Response to Referees

Dear editor,

We are submitting a revised version of our manuscript entitled "Source-to-Sink Pathways of Dissolved Organic Carbon in the River-Estuary-Ocean Continuum: A Modeling Investigation". Based on the comments and suggestions provided by the anonymous reviewers of our work, we have made corresponding modifications to the manuscript.

We appreciate the valuable feedback from the reviewers and the editor, which has helped us improve our paper. Our detailed responses to the comments are listed below.

Referee #1 (Responses in *italics*, changes in manuscript in *red*)

General comment

This manuscript aims at applying a model that describes dissolved organic carbon dynamics at the Changjiang Estuary, in order to identify the different processes affecting DOC dynamics in this particular site.

In general the manuscript is well written and easy to follow in all its parts. Although I am not an expert on modeling, I was able to follow the description and the application of the model that the authors used. I cannot comment on the specifics on the model used, as I am not an expert in this field, but it was clear enough that the model was properly validated by observational data over a large time scale.

In my opinion however, the authors need to work on the discussion part of the manuscript to highlight the importance of this study. Some important questions need to be answered, such as: why is this model important? what new information it gives that improves the knowledge on this region? how these results/model can be of use in other regions?

The discussion needs therefore to be re written taking these questions in mind. In the current form the discussion contains mostly a literature review on previous studies, not properly compared to the results of this study.

Also the introduction strongly needs a revision in order to have an updated bibliography. There are too many outdated references, sometimes as the only ones, that can be updated with much more recent studies.

Many thanks to the reviewer for the helpful suggestions.

We expanded the discussion section to highlight the significance of our study. We emphasized that our model study distinguishes between terrigenous and marine sources of DOC in the *river-estuary-ocean continuum. By quantifying the contributions of different source and sink processes, and integrating results from other studies, we highlighted the importance and discussed the implications of our work. In addition, we improved the Introduction by referring more recent studies.*

Added to 4.1 (lines 320-327): "Our study employed a physics-biogeochemistry coupled model to investigate the transport and transformation of DOC in the Changjiang Estuary. Although previous studies have included simulations of DOC in estuaries (Anderson et al., 2019; Clark et al., 2022; Druon et al., 2010), they have not explicitly addressed the transport and transformation based on different source-to-sink pathways of terrigenous and marine DOC within a three-dimensional model of the river-estuary-ocean continuum. Our results reveal variations in the rates of distinct processes and their contribution proportions in the Changjiang Estuary, not only as an important transport route for export of terrigenous DOC to open ocean but also as a reactor for biogeochemical cycling of DOC from both terrigenous and marine origins."

(lines 351-356): "Our study distinguished between terrigenous and marine components of DOC and applied them to a three-dimensional hydrodynamic-biological model to evaluate the transport and transformation of DOC in the river-estuary-ocean continuum. Our results emphasize that terrestrial DOC undergoes photodegradation and microbial decomposition, with up to 60% of the riverine input being consumed before reaching the ocean, which resulting in the transition of DOC from terrigenous-source dominant to marine-source dominant in the plume area. In contrast, mDOC makes a larger contribution to export, especially from phytoplankton production."

Specific comments

Line 15: salinity has no units. To be checked throughout the entire manuscript.

Thank you. The units of salinity have been included in the line 15 as indicated in the original submission. Also, we checked throughout the manuscript.

Lines 23-24: "DOC is defined as the nonliving organic matter in the ocean that can pass a 0.5µm pore size filter…". This definition is not correct. DOC is operationally defined as the organic carbon that passes through a 0.2 µm pore size filter. Sometimes also 0.77 µm pore size filter is used. Also the references here needs to be adjourned.

Rephrased (lines 23-25): "DOC is typically defined as the fraction of organic carbon in the ocean that can pass a pore size filter ranging from 0.2-0.77µm, with decomposition time scales varying from hours to years (Asmala et al., 2014; Carlson and Hansell, 2015; He et al., 2016)."

Lines 27-28: "DOC in estuaries is predominantly derived from river inputs and marine production". In situ production processes should be mentioned too here. Also because they are mentioned later in the manuscript.

