Author response

We deeply appreciate the Editor and the Anonymous Referees for the thorough review of our manuscript. Our manuscript has been revised according to the comments and our responses to the comments are as follows. For clarity, the comments are reproduced in blue, authors' responses are in black and changes in the manuscript are in red color text.

Reply to the comments from Anonymous Referee #3

This manuscript describes a thorough analysis of the life cycle of DOC concerning concentrations in seawater, the SML, and integration into SSA during a phytoplankton bloom. Using various methods, the concentration and enrichment of DOC across these layers of the air-sea interface are quantified and related to the biological activity and interactions occurring. Namely, the non-linear relationships between aerosolized DOC and chlorophyll concentrations point to complex interactions leading to issues with current limitations on understanding the DOC aerosolization cycle.

Major Comments:

- The figures with timeseries are misleading due to inconsistent time intervals. It is recommended to update the figures with consistent and evenly distributed intervals to better present changes and make it easier to compare between plots when measurements were taken on different days and at different intervals.

Author Reply

We have updated all figures in the revised manuscript to ensure consistent time intervals. Due to the adoption of a new time interval approach, the original area accumulation chart, which was based on continuity, is no longer applicable. We have made additional modifications to the relevant content. The modified figures are shown below:

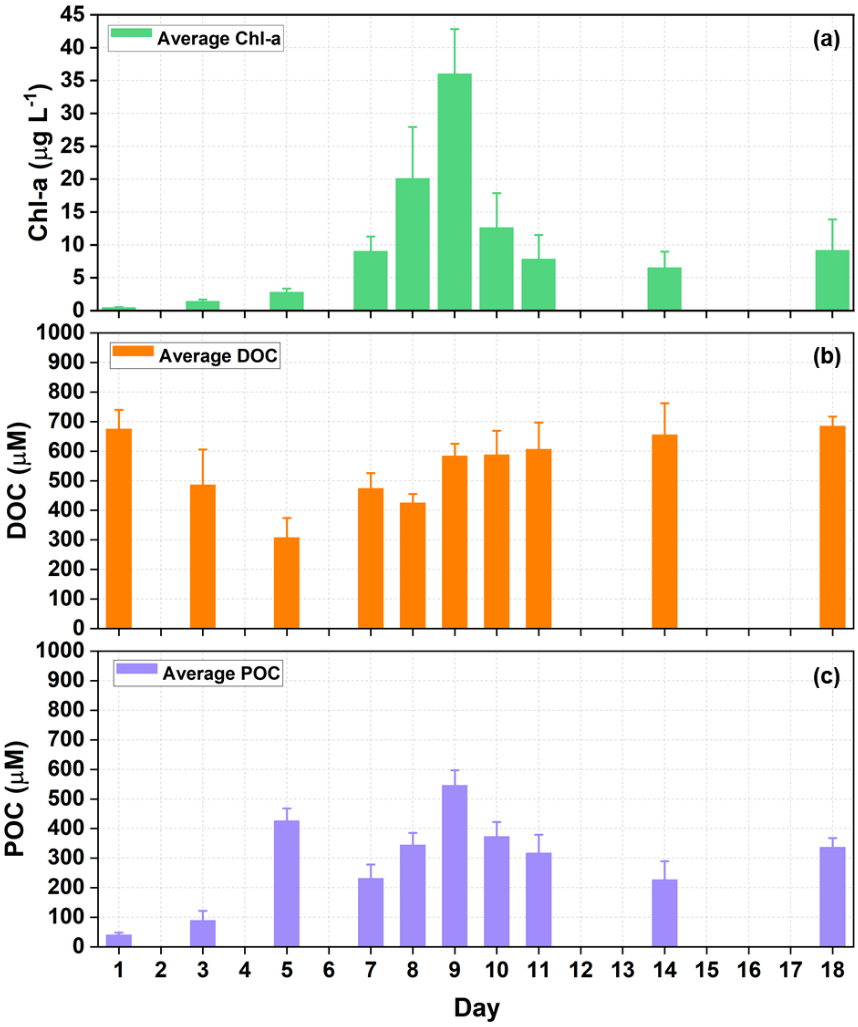

Figure 1. Time series of physicochemical properties of seawater during the phytoplankton bloom. (a) chlorophyll-a (Chl-a), (b) dissolved organic carbon (DOC), and (c) particulate organic carbon (POC) concentrations in seawater. Mean and standard deviations are for three containers of seawater in each experiment.

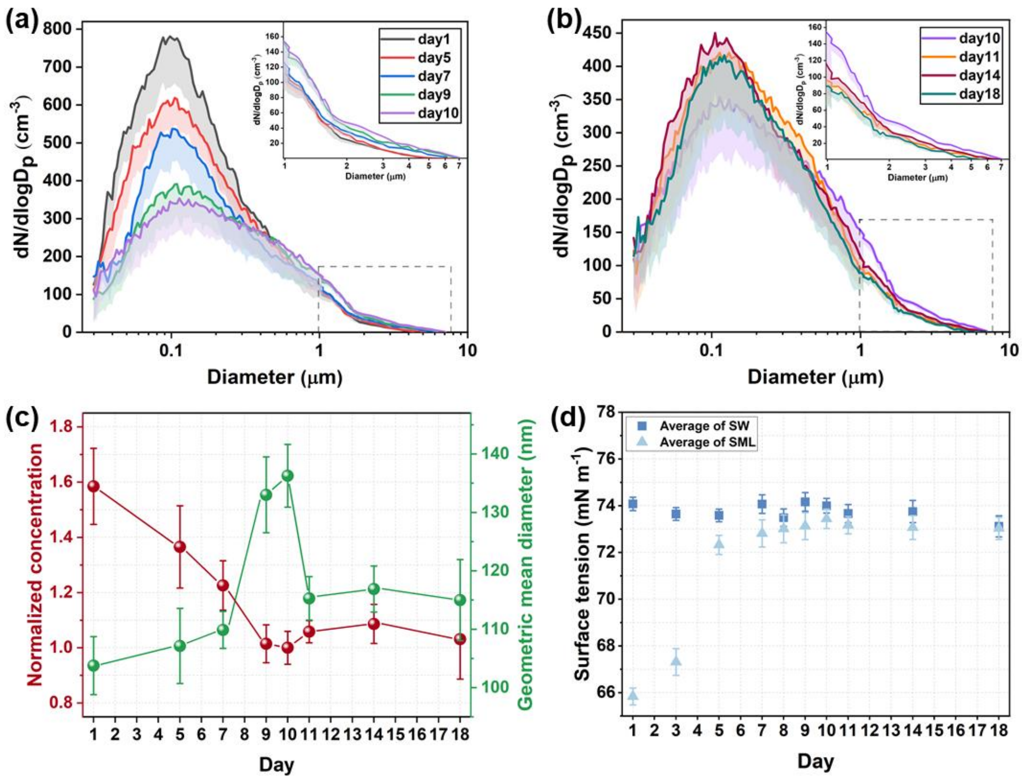

Figure 2. Time series of SSA formation during the phytoplankton bloom. (a) Particle size distributions of SSA from Day 1 to Day 10; (b) Particle size distributions of SSA from Day 10 to Day 18. For clarity, the gray dashed box area is the result of the aerodynamic particle sizer and is enlarged to the upper right corner. Shading is the standard deviation in the negative direction. (c) Number concentrations and geometric mean diameters of SSA. Error bars are standard deviations for SSA size distribution results measured by SMPS and APS at 5-minute intervals during the nascent SSA sampling period. (d) Surface tension of SML and bulk seawater. Error bars are the standard deviation of three repeated measurements.

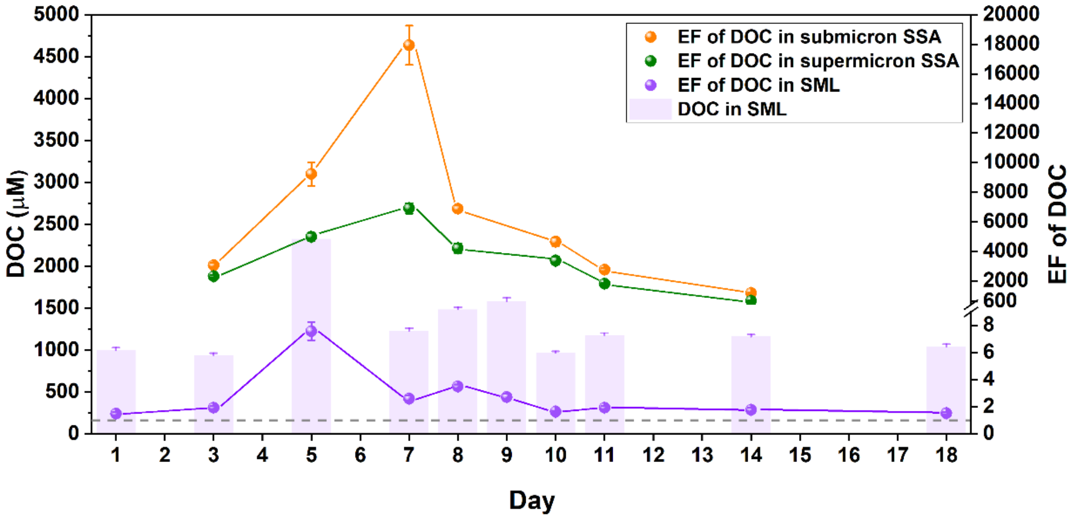

Figure 3. Time series of DOC enrichment during the phytoplankton bloom. Enrichment factors of DOC relative to Na^+ in the SML (purple), submicron SSA (orange) and supermicron SSA (green). Error bars represent the deviation of the EF, derived from the standard deviation of Na^+ concentration and DOC concentration obtained through two repeat measurements. The purple column is the concentration of DOC in the SML, and the error bars are derived from at least three repeated measurements.

