

Anonymous Referee #1

We thank the reviewer for the very insightful comments. We respond to each comment below. Reviewer comments are in black. Our responses are in blue, and changes/additions to the manuscript are in *italics*.

Review of the manuscript “SOA formation from the photooxidation of α -pinene: systematic exploration of the simulation of chamber data”

General comments:

This manuscript presents results from simulations of Caltech smog chamber experiments on photooxidation of α -pinene with the Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A). The manuscript is well written and present interesting and new experimental and theoretical results on the SOA formation from photooxidation of α -pinene at different OH concentrations. The authors perform an extensive set of sensitivity tests in order evaluate the relative role of VOC chamber wall losses, gas to particle mass transfer limitations, second and later generation oxidation products, condensed-phase photolysis and particle-phase dimerization for the SOA formation. However, according to my opinion no one of the suggested model setups is able to capture the observed evolution of the SOA formation in a convincing way for all experiments. Instead the model always tends to overestimate the SOA formation during the high OH concentration experiments and underestimate the SOA formation during the low OH concentration experiments. As the authors suggest this can possibly be because the model do not take into account the autoxidation of α -pinene and formation of first generation ELVOC oxidation products. Most of the sensitivity tests are well motivated and described but I have a few critical questions (comments) that I would like the authors to answer (consider). If this is done in an appropriate way I think the manuscript is well worth to be published in ACP.

We agree that none of the hypotheses we investigate fully explains all features of the observed SOA formation. We thank the reviewer for the comments regarding autoxidation and discuss these below. With the additional discussion of autoxidation, we believe a convincing case can be made for two of the hypotheses explaining part or all of the measurement-model discrepancy. We identify areas where additional study is needed in order to further evaluate these hypotheses.

Experiment 141125 has the highest SOA yield. Based on your modeled OH concentration of 2×10^5 molec cm^{-3} you get an overall OH reaction rate of 10^5 s^{-1} (P 33177, L 7). I compared this with how much O_3 that needs to be present in order to get the same overall O_3 reaction rate as the OH reaction rate. My calculation gave that at an O_3 concentration of 4.5 ppbv half of the α -pinene is oxidized with O_3 instead of OH ($k_{\text{O}_3} = 9.4 \times 10^{-17} \text{ cm}^3 \text{ molec}^{-1}$). According to Fig. S2 the measured O_3 concentration increases from 0 to 10 ppbv during this experiment while the modeled O_3 concentration only reaches 4 ppbv in the end of the experiment. Thus, according to the measurements I think that more than half of the consumed α -pinene reacts with O_3 and not OH. How does the model handle the O_3 oxidation of α -pinene and the chemistry beyond the formation of the Criegee biradicals? How much SOA is formed from ozonolysis of α -pinene? This is not mentioned at all in the manuscript but could potentially be a large source of error that need to be discussed. I think it is suitable to add figures to the supplementary material that shows how large fraction of the α -pinene that react with O_3 according to both the model and the measurements. Because the autoxidation mechanism that is suggested to generate ELVOCs is much more

effective when α -pinene is oxidized by O_3 instead of OH I think this could at least partly explain why the model and measurements disagree. This needs to be estimated and discussed.

We agree that ozonolysis likely explains part of the measurement-model discrepancy at low UV. A discussion of the ozonolysis of α -pinene has been added to section 2.1 along with a figure in the Supplement:

