing fast changes of DOM properties is termed the head region, while the area downstream of it is referred to as the main estuary. The salinity demarcating these two regions was often ~5 but could change to some extent with season and the DOM variable of interest (Figs. 5 and 6). Results of linear regressions for the main estuary are summarized in Table S3. At a 95% confidence level, both the slopes and intercepts were statistically no different between August and January for [DOC] and a_{330} and between all three seasons for C_h, indicating that the multi-season data on each of these occasions can be combined into a single dataset. The slope for a_{330} in November was, however, ≥32% lower than those in August and January. The slope for C_p presented significant seasonal variations, with the value in January being 23% and 89% higher than those in November and August, respectively.

The percent decrease of each variable per unit increase of salinity across the main estuary was calculated using the known regression equations shown in Table S3. a_{330} decreased 2.1 and 2.7 times faster than [DOC] in August and January, respectively (Table S4). The proxy of FDOM abundance (⟨FDOM⟩), expressed by C_p and C_h, declined faster than ⟨CDOM⟩, with November showing the largest difference (25–35%) followed by August (5–21%) and January (<10%) (Table S4).

E_2/E_3 in August and November increased quickly (by ~24%) at salinity <1.3 and then slowly in the main estuary (Fig. 7a). In January, the surge of E_2/E_3 at low salinities was less obvious. In the main estuary, all three seasons displayed similar E_2/E_3 vs. salinity patterns, each of which roughly followed the respective theoretical mixing line defined by the maximum- and minimum-salinity E_2/E_3 (Fig. 7a).

Between salinity 0 and 1.27, %C_p^{Aug} decreased by 14.2% (Fig. 7b). At higher salinities, the west transect displayed an increasing %C_p with salinity but was constantly below the main and east transects which formed a coherent %C_p vs. salinity pattern featured by a small rebound from salinity 3 to 13 and a gradual decline at salinity >13. A sharp drop of 25.3% occurred for %C_p^{Nov} from salinity 0 to 0.63, which was followed by relatively constant values (mean: 64.0% ± 4.0%). A pan shape characterized the distribution of %C_p^{Jan} showing higher values at both the lowest and highest salinities and slightly

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lower values across a wide range of salinities in between (Fig. 7b). The distributions of %C_h mirrored those of %C_p (Fig. 7c).

The HIX vs. salinity patterns (Fig. 7e) approximately corresponded to those of %C_h, leading to a strong linear correlation between the two variables (r = 0.94) (Fig. S1a). BIX displayed a distribution roughly inverse to that of HIX (Fig. 7d), as can be inferred their definitions (Sect. 2.3). The correlation between BIX and %C_p (r = 0.40) (Fig. S1b) was weaker compared with that between HIX and %C_h. Compared to the quantitative variables, a common feature for all qualitative metrics in the main estuary was their relatively small variations over the rather large salinity ranges encountered (Fig. 7).

3.4 Relationships between [DOC] and ⟨CDOM⟩ and ⟨FDOM⟩

[DOC] was linearly related to a_{330} for all three sampling seasons; the coefficient of determination was, however, lower in November (Fig. 8a, Table S5). The fitted slope was in descending order of January (32.0 ± 2.0 m μmol L^{-1}) > August (22.5 ± 1.4 m μmol L^{-1}) > November (18.8 ± 2.2 m μmol L^{-1}). Similarly, [DOC] showed a strong, linear relationship with C_p in August and January and a relatively weaker one in November (Fig. 8b, Table S5). The fitted slopes in August and January were comparable but ~2.8 times that in November (Table S5). [DOC] was also significantly related to C_h (Fig. 8c) but the coefficients of determination were considerably lower than those with C_p (Table S5).

4 Discussion

4.1 Sources of freshwater DOM endmembers

The present study confirms the large variations in [DOM] in the head region of the PRE observed by previous studies (Callahan et al., 2004; Chen et al., 2004; Lin, 2007; He, 2010; Wang et al., 2014; Lei et al., 2018; Ye et al., 2018). This phenomenon is commonly ascribed to the presence of multiple freshwater endmembers delivered by various water channels and outlets of the Pear River system (Cai et al., 2004; Callahan et al., 2004; He et al., 2010). Notably, the Humen channel takes most of the

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sewage discharge from Guangdong Province (Pang and Li, 2001), which carries the highest DOM load, while the other waterways on the west coast, less influenced by urbanization and industrialization, bear lower levels of DOM (Callahan et al., 2004; Ni et al., 2008). Although the existence of multiple "quantitative" endmembers in the PRE has been well recognized, it remains poorly understood if these endmembers differ qualitatively. Data published by Callahan et al. (2004) shows that [DOC]-normalized fluorescences of the freshwater endmembers in Jiaomen, Hongqimen, and Hengmen differed little (c.v. = 4%) while the Humen endmember was 17% higher than the mean of the other three endmembers in November 2002. Besides, fluorescence EEMs collected upstream of Humen reveal tryptophan-like fluorophores to be the dominant FDOM fraction in the Humen endmember which was considered to originate from sewage effluents (Hong et al., 2005). The present study has analyzed by far the largest number of qualitative metrics and thus offers a more robust means to assess the nature of the freshwater endmembers. In November, near-zero-salinity (<0.7) water was accessible down to Sta. M05 off Hongqimen (Fig. 1), making this season suitable for comparing the endmembers from the different water outlets. E_2/E_3^{Nov} at near zero-salinities fell in a rather small range from 5.5 to 6.8 that corresponded to a MW range from 0.83 kDa to 1.18 kDa estimated from the MW vs. E_2/E_3 relationship established by Lou and Xie (2006). The higher MW values were observed in the Humen channel, while the lower ones in water from Jiaomen and Hongqimen, both being close to the borderline separating the high- and low-MW CDOM (i.e. 1 kDa). $\%C_p^{Nov}$ varied from 70% at Sta. M01 in the Humen channel to 56% off Hongqimen, consistent with a stronger anthropogenic DOC signature in the Humen channel (He et al., 2010). Yet $\%C_p^{Nov}$ for all endmembers were >50%, demonstrating that protein-like components dominated all freshwater FDOM endmembers. BIX^{Nov} was higher (1.28 vs. 1.00) while HIX^{Nov} lower (0.53 vs. 1.34) at Sta. M01 than at Sta. M05; all BIX^{Nov} and HIX^{Nov} were, however, well above 0.8 and below 5, respectively, implying the dominance of fresh, microbial-derived FDOM in all freshwater endmembers (Sect. 2.3). Taking into account all these qualitative metrics and the linear relationships between [DOC] and (FDOM) (Sect. 3.4), we can conclude that all three

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freshwater DOM endmembers in November mainly comprised fresh, low-MW (~1 kDa) organic material of microbial origin, with the microbial signature in the Humen endmember somewhat stronger. The sewage influence could be depressed due to a rapid bacterial mineralization of the sewage-derived DOM between the point sources of pollution in the Guangzhou area and the sampling stations downstream (He et al., 2010). Note that the three endmembers also bore a perceptible terrigenous character, since the humic-like C_h, albeit generally lower in abundance than the protein-like C_p, were still a significant fraction of the total FDOM pool (Fig. 6). The values of the qualitative metrics at Sta. M01 in August and January (E_2/E_3: 5.18-6.13; %C_p: 62.2-72.2%; %C_h: 27.8-37.8%; BIX: 1.03-1.15; HIX: 0.68-1.01) were comparable to those in November, indicating that the Humen DOM endmembers in summer and winter were also of microbial origin.

Based on an estimate of the relative contributions of land-, sewage-, and phytoplankton-derived DOC, He (2010) and He et al. (2010) proposed that the land component is the dominant source of the total DOC pool in the lower reach of the Humen channel. In this estimation, the authors assigned the "natural background" [DOC] in the three major tributaries of the Pearl River (range: 114–125 μmol L^{-1}; mean: 119 μmol L^{-1}) as "land-derived". Our result suggests that, apart from terrigenous DOC leached from soil, this "land-derived" DOC contains an ample amount of river-born DOC of microbial origin. This argument is supported by the poorly-forested watershed of the Pearl River (Luo et al., 2002) and the low molar carbon-to-nitrogen (C/N) ratios of suspended particulate organic matter (7.2–9.3) (Ni et al., 2008) and DOM (range: 1.8–12; mean ± SD: 4.6 ± 2.5; median: 3.6) (Supporting Information in Ye et al., 2008) in fresh or low-salinity (<5) waters of the PRE.

4.2 Estuarine mixing and transformation of DOM

Sharp decreases in [DOC], ⟨CDOM⟩, and ⟨FDOM⟩ in the head region of the PRE have been previously observed and postulated as a result of adsorption, flocculation, biodegradation, and/or incomplete mixing of multiple freshwater endmembers (Callahan et al., 2004; Chen et al., 2004; Lin,

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2007; He et al., 2010; Ye et al., 2018). The present study confirmed the earlier observations and provided additional qualitative metrics that are instrumental for constraining the principal processes causing this quick drawdown of DOM abundance. The increases in %C_h and HIX and decreases in %C_p and BIX in the head region suggest a bacterial preferential uptake of protein-rich materials and hence a key role of biodegradation in controlling the loss of DOM. Our result corroborates the finding of He et al. (2010) showing higher fractions of biodegradable DOC and higher DOC bio-uptake rates in the head region than in the main estuary. The more scattering of the qualitative metrics data in November (Figs. 6) likely reflects an incomplete mixing of the multiple freshwater endmembers stated earlier. This partial-mixing effect may overshadow the biodegradation signal. Notably, the presence of large amounts of highly biolabile, sewage-derived DOM in the upper reach of the PRE could potentially enhance the biodegradation of the less reactive terrigenous DOM through a positive priming effect (Bianchi et al., 2011). However, the [DOC] after the rapid removal of the labile fraction within the head region (110–130 μmol L^{-1}, Fig. 3), except November, were in the same range as that of the background [DOC] in the Pearl River upstream of the Pear River Delta (114–137 μmol L^{-1}, Shi et al., 2016). This fact, alongside the enriched humic character of the residual DOM, implies a negligible priming effect. In November, the possibility of a positive priming effect could not be excluded, given that the [DOC] exiting the head region (82 μmol L^{-1}) was substantially lower than the riverine background concentrations.

