Author Comments to Referee Pontus Roldin

We thank the referee very much for providing insightful feedback on our manuscript. Below we have responded to the specific questions and suggestions from the referee.

Many of the referee's comments dealt with the issue that our model assumes well-mixed particles, whereas actual SOA may have (and likely does have) a relatively low viscosity. We have made more explicit the limitations of this assumption on our modeling by adding additional sentences, as well as addressing the specific comments.

Comment by Referee 1)"In addition, several experiments have observed slower than expected room temperature evaporation of both ambient (Vaden et al., 2011) and laboratory generated (Saleh et al., 2013; Grieshop et al., 2007; Wilson et al., 2015) SOA during isothermal dilution." Vaden et al., 2011 also studied laboratory generated SOA. Refer to Vaden et al., 2011 for the laboratory generated SOA too.

We have added a reference to Vaden.

Comment by Referee 2) P 10002, L3: You use the term "*homogeneous nucleation*" to refer to how the SOA particles were generated. I have also used this expression in previous publications when I referred to new particle formation during no-seed SOA particle formation experiments. However, I don't know if this is correct. Lately I have started to use "formation of nano condensation nuclei (nano-CN)" instead, with a reference to McMurry P. H., Kulmala, M., Worsnop D. R.: Special Issue on Aerosol Measurements in the 1 nm Range, Aerosol Sci. Technol. 45, I, 2011.

Reply: *We thank the referee for pointing out that there is other possible nomenclature that may more precisely describe the process by which particles are generated in laboratory experiments. The language has been updated to reflect this more precise definition of particle generation and now reads:*

"SOA was formed at various total C_{OA} from the formation and subsequent growth of nano-condensation nuclei that were formed from products of the ozonolysis of gas-phase α-pinene, in excess (Fig. S1)"

Comment by Referee 3) P 10005 L1-L4: "*Here, to provide for more consistent fitting and since no evaporation at room temperature was observed, the fit curves were forced to go through unity at room temperature.*"

Change to: "Here, to provide for more consistent fitting and since no evaporation was observed at room temperature, the fit curves were forced to go through unity at room temperature."

This has been changed.

Comment by Referee 4) Sect. 2.4.1 Thermodenuder model. An assumption that I think should be mentioned is that you assumed that the particles behave as liquid droplets (no mass transport limitations in the particle-phase). This may be justified by the relative high temperature in the TD but is probably not entirely true for room-temperature isothermal evaporation.

Reply: *The following has been added to Section 2.4.1 "It was assumed that there were no mass transport limitations within the particle-phase for all evaporating species, i.e. that the surface composition was always equivalent to the bulk composition."*

Comment by Referee 5) P 10006, L14-21: *"If K_{eqm} is large then all condensed-phase species would be in dimer form and, at equilibrium, all gas-phase material would be drawn into the condensed phase. Here, this situation is avoided through the following simplification to determine the initial particle state at the TD inlet. First, the gas/particle (monomer only) equilibrium distribution is calculated given the specified volatility distribution and C_{OA}. Then the monomer/dimer equilibrium in the condensed phase is calculated, and the gas-phase concentrations are set to zero to avoid large amounts of condensing material at the next time step. Since a charcoal denuder is placed immediately after the flowtube, this simplification is physically accurate."*

It is good that you clearly describe the assumptions that you use for the model setup but I think that it would be more physically reasonable to assume that monomers are not dissolved (absorbing) into the dimer SOA volume fraction if you want to limit the growth during next time step. You would then have to simulate (or iteratively derive) the SOA composition at the TD inlet. To assume that the monomers absorbs into the total C_{OA} would not be correct then. Especially for the low SOA loading experiments, I think that you actually need to explicitly simulate how the non-equilibrium SOA formation and dimer/monomer SOA composition changes in the flow-tube.

