Authors' response to the first set of egusphere-2025-4207 Referees' and community comments

We deeply appreciate the Editor, the Anonymous Referees and Ian Jenkinson for their thorough review of our manuscript. Our manuscript has been revised according to the Referees' and Ian Jenkinson's 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 Ian Jenkinson.

A very interesting and important paper!

However, quoting Lines 190--219, "Several studies have found that phytoplankton blooms can result in the formation of mucus on the water surface, which is typically an excessive accumulation of extracellular polysaccharides (Ternon et al., 2024; Medina-Pérez et al., 2021). In contract, this can increase the viscosity of SML and potentially enhance its surface tension (Jenkinson and Sun, 2010). From day 1 to day 5, the rapid increase in the surface tension of SML samples appears to be related to the rise in their saccharide concentration (see in Fig. 6a).".

As the authors say, mucus, secreted by organisms such as phytoplankton, consists of polymers can indeed increase viscosity of seawater. However, it tends to reduce surface tension below the value for "pure" (i. e. organics-free) seawater about 74 mN.m-1, not enhance (increase) it. As shown in the authors' Fig. 6d, the surface tension of SML water remained consistently less than that of subsurface water (SSW) by about 0.5 to 1 mN.m-1, consistent with enrichment in the SML. The much lower values at the beginning of the experiment remain enigmatic to me, unless they might have been caused by some tiny contaminant by a surfactant molecule such as detergent, often present on the surface of new apparatus. The subsequent increase could then have represented the incorporation of such a surfactant into other organic matter in the experiment, or its

conversion or utilization by organisms present. I think this small issue does not affect the validity of the rest of the presentation.

Author Reply

Thank you for your comment. We agree with your view that, compared to pure seawater, the presence of organic matter generally reduces surface tension. Since the sea surface microlayer (SML) typically contains higher concentrations of organic matter than subsurface water (SSW), the surface tension of SML was consistently lower than that of SSW in our experiments.

We can rule out the possibility of these compounds originating from our homemade SSA simulation tank. On the one hand, the new equipment was thoroughly scrubbed with a brush and rinsed multiple times with both tap and deionized water before the next SSA experiment. Even if contaminants remained, they are unlikely to have such a significant impact on the surface tension of SML. On the other hand, the surface tension of SML showed a gradual increase over the first five days. If these organic compounds originated from the equipment surfaces, we would expect the surface tension of the SML to rapidly return to its "original" state during the second SSA experiment.

Another possibility is that the surface-active organic matter may already exist in the coastal seawater's microlayer. To investigate this further, we analyzed the mass spectrometry data. Figure 1 shows the base peak chromatograms for three samples: SSW and SML sample on Day 1 and SML sample on Day 9. We observed a prominent peak (Peak 1) between elution times of 21.1 and 21.9 minutes in the SML on Day 1, significantly higher than in the seawater on Day 1 and SML on Day 9. Results in Figure 2(a) indicate that the ion at m/z 221.0813 is the primary contributor to Peak 1, with an assigned molecular formula of $C_{12}H_{13}O_4$ (error = 1.1 ppm). The results in Figure 2(b) show that the primary signal intensities in the secondary mass spectrometry fragments of the ion at m/z 221.0813 originate from m/z 177.0913 and 144.0964. These characteristic ions match those observed in the mass spectrum of diethyl phthalate (DEP) standard in the NIST Standard Reference Database (Figure 3). Therefore, Peak 1 can be primarily attributed to DEP. DEP is a commonly used plasticizer, and high

concentrations (in the range of mg L^{-1} or mg kg^{-1}) have been detected in various aquatic environments (Gani and Kazmi, 2016; Lu et al., 2023; Liang et al., 2024). Figure 1 reveals that high concentrations of DEP signal was present only in the Day 1 SML samples, while signals in the Day 1 seawater samples were very low. This could be due to DEP's low solubility in water and hydrophobic nature, which makes it significantly enriched in the SML. The DEP signal in the Day 9 SML sample was also low, likely due to reduced concentrations from biosorption or transformation processes (Gao and Chi, 2015; Liang et al., 2024). We further examined the relationship between DEP concentration and surface tension in artificial seawater (Figure 4). Even at extremely low concentrations, DEP can significantly reduce surface tension. For example, a DEP concentration of 2 µM can reduce surface tension to the initial SML value of 65.84 ± 0.36 mN m^{-1}, which is significantly lower than DOC concentration in the SML at that time. Therefore, the presence of DEP in the SML at the start of the experiment was a significant factor contributing to its low surface tension.

We consider that DEP was present in the seawater from the outset of the experiment, likely originating from coastal pollution or being introduced during seawater transport. SML consists of an extremely thin layer at the water's surface, ranging from 1 to 1000 µm, occupying a negligible fraction of the total seawater volume. Although DEP exhibited strong mass spectrometry signals in the day 1 SML sample, its signal in SSW sample on Day 1 were very low (Figure 1). This suggests that the concentrations of DEP in the seawater used in our study were actually quite low. As a result, we no longer consider its impact on phytoplankton blooms.

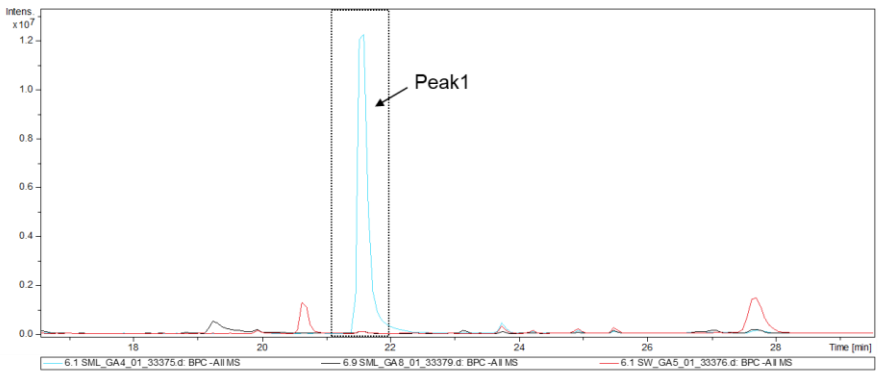


Figure 1. Base peak chromatogram for three samples: SML sample on day 1(blue line), seawater sample on day 1(red line), SML sample on day 9 (black line).

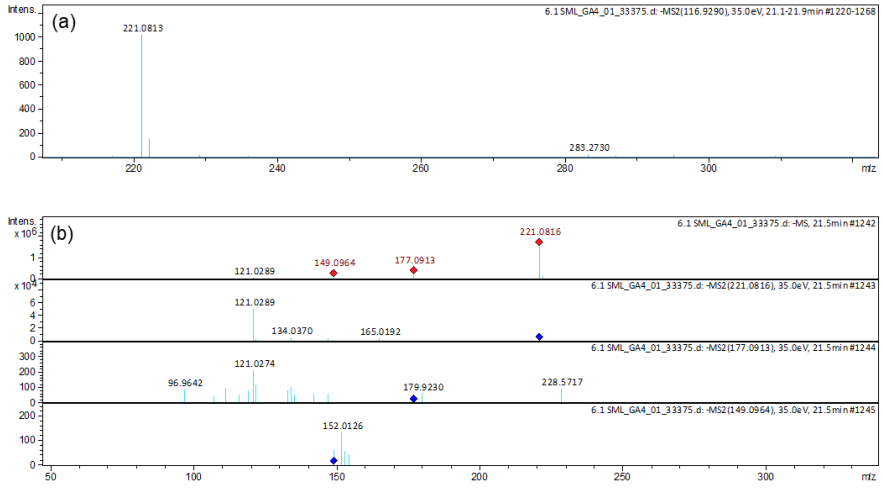


Figure 2. The primary contributing ion of Peak 1 and its secondary mass spectrometry fragments.

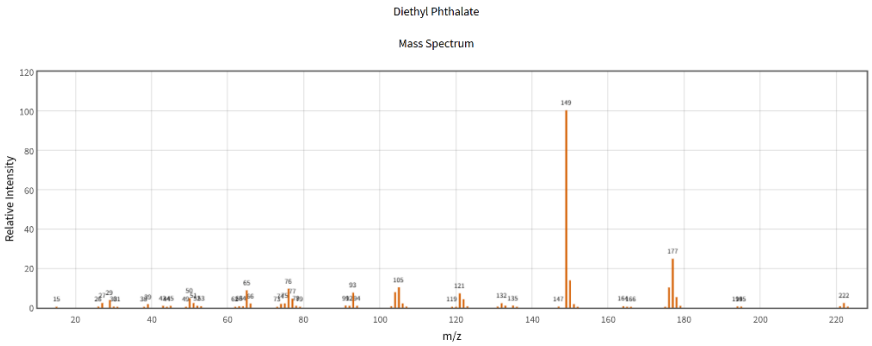


Figure 3. Standard spectrum of diethyl phthalate from NIST Standard Reference Database 69: NIST Chemistry WebBook (https://webbook.nist.gov/chemistry). Note that the standard spectrum employs electron ionization, whereas we utilize an electrospray ionization source. Nevertheless, certain characteristic ions from the standard spectrum remain useful for our identification.

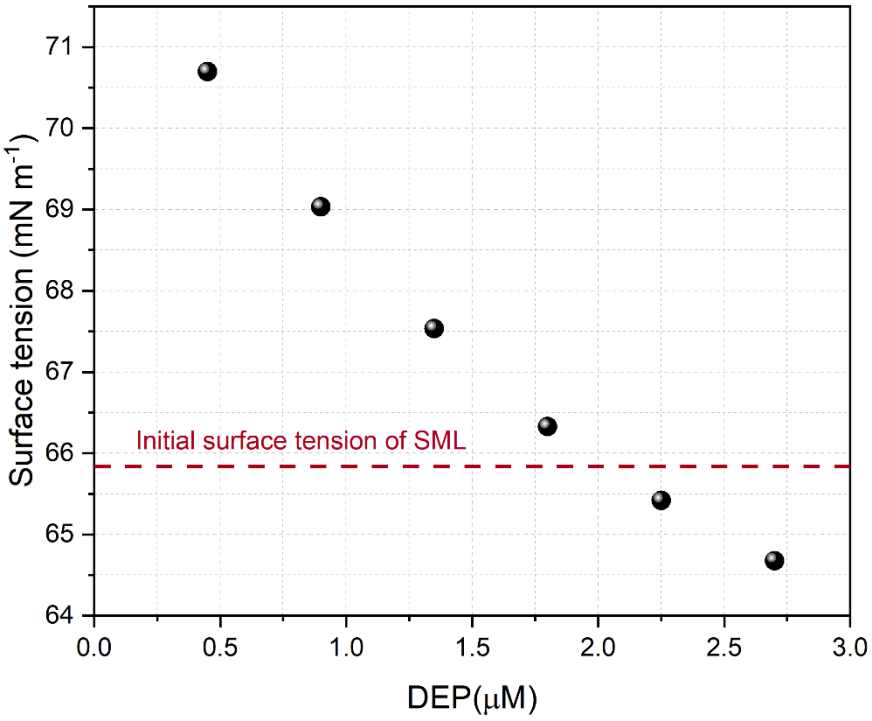


Figure 4. The relationship between different concentrations of DEP and the surface tension of artificial seawater.

We have revised the previous description in the manuscript.

Page 7, lines 186-196

As shown in Fig. 2d, the surface tension of SML at the start of the experiment was measured at 65.84 ± 0.36 mN m^{-1}, which exceeded our expectations. Using both primary and secondary mass spectrometry, we detected diethyl phthalate in the SML on Day 1. As common plasticizer, it is often found in coastal seawater and accumulates in SML due to its low solubility and hydrophobic nature (Lu et al., 2023), significantly reduce surface tension even at low concentrations (Figure S8). However, no diethyl phthalate was detected in bulk seawater on Day 1, which suggests that they likely do not influence phytoplankton blooms in bulk seawater. Detailed mass spectrometry analysis can be found in the Supplement. The surface tension of the SML increased rapidly from Day 1 to Day 5, possibly due to the rapid increase in DOC concentration in the SML during phytoplankton growth (Figure 3). Organic matter secreted by

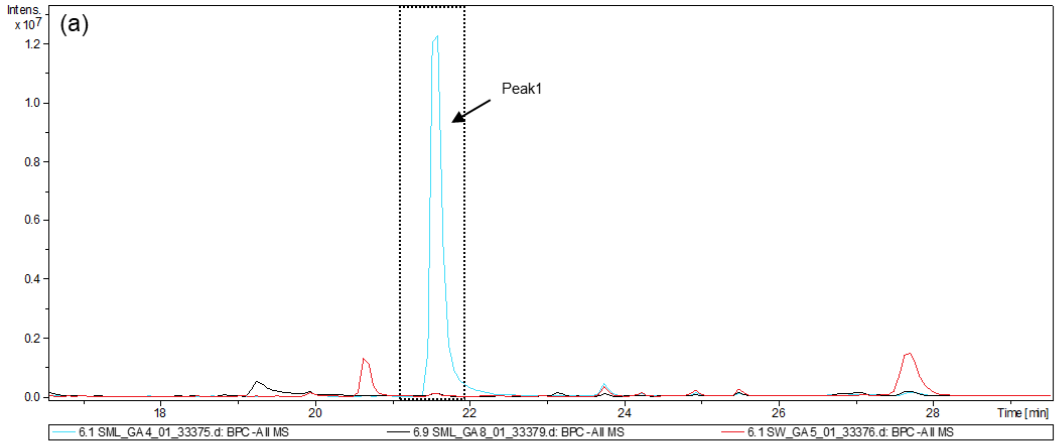
microorganisms can significantly affect the physical properties of the SML(Jenkinson and Sun, 2010; Ternon et al., 2024), which may partially mitigate the low surface tension observed at the beginning. Furthermore, the rapid increase in surface tension may also be linked to the biosorption of diethyl phthalate or transformation by marine microorganisms(Liang et al., 2024; Gao and Chi, 2015).

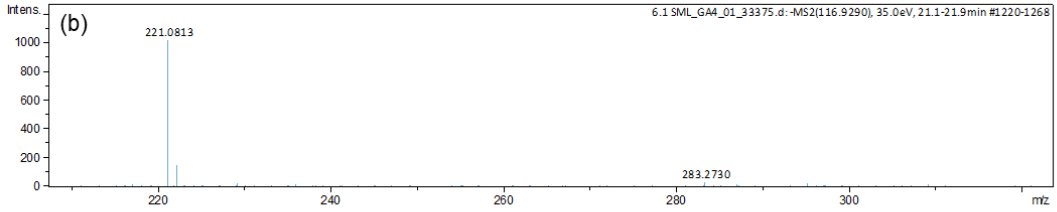
We have supplemented the content in the Supplement.

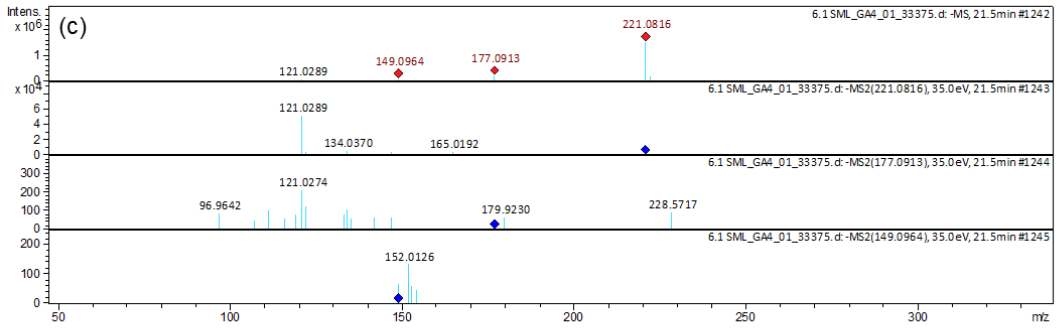
S5. Identification of phthalate esters in initial SML samples through mass spectrometry

Figure S7(a) shows the base peak chromatograms for three samples: SSW and SML on Day 1 and SML on Day 9. We observed a prominent peak (Peak 1) between elution times of 21.1 and 21.9 minutes in the SML on Day 1, significantly higher than in the seawater on Day 1 and SML on Day 9. Results in Figure S7(b) indicate that the ion at m/z 221.0813 is the primary contributor to Peak 1, with an assigned molecular formula of $C_{12}H_{13}O_4$ (error = 1.1 ppm). The results in Figure S7(c) show that the primary signal intensities in the secondary mass spectrometry fragments of the ion at m/z 221.0813 originate from m/z 177.0913 and 144.0964. These characteristic ions match those observed in the mass spectrum of diethyl phthalate (DEP) standard in the NIST Standard Reference Database (Figure S7(d)). Therefore, Peak 1 can be primarily attributed to DEP. DEP is a commonly used plasticizer, and high concentrations (in the range of mg L^{-1} or mg kg^{-1}) have been detected in various aquatic environments (Gani and Kazmi, 2016; Lu et al., 2023; Liang et al., 2024). Figure 1 reveals that high concentrations of DEP signal was present only in the Day 1 SML, while signals in the Day 1 seawater were very low. This could be due to DEP's low solubility in water and hydrophobic nature, which makes it significantly enriched in SML. The DEP signal in the Day 9 SML was also low, likely due to reduced concentrations from biosorption or transformation processes (Gao and Chi, 2015; Liang et al., 2024). We further examined the relationship between DEP concentration and surface tension in artificial seawater (Figure S8). Even at extremely low concentrations, DEP can significantly reduce surface tension. For example, a DEP concentration of 2 μM can reduce surface tension

to the initial SML value of 65.84 ± 0.36 mN m^{-1}, which is significantly lower than DOC concentration in the SML at that time. Therefore, the presence of DEP in the SML at the start of the experiment was a significant factor contributing to its low surface tension. Therefore, the presence of DEP in the SML sample at the start of the experiment was a significant factor contributing to its low surface tension.