In the main estuary, the linear decreases in [DOC] (see exceptions below), ⟨CDOM⟩, and ⟨FDOM⟩ with salinity point to the absence of net removal and input of these constituents and physical dilution being the principal mechanism dictating their estuarine mixing behaviors. The two extreme cases of near-constant [DOC] vs. salinity in May and November indicate that the loss of DOC in the head region reduced its content to the level comparable to the marine endmember and again that the removal of DOC in the main estuary, if any, was roughly balanced by the input. Potentially important DOM loss processes in the PRE are bacterial (He et al., 2010) and photochemical (Callahan et al., 2004)

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degradation. The significance of these processes relies on both their rates and the residence time of freshwater in the PRE. Using the volume of the estuary (9.6×10^9 m^3) and the freshwater discharge rate for each sampling season (Sect. 3.1), we estimated the residence time of freshwater in the top 1-m layer to be 3.1 d in May, 4.9 d in August, 4.1 d in November, and 5.6 d in January. The value for May is essentially identical to that previously reported for the wet season (Yin et al., 2000). Here the volume of the estuary was obtained from the published average depth (4.8 m) and total area (2×10^9 m^2) of the estuary (Sect. 2.1). The bacterial uptake rate of DOC in surface water of the main estuary has been reported to be 0.04 μmol L^{-1} h^{-1} in spring and 0.07 μmol L^{-1} h^{-1} in summer (He, 2010; He et al., 2010), giving a consumption of 3.0 μmol L^{-1} and 8.2 μmol L^{-1}, respectively, when multiplied by the corresponding residence time for May and August. Our unpublished data suggests that photodegradation in August could at most reduce [DOC] by 0.76 μmol L^{-1} and a_{330} by 0.11 m^{-1}, after considering the attenuation of solar radiation and the competition for light absorption by particles in the water column (Wang et al., 2014). The combined photochemical and bacterial DOC degradation in summer was thus ~9 μmol L^{-1}, ~8% of the initial [DOC] in the main estuary. The parallel photobleaching loss of a_{330} was 7%. Such small losses could be readily compensated for by DOM input from in situ primary production, sediment resuspension, and/or freshwater discharge farther downstream. Notably, chlorophyll *a* concentration maxima of up to 11.0 μg L^{-1} and turbidity maxima of up to 154 mg L^{-1} were spotted in the mid- and lower estuary during our cruises (Li et al., 2017). Nonetheless, there existed no co-variations of [DOC], ⟨CDOM⟩, and ⟨FDOM⟩ with chlorophyll *a* or suspended particulate matter (SPM) (data not shown). This observation, in conjunction with the linear DOM abundance vs. salinity relations, demonstrates that autochthonous production was unlikely a major source of DOM and that adsorption and flocculation were not a major sink of DOM in the main estuary. The short residence time of freshwater likely minimized the influences of these processes.

To reinforce the argument that the dynamics of DOM in the main estuary of the PRE was dominated by physical mixing, a principal component analysis (PCA) of the all-cruises dataset was performed in

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in R 3.5.2 using the *prcomp()* function. The dataset includes variables in addition to salinity, such as water temperature, nutrients (nitrate, nitrite, silicate), chlorophyll *a*, SPM, and freshwater discharge rate. Variables used in the PCA were zero centered and scaled to the unit variance. The first two axes of the PCA explained ~74% of the variability in the dataset (Fig. 9). DOC and a_{330}, along with nitrate and silicate, were strongly negatively related to salinity, a typical indication of a conservative mixing behavior. In contrast, DOC and a_{330} were not or only weakly linked to chlorophyll *a*, SPM, water temperature, and the freshwater discharge rate.

The completely different behaviors of [DOC] and ⟨CDOM⟩ with respect to salinity in the main estuary in November (Fig. 3c,f) led to a decoupling of the two variables. This phenomenon has also been observed for summer by Chen et al. (2004). In fact, the decoupling of [DOC] and ⟨CDOM⟩ is an extreme case of the higher salinity-based ⟨CDOM⟩ gradient relative to that of [DOC] seen in August and January (Sect. 3.4). The difference in estuarine mixing behavior between [DOC] and ⟨CDOM⟩ arose mainly from two factors. First, the main component of the freshwater DOM endmember was non- or weakly colored, as implied by its abundant fresh microbial constituents. Second, the difference in ⟨CDOM⟩ between the freshwater and marine endmembers was substantially larger than that in [DOC].

4.3 Depressed seasonal and spatial variations

The overall small variations of the qualitative metrics across the main estuary (Sect. 3.3) suggest that the chemical composition of CDOM and FDOM remained generally stable during estuarine mixing, consistent with the marginal photochemical and microbial breakdown of DOM elaborated above. As C_p was mostly >50%, BIX >1 and HIX <2.4 (Sect. 3.2), fresh, protein-enriched DOM of microbial origin dominated the DOM pool in the main estuary (Sect. 2.3), irrespective of seasons, locations, and depths. The dominance of protein-like over humic-like FDOM is in line with the low C/N ratios of DOM (range: 1.0–15; mean ± SD: 4.5 ± 2.9; median: 3.4) across the entire PRE in all seasons (Supporting

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Information in Ye et al., 2008). The higher %C_h and HIX in August than in November and January (Fig. 7c,e) point to FDOM in summer containing a larger fraction of humic-like fluorophores. The divergence in August of the west transect from the main and east transects with respect to the distributions of the FDOM metrics vs. salinity (Fig. 7c,e) suggests a different freshwater mass on the west shoal somewhat enriched with humic-like FDOM and possibly originating from Hengmen (Fig. 1). Nonetheless, the relatively higher humic-like fractions in August, particularly on the west transect, do not change the dominant signature of fresh, microbial-derived DOM in this season.

The PRE is largely homogeneous not only from a perspective of its dominant DOM source but also in terms of the vertical distribution of the quantitative variables. The bottom-surface differences for the quantitative variables are on average insignificant (particularly true for [DOC]) even in the presence of strong vertical stratification, such as in August (Sect. 3.2). This depressed vertical heterogeneity could be attributed to the reduced differences between the low-salinity and marine endmembers as elaborated above.

4.4 Indicators of a_{CDOM} and [DOC] in the main estuary

Salinity is a useful proxy of a_{CDOM} in light of their linear relationships in the main estuary for all three sampling seasons (Fig. 3). Furthermore, a common equation (Y = −0.048*X + 1.99, $p < 0.0001$) can serve as a predictive tool of a_{330} in August and January, given essentially the same statistics for each of these two months (Table S3). For [DOC], salinity can be used as an indicator in August and January but not in May and November (Fig. 3). Similar to the a_{CDOM}–salinity case, the August and January [DOC] data can be combined to formulate a single [DOC]–a_{CDOM} relationship (Y = 40.7*X + 75.6; $p < 0.0001$). Hence, [DOC] in summer and winter can in principle be retrieved from remote sensing-based a_{CDOM} data (Siegel et al., 2002; Johannessen et al., 2003; Mannino et al., 2008). C_p is also a good indicator of [DOC] in August and January (Fig. 8).

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Caution should be exercised when applying the [DOC] and a_{CDOM} predictive tools established here, since interannual variability and other factors may limit their applicability on broader time and space scales. For example, Hong et al. (2005) arrived at an a_{CDOM}–salinity relationship of $a_{355} = -0.045*\text{salinity} + 1.81$ for November 2002, which is different from ours in the main estuary ($a_{355} = -0.021*\text{salinity} + 0.98$). The data reported by Ye et al. (2018) shows a significant removal of DOC in May 2014 between salinity 5 and 22. Concurrent measurements of [DOC] and a_{CDOM} in the PRE are rare but Chen et al. (2004) reported no significant correlation between the two variables in July 1999.

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4.5 Fluxes of DOC and CDOM

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The fluxes of DOC and CDOM exported from the PRE to the South China Sea were estimated as follows (Cai et al., 2004; Lin, 2007; He et al., 2010):

$$F = Q \times C^* \quad (1)$$

where F denotes the flux of DOC or CDOM, Q the freshwater discharge rate, C^* the effective [DOC] ($[\mathrm{DOC}]^*$) or a_{330} (a_{330}^*). C^* is the y-axis intercept of the regression line of [DOC] or a_{330} vs. salinity in the main estuary (Table S3). For May and November when [DOC] remained roughly constant across the main estuary, C^* signifies the average [DOC] over this region. Monthly fluxes were computed using freshwater discharge rates for the sampling year and those averaged over 2006–2016 (http://www.mwr.gov.cn/zwzc/hygb/sqnb), under the assumption that the [DOC] or a_{330} obtained for May, August, November, and January represents the entire spring (March, April, May), summer (June, July, August), autumn (September, October, November), and winter (December, January, February), respectively. As no CDOM data was collected in May, the a_{330}^* for spring (1.99 ± 0.19 $\mathrm{m^{-1}}$) was derived from the mean of the $[\mathrm{DOC}]^*$-normalized a_{330}^* in January (1.31 L $\mathrm{mg^{-1}\ m^{-1}}$) and August (1.36 L $\mathrm{mg^{-1}\ m^{-1}}$) multiplied by the $[\mathrm{DOC}]^*$ in May (124.5 μmol $\mathrm{L^{-1}}$). This treatment, with unknown

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uncertainties, was based on the relatively small variations of the [DOC]*-normalized $a_{330}{}^*$ among the three CDOM sampling seasons (range: 1.31–1.50 L mg^{-1} m^{-1}).

Flux estimates for the sampling year are comparable to those for the 10-year period for spring and summer, whereas the former is approximately twice the latter for autumn and winter due to above-average freshwater discharge rates during the low-flow season of the sampling year (Table 1). Aggregation of the fluxes for all four individual seasons arrives at an annual export of 240 × 10^9 g C (sampling year) or 195 × 10^9 g C (10-year period) for DOC and of 329 × 10^9 m^2 (sampling year) or 266 × 10^9 m^2 (10-year period) for CDOM in terms of a_{330}. As the PRE receives ~54% of the total Pearl River freshwater discharge to the South China Sea (Mikhailov et al., 2006), including the rest 46% gives a grand annual export of 362 × 10^9 g C of DOC and 493 × 10^9 m^2 CDOM, respectively, assuming that the fluxes from the PRE are applicable to the entire Pearl River Delta.

4.5 Comparison with previous studies and other major estuaries

[DOC] obtained by this study in all four seasons are within the ranges previously reported for the PRE (Table 2). DOC stock in the PRE thus has not underwent large changes since the mid-1990s, suggesting that the gross inputs and losses of DOM remained stable during this period. Compared to [DOC], previous a_{CDOM} measurements are far fewer and none of them was made during wintertime. The summer and autumn a_{330} from this study are, however, comparable to those published (Table 2). Our DOC flux estimate for spring 2015 (5.8 × 10^8 g C d^{-1}) is close to that reported by He et al. (2010) for spring 2007 (5.3 × 10^8 g C d^{-1}). The summer 2015 value (9.0 × 10^8 g C d^{-1}) is, however, only 60% of the summer 2007's (He, 2010) due to a much lower river runoff in 2015 (7174 m^3 s^{-1} vs. 25060 m^3 s^{-1}). The DOC flux for the entire Pearl River Delta estimated by this study (362 × 10^9 g C year^{-1}) is comparable to that (380 × 10^9 g C year^{-1}) reported by Ni et al. (2008) but 44% lower than that (650 × 10^9 g C year^{-1}) obtained by Lin (2007). The estimate by Ni et al. (2008) was based on monthly [DOC]

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measurements at eight major runoff outlets of the Pearl River Delta from March 2005 to February 2006. Lin (2007) derived the estimate from data collected during three cruises carried out in winter (February 2004), early spring (March 2006), and summer (August 2005). Part of the difference between our study and Lin's could result from the different temporal coverage. The main difference, however, stems from the much greater $[\text{DOC}]^*$ obtained by Lin (2007) (147 µmol L^{-1} for the wet season and 254 µmol L^{-1} for the dry season).