Ozonolysis chemistry in GECKO-A does not explicitly include the Criegee biradicals formed from the addition of O_3 to the α -pinene double bond; rather the predicted products of the Criegee intermediates are directly assigned to the α -pinene ozonolysis reaction. This simplification overlooks potential reactions of the stabilized Criegee intermediates (SCI) with water, alcohols, acids, carbonyls, etc. (Ma et al., 2008; Tobias and Ziemann, 2001). Reaction of the SCI with water to form pinonaldehyde is thought to be significant (Capouet et al., 2008), and a direct route to pinonaldehyde has been added in GECKO-A. The initial reaction step for ozonolysis is shown in Fig. S1. Furthermore, Ma et al. (2008) proposed several later-generation intramolecular isomerization reactions to form low-volatility acids. These reactions have been implemented in GECKO-A as a sensitivity test. Virtually no change in predicted SOA concentrations is observed when adding these reactions or when changing the branching ratios of the SCI products. Separate (not shown) purely ozonolysis simulations showed very little SOA formation, indicating potential missing pathways in the ozonolysis mechanism forming low-volatility products. Updating the ozonolysis mechanism should be the subject of future studies.

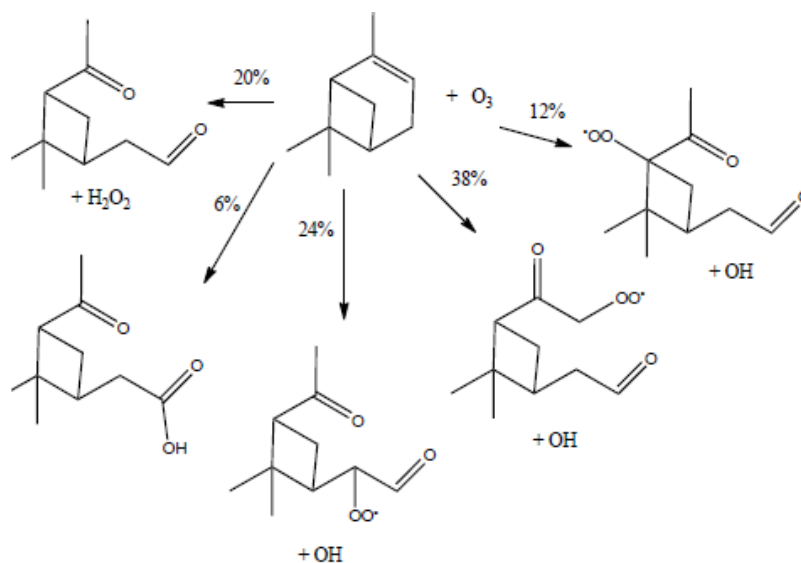


Figure S1: Overview of the α -pinene + O_3 initial reaction step in GECKO-A. All subsequent chemistry is generated according to the standard protocols in GECKO-A.

A plot has been added to the Supplement showing how much α -pinene reacts with OH vs. O_3 along with the following explanation in section 4 of the main text:

Figure S5 shows the amount of α -pinene predicted to react with OH vs. O_3 , using both the modeled and measured O_3 concentration. For the 100% UV experiments, ~2-3% of the total α -pinene is predicted to react with O_3 , using either the modeled or measured O_3 concentration. For the 10% UV experiments, ~20% of the total α -pinene is predicted to react with O_3 using the modeled O_3 concentration. For experiment 141113, roughly the same amount of α -pinene is predicted to react with O_3 based on the measured O_3 concentration. However, for experiment 141125, because the model underpredicts the O_3 concentration, much more α -pinene is predicted to react with the measured O_3 concentration, ~49 %.

Figure S5 is shown on the following page.