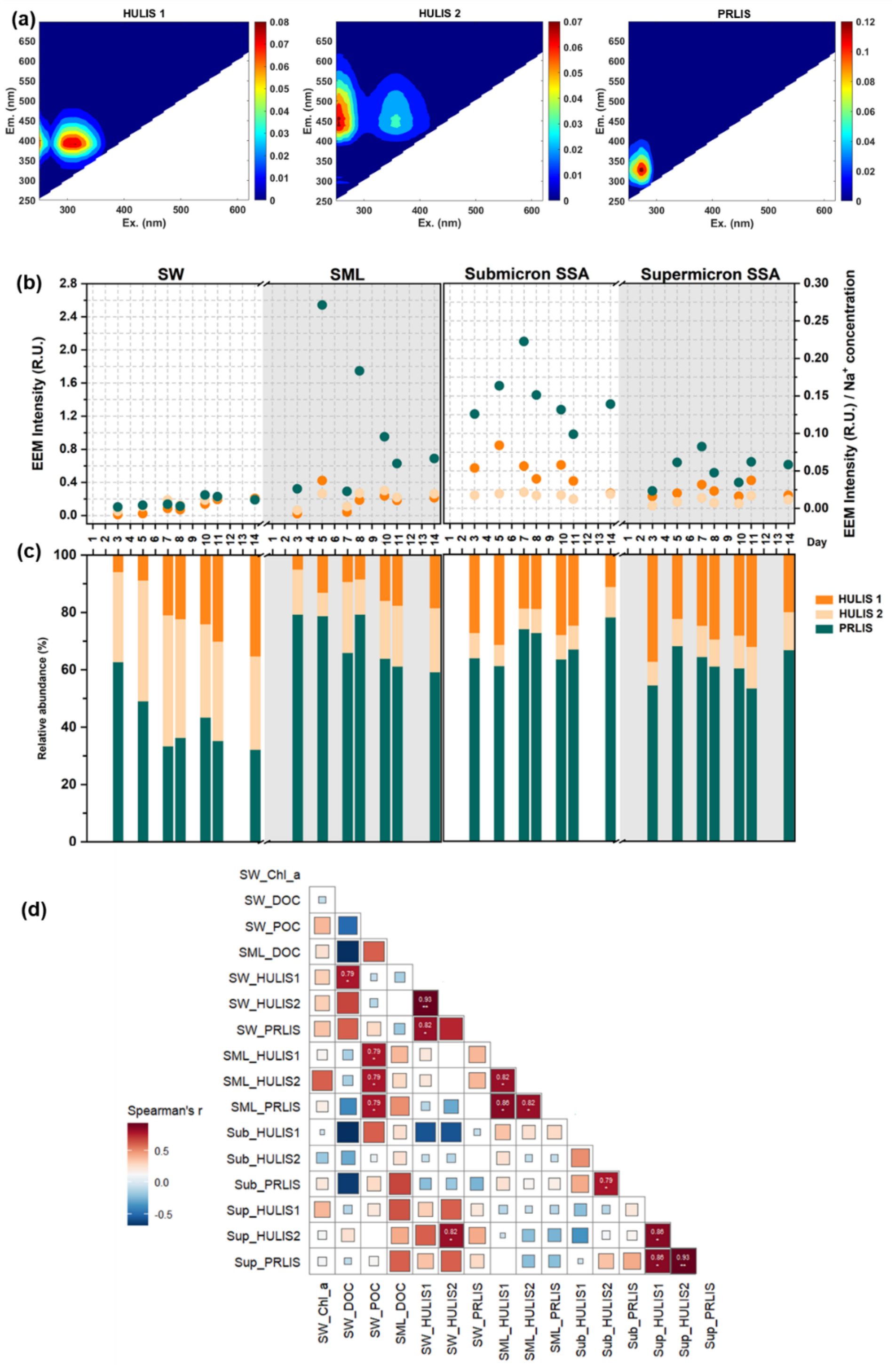

Figure 5. Sea-to-air transfer of HULIS and PRLIS. Three organics identified using the EEM-PARAFAC method: (a) HULIS 1, HULIS 2, and PRLIS. (b) EEM intensities of the three organics in different samples with respect to time. Note that in order to exclude the effect of SSA collection mass on EEM intensity, EEM intensities of SSA samples were normalized with their Na$^+$ concentrations. (c) Relative abundance of EEM intensities of the three organics in different samples with respect to time. (d) Spearman's

correlation between Chl-a, DOC and POC concentrations in seawater, POC concentration in the SML and EEM intensities of three fluorescent substances.

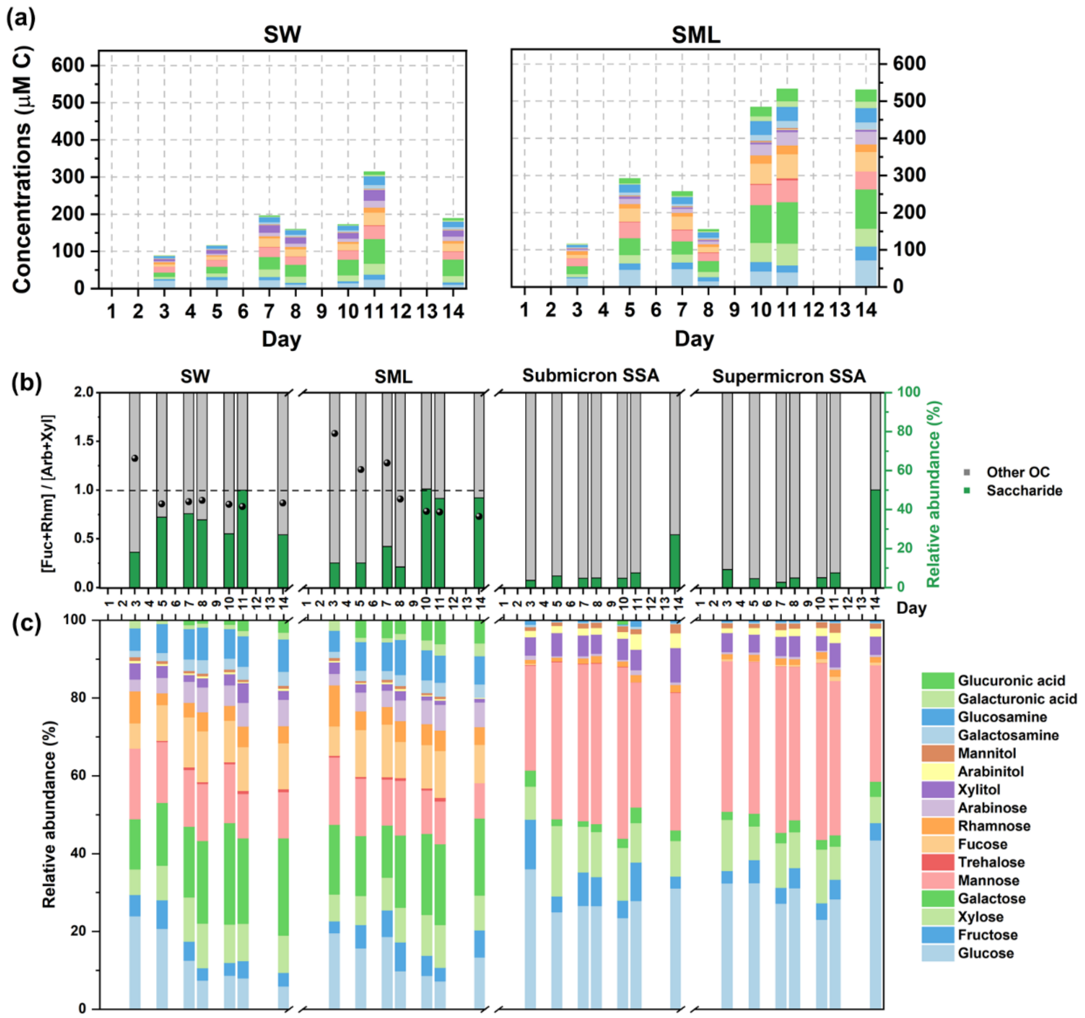

Figure 6. Sea-to-air transfer of saccharides. (a) Relative abundance of total saccharides in DOC. The bacterial activity is expressed as the ratio of the sum of the concentrations of fucose and rhamnose to the sum of the concentrations of arabinose and xylose (the black scatters). The activity is typically considered higher when the ratio is less than 1. (b) Composition and relative abundance of saccharides.

- I have a few concerns about your experimental setup and description. Firstly, were the carboys aerated or sealed? From Fig. S1, it appears they were sealed and not aerated, which would limit the type of community that thrives during the experiment. Secondly, I appreciate the updated main text concerning the air temperature fluctuations of the carboys. However, the text states the average temperature was 21C, while the SI text mentions the experiments being conducted at 25C. Can you explain this discrepancy and if the 25C is the water, aerosol stream, or room temperature? Thirdly, you mention operating the simulation tank on continuous waterfall mode with a centrifugal pump for 8-9 hours. How did you address the time-dependent destruction of the microbial community due to the centrifugal pump? What period of those 8-9 hours did you use to estimate the size distribution? Fourthly, what do you mean by line 120? Did the two distributions perfectly align at 1μm? Or how were the two distributions merged into one?

Author Reply

During the phytoplankton bloom in carboys, we sealed the environment by closing the carboys' caps to minimize external interference with the microbial communities in seawater. However, we shook the carboys three times daily and opened the lids for ventilation, ensuring that the phytoplankton maintains a good growth environment. Microbial incubation in sealed environments is a common operation. The undisturbed environment allows for the quantification and analysis of key indicators before and after incubation, such as phytoplankton-associated organic matter release and degradation (Xu et al., 2024a; Xu et al., 2024b; Flores et al., 2025) as well as nitrogen fixation rates of nitrogen-fixing microorganisms (Zhang et al., 2024; Yao et al., 2025).

Phytoplankton blooms are primarily triggered by sufficient nutrients and suitable temperatures (Cao et al., 2023; Li et al., 2024). Key indicators like Chl-a suggest that the phytoplankton bloom occurring in our experiments is comparable to that in previous studies. For example, Biermann et al. conducted six controlled experiments that induced phytoplankton blooms and found that at a seawater temperature of 8.3±0.3 °C, Chl-a peaked at approximately 35 μg L-1 between day 10 and day 12 (Biermann et al., 2014). In a different study, peak Chl-a concentrations were recorded on day 13 (Jayarathne et al., 2016). The timing and concentrations of these indicators are consistent with our results.

Additionally, under conditions where nutrients were added, phytoplankton blooms were the primary factor altering the aquatic community structure. This is due to competition for nutrients rather than effects from the culture apparatus itself. Jayarathne et al. noted that, although coastal seawater introducing directly into a large wave channel for artificial bloom experiments, laboratory conditions may favor specific species. This may result in microbial communities and distributions that differ from those in natural marine environments.

In the revised manuscript, we have elaborated on the ventilation conditions during the phytoplankton bloom and acknowledged that phytoplankton blooms under laboratory conditions may differ from those in natural environments.

Page 3, lines 82-86

The phytoplankton bloom experiment began on June 1st, 2024, and lasted for 18 days. To minimize the interference from external environmental factors, these containers remained sealed most of the time. They were shaken at least three times daily, with the caps being briefly opened during each operation to allow ventilation. It is acknowledged that phytoplankton blooms under laboratory conditions may differ from those in natural environments (Jayarathne et al., 2016). During this period, 10 simulation experiments on nascent SSA were conducted.