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[DOC] and ⟨CDOM⟩ in the PRE are the lowest among the major world rivers (Table 3). The low DOM load in the PRE could be associated with a deficiency of organic matter in soil of the Pearl River's watershed having almost no forest (Luo et al., 2002). Moreover, although sewage effluents may bring in large amounts of DOM, a large portion of it can be rapidly biodegraded before reaching the head of the estuary (He et al., 2010). The lack of correspondence between $[\text{DOC}]^*$ and a_{330}^* and the freshwater discharge rate (Fig. S2) suggests that [DOM] in the PRE be controlled by both river runoff and pollution input. In contrast, DOM in the majority of large rivers is predominantly terrigenous (Bianchi, 2011; Raymond and Spencer, 2015) and the abundance of DOM in many rivers increases with the river flow rate (Cooper et al., 2005; Holmes et al., 2013). Note that the absence of a link between [DOC] and the freshwater discharge rate in the PRE observed by this study differs from the anti-variation of the two variables reported by Lin (2007) and Ni et al. (2008). Based on this anti-variation, Lin (2007) proposed that the PRE is a typical point source-regulated system in terms of DOC concentration and distribution. It remains to be confirmed if our results imply a fundamental change of the relative importance of sewage discharge (anthropogenic DOM) and river runoff (soil-derived and river-born DOM) in controlling the PRE's DOC freshwater endmember.

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Owing mainly to the very low [DOC], our DOC export estimate for the Pearl River is the lowest among the 30 largest rivers worldwide (Raymond and Spencer, 2015), though the Pearl River is ranked the 13th largest river by discharge volume. The Pearl River value of 362×10^9 g C year^{-1} only accounts for 0.14% of the global riverine DOC flux estimate of 250 × 10^{12} g C year^{-1} (Raymond and Spencer, 2015). The estimate for CDOM export from the Pearl River is also the lowest among the limited number of estimates available for the major world rivers (Table 4). Despite its small contribution on global scales, DOM delivered by the Pearl River is rich in proteinaceous constituents that can be utilized by microbes, thereby exerting a potentially important impact on the local coastal ecosystem.

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5 Conclusions

The main estuary of the PRE manifests smaller seasonal and spatial variations in DOM than expected for a sizable estuary with a marked seasonality of hydrography. Several factors functioning in concert lead to this phenomenon. First, a combination of the poorly forested watershed, rapid degradation of pollution-derived DOM in the upper reach, and short residence time of freshwater diminishes the DOM abundance and the seasonal variations in both DOM quantity and quality. Second, the small difference between the low-salinity and marine DOM endmembers tends to lessen the vertical and lateral gradients in DOM again both qualitatively and quantitatively, despite the larger vertical and cross-estuary salinity gradients. Both the concentrations and seaward exports of DOC and CDOM in and from the PRE are the lowest among the major world rivers. However, as DOM undergoes marginal processing during its transit through the estuary, the Pearl River delivers protein-rich, labile organic matter to the continental shelf of the South China Sea where it may fuel heterotrophy.

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Author contributions. GS and HX designed the study. HX and GS interpreted the results and prepared the manuscript with input from PM. YL performed sample analysis and data processing. YL, GS, FY, and RL participated in field sampling. PM carried out PARAFAC modeling, PCA, and Openfluor database search. FY conducted ANOVA.

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Competing interests. The authors declare that they have no conflict of interest.

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Figure captions

Figure 1. Map of sampling stations in the Pearl River Estuary. Station names starting with letters M, W, E designate the main, west, and east transects, respectively. See Table S1 for coordinates of the stations. HM: Humen; JM: Jiaomen; HQM: Hongqimen; HeM: Hengmen; MDM: Maodaomen; HMH: Huangmaohai.

Figure 2. Excitation-emission contours of five components identified by PARAFAC modeling (left panels) and split-half validations of excitation and emission loadings (right panels). Excitation/emission maximum wavelengths are: C1: 275/320 nm; C2: <240(335)/426 nm; C3: 245/378 nm; C4: 255(370)/464 nm; C5: <240(290)/348 nm.

Figure 3. Mean values of salinity (a), [DOC] (b), a_{330} (c), C_p (d), C_h (e), %C_p (f), %C_h (g), E_2/E_3 (h), BIX (i), and HIX (j) in the upper (UE) and lower (LE) estuaries. UE and LE refer to areas upstream and downstream of Sta. M05, respectively (Fig. 1). Surf and btm stand for surface and bottom respectively, and surf+btm denote surface combined with bottom. Error bars are one standard deviation.

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Figure 4. Mean values of salinity (a), DOC (b), a_{330} (c), C_p (d), C_h (e), %C_p (f), %C_h (g), E_2/E_3 (h), BIX (i), and HIX (j) on the west and east transects. Surf and btm stand for surface and bottom respectively, and surf+btm denote surface combined with bottom. Error bars are one standard deviation.

Deleted: The mean values of salinity (a), DOC (b), a_{330} (c), C_p (d), C_h (e), %C_p (f), %C_h (g), E_2/E_3 (h), BIX (i) and HIX (j) in surface combined bottom waters in the west and east transects. The error bar denotes the one standard deviation.

Figure 5. DOC concentration and a_{330} versus salinity in the PRE. Red circles denote samples collected in the head region of the estuary where DOC and a_{330} showed rapid decreases or large variabilities with salinity. Blue circles denote the samples collected in the main estuary. Solid lines in panels a and c represent means of the blue circles. Solid lines in the other panels denote linear fits of the blue circles. Dashed lines signify the 95% confidence intervals. See Table S3 for fitted equations and statistics.

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Figure 6. Same as in Figure 5b,d,e–g except for FDOM components C_p and C_h.

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Figure 7. E_2/E_3 (a), %C_p (b), %C_h (c), BIX (d), and HIX (e) versus salinity for each cruise. Lines in panel a denote conservative mixing lines defined by the lowest- and highest-salinity points in the main

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estuary, red solid circles in panels c and e denote samples collected along the west transect (see Figure 1) in August.

Figure 8. DOC concentration versus a_{330} (a), C_p (b), C_h (c). Solid lines denote linear fits of data for each cruise. See Table S5 for fitted equations and statistics.

Figure 9. Principal component analysis (PCA) based on the all-cruises dataset for the main estuary. 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. The data of SPM, Chla, and nutrients were provided by Li et al. (2017).

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Table 1. Estimates for DOC and CDOM (a_{330}-based) export from the Pear River to the South China Sea based on monthly freshwater discharge rates for the sampling year and those averaged over a 10-year period from 2006 to 2016. Standard errors of the fluxes for the sampling year were derived from the standard errors of the effective [DOC] and a_{330} (Table S3), while those for the 10-year period also include the interannual variability of the freshwater discharge rate.

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	Freshwater discharge ($\times10^{10}$ m^3)		Fluxes			
			DOC ($\times10^9$ g)		CDOM ($\times10^9$ m^2)	
	Sampling year	10-year average	Sampling year	10-year average	Sampling year	10-year average
Spring	3.58	3.63±0.78	53.5±2.4	54.2±11.9	71.3±4.9	72.2±16.2
Summer	5.68	6.17±1.22	82.7±1.0	89.9±17.7	112±3	122±24
Autumn	5.06	2.75±0.74	49.6±2.1	27.0±7.3	74.1±1.4	40.3±10.8
Winter	3.71	1.65±0.45	54.3±1.2	24.3±6.7	71.0±1.5	31.8±8.7
Annually	18.0	14.2±1.7	240±4	195±24	329±6	266±32

based) export from the Pear River to the South China Sea based on monthly freshwater discharge rates for the sampling year and those averaged over a 10-year period from 2006 to 2016. Standard errors of the fluxes for the sampling year were derived from the standard errors of the effective [DOC] and a_{330} (Table 4S5), while those for the 10-year period also include the interannual variability of the freshwater discharge rate.

... [166]

Table 2. DOC concentrations and a_{330} in surface water of the Pearl River estuary reported in the literature and this study.

Month	DOC (μmol L^{-1})	Sampling Year	Reference
Jan.	71–194	2016	This study
	179–285[a]	2014	Ye et al. (2018)
Feb.	100–247[b]	2004	Lin (2007)
	62–210[a,c]	2014	Ye et al. (2018)
Mar.	109–266	1997	Dai et al. (2000)
	103–229[b]	2006	Lin (2007)
Apr.	84–278[d]	2007	He et al. (2010) He (2010)
May	110–243	2015	This study
	58–160[e]	2001	Callahan et al. (2004)
	43–194[a]	2014	Ye et al. (2018)
Jul.	109–315	1996	Dai et al. (2000)
	68–250	1999	Chen et al. (2004)
Aug.	96–167	2015	This study
	107–164[b]	2005	Lin (2007)
	94–124[d]	2008	He (2010)
Nov.	77–133	2015	This study
	82–187[e]	2002	Callahan et al. (2004)
	59–164[a]	2013	Ye et al. (2018)
Month	a_{330} (m^{-1})	Sampling Year	Reference
Jan.	0.29–3.98	2016	This study
May	0.37–7.48[f]	2014	Lei et al. (2018)
Jul.	1.01–3.38[f]	2013	Wang et al. (2014)
	0.54–1.98	1999	Chen et al. (2004)
Aug.	1.07–4.35	2015	This study
Nov.	0.54–3.35	2015	This study
	0.38–2.73	2002	Hong et al. (2005)

[a] Data were obtained from the Supporting Information of Ye et al. (2018).
[b] Ranges were estimated using the fitted [DOC]-salinity equations in Lin (2007) over salinity 0–30.
[c] Data for the Guangzhou Channel were excluded.
[d] DOC concentrations upstream of Sta. M01 in the present study are excluded.
[e] Values were retrieved from figures 5a and 8b in Callahan et al. (2004).
[f] Ranges were estimated using exponential decay equations established from data in table 1 in Lei et al. (2018).

Table 3. DOC concentrations and CDOM abundances (a_{330}) in major world rivers.