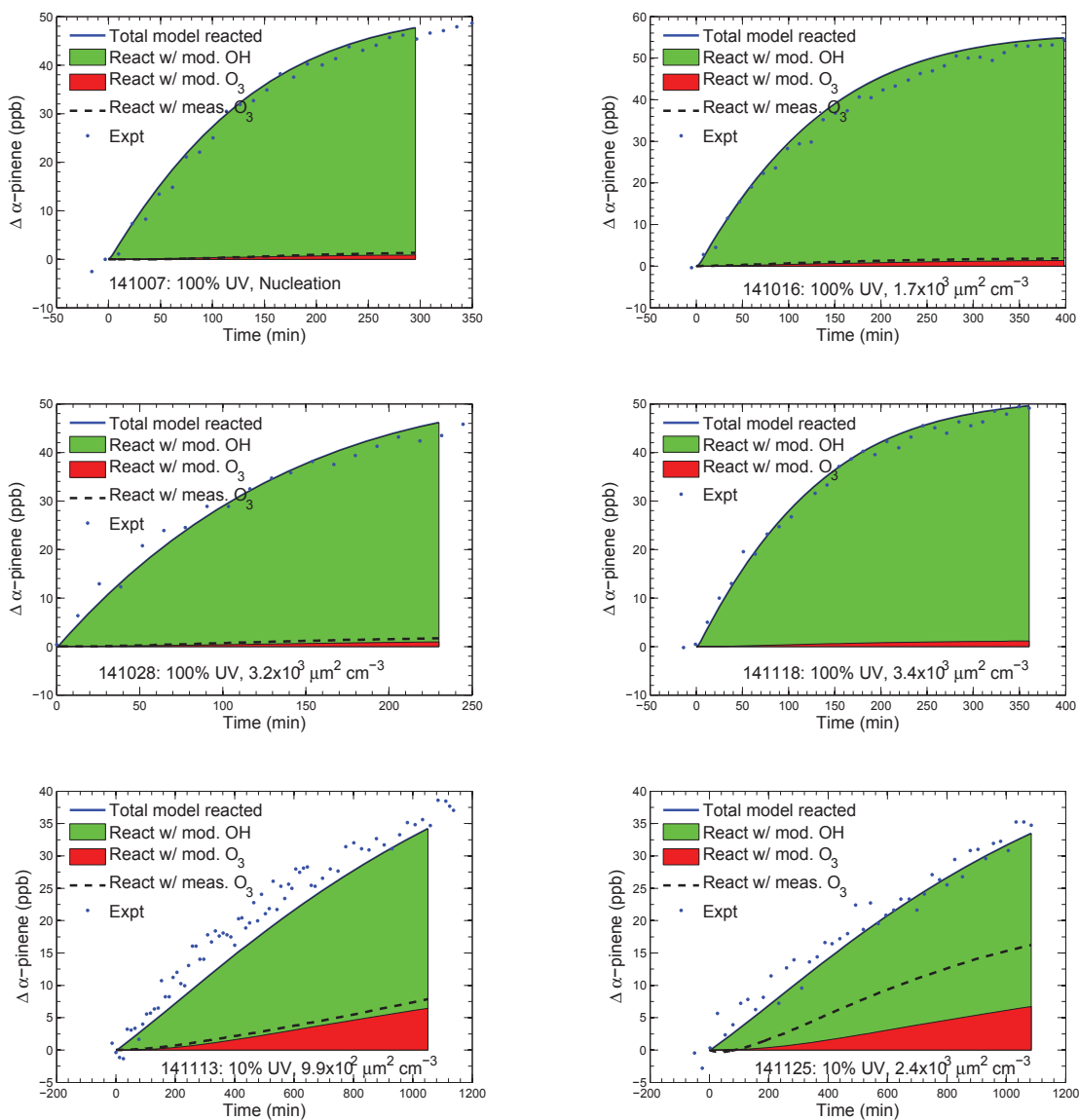


Figure S5: Amount of α -pinene predicted to be reacted with OH versus O_3 , for both modeled and measured O_3 concentrations. The solid blue line shows the total α -pinene reacted. The green area shows the amount reacted with OH based on the modeled OH concentration. The red area shows the amount reacted with O_3 based on the modeled O_3 concentration. The dashed black line shows the amount predicted to have reacted with the measured O_3 concentration. Because the O_3 monitor malfunctioned during experiment 141118, the dashed line is not shown for this experiment.