Regarding the experimental temperature, during the phytoplankton bloom, the ambient air temperature outdoors was recorded at 21.19±2.60 °C. The experiments involving nascent sea spray aerosol were conducted indoors, where the air conditioning maintained an air temperature range of 22 to 25 °C. Since the air temperature does not change significantly, the change in seawater temperature is also minimal. In the revised manuscript and supplement, we have provided further clarification regarding room temperature.

Main manuscript, Page 4, lines 102-95

All SSA generation experiments, which typically started around 9:00 AM and lasted for 8 to 9 hours, were conducted at indoor air temperatures (22–25 °C) that approximate outdoor air temperatures.

Supplement, Page 2, lines 33-34

All experiments were conducted at relatively constant room temperature (22–25 °C).

Regarding the time-dependent destruction of the microbial community raised by the Referee, during a prolonged operation of centrifugal pumps, the shear forces generated can damage phytoplankton cells. To mitigate the impact of shear forces, our home-made SSA simulation tank used a parallel configuration of three centrifugal pumps. Each pump operated at its rated speed of 3500 rpm (rounds per minute), achieving a flow rate of 20 L min^{-1} and pumping water upwards at a maximum height of 5 m. In the nascent SSA experiments, we set the total seawater circulation flow rate at 20 L min^{-1}. Assuming that each of the three parallel pumps operates at 6.7 L min^{-1} flow rate, the theoretical rotational speed for a single pump would be approximately 1167 rpm. However, given that the actual height at which water is pumped is around 1.5m, the operating speed of a single centrifugal pump should be lower than 1167 rpm. Additionally, the centrifugal pump is specifically designed for circulation at a low height, with the internal pressure not exceeding 0.2 bar under actual operating conditions.

Several studies have investigated the mechanical damage caused by shear forces during centrifugal pump operation to phytoplankton cells. Bronnenmeier and Märkl examined two green algae species, *Chlamydomonas reinhardii* and *Chlorella vulgaris*, alongside the common cyanobacterium *Anacystis nidulans* (Bronnenmeier and Märkl, 1982). Their findings indicated that *Chlamydomonas reinhardii* cells exhibited critical stress thresholds of 15 to 20 bar and 2400 rpm, whereas *Chlorella vulgaris* demonstrated significantly higher thresholds of approximately 100 bar and 3000 rpm. Furthermore, *Anacystis nidulans* shows greater tolerance to shear stress than the two green algae species. During the operation of our apparatus, the rotational speed of the pump rotor and the pressure applied were significantly below the above critical values. Vandandjon et al. investigated the effects of centrifugal pump cycling on the marine diatom *Haslea ostrearia* (with an average modal length of 37.1–77.8 μm). Their results showed that cellular damage increased with higher cycling frequency, greater number of cycles, higher pump rotor speed, and larger algal size (Vandanjon et al., 1999).

Specifically, when cells underwent over 1000 circulations within the pump at a circulation frequency of 0.033 s^{-1} and a rotor speed of 1320 rpm, the final cell damage rate remained around 10%. Our study utilized a lower circulation frequency (0.0040 s^{-1}, completing one circulation of 84 liters of seawater within the tank at a flow rate of 20 L min^{-1} over 4.2 min), a lower number of cycles (114 to 129 cycles over 8 to 9 h), a lower rotational speed (1167 rpm), and smaller algal sizes (≤50 μm). Therefore, we anticipate that the cell damage rate will be significantly lower than 10%, and may even be negligible. However, precise quantification of this damage requires further investigation.

The duration of the nascent SSA experiment is 8–9 h. Considering the potential effects from the operation of the centrifugal pump or on phytoplankton cells from growth during this period, our assessment of the SSA particle size distribution is based on the average throughout the nascent SSA experiment. During the experiment, a scanning mobility particle sizer was operated at a scan rate of 5 min to measure SSA particle with electrical mobility diameter between 0.02 and 1 μm; an aerodynamic particle sizer measured SSA particle with aerodynamic diameters between 0.5 and 10 μm at a scanning rate of 1 min, then paused for 4 min before initiating the next scan. This continuous measurement yielded approximately 90 to 100 results by the end of the nascent SSA experiment. Subsequently, we excluded 4 to 6 results from the early experimental phase where the SSA number concentration in the headspace of the tank had not yet reached a steady state. The average values were calculated from the remaining results to assess the size distribution characteristics of SSA throughout the experiment.

We have added estimates of the damage to phytoplankton cells caused by the operation of centrifugal pumps in the revised manuscript and supplement.

Manuscript, Page 4, lines 103-105:

It is estimated that during this period, the total damage rate to phytoplankton cells in seawater caused by centrifugal pump operation can be significantly lower than 10%. More details on SSA generation and cell damage assessment are provided in the Supplement.

Supplement, Page 2, lines 35-59:

S3. Assessment of damage caused by centrifugal pump operation to phytoplankton cells

During prolonged operation of centrifugal pumps, the shear forces generated can damage phytoplankton cells. To mitigate the impact of shear forces, our home-made SSA simulation tank used a parallel configuration of three centrifugal pumps. Each pump operates at its rated speed of 3500 rpm (rounds per minute), achieving a flow rate of 20 L min^{-1} and a head of 5 meters. In the nascent SSA experiments, we set the total seawater circulation flow rate at 20 L min^{-1}. Assuming each of the three parallel pumps operates at 6.7 L min^{-1} flow rate, the theoretical rotational speed for a single pump would be approximately 1167 rpm. However, given that the actual operating head is around 1.5 m, the operating speed of a single centrifugal pump should be lower than 1167 rpm. Additionally, the centrifugal pump we selected is specifically designed for low-head circulation, with internal pressure not exceeding 0.2 bar under actual operating conditions.

Several studies have investigated the mechanical damage caused by shear forces during centrifugal pump operation to phytoplankton cells. Bronnenmeier and Märkl examined two species of green algae, *Chlamydomonas reinhardii* and *Chlorella vulgaris*, alongside the common cyanobacterium *Anacystis nidulans* (Bronnenmeier and Märkl, 1982). Their findings indicated that *Chlamydomonas reinhardii* cells exhibited critical stress thresholds of 15 to 20 bar and 2400 rpm, whereas *Chlorella vulgaris* demonstrated significantly higher thresholds of approximately 100 bar and 3000 rpm. Furthermore, *Anacystis nidulans* shows greater tolerance to shear stress than these two green algae species. During the operation of our apparatus, the rotational speed of the pump rotor and the pressure applied were significantly below the above critical values. Vandandjon et al. investigated the effects of centrifugal pump cycling on the marine diatom *Haslea ostrearia* (with an average modal length of 37.1–77.8 μm). Their results showed that cellular damage increased with higher cycling frequency, greater number of cycles, higher pump rotor speed, and larger algal size (Vandanjon et al., 1999). Specifically, when cells underwent over 1000 circulations within the pump at a circulation frequency of 0.033 s^{-1} and a rotor speed of 1320 rpm, the final cell damage rate remained around 10%. Considering that our study utilized a lower circulation frequency (0.0040 s^{-1}, completing one circulation of 84 liters of seawater within the tank at a flow rate of 20 L min^{-1} over 4.2 min), a lower number of cycles (114 to 129 cycles over 8 to 9 h), a lower rotational speed (1167 rpm), and smaller algal sizes (≤50 μm), we anticipate that the cell damage rate due to the shear effect of centrifugal pumps will be significantly lower than 10%. However, precise quantification of this damage requires further investigation.

Additionally, details regarding SSA particle size distribution measurements in the nascent SSA experiment have been updated in the revised manuscript.

Page 5, lines 125-133

Particle size distributions of dried SSA were measured by a scanning mobility particle sizer (SMPS, GRIMM, Germany) and aerodynamic particle sizer (APS 3321, TSI, USA). SMPS was operated at a sampling flow rate of 0.3 L min^{-1} and a scan rate of 5 min, providing the particle size distribution with electrical mobility diameter (d_{em}) between 0.02 and 1 μm. Aerodynamic particle sizer (APS) detected SSA particles with aerodynamic diameters (d_a) ranging from 0.5 to 10 μm at a scanning rate of 1 min, then paused for 4 min before starting the next scan. Throughout the nascent SSA experiment, both SMPS and APS could provide approximately 90 to 100 results of particle size distribution. The first 4 to 6 results from the initial phase of the experiment were excluded because the SSA number concentration in the headspace of the tank had not yet reached a steady state. The average values were calculated from the remaining results to assess the size distribution characteristics of SSA in the entire experiment.

Concerning the last concern of the Referee, due to differences in measurement principles, the electromigration diameter (d_{em}) measured by SMPS and the aerodynamic diameter (d_a) measured by APS need be converted to the particle's geometric physical diameter (d_p) before they can be merged. The specific conversion formula is as follows (Stokes et al., 2013; Christiansen et al., 2019; Harb and Foroutan, 2022):

$$d_p=d_{em}=\frac{d_a}{\sqrt{\frac{\rho_{eff}}{\rho_0}}}$$

where ρ_0 is the unit density (1.0 g cm^{-3}), and ρ_{eff} is the effective density of the particles (2.0 g cm^{-3}). While merging size distributions, we found that the SSA number concentrations measured by SMPS and APS were closest at geometric diameters of approximately 1 μm. For larger diameters, SSA measurements exceeded the SMPS range, while for smaller diameters, results could not be integrated with SMPS due to the inability of APS to efficiently count small particles. Around 1 μm, the size distributions of SMPS and APS also do not perfectly align. In Figure R1, we have marked the merging point of the two size distributions with a red dashed box. The number concentration of APS remains slightly lower than that of SMPS. Similar phenomena observed during the merging process have also been reported in a previous study (Christiansen et al., 2019).

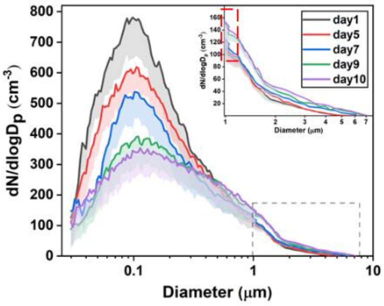

Figure R1. Integration of the SSA particle size distribution obtained from APS and SMPS around 1 μm.

The merging process for the SMPS and APS particle size distributions have been updated in the revised manuscript.

Page 5, lines 133-138

Due to differences in measurement principles, d_{em} measured by SMPS and d_a measured by APS need be converted to the particle's geometric physical diameter (d_p) before they can be merged. Assuming spherical SSA particles, the specific conversion formula is as follows (Eq. (1)) (Harb and Foroutan, 2022; Stokes et al., 2016):

$$d_p=d_{em}=\frac{d_a}{\sqrt{\frac{\rho_{eff}}{\rho_0}}} \quad (1)$$

where ρ_0 is unit density (1.0 g cm^{-3}), and ρ_{eff} is the effective density of the particles (2.0 g cm^{-3}). Since the SSA number concentrations from SMPS and APS are relatively close, we have chosen to merge them around 1 μm.