River	DOM	References
	DOC (μmol L^{-1})	
Amazon	235	Raymond and Bauer (2001)
	277	Cao et al. (2016)
	307 (122–492)	Seidel et al. (2016)
Mississippi	489 (231–672)	Bianchi et al. (2004)
	417[a]	Spencer et al. (2013)
Atchafalaya	331[a]	Spencer et al (2013)
St. Lawrence	307 (25–1333)	Hudon et al. (2017)
	231[a]	Spencer et al. (2013)
Mackenzie	375±100	Cooper et al. (2005)
	347 (258–475)	Raymond et al. (2007)
	402 (250–576)[b]	Osburn et al. (2009)
	363 (250–475)	Stedmon et al. (2011)
Yukon	533±242	Cooper et al. (2005)
	509 (217–1258)	Raymond et al. (2007)
	574[a]	Spencer et al. (2013)
	674 (200–1617)	Stedmon et al. (2011)
Kolyma	500±167	Cooper et al. (2005)
	594 (250–1025)	Stedmon et al. (2011)
Lena	724±283	Cooper et al. (2005)
	775 (542–1233)	Raymond et al. (2007
	948 (550–1600)	Stedmon et al. (2011)
Ob	733±167	Cooper et al. (2005)
	780 (458–1000)	Raymond et al. (2007)
	875 (375–1058)	Stedmon et al. (2011)
Yenisey	733±316	Cooper et al. (2005)
	638 (242–1050)	Raymond et al. (2007)
	754 (208–1250)	Stedmon et al. (2011)
Yellow	202 (151–280)	Wang et al. (2012)
Yangtze	169 (137–228)	Wang et al. (2012)
Pearl River	149 (72–243)[c]	This study
	a_{330} (m^{-1})	
Amazon	13.05[d]	Cao et al. (2016)
Mississippi	9.60[a]	Spencer et al. (2013)
Atchafalaya	11.55[a]	Spencer et al. (2013)
St. Lawrence	9.65[e]	Xie et al. (2012b)
	2.16[a]	Spencer et al. (2013)
Mackenzie	8.30 (5.19–13.30)[b]	Osburn et al. (2009)
	6.04 (3.01–9.63)	Stedmon et al. (2011)
Yukon	17.34[a]	Spencer et al. (2013)
	14.50 (2.65–37.84)	Stedmon et al. (2011)
Kolyma	13.63 (5.77–29.19)	Stedmon et al. (2011)
Lena	26.51 (15.48–52.94)	Stedmon et al. (2011)
Ob	22.43 (6.74–30.74)	Stedmon et al. (2011)
Yenisey	22.14 (3.50–44.79)	Stedmon et al. (2011)
Yangtze (Changjiang)	2.60 (2.29–3.02)[f]	Song et al. (2017)
Pearl River	2.50 (1.04–4.35)[c]	This study

[a] Retrieved from DOC and CDOM fluxes and freshwater discharge rates in Spencer et al. (2013).

[b] From data at salinities <5

[c] From data at salinities <5.

[d] Retrieved from the spectral slope and a_{350} at Sta. 10 in Cao et al. (2016)

[e] Average value at Sta. SL1 and SL2 in Xie et al. (2012b).

[f] Average value at salinities <5.

Deleted: **Table 247.** DOC concentrations and a_{330} in surface water of the Pearl River estuary reported in the literature and this study. DOC (μmol L^{-1}) ... [167]

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Table 4. CDOM fluxes (a_{330}-based) from major world rivers to the ocean reported in the literature. The flux estimated for the Pearl River by this study is also included for comparison.

River	Flux ($\times10^{9}$ m^{2} year^{-1})	Reference
Mississippi	5070	Spencer et al. (2013)
Atchafalaya	2750	Spencer et al. (2013)
St. Lawrence	490	Spencer et al. (2013)
Mackenzie	1550	Stedmon et al. (2011)
Yukon	3520	Spencer et al. (2013)
	3260	Stedmon et al. (2011)
Kolyma	1340	Stedmon et al. (2011)
Lena	17100	Stedmon et al. (2011)
Ob	7350	Stedmon et al. (2011)
Yenisey	12600	Stedmon et al. (2011)
Pearl River	266	This study

the Pearl River estuary reported in the literature and this study.
DOC (μmol L^{-1}) ... [168]

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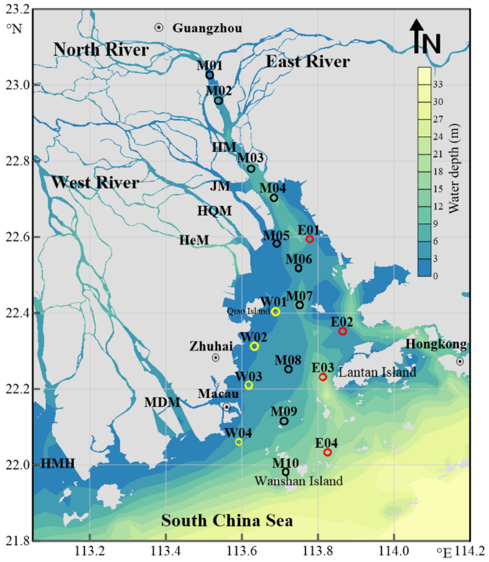


Figure 1. Map of sampling stations in the Pearl River Estuary. Station names starting with letters M, W, E designate the main, west, and east transects, respectively. See Table S1 for coordinates of the stations. HM: Humen; JM: Jiaomen; HQM: Hongqimen; HeM: Hengmen; MDM: Maodaomen; HMH: Huangmaohai.

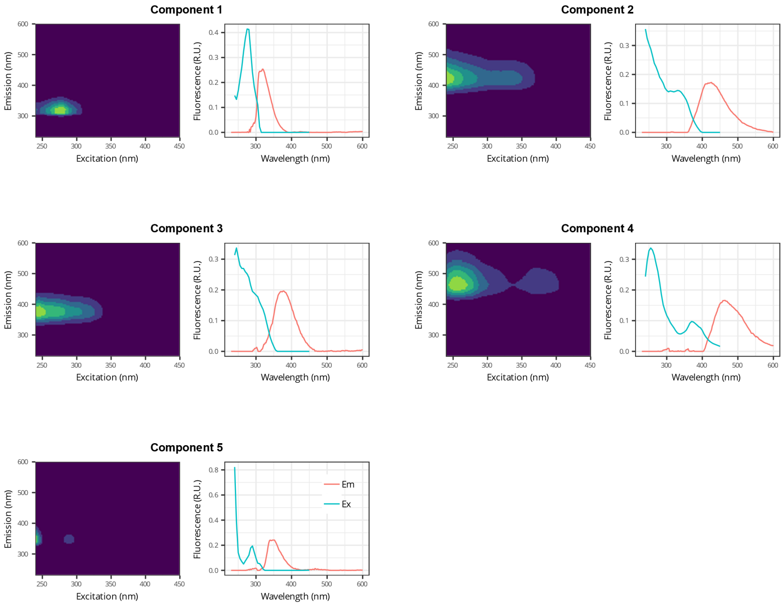


Figure 2. Excitation-emission contours of five components identified by PARAFAC modeling (left panels) and split-half validations of excitation and emission loadings (right panels). Excitation/emission maximum wavelengths are: C1: 275/320 nm; C2: <240(335)/426 nm; C3: 245/378 nm; C4: 255(370)/464 nm; C5: <240(290)/348 nm.

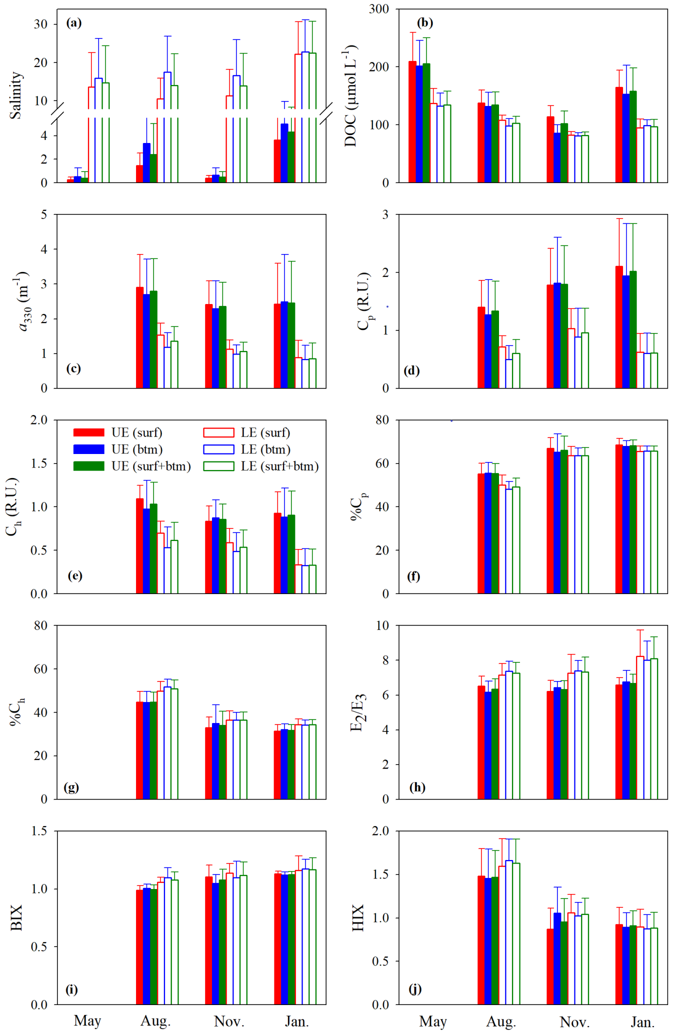
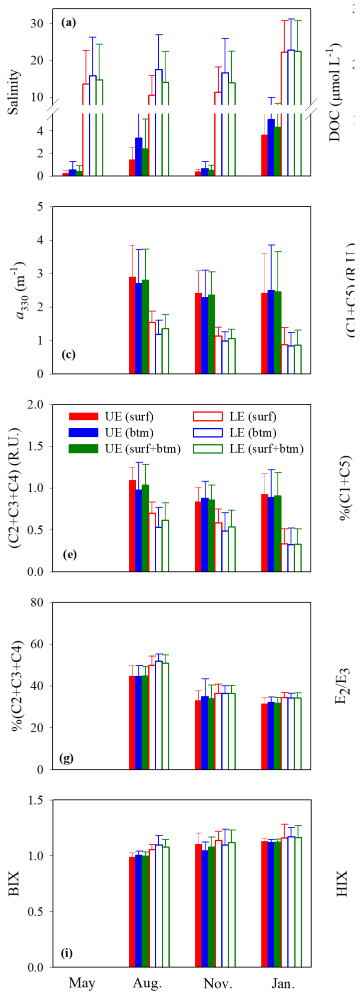


Figure 3. Mean values of salinity (a), [DOC] (b), a_{330} (c), C_p (d), C_h (e), $\%C_p$ (f), $\%C_h$ (g), E_2/E_3 (h), BIX (i), and HIX (j) in the upper (UE) and lower (LE) estuaries. UE and LE refer to areas upstream and downstream of Sta. M05, respectively (Fig. 1). Surf and btm stand for surface and bottom respectively, and surf+btm denote surface combined with bottom. Error bars are one standard deviation.



