A point-to-point response to reviewers' comments

We are very grateful for the helpful and insightful comments from the reviewers, and have carefully revised our manuscript accordingly. In the following point-to-point response, reviewers' 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.

Reviewer #4

The authors have addressed well the points brought up by the four reviewers. The manuscript has improved significantly and I am happy with the majority of the responses. However, as the authors now report the slow temperature ramping rate in their FIGAERO setup, I realized that the manuscript lacks some discussion regarding the potential effects of thermal decomposition on their observations.

Response:

We are very grateful for the insightful comments from Reviewer #4 and have revised our manuscript accordingly.

1.It should be noted that a single-peak thermogram does not always ensure that decomposition did not take place. For example, in Riva et al. (2019), SOA (alpha-pinene ozonolysis) formed onto acidic sulfate particles (a chamber study) sampled with a FIGAERO-I-CIMS had a rather unimodal thermogram with a low Tmax, but isothermal evaporation studies on similar SOA formation showed that the SOA was actually of very low volatility. The SOA measured by the FIGAERO during the Riva et al. (2019) experiments had high contributions from high double bond equivalent (DBE) compounds. Discussion about high DBE and thermal decomposition likelihoods were brought up also in Yang et al. (2021). How would Figures 3 and 4 look like if color-coded by DBE? Could you add some discussion about the potential effects of thermal decomposition and how it would affect your volatility parameterizations? Is it possible that the second ellipse (the one at generally higher molecular weights with lower O:C) in Figures 3 and 4 is greatly affected by thermal decomposition and the Tmax is significantly reduced similarly as happened in the Riva et al. (2019) experiments mentioned above?

Response:

Indeed, according to Riva et al. (2019), thermal decomposition of the oligomers in organic aerosols can lead to a misinterpretation of the SOA volatility. Riva et al. (2019) observed an increase in high DBE compounds, which were postulated to be thermal decomposition fragments of high-molecular-weight organic molecules. Besides, those thermal decomposition fragments with high DBEs could lead to an overestimation of

organic aerosol volatility. In our study, the components of ambient organic aerosols are very complex, and thus it is difficult to identify the decomposition products and their parental organic molecules based on thermograms and to quantify this effect on our volatility parameterizations.

Furthermore, Yang et al. (2021) found that the nO, DBE, and T_{max} of the parental compounds may be related to the degree of thermal decomposition by observing 29 standard compounds that include alcohols, monoacids, diacids, polyacids, and multifunctional acids. When DBE ≥ 2, $T_{max} \geq 72$ °C and nO >4, thermal decomposition of parental compounds can occur considerably. Since the parental compounds in ambient organic aerosols cannot be identified in this study, these criteria cannot be directly adopted to predict the degree of thermal decomposition of complex ambient organic aerosols.

Figure 3 and Figure 4 are now colour-coded by DBE, as shown in Figure R1 and Figure R2 (i.e., Figure S11 in the revised Supporting Information (SI)). In Figure R1 and Figure R2, the DBE distribution of these CHO and CHON compounds is random, suggesting that the effect of thermal decomposition on our volatility parameterizations may be minor.

We have added this point to the revised manuscript, which (Line 327-332) reads, "Furthermore, thermal decomposition of the oligomers in organic aerosols can lead to a misinterpretation of the SOA volatility, and double bond equivalent (DBE) has been used to determine the thermal decomposition degree of an individual compound and SOAs formed from the ozonolysis of α-pinene (Riva et al., 2019; Yang et al., 2021). The contents in Figure 4 are further colour-coded by DBE, instead of O:C, as shown in Figure S11. In Figure S11, the DBE distribution of these 181 compounds is random, thus the thermal decomposition could have a minor effect on T_{max}.".

