

Responses to the comments of Referee#1

General comments:

The organic component of aerosol is an important and uncertain aspect of aerosol composition, particularly in the marine atmosphere. Given the importance of aerosols in atmospheric chemistry and climate developing a better understand of this aerosol organic matter is valuable and this paper is a useful contribution to this goal.

This is a thorough and interesting study of aerosols during the spring bloom period in the Sea of Okhotsk. The chemical characterisation particularly of the aerosol is comprehensive, sophisticated, and well described. Overall I believe the paper is well worth publication but I do have some suggestions for modifications prior to final publication.

Reply: We appreciate the referee's valuable comments on our work. Our responses to the specific comments and details of the changes made to the manuscript are given below.

Specific comments:

Firstly I believe it would be useful to include some further descriptions of the conditions at the time of sampling.

1. There is talk of ice algae and I'm not clear whether there was a lot of ice at the time of sampling or not. This is potentially important because an ice cap can allow a build up of quite high concentrations of marine biogenic gases which are then released rapidly as the ice breaks up.

Reply 1: During the sampling period of this study, sea ice had already retreated, and there was no ice around the observed region. To show the special distributions of sea ice and their temporal changes, the maps of sea ice extent in the Sea of Okhotsk in March and April 2021 are now added as Fig. S1 in the Supplement. Also, the corresponding sentence has been revised as follows:

L.68: “*During this period when the sea ice had already melted or retreated (Fig. S1), ..*”

2. What were the wind conditions like? – this is relevant to ice break up, seawater mixing and bloom development and to seaspray emissions.

Reply 2: The average local wind speeds during each sampling duration were $\sim 4\text{--}12\text{ m s}^{-1}$ as shown below. Because sea ice had already retreated during the study period, as mentioned above, the local wind speeds were unlikely to be relevant to ice breakup during the study period. Instead, the wind speed was relevant to the atmospheric emission of sea spray aerosols, as the referee pointed out. The figure below illustrates that Na^+ concentrations in submicrometer aerosol and local wind speeds showed significant positive correlations both during the bloom ($R^2 = 0.52$; $p < 0.05$) and bloom-decay ($R^2 = 0.64$; $p < 0.05$) periods. This supports that Na^+ concentrations in submicrometer aerosols can be a suitable tracer of sea spray in this study. This information is already described in the original manuscript, but the sentence has been modified in the revised manuscript (L. 267: “*The Na^+ concentrations and surface wind speeds were positively correlated during the bloom period ($R^2 = 0.52$; $p < 0.05$) and bloom-decay period ($R^2 = 0.64$; $p < 0.05$), supporting the hypothesis that Na^+ is a suitable tracer for SSAs.*”). Note that sea spray aerosols were more efficiently produced during the bloom-decay period compared to the bloom period. It might be partly due to the difference in the physical state of the sea surface, but the exact reason is not clear.

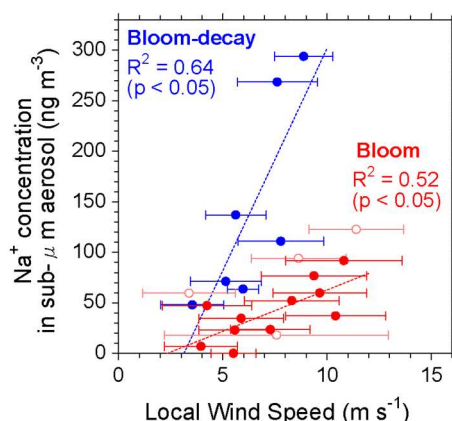


Figure: Scatterplot between sodium concentration in submicrometer aerosols vs. local wind speeds. The values of local wind speed are averages during each aerosol sampling duration and bars indicate standard deviations. The data obtained during the bloom and bloom-decay periods are shown in red and blue, respectively. Solid circles indicate the data of marine origin defined by stable carbon isotope ratios in submicrometer aerosols.

3. The apparently very low contribution of terrestrial derived atmospheric aerosol organic matter leads to a question of where the air came from during the sampling period?, so including some air-parcel back trajectories would be useful.

