

Reply to RC2 (Responses in *italic*)

General comment:

Yao et al used a physical mixing coupled with biogeochemistry model to investigate DOC cycling in the Changjiang Estuary along the land to coastal ocean continuum. They find with their model that in the summer, DOC distributions are dependent on biogeochemical processes as well as physical mixing, while in the winter, physical mixing predominates. The study found that terrestrial DOC is not susceptible to bacterial consumption in the estuarine system, but highly susceptible to marine bacteria consumption. Finally, the estuary is a source of DOC to the coastal ocean.

I found the study interesting and suitable for publication after moderate revisions, and have a few major comments for the authors to consider, listed below:

We are very grateful for the detailed and helpful suggestions. We have carefully addressed the questions from the reviewer. Our specific point-to-point responses to the reviewer's comments are listed below.

I think the authors need to go more into depth about their model set up. Why is it that refractory DOC, which makes up a large portion of the total pool, is not accounted for in the model at all? Would that simply be grouped together with the semi-refractory pool? Please clarify.

Thank you for pointing out. The nomenclature for DOC classification in the biogeochemical model ERSEM is derived from Hansell (2013). According to Hansell (2013), the lifetime of semi-refractory DOC is ~20 years, while the lifetime of refractory DOC is ~16,000 years. The biogeochemical model (ERSEM) used in this study only considers DOC with a maximum lifetime up to 70 years. This means that refractory DOC with turnover time scale >70 years is assumed to have the same turnover rate as the semi-refractory DOS in the budget calculation in our study. We believe that the potential error is minor and does not affect the overall ratio of source and sink terms in the budget analysis since our model simulation covers only a period of 5 years, which is much shorter than the turnover time of semi-refractory DOC. We will add more details regarding the DOC classification setup in the methods section. A justification as well as a discussion of the potential error in the model configuration for refractory DOC will also be provided.

It seems like the semi-refractory pool in the model is a closed loop and not connected to the semi-labile/labile pools of DOC, which the model in Figure 1 suggests are impacted mostly by phyto- and zoo-plankton. However, bacteria play a role in the conversion of labile to semi-labile DOC and semi-labile to semi-refractory (and so on). It also looks like from the arrows in the model setup in Figure 1 that bacteria are taking up non-photolabile DOC and converting it into the semi-refractory pool.

We will improve this figure to avoid this misunderstanding. Bacteria uptake all components of DOC, including T_1 , T_2 , R_1 , R_2 , and R_3 , with varying uptake rates for different pools (Table S1). The light blue box encompassing R_1 , R_2 , and R_3 was intended to indicate that bacteria uptake the entire marine DOC pool. According to the microbial carbon pump concept from Jiao (2010), bacteria convert bioavailable organic carbon into difficult-to-digest forms.

How does the model consider past work that DOM that has been photochemically altered can become more biologically labile? The authors mention something about this in the text (how aromatics are biologically resistant, but photochemically susceptible), but don't really go into detail, as far as I can tell. Photo-transformed, newly biologically labile DOM may also enhance bacterial productivity. Please at least discuss this in the paper (papers from Medeiros <https://doi.org/10.1002/2014GL062663>, Mopper, and Zhou may provide some insights) and relate to where this may fit into the model.

This is indeed a topic worth discussion. In our study, it was assumed that terrigenous DOM contains more aromatic compounds, leading to the component of T_1 (Figure 1) undergoing photochemical reactions in the surface water. The model does consider the case that DOC may become more biologically labile after photo-transformation. There is a portion of T_1 , after photolysis, transformed into the more microbially labile T_2 pool (Text S1). Nevertheless, this is still a simplification. We will add more discussions into the enhancement of DOC reactivity due to photo-transformation. The recommended papers will also be included in the discussion.

While I like Figures 4 and 5 a lot, I think an additional figure or subplot showing DOC vs. salinity and a conserved mixing line would be informative to this study to show where and when it diverges from mixing.

The figure will be improved by adopting the useful suggestion.

There could be additional discussion. I think there is a lot to be discussed relating the findings to past studies that look at priming of DOM (Bianchi work), and how DOM may be refractory in one location / time, but when transported to a different location / time / set of environmental conditions, it may be more labile (Shen & Benner, 2018, among others). A more detailed discussion of why in the winter DOC is conserved and in the summer it isn't would be valuable as well.

We will add discussion of our findings in relation to past studies on the priming of DOM. A more comprehensive analysis of these dynamics incorporating relevant literature will be added. Besides, we will incorporate a detailed discussion on the potential mechanisms driving this seasonal difference between summer and winter, considering factors such as temperature fluctuations, microbial and planktonic activity, and other hydrodynamic variables that may influence DOC transport.

The English is overall good but I noticed several typos.

Thank you for pointing out the typos. We have corrected them.

Specific comments:

Line 24: "non-living" organic matter. That's not necessarily true because DOC is between 0.2-0.77 microns and small bacteria can pass through 0.77 microns (so their biomass would technically be a part of the DOC pool).

