Dear editors and reviewers,

Thank you for the reviewers' and editor's useful comments and suggestions on our manuscript (Manuscript Number: egusphere-2025-2429). The manuscript has been carefully revised according to the reviewers' comments and suggestions. Attached please find an itemized response to reviewers' comments and suggestions in which we have addressed each of the reviewer's concerns (**blue words**).

Reviewer 1:

The manuscript presents novel and valuable data on CO concentrations across an extensive coastal zone, offering a relevant contrast between coastal and open ocean environments. These results are original and, in my opinion, worthy of publication. However, in its current form, the manuscript does not fully reach its potential. One of the main issues is that the paper seems to follow two parallel storylines: the in-situ measurements and the incubation experiments. While these approaches can certainly complement each other, they are not currently well integrated. I recommend either working more carefully to tie these two parts together into a cohesive narrative or considering separating them into two independent manuscripts.

Additionally, critical methodological details are missing, particularly regarding the photoexposure experiments. The description lacks enough clarity to allow reproducibility. For instance, key information about the use of triplicates and the overall study design is absent and should be explicitly detailed.

Thanks for the reviewer's suggestions. We have accepted the reviewer's suggestions

that some methodological details were explained more clearly in the revised manuscript.

The Introduction section would benefit from restructuring. It currently consists of three lengthy paragraphs, each containing multiple ideas, which makes it hard to follow. I suggest breaking it into shorter, more focused paragraphs (ideally 100–200 words each), each addressing a single point.

Thanks for the reviewer's suggestions. We have accepted the reviewer's suggestions, and the introduction has been restructured.

"Carbon monoxide (CO) is an indirect greenhouse gas, and it plays an important role in atmospheric chemistry (Nguyen et al., 2020). It is the predominant sink of hydroxyl radical (OH•, Conte et al., 2019; Cordero et al., 2019), which oxidizes pollutants and greenhouse gases (such as CH_4) emitted to the atmosphere by human activities (Nguyen et al., 2020). The photodegradation of dissolved organic matter (DOM) is thought to be the main source of CO in the ocean (Stubbins et al., 2006), and the ocean acts as a source of atmospheric CO (Mopper and Kieber, 2002). In addition, direct production of CO by phytoplankton has been observed in laboratory experiments (Troxler et al., 1972; Gros et al., 2009) and dark/thermal production was also inferred from modeling at Bermuda Atlantic Time Series (BATS, Kettle, 2005), and from incubations of water samples from the Delaware Bay (Xie et al., 2005) and St Lawrence estuary (Zhang et al., 2008). Microbial consumption and the sea-to-air fluxes (Doney et al., 1995; Song et al., 2015) of CO are considered to be the main sinks of oceanic CO (Zafiriou et al., 2003). The average annual sea-to-air flux accounted for 10% of the

global CO sinks estimated by Zafiriou et al. (2003), Conte et al. (2019) and Yang et al. (2024). In the ocean, CO acts as a microbial energy source that supports food webs, a link in carbon cycling that connects surface and deep waters, and a modulator of oxygen cycles. With increasing concern about atmospheric pollution and the potential role of CO, a primary goal of studying oceanic CO concentrations is to evaluate its long-term stability and distribution trends in the marine boundary layer (Conte et al., 2019; Xu et al., 2023), where the ocean and atmosphere exchange momentum, heat, moisture, and gases.

The ocean surface layer plays a vital role in climate change through the sea-to-air exchange of greenhouse gases. The sea-surface microlayer (SML) is located at the sea-to-air interface and is considered to play a critical role in global biogeochemical cycles and climate change by regulating the sea-to-air exchange of gases and aerosol particles (Liss and Duce, 1997; Cunliffe et al., 2013). In addition, SML is exposed to the most intense solar radiation of any seawater layer, especially ultraviolet (UV) light, and shows significantly higher colored dissolved organic matter (CDOM) concentration and microbial abundances compared to the subsurface layer (SSW, Obernosterer et al., 2006; Obernosterer et al., 2008; Wurl et al., 2009; Yang et al., 2022). For decades, articles have emphasized the presence and enrichment of organic matter and gases (CO and DMS) in the SML (Liss and Duce, 1997; Orellana et al., 2011; Ma and Yang, 2023; Sugai et al., 2020), but it remains unclear how this is maintained whilst CO is lost to the atmosphere.

Generally, the sea-to-air flux is estimated from CO concentration in sea surface

waters (2 to 10 m), but there is evidence that biogeochemical processes within the SML may also affect the CO flux (Sugai et al., 2020). CDOM and surfactant enrichment in the SML relative to the SSW has been reported, with an enrichment factor (EF) range of 0.4 to 6.7 (Huang et al., 2015; Shaharom et al., 2018; Yang et al., 2022), and mediates all mass transfer across the SML (Rickard et al., 2019 and 2022). Although intense solar radiation and enrichment of DOM may promote CO photoproduction involving SML (Cunliffe et al., 2013; Pereira et al., 2018; Sugai et al., 2021), and likely modify sea-to-air gas transfer velocity (k_w) of CO and other gases (Pereira et al., 2018). The role and response of the SML, along with the complex interplay of biological, geochemical, and physical processes, govern the transfer of CO from the SSW, where it can either be consumed by bacteria or released into the atmosphere. Our study hypothesized that SML-specific environmental changes (i.e., enrichment processes and biogeochemical processes) and the abundance and composition of DOM in the eastern marginal seas of China influence the rate of sea-to-air CO exchange, and they contribute to the formation of the marine boundary layer involved in atmospheric chemistry and climate regulation."(Line 46-96)

Several other aspects require clarification:

The sampling was conducted during winter only, so some discussion on seasonal effects would be relevant.

"$[CO]_{SSW}$ showed great seasonal and diel variability, as well as variability between ocean regions. $[CO]_{SSW}$ mean value in the YS in January 2020 (1.23 ± 0.40 nmol L^{-1}) was higher than in September 2010 (1.05 nmol L^{-1}, Zhao et al., 2015). $[CO]_{SSW}$ mean

value in the ECS during winter (1.23 ± 0.45 nmol L^{-1}) was also higher than in October 2021 (0.97 ± 0.86 nmol L^{-1}, Yang et al., 2024). Globally, $[CO]_{SSW}$ mean value (1.23 nmol L^{-1}) in the eastern marginal seas of China was similar to that observed in the Bohai Sea and the YS during autumn (Zhang et al., 2019, 1.22 nmol L^{-1}) and the Arctic waters of the Amundsen Gulf (Beaufort Sea) in September/October (Xie et al., 2009, 0.17–1.34 nmol L^{-1}), but was relatively lower than the Eastern Indian Ocean (Xu et al., 2023, 1.92 nmol L^{-1}).” (Line 431-440)

Day and night samples were taken, but no information about them is provided in the figures. This analysis is also very relevant: were they treated separately, and could the differences be discussed?