The second ellipse (the one at generally higher molecular weights with lower O:C) covers 47 compounds. As shown in Figure R1 and Figure R2, the DBE of most compounds (32 out of 47) in the second ellipse is smaller than or equal to 2, and there are 15 of 47 compounds with high DBE (DBE >2). Moreover, the DBE distribution of compounds in the second ellipse has no regularity. Therefore, the T_{max} values of compounds in the second ellipse are less affected by thermal decomposition.
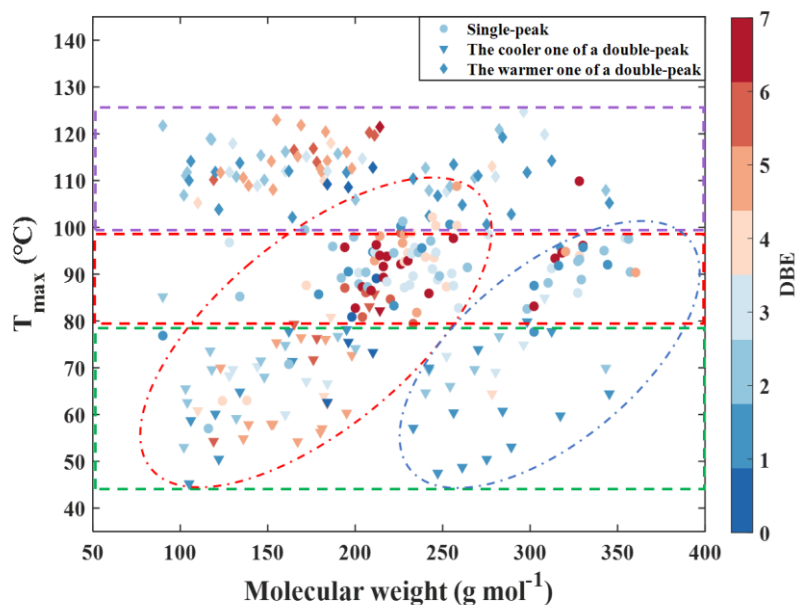
Figure R1. Evaporation and decomposition of 91 CHO and 90 CHON compounds, as colour-coded by DBE. Note that compounds with DBE equal to or greater than 7 are marked with the same colour. The signal peaks, the cooler and warmer peaks of double-peaks are denoted by circles, triangles and diamonds, respectively. Rectangular bands depict the temperature zones in which peaks appear.
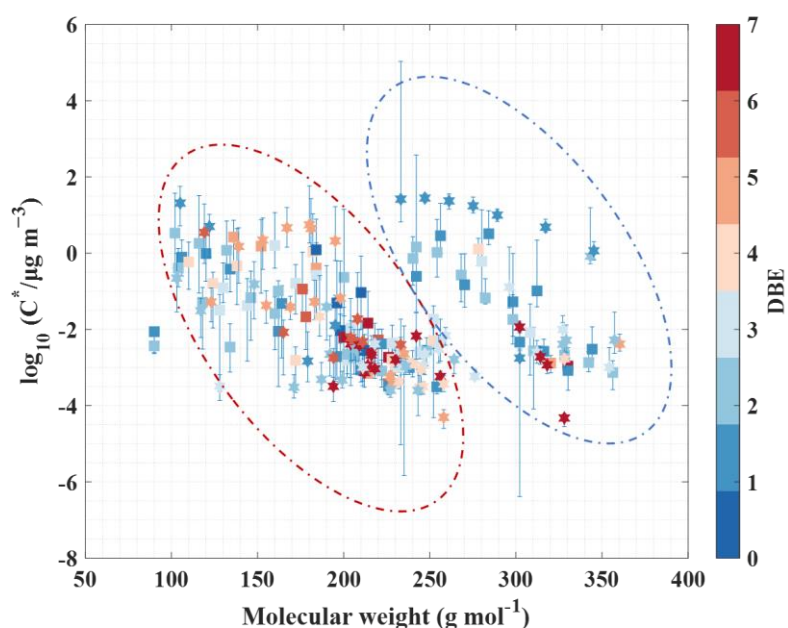

Figure R2. Saturation mass concentration of CHO and CHON compounds against their molecular weights, as colour-coded by DBE. Note that compounds with DBE equal to or greater than 7 are marked with the same colour. The CHO and CHON compounds are denoted by squares and hexagrams, respectively. Whiskers denote 25th and 75th percentile values of measured saturation mass concentration from 30 ambient samples and whiskers are ultimately due to variability in the measured T_{max} of CHO and CHON compounds.

