Author's Response to comments on

A study of volatility by composition, heating, and dilution measurements of secondary organic aerosol from 1,3,5-trimethylbenzene

Kei Sato et al.

1. Author's response to anonymous referee #1

(1) General comments: The authors have carefully addressed previous review comments. Although the manuscript is generally of good quality, I think the author should add a brief discussion on wall losses (particle and vapor). Are the SOA mass concentrations corrected for particle wall loss? It seems they did not account for particle wall loss. Does particle wall loss affect "Yield curve fit" VBS? Vapor wall loss may also contribute to the decrease in SOA mass concentrations and particle size, which was used for determining VFR and "Dilution" VBS. I don't think wall loss would affect their major conclusions. Nevertheless, it should be mentioned as possible limitations of this study.

We would like to thank anonymous referee #1 for carefully reading the manuscript and for providing valuable comments. We have revised the manuscript according to the comment provided. In the revised manuscript, revised words and sentences are written in red ink.

As for the effects of vapor wall loss on results of yield curve fit, we inserted the following sentence: Possible reasons for underestimations of low-volatility compounds by yield curve analysis will be effects of semivolatile vapor wall loss generally enhanced in batch experiments in a low concentration region or … (omitted below). Please confirm it in lines 16 – 18 of page 13 and please see also the general comment of referee #3.

The transmission efficiency of 50–250 nm sodium chloride particles was reported to >80% in the region 298–498 K for a TD with the same design as the present TD (Huffmann et al. 2008). We ignored particle wall loss in the TD during the data analysis. These sentences were added in lines 10 – 12 of page 11.

With regard to the effect of particle wall loss in the dilution chamber, one paragraph was rewritten according to comments (12) of reviewer #3. In the revised analysis, effects of particle wall loss are fully taken into account. Please see from line 23 of page 12 to line 5 of page 13.

(2) p.7 L 18. The word "referred" is misplaced.

We revised it.

(3) p.8 L7. "The saturation concentrations calculated for TMB photooxidation products ranged from -7.99 to 9.86." --> I suppose it is log of the saturation concentration (logC*), not the saturation concentration (C*) itself.

We revised it.

(4) p. 8 L 17. "The volatility versus carbon number mapping shows that low-volatility compounds with log10 C* < 0 are and dimers." --> Remove "and"

We removed it.

2. Author’s response to anonymous referee #3

We would like to thank this referee for carefully reading the manuscript and for providing valuable comments. Comments on isothermal dilution data based on his/her deep understanding were very helpful to us. We have revised the manuscript according to the comment provided. In the revised manuscript, revised words and sentences are written in red ink.

(1) Comments on previous referee reports: The authors seemed to have addressed most of the comments from the referees to a satisfactory extent. However, there are a number of places in which the text was changed and the remaining language seems vague as a result (for example, response to comment 6 in the response document). Also, the response to comment 11 includes some helpful ‘scoping’ calculations that it seems should be included in the actual paper text, as the importance of RO2+RO2 chemistry was highlighted by both referees.

As for a revision made by previous comment 6, we removed vague words. Please see also reply to comment (3) of referee #3.

In addition, we found several descriptions which refer LC/MS volatility distributions based on previous fit data. We removed these descriptions in the section of TD-AMS measurement.

As for previous comment 11, we added discussion on RO_2 + RO_2 chemistry. We added the following paragraph in lines 3 – 10 of page 10:
Since a relatively high concentration (i.e., ppm level) was used for the initial TMB concentration in this study, the auto-oxidation of RO_2 might be suppressed by fast RO_2 + RO_2 reactions. Currently, accurate rate constant values are not known for intramolecular hydrogen abstraction from RO_2 (k_1) and for the RO_2 + RO_2 reaction (k_2). We conducted the following preliminary calculations: The rate constant for the CH_3O_2 + CH_3O_2 reaction (4.74×10^{-13} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$; DeMore et al., 1997) was employed as k_2. We assumed the concentration of RO_2 during the chamber experiments under ppm level conditions to $<10^{10}$ $molecule \cdot cm^{-3}$. If this is the case, k_2 [RO_2] is determined to $<4.74 \times 10^{-3}$ s^{-1}, which is sufficiently lower than the k_1 value assumed for intramolecular hydrogen abstraction from RO_2 (0.1 s^{-1}; Praske et al., 2018). These results suggest that RO_2 auto-oxidation will dominate even under ppm level conditions.

(2) General comments: In general I found the paper to be interesting and mostly clear description of these experiments and analysis. There were a number of instances where assumptions or approaches are not well justified and this reduces confidence in the quantitative results, though the general point (that TMB SOA contains low volatility material not captured in yield experiment-based product distributions) is well supported. One general comment is that there is quite a bit of literature on the potential influence of chamber walls on SVOC/IVOC measurement, and none of that is mentioned/discussed here, either in terms of influence on your measurements or interpretation of yield experiments. I think this and other lines of evidence have pointed to the fact that the ‘traditional’ yield-experiment-based VBS parameters are probably wrong and missing material. A bit more discussion of this would be helpful.