“The EF of CO in the daytime (mean value: 1.5 ± 0.8, 7:00-19:00) was 1.6 times higher than that in the nighttime (mean value: 0.9 ± 0.3, 19:00-7:00) (Fig. 3b)). The EF of CDOM in the daytime (mean value: 2.3 ± 11.4) was 1.1 times higher than that in the nighttime (mean value: 2.1 ± 0.9) (Fig. 3b)). In addition, $[CO]_{SSW}$ in the daytime (mean value: 1.39 ± 0.47 nmol L^{-1}) was 1.3 times higher than that in the nighttime (mean value: 1.05 ± 0.22 nmol L^{-1}) and $[CO]_{SML}$ in the daytime (mean value: 1.88 ± 0.77 nmol L^{-1}) was 2.0 times higher than that in the nighttime (mean value: 0.95 ± 0.29 nmol L^{-1}), likely due to CO photoproduction in the daytime.” (Line 349-355)

“The higher EF values of CO also occurred in the daytime, suggesting that sufficient light and higher temperatures combined to facilitate the photoproduction of CO and its enrichment in the SML.” (Line 460-462)

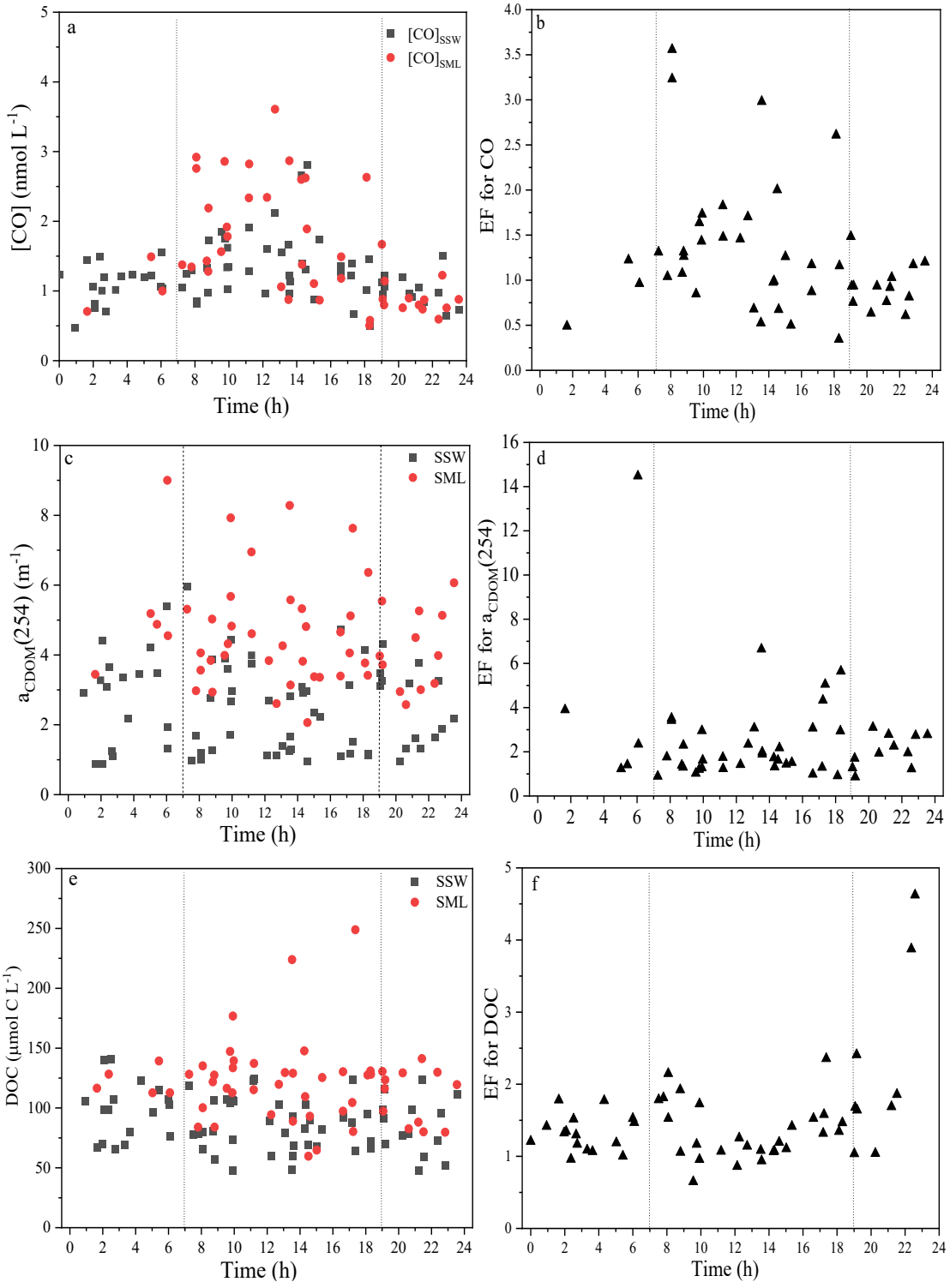

Fig. 3. Variations in the $[CO]_{SML}$, $[CO]_{SSW}$, $a_{CDOM}(254)$, and DOC, EFs of [CO], $a_{CDOM}(254)$, and DOC with the sampling time at each station (Daytime: 7:00 -19:00; Nighttime: 19:00 – 7:00).

There is also a misalignment between the aims and hypotheses stated in the Introduction and the Conclusions. For example, while the Discussion emphasizes the coastal-to-

open-ocean contrast, this topic is not introduced at the beginning. Likewise, the Results and Discussion sections should be better aligned with both the stated aims and the conclusions.

Although I have not marked individual grammar or typographical errors, I recommend that the manuscript be reviewed by a native English speaker or a professional proofreader before publication. I have attached a PDF version of the manuscript with detailed comments throughout, except for the Results and Discussion sections, which I will be happy to read more closely and assess in detail in the revised version.

In summary, the study has strong potential, and the data are of interest to the community. However, a significant revision is necessary to improve the manuscript's clarity, structure, and internal coherence before it can be considered for publication.

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript. In addition, our manuscript has been edited by a native English speaker for English language.

Our study hypothesized that SML-specific environmental changes (i.e., enrichment processes and biogeochemical processes) and the abundance and composition of DOM in the eastern marginal seas of China influence the rate of sea-to-air CO exchange, and they contribute to the formation of the marine boundary layer involved in atmospheric chemistry and climate regulation.