Section 5.4 discussing autoxidation has been significantly expanded:

Moreover, during the low UV experiments, 20-50% of α -pinene reacts with O_3 instead of OH, compared to only 2-3% for the high UV experiments. As discussed previously, the ozonolysis mechanism in GECKO-A is likely incomplete and may be lacking pathways to SOA precursors, such as autoxidation. Because autoxidation is much more efficient from the ozonolysis pathway than from the OH pathway (Ehn et al., 2014; Jokinen et al., 2014), more ELVOCs will likely be produced under low UV and will increase the amount of SOA formed. Furthermore, autoxidation could also explain the difference in SOA yield observed between the two low UV experiments. Experiment 141125 has a higher yield than experiment 141113 and also has a higher observed O_3 concentration. ELVOC production was likely higher during this experiment owing to the increased fraction of α -pinene reacted via ozonolysis.

Autoxidation is observed to occur immediately upon oxidation (Rissanen et al., 2015), indicating it is likely a first-generation process. Second-generation species are predominantly responsible for the discrepancy in model predictions between high and low UV due to the difference in OH levels (Fig. 4). Unlike second-generation products, autoxidation products will not depend on the OH concentration and will not be produced slower under low UV. Therefore, adding autoxidation pathways will likely increase the fraction of SOA composed of first-generation products, which may lead to similar predictions for high and low UV.

However, explicit mechanisms and rate constants are still lacking for autoxidation in the α -pinene system, although they have been developed for simpler cycloalkenes (Mentel et al., 2015; Rissanen et al., 2015). A recent computational study found that the cyclobutyl ring in α -pinene must open in order for intramolecular hydrogen shifts to be competitive with the peroxy bimolecular sink reactions (Kurtén et al., 2015). The currently-accepted α -pinene ozonolysis mechanism does not include rapid opening of this ring. Kurtén et al. (2015) investigated several pathways to break this ring but found none that could explain all of the characteristics of observed ELVOCs from α -pinene. In the absence of explicit mechanisms, the effect of autoxidation cannot be fully tested. To approximate the effect, a $C_{10}H_{15}O_9$ species (an ELVOC predicted by Kurtén et al. (2015)) is added with a 7% molar yield (based on the 6-8% yield measured by Ehn et al. (2014)) as a direct product from the α -pinene+ O_3 reaction. This addition has no effect on SOA concentrations for the high UV experiments but increases the final SOA concentrations for the low UV experiments by $\sim 10 \mu\text{g m}^{-3}$ (not shown). However, adding this fixed ELVOC yield does not increase SOA predictions for low UV at the beginning of the experiment, when no O_3 is present. Therefore, although autoxidation via ozonolysis is likely important towards the end of the low UV experiments, other explanations are needed to reconcile the underprediction of SOA at the start of the experiment. Autoxidation via OH oxidation could potentially resolve part of this discrepancy, but no pathways or yields are yet available. Overall, autoxidation is a likely process to explain the measurement-model discrepancy at high and low UV but is in need of more study. The presence of significant autoxidation could furthermore lead to a different best-fit vapor wall loss rate.

A sentence has been added to the abstract emphasizing the potential importance of autoxidation:

Moreover, we propose that autoxidation may alternatively resolve some or all of the measurement-model discrepancy, but this hypothesis cannot be confirmed until more explicit mechanisms are established for α -pinene autoxidation.

On page 33169, L10-12 you write that the particle number concentration remains unchanged in the model during the course of the experiments. Why do you not include particle wall losses in the

model? On page 33173, L1-2 you write that the measured particle volume distributions are corrected with the size-dependent wall loss rates. Thus, it should be straightforward to also consider these particle wall losses in the model.

We do not include particle wall losses in the model because the particle size distribution is not explicitly simulated. Only a single size bin is used so that all particles have the same radius (see below). Only the particle radius, which changes with time as condensation occurs, is tracked. Including size-dependent particle wall loss for a single particle bin could potentially over- or underestimate the amount of particle wall loss occurring because the true size distribution is not represented. Furthermore, to include particle wall loss, we would have to include a means to track the organic aerosol that deposits on the wall separate from the organic aerosol that remains suspended. GECKO-A is not currently well-equipped to handle that addition. Because SOA formation in this system does not display a dependence on particle surface area, we are confident that not including particle wall loss does not significantly affect our SOA predictions.