Because we do not think vapor wall loss is an only reason for the problem of yield curve fit, we added the following sentence in lines 16 – 18 of page 13: Possible reasons for underestimations of low-volatility compounds by yield curve analysis will be effects of semivolatile vapor wall loss generally enhanced in batch experiments in a low concentration region or constant product yields assumed in gas-particle partitioning model function.

(3) P6, L10 – This should mention particle diameter for SOA experiments. Also, ‘other processes’ is very vague and could this be attributable for different loss in the chamber? Did you monitor loss with and without oxidant?

We rewrite sentences in lines 8 -12 of page 6 as follows:
The mass concentration of SOA then decreased with a rate of (7.1 ± 0.1) × 10^{-5} s^{-1}. The geometric mean particle size after OH exposure was 558 nm, which was larger than for run 1 (395 nm). The wall loss rates of ammonium sulfate particles with sizes of 279–322 and 372–429 nm were measured using the present reaction chamber to be (1.4 ± 0.6) × 10^{-5} and (6.1 ± 3.5) × 10^{-5} s^{-1}, respectively. Particle wall loss may explain the observed decrease in SOA mass concentration.

(4) P8, L17 – there appears to be an extra or missing word: ‘are and dimers’

We revised it.

(5) P8, L31 – assuming gas-particle equilibrium? (missing word).

We revised it.

(6) P9, L10 – Not very clear what equation you’re mentioning here.

We substitute “the equation” with “Eq. (1)”. Please confirm it in line 9 of page 9. We made similar revision at other two places in pages 8 and 9.

(7) P9, L13 – There are many ways to average here, presumably this is weighted by total mass fraction? Should be specified

We added the following explanation in lines 4 – 5 of page 9: Here, the weighted averages are calculated using total mass fraction as the weighting factor. We also added a similar explanation in lines 15 – 16 of page 9.

(8) P10, L34 – I don’t believe this statement is justified. You have one ‘aged’ experiment and if error bars are similar to the one shown, they might well overlap. How is ‘significantly higher’ defined? Variation in particle loading, diameters and other properties can lead to changes in observed evaporation as well. Similarly, should not compare thermograms across studies (e.g. P11, L6).

We substituted this sentence with the following sentence: The MFR results observed between 50 and 150 °C in the aging experiment were slightly higher than those from normal photooxidation experiments, but these differences may not be significant because results of aging experiment were obtained from only one experimental run. Please confirm it in lines 6 – 8 of page 11. Similar revisions were also made in lines 23 – 24 of page 11.

We removed descriptions on comparison with previous thermogram data at this place and in the conclusions.

(9) P11, L21 – Is there evidence of thermal decomposition of dimers? Did you try LC/MS analysis on thermally treated aerosol?

No, we didn’t. We removed descriptions on thermal decomposition of dimers at this place and another place in section 3.7.

(10) P12, L2 – I think you are fitting this alpha value, but it seems like it is assumed. This section needs to be made more clear and the actual fit approach/uncertainty discussed.

We determined the alpha value by fitting. We rewrite this paragraph to make clear and to discuss actual fit approach/uncertainty. Please confirm it in lines 1 – 22 of page 12.

(11) P12, L24 – Why should volatility distribution and alpha be linked? One is thermodynamics and the other kinetics?

We removed descriptions on the link between volatility distribution and alpha.

(12) P13, L1-13 – I find this section unconvincing. Given the lack of very low concentration data, it's unclear how well constrained bins down to 0.01 ug /m3 are constrained by this dilution data. Could the same fits be achieved using a narrower range of volatility? This seems like it might be over-fitting since you're using 4 data points to fit 6 parameters (or maybe 5). Also, the effects of walls is not mentioned at all. Is the aerosol concentration measured at equilibrium used? This will reflect the loss to your secondary chamber wall, which may not be a good representation of the conditions dictating partitioning of the suspended particles (or else wouldn't things keep evaporating away?)

According to this comment, we determined the mass fraction only for $\log_{10} C^*$ of –1, 0, 1, and 2. We mentioned on particle wall loss in the external dilution chamber and explained the particle mass concentration of horizontal axis of Figure S5, which is actual concentration in the dilution chamber. Furthermore, we also conducted a similar analysis for predicted equilibrium data. We rewrote this paragraph and revised Figures 4e and S5. Please see from line 23 of page 12 to line 5 of page 13 and Figures 4e and S5.

References:

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Huffman, J. A., Ziemann, P. J., Jayne, J. T., Worsnop, D. R., and Jimenez, J. L.: Development and characterization of a fast-stepping/scanning thermodenuder for chemically-resolved aerosol volatility measurements, Aerosol Sci. Tech., 42, 395–407, doi: 10.1080/02786820802104981, 2008.

Praske, E., Otkjær, R. V., Crounse, J. D., Hethcox, J. C., Stoltz, B. M., Kjaergaard, H. G., and Wennberg, P. O.: Atmospheric autoxidation is increasingly important in urban and suburban North America, Proc. Natl. Acad. Sci. USA, 115, 64-69, doi: 10.1073/pnas.1715540115, 2018.