In our manuscript, we observed that significant CDOM accumulation and the production rates of CO in the SML significantly exceed the loss rates, which could

contribute to the significant accumulation of CO in the SML, especially in the daytime in the eastern marginal seas of China.

Reviewer 2:

General comments

The authors presented a dataset composed of CO concentrations, CO air-sea fluxes, CO production (photochemical and dark) rates, bacterial CO consumption rates, and DOM (DOC, CDOM, and FDOM) in the surface microlayer (SML) and the underlying bulk seawater (termed as subsurface water, SSW, by the authors) in the East China Sea and the Yellow Sea. Major findings include 1) the SML samples exhibited higher CO and DOM levels and higher CO photoproduction and bacterial consumption rates compared to the underlying seawater samples, and 2) the CO sea-to-air flux was negatively correlated to the CDOM absorption coefficient at 254 nm and the fluorescence intensity of the marine humic-like FDOM component. The authors concluded that while enrichment of DOM in the SML promotes CO photoproduction, the higher levels of DOM also serve as a barrier for air-sea exchange, thereby leading to a reduced CO emission to the atmosphere. After a thorough review, I found that the manuscript suffers major weaknesses and is not suitable for publication.

Dear Review,

For the continuous air-sea exchange to occur, CO must necessarily pass in and out through the sea-surface microlayer (SML), which is considered a special carbon milieu and covers the oceans' surface. Historically, the combination of CO and DOM concentrations, usually measured at 3 m depths, has been used to describe seawater´s sea-to-air system and to estimate the CO fluxes happening on the surface. Therefore, further studies should

investigate CO dynamics in the SML of various oceanic areas to accurately calculate global flux and analyze the efficiency of CO photoproduction and the consumption rate of CO in the SML to better understand CO production and consumption there, respectively. The production and consumption of CO in the SML and its sea-air emission were investigated by Sugai et al. (2020) in the coastal waters of the Sagami Bay, Japan. It is also important to measure and evaluate the influence of DOM on the flux of several gases between the sea and the atmosphere within the SML. The lack of consideration will lead to under- or over-estimation of CO fluxes where the concentration of OM is high enough to impact these fluxes.

The primary motivation of this manuscript is to assess the role of the DOM in the SML as a key component influencing the sea-to-air CO fluxes. We conducted ship-based incubation experiments in the East China Sea and the Yellow Sea to explore how CDOM photochemistry and microbial consumption processes impact CO concentration in the SSW and the SML. The results lead to a better understanding of how the SML plays a role in CO fluxes in the ocean. Our results demonstrate that DOM was more strongly enriched in the SML than CO, and elevated DOM could stimulate the photoproduction of CO, but may also decrease sea-to-air CO exchange in the SML.

Greenhouse gas measurements in the SML were direct study challenge to marine research. Therefore, we did lots of in situ investigations and incubation experiments to investigate CO accumulation and sea-to-air flux in the SML. Further, one note of the study of gases in the SML is that gases supersaturated with respect to their atmospheric

concentrations, including CO, are inevitably lost from SML samples during sampling, depending on environmental conditions such as water temperature and wind. For example, in case of dimethylsulfide (DMS), a volatile gas with large concentration difference between the atmosphere and the ocean, Yang et al. (2001) and Yang and Tsunogai (2005) showed about 50–70% and 60% (mean) of loss from SML samples collected using a mesh screen at 0–15°C and at a water temperature of 10°C and wind speed of 4 m s^{-1}, respectively. We agree that a mesh screen was also used in this study, and parameters such as $[CO]_{SML}$ and the EF of CO may have been underestimated.

My first and most serious concern for this study relates to the reliability of the Garrett screen sampler for collecting SML samples for measuring in situ CO concentrations and the production and consumption rates of CO. CO is a sparingly soluble gas and its concentrations at the water-air interface, when at non-equilibrium between the water and air phases, are sensitive to the disturbance of the SML. Sampling the SML with a Garrett screen sampler (or other types of SML samplers currently available) inevitably disrupts the integrity of the SML with respect to air-water exchange of sparingly soluble gases such as CO, thereby altering the gases' concentrations in the SML. As CO is mostly supersaturated in surface waters, the disturbance caused by the Garrett sampler would reduce the CO concentrations in the collected SML samples. Moreover, the Garrett screen sampler is usually made of stainless steel, which may contaminate the SML samples with a bunch of metals (e.g., Fe, Cu, Mn, Cr, etc.) that participate in DOM photochemistry (e.g., Fe is well known for its ability to enhance CO photoproduction from CDOM) and/or

promote (e.g., Fe) or inhibit (e.g., Cr) bacterial growth. The quality of the core data (in situ concentrations, photoproduction rates, and bacterial consumption rates of CO in the SML, and CO air-sea fluxes) reported by the authors is thus questionable. A rigorous assessment of the suitability of the Garrett screen sampler (and other types of SML samplers) for the related measurements is required prior to adopting this sampling method for research purposes.

Thanks for the reviewer's suggestions. The details of the study area and the CO samplings of the SML were also described by Sugai et al. (2016, 2018, 2021) and Xu et al. (2025). We agree that other type of SML samplers for the related measurements is required for research purposes, and we eventually chose the screen method in order to save time.

SML samples were collected from the bow of the research vessel (12 m long) on the leeward side, using a mesh screen sampler to collect microorganisms within a wide range of sizes and obtain a large number of samples over a relatively short period (Garrett 1965, Agogué et al. 2004, Momzikoff et al. 2004). Nylon mesh (mesh size: 1.25 mm; nylon diameter: 0.43 mm) was stretched over a 60 × 80 cm plastic frame. The screen was lowered vertically through the ocean surface 1.5 to 2 m away from the research vessel to minimize the disruption of the natural SML near the hull, raised horizontally through the ocean surface, and tilted to drain the SML sample into 2 l polypropylene bottles. Approximately the first 100 ml of seawater draining from the screen was discarded to prevent the inclusion of seawater adhering to the frame (Obernosterer et al. 2005). To collect a 2 l SML sample, about 20 successive dips were conducted within 1.5 h. The thickness of the collected SML was calculated to be 380 ± 9 µm following Cunliffe & Wurl (2014). SSW samples were collected at 0.5 m depth using a horizontal Niskin bottle. Seawater samples except for the analysis of TEPs were pre-filtered through 180 µm nylon mesh to remove large plankton and debris.

