

Reply to comments

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Anonymous Referee #1

General comments

The authors have addressed my comments and revised the manuscript mostly sufficiently. I can recommend publishing the manuscript after minor modifications according to below comments.

Reply

Thank you for your valuable comments; we appreciate the time and effort you have put into reviewing our paper. I have revised the manuscript based upon your input, as described below.

Specific comments

Comment 1

My original comment 3 C concerned the large differences between same oxidation conditions in figure 3. To address this comment the authors have included the following sentence in the manuscript (192-194): “There are differences between runs 1 and 6 and between runs 7 and 8, although the oxidation conditions are similar; these will be due to differences in initial reactant concentrations or uncertainties resulting from sensitivity variations.” It is not clear what the “uncertainties resulting from sensitivity variations” means here. It is also concerning if the different reactant concentrations can cause such differences e.g. between the runs 7 and 8. In figure 3 it even seems that the run 8 resembles more run 9 than run 7. This added sentence needs clarification in the manuscript. This is an important point to explain properly as the reader will need to consider how reliable the figure 3 results are and if they include reliable information on the effect of oxidation state on the composition.

Reply

“Uncertainties resulting from sensitivity variations” mean the variation of mass spectrometer sensitivity during LC analysis. The sensitivity would have an uncertainty of ~10% due to these variations; however, it cannot fully explain the difference between the results measured in runs 7 and 8 for the C17 and C18 dimers with carbon oxidation state lower than -0.6. The sentences in lines 192-194 of the previous manuscript were incorrect; thus, I removed these sentences. Instead, we added new appropriate explanations.

We added the following sentence in lines 206-209:

With regard to nine- and ten-carbon HOMs, the result of run 7 was close to that of run 8. These results suggest that the relative abundances of nine- and ten-carbon HOMs in SOAs will be independent of the initial α -pinene concentration.

Furthermore, we added the following sentences in lines 221-225:

As for the C_{17} and C_{18} dimers with carbon oxidation state less than -0.6, the results of run 9 was close to or slightly lower than that of run 8. These results suggest that the addition of OH radicals will barely affect or slightly reduce the relative abundances of these dimers in SOAs. The result of run 8 was higher than that of run 7, suggesting that the relative abundances of these C_{17} and C_{18} dimers in SOAs may increase with decreasing the initial α -pinene concentration.

Comment 2

L334-226: Please explain here how equilibration time scale was determined. I assume fitting the eq. (2) from Saleh et al. (2013) to the dilution data but this is not clear to a reader if they are not familiar with that paper.

Reply

Your assumption on equilibration time scale calculations is correct. I have added the following sentence in lines 350-351:

The equilibration scaling time was determined by fitting eq. 2 in Saleh et al. (2013) to the dilution data.

Comment 3

L347-354: It is not clear how the volatility distribution was calculated from the dilution data. This needs to be explained. What does it mean that “dilution data are only available for $C^ > \text{several } \mu\text{g m}^{-3}$ ”? Also, the statement “these results of dilution experiments might be consistent with the results of LC/MS and TD-AMS” does not seem justified. First, if volatility distribution from dilution data is determined so that only $\log C^* > 0$ is included, then there is little ground for comparing that to the figures 4 a-e. Second, if one does such comparison anyway, consistency would require that the relative amounts of bins with $\log C^*$ above 0 would be same between the distributions. This doesn't seem to be the case and even the volatility distributions from dry and 40% RH dilution experiments do not show such consistence between them two.*

We added Figure S6 to show how this distribution was determined. The following sentences describing

the procedure for determination of this distribution were added in lines 367-370:

The normalized SOA yields obtained in dilution experiments are plotted as a function of mass concentration (Figure S6). The volatility distribution was determined by fitting eq. 2 in Grieshop et al. (2007) to the plotted data.

The sentence in lines 370-371 was revised as follows:

The volatility distributions were only calculated in the range 1-1000 $\mu\text{g m}^{-3}$ because dilution data are only available in this region.

We removed the sentence, “these results of dilution experiments might be consistent with the results of LC/MS and TD-AMS.”