- I find the description of Section 3.1 and of Fig. 1 over-generalized. As I understand it, you sampled 3 of your carboys at each time point but did not have one system growing during the entire time period. Therefore, I find it overgeneralized to state the bloom peak occurred on Day 9 when we have no continuous record. For example, one of the samples on Day 8 has a higher chlorophyl concentration than one of the samples on Day 9, indicating the bloom of the day 8 sample may have peaked. And for the samples of day 10, we have no indication of when the bloom peak occurred. I suggest rephrasing the results and discussion of the manuscript to consider the lack of continuity, and therefore the ability for larger variation in the time scales of each carboy.

Author Reply

This study investigates the patterns of sea-to-air transfer of DOC by utilizing changes in Chl-a concentration as an indicator for phytoplankton blooms. Chl-a concentration data were obtained from each carboy to account for potential differences in phytoplankton growth processes, even under identical environmental conditions. In the nascent SSA experiments, the Chl-a concentration in the SSA simulation tank represented the average of measurements from all three carboys. We did not directly induce the entire phytoplankton bloom in the SSA simulation tank due to the following primary considerations: first, during SSA generation and collection, organic matter in seawater is continuously scavenged by bubbles and transported with SSA to the sampler, resulting in a gradual decrease in seawater organic matter concentration. This phenomenon that cannot be overlooked, particularly in a relatively closed tank. Second, the repeated and prolonged operation of centrifugal pumps may cause significant damage to microbial cells. This was discussed in more details in our reply to a previous

Referee's inquiry.

We acknowledge that the processes driving phytoplankton blooms may differ among various carboys. However, the average Chl-a concentration in the SSA simulation tank indicated that the peak concentration was recorded on Day 9, during the five-day monitoring period from Day 7 to Day 11. This study mainly depends on Chl-a concentration of thoroughly mixed seawater in the SSA simulation tank, as subsequent experiments, sample measurement, and result discussion were conducted using this seawater. The phytoplankton blooms induced by our method demonstrated a high level of consistency with the results of six blooms observed in the same system by Biermann et al. (2014), particularly regarding fluctuations in Chl-a and dissolved organic carbon (DOC) concentrations over time (Biermann et al., 2014).

In the revised manuscript, we emphasize that our subsequent analyses primarily rely on Chl-a concentrations in the mixed seawater from the SSA simulation tank. We also note that the absence of a continuous monitoring system may limit the precise tracking of phytoplankton bloom phenomena within each carboy over time. We also describe Day 9 as the "peak of Chl-a concentration", rather than the "peak of phytoplankton bloom" in the previous version.

Page 7, lines 209-212

The processes of phytoplankton blooms may differ among various outdoor containers, which could limit the consistency of Chl-a concentrations in each container. However, as this study primarily uses seawater in the SSA simulation tank as the liquid medium during nascent SSA experiments, future discussions on Chl-a concentrations (or concentrations of other substances) will focus exclusively on seawater within the SSA simulation tank.

Page 7, lines 193-195

Based on Chl-a concentration during the phytoplankton bloom, samples of submicron SSA, supermicron SSA, SML, and seawater collected on Day 1 Day 9 (peak of Chl-a), and Day 18 were pretreated for desalting and concentrating using a PPL solid-phase extraction column (100 mg/3 mL, Agilent Technologies).

Page 12, lines 300-301

To investigate the link between the sea-to-air transfer of DOC and biological activity, samples of submicron SSA, supermicron SSA, SML, and seawater were collected on Day 1, Day 9 (peak of Chl-a) and Day 18 for mass spectrometry analysis.

Page 16, lines 387-389

The accumulation of saccharides in seawater and phytoplankton growth processes is interrelated but not fully synchronized. In both seawater and SML, two distinct peaks in total saccharides were observed, occurring before and after the peak of Chl-a concentration (Fig. 6a).

Minor Comments:

- The sentences on lines 53-55 are unclear. Revision is recommended to clarify the point being made.

Author Reply

We have revised the sentences.

Page 2, lines 58-60

Globally, the occurrence of phytoplankton blooms in coastal regions is rapidly expanding and intensifying (Dai et al., 2023). Therefore, elucidating the mechanisms that govern the transfer of DOC from the ocean to the atmosphere will enhance our understanding of related atmospheric chemistry and climatic effects.

- Missing references on lines 58-60. What previous laboratory simulations are you referring to?

Author Reply

We have added the references.

Page 2, lines 63-65

Previous laboratory simulation studies typically employed simplified modeling systems that focused on a single organic molecule or class of compounds, overlooking the complexity of DOC and the relationship between DOC composition and biological activity (Schill et al., 2018; Hasenecz et al., 2019; Hartery et al., 2022).

- Typo on line 116, “de” should be “dem”

Author Reply

This has been corrected.

Page 5, lines 133-134

Due to differences in measurement principles, d_{em} measured by SMPS and d_a measured by APS need be converted to the particle’s geometric physical diameter (d_p) before they can be merged.

- On line 136, are you implying that the concentration of Na+ remains constant within each experiment, across days, or both?

Author Reply

The mass concentration of Na^+ in seawater, at the sea surface microlayer, and in sea spray aerosols is generally considered to be constant. Consequently, it can act as an indicator for the enrichment levels of specific substances during sea-to-air transfer (Quinn et al., 2015; Jayarathne et al., 2016; Quinn et al., 2014; Salter et al., 2016). It is defined as the concentration ratio of the target substance (X) to that of Na^+ in SSA particles or SML relative to the ratio in seawater (Eq. (2)).

$$EF=\frac{(X)_{SSA\ or\ SML}/(Na^+)_{SSA\ or\ SML}}{(X)_{SW}/(Na^+)_{SW}} \qquad (2)$$

This has been updated in the revised manuscript, and the related relevant references have been provided.

Page 6, lines 155-157

Previous studies have shown that the concentration of Na^+ is typically constant during the sea-to-air transfer. Therefore, the enrichment factor (EF) relative to the concentration of Na^+ can quantify the degree of organic matter enrichment in this transfer (Quinn et al., 2014; Quinn et al., 2015; Jayarathne et al., 2016).

- Lines 205-206: Typo-- the production of submicron SSA decreased then increased (more or less).

Author Reply

We have made the necessary corrections.

Page 8, lines 226-2227

The distributions of SSA particle size during the phytoplankton bloom are shown in Fig. 2a-b. Prior to Day 10, the production of submicron SSA first decreased, and then increased, while supermicron SSA exhibited an opposite trend.

- Lines 231-233: If changes in SML surface tension were responsible for the decrease in SSA concentration and increase in geometric mean diameter, then why is SML surface tension fairly constant after day 7 while the largest changes in SSA occur between days 7 and 9 and again between days 10 and 11?

Author Reply

We intended to clarify that surface tension is a key factor influencing the generation of SSA. Our results demonstrate a significant positive correlation between changes in surface tension and variations in the number concentration and geometric mean diameter of SSA. It is essential to clarify that this correlation is not linear; thus, surface tension does not need to maintain a precise proportional relationship with the geometric mean diameter and number concentration of SSA. Furthermore, phytoplankton blooms may influence SSA formation by altering seawater viscosity (Tammaro et al., 2021; Berny et al., 2020), which could inhibit surface tension from entirely determining SSA formation. Considering that our original wording might have been misleading, the related text has been revised as follows:

Page 9, lines 250-251

Our findings also indicate that changes in surface tension during phytoplankton blooms play a key role in influencing the formation of SSA.

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Reply to the comments from Anonymous referee #4

The paper by Hu et al. reports the findings of DOC sea-to-air transfer experiments during laboratory induced phytoplankton bloom. The study is methodologically correct and there are elements of novelty worthy of publication. However, there are numerous trivial or speculative statements which are unsupported by experimental data and obscuring the overall merit of the study. Not every experimental result should be reported, but rather only those which advance the knowledge. There are often the results which do not deserve to be published being either confusing or indecisive. Reporting every result would turn every paper into the report.

Author Reply

We have carefully revised the entire manuscript and removed unnecessary experimental results, while revising previous ambiguous content. Below are the main actions we have taken in the revised manuscript.

1. Previous studies were cited to demonstrate that sodium ion (Na^+) concentration remains constant during sea-to-air transfer and that the enrichment of target substances can be quantified by calculating the concentration ratio of the target substance to that of Na^+ in a specific sample category, relative to the ratio in seawater samples.

Page 6, lines 155-158

Previous studies have shown that the concentration of Na^+ is typically constant during the sea-to-air transfer. Therefore, the enrichment factor (EF) relative to the concentration of Na^+ can quantify the degree of organic matter enrichment in this transfer (Quinn et al., 2014; Quinn et al., 2015; Jayarathne et al., 2016).

2. The texts at page 9, lines 235-239, and page 7, lines 196-199 in the original previous manuscript version have been deleted.

3. Further clarification was provided regarding why the enrichment factor of DOC in SML increased while surface tension decreased on Day 5. The relationship between the enrichment factor and surface tension was also elucidated.

Page 10, lines 270-274

The highest EF in the SML was observed on Day 5. On this day, the increase in the EF of DOC was not contradictory to the increase in surface tension of the SML samples. The rise in surface tension of the SML samples could be attributed to a reduction in a highly surface-active organic pollutant. However, because its concentration is extremely low (below 2 μM, seeing Figure S5), it does not significantly impact the EF of the DOC (ranging from 700 to 2200 μM C) in the SML samples.

4. The speculations regarding potential climate impacts from organic matter enrichment in SSA have been revised.

Page 11, lines 280-285

Compared to particle size distribution, the significant variation in DOC's EF in SSA may have more profound implications for SSA's climate effect. The widely reported phenomenon of organic matter enveloping inorganic salt cores (as illustrated in Fig. S6) significantly influences the cloud condensation nucleation activity (Bates et al., 2020; Lee et al., 2020; Cravigan et al., 2020) and ice nucleation activity of SSA (Pandey et al.; Hartmann et al., 2025), with specific effects depending on the type of organic matter. Although the EF of DOC in SSA reflects the overall characteristics of sea-to-air transfer pattern, more detailed studies are still needed to elucidate the specific pattern of different organic species.

5. Rather than comparing the strength of correlations in the absence of significant correlations, the discussion at page 14, lines 357-365, has been revised to explain why no significant correlations exist.