2.You mention on L136 that a slower heating rate leads to a smaller number of decomposition products. Based on Yang et al. (2021), shouldn't it say the opposite or am I missing something?

Response:

Indeed, a slower heating rate leads to a larger decomposition degree of parental compounds. But Yang et al. (2021) also found that for the citric acid, there is a smaller number of products formed after the desorption process under a slower heating rate (i.e., only the primary and secondary dehydration products with no decarboxylation product).

To clarify this point, we now state in our revised manuscript (Line 124-127) that "Also, a slower ramping rate can separate compounds with similar volatilities better (Lopez-Hilfiker et al., 2014). Note that the decomposition degree of parental compounds under a slower ramping rate is higher than that under a faster ramping rate, but a slower heating rate generally leads to a smaller number of thermal decomposition products (Yang et al., 2021).".

Reviewer #3

I would like to thank the authors for carefully considering and addressing my comments (and those of my co-reviewers).
I believe the manuscript is much improved and clearer. As in my first review, I still think the manuscript overall is a carefully worked out and useful piece in our quest towards figuring out the volatility of SOA, so I recommend to accept it for publication. However, I also recommend the following minor and technical revisions:

Response:
We appreciate the insightful and positive comments from Reviewer #3 and have revised our manuscript accordingly.

Minor comments:

1.Lines 379+:
If I understand correctly, neither Zhao et al. (2013) nor Mazzoleni et al. (2010) report molecular structures, "just" molecular formulae. Please explain or correct.
However, some assumptions on molecular structures are indeed necessary to obtain vapor pressures from SIMPOL, so I wonder which assumptions were used here to arrive at the SIMPOL predictions (as in Fig. 5). I may just be missing a step here, which could be useful to point out in the text here. However, that step may be important for interpreting Fig. 5. (Specifically, for 230 of the 245 x-axis values!)
Same comment for lines 415+ (dealing with CHON instead of CHO).

Response:
Indeed, neither Zhao et al. (2013) nor Mazzoleni et al. (2010) reported molecular structures. Only molecular formulae were presented in the two studies.
We assume that the molecular structures of compounds from Zhao et al. (2013) and Mazzoleni et al. (2010) are common ones (i.e., most of function groups of their structures are included in SIMPOL, so that their volatilities can be calculated using SIMPOL).

To clarify this issue, we now state in the revised manuscript (Line 384-387) that "The molecular formulae of 230 CHO (O/C: 0.25-1) compounds are from Zhao et al. (2013) and Mazzoleni et al. (2010), and the molecular structures of these 230 compounds are predicted to be common, i.e., most of function groups of their structures are included in SIMPOL, so that the volatilities of these compounds can be estimated by SIMPOL.", and (Line 426-427) that "The molecular structures of selected species are assumed to be common. Then their saturation mass concentration (C^*) are estimated by different parameterizations and SIMPOL, respectively.".

2.Line 383:
Who or which parametrization have not been "considering covalent binding"? I suspect

that the term "covalent binding" is a too general term here for what the authors try to say. Please double-check and attempt to clarify.

Response:
Mohr et al. (2019) have not considered covalent binding. To clarify this point, we now state in the revised manuscript (Line 388-392) that "Although Mohr et al. (2019) and Stolzenburg et al. (2018) both updated parametrizations based on those 15 HOMs detected by Tröstl et al. (2016), compared to the Mohr et al. (2019) parameterization, the volatility predicted by the Stolzenburg et al. (2018) parameterization does match those by SIMPOL better, which could be attributed to the fact that Mohr et al. (2019) did not separately use parameters for dimer and monomer as Stolzenburg et al. (2018) did, so that the effect of the covalent binding is ignored.".

3.Line 388:
Which "inherent strength and deficiency of the FIGAERO method" is (are) referred to here?

Response:
We now state in our revised manuscript (Line 396-398) that "…, which reflects the inherent strength and deficiency of the FIGAERO method, i.e., the FIGAERO method replies on authentic standards that are commonly LVOCs and is thus less suitable for the more volatile compounds.".

