An itemized response (**blue words**) to reviewers' comments and suggestions

Dear Editor and Reviewers,

Thank you for your 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. The following are the reviewer's comments and suggestions related to the manuscript and how we have addressed each of reviewer's concerns (**blue words**).

Editor

In the revised version the authors have tried hard to deal with the substantial criticisms raised by the referees. But there is still some work to be done before the paper can finally be accepted. Some aspects are difficult to deal with, e.g the problems of sampling the microlayer for gases. But the problems need to be discussed in greater detail so, at least, the intrinsic problems are acknowledged. Other points from the referees can be further addressed with some revision of the text.

Thanks for the editor's comment. We have accepted the editor and reviewer's suggestions that some sampling difficulties were explained more clearly in the revised manuscript.

Reviewer 1:

This manuscript presents a comprehensive investigation into the distribution and cycling of carbon monoxide (CO) within the sea-surface microlayer (SML) and

subsurface waters (SSW) of the East China Sea and the Yellow Sea. The study effectively combines field campaigns and controlled incubation experiments.

The authors have been responsive throughout the interactive discussion, and the current version represents a substantial improvement. However, prior to final acceptance, several clarifications and minor revisions are essential to strengthen the manuscript.

Thanks for the reviewer's positive comment. We have accepted the reviewer's suggestions that some discussion details were explained more clearly in the revised manuscript.

My primary concerns are as follows:

The authors' response regarding seasonal effects merely, but this does not adequately address the more critical question of whether the mechanistic conclusions drawn from winter observations have seasonal universality. The manuscript lacks a discussion on "how seasonal changes may potentially affect the relationship between DOM enrichment and CO flux." For example, whether stronger summer light and temperature would change the relative importance of light production, microbial production and DOM (surfactants) inhibition? It must be clearly pointed out that the inference "DOM inhibits CO flux" based on the winter observations in this study remains an unanswered question in other seasons and requires further verification.

Thanks for the reviewer's comment. We have made the revision.

“During our study period (winter), surface seawater temperatures showed substantial spatial fluctuations (ranging from 2.08°C in the YS to 23.80°C in the ECS) due to the broad investigation range. In our previous manuscript (Yang et al., 2022), we observed that relatively higher nutrient enrichment in summer could enhance phytoplankton growth and promote DOM production in the SML; stronger enrichment and photochemical processes in the SML result in relatively accelerated enrichment of more locally produced marine DOM in the SML than in the SSW. During warm seasons, stronger light and temperature may alter the relative importance of light production, microbial production, and DOM (surfactants) composition, as well as the inhibition of CO flux. Therefore, the fact that DOM inhibits CO flux still requires further verification in other seasons and regions.” (Line 565-575)

While the structure of Introduction has been improved in this version, the logical progression leading to the study's hypothesis can be sharper. Currently, the introduction extensively reviews background knowledge but does not highlight the contradiction, limitation, or key unknown in current understanding that motivates the present work.

Thanks for the reviewer's comment. We have made the revision.

“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. 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 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). However, CO-related data from the SML is especially scarce, and the fate of CO in the SML remains unknown, because of the sampling limitation (Engel et al., 2017). 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." (Line81-98)

I recommend "Minor Revisions". The points raised above and the detailed comments in the below should be addressed. Upon satisfactory revision, I believe this manuscript will be a valuable contribution suitable for publication.

Thanks for the reviewer's positive comment.

Specific comments

L32-35 Considering that CDOM and FDOM are two subsets of DOM, their usage should be consistent with the actual measurement content. it is recommended to use these terms "DOM", "CDOM" and "FDOM" more precisely and carefully.

Thanks for the reviewer's comment. We have made the revision.

"Although CO, CDOM and FDOM concentrations decreased from in-shore regions to open oceans, higher enrichment factors (EFs > 2) of CO and CDOM and FDOM in the SML were generally observed in the off-shore areas." (Line 32-35)

L208 Lack of a complete definition of 'Kbio'

"The turnover time of the photochemical production (τ_{prod}) and biological consumption (τ_{cons}) in the SML (SSW) 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)

τ_{cons} = [CO] in SML/k_{bio} in SML (2)"

(Line 225-229)

L250 The "a" in "ma" should be in subscript format

Thanks for the reviewer's comment. We have made the revision.

"Where P is the standard atmosphere pressure (atm) and m_a represents the concentration of CO in the headspace when the sample reaches equilibrium." (Line 259)

L377 [CO]ssw is ambiguous. I guess it might be [CO] instead

Thanks for the reviewer's comment. We have revised.

“[CO] showed great seasonal and diel variability, as well as variability between ocean regions.” (Line 439)

Reviewer 2:

The manuscript has improved compared to the previous version; however, several important issues still need to be addressed before it can be considered fully satisfactory.

Thanks for the reviewer's positive comment.