I guess that the observed SOA growth curves displayed in e.g. Fig. 2 and 4 are not what actually were observed but the wall loss corrected SOA mass derived from the SMPS measurements. You need to explicitly write this in the manuscript. I also wonder how uncertain the corrected SOA mass is. How much did you need to correct the measured SMPS particle volume? I know from experience that chamber wall losses in Teflon smog chambers can vary from experiment to experiment because of e.g. variations in the electrical field strength of the chamber and how long time it takes between that the seed particles are added to the SOA formation starts. I think you should add the not wall loss corrected SOA or total particle mass to the panels in Fig S3.

The reviewer is correct that all measured SOA data shown in the manuscript have been particle-wall-loss corrected. We revised Fig. S3 (now Fig S2) to show the non-particle-wall-loss corrected total particle volume, as well as the total volume corrected with both the lower and upper bound (shown on following page). It is not possible to show the non-wall-loss corrected SOA; the DMA only measures the total volume of the particles, which is a mixture of organic aerosol and inorganic seed. Only by accounting for particle wall loss can the seed volume be subtracted. An explanation of this has been added to section 4:

Measured volume distributions must be corrected for particle wall loss; the DMA measures the total volume of particles, which is a mixture of organic aerosol and inorganic seed. By accounting for particle wall loss, the seed volume can be subtracted and the mass of SOA calculated.

Uncertainties in the particle wall loss correction of the data arise primarily from the assumption in terms of interactions of deposited particles on the wall with suspended vapors. As we stated in the main text: 'in the lower bound, once deposited, particles are assumed to no longer interact with the vapor. The mass of SOA present on a particle at the moment of its deposition is added when calculating the total SOA. In the upper bound, deposited particles are assumed to continue growing at the same rate as suspended particles, and this SOA is similarly added to the total SOA.' As we show in Figure S2 in the supplement (formerly Figure S3), the derived total SOA mass may differ from 1% to 22% for the high UV experiments and 200% to 315% for the low UV experiments under these two assumptions. (The very large difference between the lower and upper bound for the low UV experiments is likely an artifact resulting from the small number of particles remaining at the end of the low UV experiments. This is explained in more detail in the caption of Figure S2). Another uncertainty is related to the surface properties of $(\text{NH}_4)_2\text{SO}_4$

particles and organic coated particles. We measured the size dependent deposition rates of dry $(\text{NH}_4)_2\text{SO}_4$ particles in the particle wall loss calibration experiments. We applied the measured rates to the actual α -pinene + OH experiments to derive the total SOA mass. While we used $(\text{NH}_4)_2\text{SO}_4$ as seeds to provide sufficient surface area for partitioning of organic vapors, these seed particles are eventually coated by an organic layer, which potentially alters the surface properties and may lead to a different wall accommodation coefficient. For now, we assume the accommodation coefficient for both $(\text{NH}_4)_2\text{SO}_4$ seed particles and organic particles as unity. Finally, the reviewer raised a good point that there may be variations in the electrical field strength of the chamber. During our routine experiments, we always ground the Teflon bags and maintain a constant relative humidity (40 %) in the chamber enclosure air. In addition, we perform the particle wall loss calibration experiments before and during the actual α -pinene + OH experiments to minimize the impact of variations in the electrical field on the particle deposition rates.

We have added the following clarification to emphasize that all growth curves have been particle wall loss corrected:

In section 4:

The upper bound is therefore less appropriate to use when vapor wall loss is accounted for separately, and thus the lower bound is used to correct the SOA data, using size-dependent wall loss rates measured in the Caltech chamber. Figure S2 shows temporal plots of the experimental non-particle wall loss corrected total volume and the total volume with both the upper and lower bound particle wall loss correction.