(Sugai et al., 2018)

Sugai, Y., Tsuchiya, K., Shimode, S., Toda, T., 2021. Photochemical Production and Biological Consumption of CO in the SML of Temperate Coastal Waters and Their Implications for Air-Sea CO Exchange. J. Geophys. Res.: Oceans 125(4), 1–14. doi: 10.1029/2019JC015505

Xu, G. B., Yan, S.B., Wang, J., Xu, F., Ji, X., Ni, J., et al., 2025. Carbon monoxide cycling in the marginal sea: a case of the Yellow Sea and the East China Sea. Marine Environmental Research 210. doi: 10.1016/j.marenvres.2025.107328

"Further, one note of the study of gases in the SML is that gases supersaturated with respect to their atmospheric concentrations, including CO, are inevitably lost from SML samples during sampling, depending on environmental conditions such as water temperature and wind. For example, in case of dimethylsulfide (DMS), a volatile gas

with large concentration difference between the atmosphere and the ocean, Yang et al. (2001) and Yang and Tsunogai (2005) showed about 50–70% and 60% (mean) of loss from SML samples collected using a mesh screen at 0–15°C and at a water temperature of 10°C and wind speed of 4 m s^{-1}, respectively. A mesh screen was also used in this study, and parameters such as $[CO]_{SML}$ and the EF of CO may have been underestimated." (Line 476-485)

Second, the discussion and interpretation of the data are overall superficial and at times vague, imprecise, inaccurate, or even self-contradictory. Here are a few examples: 1) While the Abstract and Conclusions convey the message that CO and CDOM were enriched in the SML relative to the SSW, the Results clearly states that there are no significant differences in CDOM and CO between the SML and SSW (L341-342; L347-350).

Our data indicated that no significant difference was observed between $a_{CDOM}(254)$ in the SML and SSW; no significant difference was observed between [CO] in the SML and the SSW.

No significant difference means that, based on the data from our samples, the observed difference between these two group means is small enough. The absorption of CDOM and the fluorescence intensity of FDOM components in the SML were positively correlated with their respective SSW values (Fig. S2).

Such self-contradictions undermine the credibility of the paper and may lead to the reader taking wrong messages from this study since many, if not most, readers only read the

abstract and/or the conclusions of a paper; 2) In the Abstract, based on the negative correlation of the CO flux with the CDOM absorption coefficient at 254 nm, the authors claim that "elevate DOM could stimulate the photoproduction of CO, but may also decrease air-sea CO exchange in the SML". A correlation, however, does not necessarily indicate a causality. For example, low wind speeds may lead to high DOM enrichment but in the meantime give rise to low gas fluxes as well;

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript.

"The negative correlations between $a_{CDOM}(254)$ and the sea-to-air flux of CO, and between marine humic-like C3 and the sea-to-air flux of CO, suggested that CDOM concentration may reduce the CO sea-to-air gas exchange rate in our study regions (Fig. 5a and 5b). In addition, low wind speeds may lead to high DOM enrichment, but in the meantime give rise to low sea-to-air fluxes as well. Therefore, due to the complexity of the DOM pool in the SML and its may result in decreased sea-to-air flux of CO, more measurements are needed to validate our conceptual model and provide a better understanding of the flux measurements of CO in the SML." (Line 543-551)

3) The authors defined a turnover time of photochemical CO production (Tao-photo) and made comparisons of this term among various samples and with the microbial CO turnover time (Tao-bio). However, Tao-photo depended on the irradiance received by the sample during irradiation, which changed with the time of day and atmospheric/cloud conditions. Such comparisons are thus not useful or even misleading;

Thanks for the reviewer's suggestion.

According to Sugai et al. (2021) "The turnover time of the photochemical production (τ_{prod}) and biological consumption (τ_{cons}) in the SML was calculated by the following equations (Doney et al., 1995):

$$\tau_{prod} = [CO] \text{ in SML}/\text{photochemical CO production rate in SML} \quad (6)$$

$$\tau_{cons} = 1/k_{CO} \text{ in SML} \quad (7)"$$

The turnover time of the photochemical production (τ_{prod}), biological consumption (τ_{cons}), and emission to the atmosphere ($\tau_{sea\text{-}air}$) of CO in the SML was calculated by the following equations (Yang et al., 2001; Yang et al., 2005; Yang & Tsunogai, 2005; Zhou & Mopper, 1997):

$$\tau_{prod} = [CO] \text{ in SML}/\text{photochemical CO production rate in SML} \quad (6)$$

$$\tau_{cons} = 1/k_{CO} \text{ in SML} \quad (7)$$

$$\tau_{sea-air} = [CO] \text{ in SML} \times \text{SML thickness}/F \quad (8)$$

4) There is no consistency in reporting CO emission rates regarding whether CO concentrations in the SSW or in the SML were used. Moreover, the authors attributed the lower CO fluxes in the Yellow Sea to more surfactants in the SML there. However, the formula of Edson et al. (2011) used for calculating the transfer velocity does not explicitly account for the effect of surfactants. Hence, the fluxes obtained by the authors of the present study do not allow them to directly evaluate the effect of surfactants on CO fluxes. This caveat also applies to the claim discussed in example 2;

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript.

Rickard et al. (2022) observed that the first-order estimates of the potential suppression of the gas transfer velocity (*kw*) by photo-derived surfactants 12.9%–22.2% in coastal North Sea water.

Pereira et al. (2018) also noted that the observed reduction in the air-to-sea CO_2 exchange in the Atlantic Ocean was due to biological surfactants acting as physical barriers and altering turbulent transfer near the water surface.

SML CDOM and DOC concentrations were higher in the YS than in the ECS, therefore, we speculated that the relatively lower CO fluxes in the YS were due to more DOM (including surfactants) in the SML than in the ECS.

5) In L486-489, the authors stated "The EF of marine humic-like Component was significantly higher than the other fluorescence components (1.6 vs. 1.4 and 1.3), indicating that in-situ autochthonous DOM was more strongly enriched in the SML than terrestrial DOM". This over-interprets the data since "marine" humic-like signals can sometimes be found in terrestrial DOM and the other fluorescence components can be found in marine DOM as well. There are many other instances of mis-interpretations throughout the manuscript. I would stop naming them all.

Thanks for the reviewer's suggestion.

Our previous paper demonstrated that the EFs of CDOM, DOC, FDOM and Chl *a* in the SML tend to be higher in off-shore regions than those in coastal regions because of the relatively higher enrichment of nutrients which could enhance phytoplankton growth and

promote plant production and DOM production in the SML in the YS and the ECS (Yang et al., 2022). Therefore, during our sampling periods, the EF of marine humic-like Component was significantly higher than the other fluorescence components (1.6 vs. 1.4 and 1.3), indicating that in-situ autochthonous DOM was more strongly enriched in the SML than terrestrial DOM.