Diethyl Phthalate

Mass Spectrum

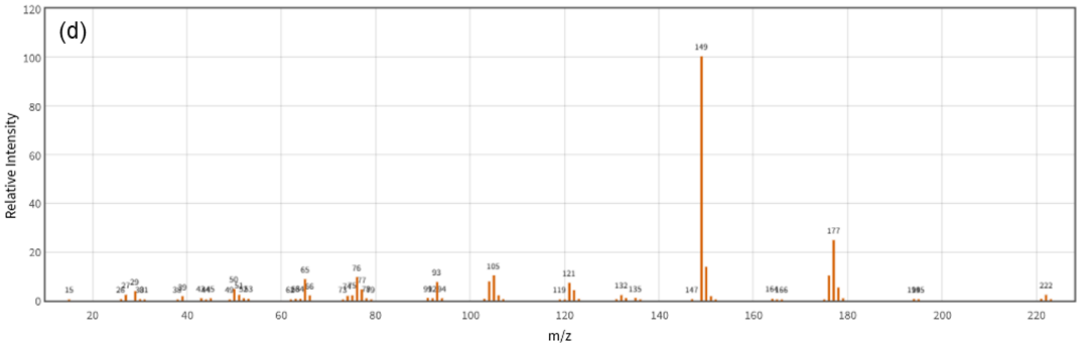


Figure S7. Identification of phthalate esters in initial SML samples through mass spectrometry (a) Base peak chromatogram for three samples: SML on Day 1(blue line), seawater on Day 1(red line), SML on Day 9 (black line); (b) The primary contributing ion of Peak 1 and its secondary mass spectrometry 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.

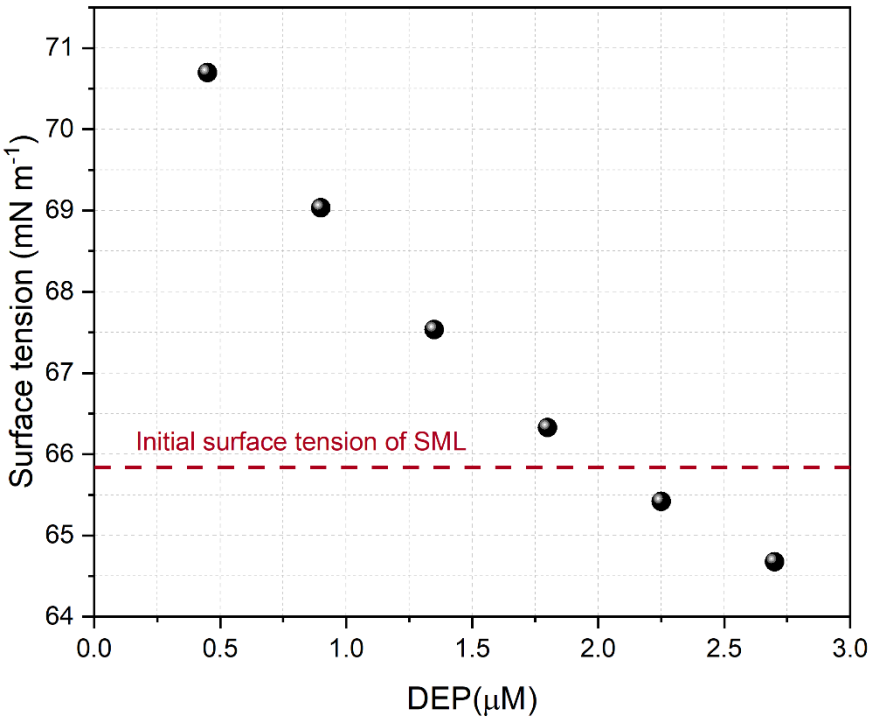


Figure S8. The relationship between different concentrations of DEP and the surface tension of artificial seawater

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Ternon, E., Dinasquet, J., Cancelada, L., Rico, B., Moore, A., Trytten, E., Prather, K. A., Gerwick, W. H., and Lemée, R.: Sea-Air Transfer of Ostreopsis Phycotoxins Is Driven by the Chemical Diversity of the Particulate Fraction in the Surface Microlayer, Environ. Sci. Technol., 58, 18969-18979, https://doi.org/10.1021/acs.est.4c06691, 2024.

Reply to the comments from Anonymous Referee #1

The aim of the paper is to highlight relationships between biological activity, DOC concentration in seawater/sea surface microlayer and sea spray aerosols.

I have several criticisms that are important to address before considering resubmitting this paper:

1. Except for the introduction, this paper is difficult to read, it is extremely long and the rationale of the study is not easy to grasp. The paper feels like adding a result to another without deep interpretation of the data. While presenting and discussing their results, the authors should make the reader understand why this experiment was performed? What was the main question? How does it relate to great questions in this field? What are the main advances obtained from this experiment? A huge effort of restructuration of the results and discussion part is needed.

Author Reply

We have carefully addressed the issues raised by the Referee by clarifying the rationale of the study, by expanding the results and discussion and by highlighting the major achievements of this study. Furthermore, we deleted unnecessary discussions and the excessive text throughout. Specifically, the following were explored:

(1) The final paragraph of the introduction presents the experimental workflow of this study and elaborates on how the molecular formula of dissolved organic carbon guides our subsequent investigations into proteins, saccharides, and humic substances.

Pages 2-3, lines 64-69

This study explored the implications of sea-to-air transfer of DOC during phytoplankton blooms. Firstly, the macroscopic effects of phytoplankton blooms on SSA formation and DOC enrichment were examined. Secondly, we employed high-resolution mass spectrometry to analyze the molecular profiles of DOC at different stages of sea-to-air transfer. Finally, by focusing on the most significant contributors, such as proteins, saccharides, and humic substances, the patterns of DOC sea-to-air transfer during phytoplankton blooms were investigated through a micro-to-macro approach.

(2) In Section 3.2 “Effects of DOC Variations on SSA Formation”, we have incorporated comparisons with previous research findings and added the atmospheric meaning of DOC fluctuations inducing changes in SSA particle size.

Page 8, lines 230-244

Previous studies have explored the relationship between surface tension and the formation of SSA by adding surfactants at varying concentrations (Sellegri et al., 2006; Tyree et al., 2007; Song et al., 2024). Our results are consistent with the findings of these studies, suggesting that increased surface tension is a key factor that contributes to decreasing the number concentration of SSA while increasing the geometric mean diameter. It was reported that increased surface tension tends to inhibit the instability of bubble film edge and the development capillary waves during bubble bursting, thereby reducing the number of film drops and increasing the droplet size (Wang and Liu, 2025; Lhuissier and Villermaux, 2012). High surface tension strengthens the attraction between liquid molecules at the surface, enabling the bubble film to withstand the pressure difference between the inside and outside of the bubble (Wu et al., 2021; Wu et al., 2022). This resulted in an extended bursting time of the bubbles population, leading to the appearance of a long-lasting foam layer on the water surface from Day 8 to Day 18 (Fig. S2), which inhibited the production of SSA. During phytoplankton blooms, surface tension is no longer solely influenced by the concentration of a single species, but by fluctuations in the composition and concentration of DOC driven by biological activity. In coastal waters where surfactants are abundant, surface tension changes are similar to those observed in SML during phytoplankton blooms may be widespread. Biologically induced DOC fluctuations will directly affect the particle size distribution of SSA, ultimately affecting SSA behavior such as atmospheric residence time and wet/dry deposition (Veron, 2015).

(3) In Section 3.3 “The Phytoplankton Bloom Promotes DOC Enrichment in SSA”, we elucidate that variations in DOC enrichment factors within SSA may have a profound impact on its climatic effects. This further leads us to focus our subsequent discussion on specific DOC species.

Page 10, lines 269-278

Compared to particle size distribution, the significant variation in DOC's EF in SSA may have more profound implications for SSA's climate effect. First, from a morphological perspective, dried SSA particles consistently exhibit an organic shell enveloping an inorganic salt core (Figure S3). Since organic matter generally has lower hygroscopicity than sea salt, the presence of an organic shell suppresses the hygroscopic growth of SSA particles, thereby affecting their cloud condensation nucleus activity. The extent of this suppression depends on the type and concentration of organic matter (Bates et al., 2020; Lee et al., 2020; Cravigan et al., 2020). Second, biogenic DOC is essential in influencing the ice nucleation activity of SSA, particularly polysaccharides and proteins, which serve as effective ice nucleation sites promoting ice crystal formation (Pandey et al.; Hartmann et al., 2025). Finally, the presence of DOC also alters SSA's radiative effects and atmospheric reactivity (Bertram et al., 2018). Based on the above, we conclude that the EF of DOC in SSA provides a macroscopic description, which requires more detailed efforts to elucidate the sea-to-air transfer pattern of different organic species.

(4) In Section 3.5, we highlighted that proteins, saccharides, and humic compounds identified through mass spectrometry may be the primary contributors to DOC during phytoplankton blooms.

Page 11, lines 309-316

As illustrated in Fig. 4c, lipid-like, protein-like, carbohydrate-like and lignin-like molecules accounted for the majority of organic molecules transferred from sea to air. Previous studies have confirmed that the DOC produced by algae consists of two major aliphatic groups: proteins and saccharides (Suo et al., 2024). Lignin-like molecules are widely considered to predominantly contribute to humic substances (Kim et al., 2003; Labeeuw et al., 2015). However, considering the effects of ionization mode and ionization efficiency, mass spectrometry results cannot directly reflect the relative abundance or concentration changes of specific DOC species. Therefore, additional methods were used to quantify the concentration fluctuations of protein, saccharides

and humic substances in DOC to better understand the link between DOC's sea-to-air transfer and biological activity.

(5) In Section 4 "Atmospheric Implications", we further expanded on the climate effects of saccharides and proteins in dissolved organic carbon on SSA.

Page 18, lines 454-4457

Polysaccharides and amino acids produced by phytoplankton have been demonstrated to be key substances for efficient ice nucleation activity and are frequently detected in SSA and low-level clouds (Triesch et al., 2021a; Triesch et al., 2021b; Hartmann et al., 2025). Therefore, given the frequent occurrence of phytoplankton blooms and the enhancing effect of ocean warming, they will ultimately exert a profound influence on climate through the sea spray process.

2. Together with the restructuration, the authors should consider reviewing deeper the literature to support their experimental evidences. At many places, citations are missing. We sometimes don't know if the results presented are from the author's work or from the literature.

Author Reply

We have re-examined the section of "Results and Discussion" and when necessary, we re-phrased the initial text or supplemented references in several places to enhance the distinctiveness of our findings from other studies.

Page 7, line 191-196

Biermann et al. found that the decline in DOC concentration during the early stages of phytoplankton blooms typically ceases after the depletion of inorganic nitrogen and phosphorus in seawater (Biermann et al., 2014). It has also been reported that the addition of inorganic nutrient not only promotes the heterotrophic consumption of DOC by phytoplankton blooms (Thornton, 2014), but also enhances bacterial production and respiration rates, thereby increasing their ability to utilize DOC (Carlson et al., 2004; Jiao et al., 2010; Cai and Jiao, 2008).

Page 7, line 206-208

The trend of SSA number concentration closely followed that of submicron SSA, as submicron SSA mainly contributes to the number concentration (Quinn et al., 2015).

Page 8, lines 230-231

Previous studies have explored the relationship between surface tension and the formation of SSA by adding surfactants at varying concentrations (Sellegri et al., 2006; Tyree et al., 2007; Song et al., 2024).

Page 8, lines 242-244

Biologically induced DOC fluctuations will directly affect the particle size distribution of SSA, ultimately affecting SSA behavior such as atmospheric residence time and wet/dry deposition (Veron, 2015).

Page 10, lines 263-268

Compared to supermicron SSA, the EF of DOC in submicron SSA consistently exhibited higher values and faster increases, which may be attributed to differences in SSA formation mechanisms. Before the bubble film ruptures at the water surface, the gravity continuously expels the liquid within it, while surface-active substances, being lighter, are pushed upward, forming a vanishingly thin film (Lhuissier and Villermaux, 2012). The resulting film drops are thus enriched with a higher concentration of organic matter. In contrast, jet drops primarily originate from the liquid at the air-water interface inside the bubble and are typically less enriched in organic matter than film drops (Crocker et al., 2022).

Page 10, lines 269-278

Compared to particle size distribution, the significant variation in DOC's EF in SSA may have more profound implications for SSA's climate effect. First, from a morphological perspective, dried SSA particles consistently exhibit an organic shell enveloping an inorganic salt core (Figure S3). Since organic matter generally has lower hygroscopicity than sea salt, the presence of an organic shell suppresses the hygroscopic growth of SSA particles, thereby affecting their cloud condensation nucleus activity. The extent of this suppression depends on the type and concentration of organic matter (Bates et al., 2020; Lee et al., 2020; Cravigan et al., 2020). Second, biogenic DOC is essential in influencing the ice nucleation activity of SSA, particularly polysaccharides

and proteins, which serve as effective ice nucleation sites promoting ice crystal formation (Pandey et al.; Hartmann et al., 2025). Finally, the presence of DOC also alters SSA's radiative effects and atmospheric reactivity (Bertram et al., 2018). Based on the above, we conclude that the EF of DOC in SSA provides a macroscopic description, which requires more detailed efforts to elucidate the sea-to-air transfer pattern of different organic species.

Page 11, lines 299-306

This suggests that the composition of DOC in seawater is influenced by biological activity during phytoplankton blooms (Meon and Kirchman, 2001), which in turn affects the sea-to-air transfer of DOC via SSA (Schmitt-Kopplin et al., 2012). For instance, our results show that the proportion of shared organic molecular formulas in SW, SML, submicron SSA, and supermicron SSA increased from 12.4% on Day 1 to 16.2% on Day 9 and 26.3% on Day 18.

Page 15, lines 371-373

Phytoplankton typically sequesters the excess carbon as saccharides in energy storage materials, cell walls, and extracellular polysaccharides, and this process is influenced by phytoplankton growth, heterotrophic bacteria, and environmental conditions (Mühlenbruch et al., 2018).

Page 15, lines 387-388

Seawater and SML exhibit different time series of bacterial activity, suggesting that they may harbor distinct microbial communities (Rahlff et al., 2023; Rahlff et al., 2019; Reinthaler et al., 2008).

Page 18, lines 454-456

Polysaccharides and amino acids produced by phytoplankton have been demonstrated to be key substances for efficient ice nucleation activity and are frequently detected in SSA and low-level clouds (Triesch et al., 2021a; Triesch et al., 2021b; Hartmann et al., 2025).

3. There is a lot of speculation in the results and discussion part, especially on the

biological side of the experiment. The authors are sometimes over interpretating the data, they should restrict their discussion to what can effectively be discussed (not the biology since the chla was the only biological parameter measured, this gives no idea of what happened in the MART).