And additionally in section 5:

Experimental particle-wall-loss corrected SOA growth curves as a function of reacted α -pinene are shown in Fig. 2 for the six photooxidation experiments.

And in the caption of Figure 2:

Figure 2. *Mass of SOA, MOA, as a function of reacted α -pinene. Experimental data are shown with filled circles, with colors corresponding to individual experiments (see Table 1), and have been corrected for particle wall loss (see text). Predictions using the default GECKO-A are shown as solid lines with the colors corresponding to the different experiments. In GECKO-A, the vapor-particle accommodation coefficient is set to $\alpha_p = 1$ and the vapor wall loss rate is set to $k_{gw} = 10^{-3} \text{ s}^{-1}$.*

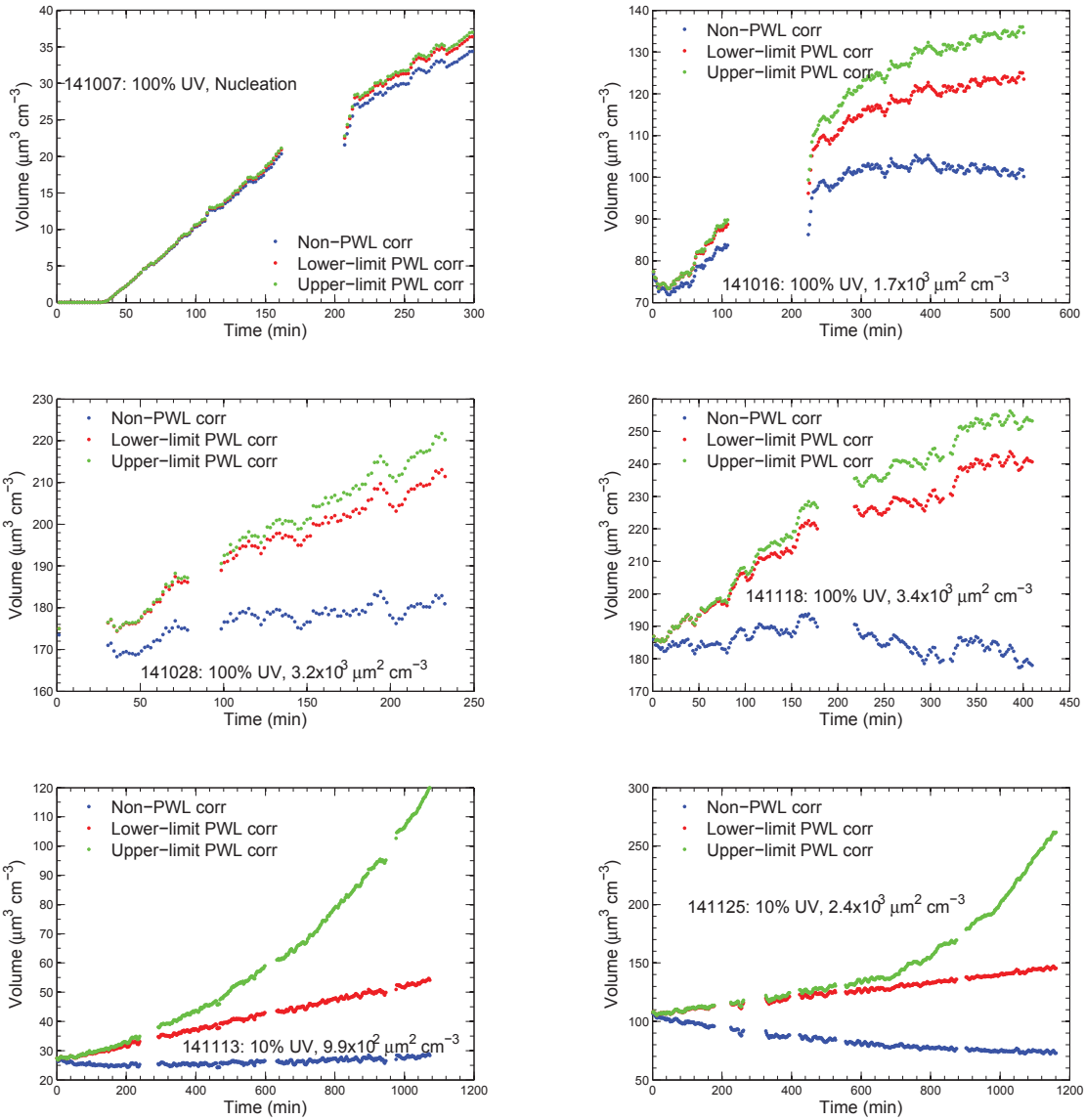


Figure S2: Caption on next page.

Figure S2: Total particle volume as a function of time, non-particle wall loss corrected (blue data points) and using two different corrections for particle wall loss. Red data points have been corrected with the lower bound assumption, in which deposited particles are assumed to not interact with vapor, and the mass of SOA present on a particle at the moment of its deposition is added to the total SOA. Green data points have been corrected with the upper bound assumption, in which deposited particles continue to grow via condensation at the same rate as suspended particles. The dramatic increase in the upper bound towards the end of the low UV experiments is likely an artifact of how the upper bound is calculated. The Aerosol Parameter Model (Pierce et al., 2008) is used to constrain the rate of condensation to particles by fitting the DMA size distribution at each time step, and this condensation rate is then applied to deposited particles. At the end of the low UV experiments, only 11% of the initial total number of particles remain suspended, as opposed to 30-40% for the high UV experiments. SOA growth in the α -pinene system is not seed surface area dependent (discussed in the Results section), and condensation to suspended particles will not decrease due to the decreased number. Therefore, at the end of the low UV experiments, the condensation rate per suspended particle is very large. With the upper bound correction, the deposited particles then grow with the same high condensation rate, despite the fact that transport to deposited particles will be slower than transport to suspended particles. The upper bound is likely a substantial overestimation for these experiments.

