

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-1006

Anonymous Referee #2

Referee comment on "Volatility parameterization of ambient organic aerosols at a rural site of the North China Plain" by Siman Ren et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-1006-RC2>, 2022

General:

The authors present the calibrations of T_{max} obtained from FIGAERO thermograms using mixed organic and inorganic calibrants, and investigate the effect of ammonium sulfate on the T_{max} of several organic standards. Then they use the calibration result from the mixture of ammonium sulfate and five organic standards to derive a formula-based parameterization for the volatility estimation of the organic compounds measured in a rural area in China, and also compare this parameterization with previous parameterizations. Studies on the effect of inorganic species on the thermogram and T_{max} behavior of organic compounds are important but scarce. From this point of view, the paper provides new input on this. However, the paper is for now a bit more technical sound, since the scientific discussion or application of this derived parameterization is not enough and feels unfinished. I would therefore recommend that this paper be published on ACP only after major revisions, with more scientific input into the paper.

Major:

- **Since the calibration results were the basis for the volatility parameterization for the ambient organic species and substantial discussions on T_{max} changes of organic standards were stated to be due to the addition of ammonium sulfate, it would be important to separate the mass loading effects and matrix effects (caused by ammonium sulfate or within these organic standards). For example, T_{max} of pure PEG-6 standard increased from 40 degC to ~50 degC**

with an increasing mass loading from 100 ng to 500 ng (for No2 and No3 experiment set, see Figure S3-S4), which could be due to the mass loading effect. The Tmax of PEG-6 mixed with ammonium sulfate (with a mass loading of 200 ng) didn't change compared to that of pure PEG-6 standard (with a mass loading of 100 ng, for No3 and No4 experiment set, see Figure S4), which may exclude the matrix effect due to the addition of ammonium sulfate. But the Tmax of PEG-6 mixed with ammonium sulfate and other organic standards (with a mass loading of 1000 ng) increased to ~60 degC compared to the Tmax (~50 degC) of PEG-6 mixed with ammonium sulfate (with a mass loading of 200 ng, for No4 and No5 experiment set, see Figure S4). This increase could be due to several reasons such as the matrix effects within these organic standards, higher mass loadings of ammonium sulfate, as well as higher total mass loadings on the filter. Since the mass loading for the calibration experiments varied between 100-1000 ng, discussions on the effect of different mass loadings and potential different matrix effects on the comparison of thermograms and Tmax for this study as well as how this would influence the derived parameterization from ambient observation is necessary.

- The derived parameterization behaves similar as Li et al (2016) and Stolzenburg et al (2018) for the 15 HOMs (O/C:0.25-1), but worse than Li et al (2016) and Stolzenburg et al (2018) for the 132 CHO (O/C:0-0.25). If this is true, I don't see why we should use this parameterization from this study instead of Li et al (2016) or Stolzenburg et al (2018). More scientific discussions on this parameterization method is needed.

Specific:

Line 41 – What do the authors mean for the “particle-associated phase”? Is it different from particle phase?

Line 49 –SIMPOL is more a structure-based estimation method of vapor pressure instead of formula-based estimation method. Check a recent work by Isaacman-vanwertz and Aumont, ACP, 2021 (<https://acp.copernicus.org/articles/21/6541/2021/>). In their work, they also mentioned about Daumit et al (2013) method for formula-based estimation method and modified version of Li et al (2016) method. Please replenish/revise this paragraph.

Line 112-113 – Please add the flow for the UHP N2 to a 0.1 mCi radioactive Am-241 source, and the ramping rate for the heating.

Line 141 – It's not very clear whether the authentic organic standards are mixed together within each experiment sets of No. 1-3, or they are injected/atomized

one by one? For No. 4 and No.5, it's more clear. Please specify in the texts or Table 1.

Line 156 – For Table 1, the mass loading for different experiments varies. According to Huang et al (2018; <https://acp.copernicus.org/articles/18/2883/2018/>) and Wang and Ruiz (2018; <https://acp.copernicus.org/articles/18/15535/2018/>), different mass loading on the filter could influence the thermogram shape and Tmax of organic compounds. It seems the author also observed similar behavior, if one compare the Tmax of PEG-6,7,8 from No.2 and No.3 experiment sets in Figure S3 and S4. Since both No.2 and No.3 experiment sets are done by atomization method but with different mass loadings on the filter, Tmax values are found to differ. For example, with 100 ng of mass loading Tmax of PEG-6 was 40 degC (Figure S4), but with 500 ng of mass loading its Tmax increased to ~50 degC (Figure S3). Since the study is based on the Tmax calibration, could the authors comment on the effect of different mass loadings on the comparison of thermograms and Tmax for this study as well as how this would influence the derived parameterization from ambient observation?

