A point-to-point response and relevant changes made in the revised manuscript

Anonymous Referee #2

The authors reported the chemical composition and evolution of volatile precursors emitted from macro-algae and their oxidation products in the gas and particle phase using a suite of mass spectrometers. But it was shallow and simple about the discussion of the transformation mechanisms of organic compound. I recommend that the authors could make more detailed explanations about the results and explore more precise reaction formulas.

Here are some questions about the methods and results in the following.

> **Re**: we thank the referee for careful examination and important comments of the manuscript. Point-to-point responses were given below. Changes were made in the revised manuscript accordingly.
>
> As a response to his/her general comment, we think for such a highly complex system with tens and even hundreds of precursors, it is very difficult for us to present a uniform reaction pattern to explain the complicated interactions among numerous precursors, intermediates and products, or to list all reaction equations that occurred in the bag reactor. Exploring precise reaction equations may be more practical for a one-precursor system. This could be the goal of a future study. More explanation is presented in our response to the last comment.
>
> More descriptions about the formation of inorganic molecules/radicals I_xO_y, $ClNO_x$ and HIO_x were added in the revised manuscript.

Method

81: "In the three ozonolysis experiments"

It seems that only one result (without error bar) is shown in this paper. What is about the remaining two experiments?

> **Re**: Mean values and standard deviations of total organic carbon, total iodine, particle number and size were presented in Table 1 for the three ozonolysis experiments.
>
> The purpose of this study is to qualitatively identify gas and particle products of algae-emitted VOCs in the simulated NPF event. Because aerosol production TOC and TI were quite constant, we measured chemical composition for only one set of experiment.

84: "In an additional OH-enhanced experiment"

The authors conducted this experiment for simulating atmospheric oxidation process, however, you didn't even give the concentration of additional OH and the limitation of the experimental design compared with the real environment wasn't discussed.

Re: OH was produced via O_3 photolysis in the UV lamp and consumed via reacting with vapor mixture and wall loss in the bag reactor. So OH concentration changed over time when air flowed through the lamp and the bag reactor. When revising the manuscript, we did SO_2 decay experiment in the bag reactor to estimate integrated OH exposure.

The following statement is added in line 90-96

"Integrated OH exposure time was determined by SO_2 decay experiment to be 2.4 days in the experimental apparatus assuming ambient average OH concentration 1.5×10^6 molecules cm^{-3} (see Supporting Material S1). Other oxidants may include $O(^3P)$ resulted from the quenching of $O(^1D)$ (Li et al., 2015). Because the purpose of this study is to identify gas and particle products of algae-emitted VOCs in the simulated NPF event, significantly higher oxidation level in the bag reactor than atmosphere should not change the conclusions in the article. Wall loss, aerosol yield, reaction rate and other kinetic factors in the bag reactor were also not evaluated."

In SM Text S2

"Integrated OH exposure measurement

SO_2 decay experiment was conducted to estimate integrated OH exposure in the experimental apparatus, following Lambe et al. 2015. We replaced the macroalgal emission flow by a humidified air flow containing 200 ppbv SO_2 from standard gas cylinder. SO_2 was consumed by the reaction with OH while flowing through 254 nm UV light and the bag reactor. SO_2 mixing ratio at the outlet of the bag reactor was measured with and without UV lamp on, using a Model 43i-TLE SO_2 analyzer (Thermo Scientific Inc.). OH exposure was calculated from the equation

$$OH_{exp}=\ln(SO_{2\ lamp\ off}/SO_{2\ lamp\ on})/k_{OH+SO2}$$

where k_{OH+SO2} is 9.49×10^{-13} cm^3 $molecule^{-1}s^{-1}$ (Burkholder et al. 2015) .

$SO_{2\ lamp\ off}$ and $SO_{2\ lamp\ on}$ were measured to be 18 and 13 ppbv, respectively. OH_{exp} was then calculated to be to be 3.2×10^{11} molecules cm^{-3} s. This is equivalent to 2.4 days assuming 1.5×10^6 molecules cm^{-3} ambient average OH.

Reference

Burkholder, J. B., Sander, S. P., Abbatt, J., Barker, J. R., Huie, R. E., Kolb, C. E., Kurylo, M. J., Orkin, V. L., Wilmouth, D. M. and Wine P. H. "Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 18," JPL Publication 15-10, Jet Propulsion Laboratory, Pasadena, 2015.