How was the particle number size distribution described in the model? Did you only consider one particle size or did you include several size bins? This should be mentioned in the article. If you only use one effective particle size bin how was the initial particle radius of the seed aerosol estimated?

The following explanation has been added to section 3.1:

In the model, a single particle size bin is used, so that all particles have the same radius. For all experiments except nucleation, the initial inorganic seed radius is set at 50 nm, and the initial number concentration is calculated from the measured initial seed surface area. GECKO-A does not currently include a mechanism for nucleation; therefore, for the nucleation experiment, an initial seed concentration of 10^4 cm^{-3} was assumed with an initial radius of 5 nm.

On page 33173 L24-25 you write that the background levels of NO_x in the chemical model was set to 0.1 ppb and split evenly between NO and NO_2 . I thought that you explicitly modeled the NO and NO_2 concentration. How were the inorganic gas-phase chemistry treated by the model?

The reviewer is correct that NO and NO_2 are explicitly simulated in the model. We meant to imply that the initial concentration of NO_x was split evenly between NO and NO_2 . The following clarification has been added to the paper:

Therefore, the initial background concentration in the simulations was set to 0.1 ppb, split evenly between NO and NO_2 . NO and NO_2 then evolve throughout the simulation according to the standard inorganic gas-phase reactions.

On page 33178 L5-7 you write “A reduction to 10% and a wall loss rate of 10^{-5} s^{-1} results in the best fit to both high and low UV experiments (Fig. 6), albeit with a slight overprediction for the high UV experiments and slight underprediction for the low UV experiments.” I would not say that the model underprediction for experiment 141125 is a “slight” underprediction but a rather substantial underprediction of about 40 %. I suggest that instead of using the terms “slight overprediction” and “slight underprediction” give values of how much in % that the model over- and underpredicts the SOA mass in the end of the experiments.