Author Reply

We have restricted our interpretation of the biological processes occurring in MART to avoid overinterpretation. The revised texts are as follows:

Page 7, lines 191-196

Biermann et al. found that the decline in DOC concentration during the early stages of phytoplankton blooms typically ceases after the depletion of inorganic nitrogen and phosphorus in seawater (Biermann et al., 2014). It has also been reported that the addition of inorganic nutrient not only promotes the heterotrophic consumption of DOC by phytoplankton blooms (Thornton, 2014), but also enhances bacterial production and respiration rates, thereby increasing their ability to utilize DOC(Carlson et al., 2004; Jiao et al., 2010; Cai and Jiao, 2008).

Page 8, lines 224-229

The surface tension of the SML increased rapidly from Day 1 to Day 5, possibly due to the rapid increase in DOC concentration in the SML during phytoplankton growth (Figure 3). Organic matter produced by microorganisms can significantly affect the physical properties of the SML (Jenkinson and Sun, 2010; Ternon et al., 2024), which may partially mitigate the low surface tension observed at the beginning.

Page 15, lines 371-373

Phytoplankton typically sequesters excess the carbon as saccharides in energy storage materials, cell walls, and extracellular polysaccharides, and this process is influenced by phytoplankton growth, heterotrophic bacteria, and environmental conditions (Mühlenbruch et al., 2018).

Page 15, lines 387-388

Seawater and SML exhibit different time series of bacterial activity, suggesting that they may harbor distinct microbial communities (Rahlff et al., 2023; Rahlff et al., 2019; Reinthaler et al., 2008).

Page 15, lines 392-395

However, the percentage of saccharides in SSA remained consistently below 10%, with a significant increase only observed on Day 14, corresponding to the peak bacterial activity in the SML. Hasenecz et al. found that addition of heterotrophic bacteria significantly increased the saccharide enrichment in SSA, as the enzymes released by these bacteria further modified the saccharides (Hasenecz et al., 2020).

Page 16, lines 422-426

For example, our experimental results showed that fucose was scarcely detected in submicron SSA, but was only enriched in the SML and supermicron SSA. Previous studies indicate that fucose-constituted polysaccharides primarily range from 50 nm (≈ 100 kDa) to 450 nm, representing a relatively large size (Jayarathne et al., 2022). It was also suggested that these polysaccharides resist bacterial hydrolysis (Murray et al., 2007). This may explain why these polysaccharides did not effectively enter the submicron SSA during our experimental period.

4. Regarding the experimental scheme, my main criticism is the method used to get a phytoplankton bloom. The carboys filled with SW were left at the sun for 18 days, and the temperature inside was never measured. Were they even ventilated ? The expected temperature increase could have drastically modified the microbial community with strong pH modification. The first incubation is probably involving larger phytoplankton communities while the others most likely smaller communities and lots of bacteria. Were there any microscope observations made over the course of the experiment? It has been shown that the physiology of phytoplankton can influence the formation of SSA: species, growth phase… This is only acknowledged once in the discussion (page 14, line 338).

Author Reply

Our phytoplankton bloom experiment was conducted from June 1 to June 18, 2024, on an open plot at Shandong University's Qingdao Campus (120.685°E, 36.364°N) (Figure 2a). During this period, the local outdoor temperature remained relatively stable,

varying between 19.39 ± 2.06 ℃ and 22.98 ± 1.82 ℃ (Figure 2b). The temperature variation of seawater inside the containers primarily depends on air heat conduction and direct solar heating. Considering that seawater has a specific capacity approximately 3000 times that of air and a large volume (≈30 L), we speculate that the diurnal fluctuation in seawater temperature within the containers may not exceed the diurnal fluctuation in air temperature, which is 3.59 ± 1.21 ℃. The fluctuations in seawater temperature during our phytoplankton blooms differ from actual conditions, as records show that the diurnal fluctuation in surface seawater temperature at a coastal station in Qingdao (120.302°E, 36.052°N) from June 1 to 18, 2019, was 1.06 ± 0.42 ℃ (Figure 2c) (Cao et al., 2024). Although these temperature variations could influence the development of phytoplankton blooms and seawater pH, it is unlikely that they could undermine the conclusions. During the experiment, instead of the ventilation, the containers at were shaken at least three times daily to promote better mixing of the seawater and the growth of phytoplankton growth.

Our experimental design focused primarily on the impact of phytoplankton blooms on the sea-to-air transfer of dissolved organic carbon via SSA. During the experiment, phytoplankton biomass was characterized using chlorophyll a concentration, while bacterial activity in seawater was assessed via the concentration ratio [fucose + rhamnose] / [arabinose + xylose] (Jayarathne et al., 2022). We explored potential conversion relationships between POC and DOC and used multiple methods to identify and quantify the sea-to-air transfer processes of the most abundant proteinaceous, saccharide, and humic substances in DOC. The experimental design and results presented in this manuscript adequately meet the research objectives. Nevertheless, we recognize that microscopic observations of changes in marine microbial communities during different stages of phytoplankton blooms would enhance our understanding of the relationship between biological activity and DOC sea-to-air transfer. However, due to the scope of the research and resource constraints, this aspect was not included in the current experimental design. In our future studies, it will be fully considered and integrated.

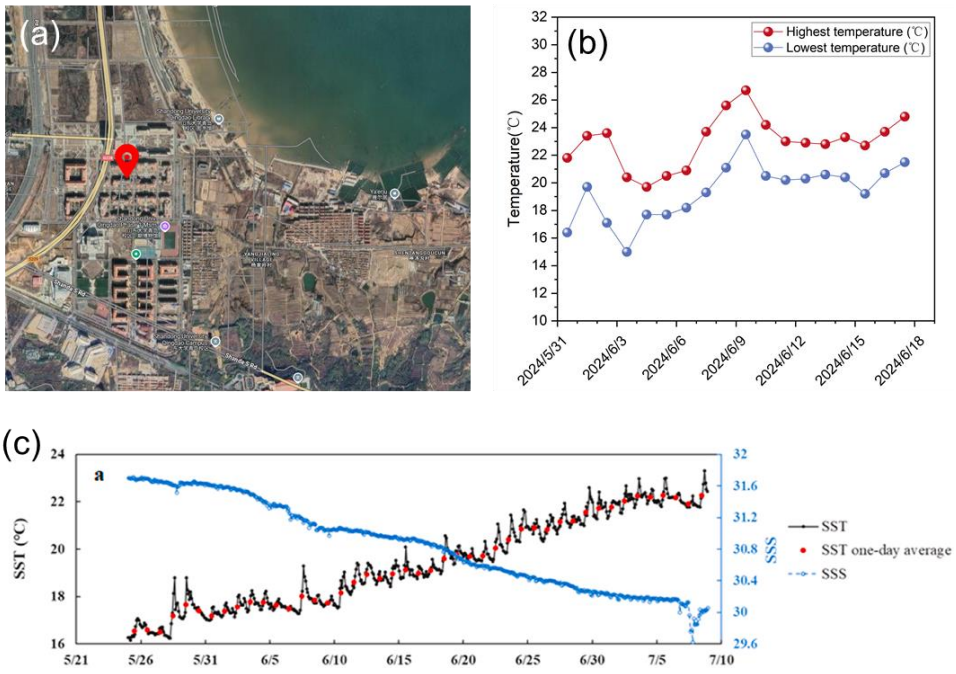

Figure R1. (a) Location where phytoplankton bloom experiments were conducted; (b) Local air temperature; (c) Sea surface temperature along the Qingdao coast.

Finally, we clarified the discrepancy in seawater temperature between natural environmental conditions and our experiments during phytoplankton blooms, and elaborated on the associated limitations and potential implications.

Page 3, lines 77-83

The average diurnal fluctuation in local outdoor air temperature is 3.59 ℃ (temperature average: 21.19 ± 2.60 ℃). Seawater temperature fluctuations in the containers primarily depends on air heat conduction and direct solar heating. However, given seawater's high specific heat capacity, its diurnal variation is likely smaller than that of air temperature, with an average comparable to air temperature. This value is slightly higher than the 1.04 ℃ diurnal variation (temperature average: 18.72°C ± 1.02 ℃) recorded for coastal seawater in Qingdao during the same period (Cao et al., 2024). Although this temperature discrepancy could influence the development of phytoplankton blooms, it is unlikely to significantly affect the conclusions.

The text format should be revised as many extra dots and extra space are present in the

text.

Author Reply

We have revised the manuscript and removed extra dots and extra spaces from the revised manuscript.

Here are some examples in the text:

Section 3.1

We don't know the duration of the MART experiments

Author Reply

We have made the necessary revisions on page 3, lines 93-94.

All SSA generation experiments were conducted at a constant room temperature, typically starting around 9:00 AM and lasting for 8 to 9 hours.

Did you measure the N and P content to say they are depleted? How do you know?

Author Reply

We cited the experimental results from Biermann et al. (Biermann et al., 2014), who conducted mesoscale experiments using Baltic Sea water at two temperatures (T = 2.7 ± 0.3 ℃ and T + 6 = 8.3 ± 0.3 ℃) under three light conditions (high light (HL ~ 8.9 mol quanta m^{-2} day^{-1}), intermediate light (IL ~ mol quanta m^{-2} day^{-1}), and low light (LL ~ mol quanta m^{-2} day^{-1})). In all six mesocosm setups, dissolved organic carbon (DOC) concentrations in seawater gradually decreased over the first 10 days. This decline ceased only after the depletion of inorganic phosphorus (DIP), inorganic nitrogen (DIN), and silicate, after which DOC concentrations began to rise again (Figure R2). The authors reported that DOC concentrations declined at the beginning of their experiment in all mesocosms from an initial overall average of 311 ± 33 µmol L^{-1} to a minimum of 239 ± 5.2 µmol L^{-1} between Days 8 and 10, and started to increase again after exhaustion of DIP and DIN, and hence earlier in T + 6 treatments. This hypothesizes that the observed DOC decline in our experiments may be linked to the depletion of nitrogen and phosphorus nutrients in the seawater, despite these indicators have not been measured directly.

To further the potential association between the decline in DOC concentrations and N and P depletion in this study, we inserted the following in the revised manuscript.

Page 6, lines 176-178

Biermann et al. found that the decline in DOC concentration during the early stages of phytoplankton blooms typically ceases after the depletion of inorganic nitrogen and phosphorus in seawater (Biermann et al., 2014).

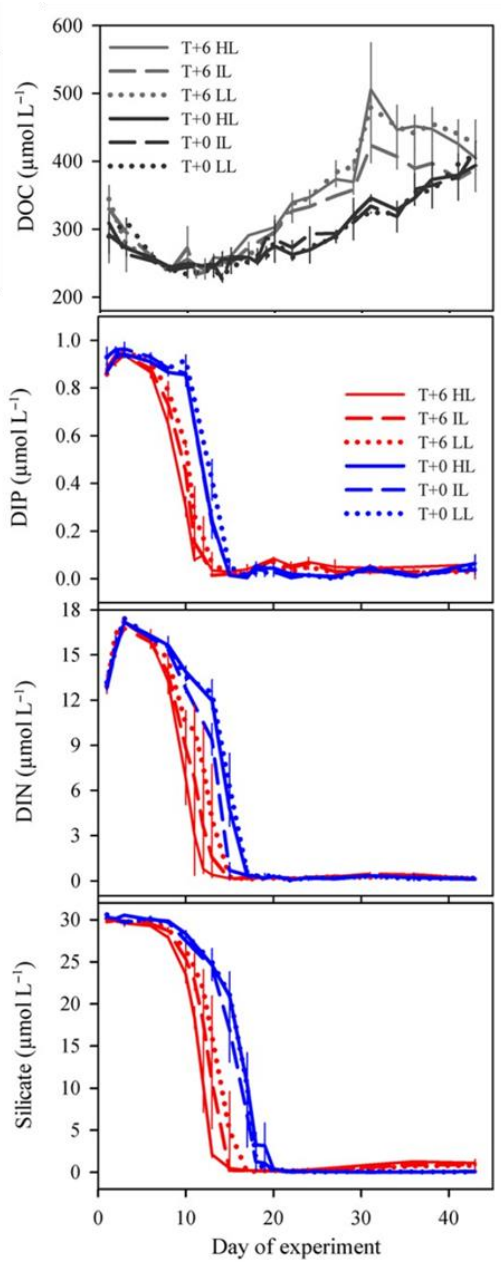

Figure R2. Six mesocosm experiments conducted by Biermann et al. (Biermann et al., 2014). The trends in dissolved organic carbon (DOC) concentrations in seawater are compared with those of inorganic phosphorus, inorganic nitrogen, and silicate.

Phytoplankton may also use DOC

Author Reply

We have made the necessary addition to the manuscript.

Page 7, lines 193-196

It has also been reported that the addition of inorganic nutrient not only promotes the heterotrophic consumption of DOC by phytoplankton blooms (Thornton, 2014), but also enhances bacterial production and respiration rates, thereby increasing their ability to utilize DOC (Carlson et al., 2004; Jiao et al., 2010; Cai and Jiao, 2008).

Line 165 – no measurement of bacterial activity

Author Reply

The corresponding text has been deleted to remove any ambiguity.

Section 3.2

Why presenting the chla first and not presenting the DOC right away as it is the aim of this section?

Author Reply

The original sentence has been modified in the revised manuscript to link Chl-a concentration to SSA particle size distribution.

Page 6, lines 205-206

Prior to Day 10, the production of submicron SSA increased and then decreased while supermicron SSA exhibited an opposite trend.

Citation expected line 179

Author Reply

We have added the citation.

Page 8, line 210-211

Prior to Day 10, the production of submicron SSA increased and then decreased, while supermicron SSA exhibited an opposite trend. The trend of SSA number concentration closely followed that of submicron SSA, as submicron SSA mainly

contributes to the number concentration (Quinn et al., 2015).

Line 180: when? At each experiment?

Author Reply

To further clarify our original idea, we have rewritten the sentence as:

Page 8, lines 208-209

During the phytoplankton bloom, the geometric mean diameter of SSA increased from 103.8 ± 5.0 nm on Day 1 to 136.3 ± 5.4 nm on Day 10, before gradually decreasing to 115.0 ± 6.9 nm (Fig. 2c).

Line 181: where is the data to support this?

Author Reply

This statement represents one of our key points. It introduces the idea that fluctuations in DOC concentrations during phytoplankton blooms are a significant factor driving substantial changes in the formation of sea spray aerosol. In the original manuscript, we placed this statement at the end of the first paragraph. After careful consideration, we have moved it to the beginning of the second paragraph to minimize potential misunderstandings.

Page 8, lines 205-212

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 increased and then decreased while supermicron SSA exhibited an opposite trend. The trend of SSA number concentration closely followed that of submicron SSA, as submicron SSA mainly contributes to the number concentration (Quinn et al., 2015). During the phytoplankton bloom, the geometric mean diameter of SSA increased from 103.8 ± 5.0 nm on Day 1 to 136.3 ± 5.4 nm on Day 10, before gradually decreasing to 115.0 ± 6.9 nm (Fig. 2c).

The dynamic accumulation of DOC during phytoplankton blooms may have a significant impact on bubble bursting and SSA formation by modifying seawater

properties. As an important surface property, surface tension has been proven to be an influential parameter in controlling bubble bursting and SSA formation (Tammaro et al., 2021; Sellegri et al., 2006).

Section 3.3- title: in seawater? In ssa?

Author Reply

We have revised the title of Section 3.3.

3.3 Phytoplankton Bloom Promotes DOC Enrichment in SSA

Lines 218 – 224 = this is method and should be moved

Author Reply

We have moved the content to the Methods section.

Line 224: targeted analysis of which compounds?

Author Reply

We performed mass spectrometry analysis on the dissolved organic carbon (DOC) in SSA samples collected on Day 1, Day 9, and Day 18. This non-targeted analysis used the MFAssignR program to identify all molecular formulas and their intensities through steps such as noise control, isotope filtering, internal mass recalibration, and molecular formula assignment. MFAssignR is widely recognized for its effectiveness in performing consistent and efficient non-targeted analysis of complex environmental mixtures (Schum et al., 2020; Radoman et al., 2022). The assigned molecular formulas were then plotted on the Van Krevelen diagram (O/C on the *X*-axis, H/C on the *Y*-axis). By examining the distribution of different compound categories on the VK diagram (Suo et al., 2024), we assessed the contributions of various chemical classes to the DOC. Our findings revealed that proteins, saccharides, and humic compounds are significant contributors to DOC. Based on these results, we subsequently employed a fluorescence spectrometer to investigate the sea-to-air transfer of proteins and humic compounds, and an ion chromatograph to explore the transfer of saccharides.

A brief explanation to this was provided in the revised manuscript.