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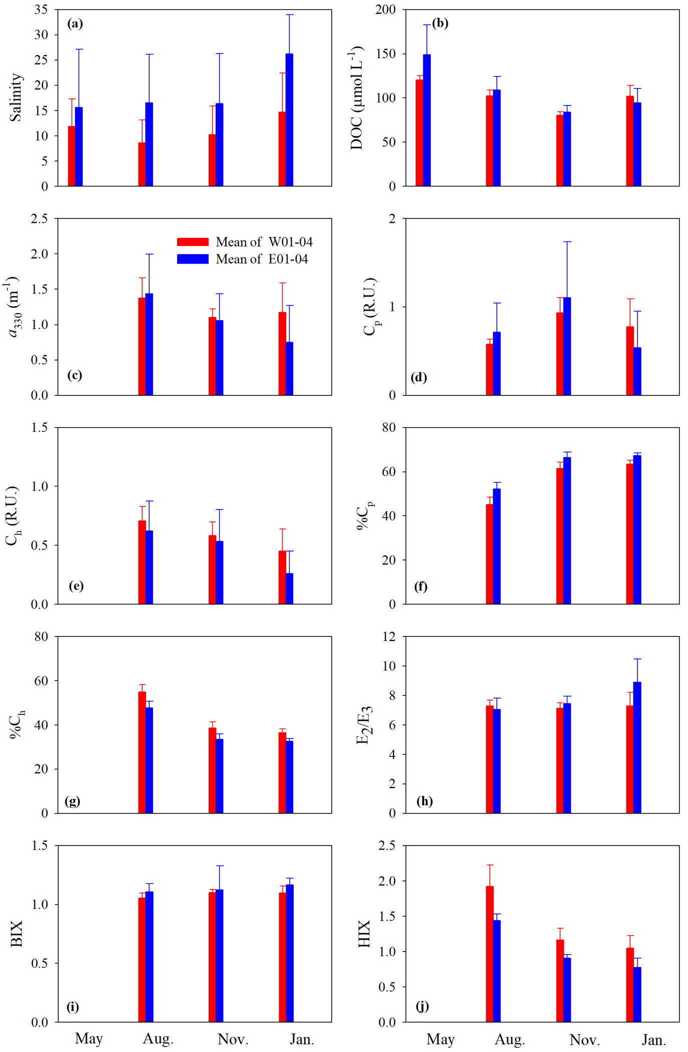
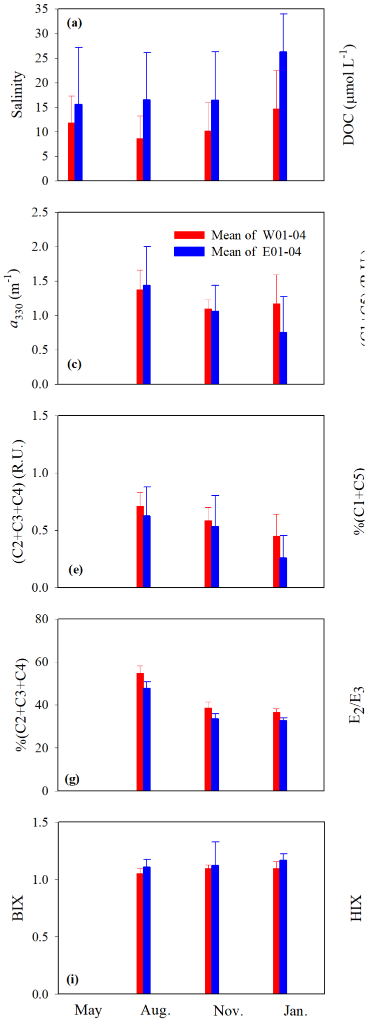


Figure 4. Mean values of salinity (a), DOC (b), a_{330} (c), C_p (d), C_h (e), %C_p (f), %C_h (g), E_2/E_3 (h), BIX (i), and HIX (j) on the west and east transects. Surf and btm stand for surface and bottom respectively, and surf+btm denote surface combined with bottom. Error bars are one standard deviation.



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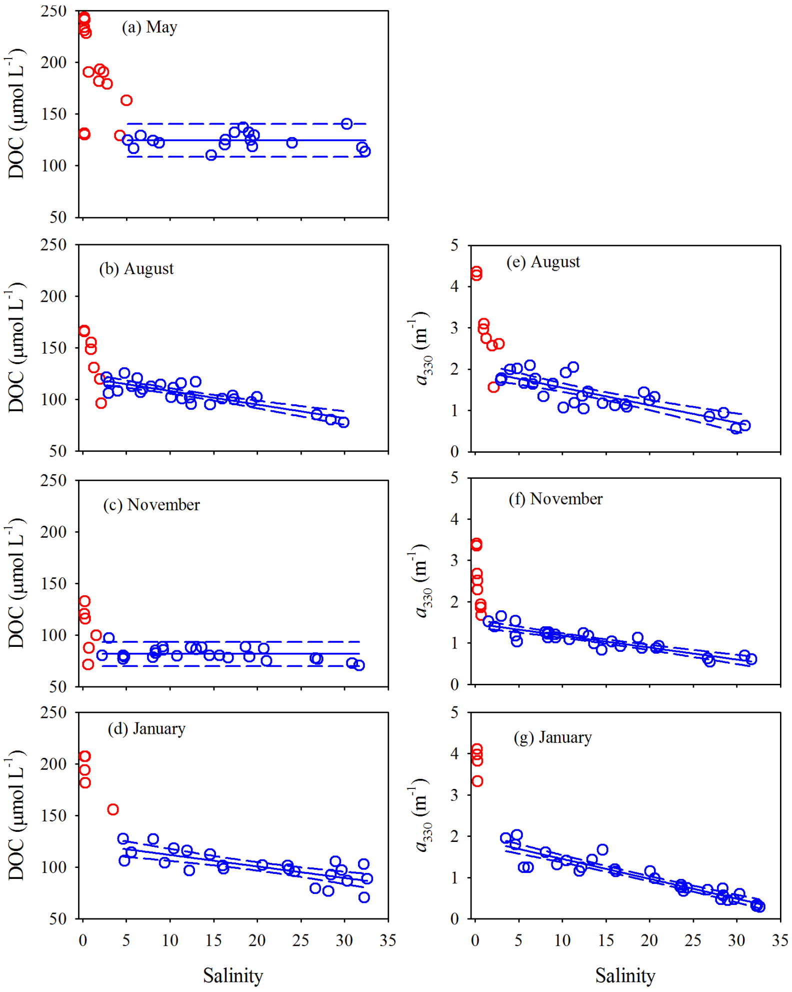

Figure 5. DOC concentration and a_{330} versus salinity in the PRE. Red circles denote samples collected in the head region of the estuary where DOC and a_{330} showed rapid decreases or large variabilities with salinity. Blue circles denote the samples collected in the main estuary. Solid lines in panels a and c represent means of the blue circles. Solid lines in the other panels denote linear fits of the blue circles. Dashed lines signify the 95% confidence intervals. See Table S3 for fitted equations and statistics.

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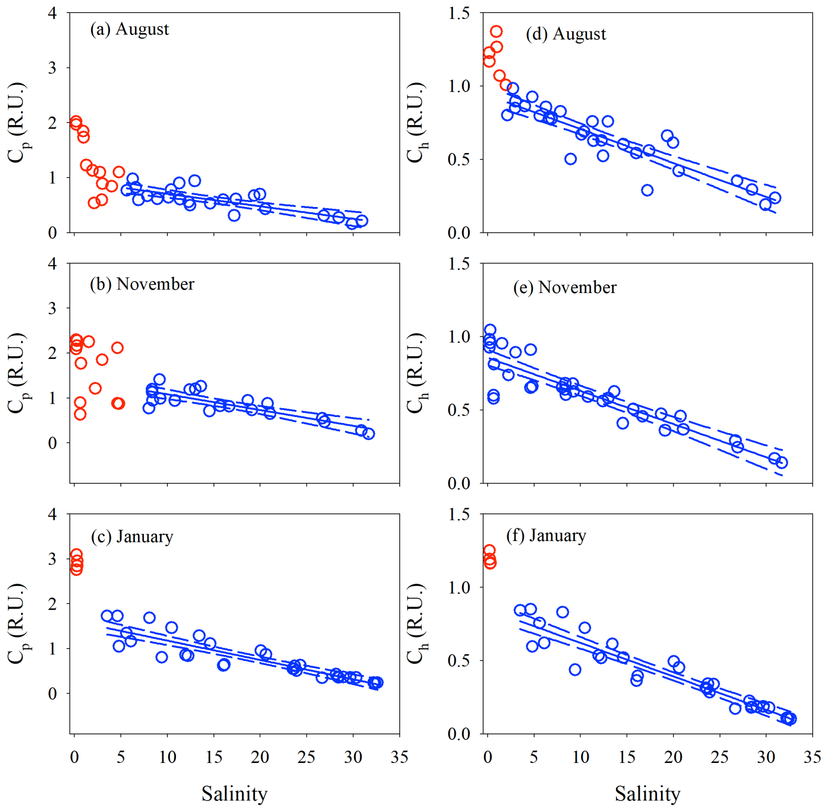

Figure 6. Same as in Figure 5b,d,e–g except for FDOM components C_p and C_h.

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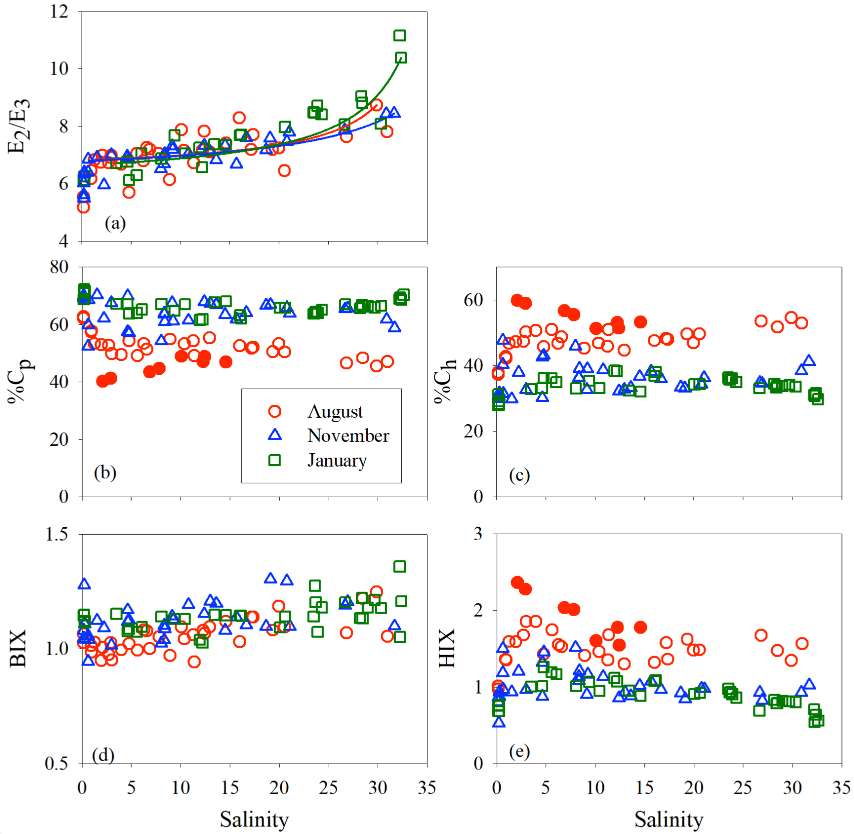

Figure 7. E$_2$/E$_3$ (a), %C$_p$ (b), %C$_h$ (c), BIX (d) and HIX (e) versus salinity for each cruise. Lines in panel a denote conservative mixing lines defined by the lowest- and highest-salinity points in the main estuary, red solid circles in panels c and e denote samples collected along the west transect (see Figure 1) in August.