Rephrased (lines 27-28): "DOC in estuaries is predominantly derived from river inputs and marine in situ production"

Line 78: SPM needs to be defined.

Added (line 76): "FVCOM encompasses a sediment transport model to simulate sediment and suspended particulate matter (SPM) dynamics."

Lined 89-92: Here the authors introduce DOM, however in the manuscript only DOC is discussed. Either the authors mention only DOC or it should be clarified the link between DOC and DOM.

Added (line 87): "DOC represents the carbon fraction within dissolved organic matter (DOM) (Hopkinson and Vallino, 2005)."

Line 96: Why the turnover time scales taken into account are limited to 70 years. Refractory DOC has a turnover time that is much larger than 70 years. For turnover time of DOC see Hansell, 2013 (https://doi.org/10.1146/annurev-marine-120710-100757).

Following classification and nomenclature of DOC by Hansell (2013), 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 DOC 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.

Added (lines 100-102): "This classification is determined by considering degradation timescales and production mechanisms. Based on the nomenclature by Hansell (2013), the existing biological model does not account for the century-scale lifespan of refractory DOC (Butenschön et al., 2016; Polimene et al., 2007). Given that our simulation period ranges for five years, this simplification is considered reasonable."

Line 145: Table 1. Some data miss the data source. Where are these data coming from?

The missing source in the table was due to data from different time periods being derived from the same reference, hence the cells in the table were merged.

The Table 1 has been added separating line to distinguish data from different references.

Line 159: Reference to figure S1. There should be also figure S2. These two figures are useful to understand the comparison between the observational data and the model data. However being two different figures and being the images (surface/bottom, summer/winter) displaced in a different order a comparison is difficult to make. I would suggest to merge these two figure together and displace the observational/modeled data next to each other.

By looking at these figures, I think it would be interesting to also highlight where there is least correspondence between the observations and the model and discuss that too.

Figure S1 and S2 have been merged and rearranged.

The least correspondence between the observations and the model has been added to 4.4 (lines 427-432): "Additionally, the DOC in model exhibits limitations in effectively capturing the north-eastward expansion of DOC during the summer (Fig. S1). This inconsistency may be attributed to the uncertainties in both measurement and modeling, including the uncertainty in sampling time, as most of the sampling data only covered a few days within a month. Additionally, there were variations in the locations where data was collected, with some points having more data collected than others, and there was limited availability of collected data. Nevertheless, a general agreement in the DOC concentration between model and observational data is shown."

Lines 167-168: "the seasonal average of the model results over the years 2013-2017 was calculated for all four seasons". Why only summer and winter were chosen?

The focus on summer and winter in our interpretation is primarily due to the following reasons:

Most observational data (Table 1) were collected during summer and winter, allowing for a corresponding and extended analysis and discussion based on the observational studies.

Additionally, these two seasons exhibit significant and representative differences in hydrological and ecological characteristics. Summer is marked by the flood season of the Changjiang Estuary, whereas winter is the dry season. The prevailing wind directions also differ between these seasons, leading to notable variations in hydrodynamics. Moreover, the higher temperature, strong stratification and abundant nutrients in summer enhance ecosystem activity and primary productivity, while the colder temperatures and stronger vertical mixing in winter reduce ecological activity. These factors directly impact the DOC cycling in the estuary. Therefore, discussing the source-to-sink pathways of DOC in terms of summer and winter makes the study more representative and concise. The other two seasons, namely spring and autumn, act as transition periods between the two distinct regimes in terms of hydrological and ecological characteristics and therefore not the focus in the main text descriptions.

Explanation was added to 4.3 (lines 388-390): "The hydrodynamic and ecological environments of the Changjiang Estuary exhibit representative characteristics in both summer and winter. Moreover, most observational voyages are concentrated in these two seasons. Therefore, our study focuses on the distributions and source-sink patterns of DOC during summer and winter."

Line 181: In the caption of Figure 4 there is no details on the 6 panels. Also it is not specified if these plots are from observational or model data.

Thanks for pointing this out.

The caption of Figure 4 has been added (lines 183-184).

Line 242: “The released mDOC from bacteria is converted into semi-refractory mDOC”. This statement needs to be supported by a reference.

