

A point-to-point response to editor's comments

We are very grateful for the helpful and insightful comments from the editor, and have carefully revised our manuscript accordingly. In the following point-to-point response, editor's comments are repeated in *italics*, whereas our responses are in plain texts labelled with **[Response]**. Line numbers in the responses correspond to those in the revised manuscript (the version with all changes accepted). Modifications to the manuscript are in blue.

1. Yang et al. illustrated how the screening criteria combined with thermogram data can be used to examine the presence of thermal decomposition in ambient organic aerosol datasets (Figure 8 in Yang et al. and associated discussions). Could you make similar evaluations to further support the statement that the effect of thermal decomposition is minor?

Response:

Yang et al. (2021) identified in their ambient dataset that $C_5H_8O_6$ met the screening criteria for considerable thermal decomposition ($DBE \geq 2$, $T_{max} \geq 72$ °C and $nO > 4$) by investigating thermograms of the parental compound ($C_5H_8O_6$) and possibly its decarboxylation product ($C_4H_8O_4$) to confirm the presence of thermal decomposition.

In our case, we analyzed 181 compounds (91 CHO and 90 CHON) according to the screening criteria of Yang et al. (2021). Thermograms of 78 compounds show bimodal peaks, most of the warmer of which correspond to thermal decomposition of higher molecular weight organic compounds (Huang et al., 2018) but not included in the following analysis.

Therefore, we used the screening criteria of Yang et al. (2021) to screen the remaining 103 compounds with unimodal thermograms. Among the 103, there are 33 compounds that meet the screening criteria for considerable thermal decomposition ($DBE \geq 2$, $T_{max} \geq 72$ °C and $nO > 4$), and the thermograms of these 33 compounds generally present a single-peak without broad tailing and fronting, as shown in Figure R1a and c (i.e., Figure S9a and c in the revised Supporting Information).

We then investigated possible thermal decomposition products of these 33 compounds. Although thermal decomposition could be very complex, here we only considered dehydration products and decarboxylation products. Two compounds were identified to be potential thermal decomposition products, i.e., $C_9H_{17}O_3N$ and $C_{10}H_{13}O_4N$ could be a decarboxylation product of $C_{10}H_{17}O_5N$ and a secondary dehydration product of $C_{10}H_{17}O_6N$, respectively. T_{max} of $C_9H_{17}O_3N$ was higher than that of $C_{10}H_{17}O_5N$ by about 8 °C and T_{max} of $C_{10}H_{13}O_4N$ was higher than that of $C_{10}H_{17}O_6N$ by about 4 °C, which is close to the results of Yang et al. (2021). However, this observation can also be explained by isomers with vastly different vapor pressures (Huang et al., 2018; Lopez-Hilfiker et al., 2015). For a quick identification of these compounds, $C_9H_{17}O_3N$,

$C_{10}H_{17}O_5N$, $C_{10}H_{13}O_4N$ and $C_{10}H_{17}O_6N$ have been marked in Figure R2 (i.e., Figure 3 in the revised manuscript).

The O/C ratios of $C_9H_{17}O_3N$ and $C_{10}H_{13}O_4N$ are in the range of 0.25-1, we fitted the volatility parameterization, and obtained Eq. (4-R3) using compounds in the left dashed ellipse in Figure R2 that do not contain $C_9H_{17}O_3N$ and $C_{10}H_{13}O_4N$, and Eq. (4-1) by compounds in the left dashed ellipse in Figure R2 that contain $C_9H_{17}O_3N$ and $C_{10}H_{13}O_4N$. We used measured saturation mass concentration as benchmarks to compare the quality of Eq. (4-1) and Eq. (4-R3). It turned out that the volatilities of compounds in the left dashed ellipse in Figure R2 estimated by Eq. (4-1) are very close to those by Eq. (4-R3), as shown in Figure R4. Thus, the effect of potential thermal decomposition of our ambient sample is minor.