Lambe, A. T., Chhabra, P. S., Onasch, T. B., Brune, W. H., Hunter, J. F., Kroll, J. H., Cummings, M. J., Brogan, J. F., Parmar, Y., Worsnop, D. R., Kolb, C. E., and Davidovits, P.: Effect of oxidant concentration, exposure time, and seed particles on secondary organic aerosol chemical composition and yield, Atmos. Chem. Phys., 15, 3063-3075, 10.5194/acp-15-3063-2015, 2015."

120: "TI or TOC in the particles was obtained by subtracting the amount on the back filter from that on the front filter"

I am confused about the calculation. As you said that "The front filter of the double filter pack collected the particles, while the back filter placed downstream of the front filter was supposed to adsorb the same amount of volatile species as the front filter", may I think of it this way: particles in the front filter and volatile species in the back filter. Why the TI in the particle is not the amount on the front filter? Why it needs to subtracting the amount on the back filter?

Re: We are sorry to make this confusion. The front filter collected particles + adsorbed volatile species; the back filter adsorbed volatile species only.

We change the sentence in line 110-113.

"The front filter of the double filter pack collected the particles and also adsorbed some volatile species as positive artifact, while the back filter placed downstream of the front filter was supposed to adsorb the same amount of volatile species as the front filter."

128: "Only the compounds that existed solely in the front filter or with ion intensity in the front filter higher than that in the back filter by a factor of 3 were regarded as the organic compounds in the particle phase"

Please cite suitable literature.

Re: we cite the following paper

"Wang, X., Hayeck, N., Brüggemann, M., Yao, L., Chen, H., Zhang, C., … Wang, L. (2017). Chemical characteristics of organic aerosols in shanghai: A study by ultrahigh-performance liquid chromatography coupled with Orbitrap mass spectrometry. Journal of Geophysical Research: Atmospheres, 122, 11,703–11,722."

Results and discussion

135, 138: "new particles larger than 14 nm were observed only 58 minutes after the injection of ozone flow", "With a prolonged residential time of 67 min…"

The authors talked about the results after 58 or 67 minutes. But the maximum of axis about the elapsed time in the Figure. 2 was 50.

Re: This is because Time zero of Figure 2 was set as the time when gaseous products first appeared, not when ozone was injected. We could not observe any new particle or gas-phase product during the first 48 minutes after O_3 were added. So we did not show the data during that early period in Figure 2.

In line 142-147 we add:

"No particles formed in the absence of room light or O_3. Therefore, light was on throughout the experiments reported in the article. In the static mode experiments, we could not observe gas-phase products until 48 minutes after O_3 injection. New particles larger than 14 nm were observed only 58 minutes after O_3 injection. Afterwards, new particles begun to grow to form a typical banana-shape particle size spectrum (Figure 2a). This relatively long waiting time was likely due to the build-up of O_3 and oxidation products. Time zero of Figure 2 was thus set as the time when gaseous products first appeared."

136: "No particles were formed in the absence of room light or ozone".

I don't see the relevant results (table or figure) shown in the paper.

Re: our pilot study showed that no particles formed in the absence of room light or O_3. We did not collect continuous time evolution data of particle and gaseous products in those pilot experiments. So we did not show those results.

On the other hand, O_3 and room light were always supplied for the chemical measurement experiments shown in the manuscript,

154: "But those small new particles are expected to grow into CCN active sizes, given longer residence time and uptake of more condensing vapors in the atmosphere".

Please cite suitable literature.

Re: this paper is cited now:

"He, X. C et al. Role of iodine oxoacids in atmospheric aerosol nucleation, Science, 371, 589-595, https://doi.org/10.1126/science.abe0298, 2021."

156: "3.2 Macroalgal emission"

I think it is more suitable to remove this section to the first part of the Results and discussion

Re: Thank you for pointing out this. Now the order of subsections in "Results and discussion" is changed to

3. Results and discussion

3.1 Macroalgal emission

3.2 Gaseous products

3.2.1 Gaseous inorganic molecules and radicals

3.2.2 Gaseous organic products

3.3 Particulate products

3.3.1 Relative mass contribution of organic carbon and iodine to new particles

3.3.2 Particulate organic products

187, 188: "IO, IO2 and ClIO could be from the reactions between I, ClI and O3", "ClNO2 was likely to form upon similar reaction between Cl and NO2 in the bag reactor"

Give the reaction mechanisms or cite literatures.