The explanations with reference have been added (lines 244-247): “The ecosystem model ERSEM includes the bacteria-mediated production of recalcitrant DOC (Hansell, 2013), which represents the most difficult-to-digest semi-refractory DOC in the model. Therefore, the newly produced mDOC from bacteria is added to the pool of semi-refractory mDOC, thereby an implementation of microbial carbon pump (Jiao and Azam, 2011; Jiao et al., 2014).”

Line 250: Figure 5 is difficult to read, especially the dotted lines, which are too similar as color and too thin

The Figure 5 has been updated with new colours and a bolder dotted line.

Referee #2 (Responses in *italics*, changes in manuscript in *red*)

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.

Explanation added to 2.2 (lines 100-102): "This classification is determined by considering degradation timescales and production mechanisms. Based on the nomenclature by Hansell (2013), the existing biological model does not account for the century-scale lifespan of refractory DOC (Butenschön et al., 2016; Polimene et al., 2007). Given that our simulation period ranges for five years, this simplification is considered reasonable."

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.

Bacteria uptake all components of DOC, including T_1 (photolabile tDOC), T_2 (non-photolabile tDOC), R_1(labile mDOC), R_2 (semi-labile mDOC), and R_3 (semi-refractory mDOC), 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.

Figure 1 has been changed to indicate that bacteria uptake all components of DOC.

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 added discussions into the enhancement of DOC reactivity due to photo-transformation. The recommended papers were also included in the discussion.*

Added to 4.2 (lines 357-369):" 4.2 Factors influencing DOC lability

In our study, it was considered that terrigenous DOM contains more aromatic compounds, leading to the component of T1 undergoing photochemical reactions at the surface layer. In actual experiments and observations, DOC exposed to sunlight undergoes a certain degree of photo-transformation and becomes more biologically labile. The model considers that a portion of T1, after photolysis, transitions into the more microbially labile T2 pool (Text S1). However, this consideration remains somewhat simplified, as some studies have reported the complexity of DOC reactivity during photo-transformation (Medeiros et al., 2015a; Aarnos et al., 2018). Experimental evidence indicates that photodegradation can significantly impact subsequent biodegradation by producing biologically labile substrates (Benner and Kaiser, 2011; Mopper and Kieber, 2002). The photo-transformed, biologically labile DOM components may enhance bacterial productivity, as indicated by the increase in unsaturated aliphatic observed in near-surface waters (Medeiros et al., 2015a). Sunlight could significantly impact the biodegradation of DOM in streams, particularly semi-labile DOM, indicating that sunlight not only alters the chemical structure of DOM but also changes its susceptibility to microbial degradation (Bowen et al., 2020). These findings indicate that photodegradation and biodegradation processes can mutually influence each other."

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.

Figure 10 has been added to 4.3.

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 expanded the discussion of our findings in relation to past studies on the priming of DOM.

Added to 4.2 (lines 370-386): "In addition to photodegradation increasing the biological lability of DOC, the priming effect also influences DOC transport from rivers to the ocean. This effect occurs when labile organic matter interacts with stable organic matter, altering the mineralization rate of the latter (Bianchi, 2011; Sanches et al., 2021). The priming effect may likewise be induced by bacteria and archaea, utilizing various pools of organic carbon (Kirchman et al., 2007). The addition of algal DOC or trehalose in laboratory microcosm *experiments has demonstrated that the priming effect significantly enhances the remineralization rate of tDOC (Bianchi et al., 2015). A substantial positive priming effect (15%–34% of initial stable DOM) occurred exclusively with the presence of mixed labile DOM (glucose and amino acids) or complex labile DOM (disaccharide) in incubation experiments, which is temporary and lasting for around two weeks (Laffet et al., 2023). Labile organic matter enhances microbial metabolism and enzyme production, thereby altering the mineralization of refractory DOC (Guenet et al., 2010). Besides the influence of labile DOC addition on the lability of refractory DOC, the impact of other environmental factors has also drawn attention. For example, the existence of sediments in the incubation did not increase the priming effect (Laffet et al., 2023). In a 346-day incubation experiment where the native microbial assemblage of the Atlantic was replaced with a coastal microbial assemblage, it was found that coastal microbes consumed 2.3-8.7% of the refractory DOC (Shen and Benner, 2018), indicating different microbial communities have varying effects on refractory DOC (Carlson et al., 2004). Additionally, other research indicates that microbes can degrade more refractory compounds, which exhibit higher temperature sensitivity (Lønborg et al., 2018). These studies indicate that the reactivity of DOC is influenced by various factors, leaving substantial scope for further theoretical and experimental and modeling research."*

Besides, we incorporated a detailed discussion on the potential mechanisms driving this seasonal difference between summer and winter.