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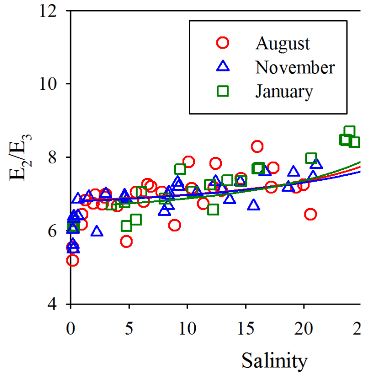
Moved up [5]: Figure 6. Same as in Figure 3b,d,e–g except for FDOM components C1+C5 and C2+C3+C4.



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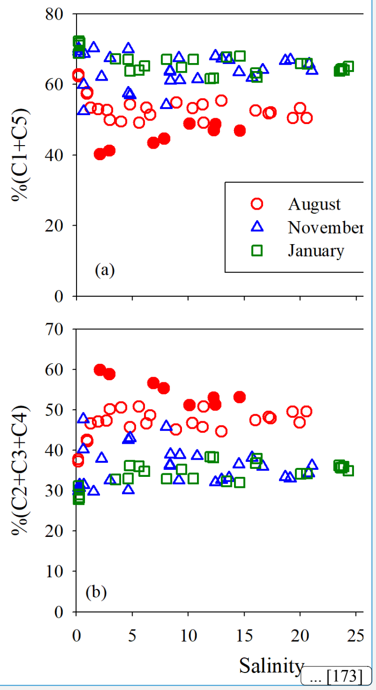

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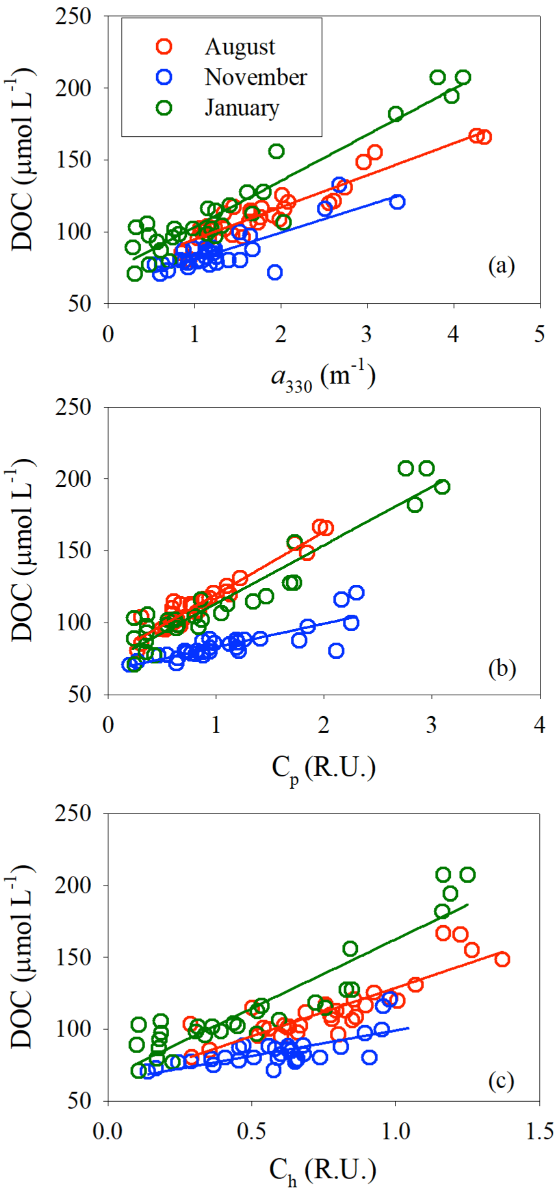
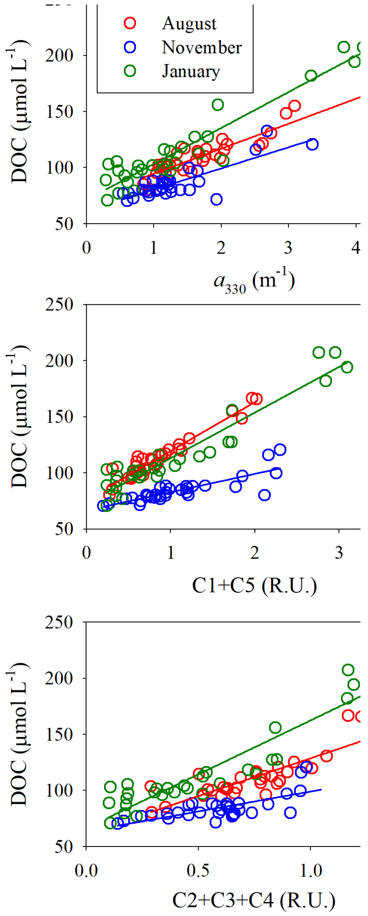


Figure 8. DOC concentration versus a_{330} (a), C_p (b), C_h (c). Solid lines denote linear fits of data for each cruise. See Table S5 for fitted equations and statistics.



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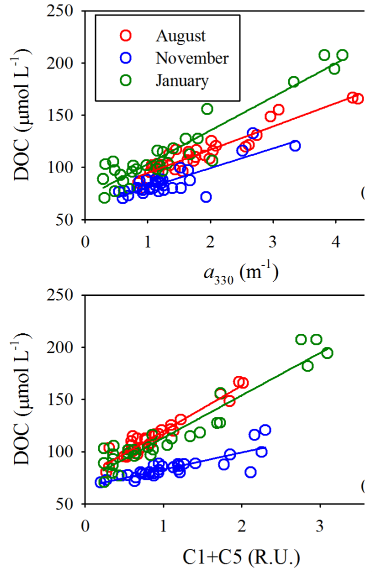

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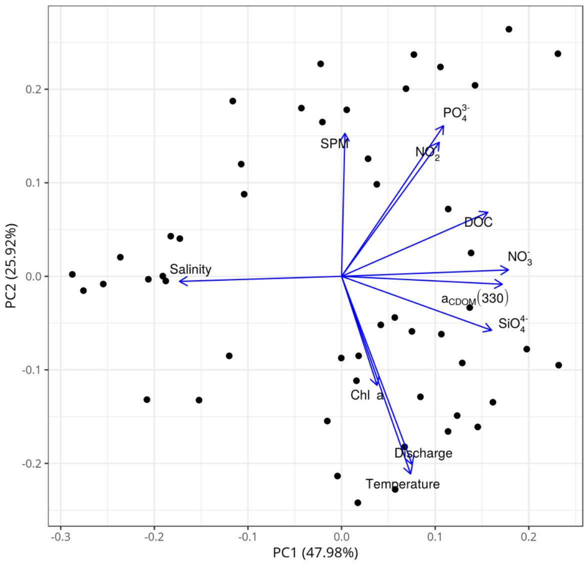

Figure 9. Principal component analysis (PCA) based on the all-cruises dataset for the main estuary. SPM: suspended particulate matter; PO_4^{3-}: phosphate; NO_2^-: nitrite; DOC: dissolved organic carbon; $a_{CDOM}(330)$: CDOM absorption coefficient at 330 nm; NO_3^-: nitrate; Chla: chlorophyll a; SiO_4^{4-}: silicate; discharge: freshwater discharge rate. The data of SPM, Chla, and nutrients were provided by Li et al. (2017).

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Response to Editor's comments

Responses are *italicized*.
AR stands for authors' response

1. Main conclusions of the article are difficult to follow since there is repetition of results throughout the text, and there are results that are not considered in the discussion, deviating attention to main points of the article. Examples: a) Water temperature is shown but there is no discussion of it, b) idem with results on water column mixing, c) in page 263, "Bottom water salinity at most stations was nearly identical to SWS in January, slightly greater in May, moderately elevated in November, and much higher in August (Fig. S2)". There is no discussion of it in the text. If there is a meaning for this, then it needs to be quantitatively explained, not as currently written (slightly, much, etc.).

AR: *We have re-organized the structure of the article to minimize the repetition of the results. a) water temperature has now been incorporated into the principal component analysis (PCA) for discussion (lines 453-461); b) & c) the effect of water column mixing/stratification on the vertical distribution of DOM has now been briefly discussed (lines 486-491); c) this sentence has been modified (lines 253-256).*

2. There is an excessive use of Supplementary tables and figures around relevant discussion and conclusions. Supplementary figures and tables are meant to back up tables and figures of the main text. A new version will require rethinking and reorganizing tables and figures accordingly.

AR: *We have substantially reduced the supplementary tables and figures in the new version.*

3. Qualitative assessments should be avoided. such as saltier, less salty (Reviewer 3 suggests using well-known and accepted terminology by the estuarine community).

AR: *The "head region" is now used to refer to the narrow low-salinity zone and "main estuary" to denote the saltier zone.*

4. Hypothesis. "… hypothesize that DOM in the PRE presents substantial seasonal variability in terms of both abundance and chemical composition and that the PRE is an important source of DOM to global oceans. "Chemical composition you are referring to is targeting a quantitatively minor fraction of DOC pool (in the order of 2%), therefore you cannot test that hypothesis for the entire pool using this approach.

AR: *The hypothesis has been modified to "Given the large volume and seasonality of the freshwater discharge of the Pearl River, we hypothesize that the quantity of DOM and the quality of CDOM in the*

PRE present substantial seasonal variability and that the PRE is an important source of DOM to the global ocean".

5. What are units of DOC and CDOM fluxes in Table 6. Nowhere is mentioned how you estimated fluxes from absorbance data.

AR: *The units are already there: grams for DOC and m^2 for CDOM. The first 4 rows are for each season and the last row for one year. The equation and procedure for estimating the CDOM flux are already given in the original version (first paragraph of section 4.4).*

6. Keep in mind Short Comment:
" 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…."

AR: *Following the reviewer's comments, we have restructured and shortened the Introduction and Results sections.*

7. Section on Pearl River estuary is definitely too long, so it is background on DOM.
Please choose the most relevant aspects.