This implies that DOC in the SML might mainly originate from POC in seawater. Within the same type of samples (seawater, SML, submicron SSA, or supermicron SSA), PRLIS, HULIS 1, and HULIS 2 often maintained significant positive correlations; however, when sample types differ, significant correlations between them are rarely observed (Fig. 5d). In seawater and SML samples, the non-significant correlation may be due to the fact that these three organic fractions originate from different organic carbon pools in seawater. For submicron and supermicron SSA, the non-significant correlation may result from DOC undergoing different air-water interfacial fractionation processes (Quinn et al., 2015). The concentration variations of DOC resulting from multiple enrichment processes at different air-water interfaces may obscure its consistency with the concentration variations induced by microbial activity in seawater. Typically, DOC in submicron SSA undergoes more pronounced interfacial fractionation than DOC in supermicron SSA.(Crocker et al., 2022).

6. The discussion regarding chlorophyll a concentration being unsuitable as an effective indicator for assessing organic matter sea-to-air transfer has been revised.

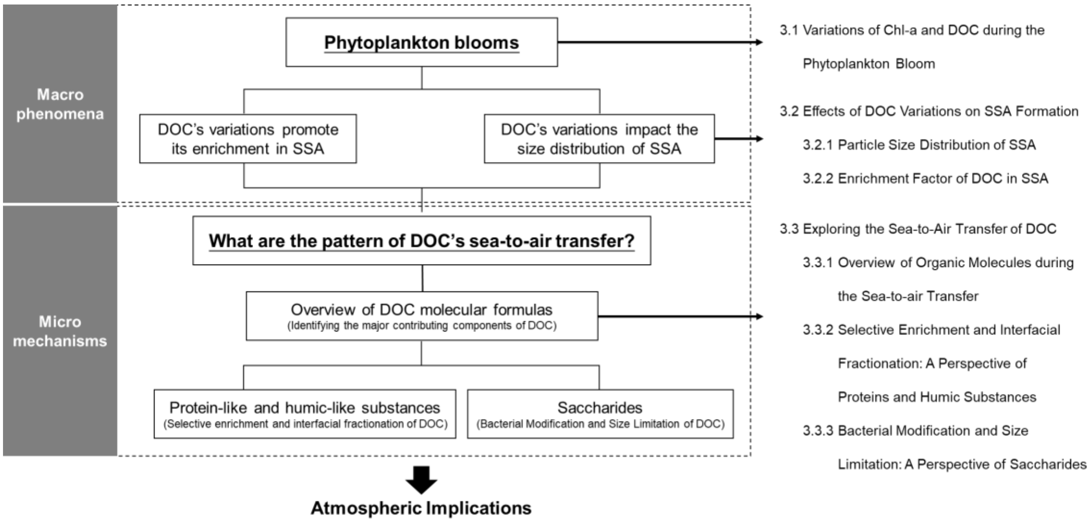
Page 19, lines 474-482

Although there are ongoing debates about the effectiveness of Chl-a concentrations in predicting the organic spray emissions (O'dowd et al., 2008; Bates et al., 2012; Rinaldi et al., 2013; Quinn et al., 2014), it can be asserted that Chl-a, as readily available from global satellite data, remains essential in these predictions, especially when it is constrained with appropriate parameters. The current study indicates that Chl-a is a driven factor to regulating the sea-to-air transfer of DOC. However, the influence of microbial cycling and SSA formation mechanisms complicates this regulatory role, preventing it from manifesting as a straightforward linear relationship. For the future organic spray emission models, it is advisable to incorporate time-series variations in Chl-a concentrations, as they could reflect the progression of phytoplankton blooms. Additionally, careful consideration should be given to dividing different biogeochemical ocean regions, which includes identifying both Chl-a concentration control regions (O'dowd et al., 2008) and non-control regions (Quinn et al., 2014), to enhance the spatiotemporal resolution.

The flow of the paper needs to be improved too, by starting with the most unique and clear results, like sacharides and molecular composition while other sections do not report as clear cut results as the mentioned above.

Author Reply

In the revised manuscript, we have restructured the section headings in "Results and Discussion" to better reflect the logical flow illustrated in the figure below:



First, we present the variations of chlorophyll-a, DOC, and POC concentrations in seawater during phytoplankton blooms (Section 3.1). Second, the fluctuations in DOC concentration induced by phytoplankton bloom (Section 3.2) significantly affect the particle size distribution (Section 3.2.1) and DOC's enrichment factors (Section 3.2.2) of SSA. In order to elucidate the sea-to-air transfer patterns of DOC via SSA during phytoplankton blooms (Section 3.3), high-resolution mass spectrometry provided an in-depth overview of DOC molecular composition across different transfer stages, confirming that phytoplankton blooms influence DOC sea-to-air transfer and identifying protein, humic, and saccharide-like DOC as major contributors (Section 3.3.1). For protein and humic-like DOC, we used a three-dimensional fluorescence spectrometer in combination with parallel factor analysis to investigate their sea-to-air transfer patterns during phytoplankton blooms. Given the significant differences in surface activity between protein and humic-like DOC, we focused on analyzing their selective enrichment in SSA and fractionation at the air-water interface (Section 3.3.2). Saccharide-like DOC was detected using high-performance anion-exchange chromatography with pulse amperometric detection. We found that although saccharides in SSA increased significantly only during the late phase of phytoplankton blooms, this was inconsistent with the consistently high contribution of saccharides in seawater. By indirectly indicating bacterial activity and considering SSA production mechanisms, we speculate that saccharides produced by phytoplankton may require bacterial modification into smaller saccharides before being effectively transported into SSA (Section 3.3.3).

The title is unclear too where sea spray does not promote but directly transfers DOC and other species to sea spray and there is no mention of laboratory study in the title. Possibly, title can be amended to: Sea-to-air transfer of dissolved organic carbon by sea spray during artificially induced phytoplankton bloom.

Author Reply

Throughout the manuscript, we primarily employed various detection methods to investigate the sea-to-air transfer of DOC via SSA during phytoplankton bloom. Based on this, the title has been revised to:

Sea-to-Air Transfer of Dissolved Organic Carbon via Sea Spray Aerosol during Phytoplankton Bloom

There are many comments in their sequence of appearance which needs careful attention before the paper can be reconsidered for publication.

Line 20. Authors claim to have made comprehensive study, but there is a single quantitative number in the abstract with all statements being descriptive. The value of the study is not in attempting various things, but rather its quantitative outcomes.

Author Reply

We have revised the Abstract and incorporated more quantifiable details.

Page 1, lines 16-24

In this study, we induced a phytoplankton bloom using coastal seawater and employed various characterization tools to investigate the sea-to-air transfer of DOC. During the phytoplankton bloom, the dynamic accumulation of DOC in coastal seawater leads to fluctuations in the number concentration and mean geometric diameter of SSA by approximately 60% and 30%, respectively; in the meantime, the enrichment factors of DOC in sea surface microlayer, supermicron SSA, and submicron SSA can increase up to ~5-fold, 10-fold, and 30-fold, respectively. The sea-to-air transfer of DOC depends on its selective enrichment as well as the fractionation process at the air-water interface. Interestingly, the particulate property of operationally defined DOC still needs to be considered during SSA formation. Additionally, the sea-to-air transfer of DOC is influenced by the synergistic effects of phytoplankton production and heterotrophic microbial processing, rather than being solely dependent on chlorophyll-a concentration.

Line 33. All aerosol with a possible exception of black carbon mitigates global warming. Why making SSA exceptional here?

Author Reply

Although all aerosols except black carbon can mitigate global warming, sea spray aerosol (SSA) play a more prominent role in this mitigation. Covering approximately 71% of the Earth's surface, the ocean emits SSA, which represent the largest natural mass source of aerosols worldwide. These aerosols enhance the brightness of marine clouds, reflecting more sunlight back into space (Quinn et al., 2015). Due to the strong scattering properties of sea salt components, international organizations and institutions have advocated for the development of marine cloud brightening programs to mitigate global warming, with a particular focus on artificially enhancing atmospheric SSA emissions (Diamond et al., 2022; Feingold et al., 2024; Li et al., 2025). Therefore, we provide descriptions regarding the SSA's mitigation of global warming here. The related text has been revised.

Page 2. Lines 35-39

Since SSA can directly or indirectly scatter solar radiation by acting as cloud condensation and ice nuclei, it has considerable potential for net climate cooling and has therefore been prioritized as a key focus of the marine cloud brightening program (Cochran et al., 2017; Ahlm et al., 2017; Diamond et al., 2022; Feingold et al., 2024). However, there are still significant uncertainties associated with the effects of SSA on climate, particularly in terms of aerosol-cloud interactions.

Line 74. What was the qualifier that the collected water did not have an already finished bloom or not enough phytoplankton to start the bloom in the first place?

Author Reply

The Chl-a concentration data from the Copernicus Marine Data Store was determined to know whether the collected seawater has undergone a phytoplankton bloom (https://data.marine.copernicus.eu/products). The figure below illustrates the average Chl-a concentration data for the Yellow Sea and Bohai Sea in China from May 18 to May 31, prior to our experiments (June 1 to June 18). During this period, the average Chl-a concentration at the seawater sampling location (120°33’28” E, 36°6’37” N) was 0.54 ± 0.04 mg m^{-3}, similar with our measurement of 0.43 ± 0.05 mg m^{-3} on Day 1. These concentrations are lower than that typically observed during coastal phytoplankton blooms (Delgado et al., 2023; Radoman et al., 2022). Therefore, we consider that the coastal seawater samples had not undergone a significant phytoplankton bloom prior to our experiments.

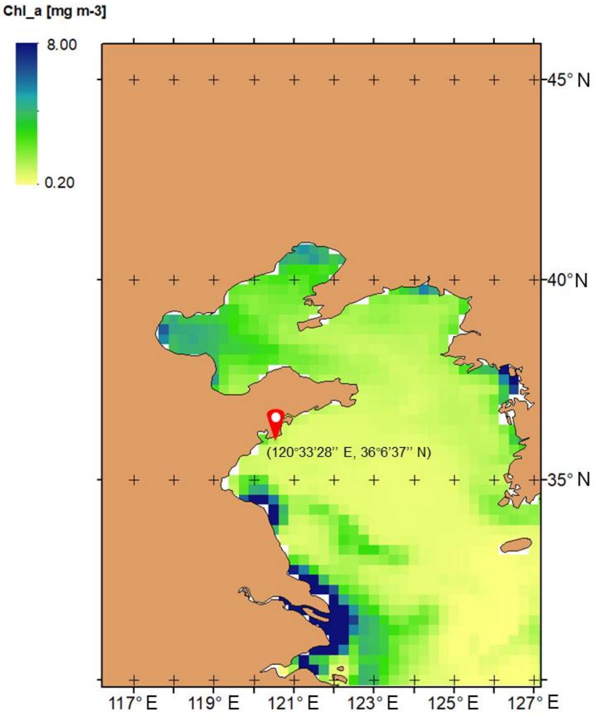


Figure R1. Coastal seawater sampling locations and the average chlorophyll-a concentration (0.54 ± 0.04 mg m^{-3}) in seawater two weeks prior to sampling.