Reply: *The reviewer raises an important point regarding the initial conditions assumed in the modeling of the SOA evaporation in the TD. There are two important considerations: the nature and distribution of the monomers within the particle phase, independent of dimerization, and the monomer/dimer distribution. Of course, these are coupled phenomena. However, given that our model assumes that the lowest saturation concentration of condensing monomers is 0.1 micrograms/*m^3 *and further that the abundance of these are very small, the dimer model is—to a reasonable extent—independent of the exact distribution of monomers with respect to their volatility and much more sensitive to the monomer/dimer distribution. Thus, it is reasonable to think of the different* K_{eqm} *simulations as the key case studies with the initial volatility distribution of monomers as a secondary concern. Put another way, since the monomers in our model evaporate "fast" given their relatively high volatilities the dimer model(s) are not overly sensitive to the monomer volatility distribution. This is not to imply that the exact monomer distribution at the start does not matter, as it certainly does, only that it is substantially less consequential than the monomer/dimer distribution. We fully agree that comprehensive simulation of both formation and evaporation would be the ideal, as it would allow for demonstration of closure. However, accurate simulation of nucleation is no trivial task and beyond the scope of this work.*

In addition, Cappa and Wilson (2011) developed a model that effectively considers particle formation and growth under the assumption that all of the absorbing mass in the particle is converted to non-absorbing at every time step. This is similar to the suggestion of the reviewer that the formation of dimers (non-absorbing mass) be accounted for during particle growth. The particle composition at any given concentration (see their Figure 6) was reasonably similar to the composition predicted from a standard absorptive partitioning model. This implies that more explicit consideration of particle formation, at least in the manner suggested here, will not influence the general conclusions presented in the current work.

We have added the following sentences that describe the nature of model simplifications regarding formation and the likely influence on the current simulations:

"The above simplification for the initial particle state most likely does not provide a true representation of the actual particle composition, just as the assumption regarding only homodimers (discussed below) is a simplification. However, as we ultimately find that the simulation results are much more sensitive to the initial distribution of particulate mass with respect to monomers and dimers than to the specific distribution of monomers with respect to their volatility, these simplifications will influence the details but not the general conclusions arrived at here."

Comment by Referee 6) It would also be good to simulate the vapor stripping in the charcoal denude and not just assume perfect gas-phase removal. Do you have some experimental results to justify this assumption?

Reply: *First, in case it was not clear, we note that transport of the vapors to the TD walls is explicitly simulated within the model such that there is a gradient in vapor concentration from the walls to the center of the cylindrical denuder tube. It is only in the cylindrical "bin" nearest to the wall that perfect gas-phase removal is assumed. That said, the strongest evidence we have for perfect gas-phase removal at the denuder walls, i.e. to the charcoal, comes from experiments performed using lubricating oil (Cappa and Wilson, 2011). In that work, it was found that a model of lubricating oil evaporation, using a separately determined volatility distribution, gave good agreement with observations. If gas-phase removal of vapors at the denuder walls were not "perfect" then the model would have failed and underestimated the extent of evaporation, especially at room temperature. This implies that vapor losses to the walls a near perfect, as would be expected for uptake onto charcoal. We have modified the text as below:*

"Since a charcoal denuder is placed immediately after the flowtube, this simplification is physically reasonable as we have previously found that vapor stripping in charcoal denuders is efficient (Cappa and Wilson, 2011)."

Comment by Referee 7) P 10007, L3-L4: "*The rate at which dimers decompose is governed by k_r and k_f, both of which are likely to be temperature dependent*"

To me it is not entirely clear if you always assume dimer/monomer equilibrium in the model or if you explicitly simulates the non-equilibrium dimer and monomer composition and how it changes in the TD as a function of temperature and evaporation. You need to explain this more clearly.

Reply: *We do not always assume dimer/monomer equilibrium. Dimer/monomer equilibrium is only assumed at the start of the evaporation simulations, i.e. is an initial condition. Once the particles enter the (model) thermodenuder, the kinetics of dimer formation/decomposition are treated explicitly. Several sentences have been added to clarify that the driving force behind evaporation is the perturbation of the dimer/monomer equilibrium by evaporation of monomers and changing* K_{eqm} *with increasing temperature.*

"As the semi volatile monomers evaporate the equilibrium state is perturbed and the dimers decompose in response, according to the temperature dependent K_{eqm}*, to re-establish dimer/monomer equilibrium. Depending on the timescale of dimer formation and decomposition, the dimers and monomers may not be in equilibrium at every step of the model, yet they are constantly forming and decomposing to move towards equilibrium."*

Comment by Referee 8) P 10009, L23-24: "*Regardless, it is apparent that the effective volatility of the SOA at C_{OA} is not higher than at low C_{OA} and that, despite the slights differences, the response to heating*"

Add "high"

"Regardless, it is apparent that the effective volatility of the SOA at high C_{OA} is not higher than at low C_{OA} and that, despite the slights differences, the response to heating"

This has been changed.