AR: *Theses two sections have been restructured and shortened.*

8. "… [DOM], [CDOM], and [FDOM] stand for the abundances of…". Square brackets are used in chemistry to denote concentration and [CDOM] and [FDOM] are not; they could be considered proxies of concentration. Different things.

AR: *Now* $\langle CDOM\rangle$ *and* $\langle FDOM\rangle$ *are used to denote the proxies of CDOM and FDOM abundances.*

9. Use of non-standard acronym such as SWS only makes reading more difficult (It is used only 7 times in the text, all in one page).

AR: *This acronym has now been spelled out throughput the text.*

10. P, 286, P 409, etc.. Correlation and regression are not the same. In correlation there is no independent variable and coefficient of correlation (r) ranges from -1 to +1. In regression, there is X and Y, and coefficient of determination (R2) ranges from 0 to 1 (0 to 100%). Please check and revise accordingly

AR: *This has been checked and revised.*

11. Method. "Hansell's low carbon ([DOC]: 1–2 µmol L−1) and deep Florida Strait ([DOC]: 41–44 µmol L−1) reference waters "
What was the quantitatively results of this calibration?

AR: *The calibration results have been added to the revised version (lines 153-154)*

12. About the analytical uncertainty mentioned by Reviewer 2. #8. " … aCDOM at 330 nm (a330) was 2.19 m−1 (range: 1.19–4.37 m−1)…" corresponds to the range of values of a330 measured in the river during the August cruise. Analytical uncertainty on the other hand, deals with dispersion of values associated to a measure and, therefore samples has to be as similar as possible.

AR: *Now the uncertainty of measurements on 6 replicates of the same sample is reported. (lines 160-163).*

13. Lines 375-376. Please explain what you want to say here

AR: *This sentence does not exist anymore in the revised version.*

14. Lines 235-236 should be in methods

AR: *Now moved to the Methods (lines 225-227).*

Response to Reviewer 1

Responses are *italicized*.
AR stands for authors' response

The paper entitled "Distribution, seasonality, optical characteristics, and fluxes of dis- solved organic matter (DOM) in the Pearl River (Zhujiang) estuary, China" investigated seasonal and spatial variations of CDOM and FDOM characterized by absorption and fluorescence spectroscopy. Since I am an organic geochemist focusing on the organic carbon and nitrogen cycling mechanism in estuarine coastal zones and the role of microbes during the organic matter cycling, I am very familiar with the topic of this manuscript. This manuscript identified the compositional characteristics and sources of DOM. The main conclusion is that (i) microbial inputs and anthropogenic inputs are important sources of DOM in the freshwater end; (ii) small seasonal variations with respect to DOC and CDOM; and (iii) PR exports the lowest quantality of DOC among 30 large world rivers, although the size of PR watershed ranked the thirteenth largest in the world by area. Considering the anthropogenic activities can influence the quality and quantity of DOM in aquatic ecosystems and urbanization trends continue in response to human population growth, anthropogenic influences on DOM composition will likely become more widespread. Such human effects on DOM quality could have strong impacts on carbon cycles and need to be better understood. Therefore, this study provides a typical case study to approach the scientific questions mentioned above. However, some points need to be addressed as follows. Nevertheless, this work did provide interesting findings, and the data is reasonably strong to make the conclusions, and there I suggest a moderate revision needs to perform before the acceptance of this manuscript.

General comments:

1. In terms of English, I suggest the writing should be improved further.

AR: *We did further language polishing.*

2. The description of "overview of DOM" is great. However, I realize that it is too general. I hope the authors could provide introduction related with their discussion or the questions that need to be solved (or knowledge gap). In addition, the transition from 1.1 to 1.2 seems not that smooth to me.

3. The chapter "1.2 The Pearl River estuary (PRE)" is too lengthy to describe the important focus and

question, and some of descriptions can be moved to "Site description", otherwise part of the information seems duplicated. For instance, the authors spent 9 paragraphs to describe the PRE, and some of the information is not closely related with the results/discussions. This needs to be shortened and be questions oriented.

AR: *Re comments 2&3. The introduction has now been restructured and shortened.*

4. The authors mentioned precipitation is an important factor affecting soil flushing, which may affect both DOM equality and quantity. It would be great if the author could incorporate some monthly or seasonal precipitation data to support their claims. In particular, the article indicated the terrigenous DOM is the main source of investigated areas, but it did not describe the influences of land runoff and rainfall on seasonal variations of DOM.

AR: *The freshwater discharge to the PRE, which has already been described in the paper, is directly correlated to precipitation over its watershed and is a more direct indicator of the impact of precipitation (than precipitation itself) on the study area.*

Note that the article does not conclude that terrigenous DOM is the main source of DOM in the PRE. Instead, it underscores the microbial nature of this DOM pool and a potentially important contribution from river-borne DOM (line 462-471 in the original version).

5. In this manuscript the author suggested that the low DOC concentrations in PRE (especially the low salinity region) was affected by biological degradation (due to input of labile DOM) and low inputs due to the low forest cover. This is a good point! I suggest the author expand this description a little bit. For instance, (i) the addition of labile DOM may "prime" the degradation of terrestrial (relatively more recalcitrant) DOM; (ii) the author could specify the land use percentages of the PR watershed and compare it with the other large river-estuarine systems (such as the Amazon River). Some of the land use% data has been organized in Wagner et al. (2015), and I believe the land use% data is not that difficult to find for PR watershed; (iii) since the authors claim that the PRE is a super eutrophic system, it would be interesting at least present some nutrient data (from literatures) to further support their main findings.

AR: *(i) The "priming" concept is a good suggestion. Nonetheless, our results indicate that this effect, if any, was minor, at least in May, August, and January. In the low-salinity section, the [DOC] after the rapid removal of the labile constituents (Fig. 3), except November, was in the same range as that of the* *background [DOC] reported for the Pearl River upstream of the Pearl River Delta (114-137 uM, line 122 and line 465-466 in the original version), demonstrating little "priming". Downstream of the upper reach, [DOC] either decreased (August and January) or remained roughly constant (May and November) with increasing salinity, again disproving a major DOC loss process caused by priming. We believe that the land-derived DOC in the Pearl River is either priming-resistant or the short residence times of freshwater in the PRE (a few days, line 496-498 in the original version) prevented a significant priming effect from occurring.*

In the revised manuscript, we have briefly discussed the potential role of the priming effect, particularly for November when the [DOC] at the downstream side of the low-salinity section was substantially lower than the land-derived background [DOC].

(ii) Sorry, we exhausted our resources but could not find the land use% data for the Pearl River region. The landscape information reported by Luo et al. (2002), which we cited, though in a more general nature, provides a similar support for the relevant discussion.

(iii) We thoroughly checked the manuscript and found that ***nowhere*** *does the article claim the PRE to be a super eutrophic system. The word "eutrophic" does not exist in this article.*

6. I really like the main findings in the manuscript, but these findings are not well reflected in the abstract. I suggest the author re-organize their abstracts and focusing on the main findings. Reporting numbers are great, but there seem to be too many. Keep the important ones would be good enough.

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

7. Considering the author spent a huge effort collecting all these samples, it would be very interesting to perform some statistical analysis such as the principal component analysis (PCA) to further confirm the major controls to the DOM variability across the whole dataset.

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 nitrate and silicate) 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 linked to the freshwater discharge rate, again consistent with our result (line 604-606 & Fig. S9 in the original version).*

We have added the plot to the main text (Fig. 9) and briefly discussed it in the revised manuscript (lines 453-461).

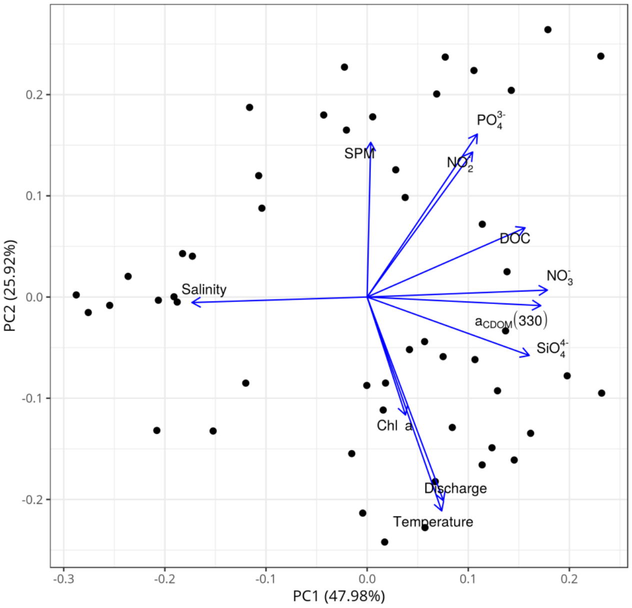

Figure: PCA analysis based on the all-season dataset. SPM: suspended particulate matter; PO_4^{3-}: phosphate; NO_2^-: nitrite; DOC: dissolved organic carbon; $a_{CDOM}(330)$: CDOM absorption coefficient at 330 nm; NO_3^-: nitrate; Chla: chlorophyll a; SiO_4^{4-}: silicate; discharge: freshwater discharge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

Specific comments:

1. There was no explanation about the inverse changes of BIX and HIX in Fig.7

AR: *This is self-evident according to the definitions of BIX and HIX (now in the Methods section): BIX denotes the relative contribution of fresh, microbial-derived FDOM, while HIX signifies the degree of humification, with old, humified FDOM having higher HIX values.*

Now a statement as follows has been added in the second last paragraph of section 3.5:

"BIX displayed a distribution roughly inverse to that of HIX (Fig. 7d), as can be inferred their definitions (Sect. 2.3)."

2. I suggest the author make it clear what is “the saltier zone” because this is a ambiguous description.

***AR:** The saltier zone is indirectly defined between line 358 and 361 in the original version. It refers to the zone with salinity generally >5, where the reported DOM variables showed much slower changes with increasing salinity as compared to the rapid changes near the head of the estuary (i.e. the low-salinity zone). However, the salinity separating these two areas was at times slightly season- and/or variable-specific.*

Following relevant comments from reviewer 3 and the associate editor, we have now termed the low-salinity zone as the head region of the estuary and the saltier zone as the main estuary.

3. Considering there are way too many tables. I suggest move some of the tables (e.g., Table 1) to the supplementary information. The DOC (μmol L-1) needs to be moved to the second column.

***AR:** Tables 1, 4, and 5 were moved to Supplemental Material. DOC was moved to the second column in Table 8.*

4. Would be wonderful if the author could point out the major metropolitan areas (or even land use patterns) in Figure 1 since it closely related with the major discussions in this manuscript.