The following texts have been added the revised manuscript and revised supplement.

Manuscript, Page 3, lines 77-79

Seawater was collected on May 31, 2024, at Shazikou Pier (120°33’28” E, 36°6’37” N) Qingdao, China, and immediately transported to the laboratory. Satellite-derived chlorophyll-a (Chl-a) concentrations indicate that no previous phytoplankton blooms had occurred at the sampling sites. Details are presented in the Supplement.

Supplement, Page 2, lines 17-23

S1. Assessing the phytoplankton bloom in the costal seawater

The Chl-a concentration data from the Copernicus Marine Data Store was determined to check whether the collected seawater has undergone a phytoplankton bloom (https://data.marine.copernicus.eu/products). Fig. S1 illustrates the average Chl-a concentration data for the Yellow Sea and Bohai Sea in China from May 18 to May 31, prior to our experiments (June 1 to June 18). During this period, the average Chl-a concentration at the seawater sampling location (120°33’28” E, 36°6’37” N) was 0.54 ± 0.04 mg m^{-3}, similar with our measurement of 0.43 ± 0.05 mg m^{-3} on Day 1. These concentrations are lower than that typically observed during coastal phytoplankton blooms (Delgado et al., 2023; Radoman et al., 2022). Therefore, the coastal seawater samples have not undergone a significant phytoplankton bloom prior to our experiments.

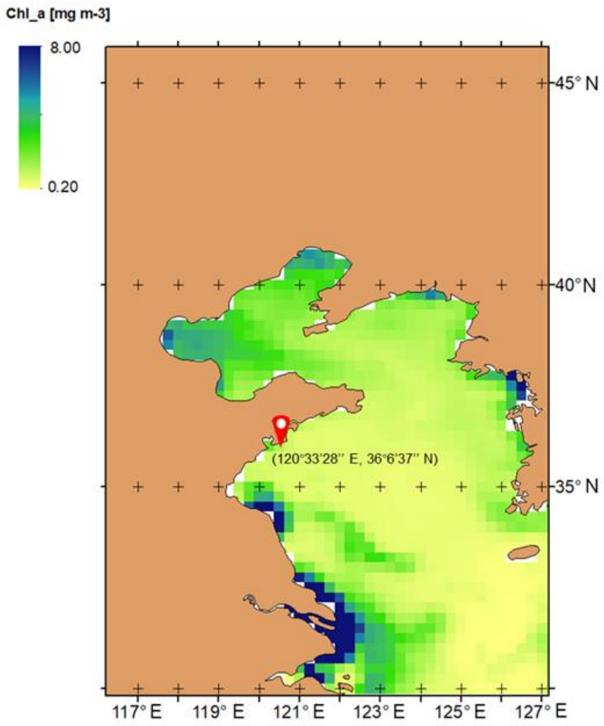


Figure S1. Coastal seawater sampling locations and the average chlorophyll-a concentration (0.54 ± 0.04 mg m^{-3}) in seawater two weeks prior to sampling.

Line 104. What is the meaning and the rationale of SML using continuous waterfall and, therefore, continuous disruption of SML? Maybe it is better to use interfacial (micro)layer?

Author Reply

Considering that sea surface microlayer (SML) will be continuously disrupted during the waterfall operation, we collected SML using the glass plate method within 30 minutes prior to the waterfall operation. At this point, the samples collected belong to the SML since it remained undisturbed.

The formation of SSA always requires disruption of SML. Due to air entrainment or bubble rupture, the interfacial microlayer during SSA formation undergoes real-time changes, complicating the acquisition of representative samples. Therefore, we consider that SML obtained under calm conditions may be more representative. We have provided an explanation in the revised manuscript.

Page 4, lines 117-118

Prior to the waterfall operation, seawater and sea surface microlayer (SML) samples were collected in SSA simulation tank while maintaining a uniformly mixed and calm state.

Line 114. How various samplers (SMPS, Dekati) sampled from the tank? Common/separate inlets?

Author Reply

We have presented the connection configuration between the SSA simulation tank and various samplers during the nascent SSA experiment using a schematic diagram. This is updated in the revised manuscript and the revised Supplement.

Manuscript, Page 4, lines 112-113

More information on the schematic diagram of the nascent SSA experiments and the connection between the tank and different samplers is provided in Fig. S3.

Supplement:

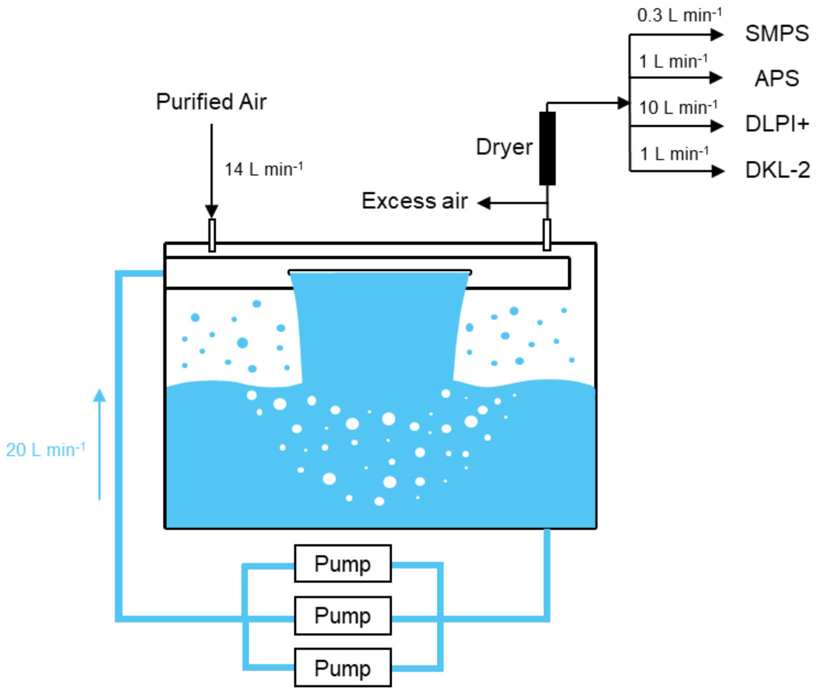


Figure S3. A schematic diagram of the nascent SSA experiments.

Line 136. Was this assumption confirmed given all available measurements of Na? There have been reports that Na or other sea salt ions do not remain the same during the transfer in dynamically enriched sea water. If Na is constant, then why Na notation is different in nominator and denominator? If the same, they would cancel out.

Author Reply

The mass concentration of Na^+ in seawater, at the sea surface microlayer, and in sea spray aerosols is generally considered to be constant. Consequently, it can act as an indicator for the enrichment levels of specific substances during sea-to-air transfer. Previous studies have shown that Ca^{2+} and Mg^{2+} can enrich in SSA, because organic matter in seawater can form complexes with these divalent cations, thereby promoting their enrichment in SSA (Carter-Fenk et al., 2021; Hasenecz et al., 2019; Schill et al., 2018). Except for the potential instability in Na^+ concentrations during sea-to-air transfer caused by sodium salt precipitation during sea ice formation in polar regions (Hara et al., 2012), to our knowledge, there is no further reports on the significant enrichment or depletion of Na^+ during the sea-to-air transfer. This has been addressed in the revised manuscript.

Page 6, lines 155-157

Previous studies have shown that the concentration of Na^+ is typically constant during the sea-to-air transfer. Therefore, the enrichment factor (EF) relative to the concentration of Na^+ can quantify the degree of organic matter enrichment in this transfer (Quinn et al., 2014; Quinn et al., 2015; Jayarathne et al., 2016).

The enrichment factor is defined as the concentration ratio of the target substance (X) to that of Na^+ in SSA particles or SML relative to the ratio in seawater (Eq. (1)):

$$\mathrm{EF}=\frac{(\mathrm{X})_{\mathrm{SSA\ or\ SML}}/(\mathrm{Na^+})_{\mathrm{SSA\ or\ SML}}}{(\mathrm{X})_{\mathrm{SW}}/(\mathrm{Na^+})_{\mathrm{SW}}} \qquad (1)$$

Taking the DOC enrichment factor as an example, the value of the denominator $(\mathrm{DOC})_{\mathrm{SW}}/(\mathrm{Na^+})_{\mathrm{SW}}$ can be calculated by directly measuring the DOC concentration and Na^+ concentration in seawater. For the numerator $(\mathrm{DOC})_{\mathrm{SSA}}/(\mathrm{Na^+})_{\mathrm{SSA}}$, constrained by the minimum sample volume limitations of relevant detection instruments, this value cannot be calculated by directly measuring the DOC concentration and Na^+ concentration within SSA. Instead, SSA samples were extracted with 10 mL ultrapure water, followed by measuring the DOC concentration and Na^+ concentration in the extract. The ratio of DOC concentration to Na^+ concentration in the extract then represents the value of numerator $(\mathrm{DOC})_{\mathrm{SSA}}/(\mathrm{Na^+})_{\mathrm{SSA}}$. When calculating the enrichment factor in SML, Na^+ concentration in SML and that in seawater can be directly offset. Thus, the enrichment factor formula can be further simplified to (Eq. (2)):

$$\mathrm{EF}=\frac{(\mathrm{X})_{\mathrm{SML}}}{(\mathrm{X})_{\mathrm{SW}}} \qquad (2)$$

On the one hand, Eq. (1) better reflects the definition of the enrichment factor. On the other hand, to maintain continuity with previous studies (Quinn et al., 2015; Jayarathne et al., 2016; Quinn et al., 2014; Salter et al., 2016), Eq. (1) was maintained in the manuscript.

Line 196. Last two sentences are trivial and out of point. POC reaches similar concentration during the bloom and is major component too. Given only two components in TOC, one is obviously higher than the other and makes the "major" claim obvious or trivial.

Author Reply

These sentences have been removed from the revised manuscript.

Line 220. The key question is the source of diethyl phthalate because of (1) plastic tank and plumbing or (2) biological? Was the source addressed by conducting blank experiment?

Author Reply

We hypothesize that this contaminant may be derived directly from the collected coastal seawater, which is supported by the following three points of evidence:

(1) Prior to the usage, the home-made SSA simulation tank was thoroughly cleaned according to the procedure described by Stokes et al. (Stokes et al., 2013). Briefly, the entire system was initially flushed with 100% isopropyl alcohol for one hour while the tank was scrubbed with a brush. This process was subsequently followed by a one-hour rinse with a 10% isopropyl alcohol and deionized water solution. Finally, the entire system was subjected to multiple rinses with deionized water, each lasting one hour. The surface tension of the deionized water reached 72 mN m^{-1} after the final rinse before we proceeded with the subsequent experiments. The aforementioned cleaning procedure ensured the removal of surface-active contaminants from the system.