Yang, L., Zhang, J., Engel A., Yang, G.P., 2022. Spatio-temporal distribution, photoreactivity and environmental control of dissolved organic matter in the sea-surface microlayer of the eastern marginal seas of China. Biogeosciences, 19, 5251–5268. doi: 10.5194/bg-19-5251-2022

Specific comments (incomplete due to lack of time. But it's the authors' responsibility to submit a manuscript in a sufficiently good shape for peer-reviewing)

Introduction

The Introduction needs to be better streamlined to improve its fluidity and readability. I would suggest starting with the biogeochemical significance of the SML (particularly DOM cycling including enrichment and photodegradation, and air-sea gas exchange) (first paragraph) followed by the importance, sources, and sinks of CO (briefly, second paragraph) and the possible influences of the SML on the cycling and air-sea fluxes of CO (third paragraph). The Introduction should conclude with a description of the current knowledge gaps and the objectives of this study (fourth paragraph).

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript.

“Carbon monoxide (CO) is an indirect greenhouse gas, and it plays an important role in atmospheric chemistry (Nguyen et al., 2020). It is the predominant sink of hydroxyl radical (OH•, Conte et al., 2019; Cordero et al., 2019), which oxidizes pollutants and greenhouse gases (such as CH_4) emitted to the atmosphere by human activities (Nguyen et al., 2020). The photodegradation of dissolved organic matter (DOM) is thought to be the main source of CO in the ocean (Stubbins et al., 2006), and the ocean acts as a source of atmospheric CO (Mopper and Kieber, 2002). In addition, direct production of CO by phytoplankton has been observed in laboratory experiments (Troxler et al., 1972; Gros et al., 2009) and dark/thermal production was also inferred from modeling at Bermuda Atlantic Time Series (BATS, Kettle, 2005), and from incubations of water samples from the Delaware Bay (Xie et al., 2005) and St Lawrence estuary (Zhang et al., 2008). Microbial consumption and the sea-to-air fluxes (Doney et al., 1995; Song et al., 2015) of CO are considered to be the main sinks of oceanic CO (Zafiriou et al., 2003). With increasing concern about atmospheric pollution and the potential role of CO, a primary goal of studying oceanic CO concentrations is to evaluate its long-term stability and distribution trends in the marine boundary layer (Conte et al., 2019; Xu et al., 2023), where the ocean and atmosphere exchange momentum (via wind stress), heat, moisture, and gases (CO and CO_2).

The ocean surface layer plays a vital role in climate change through the air-sea exchange of CO. The sea-surface microlayer (SML) is located at the sea-to-air interface and is considered to play a critical role in global biogeochemical cycles and climate change by regulating the sea-to-air exchange of gases and aerosol particles (Liss and

Duce, 1997; Cunliffe et al., 2013). For decades, articles have emphasized the presence and enrichment of organic matter and gases (DMS and CO) in the SML (Liss and Duce, 1997; Orellana et al., 2011; Ma and Yang, 2023; Sugai et al., 2020). In addition, SML is exposed to the most intense solar radiation of any seawater layer, especially ultraviolet (UV) light, and shows significantly higher colored dissolved organic matter (CDOM) concentration and microbial abundances compared to the subsurface layer (SSW, Obernosterer et al., 2006; Obernosterer et al., 2008; Wurl et al., 2009; Yang et al., 2022).

Generally, the sea-to-air flux is estimated from CO concentration in surface waters (2 to 10 m), but there is evidence that biogeochemical processes within the SML may also affect the CO flux (Sugai et al., 2020). CDOM and surfactant enrichment in the SML relative to the SSW has been reported, with an enrichment factor (EF) range of 0.4 to 6.7 (Huang et al., 2015; Shaharom et al., 2018; Yang et al., 2022), and mediates all mass transfer across the SML (Rickard et al., 2019 and 2022). Generally, strong spatiotemporal gradients in gas transfer velocity (k_w) were inversely correlated with natural surfactants, especially in the SML and in the SSW and the underlying near-surface seawater (Pereira et al., 2018). Bubble mediated enhancement of the transfer velocity, k, which exhibits a relationship with wind speed, has emerged as a key issue for flux parameterization in high wind regions (Edson et al., 2011). An estimated 10% of surface CO is released into the atmosphere via the sea-to-air interface (Zafiriou et al., 2003; Conte et al., 2019; Yang et al., 2024). Although intense solar radiation and enrichment of DOM may promote CO photoproduction involving SML (Cunliffe et al.,

2013; Pereira et al., 2018; Sugai et al., 2021), and likely modify sea-to-air gas transfer velocity (k_w) of CO and other gases (Pereira et al., 2018). The role and response of the SML, along with the complex interplay of biological, geochemical, and physical processes, govern the transfer of CO from the SSW, where it can either be consumed by bacteria or released into the atmosphere. Our study hypothesized that SML specific environmental changes (i.e., enrichment processes and biogeochemical processes) and the abundance and composition of DOM in the eastern marginal seas of China influence the rate of sea-to-air CO exchange, and they contribute to the formation of the marine boundary layer involved in atmospheric chemistry and climate regulation. Thus, the present study aimed to clarify the influence of the enrichment of DOM in the SML on sea-to-air CO exchange by relating seawater DOM concentrations to CO emissions to the atmosphere."

Materials and Methods

This section is often confusing and poorly organized. The "Study Area" is largely focused on the physical oceanography but lacks a synthesis of the results of earlier studies on DOM and CO, which are the main science of this study. There are substantial, unnecessary repetitions, e.g., the use of the Garrett screen for SML sampling (L137-147; L148-151), the measurement of solar irradiance (L169-174; L197-200). Some crucial claims are put forward without proof, e.g., the stability of [CO] during the sampling (L144) and the linear relationship between CO photoproduction and irradiation time (L195-197, note that the solar irradiance changes significantly over a 4-hour time period, particularly in winter, the sampling season of this study). The description of the photoexposure experiment is

confusing and does not follow a logical sequence: It first gives the impression that samples were placed in brown glass bottles for solar exposure (L182-183) but then it suddenly pops up the quartz tubes (L185) without a prior explanation of the dimensions of the tubes and the configuration of the experiment (this explanation is somehow placed at the end). The phrase of “In addition” in L189 would lead to the reader thinking that both brown glass bottles and quartz tubes were used as irradiation vessels. Please clarify. The Materials and Methods section also contains imprecise phrases or lacks essential info in several instances (see specific comments below).

