Reply to interactive 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. Reply to anonymous referee #1

General comment

This paper investigates the volatility of SOA produced from the photooxidation of 135-trimethylbenzene through the combination of composition analysis by LC-MS, evaporation upon heating (TD-AMS), and isothermal dilution in the smog chamber. The estimated VBS varied substantially due to the limitations of each approach. This paper is an extension of a recent study from this research group on alpha-pinene SOA into anthropogenic SOA. SOA formation from aromatic hydrocarbons is regaining attention in recent years as it may involve the formation of highly oxygenated molecules (HOMs) via auto-oxidation. This paper presents an impressive set of data and is generally well written. However, I found some discussions confusing or missing details. The following are my specific comments, which I am sure the authors can address.

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.

(1) C* from LC-MS was calculated using the linear fit to MW versus logC* relationship shown in Figure S3. The molecular structures of each compound are taken from MCM and previous experimental studies (Table S3). The corresponding logC* values were calculated using SPARC. I do not understand why you would use only one line to represent the relationship between MW and logC* since C* strongly depends on MW and O/C. In Figure 3, they show that O/C varies widely from 0.3 to 0.9. Thus, applying one line to all of the data does not seem reasonable. Since empirical formulae are available from LC-ToF-MS analysis, I do not see the need for the single-line calibration that neglects O/C distribution (Figure S3). Am I missing something? Since Li et al.'s molecular corridor parameterization accounts for the number of C, H, O, and N, I believe Li et al. parameterization is much more appropriate than the "linear fit" of this study (Figure S3 and Figure 4ab).

The root mean squared error (RMSE) of predicted log C^* data was calculated to be 1.91 for a multivariable function of Li et al. adapted to TMB photooxidation products. This RSME result was lower than that of log C^* predicted by a linear function adapted to TMB products, 2.47 (Figure R1). As mentioned by the reviewer, these results suggest that the multivariable fit function predicts a saturation concentration with a lower uncertainty than that of the linear fit function.

In the revised manuscript, we have rejected the linear fit and instead employed a multivariable equation adapted to TMB photooxidation products. We fitted an equation of Li et al. to log C^* data calculated by SPARC for TMB photooxidation products. In accordance with these revisions we revised the related descriptions in Sections 3.3 and 3.4 together with Figures 3, 4, and S3, and Table S2.

(2) Therefore, I think this statement in P.32 needs more considerations. "The results from the method by Li et al. were higher probably because the TMB photooxidation products had lower volatilities than a wide range of organic compounds referred to in the analysis of Li et al." Li et al.'s dataset included ELVOC with logC0 down to even -10 or less. It seems unlikely that TMB products had lower volatilities than what was considered by Li et al.

In the revised manuscript we have removed the description: "the results from the method by Li et al. were higher probably because the TMB photooxidation products had lower volatilities than a wide range of organic compounds referred to in the analysis of Li et al."

(3) Please provide more details on the equilibrium time-scale calculations. I don't see a definition of the "effective saturation ratios" (SR_eff). P.11, L.14-15 refers to eq. 2 in Saleh et al., but the equation is SReff = 1 -exp(-t/tau). I suppose it is meant to be eq.1 in Saleh et al. that defines SReff. Since eq. 1 and 2 in Saleh et al. are quite simple equations, I think it should be shown in this manuscript.

We have included an explanation of SR_{eff} and the fitting curve used in Figure S4 in the revised manuscript.

(4) Similarly, I would like to see more details on volatility estimation using the PTR-MS. Although the text refers to Inomata et al. (2014), there should be a brief description of the procedures. Did the analysis assume a certain value of the heat of vaporization?

We have added an explanation of the procedure used to calculate the saturation concentration in Section S1 of revised supplementary material. A sentence informing the reader of this has also been added to Section 2.3 of the revised manuscript.

(5) The error bars in Figure 3cd are based on assumed "maximum uncertainty of 20% -for the total EIC peak intensity" and error propagation analysis. Is there any basis for choosing 20%? As authors must be well aware, the sensitivity of ESI-MS is highly compound specific.

