Response to Reviewer#1

We appreciate the reviewer's constructive comments. Our 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 quantity 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. In addition, please see the positive comment in SC1 on the readability of the manuscript ("…the manuscript is well written and reads easily…").

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: As comments 2&3 both concern the Introduction, we respond to them together.

The Introduction was condensed and the details of the PRE were moved to a new section "2.1 Study area" in the Methods (as suggested by RC2). The new Introduction is not divided into subsections.

*It should be noted that, for a paper of multidisciplinary nature like this, it is essential to place the targeted research question into a broad and multifaceted context. **This is particularly helpful for the readers who are not familiar with the PRE**. The Introduction follows a typical logic line proceeding from the general to the specific to the knowledge gap and eventually to the objectives. Section 1.1 unfolds with describing the importance of DOM in the marine ecosystem, followed by the key processes affecting the quantity and quality of DOM in coastal and estuarine environments. The latter serves not only as the basis for discussing the results and interpreting the data later on but also as an overture for presenting the relevant information on the PRE. Section 1.2 summarizes the geography, topography, hydrography, and biology of the PRE (now moved to a new section "2.1 Study area" in the Methods) preceding a brief review of previous DOM studies in this environment and a statement of the knowledge gap. We carefully checked the entire manuscript and can confirm that **every element presented in the Introduction is indispensable to and echoed in the later sections**. For example, the geographical information is required for describing the sampling scheme, while the topographic (water depths, shoals, channels), hydrographic (freshwater discharge rates, freshwater flow paths, water column stratification, turbidity), biological (phytoplankton biomass), and pollution-related information all provides fundamental context for data presentation and interpretation. Besides, the separate*

*treatment of quantitative and qualitative DOM variables in the Introduction foreshadows a similar structural arrangement in data presentation in the Results section. **The manuscript is such structured that removing any element in the Introduction (and section "2.1 Study area" in the revised version) would compromise the integrity of the entire article.***

The manuscript currently does not have a "Site description" section and we could not find information in the Introduction is repeated somewhere else (as the reviewer mentioned in the comment 3).

4. The authors mentioned precipitation is an important factor affecting soil flushing, which may affect both DOM quality 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. However, we have added the dissolved inorganic nitrogen values in the revised manuscript.*

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 a bunch of other variables (e.g. nitrate, nitrite, silicate, chl-a), are strongly negatively correlated to salinity, which is a typical indication of a conservative mixing behavior. In contrast, DOC and a_{330} are only weakly (negatively) linked to the freshwater discharge rate, again consistent with our result (line 604-606 & Fig. S9 in the original version).

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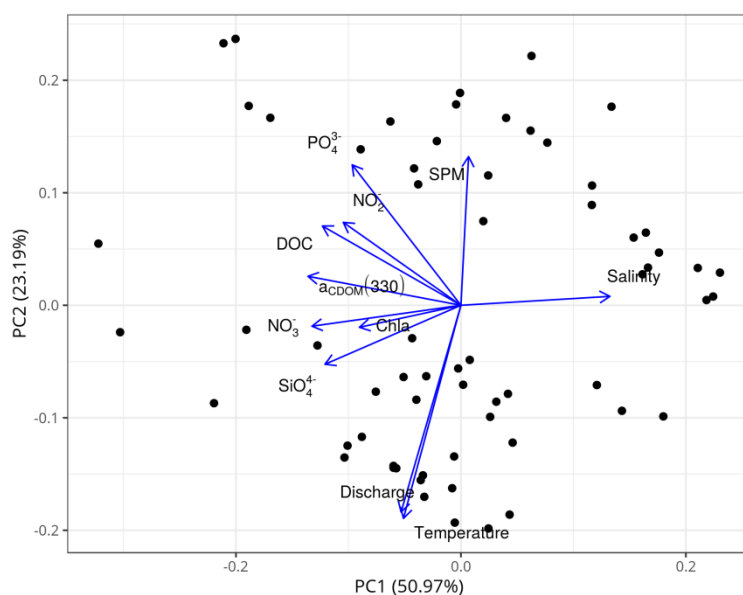

Figure: PCA analysis based on the all-season dataset. SPM: suspended particulate matter; PO_4^{3-}: phosphate; NO_2^-: nitrite; DOC: dissolved organic carbon; $a_{CDOM}(330)$: CDOM absorption coefficient at 330 nm; NO_3^-: nitrate; Chla: chlorophyll a; SiO_4^{4-}: silicate; discharge: freshwater discharge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

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 (section 3.3): 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 and HIX displayed roughly inverse distributional patterns against salinity, as can be inferred from their definitions (Sect. 3.3)."

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. We have now explicitly defined the low-salinity and saltier zones in the first paragraph of section 3.4 as follows:

"Hereafter, the head region of the estuary showing fast change or high variability of DOM is termed "the low-salinity zone", while the downstream area exhibiting much gentler variations in DOM is referred to as "the saltier zone." The salinity demarcating the low-salinity and saltier zones was generally ~5 but could change slightly with season and the DOM variable of interest (Figs. 3 and 4)."

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. In fact, adding the metropolitan areas reduces the legibility of the map.

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 a table showing the results of comparison is provided in the Supplemental Material.

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

AR: Thanks. Done.