2.3 Photoexposure experiments

The in-situ natural sunlight incubation experiment was conducted to estimate the CO photoproduction rates in different seawater layers. SSW and SML samples for photochemical incubation were collected from stations B1 and C4, as well as E2, FJ5, P1, and P7, located in the YS and the ECS, respectively (Fig. 1). SML and SSW (5 m below seawater surface) samples (SSW: 2 L; SML: 500 mL) were passed through a 0.22 μm PES filters (Pall Corp. Port Washington, NY, USA) immediately to remove the majority of the bacteria and was then placed in an acid-washed and pre-combusted quartz tubes (120 mL, acid-washed and pre-combusted) in a natural sunlight incubation and sealed without headspace or air bubbles. Photo incubation experiments were conducted on the ship immediately after sample collection. To measure the photoproduction at solar radiation production rates of CO, the quartz tubes were treated as follows: (1) uncovered quartz tubes exposed to full-spectrum irradiation; (2) quartz

tubes wrapped in multiple layers of aluminum foil to eliminate all light transmission. Treatment (2) was subtracted from light-exposed treatments to remove the fraction of CO produced by dark production. The quartz tubes were positioned under the in-situ irradiation source to maximize the exposure of the sample; the water depth in each tube was 5 cm (i.e., the diameter of the tube). SML and SSW quartz tubes were irradiated for 4 hours and were exposed to direct solar irradiation while being held in a water bath with circulating seawater. The change in the CO photoproduction with time can be seen as a constant due to the relatively small amount of total radiation during the short exposure time. The intensity of incident solar radiation was measured and recorded at half-hour intervals using an OL 756 UV-visible spectroradiometer (Li et al., 2020) fitted with an OL IS-270 2-inch integrating sphere (wavelength accuracy: ± 0.15 nm; wavelength repeatability: ± 0.05 nm; spectral radiance accuracy: 1%, Table S1).

The turnover time of the photochemical production (τ_{prod}) and biological consumption (τ_{cons}) in the SML was calculated by the following equations (Doney et al., 1995; Jones and Amador, 1993):

τ_{prod} = [CO] in SML/photochemical CO production rate in SML (1)

$\tau_{cons} = 1/k_{CO}$ in SML (2)

2.4 Microbial consumption and dark production experiments

Six stations were selected to determine the microbial consumption rates of CO (YS: stations A1, B1, and C4; ECS: stations E2, T2, and S6). CO concentrations in seawater samples were measured immediately after collection from the SSW and the

SML and used as background values. Seawater was used to fill 1 L glass syringes equipped with a 3-way nylon valve, which were pre-cleaned with 10% HCl-Milli-Q water and Milli-Q water, until free of headspace, and wrapped with aluminum foil. The syringes were immersed in a shallow tank of flowing water that was continuously pumped from the sea to maintain the temperature of the incubation experiments equal to that of the ambient surface seawater. Each sampling series consisted of 4–5 points, and the data from each series were fitted exponentially to determine the consumption rate constant (k_{bio}).

Shipboard incubations were conducted to measure CO dark production rates. According to Zhang et al. (2008), the dark production is the abiotic dark production. Seawater was first filtered through 0.2 μm polyethersulfone membranes and bubbled with CO-free gas (ultrahigh-purity N_2, China) to reduce the background CO values before being put into the 1 L syringes as previously described. Then syringes were rinsed with the sample water and then overflowed with the sample twice their volumes before they were closed without headspace. All incubations were conducted in duplicate and placed in the same environment. The water bath was completely darkened with opaque foam and black garbage bags. Samples were collected at 0, 0.5, 1, 2, and 4 h during incubation. The dark production incubations were used to eliminate the effect of dark production from the microbial CO consumption measurements. CO incubation experiment was performed under the same conditions as the CO degradation processes according to the method of Xie et al. (2005) and Xu et al. (2023).

Shipboard incubations were carried out to measure CO dark production rates.

According to Zhang et al. (2008), dark production is abiotic. Seawater was first filtered through 0.2 μm polyethersulfone membranes and bubbled with CO-free gas (ultrahigh-purity N_2, China) to reduce background CO levels before being transferred into 1 L syringes, as previously described. The syringes were then rinsed with the sample water and overflowed twice their volume with the sample before being sealed without headspace. All incubations were performed in duplicate and kept in the same environment. The water bath was completely darkened using opaque foam and black garbage bags. Samples were collected at 0, 0.5, 1, 2, and 4 hours during incubation. The dark production incubations were used to eliminate the effect of dark production from microbial CO consumption measurements. The CO incubation experiments were conducted under the same conditions as the CO degradation processes, following the method of Xie et al. (2005) and Xu et al. (2023).

L33-36: The EF of [CO] in the SML is the ratio of [CO] in the SML to that in the SSW. Without comparing the CO photoproduction and consumption rates in the SML with those in the SSW, it does not make much sense to say that the EF of [CO] in the SML showed a large diurnal variation.

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript.

"The mean value of K_{photo} in the SML was slightly higher than that in the SSW." (Line)

L33-34: add ranges and number of samples as well.

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript.

"Chromophoric DOM (CDOM) (92%) and fluorescent DOM (FDOM) (92%) were frequently enriched in the SML during winter. The enrichment of CO was lower than the enrichments of CDOM and FDOM. CO ranged from 0.48 to 2.81 nmol L^{-1} (1.22 ± 0.85 nmol L^{-1}) and 0.50 to 3.61 nmol L^{-1} (1.54 ± 1.61 nmol L^{-1}) in the subsurface layer (SSW) and the SML, respectively, with higher concentration observed in the SML due to CDOM enrichment." (Line 27-32)

L60: what potential role of CO?

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript.

"In the ocean, CO acts as a microbial energy source that supports food webs, a link in carbon cycling that connects surface and deep waters, a modulator of oxygen and nitrogen cycles. With increasing concern about atmospheric pollution and the potential role of CO, a primary goal of studying oceanic CO concentrations is to evaluate its long-term stability and distribution trends in the marine boundary layer (Conte et al., 2019; Xu et al., 2023), where the ocean and atmosphere exchange momentum (via wind stress), heat, moisture, and gases." (Line 61-67)

L93-95: I do not think the cited articles reported these findings. Please re-check.

Thanks for the reviewer's suggestion. We have deleted this sentence.

L96-97: This statement gives readers the impression that the 10% value applies to global ocean scales while in fact this result was obtained from the East China Sea only.

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have revised the manuscript.

"The average annual sea-to-air flux accounted for 10% of the global CO sinks estimated by Zafiriou et al. (2003), Conte et al. (2019) and Yang et al. (2024)." (Line 59)

L132-135: There were 70 stations in total but only 52 pairs of samples. So not every station was sampled for both SML and SSW?