Here, we intended to say that an uncertainty is limited to that which has originated from the reproducibility capabilities of the LC/MS instrument. However, we consider that describing this here may lead to readers' misunderstanding. In the revised manuscript we have therefore removed these descriptions and the error bars from Figure 3. Instead, we have added the following sentence: "We note that the sensitivity of ESI mass spectrometry is compound specific, thus the calculated distribution includes the uncertainties that result from compound specific sensitivities."

(6) Figure 2: Is this a result of direct infusion to ESI-MS? Please clarify.

Yes, it is. In the revised manuscript we have clarified this point in Section 3.2 and in the caption of Figure 2.

2. Reply to anonymous referee #2

Summary and Recommendation:
This study examines the volatility distribution of secondary organic aerosol (SOA) produced from the photooxidation of 1,3,5-trimethylbenzene (TMB) under dry conditions (RH < 1%) and in the absence of pre-existing aerosol particles. The volatility distribution was determined from chemical composition data obtained by LC/MS and AMS as well as from heating and dilution experiments. With the LC/MS data, the authors used models to predict the volatility distribution of the SOA and compared this with the heating and dilution measurements. The LC/MS data revealed the presence of $C_9H_{14}O_x$ monomers (x= 4-7) and $C_{18}H_{26}O_x$ dimers (x = 8-12). The combined results from the LC/MS, heating, and dilution measurements may suggest that TMB-derived SOA has constituents that have volatilities less than those predicted from conventional SOA yield curve analyses. Overall, the approach is quite nice and I find that this paper will be of interest to readers of ACP. I have a number of specific questions below that the authors need to address before publication can be fully considered in ACP. Due to the nature of these comments, I most recommend this paper be accepted with major revisions.

We would like to thank anonymous referee #2 for carefully reading the manuscript and for providing valuable comments. We have revised the manuscript according to the comments provided.

(1) Concentrations of TMB: The concentrations of TMB are quite high; specifically ppm levels. Do the authors have concerns about the RO2 radical dynamics being relevant to ambient atmospheres? Are there any concerns that RO2 + RO2 reactions could become more dominate than what might be expected in actual urban atmospheres? Basically, why are the concentrations of VOC and NO selected for these experiments? It seems unclear from the experimental description.

We had to set the SOA mass concentrations to several hundreds of micrograms per cubic meter for the PTR-MS analysis of SOA gas/particle partitioning and for the dilution measurements at high dilution ratios. In order to obtain the required amounts of SOA we set the initial TMB concentrations to ppm levels. During the experiments, a TMB concentration higher than ambient levels may induce RO_2 + RO_2 reactions in comparison to ambient conditions. We have added a discussion of this in Section 2.1 of the revised manuscript.

(2) RH Conditions: It appears from the experimental description that the RH was < 1% in all experiments conducted. Do the authors have any concerns for the lack of possible aqueous-phase chemistry? Previous work by the Kamens

group (e.g., Zhou et al., 2011, Atmos. Environ.; Kamens et al., 2011, Atmos. Environ.) showed that aromatic VOCs oxidized in the absence of particle water produced less SOA than those with particle water at higher RH conditions. Do you worry your reaction conditions may not capture what could occur in more humid urban atmospheres? Related to my concerns about having particle-associated water to help further promote SOA, it appears your experiments relied on nucleation mechanisms to yield SOA. Can the authors clarify in the experimental approach why this condition was selected?

The relative humidities (RHs) employed in the wet condition experiments of Zhou et al. (2011) and Kamens et al. (2011) are between 45% and 89%. If we inject a similar level of water into our chamber, the lifetimes of the reactive species, including O_3 and NO_2, become shorter due to the change in wall surface conditions. The changes in the lifetimes of reactive species would affect the secondary pollutant levels simulated in the chamber. We needed to bake the chamber and expose a high level of ozone to the chamber wall repeatedly in order to recover the lifetimes of the reactive species (Akimoto et al., 1979). It takes more than several weeks to recover lifetimes of reactive species. Therefore, we basically avoided wet condition experiments. Thus the present results may not provide good approximations of a humid urban atmosphere. In Section 2.1 of the revised manuscript we have described the reason why we chose dry conditions, and have stated that the present experiments only simulate a dry atmosphere.