Comment 4

L366: What does “current VBS model” mean here? Do you mean the current VBS parameterizations used in global models?

Reply

No we don't. We revised the sentence in lines 384-386 as follows:

In the standard VBS approach, the product volatility distributions determined by SOA yield curves are employed. Further improvement of the atmospheric simulation model will be necessary to explain both laboratory and ambient SOA levels.

Referee #2: Andrew Grieshop, agrieshop@ncsu.edu

General comments

Overall, I'm quite happy with the updates that the authors made to the manuscript and believe that this will make a valuable addition to the literature. I have a number of hanging questions/concerns related to the way in which my original comments were addressed, listed below. Some of this is simply clarification, but I do have some concerns about how inter-experiment variation is treated, especially with regards to the thermodenuder measurements. If a potential reason for variation, it should be explored or supported with available evidence, rather than being presented as a supposition without supporting evidence. I would like to see these comments addressed in a revised manuscript.

Reply

Thank you for your valuable comments; we appreciate the time and effort you have put into reviewing

our paper. We have revised the manuscript based upon your comments. Descriptions on the thermodenuder measurements have been revised based upon your comments 1 and 2.

Specific comments

Comment 1

Line 301-302: This is not a satisfying explanation, unless it is experimentally verified... Based on sensitivity implied by line in Fig. S4, there would need to be a variation of ~25 C across these experiments, which is a lot. The 40 degree pinonic acid data don't have nearly so much scatter. This issue needs to be discussed further. Was the residence time in the TD closely controlled? Were calibration experiments on TD temperature control or experiments with single component aerosols conducted?

Reply

No experimental evidence is available for the original explanation; therefore, I removed the sentences of the original explanation.

The MFR plotted in Figure S4 was defined to be the fraction of the mass concentration measured at a target temperature to that measured at 25°C; thus, MFR determined for 25°C is defined to be unity in this study (there is no uncertainty).

The number of TD measurements of pinonic acid particles was much smaller than that of TD measurements of SOA. Thus, we cannot simply compare the variation of pinonic acid particle data with that of SOA particle data.

We did not monitor the flow rate during TD measurements although we check it prior to every day TD measurement. Thus, the variation of residence time may be a potential reason of the variation of present TD data.

We conducted the measurements of pinonic acid particles as described in the manuscript. The present pinonic acid particle measurements provided a saturation concentration consistent with the literature data (please see the reply to specific comment 3 given by Prof. Grieshop on the first discussion paper).

We show two examples of TD-AMS data. Figure R1 shows time series of SOA concentration measured by TD-AMS in runs 1 and 2. The TD equipped with a bypass line. During each cycle of TD-AMS measurement, we used the bypass for first 9 min to obtain the reference data and then used the TD of a specific temperature for 15 min. During the measurements shown in Figure R1, the TD mode was programmed to be bypass (0-3 min), TD of 50°C (3-18 min), bypass (18-27 min), TD of 100°C (27-42 min), bypass (42-51 min), TD of 150°C (51-66 min), bypass (66-75 min), TD of 200°C (75-90 min), and bypass (90-99 min). MFR was determined by accounting for SOA wall loss. As shown in Figure R1, the

bypass data decreased with time. In standard cases, the SOA concentration decreased by 5–9% for each measurement cycle (24 min) due to chamber wall loss. On the other hand, irregular fast decay was observed during the measurement of 50°C in run 2; the bypass data decreased by 19% for 24 min. Similar irregular results were also observed in runs 3 and 4. Irregular decay may result from the variation of the residence time which affects wall loss in the bypass.

Consequently, the variation of residence time may be a potential reason of the variation of present MFR data. I added the following sentences in lines 310-313:

The variation of MFR could be caused by the variation of the residence time. Although the flow rate was not monitored during present TD-AMS measurements, the SOA concentration was monitored through the bypass as the reference. The bypass result decreased by 5–9% for each TD measurement cycle (24 min) due to the SOA loss on the chamber wall (Figure S5); however, it decreased by 17–19% for 24 min in irregular cases observed during runs 2, 3, and 4. These results suggest that there may be the variation of the residence time in these runs.