Thanks for the reviewer's suggestion. Not every station was sampled for both SML and SSW.

L137-138: the specifications for the screen sampler given here seem to be different from those in L150-151. Please clarify.

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript.

"SML sampling used a Garrett Screen (Garrett, 1965; Chen et al., 2016; Ma and Yang, 2023) (mesh: 16 mm, wire diameter: 0.36 μm; effective surface area: 2.025 cm^2) according to standard procedures (Pereira et al., 2016; Sabbaghzadeh et al., 2017) when seawater conditions were calm. While SML integrity is disrupted by a moving vessel, or when sampling from its stern (Cunliffe and Wurl, 2014; Wurl et al., 2016), the SML can be

successfully sampled from a vessel's bow while on-station (Sabbaghzadeh et al., 2017) with the ambient waterflow toward the RV (Cunliffe and Wurl, 2014).” (Line 121-128)

L143-144: what do you mean by “the sampling distance”? Relative to what? “CO did not change during the sampling”, for SSW or SML, or both?

The sampling distance is at a certain distance (5 ~ 8 m) where the CTD sampler was deployed, and both SSW and SML CO did not change during the sampling. We collected and measured CO samples first.

L166-167: Could the CTD sensor measure the SST and SSS for the SML?

“Seawater temperature and salinity in the SML were measured *in situ* using a pre-calibrated multi-parameter water quality probe (AP-5000, Aquaread Co., UK).” (Line 175-177)

L169-173: the measurement of solar irradiance was conducted over what wavelength range and at what wavelength resolutions?

Thanks for the reviewer's suggestion. According to the reviewer’s suggestion, we have made the revision in the revised manuscript.

> “Net solar radiation is the balance between all incoming and outgoing radiant energy fluxes at the Earth's surface. Our ocean surface net solar radiation was measured and recorded using a net radiometer (Table S1). Ocean surface net solar radiation is significant in research on the Earth’s heat balance systems, sea-to-air interactions, and other applications.” (Line 179-183)

L191: how were the quartz tubes sealed (plastic screw caps? Glass stoppers?)

It is the plastic screw cap.

L218: These were not cultures (essentially bugs-free). You can call them “incubations”.

L219: the same incubator as what?

Thanks for the reviewer's suggestion. According to the reviewer’s suggestion, we have made the revision in the revised manuscript.

“All incubations were conducted in duplicate and placed in the same incubator environment.” (Line 229-231)

L221: using a syringe. Glass syringe? What volume?

L231: gas-tight syringe. Glass syringe? What volume?

“Samples were collected at 0, 0.5, 1, 2, and 4 hr during incubation.” (Line 231)

L272: units of beta?

β is the Bunsen solubility coefficient, which is dependent on salinity and temperature (Wiesenburg and Guinasso, 1979), and has no unit.

L289: the photoproduction rate depends on a lot of variables, particularly the solar irradiance, which changes as a function of the time of day, season, latitude, atmospheric conditions, etc. What is the point of defining the photochemical turnover time?

The turnover time of the photochemical production (τ_{prod}), biological consumption (τ_{cons}), and emission to the atmosphere ($\tau_{sea\text{-}air}$) of CO in the SML was calculated by the following equations (Yang et al., 2001; Yang et al., 2005; Yang & Tsunogai, 2005; Zhou & Mopper, 1997):

$$\tau_{prod} = [CO] \text{ in SML} / \text{photochemical CO production rate in SML} \quad (6)$$

$$\tau_{cons} = 1/k_{CO} \text{ in SML} \quad (7)$$

$$\tau_{sea-air} = [CO] \text{ in SML} \times \text{SML thickness}/F \quad (8)$$

(Sugai et al., 2020)

We follow Sugai et al. (2020) methods.

Section 2.5: list the essential equations only. Refer the reader to the relevant literature for the other equations.

"*2.5 Calculation of sea-to-air flux of CO*

The two-layer model proposed by Liss and Merlivat (1986) was used to calculate the instantaneous sea-to-air flux of CO according to the following equation:

$$F = k([CO]_{surf} - [CO]_{eq}) \quad (1)$$

where F refers to the sea-to-air flux of CO (nmol m^{-2} h^{-1}); and k is the gas transfer coefficient (cm h^{-1}) as a function of wind speed u (m s^{-1}) and the Schmidt number of CO (Sc). In this paper, we used empirical formula E2011 (Edson et al., 2011), which applies to wind speeds from 0 to 18 m s^{-1} (Wind speed ranged from 0.68 m s^{-1} to 12.00 m s^{-1}), to calculate the gas transfer coefficient as follows:

$$k = (0.029u^3 + 5.4)\,(Sc/660)^{-1/2} \quad (2)$$

The Schmidt number of CO was referenced from the research of Zafiriou et al. (2008):

$$Sc = -0.0553t^3 + 4.3825t^2 - 140.07t + 2134 \quad (3)$$

where t is seawater temperature (°C).

$[CO]_{surf}$ represents the concentration of CO in the initial SML and SSW seawater, calculated by the following equation:

$$[CO]_{surf} = pm_a\,(\beta pV_w + V_a)/(RTV_w) \quad (4)$$

where *P* is the standard atmosphere pressure (atm) and *ma* represents the concentration of CO in the headspace when the sample reaches equilibrium. β is the Bunsen solubility coefficient which is dependent on salinity and temperature (Wiesenburg and Guinasso, 1979). *Vw* and *Va* are the volumes of seawater and headspace in the sample bottle, respectively. *T* is temperature (in Kelvin) and *R* is the gas constant with the value of 0.08206 atm L $(mol\ K)^{-1}$."

Section 2.7: EF has already been defined earlier. It's a simple concept and thus does not need a repetition in full detail.

Thanks for the reviewer's suggestion. We have deleted this section.

Technical notes

L23: how do DOM enrichment in the SML control how DOM enrichment in the SML controls

L24: the flux of several gasesàair-sea gas exchange.

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript.

"However, how DOM enrichment in the SML controls the flux of several gases in sea-to-air exchange remains poorly understood."

L26: Enrichment factor is a jargon that a general reader may not understand. Define it.

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript.

"Enrichment in the SML was expressed as enrichment factors (EFs) defined as the ratio of values in the SML to those in the SSW."

L30: open oceanàopen oceans.

L32: EFsàthe EFs and many other similar cases.

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript.

"Although CO, CDOM and FDOM concentrations decreased from in-shore regions to open oceans, higher enrichment factors (EFs > 2) of CO and DOM in the SML were generally observed in the off-shore areas."

L36: Fluxàflux.

L37: delete “a_{CDOM}(254). Replace “CDOM absorption” with “the CDOM absorption coefficient at 254 nm”.

