

Responses to the comments

We appreciate the additional comments on our work given by the editor and referee. Our responses to the specific comments and details of the changes made to the manuscript are given below.

The editor's comments and our responses

In addition to the revisions requested by the anonymous reviewers, please address also the following requests.

In section 2.4.5:

- Add the list of all target analytes that were investigated in the study.

Reply 1: Because the target compounds are only two (2-methyltetrols and 3-MBTCA) in this study and because they are already listed in Tables 3 and S2, we do not think it is necessary to additionally provide them in an individual list.

- Provide full experimental details for the GC-MS method used. This should include: chromatographic column used, elution method, amount injected, retention times of the analytes, quantification method, any use of calibration standards, method for determining recovery, method for determining reproducibility (or repeatability), limits of detection of the analytes.

Reply 2: According to the comment, we have provided the details for the GC-MS experimental method, except for the retention time, as follows (L.165):

“...After the derivatization, the derivative was diluted with hexane containing the internal standard (n-Tridecane (C₁₃) with concentration of 1.43 µg µL⁻¹ in hexane). Two µL of the TMS derivative was then injected into a capillary gas chromatograph (GC8890, Agilent) equipped with a DB-5MS fused silica capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness) coupled to a mass spectrometer (MSD5977B, Agilent) to determine the concentration of each molecular tracer. The mass spectrometer was operated in the electron ionization (EI) mode at 70 eV. The sample injection was made in splitless mode. The peaks of the target compounds in total ion chromatograms (TICs) were identified by

comparison of mass spectra with those of authentic standards or literature data. 3-MBTCA was estimated using the response factor of pimelic acid, which was determined using an authentic standard. 2-methyltetrols was quantified using the response factor of meso-erythritol (Fu et al., 2009). The mass concentrations of molecular tracers were determined by the MS peak area of TMS derivative relative to that of the 140 µl internal standard injected into the GC-MS. Recoveries of each organic compound were measured using the surrogates that were spiked into precombusted quartz-fiber filters (n=3), which were higher than 81% for all the compounds measured. Reproducibility of the measurements is based on relative standard deviation of the concentrations based on duplicate analysis, which was generally <13%. ...”

Retention time of a peak of a target compound depends on the length of the column in the GC instrument, which requires regular cutting during maintenance. The cutting includes removing short sections from the inlet end of the column to remove contaminants that are permanently retained on the column. Because the retention time changes depending on the length of the column, we do not include the information on it.

Table S2: report results for all analytes investigated and report detection limits for all analytes reported in the table.

Reply 3: According to the comment, all the aerosol chemical parameters investigated in this study are shown in Table S2 together with their lower detection limits of the concentrations for parameters directly measured.

Please note typo at line 188 of the tracked-changes version: “chl.a”.

Reply 4: Corrected as pointed out (L.198).

Comments by the referee and our responses

The authors have addressed almost all of my comments and I am content for the manuscript to be published. I would suggest a couple of changes that might be made.

Line 80 explain briefly the “blank procedure”, since there are several ways to do this.

Reply 1: Four field blanks were collected with quartz-fiber filters mounted on the impactor without running the HVAS, which were obtained on the ship during the expedition. This has been additionally described in the revised manuscript (L. 80).

Line 223 I would prefer molar units, but if you use mass units please specify them more ng/m³ SO₄ for example should specify if the weight is as S or SO₄.

Reply 2: The mass unit is used for sulfate, because the mass concentrations are compared with those of the other chemical component (i.e., OM, etc.) in this context. Also, as we clearly mention “Sulfate (SO₄²⁻)” at the beginning of a sentence, we believe it is apparent that the concentration is for the sulfate mass rather than S. Therefore, we decided to keep them as they are.

The paper usefully demonstrates that fine mode organic aerosol composition in this area is dominated by marine probably gaseous sources. I would however, suggest that the argument about the mechanism can be clarified a bit.

Firstly in line 220 the data seems to suggest that aerosol WSOC is similar before the bloom, so are the results really bloom period specific?

Reply 3: First, the WSOC concentrations shown in Section 3.1 are those for all the data obtained during each period. Meanwhile, the difference in the WSOC concentrations of “marine origin” between the bloom (803±555 ngC m⁻³; Table 1) and the pre-bloom (545±332 ngC m⁻³) periods is larger than that for all the data. In addition, the contribution of sea spray aerosols to WSOC was more significant during the pre-bloom period (Miyazaki et al., 2018) compared to the bloom period in this study. Therefore, these results support our conclusion that aerosol WSOC and WSON of marine origin were likely affected by secondary formation from precursors of marine origin rather than primary emissions of sea spray aerosols.

Secondly there seems some contradiction in the suggested sources of some of the WSOC and WSON in aerosols.

In lines 325 and 370 there is discussion of proteins in seawater, but I assume the authors are not suggesting that these are volatile.

The discussion around line 335 links the seawater DOC and DON to the aerosol WSOC and WSON, but most of the DOC and DON in seawater is not volatile – indeed we know it is high molecular weight and recalcitrant- and the authors acknowledged in the response to reviewers that amines while volatile form seawater are at very low concentrations.

I would suggest the authors clarify (or remove) the mechanisms they are proposing

Reply 4: We do not intend to mention that the seawater DOC and DON compositions were preserved during their sea-to-air emissions, but some parts of them may have been affected by photodegradation and/or biodegradation in the air-sea interface to produce more volatile compounds. Although it is difficult to provide a clear explanation of the exact mechanism for the aerosol WSON formation including the processes in the air-sea interface, we have added the following statement in the revised manuscript, taking account of the referee's comment:

L. 407: "It is noted that the majority of DOC and DON discussed in this study are generally high molecular weight compounds and have low volatility. Therefore, photodegradation and/or biodegradation of DOC and DON in the air-sea interface are likely important to produce more volatile compounds for the atmospheric emissions, which needs further investigation in future studies."

Reference

Miyazaki, Y., Yamashita, Y., Kawana, K., Tachibana, E., Kagami, S., Mochida, M., Suzuki, K., and Nishioka, J.: Chemical transfer of dissolved organic matter from surface seawater to sea spray water-soluble organic aerosol in the marine atmosphere, Scientific Reports, 8(1), 14861, <https://doi.org/10.1038/s41598-018-32864-7>, 2018.