In order to explain the bypass of TD, I also added Figure S2 and the following sentences in lines 103-105:

The TD was equipped with a bypass line. During each cycle of TD-AMS measurement, we used the bypass for first 9 min to obtain the reference data and then used the TD for 15 min to obtain the data of a specific temperature.

Comment 2

Line 309-310: The description of residence time as 'close to' that of Faulhaber is vague. Please specify the residence time of the TD used in experiments. Was it help constant across all experiments?

Reply

We explicitly describe the residence time in the sentence in lines 321-323 :

We used the results of the calibration curve from Faulhaber et al. (2009) directly because the TD in our study has a residence time (~13 s at room temperature) close to that used for their TD (~15 s at room temperature).

In our study, the flow rate was about 1 L min⁻¹. However, we did not control flow rate; this may also be a potential reason of TD data variation as described in the reply to your specific comment 1.

Comment 3

Line 343: 'slow' is a vague term, as is kinetic inhibition. There is some kinetic inhibition, but this is not

slow relative to what others have claimed as time scales (e.g. Vaden et al 2011) or slow with respect to a time step in most atmospheric models.

I removed the term, “slow”, and revised this sentence in lines 361-362 as follows:

These results suggest that kinetic inhibition may **explain the equilibration time scale measured in this study.**

I also made a similar revision in the abstract.

Comment 4

Line 343-344: Comparison with Diesel emission evaporation is not appropriate for comparison evaporation rates, as the materials likely have very different volatility distributions, and the change in vapor concentration will be a function of the underlying volatility distribution and the relative change in concentration. Evaporation time scales or evaporation coefficients can/should be compared instead.

Reply

I removed this sentence. Instead, we revised the following sentence in the introduction (lines 40-42) to mention volatility studies of diesel exhaust particles.

Yet another technique used to study volatility distribution is dilution-induced evaporation, **which has been successfully applied to the volatility studies of diesel exhaust particles (Robinson et al., 2007; Fujitani et al., 2012).**

Comment 5

Line 345-346: Kinetic inhibition being linked to thermodynamic properties is not appropriate, unless a mechanism is discussed. This is conflating thermodynamics (volatility) with kinetics (inhibition).

Reply

I have added the discussion of the mechanism in lines 357-360 as follows:

The mass accommodation coefficient subsumes all resistances to gas–particle partitioning other than gas phase diffusion; and a mass accommodation coefficient smaller than 1 would indicate that the condensed phase is highly viscous and exhibits substantial kinetic limitations.

Comment 6

Line 349-354: Not very clear how this distribution was determined. How many data points? Why not compare to our volatility distribution in Saha and Grieshop (2016)? If you are comparing VFRs after 3

hours, this should be something like $6 \cdot \tau$ (considering your τ are ~ 30 min), so I'm not so sure kinetic inhibition would be an issue. Wall losses may be?

We added Figure S6 to show how this distribution was determined. The following sentences describing the procedure for determination of this distribution were also added in lines 367-370.

The normalized SOA yields obtained in dilution experiments are plotted as a function of mass concentration (Figure S6). The volatility distributions were determined by fitting eq. 2 in Grieshop et al. (2007) to the plotted data.

We showed the data from Saha and Grieshop (2016) in Figure 4f. We added the following sentences in lines 332-333:

Figure 4f includes the volatility distribution determined from the previous TD study (Saha and Grieshop, 2016). This previous result is similar to present TD-AMS results.

We completely removed the sentence, "However, note that the volatility determined from dilution experiments will be underestimated due kinetic inhibition."

Comment 7

Line 366: There is no one 'current VBS model', and it's not true that every model necessarily exclusively uses chamber yields (though that is definitely the standard approach).

Reply

I revised this sentence in lines 384-386 as follows:

In the standard VBS approach, the product volatility distributions determined by SOA yield curves are employed. Further improvement of the atmospheric simulation model will be necessary to explain both laboratory and ambient SOA levels.