***AR:** As stated in our response to comment#5, we could not find the land use data for this region. The major cities are already labeled. The discussion does not require information on the metropolitan borderlines.*

5. When the authors describe each PARAFAC component, I suggest the author use DOM Open- fluor database to compare the components in this study with literature data. Murphy, K. R., Stedmon, C. A., Wenig, P., & Bro, R. (2014). OpenFluor–an online spectral library of auto-fluorescence by organic compounds in the environment. Analytical Methods, 6(3), 658-661.

***AR:** This has now been done and added to the Methods section.*

6. R.U. should be defined in the abstract.

***AR:** Thanks. Done.*

Response to Reviewer 2

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 Introduction has been re-arranged and shortened. Details of the PRE are moved to a separate section (2.1. Site description) in the Methods.*

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:** This sentence does not exist anymore in the revised Introduction.*

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:** Now the uncertainty of measurements on 6 replicates of the same sample is reported. (lines 160-163).*

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* $S_{275\text{-}295}$ *(lines 205-210).*

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 and t-test have been conducted. The results indicate 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. The results of ANOVA and t-test are incorporated into the Results section.*

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 nitrate and silicate) 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 linked to the freshwater discharge rate, again consistent with our result (line 604-606 & Fig. S9 in the original version).*

We have added the plot to the main text (Fig. 9) and briefly discussed it in the revised manuscript (lines

453-461).

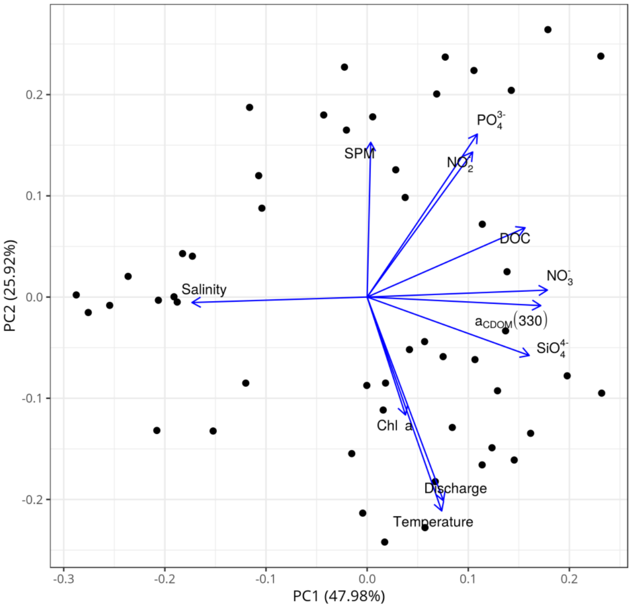

Figure: PCA analysis based on the all-season dataset. SPM: suspended particulate matter; PO_4^{3-}*: phosphate;* NO_2^-*: nitrite; DOC: dissolved organic carbon;* $a_{CDOM}(330)$*: CDOM absorption coefficient at 330 nm;* NO_3^-*: nitrate; Chla: chlorophyll a;* SiO_4^{4-}*: silicate; discharge: freshwater 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. A river-born component (from phytoplankton and/or bacterial activities) is added to this proposition (lines 568-570).*

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.

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.

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.

Response to Reviewer 3

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 nitrate and silicate), 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 linked to the freshwater discharge rate, again consistent with our result (line 604-606 & Fig. S9 in the original version).*

We have added the plot to the main text (Fig. 9) and briefly discussed it in the revised manuscript (lines 453-461).

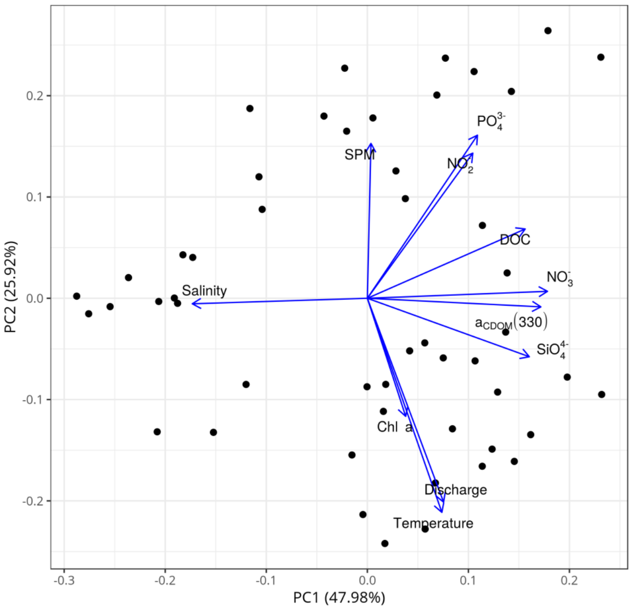

Figure: PCA analysis based on the all-season dataset. SPM: suspended particulate matter; PO_4^{3-}*: phosphate;* NO_2^-*: nitrite; DOC: dissolved organic carbon;* $a_{CDOM}(330)$*: CDOM absorption coefficient at 330 nm;* NO_3^-*: nitrate; Chla: chlorophyll a;* SiO_4^{4-}*: silicate; discharge: freshwater 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: *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 (including chlorophyll and SPM) 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: *The "head region" is now used to refer to the narrow low-salinity zone and "main estuary" to denote the saltier zone.*

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: *There are several points to support 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 the 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 ($S_{275\text{-}295}$, $S_{350\text{-}400}$ 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 $S_{275\text{-}295}$ and MW.

We have explicitly stated in the revised manuscript that E_2/E_3 serves similar functions to those of $S_{275\text{-}295}$ (lines 205-210).

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 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 is 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 in part 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 main estuary (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 494-497 in the original version; 2) the competition of light absorption by particles (water in the PRE is turbid); and 3) self-shading due to 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 causes 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).*

References: X. Lei, J. pan, A. T. Devlin. 2018. Mixing behavior of chromophoric dissolved organic matter in the Pearl River Estuary in sprig. Continental Shelf Research, 154, 46-54.

F. Ye, W. Guo, G. Wei, and G. Jia. 2018. The sources and transformations of dissolved organic matter in the Pearl River Estuary, China, as revealed by stable isotopes. J. Geophys. Res.: Oceans, 123, 6893-6908.

***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.*

References cited in this response:

Aarnos, H., Gélinas, Y., Kasurinen, V., Gu, Y., Puupponen, V.M. and Vähätalo, A.V., 2018. Photochemical mineralization of terrigenous DOC to dissolved inorganic carbon in ocean. Global Biogeochemical Cycles, 32(2), 250-266.

Bianchi, T.S. and Allison, M.A., 2009. Large-river delta-front estuaries as natural "recorders" of global environmental change. Proceedings of the National Academy of Sciences, 106(20), 8085-8092.

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Cauwet, G., 2002. DOM in the coastal zone. Biogeochemistry of marine dissolved organic matter.

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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.

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Hong, J., Xie, H., Guo, L. and Song, G., 2014. Carbon monoxide photoproduction: implications for photoreactivity of arctic permafrost-derived soil dissolved organic matter. Environmental science & technology, 48(16), 9113-9121.

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

Mann, P.J., Davydova, A., Zimov, N., Spencer, R.G.M., Davydov, S., Bulygina, E., Zimov, S. and Holmes, R.M., 2012. Controls on the composition and lability of dissolved organic matter in Siberia's Kolyma River basin. Journal of Geophysical Research: Biogeosciences, 117(G1).

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Osburn, C.L., Retamal, L. and Vincent, W.F., 2009. Photoreactivity of chromophoric dissolved organic matter transported by the Mackenzie River to the Beaufort Sea. Marine Chemistry, 115(1-2), 10-20.

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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.

Raymond, P.A. and Spencer, R.G., 2015. Riverine DOM. In Biogeochemistry of marine dissolved organic matter (pp. 509-533). Academic Press.

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Song, G., Li, Y., Hu, S., Li, G., Zhao, R., Sun, X. and Xie, H., 2017. Photobleaching of chromophoric dissolved organic matter (CDOM) in the Yangtze River estuary: kinetics and effects of temperature, pH, and salinity. Environmental Science: Processes & Impacts, 19(6), 861-873.

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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.

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Response to Public Short Comment

Responses are *italicized.*
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:** Following the reviewer's comments, we have restructured and shortened the Introduction and Results sections.*

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.*

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 and now the PCA* *analysis as well) suggest that this effect was minor. Note that the effect of sediment resuspension, if any, 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 ($S_{275-295}$, $S_{350-400}$ 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 $S_{275-295}$ (lines 205-210).

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 nitrate and silicate) 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 linked to the freshwater discharge rate, again consistent with our result (line 604-606 & Fig. S9 in the original version).*

We have added the plot to the main text (Fig. 9) and briefly discussed it in the revised manuscript (lines 453-461).

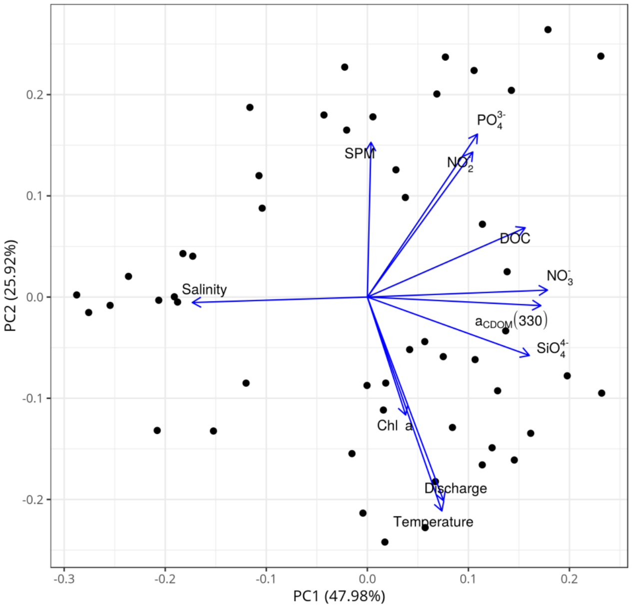

Figure: PCA analysis based on the all-season dataset. SPM: suspended particulate matter; PO_4^{3-}*: phosphate;* NO_2^-*: nitrite; DOC: dissolved organic carbon;* $a_{CDOM}(330)$*: CDOM absorption coefficient at 330 nm;* NO_3^-*: nitrate; Chla: chlorophyll a;* SiO_4^{4-}*: silicate; discharge: freshwater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

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*** *our finding, 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 Introduction is greatly shortened and this kind of non-essential information is not provided in the revised version in part because different papers reported widely different values and in part because we conducted a PCA that includes the chl-a values from our cruises.*

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).*

The revised manuscript does not contain this content anymore in order to restructure and condense the Results section.

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 believe that our explanation is sound. These points are made clearer in the revised version.

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.*

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