Re: we revised the two paragraphs in line 181-193, following community comments

> *"2. IO_2, IO and ClIO in gas phase: these species showed a similar time evolution to I and Cl atoms. They could be from the reactions between I, ClI and O_3 (Saiz-Lopez et al., 2014). Sequential oxidation and aggregation reactions might have formed other halogen oxides (Gómez Martín et al., 2013), but they might not be detectable by iodide-CIMS.*
>
> *3. INO_2, $ClNO_2$ and INO_3: INO_2 and $ClNO_2$ were detected in gas phase with similar time evolution with halogen atoms and halogen oxides (Figure 2d). INO_3 was found in both gas and particle phases. INO_2 and INO_3 were usually thought to form upon the reactions $I+NO_2+M \rightarrow IONO+M$ and $IO+NO_2+M \rightarrow IONO_2+M$ in the atmosphere (Saiz-Lopez et al., 2012), which seems to be unlikely in our bag reactor because NO_2 was not added. Considering NO_3^- was ubiquitous in the bag reactor of our experiment, it is likely that INO_2 and INO_3 formed via $I_2O_2+NO_3^- \rightarrow IO_3^-+IONO$ and $I_2O_3+NO_3^- \rightarrow IO_3^-+IONO_2$. These reaction pathways have been supported by theoretical calculation and flow tube mass spectrometry experiments (Gómez Martín et al., 2022; Gómez Martín et al., 2020). $ClNO_2$ was likely to form upon similar reaction between Cl_2O_2 and NO_3^- in the bag reactor."*
>
> *"*

195: "which is contrary to the observation by HPLC-ICP-MS that total iodine was mostly dominated IO3- peak"

Could the authors explain the contrast?

Re: In line 199, we add

> *"We speculate that HIO_3 might have been dehydrated to I_2O_5 under thermal desorption temperature up to 180 ℃ in FIGAERO."*

259: Scheme II

The formulas are too simple to understand the mechanism of particle formation. It might be meaningful to give formulas like Scheme I for several specific species.

Re: it is not appropriate to give exact reaction equations in *Scheme II* for the following reasons:

1. Particulate dimer products like $C_{14}H_{16\text{-}26}O_{6\text{-}12}$ and $C_{16}H_{20\text{-}32}O_{6\text{-}12}$ have higher carbon number and thus more complex molecular structure than those small molecules in *Scheme I*. CIMS analysis provided molecular formula information only. It is thus not realistic to propose an exact molecular structure and reaction equation. Any speculative molecular structure or reaction equation is unfounded and may be misleading.

2. For the highly complex system with tens and even hundreds of precursors, it is not realistic to present a general or uniform reaction equation to explain the complicated interactions among numerous precursors, intermediates and products, or to list all reaction formulas that occurred in the bag reactor.

3. A variety of accretion reactions without uniform oligomerization pattern (e.g., esterification, aldol condensation, hemiacetal reactions, peroxyhemiacetal formation and SCI reactions, etc.) might have occurred in the particles. It is again not realistic to present equations for just several specific species.

On the other hand, the two equations in our old manuscript, strictly speaking, can not be called a "scheme". In line 292-298, we rephrase to :

"As an example, we used two simplified reaction equations to illustrate addition-type cross-oligomerization between C_6 and C_8 monomers and self-oligomerization of C_8 monomers, respectively:

$$C_6H_{6\text{-}12}O_{3\text{-}6}+C_8H_{10\text{-}16}O_{3\text{-}6}\rightarrow C_{14}H_{16\text{-}26}O_{6\text{-}12}$$

$$C_8H_{10\text{-}16}O_{3\text{-}6}+C_8H_{10\text{-}16}O_{3\text{-}6}\rightarrow C_{16}H_{20\text{-}32}O_{6\text{-}12},$$

in which the C_6 , C_8, C_{14} and C_{16} formulas are among the most abundant ones observed in the particle phase by the iodide-CIMS."