Technical comments:

4.Figure 1:
The authors could point out which vapor pressures correspond to which compound, at least for the compounds used in this study. That would be particularly useful because not only PEG-n are used, but also erythritol and citric acid. Also, a slightly discrepant behavior is referred to in the text (line 253), which will be much easier to make out then. ... Oh, that has been done actually in Figs. S4-S6! That helps. It might still help to add some labels like that to Fig. 1 too. I'll leave that to the authors.
The other thing, however, is that it is unclear from Fig. 1, which line the "fitted parameters" (legend) correspond to. Please clarify, at least in the caption.

Response:

We have added more labels to Figure R3 (i.e., Figure 1 in the revised manuscript) to point out vapor pressures of corresponding compounds.
We have clarified the "fitted parameters" in the caption of Figure 1, which (Line 233) reads "The fitted parameters correspond to the dark green line.".
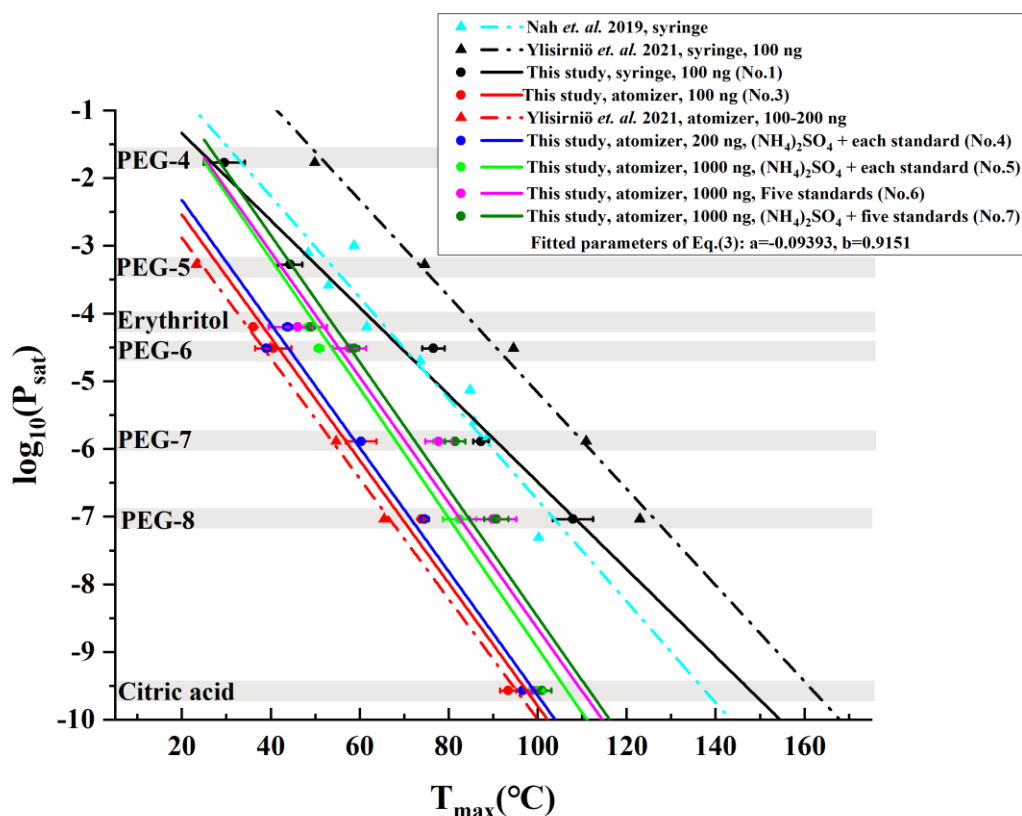
Figure R3. Comparison of calibration results obtained in this study with those reported previously. These solid lines denote the calibration results obtained in this study. Error bars represent ± one standard deviation of T_{max} from four replicate experiments. The fitted parameters correspond to the dark green line.

5.Lines 376:
I believe those 15 HOM have not yet been brought up, so I think "the" should be removed.
In fact, it should be moved to line 378.