Line 163-166 – What's the aerosol mass loading on the filter? Please add this information.

Line 170-190 – Could the authors comment on the uncertainty for the C* calculation as well as the uncertainty using this parameterization method?

Line 226-229 – From Figure S4 caption, it seems the No.3 set was done for each standard one by one using atomization method. If that is the case, the figure shows the PEGs 6-8 Tmax for No.4 set (AS+each standard) was similar to those for No. 3 set (Each standard). It thus would indicate the increase of PEGs 6-8 Tmax for No. 5 set (AS+five standards) is probably not (only) due to the matrix effects caused by the addition of ammonium sulfate, but due to the matrix effects within these organic standards. Besides, as the authors mentioned in Line 237-240, the Tmax increase could also be due to higher mass loadings for No. 5 set. It would be important to separate these different reasons, i.e., matrix effects within organic standards or due to the addition of ammonium sulfate, or mass loading effects.

Line 229-231 – Clear connection between more partitioning of organic acids and lower volatility of particulate organic compounds is missing. For example, partitioning of SVOC would increase the volatility of particles. Please explain/clarify a bit more.

Line 245-247 – As for the calibration line is similar to that of Nah et al (2019), do the authors mean the lines are quite close to each other? But the slope is a bit

different from that of Ylisirniö et al (2021) and Nah et al (2019). Could it be due to Nah et al (2019) used acids with $O/C < 0.25$?

Line 259-261 – It would be informative to add the fitted equation (or the fitted parameters a and b of Eq. (3)) of No.5 experiment set here or in Figure 1.

Line 264-267 – Please add the contribution of each group (CHO, CHON, other, unidentified) to the total signal in brackets after each group.

Line 280-281 – What are these dominated compounds and their potential sources? $C_6H_{10}O_5$ could be levoglucosan from biomass burning. How about the others?

Line 324-330 – Would be nice to mark $C_6H_{10}O_5$, $C_{16}H_{32}O_2$, $C_{17}H_{34}O_2$, $C_{18}H_{32}O_2$, and $C_{18}H_{34}O_2$ in Figure S7.

Line 338-341 – The authors mentioned in Line 280-281 about the dominated compounds including $C_{13}H_{25}NO_2$, $C_9H_{17}NO_2$ etc. It seems these CHON with $nO \leq 2$ are quite important. Would the Equation (4) still be applicable to them since the equation subtract $3nN$ for each nO ? Besides, the Equation 4 is a modified parameterization in Mohr et al (2019) specified for HOM with big nO . Maybe the modified Li et al (2016) parameterization equation by Isaacman-vanwertz and Aumont, ACP, 2021 would be a better option considering the fits in Table 2 are mainly based on SVOC and LVOC?

Line 377-379 – Since Isaacman-vanwertz and Aumont (2021) found that the vapor pressures of CHON compounds estimated by Li et al. (2016) significantly biased with an increase of the number of nitrogen atoms, it would be important to add the comparison of the $\log C^*$ (Formula) vs. $\log C^*$ (SIMPOL) for CHON compounds as an additional panel in Figure 5.

Line 397-404 – In general Eq. (4-1) and (4-2) parameterization behaves better than Donahue et al (2011) and Mohr et al (2019). Based on Figure 5, Eq. (4-1) behaves similar as Li et al (2016) and Stolzenburg et al (2018) for the 15 HOMs ($O/C:0.25-1$), but Eq. (4-2) behaves worse than Li et al (2016) and Stolzenburg et al (2018) for the 132 CHO ($O/C:0-0.25$). If this is the case, could the authors comment on why we should use this parameterization from this study instead of Li et al (2016) or Stolzenburg et al (2018)?

Technical:

Line 17 – Change to “formulae” throughout the manuscript.

Line 30 – Change to “for organic compounds with different O/C ratios”.

Line 33 – Either say “a significant mass fraction” or “total submicron particulate mass”.

Line 110 – A typo for “UHP N2”.

Line 197 – Refer to Figure S3 when describing the results.

Line 224 and 226 – Refer to Figure S4 when describing the results.

Line 350 – Either “O:C” or “O/C”. Make it consistent throughout the text.

Line 399-404 – Too long sentence. Please reformulate.