(2) Based on existing literature, diethyl phthalate is employed as a plasticizer in the synthesis of polyvinyl chloride, polystyrene, and polylactic acid to improve their flexibility and plasticity (Yan et al., 2021; Paluselli et al., 2019; Mao and He, 2023; Zhao et al., 2022; Ye et al., 2020). The body of our SSA simulation tank was constructed from polymethyl methacrylate, while the pipe connections were comprised of silicone. The containers utilized to promote phytoplankton blooms were made of polycarbonate. The synthesis of these materials does not necessitate the use of phthalate plasticizers; therefore, our experimental vessels and piping cannot be considered to be direct sources of diethyl phthalate.

(3) The Shazikou Pier, from which coastal seawater is collected, serves as a significant fishing port. The surrounding waters may be adversely affected by plastic waste, fishing nets, and plastic packaging, which could potentially result in phthalate contamination (Akhbarizadeh et al., 2017; Mi et al., 2019). In fishing ports along China's Yellow and Bohai Seas, diethyl phthalate is frequently identified as the phthalate plasticizer with the highest concentration (Liu et al., 2021). Due to their high octanol-water partition coefficient and low water solubility, these compounds tend to accumulate in the sea surface microlayer relative to the bulk seawater.

We have added the source analysis of diethyl phthalate in the revised manuscript and the revised Supplement.

Manuscript, Page 9, lines 245

Detailed mass spectrometry and source analysis can be found in the Supplement.

Supplement, Page 6, lines 134-159

We hypothesize that this contaminant may be derived directly from the collected coastal seawater. This is supported by the following three points of evidence:

(1) Prior to the usage, the home-made SSA simulation tank was thoroughly cleaned according to the procedure described by Stokes et al. (Stokes et al., 2013). Briefly, the entire system was initially flushed with 100% isopropyl alcohol for one hour while the tank was scrubbed with a brush. This process was subsequently followed by a one-hour rinse with a 10% isopropyl alcohol and deionized water solution. Finally, the entire system was subjected to multiple rinses with deionized water, each lasting one hour. The surface tension of the deionized water reached 72 mN m^{-1} after the final rinse before we proceeded with the subsequent experiments. The aforementioned cleaning procedure ensured the removal of surface-active contaminants from the system.

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Line 225. Why would rapid increase of surface tension be expected with rapid increase in DOC? Why not the opposite expectations given known surfactant properties of certain DOC species?

Author Reply

Theoretically, the presence of organic matter in pure water typically leads to a decrease in its surface tension. The initial presence of diethyl phthalate in the sea surface microlayer (SML) significantly reduced its surface tension. During phytoplankton blooms, diethyl phthalate may undergo biosorption or microbial degradation, resulting in reduced concentrations in the SML sample. The increase in surface tension due to reduced diethyl phthalate concentrations may outweigh the decrease in surface tension caused by phytoplankton releasing more DOC. Consequently, the surface tension of SML sample exhibited a significant increase during the initial phase of the phytoplankton bloom. The related description has been corrected in the revised manuscript:

Page 9, lines 245-248

Surface tension of the SML increased rapidly during the initial phase, being potentially associated with declining concentrations of diethyl phthalate. This compound was undetectable in the SML sample on Day 9, which could result from the biosorption or transformation by marine microorganisms (Liang et al., 2024; Gao and Chi, 2015).

Line 240. The sentence is not supported by evidence or is trivial, because surfactant accumulation in SML will always affect surface tension given the right compounds and concentrations.

Author Reply

This sentence has been removed from the revised manuscript.

Line 256. Is the low EF in SML not the consequence of Na concentration in SML which is different from the bulk as I enquired above. If Na was already depleted in SML due to DOC enrichment, one would easily get diminished EF in SML. What was EF in SML relative to Na in bulk sea water? Also how is it possible that highest EF on DAY5 causes surface tension to return to water tension? Why EF is important in the first place if it has no relevance to surface tension? There are so many questions and consequential interpretations that it is very difficult to assess the entire section of EF.

Author Reply

The concentration of Na^+ in seawater and SML is typically constant (Jayarathne et al., 2016). The SML accumulates organic matter with surface-active properties. These surface-active substances readily aggregate at the air-water interface due to their hydrophobic/hydrophilic structure (Cheng et al., 2020). Generally, organic matter with stronger surface activity or greater hydrophobicity exhibits higher enrichment levels in the SML. Na^+, however, is a non-surfactant electrolyte lacking the ability to form complexes with organic matter like divalent cations Ca^{2+} and Mg^{2+}. Consequently, it possesses no driving force to aggregate at the air-water interface. Since Na^+ concentrations remain constant in both seawater and the SML, Eq (2) can be directly applied in practical calculations:

$$EF=\frac{(X)_{SML}}{(X)_{SW}} \qquad (2)$$

We have clarified in the revised manuscript that the concentration of Na^+ remains constant during the sea-to-air transfer.

Page 6, lines 155-157

Previous studies have shown that the concentration of Na^+ is typically constant during the sea-to-air transfer. Therefore, the enrichment factor (EF) relative to the concentration of Na^+ can quantify the degree of organic matter enrichment in this transfer (Quinn et al., 2014; Quinn et al., 2015; Jayarathne et al., 2016).

In the SML, the enrichment factor of DOC does not show a perfect correlation with surface tension. We first demonstrated that, in the presence of diethyl phthalate at concentrations ranging from 1.5 to 2 μM, the surface tension of water can decrease to 65.84 ± 0.36 mN m^{-1} (See Fig. S5 in the Supplement). This suggests that the concentration of this substance influencing surface tension could be extremely low. The DOC enrichment factor is calculated as the ratio of DOC concentration in the SML (typically ranging from 700 to 2200 μM C) to that in seawater (generally between 300 and 700 μM). Since predicted diethyl phthalate concentrations are far below total DOC levels, its impact on the DOC enrichment factor is negligible.

During the initial phase of phytoplankton blooms, the low surface tension observed in SML samples may arise from organic matter, including diethyl phthalate, that pre-existed in coastal seawater. However, as the bloom progresses, these pollutants—which significantly reduce surface tension—undergo degradation or adsorption, resulting in declining concentrations and a restoration of surface tension. Fig. S4 in the Supplement displays that diethyl phthalate was undetectable in the SML sample collected on Day 9 when compared to samples from Day 1.

Surface tension primarily influences the rupture behavior of surface bubbles, with its most significant effect being on the particle size distribution of SSA. The enrichment factor reflects the sea-to-air transfer capacity of organic matter, primarily affecting the chemical composition and morphological structure of SSA. Surface tension and the enrichment factor synergistically govern SSA formation in the aforementioned aspects. This has been addressed in the revised manuscript.

Page 10, lines 270-274

The highest EF in the SML was observed on Day 5, during which the increase in the EF of DOC was not contradictory to the increase in surface tension of the SML samples. The rise in surface tension of the SML samples could be attributed to a reduction in a highly surface-active organic pollutant. However, because its concentration is extremely low (below 2 μM, seeing Fig. S5), it does not significantly impact the EF of the DOC (ranging from 700 to 2200 μM C) in the SML samples.

Line 265. The most significant EF and potential implications are with submicron particles and not SML unless corroborated as commented above.

Author Reply

Our experimental results show that during phytoplankton blooms, the DOC enrichment factor more significantly in submicron SSA increases than in the SML. Carbon isotope studies indicate that the organic matter enriched in submicron SSA closely resembles that in the SML, suggesting that the SML functions as a "pre-enrichment" zone for DOC enriching into submicron SSA (Crocker et al., 2022). However, in our experiments, the DOC enrichment factors in the SML and in submicron SSA did not show expected temporal consistency. Therefore, in the subsequent results and discussion, we sought to qualitatively and quantitatively analyze different types of DOC using various methods to investigate this temporal misalignment. This has been clarified in the revised manuscript.

Page 11, lines 274-280

Carbon isotope studies indicate that the SML functions as a "pre-enrichment" zone for DOC enriching into SSA, especially for submicron SSA (Crocker et al., 2022). However, the highest EFs in submicron and supermicron SSA were on Day 7 (given the low EF of DOC in the SML on Day 9, it is unlikely that DOC's EF in SSA at this time would reach its highest value), and the morphological structural images of SSA also illustrate a significant enhancement in DOC enrichment (Fig. S4). The time series of DOC's EF in the SML and SSA do not align, indicating that the sea-to-air transfer of DOC is likely to be complex. Temporal fluctuations in DOC compositions and concentrations triggered by biological cycles during phytoplankton blooms may play an important role in influencing DOC's sea-to-air transfer.

Line 270. The whole paragraph is speculative as to what the implications may be as the references were gathered to the authors liking to support the narrative. I do not necessarily disagree, but there is no solid proof to the discussion or no added value of the study results, just free-style considerations.

Author Reply

In the revised manuscript, we have removed this paragraph and clarified that the enrichment of DOC in SSA significantly influences the climatic impact of SSA, thus leading into our subsequent research on the patterns of sea-to-air transfer for various types of DOC.

Page 11, lines 287-292

Compared to particle size distribution, the significant variation in DOC's EF in SSA may have more profound implications for SSA's climate effects. The widely reported phenomenon of organic matter enveloping inorganic salt cores (as illustrated in Fig. S6) significantly influences the cloud condensation nucleation activity (Bates et al., 2020; Lee et al., 2020; Cravigan et al., 2020) and ice nucleation activity of SSA (Pandey et al.; Hartmann et al., 2025), with specific effects depending on the type of organic matter. Although the EF of DOC in SSA reflects the overall characteristics of sea-to-air transfer pattern, more detailed studies are still needed to elucidate the specific pattern of different organic species.

Line 306. Precision and accuracy cannot be attained at 0.1%, so should be reduced to two significant digits in percentages. Furthermore, is 4% difference statistically significant from Day1 & 9? If not it should be reported that there was no significant difference up until Day9, but increased on Day 18.

Author Reply

From a computational perspective, maintaining a precision of 0.1% is critical. This value is calculated as the number of common molecular formulas divided by the number of distinct molecular formulas among the four sample types. For example, on Day 1, utilizing the molecular formula assignment method outlined by Schum et al. (Schum et al., 2020), the mass spectrometry analysis of these four sample types yielded a total of 4,807 distinct molecular formulas. Among these, 596 formulas were found to be shared across all four sample categories. Consequently, the proportion of shared molecular formulas among the four sample categories is 596 out of 4,807, which is approximately 12.4%. Rounding this value to two significant digits (*i.e.,* 12%) would result in insufficient precision, as the 0.4% difference reflects a meaningful quantity of common molecular formulas that should not be overlooked in our analysis.