Page 9, lines 254-256

Due to the limited SSA collection, samples on Day 1, 9, and 18 were not analyzed for the EF of DOC, which were only used for mass spectrometry analysis to identify the primary DOC molecular types.

Line 226 – is it from the literature or is it your result?

Author Reply

This result stems from our own research. We have explained this in the manuscript.

Page 9, lines 255-257

In our phytoplankton bloom experiments, the EFs of DOC in SML, supermicron SSA, and submicron SSA increased by up to ~4-fold, 10-fold, and 30-fold, respectively.

Please check the literature on the effect of microalgal growth phases and formation of SSA. There is no discussion on the differences observed between EF for submicron and supermicron SSA. The authors could try to interpret this difference, especially after the peak of the bloom where submicron is produced. Were atmospheric reactions allowed to form nanoparticles?

Author Reply

We have incorporated a discussion on the differences in EF between submicron and supermicron SSA. Additionally, volatile gases released by phytoplankton, such as dimethyl sulfide, have been shown to form nanoparticles through atmospheric chemical reactions or by directly participating in microdroplet interface reactions to form organic sulfate esters (Jang et al., 2025). Organic aerosol particles formed by the secondary oxidation of isoprene released by phytoplankton (Meskhidze and Nenes, 2006) may also be present in our collected SSA samples. However, regarding these nanoparticles: first, the scanning electrical mobility size analysis we employed cannot detect particle number concentrations below 10 nm; second, even if these particles are sufficiently abundant, their extremely small size limits their overall impact; and finally, since our experiments did not focus on secondary organic aerosol formation, an effective discussion on this matter is beyond the scope of this study. This was clarified in the

revised manuscript.

Page 10, lines 263-268

Compared to supermicron SSA, the EF of DOC in submicron SSA consistently exhibited higher values and faster increases, which may be attributed to differences in SSA formation mechanisms. Before the bubble film ruptures at the water surface, gravity continuously expels the liquid within it, while surface-active substances, being lighter, are pushed upward, forming a vanishingly thin film (Lhuissier and Villermaux, 2012). The resulting film drops are thus enriched with a higher concentration of organic matter. In contrast, jet drops primarily originate from the liquid at the air-water interface inside the bubble and are typically less enriched in organic matter than film drops (Crocker et al., 2022).

Section 3.4

Line 238 What samples are considered here?

Author Reply

We have provided more detailed descriptions of the samples selected for mass spectrometry analysis in the manuscript.

Page 11, lines 285-287

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 during the early (Day 1), peak (Day 9), and late (Day 18) stages of the phytoplankton bloom for mass spectrometry analysis.

Line 257 this assumption should be put in perspective with other studies

Author Reply

Appropriate citations have been included.

Page 11, lines 302-304

This suggests that the composition of DOC in seawater is influenced by biological activity during phytoplankton blooms (Meon and Kirchman, 2001), which in turn affects the sea-to-air transfer of DOC via SSA (Schmitt-Kopplin et al., 2012).

Line 260: this is probably due to the biology in the MART

Author Reply

Indeed, we acknowledge that the increase in the proportion of dissolved organic carbon molecular formulas shared among seawater, sea surface microlayer, submicron SSA, and supermicron SSA can be attributed to biological activity, which results from phytoplankton blooms. Our hypothesis is further supported by previous findings.

Page 11, lines 301-306

As shown in Figure 4a, the total intensity of molecular formulas assigned to seawater remained relatively stable across the three stages of the phytoplankton bloom, while the total number exhibited a stepwise decline. This suggests that the composition of DOC in seawater is influenced by biological activity during phytoplankton blooms (Meon and Kirchman, 2001), which in turn affects the sea-to-air transfer of DOC via SSA (Schmitt-Kopplin et al., 2012). For instance, our results show that the proportion of shared organic molecular formulas in SW, SML, submicron SSA, and supermicron SSA increased from 12.4% on Day 1 to 16.2% on Day 9 and 26.3% on Day 18.

Section 3.5

This is difficult section, What is HULIS? This should be explained in details and the authors should use another wording than HULIS 1, PRLIS, there are too many acronyms, it's difficult to remember at this stage of the paper without previous description and introduction.

Author Reply

HULIS refers to humic-like substances, where HULIS 1 denotes substances with excitation wavelengths < 245 nm or 320 nm and emission wavelengths at 396 nm, while HULIS 2 denotes substances with excitation wavelengths at 260 or 360 nm and emission wavelengths at 450–455 nm. PRLIS refers to protein-like substances with excitation wavelengths at 280 nm and emission wavelengths at 330 nm. We have restructured the final paragraph of the Introduction for a better flow in the following sections.

Page 2, lines 64-69

This study explored the implications of sea-to-air transfer of DOC during phytoplankton blooms. Firstly, the macroscopic effects of phytoplankton blooms on SSA formation and DOC enrichment were examined. Secondly, we employed high-resolution mass spectrometry to analyze the molecular profiles of DOC at different stages of sea-to-air transfer. Finally, by focusing on the most significant contributors, such as proteins, saccharides, and humic substances, the patterns of DOC sea-to-air transfer during phytoplankton blooms were investigated through a micro-to-macro approach.

In Section 3.5, we provided further clarification on the definition of "HULIS."

Page 13, lines 325-329

The peaks of protein-like substances (PRLIS) are mainly at (280 nm)/ (330 nm), and most of them were due to tryptophan-like substances (Santander et al., 2022). The humic-like substances (HULIS) peaks mainly appear at the excitation/emission wavelengths of (<245 nm or 320 nm) / (396 nm) for HULIS 1, and at (260 or 360 nm) / (450-455 nm) for HULIS 2. The production of HULIS 1 is primarily linked to heterotrophic processes, whereas HULIS 2 is a photooxidation product and, as such, contains a higher oxygen content than HULIS 1 (Santander et al., 2023; Barsotti et al., 2016).

Lines 280 – 283: this is method and should be moved

Author Reply

Since this text describes the three fluorescent substances that coexist in seawater, sea surface microlayer, submicron SSA, and supermicron SSA, as revealed by the results of excitation-emission matrix combined with parallel factor, we believe it is at the appropriate place.

In the revised manuscript, we have further modified these sentences.

Page 13, lines 323-329

By EEM-PARAFAC method (Fig. 5a), three fluorescence compounds co-exiting

in SW, SML, submicron SSA, and supermicron SSA were identified. The peaks of protein-like substances (PRLIS) are mainly at (280 nm)/ (330 nm), and most of them were due to tryptophan-like substances (Santander et al., 2022). The humic-like substances (HULIS) peaks mainly appear at the excitation/emission wavelengths of (<245 nm or 320 nm)/ (396 nm) for HULIS 1, and at (260 or 360 nm)/ (450-455 nm) for HULIS 2. The production of HULIS 1 is primarily linked to heterotrophic processes, whereas HULIS 2 is a photooxidation product and, as such, contains a higher oxygen content than HULIS 1 (Santander et al., 2023; Barsotti et al., 2016).

Line 284: be more specific, what compounds are you talking about?

Author Reply

We have further explained this.

Page 13, lines 330-331

The EEM intensities of PRLIS, HULIS 1, and HULIS 2 in seawater, sea surface microlayer, submicron SSA, and supermicron SSA are shown in Figure 5b.

Line 291: not sure what's the conclusion of the authors here.

Author Reply

We have removed this conclusion and revised the sentence.

Page 13, lines 336-337

Due to their hydrophilic groups (-NH_2 and -COOH) and hydrophobic carbon chains, they have been reported to exhibit strong enrichment potential in the SML and SSA (Triesch et al., 2021a; Triesch et al., 2021b).

Line 293: where is this match visible in the manuscript?

Author Reply

We have rewritten this conclusion to make the expression clearer.

Page 13, lines 337-340

As shown in Figure 5b, the EEM intensity of PRLIS in SSA rapidly peaks on Day 7 before declining. This pattern closely aligns with the DOC's enrichment factor trend

in SSA presented in Figure 3, indicating that PRLIS was the primary contributor to the increase of DOC's EF during the phytoplankton bloom.

Line 300: this is vague regarding the results provided

Author Reply

Considering also the Referee's previous suggestions, we have moved the discussion regarding organic matter enrichment in submicron SSA and supermicron SSA to Section 3.3 "The Phytoplankton Bloom Promotes DOC Enrichment.", and a simplified discussion of the results is given as:

Page 13, lines 342-345

Compared to supermicron SSA, the EEM intensities of the three organic compounds are higher in submicron SSA. Consistent with previous studies, besides the properties of the organic matter itself, the sea-to-air transfer of DOC is also influenced by the different generation mechanism of SSA (Crocker et al., 2022).

Line 304-305: this is difficult to understand

Author Reply

We have restructured the relevant discussion.

Page 13, lines 347-351

We found that the EEM intensities of the three compounds in seawater are positively correlated with the DOC concentration, while in the SML, these compounds are significantly positively correlated with the POC concentration in seawater. This implies that DOC in the SML likely originates from POC in seawater rather than DOC. Within the same samples (seawater, SML, submicron SSA, or supermicron SSA), PRLIS, HULIS 1, and HULIS2 maintained significant or near-significant positive correlations; however, their correlation weakened across different samples (Fig. 5d).

Section 3.6

Line 328, 329 and 330: missing citations, are they results obtained in your study?

Author Reply

This is not our results and now, we have added the relevant citations.

Page 15, lines 371-373

Phytoplankton typically sequesters excess carbon as saccharides in energy storage materials, cell walls, and extracellular polysaccharides, and this process is influenced by phytoplankton growth, heterotrophic bacteria, and environmental conditions (Mühlenbruch et al., 2018).

Line 340: how do you know about the degradation of saccharides; do you have data to support this assumption?

Author Reply

The hypothesis in question does not have direct empirical data from our experiments; we cited the a previous study to support this (Hasenecz et al., 2020). We removed this assumption in the revised manuscript to help reduce overinterpretation in our biological analyses.

Line 346: I doubt this study monitored the bacterial activity, they measured chla and saccharides. If they did then you can use their conclusion, if they suggested it, then it's not the conclusion of their study and cannot be used as such.

Author Reply

Upon verification, we confirm that the study by (Jayarathne et al., 2022) employed the molar ratio of (Fuc + Rha): (Ara + Xyl) to assess bacterial activity and concentration in seawater during phytoplankton blooms. To further validate whether this ratio effectively represents bacterial activity in seawater, we conducted a detailed examination. This molar ratio is commonly used to describe microbial metabolic pathways for saccharides and reflects the bacterial capacity to metabolize specific carbon sources. It holds particular significance in studies of bacterial growth, metabolic pathways, and environmental adaptation. Generally, (Fuc + Rha) : (Ara + Xyl) serves as a key indicator for estimating microbial degradation levels, especially in research on recalcitrant dissolved organic matter degradation (Jiao et al., 2010). When the molar ratio falls below 1, it typically indicates environments characterized by high microbial

(primarily bacterial) activity and extensively degraded humus, where microorganisms preferentially metabolize arabinose (Ara) and xylose (Xyl). In such conditions, fucose (Fuc) and rhamnose (Rha) are either present at lower concentrations or have been degraded (Engbrodt and Kattner, 2005; Frimmel, 1998). Therefore, a molar ratio below 1 can serve as an indirect biological indicator of the biodegradation state in the environment.

Line 346: this has been shown in many papers, they should be cited here

Author Reply

We have supplemented the references.

Page 15, lines 387-388

Seawater and SML exhibit different time series of bacterial activity, suggesting that they may harbor distinct microbial communities (Rahlff et al., 2023; Rahlff et al., 2019; Reinthaler et al., 2008).

Other details

Section 2.1: medium F/2

Author Reply

We considered that using Guillard's F/2 medium might cause the phytoplankton bloom process to proceed too rapidly. Hence, we opted for Guillard's F/4 medium instead, at half the concentration of Guillard's F/2 medium.

We have revised the description in the manuscript.

Page 3, lines 74-75

Guillard's F/4 medium was added to each container, and these containers were placed outdoors on a flat to promote phytoplankton blooms under natural sunlight (Fig. S1).

Section 2.2: how long was each MART incubation? What time of the day were the seawater sampling made (this would influence the chemical composition of the phytoplankton community)?

Author Reply

We have added the duration of each MART experiment and the sampling times for seawater to the manuscript.

Page 3, line 93-94

All SSA generation experiments were conducted at a constant room temperature, typically starting around 9:00 AM and lasting for 8 to 9 hours.

Page 4, line 105-106

Seawater samples were collected within the half-hour preceding the start of the nascent SSA generation.

How was chosen the extraction method of the SSA? Why using ultrapure water only and not other solvents?

Author Reply

Since the current research primarily focuses on the sea-to-air transfer of dissolved organic carbon, water was used to extract organic matter from SSA. We have provided an explanation in the manuscript.

Page 4, lines 98-99

Since this study focuses on the sea-to-air transfer of DOC, all SSA samples were extracted with ultrapure water (>18.2 MΩ·cm, 25 °C, Millipore) and the extractions were filtered with 0.45 μm filters.

How was POC sampled?

Author Reply

In Section 2.2, we have described the operation of filtering seawater using GF/F membranes in our original manuscript: “Seawater was collected at a depth of 10 cm in each container and immediately filtered at low pressure (≤0.2 MPa, avoiding the Chl-a loss) through a GF/F filter (47 mm, Whatman, UK).”

To clarify further, we emphasize in Section 2.3.2 that the POC measurements were conducted using the GF/F filters described in Section 2.2.

Page 4, lines 123-125

Quantitative measurements of POC and Chl-a concentrations in seawater were carried out using the GF/F filters described in Section 2.2. Specifically, the concentration of POC in seawater was determined using an elemental analyzer (Elementar, UNICUBE), which measured the POC content in a 1 cm diameter circular area on the GF/F filter.

Section 2.3.1 - Chemical analysis of SSA or all chemical analysis?

Author Reply

We are referring to all chemical analysis. The title of Section 2.3 has been changed from "**Aerosol Characterization and Chemical Analysis**" to "**Characterization and Chemical Analysis**".

The methods should describe

- sampling of seawater and bloom inducing

Author Reply

The description of seawater collection has been provided in Section 2.2 of the original manuscript: "Seawater was collected at a depth of 10 cm in each container and immediately filtered at low pressure (≤0.2 MPa, avoiding the Chl-a loss) through a GF/F filter (47 mm, Whatman, UK). Both filters and filtered seawater were stored at -20 ℃ in a dark environment."

Now, we provide a more detailed description of the triggering phytoplankton blooms, including nutrient additions and temperature changes during the period.

Page 3, lines 72-83

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, where it was filtered through a 1-mm mesh sieve and transferred into 30 transparent polycarbonate containers, each with a capacity of 28 liters. Guillard's F/4 medium was added to each container, and these containers were placed outdoors on a flat to promote phytoplankton blooms under natural sunlight (Fig. S1). The phytoplankton bloom experiment began on June 1st, 2024, and lasted for 18 days. During this period, 10

simulation experiments on nascent SSA were conducted. The average diurnal fluctuation in local outdoor air temperature is 3.59 ℃ (temperature average: 21.19 ± 2.60 ℃). Seawater temperature fluctuations in the containers primarily depend on air heat conduction and direct solar heating. However, given seawater's high specific heat capacity, its diurnal variation is likely smaller than that of air temperature, with an average comparable to air temperature. This value is slightly higher than the 1.04 ℃ diurnal variation (temperature average: 18.72°C ± 1.02 ℃) recorded for coastal seawater in Qingdao during the same period (Cao et al., 2024). Although this temperature discrepancy could influence the development of phytoplankton blooms, it is unlikely to significantly affect the conclusions.

- experiment: time of sampling, sampling methods for all parameters, sub-sampling for different analysis and storing

- analysis of the different samples, each of the samples must have a specific name, "sample" is too vague and the reader doesn't know what sample the authors are considering

Author Reply

We thank the Referee for the valuable feedback. We have revised the experimental and analytical sections to provide clearer descriptions in line with the Referee's suggestions. Specifically, we have detailed the collection times for each parameter, the sampling methods employed, and the sub-sampling and storage procedures for the different analyses. To eliminate any ambiguity associated with the term "sample", we have assigned specific names to each sample and consistently label them throughout the manuscript, ensuring that readers can easily identify the samples being referenced.

Below, we outline the major revisions to the experimental methods section.

(1) The sampling time of nascent sea spray aerosol

Page 3, lines 93-94

All SSA generation experiments were conducted at a constant room temperature, typically starting around 9:00 AM and lasting for 8 to 9 hours.

(2) Drying, collection, particle size classification, and extraction of SSA.