(3) HOMs: The authors mention HOMs in their paper and this is likely associated with the high oxygen atom content of your monomer and dimer species measured by LC/MS. Related to my comment above about the lack of particle-associated water, couldn't this potentially prevent HOMs from further reacting to make particle-phase re-action products like peroxyhemiacetals? I'm assuming some of these HOMs may contain hydroperoxide functionalities and thus may be able to react with carbonyl species in the aqueous phase to form such products. I would suggest to the authors that they at least acknowledge that this is one drawback from their study; specifically, the lack of examination of the volatility distribution at higher RH conditions and that further work is warranted at these conditions.

The assumption suggested by the reviewer may be possible under humid conditions. HOM and peroxyhemiacetal formation may be promoted under humid conditions. As described previously, we have discussed this in Section 2.1 of the revised manuscript: the present experiments only simulate a dry atmosphere. Furthermore, we have suggested in the conclusions, that further studies would be necessary to understand the effects of relative humidity on SOA volatility.

(4) Dilution measurements: For your dilution experiments you added 20 ppm of CO. How much of this could have reacted away with OH radicals in your chamber? I'm assuming the OH levels are low enough to not matter in converting large quantities to CO2? It would be good to know in the text that you considered how much of the loss of CO was due to dilution rather than reaction with OH radicals.

The required duration for gas transfer from the reaction chamber to the dilution chamber was 13 min or less. During gas transfer CO might decrease due both to a dilution effect and to the reaction with OH radicals. We ignored the reaction of CO in the dilution chamber because the dilution chamber was not irradiated. However, before gas transfer was completed, a portion of diluted gas remained in irradiated reaction chamber; the decrease in this portion might lead to an overestimation of the dilution ratio. Even though we assumed a maximum level of OH radicals (10^7 molecule·cm^{-3}), CO decreases by only ≤2% due to the reaction with OH radicals for ≤13 min. Thus we ignored the overestimation of the dilution ratio due to the reaction of CO with OH radicals. We have added these descriptions in Section 2.4 of the revised manuscript. To account for this discussion, we have made the effective digit of DR values smaller (2 digits) in the revised manuscript than the original one (3 digits).

(5) LC/ESI-TOFMS: Can the authors clarify how exactly the calibration of the LC/ESITOFMS system was done? Did you use a commercially available turning mixture? If so, what compounds are in this mixture and does it cover your entire mass axis? What was your mass resolution during your LC/ESI-TOFMS runs? Did you use a lock-mass correction approach for more accurately calculating elemental formulas of observed ions reported in Tables S1 and S2?

The mass calibration and lock-mass correction were conducted using G1969-85000 and G1969-85001 tuning mixtures (Agilent Technologies, UK), respectively. A mass resolution of the mass spectrometer (full width at half maximum) was >20,000. This information has been added to Section 2.2 of the revised manuscript.

Compounds included in the G1969-85000 tuning mixture are:
1. betaine,
2. hexamethoxyphosphazine,
3. hexakis(2,2-difluoroethoxy)phosphazine,
4. hexakis(1H,1H,3H-tetrafluoropropoxy)phosphazine,
5. hexakis(1H,1H,5H-octafluoropentoxy)phosphazine,
6. hexakis(1H,1H,7H-dodecafluoroheptoxy)phosphazine,
7. hexakis(1H,1H,9H-perfluorononyloxy)phosphazine,
8. hexakis(1H, 1H, 4H-hexafluorobutyloxy)phosphazine,
9. hexakis(1H,1H,6H-decafluorohexyloxy)phosphazine,
10. hexakis(1H,1H,8H-tetradecafluorooxtyloxy)phosphazine,
11. tris(trifluoromethyl)-1,3,5-triazine, and tris(heptafluoropropyl)-1,3,5-triazine.