We have added this point to the revised manuscript, which (Line 332-342) reads, “On the other hand, 33 out of the 103 unimodal compounds meet the screening criteria of Yang et al. (2021) for considerable thermal decomposition ($DBE \geq 2$, $T_{max} \geq 72$ °C and $nO > 4$), and the unimodal thermograms of these 33 compounds generally do not present broad tailing and fronting, as shown in Figure S9a and c. The possible thermal decomposition products of these 33 compounds are then investigated. Although thermal decomposition could be very complex, here we only considered dehydration products and decarboxylation products. $C_9H_{17}O_3N$ and $C_{10}H_{13}O_4N$ could be a decarboxylation product of $C_{10}H_{17}O_5N$ and a secondary dehydration product of $C_{10}H_{17}O_6N$, respectively. T_{max} of $C_9H_{17}O_3N$ is higher than that of $C_{10}H_{17}O_5N$ by about 8 °C and T_{max} of $C_{10}H_{13}O_4N$ is higher than that of $C_{10}H_{17}O_6N$ by about 4 °C, which is close to the results of Yang et al. (2021). However, this observation can also be explained by isomers with vastly different vapor pressures (Huang et al., 2018; Lopez-Hilfiker et al., 2015). For a quick identification of these compounds, $C_9H_{17}O_3N$, $C_{10}H_{17}O_5N$, $C_{10}H_{13}O_4N$ and $C_{10}H_{17}O_6N$ have been marked in Figure 3. Since only two compounds may be thermal decomposition fragments, thermal decomposition likely has little effects on our subsequent analysis.”.

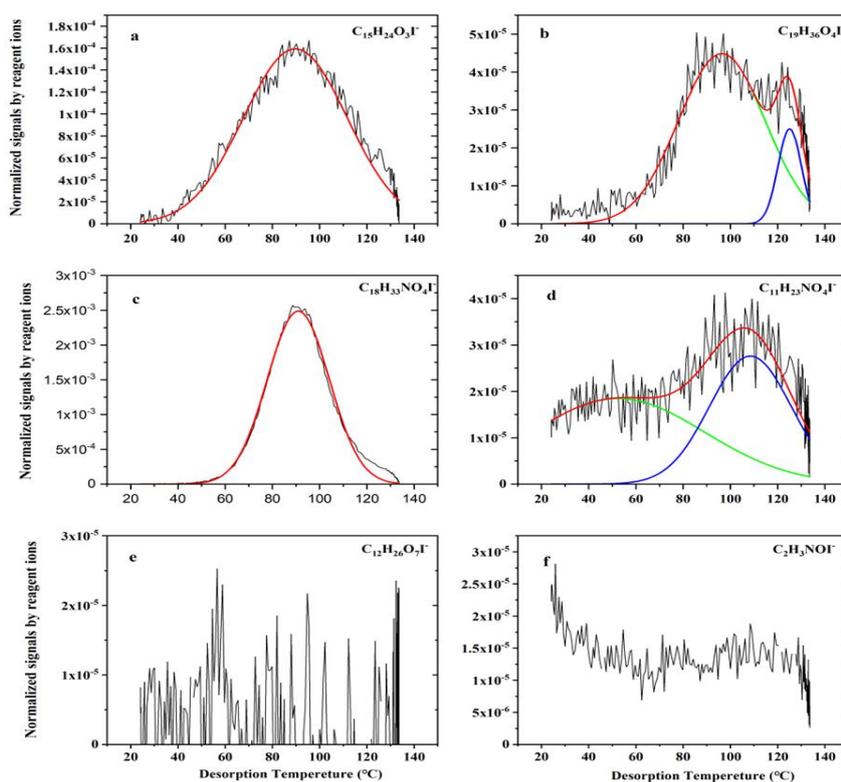


Figure R1. Four representative types of thermograms. Red, green and blue lines represent fitting curves for the overall thermogram, the first desorption peak, and the second desorption peak, respectively.