Page 4, lines 93-103

More details on SSA generation are provided in the Supplement. Nascent SSA was transported with purified air (Zero Air Supply, Model 111, Thermo Scientific), and the airflow was dried to a relative humidity below 30% (Monotube Dryer, MD700-12F-3, Perma Pure, USA) before collection and measurement. At this relative humidity, nascent SSA can become completely dry. Single particles of SSA were collected by a single particle sampler (DKL-2, Genstar electronic technology Co., Ltd., China) and then analyzed by transmission electron microscopy (TEM, FEI Tecnai G2 F20, Thermo Fisher Scientific, USA). Using a low-pressure cascade impactor (DLPI+, Dekati Ltd., Finland), nascent SSA particles were collected with 14 different particle size classifications (Table S2) and distributed into submicron SSA (0.016-0.94 μm) and supermicron SSA (1.62-10 μm) samples. Since the current study focuses on the sea-to-air transfer of DOC, all SSA samples were extracted with ultrapure water (>18.2 MΩ·cm, 25 ℃, Millipore) and the extractions were filtered with 0.45 μm filters. Further collection details are provided in the Supplement. Blanks were prepared by unexposed quartz fiber filters with the same treatment as for SSA samples.

(3) Sampling times for seawater and the sea surface microlayer

Page 4, lines104-105

Seawater and sea surface microlayer (SML) samples were collected within the half-hour preceding the start of the nascent SSA generation.

(4) Determination of chlorophyll a and particulate organic carbon concentrations

Page 4, lines 122-123

Quantitative measurements of POC and Chl-a concentrations in seawater were carried out using the GF/F filters described in Section 2.2. Specifically, the concentration of POC in seawater was determined using an elemental analyzer (Elementar, UNICUBE), which measured the POC content in a 1 cm diameter circular area on the GF/F filter.

(5) Determination of sodium ion concentration

Page 5, lines 131-134

The seawater and SML samples were diluted 5,000-fold, while the submicron and

supermicron SSA extracts were diluted 5-fold, ensuring that their Na^+ concentrations fall within the 0.1 to 10 μg mL^{-1} range of a seven-point calibration curve for quantification. Repeated measurements confirmed that the relative standard deviation of the Na^+ peak area remained within 6.2%.

(6) Determination of sea surface tension

Page 5, lines 134-135

The surface tension of filtered seawater and SML samples was measured by the platinum plate method using a surface tension meter (Powereach, JB99B, China). Each measurement was repeated three times, and the average value was taken.

(7) Determination of fluorescent organic compounds

The EEM results for all samples were normalized to Raman units (R. U.) by the Raman peak of water (Ex=350 nm) after subtracting the background signal obtained from Milli-Q water (Chen et al., 2023). EEM data analysis using parallel factor analysis (PARAFAC) with non-negativity constraints were performed with the DOMFlour toolbox by MATLAB R2020a (Stedmon and Bro, 2008). It is important to consider the matrix effects resulting from differences in pH and salinity between seawater samples (seawater and sea surface microlayer) and SSA samples (submicron and supermicron SSA extracts), as well as potential deviations from the variability assumptions of the PARAFAC model due to variations in DOC concentrations across the samples. Therefore, we followed the method outlined by Murphy et al. to normalize each sample's EEMs based on their total signal intensity (Murphy et al., 2013). After validating the PARAFAC model through split-half verification and random initialization analysis, the normalization was cancelled by multiplying the fractions by each sample's total signal intensity.

(8) Estimation of the uncertainty in saccharides determination

Page 6, lines 169-171

According a previous assessment, the desalting dialysis step retains over 90% of high-molecular-weight DOC (Engel and Händel, 2011); after acidification and hydrolysis, the average recovery rate for most saccharides ranges from 81% to 107%.

(9) Processing and gradient elution methods for DOC in high-resolution mass

spectrometry analysis.

Page 6, lines 178-181

Water with 0.1% (v/v) formic acid (eluent A) and acetonitrile (eluent B) was applied for the SSA, SML, and seawater extractions, with a flow rate of 0.3 mL min^{-1}. Gradient elution was performed as follows: eluent B, initially set to 5% for 4 min, increased to 100% in 36 min, was held for 3 min, decreased to 5% in 0.5 min and was held for 12.5 min to recondition the column.

Section 2.3.2

Did you perform visual observations of the communities over the course of the experiment?

Author Reply

Although we recognize that this operation would be beneficial for deepening our understanding of the relationship between biological activity and the sea-to-air transfer, we did not perform it here. However, it will be incorporated into the experimental design in our future study.

Section 2.3.4 Why saccharides?

This family of compounds was not introduced in the introduction, the reason for their analysis should appear somewhere, it could be in the discussion part, but it is not clear anywhere why this specific analysis was performed.

Author Reply

We have made the following revisions in the revised manuscript:

In the final paragraph of the introduction, we restructured the content to seamlessly transition into the relevant sections on saccharides within the experimental methods and results and discussion sections.

Page 3, lines 64-69

This study explored the implications of sea-to-air transfer of DOC during phytoplankton blooms. Firstly, the macroscopic effects of phytoplankton blooms on SSA formation and DOC enrichment were examined. Secondly, we employed high-

resolution mass spectrometry to analyze the molecular profiles of DOC at different stages of sea-to-air transfer. Finally, by focusing on the most significant contributors, such as proteins, saccharides, and humic substances, the patterns of DOC sea-to-air transfer during phytoplankton blooms were investigated through a micro-to-macro approach.

In the conclusion, we emphasized that studying the entry of sugars and proteins into the atmosphere via marine aerosols will have profound implications for climate.

Page 18, lines 454-457

Polysaccharides and amino acids produced by phytoplankton have been demonstrated to be key substances for efficient ice nucleation activity and are frequently detected in SSA and low-level clouds (Triesch et al., 2021a; Triesch et al., 2021b; Hartmann et al., 2025). Therefore, given the frequent occurrence of phytoplankton blooms and the enhancing effect of ocean warming, they will ultimately exert a profound influence on climate through the sea spray process.

The word sample is used every single sentence without further details. More precision is needed each time, what samples are mentioned? This is the same in all sections (2.3.5 …)

Author Reply

We have revised the description of the sample in the manuscript.

Page 6, lines 160-162

Except for the samples collected on Days 1, 9, and 18, samples of submicron SSA, supermicron SSA, SML, and seawater collected on other days were subjected to dialysis for desalting, followed by acid hydrolysis, nitrogen blowing, and re-solubilization (Engel and Händel, 2011).

Page 6, lines 173-175

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

Section 2.3.5

How can you know about the phases of the bloom without visual observations?? Clearly you could have two different successive blooms with different communities, and this is well supported by the color of your carboys. Chl-a is a weak proxy here.

Author Reply

We acknowledge that the stage of phytoplankton blooms cannot be determined without visual observation. Therefore, we have revised the manuscript to clarify that samples for mass spectrometry analysis were selected based solely on Chl-a concentrations.

Page 6, lines 173-175

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

The gradient elution should be written in the text, no table is needed in the Supplementary

Author Reply

We have described the elution method in Section 2.3.5 and deleted the table in the Supplement.

Page 6, lines 178-181

Water with 0.1% (v/v) formic acid (eluent A) and acetonitrile (eluent B) was applied for the SSA, SML, and seawater extractions, with a flow rate of 0.3 mL min^{-1}. Gradient elution was performed as follows: eluent B, initially set to 5% for 4 min, increased to 100% in 36 min, was held for 3 min, decreased to 5% in 0.5 min and was held for 12.5 min to recondition the column (Wan et al., 2022).

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Reply to the comments from Anonymous Referee #2

Sea spray aerosol (SSA) formation is an important pathway for the transfer of marine substances to the atmosphere. This study investigates how phytoplankton blooms promote the sea-to-air transfer of dissolved organic carbon (DOC) through SSA formation. Natural seawater was incubated outdoors to induce phytoplankton blooms, and a laboratory waterfall-type SSA simulation tank was used to reproduce the sea–air exchange process. The DOC enrichment in SSA can increase by 10–30 times during phytoplankton blooms, mainly driven by protein-like components (PRLIS), with a secondary contribution from polysaccharides modified by heterotrophic bacteria. The study is well designed and methodologically sound, covering the continuous chain from seawater to the sea surface microlayer and SSA, and it provides scientifically meaningful insights. The following suggestions are provided to the authors for further revision before the final publication.

The continuous plunging waterfall mode was adopted to improve SSA sampling efficiency; however, this configuration may not accurately reproduce the bubble dynamics and turbulence of real oceanic wave-breaking. Please discuss the representativeness and possible implications of this setup.

Author Reply

Plunging waterfall type has been proven as an efficient laboratory simulation method to generate sea spray aerosols (Stokes et al., 2013), and has been used widely in many research studies (Callaghan et al., 2014; Van Acker et al., 2021; Harb and Foroutan, 2022; Jayarathne et al., 2022). Collins et al. conducted a detailed comparison between intermittent and continuous plunging waterfall systems, focusing on differences in sea spray aerosol particle size distribution and organic enrichment (Collins et al., 2014). The main difference between intermittent and continuous modes lies in how surface foam behavior affects the formation of sea spray aerosol. In intermittent operation, surface foam breaks and dissipates during operational gaps, whereas in continuous operation, foam gradually dissipates as it moves away from the impact point. At lower dissolved organic carbon concentrations (≈85 μM), SSA produced by both methods shows minimal differences, while the differences become

more important at higher DOC concentrations (≈400 μM). However, compared to other laboratory SSA production methods (wave breaking and sintered filter glass), the differences between intermittent and continuous plunging waterfalls are relatively minor (Collins et al., 2014). During the phytoplankton bloom period, the use of a continuous plunging waterfall would help reduce our sampling time.

In the revised manuscript, we briefly discuss this configuration.

Page 3, lines 90-94

These two types of plunging waterfalls differ mainly in the behavior of surface bubbles as they rupture and dissipate: in intermittent waterfalls, surface bubbles breaks and dissipates during operational gaps, whereas in continuous waterfalls, surface bubbles gradually dissipates as it moves away from the impact point (Collins et al., 2014).

The enrichment factor (EF) is normalized to Na^+, assuming its concentration remains constant. However, Na^+ levels may vary with particle size and humidity. The authors should clarify the measurement range, precision, and variability of Na^+ and discuss how potential deviations from this assumption could affect the calculated EF values.

Author Reply

The size of SSA is related to relative humidity (RH) as it equilibrates either by absorbing or evaporating water. At different RH, the empirical relationship among the sizes of SSA is: Dp (at 100%RH) ≈ 2Dp (at 80% RH) ≈4Dp (below 50% RH) (Veron, 2015). In other words, when RH falls below 50%, it is generally considered that water within the SSA has evaporated completely, and the diameter is no longer affected by the water content. In order to exclude the influence of RH on SSA's size, we employed a drying tube to dehumidify the airflow carrying the SSA. After drying, the airflow's RH was kept below 30%, ensuring that the nascent SSA underwent a phase transition from liquid to solid.

Dried SSA particles were collected by a low-pressure cascade impactor (DLPI+, Dekati Ltd., Finland) and classified into submicron and supermicron SSA. Submicron SSA and supermicron SSA were extracted using 10 mL Milli-Q water. In order to

quantify the Na^+ concentrations, a seven-point calibration curve of 0.1 to 10 μg mL^{-1} range was created. Samples of seawater and sea surface microlayer were diluted 5,000-fold, and extracts of submicron SSA and supermicron SSA were diluted 5-fold, making the Na^+ concentrations fall within the range of the calibration curve. The relative standard deviation of Na^+ concentration after repeated measurements was controlled within 6.2%.

We have added the necessary information in the revised manuscript.

Page 3, lines 94-98

Nascent SSA was transported with purified air (Zero Air Supply, Model 111, Thermo Scientific), and the airflow was dried to a relative humidity below 30% (Monotube Dryer, MD700-12F-3, Perma Pure, USA) before collection and measurement. At this relative humidity, nascent SSA can be completely dried into solid particles.

Additionally, the information regarding the sample dilution, the measurement range of Na^+ concentration, and the relative standard deviation ranges for multiple measurements has been updated.

Page 5, lines 131-134

Sodium ions (Na^+) concentrations were measured using an ion chromatograph (Dionex ICS-600, Thermo Fisher Scientific, USA). The seawater and SML samples were diluted 5,000-fold, while the submicron and supermicron SSA extracts were diluted 5-fold, ensuring that their Na^+ concentrations fall within the 0.1 to 10 μg mL^{-1} range of a seven-point calibration curve for quantification. Repeated measurements confirmed that the relative standard deviation of the Na^+ peak area remained within 6.2%.

In the original manuscript, the enrichment factors for organic matter were calculated using the average of multiple measurements. In this revision, we apply uncertainty propagation formulas to incorporate measurement uncertainties into the enrichment factor results. The formulas for calculating the DOC enrichment factor and

relative standard deviation (RSD) are as follows:

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

$$RSD_{enrichment\ factor}=\sqrt{(RSD_{DOC|SSA\ or\ SML})^2+(RSD_{Na^+|SSA\ or\ SML})^2+(RSD_{DOC|SW})^2+(RSD_{Na^+|SW})^2}$$

In the revised manuscript, we have added explanations regarding the propagation of measurement uncertainty to the enrichment factor calculations and presented the specific settlement results in Figure 3.

Page 5, lines 139-140

Using the uncertainty transfer formula to propagate the uncertainties from multiple measurements results into the calculation of the enrichment factor.

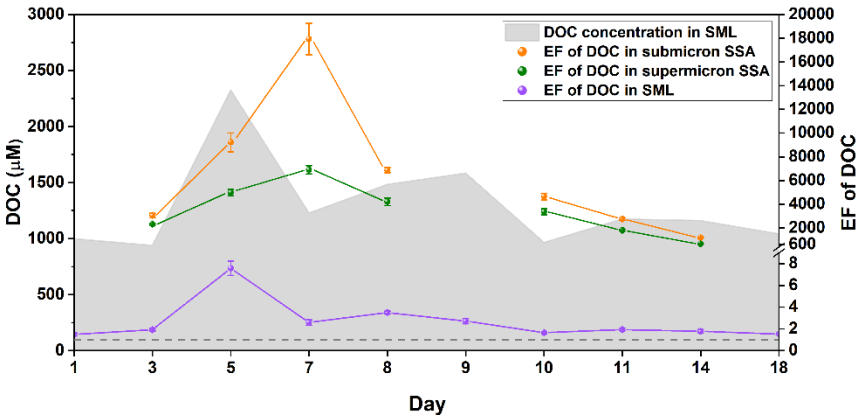


Figure 3. Time series of DOC enrichment during the phytoplankton bloom. Enrichment factors of DOC relative to Na^+ in the SML (purple), submicron SSA (orange) and supermicron SSA (green). The gray background is the concentration of DOC in the SML. Error bars represent the standard deviation of the EF, derived from the standard deviation of Na^+ concentration and DOC concentration obtained through multiple measurements.

The fluorescence intensities used in the EEM–PARAFAC analysis may be influenced by matrix effects such as salinity, pH, and the polarity of DOM. These factors can alter fluorescence yield and spectral properties, potentially leading to biases when comparing different sample types (e.g., seawater or SSA extracts). Please include some discussions on how these matrix effects were considered or minimized, and whether

they may influence the comparability of EEM results.

Author Reply

Regarding the potential influence of matrix effects—such as salinity, pH, and the polarity of DOM—on fluorescence intensity, these factors could indeed introduce bias between different samples (e.g., seawater versus SSA extracts), which may in turn affect the results of the EEM-PARAFAC analysis.

Changes in pH can alter the ionization state of certain fluorescent compounds, thereby affecting their fluorescence yield (Timko et al., 2015). Seawater and seawater surface microlayer samples used for EEM detection should have a pH of approximately 8.2. In contrast, extracts of submicron and supermicron SSA (extracted with 10 mL of Milli-Q water) contained very low amounts of SSA, leading to pH values close to 7 for these samples.

Salinity variations can influence the aggregation state of fluorescent molecules, thereby altering their fluorescence emission characteristics (Kholodov et al., 2024). While some studies have reported significant enrichment of divalent cations in sea surface microlayer compared to seawater (Salter et al., 2016; Schill et al., 2018), it is important to note that sodium chloride is the main contributor to seawater salinity, with divalent cations contributing relatively little. Therefore, it can be assumed that the salinity of seawater samples and that of SML samples used for EEM fluorescence detection should be quite similar. In contrast, the salinities of submicron and supermicron SSA samples' extracts are both close to and significantly lower than that of seawater.