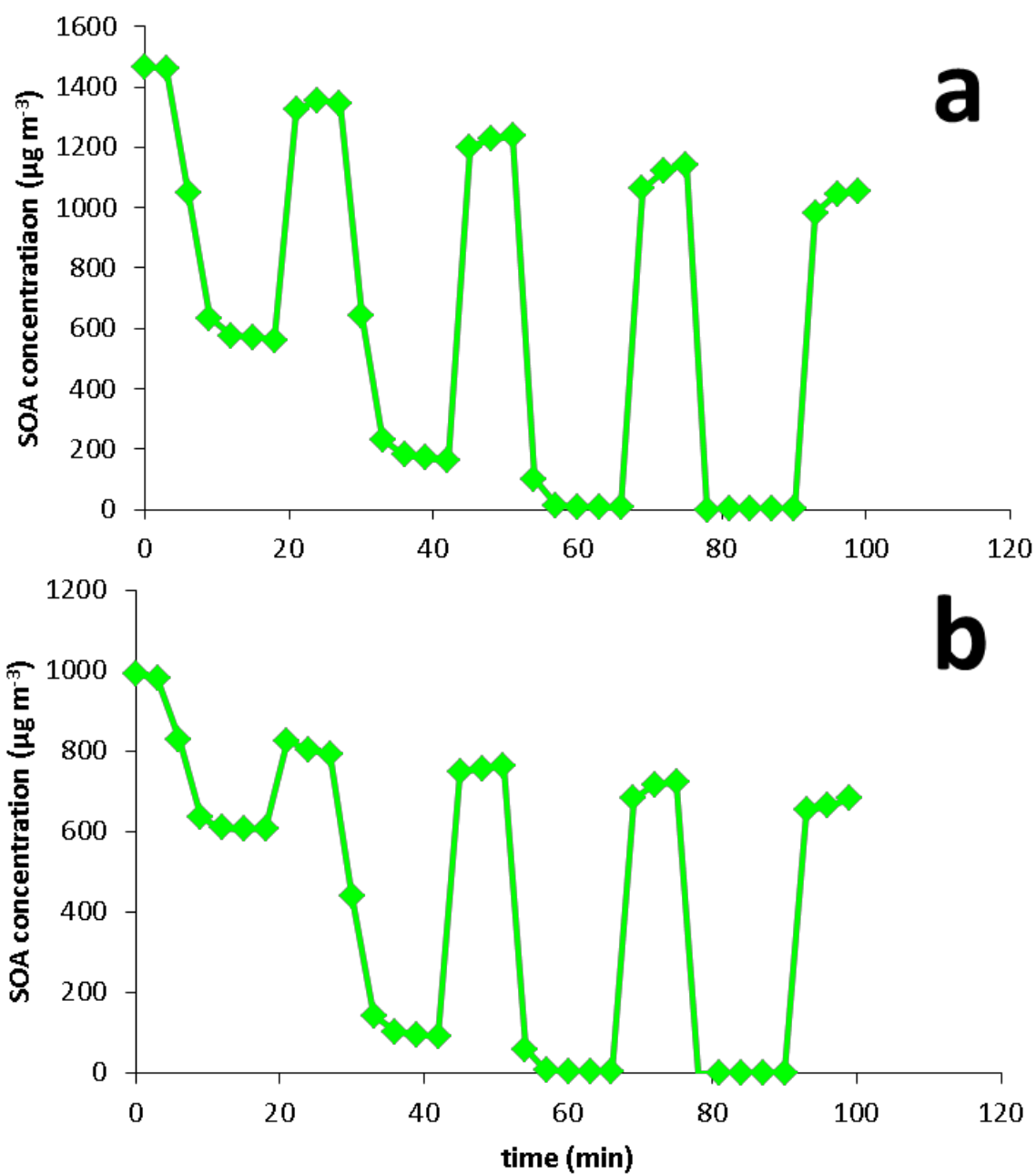


Figure R1: Time series of SOA concentration measured by TD-AMS during the heating measurement in (a) run 1 and (b) run 2; the TD mode was programmed to be bypass (0-3 min), TD of 50°C (3-18 min), bypass (18-27 min), TD of 100°C (27-42 min), bypass (42-51 min), TD of 150°C (51-66 min), bypass (66-75 min), TD of 200°C (75-90 min), and bypass (90-99 min).