L38: replace “fluorescence marine humic-like Component 3” with “marine-humic-like FDOM”.

Thanks for the reviewer's suggestion. According to the reviewer’s suggestion, we have made the revision in the revised manuscript.

The flux of CO exhibited a significantly negative correlation with the CDOM absorption coefficient at 254 nm and marine-humic-like FDOM in the SML, suggesting that elevated DOM could stimulate the photoproduction of CO, but may also decrease sea-to-air CO exchange in the SML.”

L97-100: Not a grammatically correct sentence.

Thanks for the reviewer's suggestion. According to the reviewer’s suggestion, we have made the revision in the revised manuscript.

“The average annual sea-to-air flux accounted for 10% of the global CO sinks estimated by Zafiriou et al. (2003), Conte et al. (2019), and Yang et al. (2024).”

L100-103: very complicated and confusing sentence. Rewrite.

Thanks for the reviewer's suggestion. According to the reviewer’s suggestion, we have made the revision in the revised manuscript.

"The role and response of the SML, along with the complex interplay of biological, geochemical, and physical processes, govern the transfer of CO from the SSW, where it can either be consumed by bacteria or released into the atmosphere."

L118: delete "very".

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript.

Seawater in the Kuroshio presents high temperatures (20–29°C), high salinities (34.2–34.8), and low suspended particulate concentrations (SPC) (< 2 mg L^{-1}) (Yang et al., 2022)."

L119-130: Eliminate the redundancies and consolidate the sentences.

"The Yellow Sea (YS) and the East China Sea (ECS) are marginal seas of the western Pacific Ocean with complicated hydrological characteristics and are substantially affected by the Yellow Sea Cold Water Mass (YSCWM), the Kuroshio Current, and the coastal currents (Fig. 1). The YSCWM is a low-temperature (< 10°C) and high-salinity (32.0–33.0) water mass. Seawater in the Kuroshio presents high temperatures (20–29°C), high salinities (34.2–34.8), and low suspended particulate concentrations (SPC) (< 2 mg L^{-1}) (Yang et al., 2022). The Changjiang River contributed more than 80% of the total freshwater inflow to the YS and the ECS (Wang et al., 2020). In addition, the atmospheric circulation in the study area was generally governed by the East Asian monsoon, with strong northerly winds prevailing from September to April, and low pressure over the northwestern Pacific Ocean

producing offshore winds that transport continental air masses into the study area (Li et al., 2019). This interaction significantly influences the hydrological conditions, circulation structures, material exchange, ecological environment, and the biogeochemical processes of CO and DOM in the region (Chen, 2009; Yu et al., 2025; Zhang et al., 2007).”

L129: use present tense of “transport”.

Thanks for the reviewer's suggestion. According to the reviewer’s suggestion, we have made the revision in the revised manuscript.

“In addition, the atmospheric circulation in the study area was generally governed by the East Asian monsoon, with strong northerly winds prevailing from September to April, and low pressure over the northwestern Pacific Ocean producing offshore winds that transport continental air masses into the study area (Li et al., 2019). ”

L191-192: “The quartz tubes….to maximize the exposure of the sample”. I do not get it.

Thanks for the reviewer's suggestion. According to the reviewer’s suggestion, we have made the revision in the revised manuscript.

“The quartz tubes were positioned under the in-situ irradiation source to maximize the exposure of the sample; the water depth in each tube was 5 cm (i.e., the diameter of the tube).”

L193-194: the diameter of the tube was the maximum water depth since the tube was cylindric (I assume).

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript.

"The quartz tubes were positioned under the in-situ irradiation source to maximize the exposure of the sample; the water depth in each tube was 5 cm (i.e., the diameter of the tube)."

L193: both types of samples (SSW and SML).

L194: 4 hours, from when to when? always over the same time period for different samples?

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript.

"SML and SSW quartz tubes were irradiated for 4 hours and were exposed to direct solar irradiation while being held in a water bath with circulating seawater."

L205-207: awkward sentence. Re-write.

L207: aluminum (lower-case a)

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript.

"Seawater was used to fill 1 L glass syringes (with a 3-way nylon valve, pre-cleaned with 10% HCl-Milli-Q water and Milli-Q water) until headspace-free, and wrapped with aluminum foil."

L208: which was (not were).

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript.

"The syringes were immersed in a shallow tank of flowing water, which was continuously pumped from the sea in order to keep the water temperature of the incubation experiments to that of the ambient surface seawater. Each time series of sampling consisted of 4–5 points, and the data from each time series were fitted exponentially to obtain the consumption rate constant (k_{bio})."

L221: what do you mean by "taking care to evacuate the headspace after each sampling"?

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript.

"taking care to evacuate the headspace after each sampling" means no air in the 1 L glass syringes incubators."

L246: eq. 4 was cited prior to eqs. 1-3.

Thanks for the reviewer's suggestion. According to the reviewer's suggestion, we have made the revision in the revised manuscript.

"The measured equilibrated headspace mixing ratio of CO (ppbv) was corrected using the saturated water vapor pressure and standard atmospheric pressure (Stubbins et al., 2006) and then converted to obtain the concentration of dissolved CO (nmol L^{-1}) in seawater (eq. 3-6)."

The authors claim that the screen sampler reveals larger enrichments than the glass plate sampler, implying it is more effective, but that is because screen sampler collects a rather thick layer). The cited paper is unfortunately not in the reference list. What is indeed needed are proper validation data that SML samples can be collected for reliable gas analysis. For gases with strong ocean molecular sublayer resistance (CO), the exchange is significantly increased with higher wind speeds, wave breaking, production of bubbles, and enhanced underwater turbulent processes.

Further, one note of the study of gases in the SML is that gases supersaturated with respect to their atmospheric concentrations, including CO, are inevitably lost from SML samples during sampling, depending on environmental conditions such as water temperature and wind. For example, in case of dimethylsulfide (DMS), a volatile gas with large concentration difference between the atmosphere and the ocean, Yang et al. (2001) and Yang and Tsunogai (2005) showed about 50–70% and 60% (mean) of loss from SML samples collected using a mesh screen at 0–15°C and at a water temperature of 10°C and wind speed of 4 m s^{-1}, respectively. A mesh screen was also used in this study, and parameters such as $[CO]_{SML}$ and the EF of CO may have been underestimated.

Yang, G.P., Watanabe, S., Tsunogai, S., 2001. Distribution and cycling of dimethylsulfide in surface microlayer and subsurface seawater. Mar. Chem. 76(3), 137–153. doi: 10.1016/S0304-4203(01)00054-8