The matrix effect can potentially influence the absolute intensity of EEM across different samples, particularly due to salinity differences between seawater-type samples (seawater and seawater micro-surface layer) and SSA-type samples (submicron and supermicron SSA). As a result, the comparability of EEM's absolute intensities between these two categories requires careful verification. Therefore, in the manuscript, our discussion of EEM's absolute intensity in Figure 5(b) is limited to comparisons within each category—either between seawater and sea surface microlayer, or between submicron and supermicron SSA.

When performing EEM-PARAFAC analysis, we accounted for matrix effects and variations in DOC concentrations between seawater and SSA samples. Following the methodology outlined by Murphy et al. (Murphy et al., 2013), we normalized the EEM for each sample to its total signal using the signal normalization module within the drEEM toolbox. This normalization ensures that each sample's EEM contributes equally during the PARAFAC analysis, enabling the model to focus on chemical variations between samples rather than the overall signal magnitude. Additionally, this approach enhances the detection of minor peaks. After model validation, normalization can be cancelled by multiplying the fractions by each sample's total signal intensity.

A discussion on matrix effects, emphasizing their potential impact on fluorescence spectra and acknowledging that these variability sources were considered during data analysis was updated in the revised manuscript

Page 5, lines 144-154

The excitation-emission matrix (EEM) of DOC was obtained using a fluorescence and absorbance spectrometer (Duetta™, Horiba Scientific, Japan). The excitation wavelength of EEM was in the range of 250-620 nm, the emission wavelength was in the range of 250-700 nm, the scanning intervals were set to 5 nm and 2 nm, respectively, and the slit width was fixed at 5 nm. The EEM results for all samples were normalized to Raman units (R. U.) by the Raman peak of water (Ex=350 nm) after subtracting the background signal obtained from Milli-Q water (Chen et al., 2023). EEM data analysis using parallel factor analysis (PARAFAC) with non-negativity constraints were performed with the DOMFlour toolbox by MATLAB R2020a (Stedmon and Bro, 2008). It is important to consider the matrix effects resulting from differences in pH and salinity between seawater samples (seawater and sea surface microlayer) and SSA samples (submicron and supermicron SSA extracts), as well as potential deviations from the variability assumptions of the PARAFAC model due to variations in DOC concentrations across the samples. Therefore, we followed the method outlined by Murphy et al. to normalize each sample's EEMs based on their total signal intensity (Murphy et al., 2013). After validating the PARAFAC model through split-half verification and random initialization analysis, the normalization was cancelled by

multiplying the fractions by each sample's total signal intensity.

The method recovery, reproducibility, and the detection limit of organic species are suggested to be provided in the method.

Author Reply

We have added this information to the Methods section of the manuscript:

(1) We provided additional details on the dilution factor for the samples, the concentration range of the standard curve, and the relative standard deviation of repeated measurements when measuring Na^+ concentration using ion chromatography.

Page 5, lines 131-134

Sodium ions (Na^+) concentrations were measured using an ion chromatograph (Dionex ICS-600, Thermo Fisher Scientific, USA). The seawater and SML samples were diluted 5,000-fold, while the submicron and supermicron SSA extracts were diluted 5-fold, ensuring that their Na^+ concentrations fall within the 0.1 to 10 μg mL^{-1} range of a seven-point calibration curve for quantification. Repeated measurements confirmed that the relative standard deviation of the Na^+ peak area remained within 5.2%.

(2) The number of repetitions for the surface tension measurements, previously described in the caption of Figure 2, has been added to the Methods section.

Page 5, lines 135-136

The surface tension of filtered seawater and SML samples was measured by the platinum plate method using a surface tension meter (Powereach, JB99B, China). Each measurement was repeated three times, and the average value was taken.

(3) In the EEM-PARAFAC method, we have clarified how matrix effects are accounted for during data processing and how variations in dissolved organic carbon concentrations across different samples are addressed.

Page 5, lines 146-154

EEM data analysis using parallel factor analysis (PARAFAC) with non-negativity

constraints were performed with the DOMFlour toolbox by MATLAB R2020a (Stedmon and Bro, 2008). It is important to consider the matrix effects resulting from differences in pH and salinity between seawater samples (seawater and sea surface microlayer) and SSA samples (submicron and supermicron SSA extracts), as well as potential deviations from the variability assumptions of the PARAFAC model due to variations in DOC concentrations across the samples. Therefore, we followed the method outlined by Murphy et al. (Murphy et al., 2013) to normalize each sample's EEMs based on their total signal intensity. After validating the PARAFAC model through split-half verification and random initialization analysis, the normalization was cancelled by multiplying the fractions by each sample's total signal intensity.

(4) In Section 2.3.5, we supplemented the average recovery rate for carbohydrate detection.

Page 6, lines 168-170

The quantification was performed using seven-point standardized calibration curves with concentrations ranging from 10 nM to 10 μM. According a previous assessment, the desalting dialysis step retains over 90% of high-molecular-weight DOC (Engel and Händel, 2011); after acidification and hydrolysis, the average recovery rate for most saccharides ranges from 81% to 107%.

Please specify in the abstract whether the reported "10-fold to 30-fold enrichment" of DOC refers to SW or to the SML.

Author Reply

We have included the specification in the revised abstract.

Page 1, lines 17-19

In this study, we observed that the phytoplankton bloom can promote DOC enrichment in SSA by 10- to 30-fold compared to seawater and investigated the mechanism of DOC sea-to-air transfer using various characterization tools.

Ensure consistent color scales in Figure 5 EEM panels to enable visual comparison.

Author Reply

After careful consideration of the Referee's suggestion and reviewing relevant literature, we have decided to retain the different color scales. The specific reasons are as follows:

Figure 5a shows the three types of fluorescent chromophores, which coexist in seawater, the SML, submicron SSA, and supermicron SSA, identified through the EEM-PARAFAC method. Since the identification of fluorescent chromophores relies primarily on the excitation and emission wavelengths corresponding to the peak fluorescence signals, selecting an appropriate color scale is crucial for accurately depicting the positions of these peaks.

The fluctuations in both absolute and relative fluorescence intensities of these three fluorescent substances during different phytoplankton blooms are shown in Figures 5b and 5c, allowing for visual comparison.

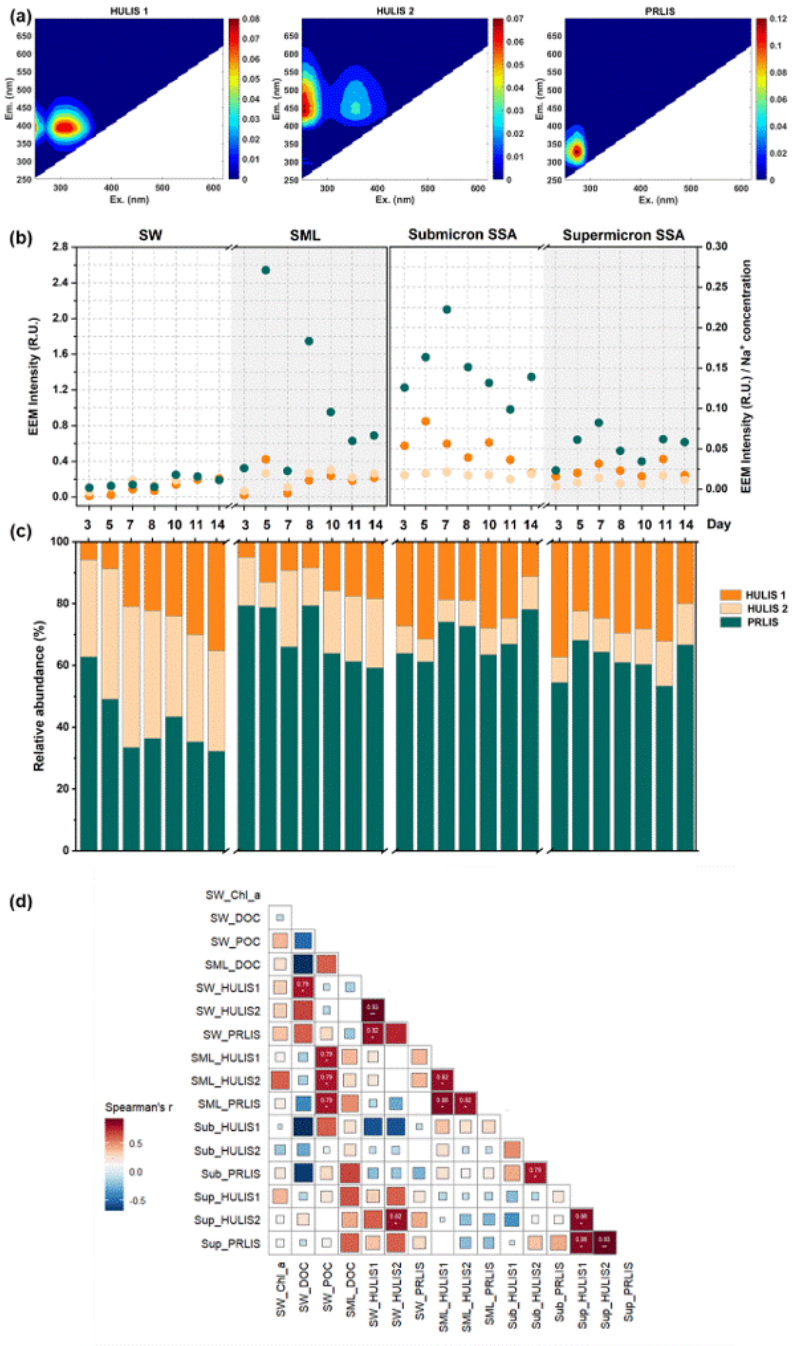


Figure 5. Sea-to-air transfer of HULIS and PRLIS. Three organics identified using the EEM-PARAFAC method: (a) HULIS 1, HULIS 2, and PRLIS. (b) EEM intensities of the three organics in different samples with respect to time. Note that in order to exclude the effect of SSA collection mass on EEM intensity, 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.

Add standard deviation or error bars for EF values to better exhibit measurement uncertainty.

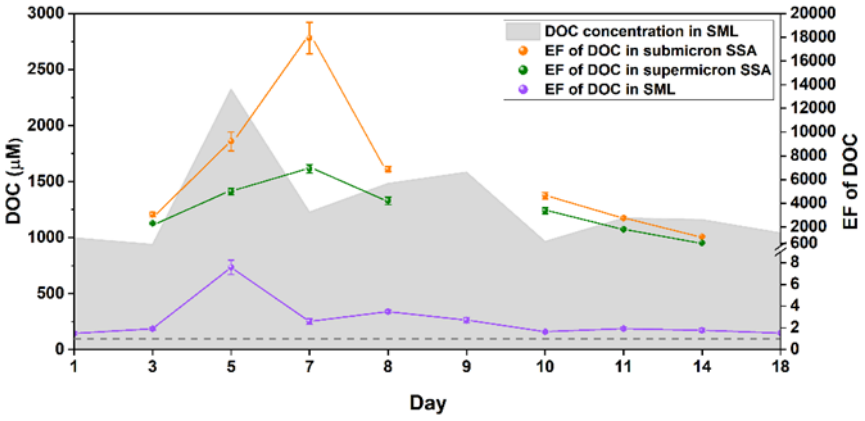
Author Reply

Measurement uncertainties into the enrichment factor results were obtained by applying the uncertainty propagation formulas. These formulas for calculating the DOC enrichment factor and relative standard deviation (RSD) are as follows:

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

$$RSD_{enrichment\ factor}=\sqrt{(RSD_{DOC|SSA\ or\ SML})^2+(RSD_{Na^+|SSA\ or\ SML})^2+(RSD_{DOC|SW})^2+(RSD_{Na^+|SW})^2}$$

We have added error bars to Figure 3 and updated the figure.



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Authors' response to the second set of egusphere-2025-4207 Referees' comments

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:

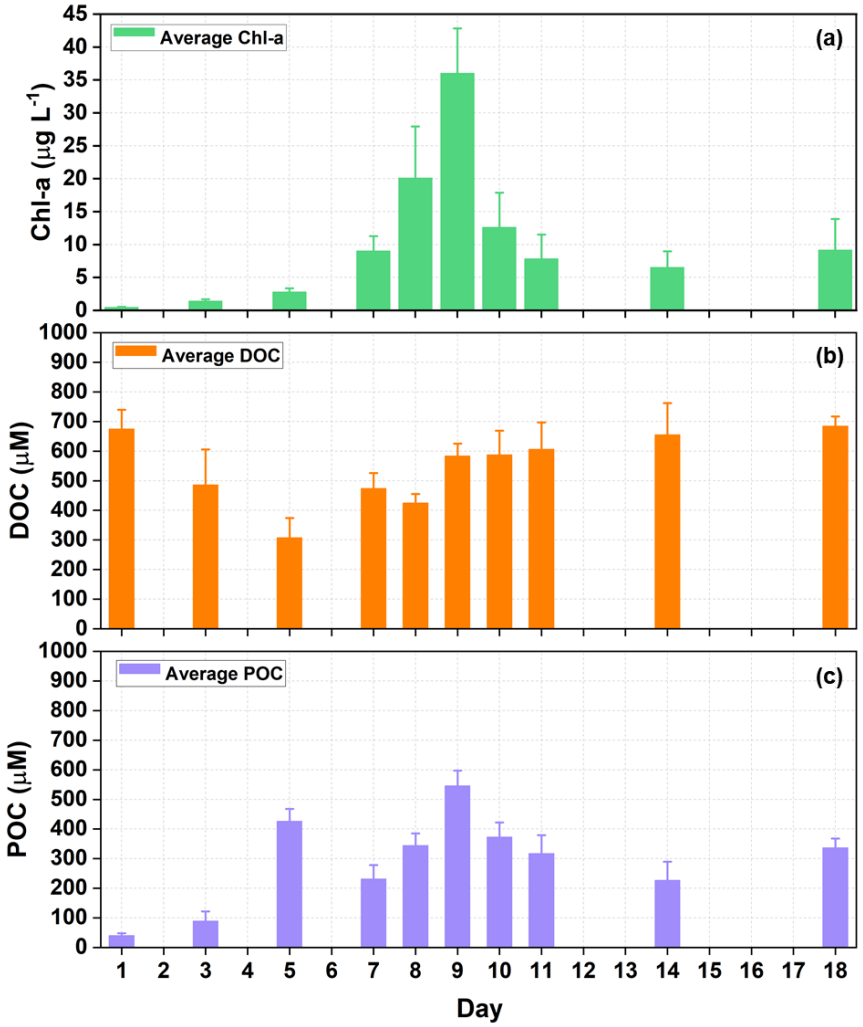


Figure 1. Time series of physicochemical properties of seawater during the phytoplankton bloom. (a) chlorophyll-a (Chl-a), (b) dissolved organic carbon (DOC), and (c) particulate organic carbon (POC) concentrations in seawater. Mean and standard deviations are for three containers of seawater in each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