Reply 3: As the referee suggested, we have added representative backward trajectories calculated from the sampling points during the bloom and bloom-decay periods (as Figure S2) to show the origins of the typical air mass. The backward trajectory frequencies showed that air masses with frequencies $>40\%$ were indeed transported or

originated over the southern Sea of Okhotsk, with minor contributions (e.g., <20%) from land surfaces, such as Hokkaido and eastern Eurasian continent. This supports the results of stable carbon isotope ratios in this study.

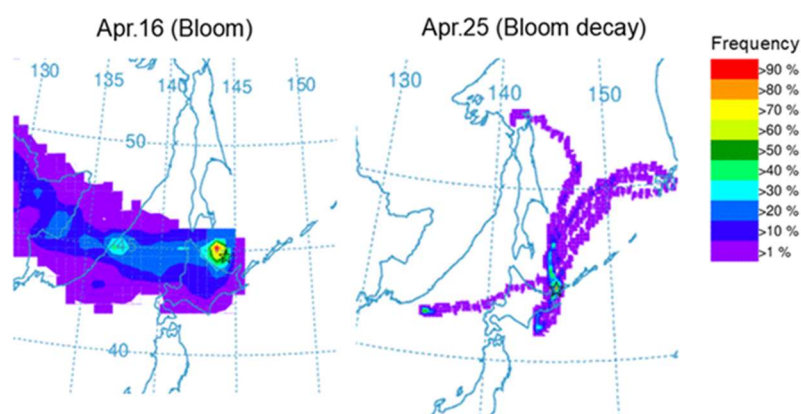


Figure S2: Typical 48-hour backward trajectory frequencies calculated from the sampling points for the bloom and bloom-decay periods.

The corresponding statement on the trajectory has been added to the text in the revised manuscript.

L.257: “..To support the source apportionment, Fig. S2 shows typical 48-hour backward trajectory frequencies calculated from the sampling points for the bloom and bloom-decay periods. The backward trajectory frequencies showed that air masses with frequencies >40% were indeed transported or originated over the southern Sea of Okhotsk, with minor contributions (e.g., <20%) from land surfaces, such as Hokkaido and eastern Eurasian continent. The trajectory supports the results of $\delta^{13}\text{C}$ values in this study.”

Throughout the discussion the authors should be clear which size of aerosol particles they are discussing. I became confused at several points. Gas phase emissions from seawater will form fine mode particles, while ejection of seawater itself will produce coarse mode particles. Some of the correlations such as in Figure 5 are not really useful given these differences.

Reply 4: In this study, we focused on the submicrometer particle as its size range is important for CCN activity. Supermicrometer particles or coarse mode particles are not discussed in this study, because their atmospheric residence time is much shorter than that of submicrometer particles. Moreover, the size distributions of WSOC shown in Figure 7 clearly support the importance of submicrometer particles in terms of the formation process of WSOC in this study. Based on these, we believe that Figure 5 is

still useful to discuss the origin and formation processes of submicrometer particles that can contribute to CCN.

In the revised manuscript, we have clearly mentioned that (L. 76) *“we focused on the analytical results obtained from the bottom stage of the impactor, which collected particles with an aerodynamic diameter (D_p) of $< 0.95 \mu\text{m}$ and are referred to as submicrometer particles.”*

Additionally, we added the following statement at the end of section 2.2: (L. 92) *“In this study, the results of submicrometer particles collected by the HVAS are mainly shown, whereas the results of aerosol particles collected by the cascade impactor are presented only to show the size distributions of water-soluble fractions of organic matter (section 3.3).”*

Also in the captions of Figures 5, 6, and 9, the words “submicrometer aerosols” have been added.

Section 3.2 is a bit misleading. As the authors correctly note at the end of this section (line 271-2) the tracer species they use represent only a tiny fraction of the WSOM and so the origin of this material is still essentially unknown, although the correlations to MSA and 3MBTCA are intriguing. I would suggest reorganising this section to avoid any misunderstandings over what can and cannot be said about the sources of the WSOM.