Indeed, we will refine this sentence to make the definition more precise.

Line 31: Marine DOC is not mainly derived from local production. At the surface ocean, maybe 30-50% of it is autochthonous; the other >50% is refractory and allochthonous.

The original statement was used to emphasize that DOC produced by marine phytoplankton undergoes rapid biodegradation. We agree with the reviewer and will revise this statement to avoid such misunderstanding.

Line 58: Anthropogenic activities are mentioned here as being a part of the study but then aren't referred to again.

Since our study focuses on the source-to-sink pathways of terrigenous and marine DOC in the estuary, the direct impact of anthropogenic activities is beyond the scope of this study, and we will remove this term.

Line 91- why would aromatic compounds precipitating with metal ions have anything to do with photo-oxidation? That line comes out of place.

We will remove this statement to avoid confusion.

Lines 93-95: I understand for simplicity sake to keep the model as two types of DOC, but recent studies have shown that DOC that is photodegraded can become more biologically labile. So does then this photodegraded DOC move into the other pool of DOC? (see major comment above)

Based on the work from Medeiros et al. (2015) and Mopper et al. (1991), deep-sea DOM undergoes photochemical alteration when brought to the surface water. While DOC in the deep ocean primarily consists of biologically resistant compounds, it can become biologically reactive when exposed to sunlight. Additionally, Fichot and Benner (2014) mentioned that photodegradation might not directly mineralize dissolved lignin but rather break it down into smaller molecules that are more readily consumed by organisms. In experiments conducted in the Satilla Estuary, where DOC was exposed to simulated sunlight, it was observed that light increased the biodegradation rate. The sensitivity of DOC to biodegradation increased with the extent of photobleaching (Moran et al., 2000). These studies indicate that photodegradation of DOC facilitates its subsequent biodegradation. In the model, a portion of the T1 would transition into T2 after photolysis, which is more easily degraded by bacteria. We have addressed the question in our previous response to the major comment, and will add more detailed discussions in the manuscript.

Figure 2b. The sampling points are very difficult to see on top of the bathymetry background (those points for 2006 are virtually impossible to distinguish). I suggest changing the way the points look (maybe filling in the color, increasing the contrast).

This figure will be improved by highlighting the points.

Line 143: "757 data points are for the bottom water" – What is the depth range of this bottom water?

The bottom water corresponds to a location 2-5 meters above the local seabed at which each observation is taken. In our study area, the depth of the bottom water layer ranges from 5 m inside the river to 90 m on the mid-shelf. This information will be added in the revised version.

Line 175: “significant contract” – is it statistical? If not please avoid using that term. Also, this is referring to DOC, right?

We will revise this expression and refer to DOC.

Lines 239-240 : Please re-orient the reader to Figure 1 when discussing phyto-/zooplankton and bacteria.

Thanks, we will refer to Figure 1.

Line 280: Rates are reduced in winter. Makes sense. Please tie together biogeochemically / seasonally better why in the winter it’s mostly just physical processes, whereas in the summer there are biogeochemical influences.

The metabolic activities of bacteria and plankton are regulated by temperature and nutrient availability, while phytoplankton are influenced by temperature and light limitation. Additionally, seasonal differences in river discharge between summer and winter play a role. These factors jointly contribute to the rate difference. We will elaborate on this seasonal difference to gain a deeper understanding of this pattern in a revised manuscript.

References used in our response

- Fichot, C. G., & Benner, R. (2014). The fate of terrigenous dissolved organic carbon in a river-influenced ocean margin. *Global Biogeochemical Cycles*, 28(3), 300-318. <https://doi.org/10.1002/2013gb004670>.
- Hansell, D. A. (2013). Recalcitrant Dissolved Organic Carbon Fractions. In C. A. Carlson & S. J. Giovannoni (Eds.), *Annual Review of Marine Science, Vol 5* (Vol. 5, pp. 421-445). <https://doi.org/10.1146/annurev-marine-120710-100757>
- Medeiros, P. M., Seidel, M., Powers, L. C., Dittmar, T., Hansell, D. A., & Miller, W. L. (2015). Dissolved organic matter composition and photochemical transformations in the northern North Pacific Ocean. *Geophysical Research Letters*, 42(3), 863-870. <https://doi.org/10.1002/2014gl062663>.
- Mopper, K., Zhou, X., Kieber, R., Kieber, D., Sikorski, R., & Jones, R. (1991). Photochemical degradation of dissolved organic carbon and its impact on the oceanic carbon cycle. *Nature*, 353, 60-62. <https://doi.org/10.1038/353060a0>.
- Moran, M. A., Sheldon Jr, W. M., & Zepp, R. G. (2000). Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter. *Limnology and Oceanography*, 45(6), 1254-1264. <https://doi.org/10.4319/lo.2000.45.6.1254>.