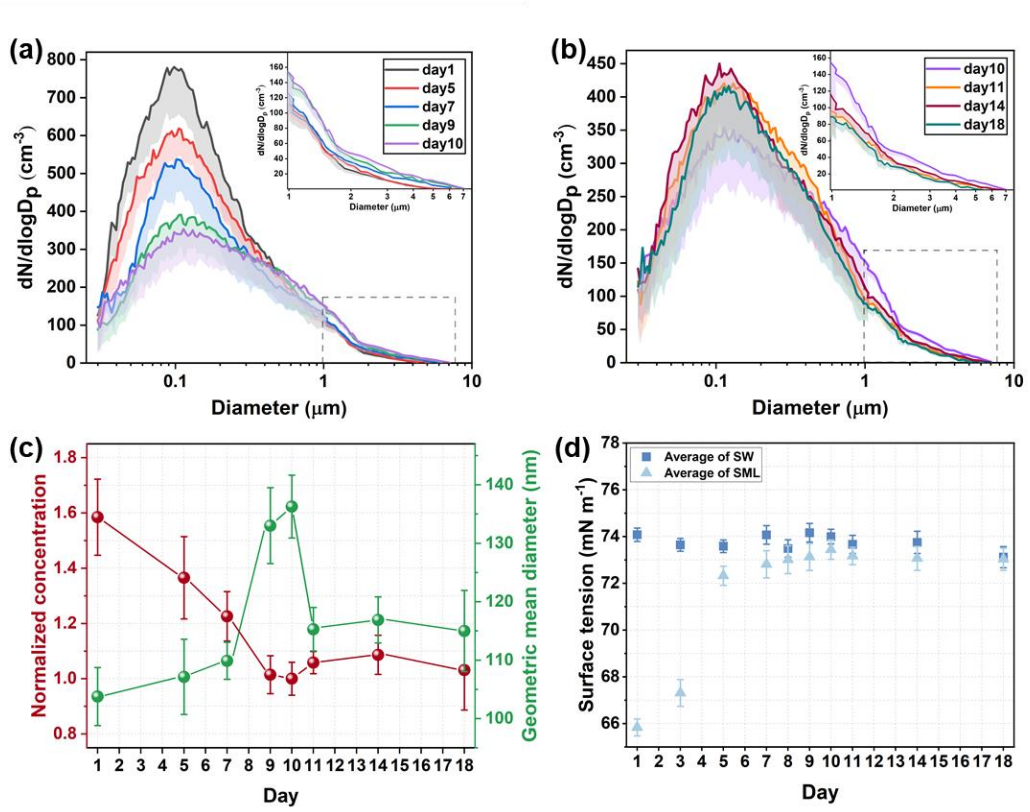
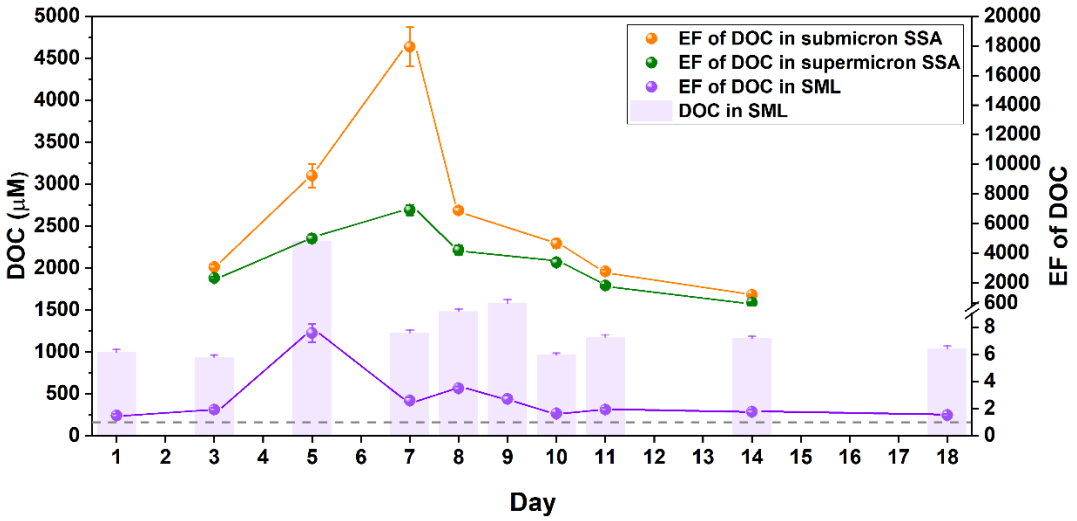


Figure 2. Time series of SSA formation during the phytoplankton bloom. (a) Particle size distributions of SSA from Day 1 to Day 10; (b) Particle size distributions of SSA from Day 10 to Day 18. For clarity, the gray dashed box area is the result of the aerodynamic particle sizer and is enlarged to the 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.



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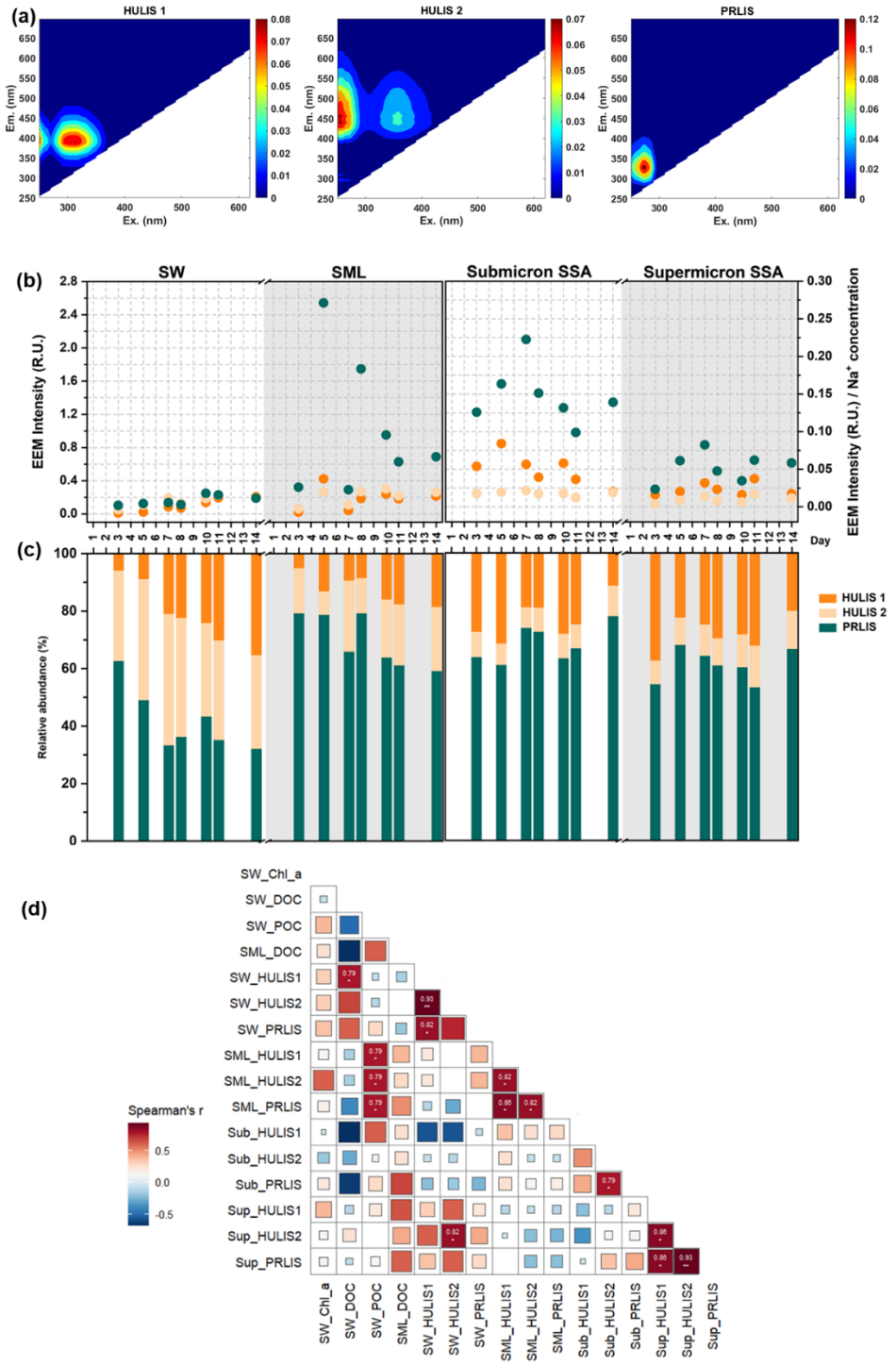

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correlation between Chl-a, DOC and POC concentrations in seawater, POC concentration in the SML and EEM intensities of three fluorescent substances.

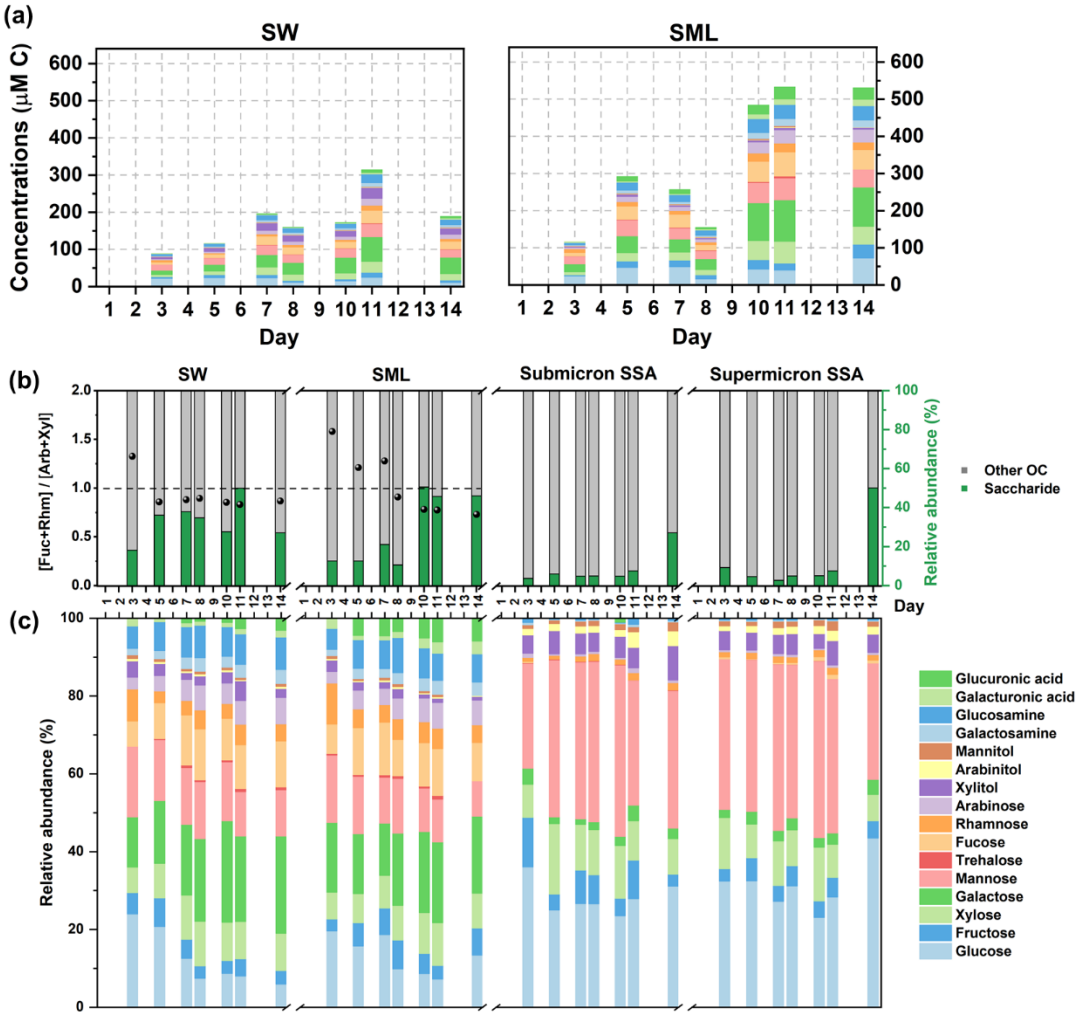

Figure 6. Sea-to-air transfer of saccharides. (a) Relative abundance of total saccharides in DOC. The bacterial activity is expressed as the ratio of the sum of the concentrations of fucose and rhamnose to the sum of the concentrations of arabinose and xylose (the black scatters). The activity is typically 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 ℃, 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 ℃. The experiments involving nascent sea spray aerosol were conducted indoors, where the air conditioning maintained an air temperature range of 22 to 25 ℃. 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 ℃) that approximate outdoor air temperatures.

Supplement, Page 2, lines 33-34

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

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).

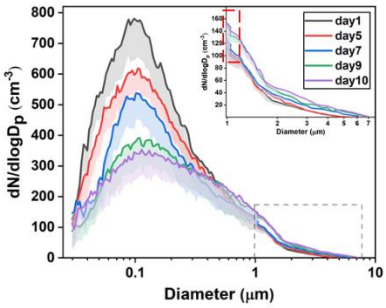

Figure R1. Integration of the SSA particle size distribution obtained from APS and SMPS around 1 μm.

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)).

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

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.

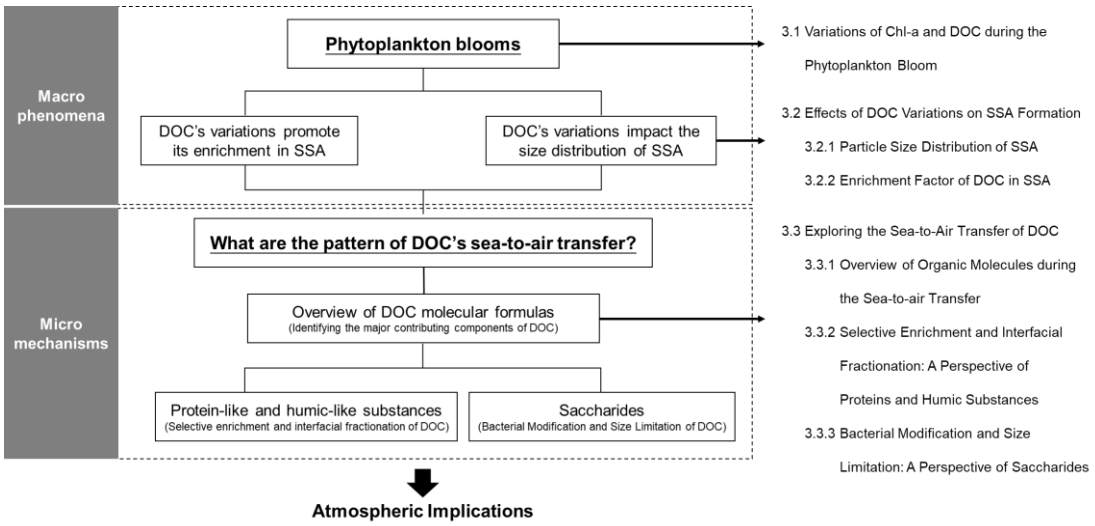
Page 19, lines 474-482

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.

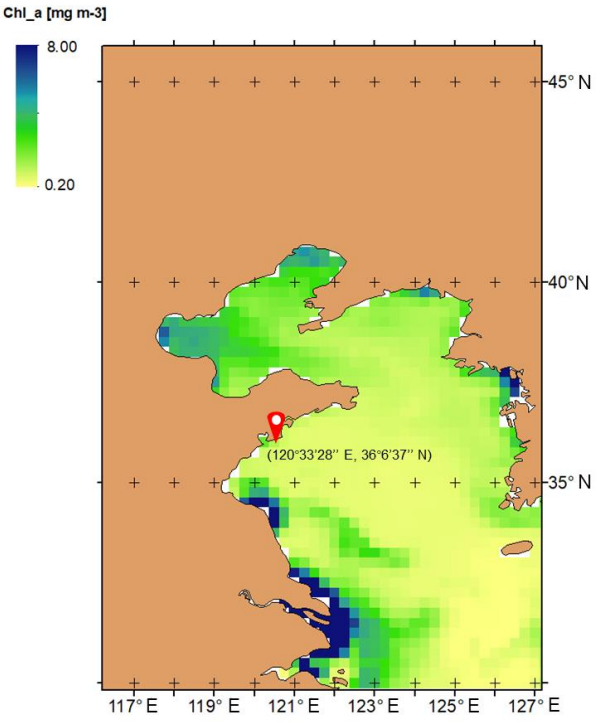


Figure R1. Coastal seawater sampling locations and the average chlorophyll-a concentration (0.54 ± 0.04 mg m^{-3}) in seawater two weeks prior to sampling.

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.

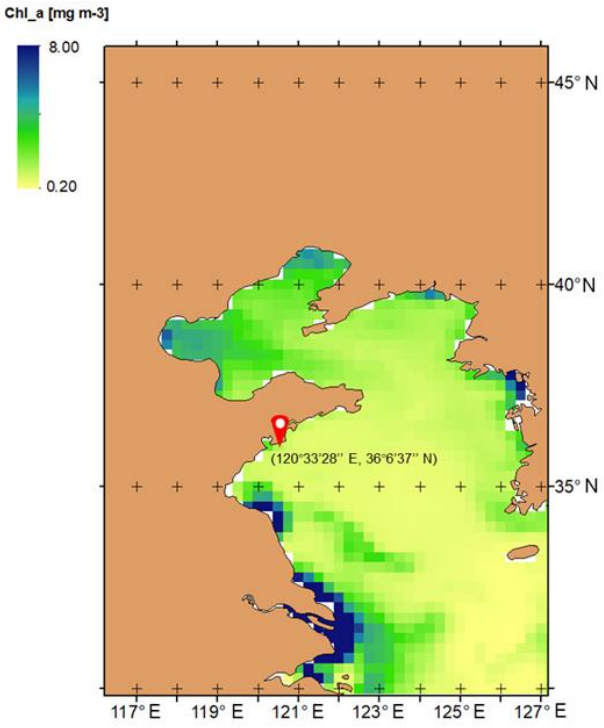


Figure S1. Coastal seawater sampling locations and the average chlorophyll-a concentration (0.54 ± 0.04 mg m^{-3}) in seawater two weeks prior to sampling.