Compounds included in the G1969-85001 tuning mixture are:
1. purine,
2. trifluoroacetic acid ammonium salt,
3. hexakis(1H,1H,3H-tetrafluoropropoxy)phosphazine.

(6) Page 5, Lines 27-29: How do you know for sure that "the decrease in mass concentration was not only due to particle wall loss but also the photolysis of organic compounds in the particle phase or dissociative photooxidation of semivolatile compounds in the gas phase?" I don't see any clear data yet to back up this conclusion from the results presented in Figure 1.

To account for this comment we have revised the former sentence to: "the decrease in mass concentration was not only due to particle wall loss but also to other processes."

(7) On Page 6, Line 10, the authors note that they didn't add sodium to their mobile phase or analytical samples. I'm curious why they didn't? Would adding some constant amount of sodium salt improve the ionization efficiency of such compounds, thus improving your detection sensitivities with ESI-MS? Are you at risk for missing any compounds in your SOA samples? Is it also possible the ESI-MS missed some of your compounds? Or what I mean is does ESI make you blind to other potentially present SOA constituents?

Indeed, the addition of sodium salt in a mobile phase might lead to higher sensitivities, and thus this would allow us to identify minor products that are not observed under the present conditions. However, we did not use sodium salt because we wanted to avoid interference from the memory effects of sodium salt on the LC/MS instrument shared with other laboratories. Kruve et al. (2013) studied the effect of sodium salt concentration in the mobile phase on the relative sensitivities for the formation of sodium adducts from 19 organic compounds. They reported that the ionization efficiency ratio of two different compounds was independent of the sodium salt concentration. Their results suggest that the log C^* distribution calculated from LC/MS data will be similar to that obtained at higher sensitivities even though minor sodium adduct signals were not observed.

As suggested by the reviewer, ESI may blind us to other potentially present SOA constituents. We have added the following sentences to Section 3.4 of the revised manuscript: "We note that the sensitivity of ESI mass spectrometry is compound specific, thus the calculated distribution includes the uncertainties that result from compound specific sensitivities. In this regard, however sodium adduct formation during ESI can ionize a wide range of oxygenated organic compounds, including carbonyls, peroxides, and alcohols (Kruve et al., 2013; Zhang et al.,2017)."

(8) Can the authors be more clear about what they mean by blank samples? Were these blank filters that were extracted in the same fashion as the filter samples collected from the chamber experiments?

A blank sample was prepared by extracting a new Teflon filter. The method of extraction was similar to that used for SOA samples. These descriptions have been added to Section 3.2 of the revised manuscript.

(9) For Table S2, should you normalize the EIC peak areas for each ion by the volume of air sampled through the filter in order to compare each experiment? Or did you collect the same volume of air for each experimental filter?

We collected the same volume of air for each experimental filter. We have added this information in the caption of Table S2 of the revised supplement.

(10) I noted that the LC/MS data presented in the SI (Tables S1 and S2) don't provide any suggestions on chemical structures. This is reasonable at this stage of your work, as in order to propose reasonable structures a combination of tandem MS experiments and synthesis of putative structures would be needed to really propose reasonable structures. However, without knowing actual structures, do the authors worry about how certain organic functionalities differ in their contribution to vapor pressures? That is, if you only use the total number of Cs, Hs, Os, etc., how uncertain is this prediction for volatility?

As described in the reply to comment (2) by reviewer #1, the RMSE of log C^* (predicted using the number of C, O, and N atoms) was determined as 1.91. We have added this result to Section 3.3. of the revised manuscript.

(11) Seeing that RO2+RO2 reactions may have dominated in your experiments owing to the high levels of VOC used, do the authors have any questions about whether this allowed for enough RO2 autooxidation to happen? What I mean is could there have been more oxygeanted products formed if the VOC concentrations were closer to atmospheric mixing ratios?