We have revised this sentence as follows:

A reduction to 10% and a wall loss rate of 10^{-5} s^{-1} results in the best fit to both high and low UV experiments (Fig. 5), albeit with an overprediction up to 75% for the high UV experiments and a 20-40% underprediction for the low UV experiments.

On page 33180, L4-10 you conclude that the underprediction of vapor pressure is likely not responsible for the enhanced contribution of later-generation species to SOA. I am not totally convinced about this. It might be correct but I don't think that you can base these conclusions only based on a comparison of different functional group contribution methods since they all have in common that they estimate the vapor pressures by summing up the contribution from different functional groups and in the best case take into account some interactions between the different functional groups. It might very well be that all these methods systematically underestimate (or overestimate) the vapor pressures of compounds with many functional groups.

We have revised this discussion to read:

While the Nannoolal et al. (2008) method generally led to the highest volatilities and the lowest SOA predictions when compared to the Myrdal and Yalkowsky (1997) method and the SIMPOL-1 method from Pankow and Asher (2008), each of these methods estimates vapor pressures via a group contribution method (i.e. summing the contributions of all functional groups). If this approach is less accurate for compounds with many functional groups, the volatilities may be underpredicted and these species may be overpredicted in SOA.

The difference in seed aerosol (SA) surface area (a proxy for the condensation sink) is not that great between the experiments called low SA, medium and high SA. Maybe you could give the value of the initial seed surface area in the figure legends instead of calling the experiments “Low SA”, “Medium SA” and “High SA”.

We have changed all legends to give the value of the initial seed surface area instead of using the labels “Low SA,” “Medium SA,” and “High SA.”

For the nucleation experiment I think that one possible reason for the relatively high SOA yield is caused by substantially lower wall losses of these particles. This is because I suspect that the particles that are formed via new particle formation are under charged with respect to the Boltzmann charge distribution. I guess the SA was neutralized before it was introduced to the chamber. Thus I don't think it is appropriate to do the same wall loss correction for the nucleation experiment as for the SA experiments. Did you use different size resolved wall loss corrections for the SA experiments and the nucleation experiment?

No, we did not use different size-resolved wall loss corrections for the SA experiments and the nucleation experiment. The nucleation experiment was hardly affected by the particle wall loss correction (shown in Figure S2 previously). Because the particle wall loss correction affected the nucleation experiment so insignificantly, it is unlikely that this explains the high SOA yield in the nucleation experiment.

Technical correction:

The text is very small in Fig. 3 and hard to read. If Fig. 3 should be included in the final manuscript the font of the text needs to be larger. I personally think that Fig. 3 can be removed from the manuscript because it adds very little to the article and you only refer to it once in the text.

We agree that Fig. 3 does not add significantly to the article, and we have removed it.

Added references:

*Kurtén, T., Rissanen, M. P., Mackeprang, K., Thornton, J. A., Hyttinen, N., Jørgensen, S., Ehn, M., and Kjaergaard, H.G.: Computational study of hydrogen shifts and ring-opening mechanisms in α -pinene ozonolysis products, *J. Phys. Chem. A*, **119**, 11366–11375, 2015.*

*Ma, Y., Russell, A. T., and Marston, G.: Mechanisms for the formation of secondary organic aerosol components from the gas-phase ozonolysis of α -pinene, *Phys. Chem. Chem. Phys.*, **10**, 4294–4312, 2008.*

*Tobias, H. J., and Ziemann, P. J.: Kinetics of the gas-phase reactions of alcohols, aldehydes, carboxylic acids, and water with the C13 stabilized Criegee intermediate formed from ozonolysis of 1-tetradecene, *J. Phys. Chem. A*, **105**, 6129–6135, 2001.*