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:

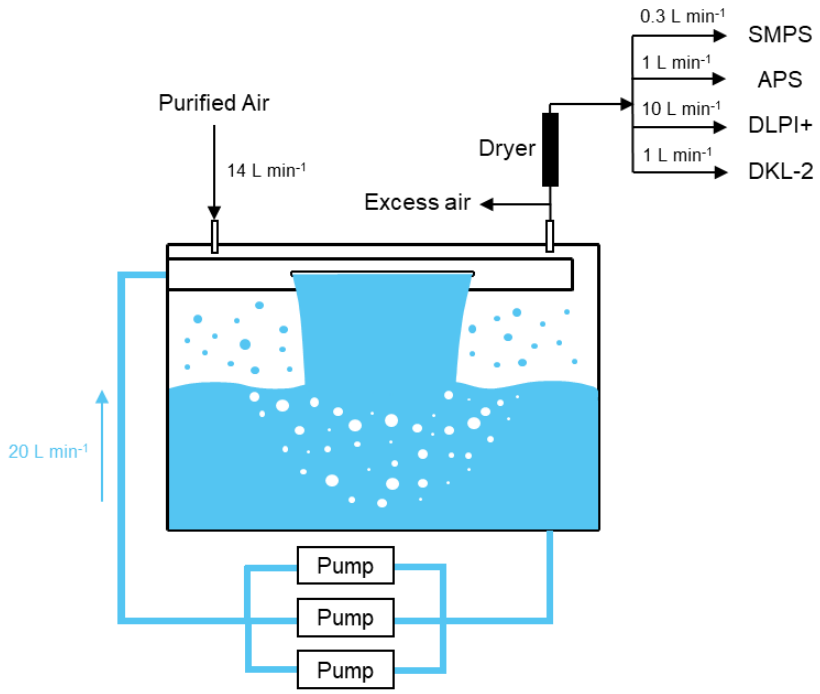


Figure S3. A schematic diagram of the nascent SSA experiments.

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)):

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

Taking the DOC enrichment factor as an example, the value of the denominator $(DOC)_{SW}/(Na^+)_{SW}$ can be calculated by directly measuring the DOC concentration and Na^+ concentration in seawater. For the numerator $(DOC)_{SSA}/(Na^+)_{SSA}$, 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 $(DOC)_{SSA}/(Na^+)_{SSA}$. 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)):

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

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

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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:

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

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.

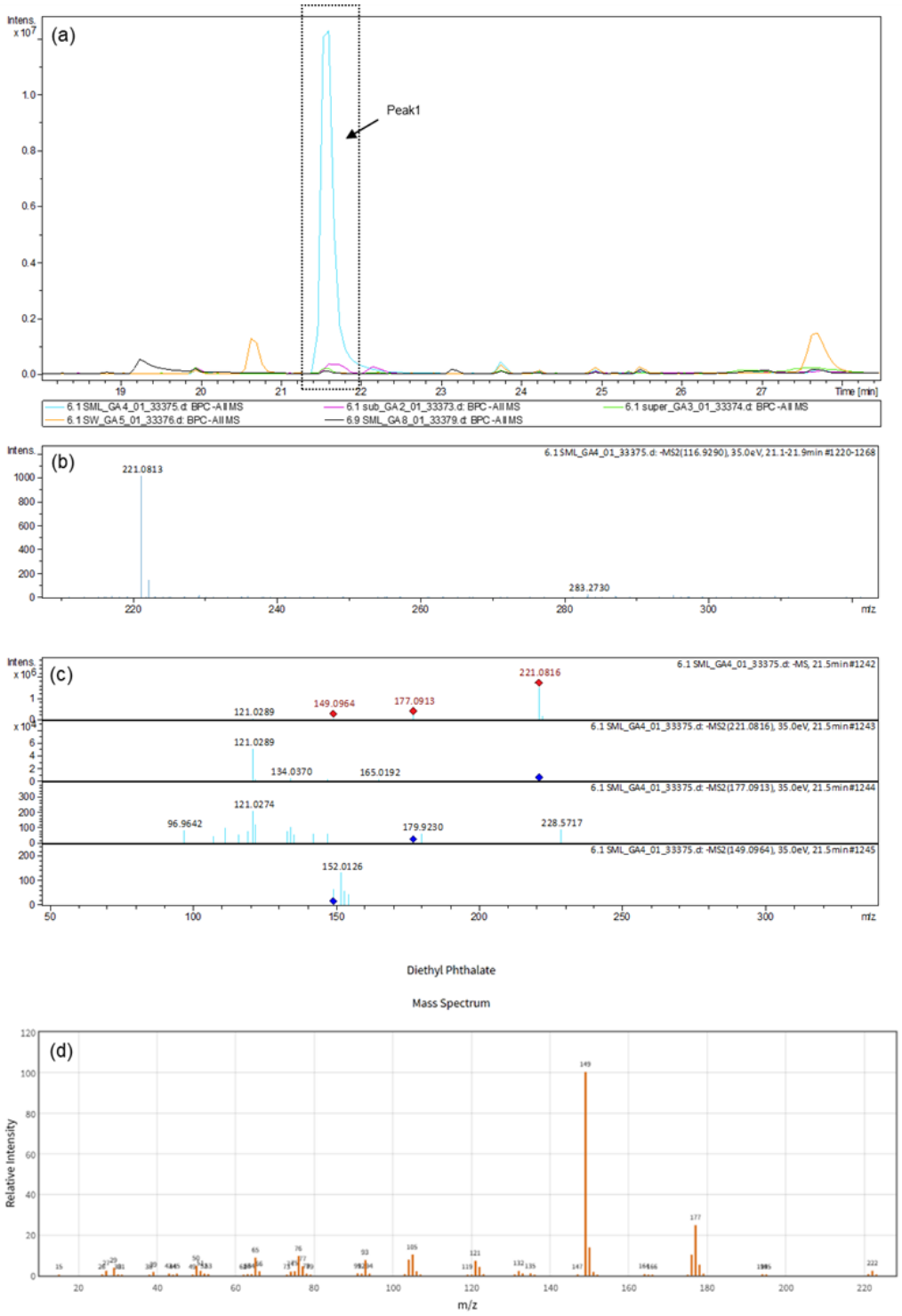

Figure S4. Identification of phthalate esters in initial SML samples through mass spectrometry. (a) Base peak chromatogram for three samples: SML sample on day 1 (blue line), seawater sample on day 1 (orange line), submicron SSA sample on Day 1 (purple line), supermicron SSA sample on Day 1 (green line), 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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Authors' response to the third set of egusphere-2025-4207 Referees' and comments

Reply to the comments from Anonymous Referee #3

We deeply appreciate Anonymous Referee #3 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.

Hu et al. describe the wealth of measurements they applied to a multi-part phytoplankton bloom experiment. Specifically, they characterized the POC-DOC cycle across the bloom and through the enrichment and transfer processes among seawater, sea surface microlayer, and sea spray aerosols (separated into submicron and supermicron populations).

I commend the authors in this version of the manuscript. I believe the content and figures are clearer and more specific, and the paper is much stronger than the previous version. The authors have fully addressed the concerns raised during the last round of revisions, and I believe this paper is much stronger. I do recommend for publication after addressing a few more minor edits, see below.

1. The paper would benefit from a final pass through correcting grammatical errors, namely issues with article placement in sentences and use of consistent tenses.

Some examples are below:

a. Line 241: "As a common…"

b. Line 242: "…accumulates in the SML…"

c. Line 243: "…significantly reduces surface…"

d. Line 252: "…the development of capillary waves…"

e. Line 254: "…observed in the SML…"

f. Line 283: "…are pushed upward, form a…"

g. Line 287: "Compared to the particle size distribution…"

h. Line 456: "…are "pulse events" in the ocean-atmosphere organic…"

i. Line 478: "…Chl-a is a driving factor regulating…"

j. Supplement line 17: "…Copernicus Data Store was checked to determine whether…"

Author Reply

We have made the corresponding corrections and they are highlighted in the revised manuscript and revised Supplement. Additionally, we have proofread the entire text and corrected grammatical errors, ensuring proper article usage and consistent verb tenses.

2. On line 356, it's stated "Consequently, HULIS1 have greater abundance in the SML and SSA compared to HULIS2 (Fig. 5c)." However, looking at Fig. 5c, it appears that HULIS2 has a greater relative abundance than HULIS1 in the SML. But I agree that HULIS1 > HULIS2 is a valid statement for SSA.

Author Reply

We have made the modifications in the revised manuscript.

Page 14, lines 356-357

As a less oxidized organic matter, HULIS 1 exhibits a greater enrichment capacity than HULIS 2 in SSA. Consequently, HULIS1 has a greater abundance in SSA compared to HULIS2 (Fig. 5c).

3. On line 366, it's stated "…however, when sample types differ, significant correlations between them are rarely observed (Fig. 5d)." While I agree with what you're trying to say, of the 14 squares with high correlation (where I'm assuming the white text in the colored box indicates high significance), 4 are between different sample types. I would suggest rephrasing the sentence to better clarify that while most of the high significance correlations occur between samples of the same type, there are 4 cases between samples of different types that exhibit significant correlations.

Author Reply

We have modified the structures of these sentences.

Page 14, lines 363-368

As illustrated in Fig. 5d, although most strong correlations occur between samples of

the same type (seawater, SML, submicron SSA, or supermicron SSA), there are four cases where strong correlations are observed between samples of different types. Among them, the EEM intensities of three dissolved fluorescent components in the SML exhibit significantly positive correlations with the POC concentration in seawater, suggesting that they may be directly derived from seawater POC. Another case is when the strong correlation is observed between HULIS 2 in supermicron SSA and HULIS 2 in seawater, providing indirect evidence that the composition of supermicron SSA and seawater may be closely related.

4. On lines 407-409, the increased percentage of saccharides in SSA is connected to the peak biological activity in the SML. While I think there is a connection, the biological activity and saccharide abundance in the SML doesn't appear to change significantly from day 10 to 14, so I have a hard time believing that's the cause for the shift in SSA saccharide abundance increase on Day 14. I agree they are linked, but I think the statement currently is an over-generalization.

Author Reply

We have provided a more detailed description of this in the revised manuscript.

Page 16, lines 409-412

However, the percentage of saccharides in SSA remains below 10%, with a significant increase only observed on Day 14. This suggests that the abundant saccharides observed in the SML on Day 10 are not immediately and efficiently transferred to SSA. Instead, they likely undergo bacterial modification before manifesting as a significant increase in SSA on Day 14.

5. On lines 435-436 there's a typo with an incomplete reference to a Figure and an accidental paragraph break.

Author Reply

This has been corrected.

Page 17, line 436

Therefore, they exhibit higher EFs in both submicron and supermicron SSA (see Fig.

S8).

6. The caption for Figure 6 is incomplete. It's missing a description of panel a, where the current description of a applies to b, and b to c.

Author Reply

We thank the Referee for this remark. We have revised the caption of Figure 6.

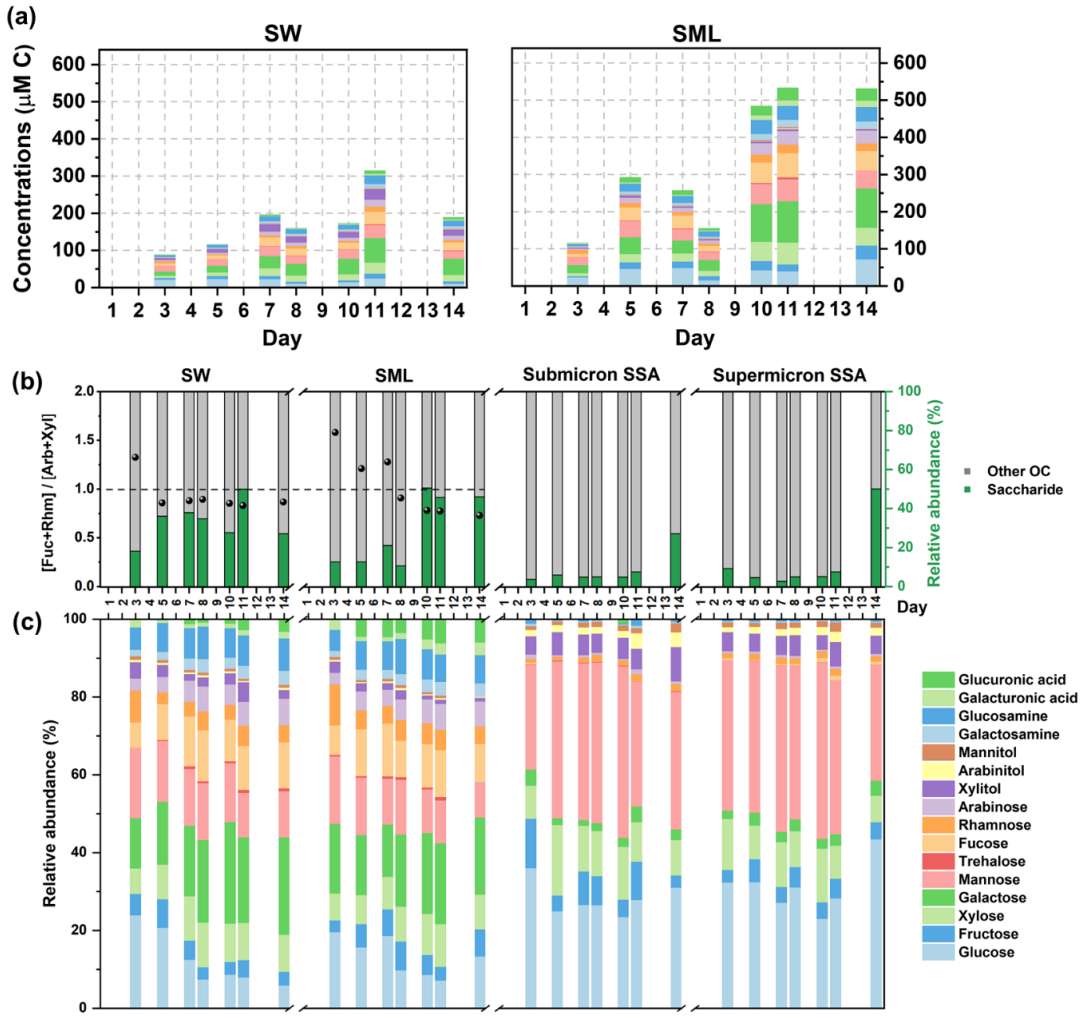

Figure 6. Sea-to-air transfer of saccharides. (a) Time series of saccharides' concentrations in seawater and the SML. (b) Relative abundance of total saccharides in DOC. The bacterial activity is expressed as the ratio of the sum of the concentrations of fucose and rhamnose to the sum of the concentrations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

7. A general comment for section 3.3.3: I agree with all of the information as it is presented. However, I think it's a bit of an over-generalization to only talk about film drop production impacting submicron SSA and jet drop production impacting supermicron SSA when jet drops produce up to 43% of submicron SSA (see Wang & Deane et al., 2017, PNAS). It's common to generalize with the distinction of film/jet for submicron/supermicron, but I think this paper would be strengthened with a statement acknowledging this generalization and the influence of jet drop production in determining submicron SSA composition.

a. Wang, Xiaofei, Grant B. Deane, Kathryn A. Moore, et al. "The Role of Jet and Film Drops in Controlling the Mixing State of Submicron Sea Spray Aerosol Particles." Proceedings of the National Academy of Sciences of the United States of America 114, no. 27 (2017): 6978–83. https://doi.org/10.1073/pnas.1702420114.

Author Reply

We have provided a generalized explanation and appropriate references on this point.

Page 17, lines 433-437

Distinguishing film drops from jet drops based on submicron SSA and supermicron SSA is a generalized approach, since submicron SSA also contains a non-negligible contribution from jet drops (~43%) (Wang et al., 2017). However, compared to supermicron SSA (which can be considered entirely composed of jet drops), both film drops and jet drops in submicron SSA are generally inefficient in transferring large particles (Dubitsky et al., 2023; Dubitsky et al., 2024). This may further influence the sea-to-air transfer of polysaccharides.

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