Response:
We have revised our manuscript accordingly.

6.Line 440:
"owning" -> "owing" (I believe)

Response:
We have replaced "owning" with "owing" in the revised manuscript.

7.Figure S11:
I suggest adding a sentence to the caption, explaining which are the compounds explicitly pointed to in the figure. That info is found in the main text, but it would be helpful for the reader to receive some explanation in the figure caption as well.

Response:

We have added a sentence to the caption of Figure S12 in the revised SI, which (Line 59-61) reads "Marked compounds are oleic acid ($C_{18}H_{34}O_2$), levoglucosan or related isomers ($C_6H_{10}O_5$), margaric acid ($C_{17}H_{34}O_2$), linoleic acid ($C_{18}H_{32}O_2$), and palmitic acid ($C_{16}H_{32}O_2$), respectively.".
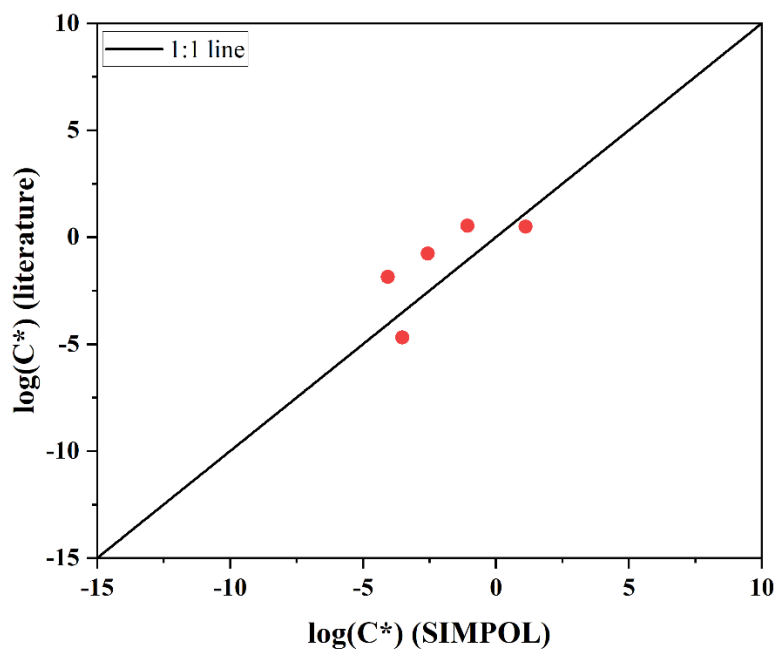
8.Figures S13:
Please explicitly name the 5 compounds.
(Also, "SIMPOL" is missing its I in both axis label and caption.)

Response:
We have explicitly named the 5 compounds in the caption of Figure R4 (i.e., Figure S14 in the revised SI).
And the typos have been revised.

Figure R4. Saturation mass concentration (C*) of five organic compounds (i.e., erythritol, PEG-6, PEG-7, PEG-8, and citric acid) from Krieger et al. (2018), Emanuelsson et al. (2016) and Ye et al. (2019) against those calculated by SIMPOL.

References

Emanuelsson, E. U., Tschiskale, M. and Bilde, M.: Phase State and Saturation Vapor Pressure of Submicron Particles of meso-Erythritol at Ambient Conditions, J. Phys. Chem. A, 120(36), 7183–7191, doi:10.1021/acs.jpca.6b04349, 2016.

Krieger, U. K., Siegrist, F., Marcolli, C., Emanuelsson, E. U., Gøbel, F. M., Bilde, M., Marsh, A., Reid, J. P., Huisman, A. J., Riipinen, I., Hyttinen, N., Myllys, N., Kurtén, T., Bannan, T., Percival, C. J. and Topping, D.: A reference data set for validating vapor pressure measurement techniques : homologous series of polyethylene glycols, , 49–63, 2018.

Mazzoleni, L. R., Ehrmann, B. M., Shen, X., Marshall, A. G. and Collett, J. L.: Water-Soluble Atmospheric Organic Matter in Fog: Exact Masses and Chemical Formula Identification by Ultrahigh-Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, Environ. Sci. Technol., 44(10), 3690–3697, doi:10.1021/es903409k, 2010.