Added to 4.3 (lines 387-410): "4.3 Distribution pattern of DOC between summer and winter

The hydrodynamic and ecological environments of the Changjiang Estuary exhibit representative characteristics in both summer and winter. Moreover, most observational voyages are concentrated in these two seasons. Therefore, our study focuses on the distributions and source-sink patterns of DOC during summer and winter. The average concentration of DOC in summer and winter across the salinity gradient (Fig. 10) indicates that DOC concentration gradually decreases from freshwater to saltwater. DOC in winter exhibits more conservative mixing at low- and mid-salinity compared to summer. Near the plume region, the influence of the DOC source becomes significant. The change in the slope of the curve is more pronounced in the summer, indicating that the source-sink variations are more pronounced in summer compared to winter. This seasonal variation is closely linked to the hydrological environment and biological activities in the estuary. In the summer, the mixing in the Changjiang Estuary is relatively weaker compared to winter, resulting in a deeper euphotic zone that benefits the primary production activities of phytoplankton (Zhu et al., 2009). Chlorophyll-a concentrations are higher in summer than in winter, which depends on temperature and nutrient levels, with higher river discharge in summer (Yang et al., 2014; Liu et al., 2016). In the ECS, it was observed that the growth rates of phytoplankton correlate positively with surface water temperature. Microzooplankton grazing effectively regulated primary production in summer, whereas grazing activity was minimal in winter due to the colder temperature (Zheng et al., 2015). Simultaneously, the seasonal pattern of planktonic bacterial productivity is similar to that of water temperature, resulting in higher rates during the summer (Peierls and Paerl, 2010). Research indicates that higher inflow with more DOC *loading would stimulate heterotrophic bacterioplankton production in the upper estuary (Hitchcock et al., 2010; Letourneau and Medeiros, 2019). Bacterial respiration and production are intimately connected to DOC originating from plankton. In summer, peak rates are frequently observed at mid-salinity levels in waters with elevated carbohydrate concentrations (Benner and Opsahl, 2001; Kinsey et al., 2018). The observed increase in DOC around the edge of plume area, which is more pronounced in summer than in winter, is consistent with previous research findings (Song et al., 2017; Shen et al., 2016; Guo et al., 2021). Our results further explain the transport variations of tDOC from river inputs and mDOC within the estuary, as well as quantify the contributions of phytoplankton, zooplankton, and bacteria to estuarine DOC."*

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).

Rephrased (lines 23-25): "DOC is typically defined as the fraction of organic carbon in the ocean that can pass a pore size filter ranging from 0.2-0.77μm, with decomposition time scales varying from hours to years (Asmala et al., 2014; Carlson and Hansell, 2015; He et al., 2016)."

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 revised this statement to avoid such misunderstanding.

Revised (line 31): "while marine DOC (mDOC) derived from fresh marine plankton production, tends to be consumed biochemically."

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 have removed this term.

Revised (line 57): "In this highly dynamic estuary, terrigenous input, and the functioning of the coastal ecosystem jointly control the cycling of DOC."

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

We removed 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.

Revisions and discussions have been made in accordance with the previous comments (see above for changes).

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 contract).

Figure 2 has been changed by filling the data 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 added in the revised version.

Added (line 143): “In this compiled dataset, 869 data points are for the surface water, and 757 data points are for the bottom water which corresponds to a location 2-5 meters above the local seabed.”

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

We revised this expression and referred to DOC.

Revised (line 176): "there is a more distinct difference of DOC between the surface and bottom layer."

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

Added (line 242).

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 elaboration of this seasonal difference has been added in the discussion 4.3 (see changes above).