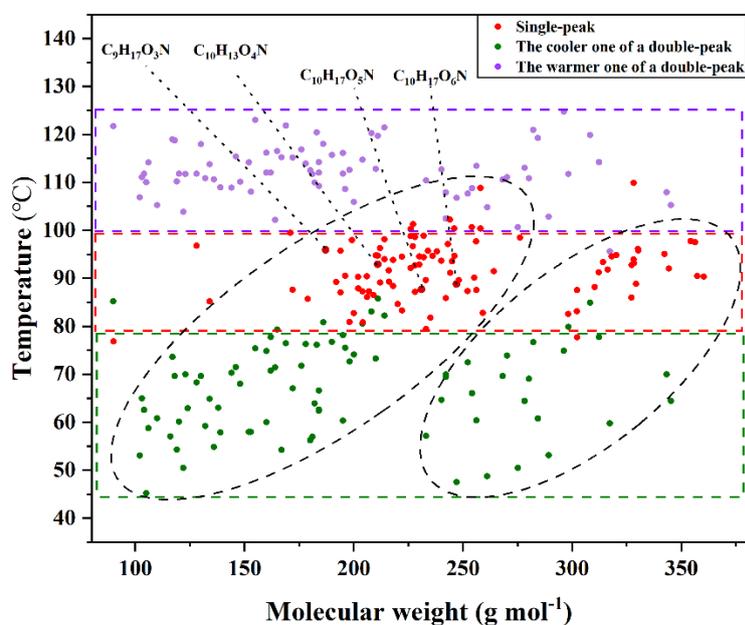


Figure R2. Evaporation and decomposition of 91 CHO and 90 CHON compounds, of which the reagent ion (I^-) is excluded from their formulae. The signal peaks, the cooler and warmer peaks of double-peaks are denoted by red, green and purple circles, respectively. Rectangular bands depict the temperature zones in which peaks appear.

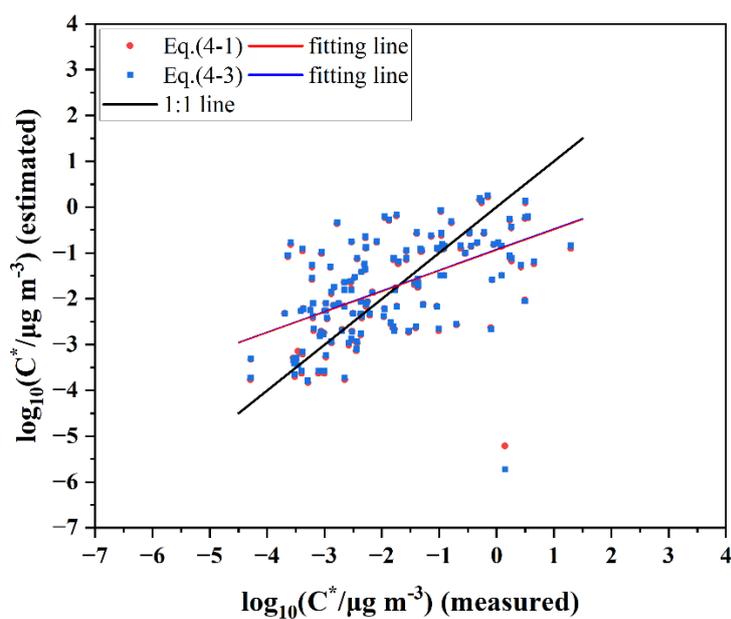


Figure R3. Saturation mass concentration (C^*) of compounds in the left dashed ellipse in Figure R2 as estimated by the Eq. (4-1) and Eq. (4-R3) against.

2. Suggest to remove the word generally in "... but a slower heating rate generally leads to a smaller number of thermal decomposition products (Yang et al., 2021)." since only citric acid was tested.

Response:

The word "generally" has been removed in the revised manuscript.

References

- Huang, W., Saathoff, H., Pajunoja, A., Shen, X., Naumann, K. H., Wagner, R., Virtanen, A., Leisner, T. and Mohr, C.: α -Pinene secondary organic aerosol at low temperature: Chemical composition and implications for particle viscosity, *Atmos. Chem. Phys.*, 18(4), 2883–2898, doi:10.5194/acp-18-2883-2018, 2018.
- Lopez-Hilfiker, F. D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T. F., Carrasquillo, A. J., Daumit, K. E., Hunter, J. F., Kroll, J. H., Worsnop, D. R. and Thornton, J. A.: Phase partitioning and volatility of secondary organic aerosol components formed from α -pinene ozonolysis and OH oxidation: The importance of accretion products and other low volatility compounds, *Atmos. Chem. Phys.*, 15(14), 7765–7776, doi:10.5194/acp-15-7765-2015, 2015.
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