Two types of RO_2 autoxidation are possible for RO_2 formed during the oxidation of aromatic hydrocarbons; one is formation of oxygen-bridged bicyclic radical whereas the other is intramolecular hydrogen abstraction from an alkyl group (Molteni et al. 2018). During present chamber experiments, we detected methylglyoxal as a major product, suggesting that the formation of bicyclic radical from RO_2 dominated even though the VOC concentration is a ppm level. Here, methylglyoxal is believed to be a product formed from the decomposition of bicyclic radical.

Currently we do not know the accurate rate constant values for intramolecular hydrogen abstraction from RO_2 (k_1) and for the RO_2 + RO_2 reaction (k_2). We have conducted the following preliminary calculations. The rate constant for the CH_3O_2 + CH_3O_2 reaction (4.74×10^{-13} cm^3·molecule^{-1}·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 VOC conditions to $<10^{10}$ molecule·cm^{-3}. If this is the case, k_2 [RO_2] is $<4.74 \times 10^{-3}$ 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 autoxidation will dominate even under ppm level VOC conditions. Since these calculations are preliminary, the results are not included in the revised manuscript. As described in the reply to comment (1) of reviewer #2, in Section 2.1 of the revised manuscript, we have discussed that a TMB concentration higher than ambient levels may induce RO_2 + RO_2 reactions in comparison to ambient conditions.

(12) Page 9, Line 33: Correct the spelling of "Kalbere et al." to "Kalberer et al."

We have revised this.

(13) Page 10, lines 20 and 21: "Baltenspelger et al. 2005" is misspelled. It should be "Baltensperger et al."

We have revised this.

(14) Conclusions, Line 21-22: Please provide citations to the published literature to support the statement "in accordance with previous results of heating measurements."

We have added the citations of Baltensperger et al. (2005).

References

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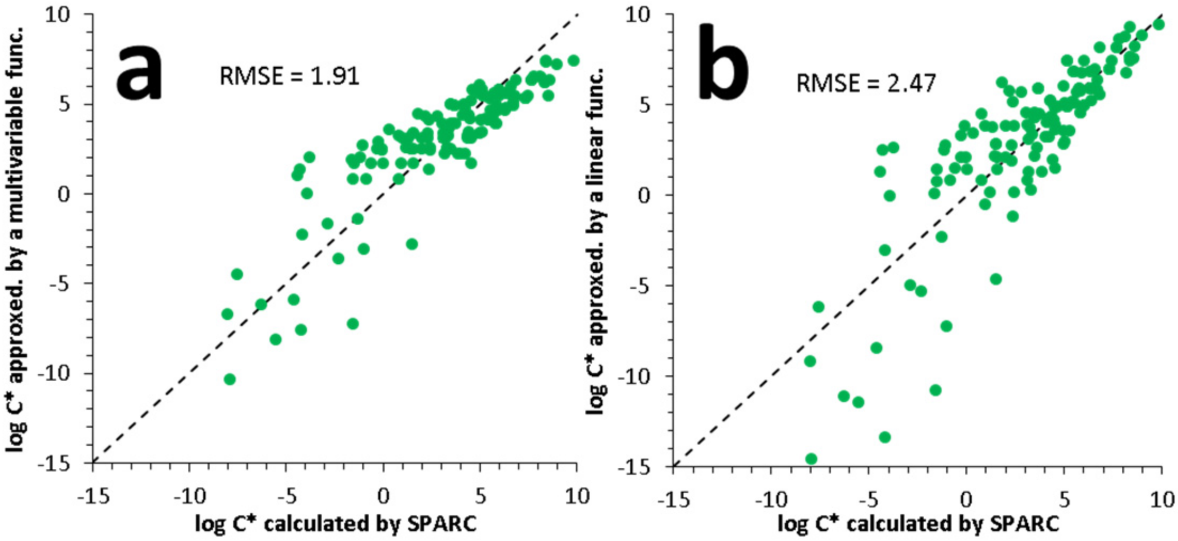

Fig R1. Plots of saturation concentrations approximated by (a) multivariable, and (b) linear functions adapted to TMB products as a function of saturation concentration calculated by SPARC.