Separation of the Two Research Lines

My earlier comment regarding the two distinct lines of investigation has not been adequately addressed. The authors continue to mix the two aspects throughout the text, which weakens the narrative and makes it difficult to follow the study's logic. These components should be more clearly differentiated, better structured, and explicitly connected where appropriate.

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

Thanks for the reviewer's suggestion. We have made the revision.

“During our study period (winter), surface seawater temperatures showed substantial spatial fluctuations (ranging from 2.08°C in the YS to 23.80°C in the ECS) due to the broad investigation range. In our previous manuscript (Yang et al., 2022), we observed that relatively higher nutrient enrichment in summer could enhance phytoplankton growth and promote DOM production in the SML; stronger enrichment and photochemical processes in the SML result in relatively accelerated enrichment of more locally produced marine DOM in the SML than in the SSW. During warm seasons, stronger light and temperature may alter the relative importance of light production, microbial production, and DOM (surfactants) composition, as well as the inhibition of

CO flux. Therefore, the fact that DOM inhibits CO flux still requires further verification in other seasons and regions." (Line 561-571)

(2) 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?

Thanks for the reviewer's suggestion. We have made the revision.

"There were 38 sampling stations during the daytime (7: 00-19: 00) and 32 sampling stations during the nighttime (19: 00-7: 00, Table S1)." (Line 119-121)

"The higher EF values of CO also occurred in the daytime (Fig. 3b), suggesting that sufficient light and higher temperatures combined to facilitate the photoproduction of CO and its enrichment in the SML." (Line 468-470)

"Notably, the enrichment of CO in the SML was more common during the daytime when photochemical processes were more active, but natural sunlight can inhibit the microbial consumption of CO. CO was maximal in the SML, leading to the significant enrichment and supersaturation." (Line 615-618)

Use of the Garrett Screen

The use of a Garrett screen in this context is problematic. As it stands, the justification for employing this method is insufficient. If the authors wish to retain it, they must provide a much stronger scientific rationale that addresses its known limitations and explains why it remains appropriate for their objectives.

Thanks for the reviewer's suggestion. We have made the revision.

"CO data from the SML samples is scarce. The SML samples were collected in 500 mL brown sample bottles. The screen was held level and dipped into the sea surface, moved laterally to sample from an undisturbed film, and then withdrawn slowly from the surface. Repeated dipping (11 times, 600 mL) was conducted until the desired volume was collected (the depths of the SML samples ranged within 100–500 μm, Garrett, 1965). The screening method is often applied during field studies because of its relative quickness and large sample volume compared to other techniques (Chen et al., 2016). CO in seawater samples was collected and measured first on board, immediately after collection. A comparison showed that screen-collected samples usually exhibit greater microlayer enrichment of gas than the plate-collected samples, indicating that the screen sampler might be more effective for in-situ measurements (Yang et al., 2001). Although established sampling techniques of the SML (Garrett screen and glass plate) are associated with high losses for the volatile trace gases (Engel et al., 2017). As the Garrett screen is widely used and can collect a large number of SML samples in the short term (Turner and Liss, 1985; Walker et al., 2016; Yang et al., 2001), we chose the Garrett screen." (Line 162-177)

Surfactants vs. DOM

The manuscript continues to equate surfactants with DOM, which is not strictly correct. Surfactants represent only a fraction of the dissolved organic matter pool, and this distinction is essential for interpreting the results. The authors should revise the text to better reflect this nuance.

Thanks for the reviewer's suggestion, we agree with the reviewer's views. Now, we only discussed the surfactants in Section 4.3.

"As noted above, the most probable sources of CO in the SML of these sea regions are in-situ photoproduction from DOM and/or vertical export through underlying SSW water. Actually, surface-active surfactants are ubiquitous and accumulate in the uppermost < 1000 μm in seawater (Rickard et al., 2019), where they slow the rate of gas exchange between seawater and air (Cunliffe et al., 2013). Although surfactants represent only a fraction of the dissolved organic matter pool, Rickard et al. (2022) observed that the first-order estimates of the potential suppression of the gas transfer velocity (*kw*) by photo-derived surfactants were 12.9%–22.2% in coastal North Sea water. The highest SML enrichments in surfactants have been seen in low productivity, oligotrophic regions away from terrestrial influences, where surfactant concentrations in SSW are generally low (Wurl et al., 2016). 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. Therefore, the relatively lower fluxes of CO observed in the YS may indicate that seawater contains lots of DOM (surfactants) in the SML. Despite the clear importance of surfactants at the sea-to-air interface, we did not conduct surfactant-specific analyses due to the analytical limitations. In our experiments, the CO flux varied by 131% in winter. 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 535-560)

The manuscript shows progress, but key conceptual and methodological issues remain unresolved. With clearer separation of the research components, a more robust justification of the sampling method, and more precise terminology, the work could be significantly strengthened.

Thanks for the reviewer's positive comment. We have made the revision.

To unravel the relevance of the SML on air-sea gas exchange and its potential as a source or sink for CO, it is necessary to sample the SML efficiently and accurately.