Riva, M., Heikkinen, L., Bell, D. M., Peräkylä, O., Zha, Q., Schallhart, S., Rissanen, M. P., Imre, D., Petäjä, T., Thornton, J. A., Zelenyuk, A. and Ehn, M.: Chemical transformations in monoterpene-derived organic aerosol enhanced by inorganic composition, npj Clim. Atmos. Sci., 2(1), 1–9, doi:10.1038/s41612-018-0058-0, 2019.

Stolzenburg, D., Fischer, L., Vogel, A. L., Heinritzi, M., Schervish, M., Simon, M., Wagner, A. C., Dada, L., Ahonen, L. R., Amorim, A., Baccarini, A., Bauer, P. S., Baumgartner, B., Bergen, A., Bianchi, F., Breitenlechner, M., Brilke, S., Mazon, S. B., Chen, D., Dias, A., Draper, D. C., Duplissy, J., Haddad, I. El, Finkenzeller, H., Frege, C., Fuchs, C., Garmash, O., Gordon, H., He, X., Helm, J., Hofbauer, V., Hoyle, C. R., Kim, C., Kirkby, J., Kontkanen, J., Kürten, A., Lampilahti, J., Lawler, M., Lehtipalo, K., Leiminger, M., Mai, H., Mathot, S., Mentler, B., Molteni, U., Nie, W., Nieminen, T., Nowak, J. B., Ojdanic, A., Onnela, A., Passananti, M., Petäjä, T., Quéléver, L. L. J., Rissanen, M. P., Sarnela, N., Schallhart, S., Tauber, C., Tomé, A., Wagner, R., Wang, M., Weitz, L., Wimmer, D., Xiao, M., Yan, C., Ye, P., Zha, Q., Baltensperger, U., Curtius, J., Dommen, J., Flagan, R. C., Kulmala, M., Smith, J. N., Worsnop, D. R., Hansel, A., Donahue, N. M. and Winkler, P. M.: Rapid growth of organic aerosol nanoparticles over a wide tropospheric temperature range, Proc. Natl. Acad. Sci. U. S. A., 115(37), 9122–9127, doi:10.1073/pnas.1807604115, 2018.

Yang, L. H., Takeuchi, M., Chen, Y. and Ng, N. L.: Characterization of thermal decomposition of oxygenated organic compounds in FIGAERO-CIMS, Aerosol Sci. Technol., 55(12), 1321–1342, doi:10.1080/02786826.2021.1945529, 2021.

Ye, Q., Wang, M., Hofbauer, V., Stolzenburg, D., Chen, D., Schervish, M., Vogel, A., Mauldin, R. L., Baalbaki, R., Brilke, S., Dada, L., Dias, A., Duplissy, J., El Haddad, I., Finkenzeller, H., Fischer, L., He, X., Kim, C., Kürten, A., Lamkaddam, H., Lee, C. P., Lehtipalo, K., Leiminger, M., Manninen, H. E., Marten, R., Mentler, B., Partoll, E., Petäjä, T., Rissanen, M., Schobesberger, S., Schuchmann, S., Simon, M., Tham, Y. J., Vazquez-Pufleau, M., Wagner, A. C., Wang, Y., Wu, Y., Xiao, M., Baltensperger, U., Curtius, J., Flagan, R., Kirkby, J., Kulmala, M., Volkamer, R., Winkler, P. M., Worsnop, D. and Donahue, N. M.: Molecular Composition and Volatility of Nucleated Particles

from α-Pinene Oxidation between -50 °c and +25 °c, Environ. Sci. Technol., 53(21), 12357–12365, doi:10.1021/acs.est.9b03265, 2019.

Zhao, Y., Hallar, A. G. and Mazzoleni, L. R.: Atmospheric organic matter in clouds: Exact masses and molecular formula identification using ultrahigh-resolution FT-ICR mass spectrometry, Atmos. Chem. Phys., 13(24), 12343–12362, doi:10.5194/acp-13-12343-2013, 2013.