Following an independent samples t-test, no significant difference was observed between the rates of 12.4% on Day 1 and 16.2% on Day 9. This finding has been addressed in the revised manuscript:

Page 12, lines 318-320

For instance, our results show that the proportion of shared organic molecular formulas in SW, SML, submicron SSA, and supermicron SSA was 12.4% on Day 1, 16.2% on Day 9, and significantly increased to 26.3% on Day 18.

Line 310. suggested, not confirmed, as one study is not the ultimate confirmation.

Author Reply

This has been corrected.

Page 12, lines 324-325

A previous study has suggested that the DOC produced by algae consists of two major aliphatic groups: proteins and saccharides (Suo et al., 2024).

Line 349. There is no consideration or discussion of POC enrichment and now one is considered for the other which is an apparent ambiguity and confusion. POC enrichment is super important and which is almost completely neglected in the paper.

Author Reply

We recognize that the enrichment of particulate organic carbon (POC) is an important research topic. However, since this manuscript primarily addresses the sea-to-air transfer pattern of DOC, exploring the pattern of POC is beyond the scope of this study.

In fact, the enrichment of POC in the SML or SSA has not been extensively discussed here. Instead, we have observed a noteworthy phenomenon that has not been previously reported in the literature: the fluorescence signal intensity of three fluorescent components in seawater showed a significant positive correlation with DOC concentration in seawater, whereas the fluorescence signal intensity of these components in the SML demonstrated a significant positive correlation with POC concentration in seawater. This finding implies that DOC within the SML may directly result from the degradation of POC present in seawater. This discovery provides essential evidence for our subsequent explanation regarding the lack of significant positive correlation between the three fluorescent components in seawater and those in the SML.

Line 351. Significance of the correlation has a measure ($P<0.0X$), meanwhile, near-significance is arbitrary and should be deleted.

Author Reply

This has been deleted, and the related text revised.

Page 14, lines 364-366

Within the same type of samples (seawater, SML, submicron SSA, or supermicron SSA), PRLIS, HULIS 1, and HULIS 2 often maintained significant positive correlations; however, when sample types differ, significant correlations between them are rarely observed (Fig. 5d).

Line 352. Why weaker correlation is important? Only significant correlations are worth exploring and reporting. Weak and statistically insignificant correlation is irrelevant.

Author Reply

We acknowledge that comparing the correlations strength without statistical significance is inappropriate. This statement has been revised to focus on analyzing why significant correlations do not exist between the three fluorescent DOC components in SML and seawater samples.

Page 14, lines 366-368

In seawater and SML samples, the non-significant correlations may be due to the fact that these three organic fractions originate from different organic carbon pools in seawater.

Line 356. This sentence is a pure speculation as weak correlations do not merit attention altogether.

Author Reply

In the revised manuscript, we no longer compare the correlations strength but instead analyze the possible reasons why no significant correlations exist in submicron SSA and supermicron SSA.

Page 14, lines 368-372

For submicron and supermicron SSA, the non-significant correlation may result from DOC undergoing different air-water interfacial fractionation processes (Quinn et al., 2015). The concentration variations of DOC resulting from multiple enrichment processes at different air-water interfaces may obscure its consistency with the concentration variations induced by microbial activity in seawater. Typically, DOC in submicron SSA undergoes more pronounced interfacial fractionation than DOC in supermicron SSA (Crocker et al., 2022).

Line 359. Good positive correlation has a number and statistical significance. Otherwise, does not matter.

Author Reply

The related sentence has been removed from the revised manuscript.

Line 461. It is fair to state that Chl-a concentration may not be the best predictor of organic matter sea-to-air transfer, but that statement requires a proposition of a better metrics, otherwise, the former statement is pointless. How one can retire something without proposing the alternative.

Line 466. The authors must suggest what the alternative parameter would reduce the uncertainties, better from their study.

Author Reply

We are addressing the two comments above in a joint reply, as we believe that merely highlighting the limitations of Chl-a in predictive models without suggesting alternative indicators would undermine the validity of our argument.

Although our study utilized various detection methods to investigate the sea-to-air transfer transport patterns of dissolved organic carbon during phytoplankton blooms, leading to several novel findings, a definitive alternative based solely on our research cannot be proposed. After thoughtful consideration, we have revised our statements regarding Chl-a concentrations and provided several recommendations based on the findings of this study.

Page 19, lines 475-483

Although there are ongoing debates about the effectiveness of Chl-a concentrations in predicting the organic spray emissions (O'dowd et al., 2008; Bates et al., 2012; Rinaldi et al., 2013; Quinn et al., 2014), it can be asserted that Chl-a, as readily available from global satellite data, remains essential in these predictions, especially when it is constrained with appropriate parameters. The current study indicates that Chl-a is a driven factor to regulating the sea-to-air transfer of DOC. However, the influence of microbial cycling and SSA formation mechanisms complicates this regulatory role, preventing it from manifesting as a straightforward linear relationship. For the future organic spray emission models, it is advisable to incorporate time-series variations in Chl-a concentrations, as they could reflect the progression of phytoplankton blooms. Additionally, careful consideration should be given to dividing different biogeochemical ocean regions, which includes identifying both Chl-a concentration control regions (O'dowd et al., 2008) and non-control regions (Quinn et al., 2014), to enhance the spatiotemporal resolution.

Suppl. S1. It is important to note separation distance between the air inlet and outlet.

Author Reply

This is provided in the Supplement:

Page 2, lines 30-31

The distance between the air inlet and the air outlet is set to 40 cm.

Suppl. S5. Where tests conducted to know whether phthalates (major compounds in a variety of plastics) did not significantly contribute to the observed SSA composition?

Author Reply

We have added the explanation regarding this issue in the revised Supplement. Fig. S4 includes the detection results of diethyl phthalate in submicron SSA and supermicron SSA on Day 1.

Page 6, lines 133-137

Fig. S4a shows that DEP peaks also appeared at the same elution time in both submicron SSA and supermicron SSA samples collected on Day 1, indicating that DEP is detectable in SSA collected on that day. Due to the very low concentration of DEP compared to the total DOC concentration, the signal intensity of DEP at m/z 221.0813 accounted for 0.93% and 0.38% of the total ion current signal intensity (m/z range 150–1000) in the submicron and supermicron SSA samples on Day 1, respectively, indicating that DEP does not significantly contribute to the SSA composition.

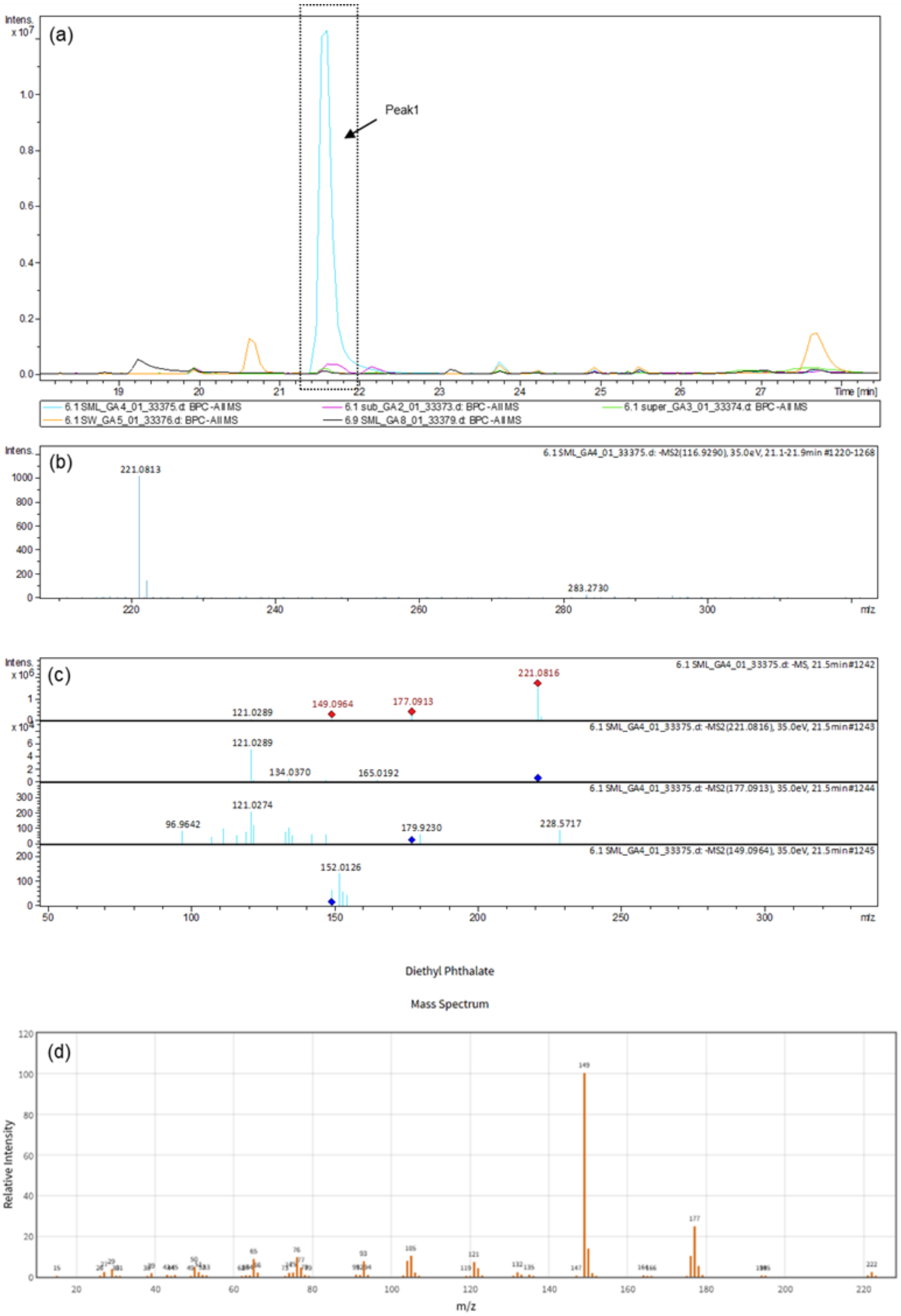

Figure S4. Identification of phthalate esters in initial SML samples through mass spectrometry. (a) Base peak chromatogram for three samples: SML sample on day 1 (blue line), seawater sample on day 1 (orange line), submicron SSA sample on Day 1 (purple line), supermicron SSA sample on Day 1 (green line), SML sample on day 9 (black line); (b) Primary contributing ion of Peak 1 and its secondary mass spectrometry fragments; (c) Standard spectrum of diethyl phthalate from NIST Standard Reference

Database 69: NIST Chemistry WebBook (https://webbook.nist.gov/chemistry). Note that the standard spectrum employs electron ionization, whereas we utilize an electrospray ionization source. Nevertheless, certain characteristic ions from the standard spectrum remain useful for our identification.

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