Reply 5: As the referee pointed out, we cannot identify the chemical structure or compositions of the majority of WSOM here, only from the relations of WSOM with those molecular tracers. Nevertheless, the correlations with 3-MBTCA and MSA together with a lower correlation with sodium at least suggest secondary formation of OA of marine biogenic origin rather than primary sea spray as the formation process of WSOC. That is what we intend to emphasize. In the revised manuscript, some sentences that were overstated have been modified as follows:

L.279: *“The WSOC concentration showed positive correlations with those of MSA (Fig.S4a; $R^2 = 0.62$ and 0.73 ($p < 0.05$) during the bloom and bloom-decay periods, respectively), suggesting that WSOC, which dominated the OC mass, was affected by the secondary production through the oxidation of DMS or DMS-relevant precursors.”*

L.289: *“The overall results suggest that the observed ocean-derived WSOC was affected by secondary formation from DMS-relevant compounds and α -pinene rather than primary sea spray emissions.”*

I was also a little confused by the logic of the argument in sections 3.3 and 3.4. The DOC and DON in seawater is overwhelmingly of high molecular weight and long lived. The observed relationships of DOC and DON in seawater (Fig 9) reflect the fact that they are probably actually bonded together in the same complex organic matter and the variations in concentrations in both compounds may reflect changes in production and consumption, or alternatively may reflect physical mixing of water masses. The correlations of DOC and DON in the aerosols look less convincing in Figure 9, and this correlation too could also represent mixing of air masses. Given its molecular weight, the direct emissions of seawater DOC and DON into the atmosphere will be via bubble bursting type processes and hence associated with coarse mode aerosol, as with sodium. This process cannot therefore explain the fine mode WSOM or the relationships of WSOM to MSA and other gaseous marine biogenic emissions reported here. All the data I have seen published suggests that marine amine emissions are very small, particularly in comparison to say ammonia emissions. Hence the emission of gaseous organic compounds from seawater into the atmosphere does not seem to be able to explain aerosol DON, although it could arise from marine biogenic gas emissions of other non-nitrogenous compounds with nitrogen being subsequently incorporated during aerosol formation. So I find the authors observations valuable and interesting, I am not sure they do provide a clear explanation of the formation mechanism for the aerosol WSON as implied particularly in the abstract. I would suggest that the logic of the argument in sections 3.3 and 3.4 might therefore be clarified.

Reply 6: If the direct atmospheric emissions of seawater DOC and DON via bubble bursting processes were significant to form the observed WSOC and WSON, their size distributions should show a dominant mode in the supermicrometer size range (or coarse mode). However, as shown in Figure 7, the mass of WSOC and WSON of marine origin resided mostly in the submicrometer size range in this study. This result of size distribution, together with the correlation with molecular tracers suggested the secondary formation of WSON rather than primary emissions with the dominant mode in supermicrometer size or coarse mode particles.

We agree that the sea-to-air emissions of amines are small compared to that of the bulk WSON and ammonia. In the current discussion, amines are raised as a candidate compound group associated with sea-ice microbiota, but they are not regarded as a major compound group of WSON. As the referee pointed out, it is possible that marine biogenic gas emissions of other non-nitrogenous VOCs, along with ammonia or reactive nitrogen, are subsequently converted to particles and/or incorporated into the existing particles (e.g., aqueous phase). As it is difficult to provide a clear explanation of the exact mechanism for the aerosol WSON formation in this study, we can just describe it as (L.354) *“the preferential formation of N-containing water-soluble OAs ... during the bloom period.”*

Taking into account the comment, we revised the statement in section 3.3 regarding the points above as follows:

L. 331: *“..The peaks measured in the submicrometer size range suggest gas-to-particle conversion of the majority of WSOC and WSON and/or accommodation of VOCs and nitrogenous compounds into the existing particles (e.g., in aqueous phase) rather than being emitted as primary aerosols (i.e., sea spray aerosols). In this study, the R^2 value between WSON and Na^+ concentrations in submicrometer aerosols was below 0.01 ($p = 0.05$) during the bloom, as expected from the relationship between WSOC and Na^+ concentrations. This also suggests the minor contribution of primary emission of sea spray to WSON, and the major contribution of SOA to WSON in the current study. These results support the secondary formation of WSOC suggested by its relationship with molecular tracers, as discussed previously in Section 3.2.”*