Comment by Referee 9) P 10013, L20-24: "At smaller K_{eqm} extensive room temperature evaporation occurred as a result of the increasing initial fraction of semi-volatile monomers, a result that is inconsistent with the observations. However, even for the simulations at larger K_{eqm} some evaporation at room temperature was always predicted."

Yes but this is partly because you assumed liquid SOA particles. If the SOA particles are solid-like at room temperature (as suggested by several studies), the evaporation of monomers would slow down substantially once the particle surface layer has been filled with non-volatile dimers.

Reply: *The reviewer raises an important point in noting that the extent of evaporation at room temperature would decrease further if evaporation of the semi-volatile monomers was inhibited by barriers to mass transfer within the particle. We now note this as a potential reason for the room temperature evaporation, although use the terminology "low viscosity" as opposed to "solid" as it is more precise. We have additionally added language in Section 2.4.1 to clarify the assumption of liquid SOA particles, as discussed above.*

"It was assumed that there were no mass transport limitations within the particle phase for all evaporating species, i.e. that the surface composition was always equivalent to the bulk composition."

and

"The simulated room temperature evaporation at larger K_{eqm} may result from the model assumption of liquid-like particles in that if mixing within the particles were slow such that there were a build up at the particle surface of non-volatile dimers then evaporation of monomers that are buried below the surface would be slowed (Roldin et al., 2014)."

Comment by Referee 10) P10015, L15-18: "The range of k_r independently determined here are somewhat larger than the room-temperature k_r suggested by Trump and Donahue (2014) (=1.1×10^{-4} s^{-1}) and Roldin et al. (2014) (=2.8×10^{-5} s^{-1}), which were based on needing an evaporation timescale of ~1 hr for isothermal evaporation (Grieshop et al., 2007;Vaden et al., 2011). However, their estimates may not have fully accounted for the dynamic nature of the system, and thus underestimated the actual dimer decomposition rates compared to that obtained here."

It is true that we used $k_r = 2.8 \times 10^{-5}$ s^{-1} for the results presented in Fig. 6 in Roldin et al. (2014) but we also tested other values of k_r. Including $k_r = 12$ h^{-1} (0.0033 s^{-1}) for a group of relatively abundant (~20 mass %) and shout-lived dimers, in combination with more long-lived but less abundant (1-2 mass %) dimers with $k_r = 1/30$ h^{-1}. We were then able to accurately simulate the nearly particle size independent evaporation of fresh SOa particles from the experiments in Vaden et al. (2011) (Fig. 77 and Fig. S9-S10 in Roldin et al. (2014)). For these simulations we considered that the particles had a high viscosity in agreement with Abramson et al. (2013). However, with this setup we substantially overestimated the effect of particle ageing in the Teflon chamber on the observed evaporation rates. This can be an indication that the actual oligomer (dimer) fraction of the short-lived dimers was larger than 20 % (maybe close to 100 % as you suggest). This would have limited the effect that VOC wall losses had on the particle composition (and evaporation behavior) when they were aged in the Teflon chamber by Vaden et al. (2011). For these type of experiments I generally think that it is important to also explicitly simulate the SOA formation phase and not just the evaporation stage of the experiments because if you don't get the model to agree with the observations both for the formation and the evaporation experiments something is not correct in the model.

Reply: *As noted above, we completely agree that comprehensive simulation of formation and evaporation is the ideal. However, simulation of nucleation is non-trivial and beyond the scope of this work. Future efforts will aim to explicitly simulate formation in a dynamic manner. That said, we have changed that last sentence above to be:*

"Ultimately, reconciliation of the different timescales indicated for dimer decomposition between the different studies likely will require more detailed consideration of the exact nature of various dimer types with respect to their decomposition and formation timescales, which may not all be identical as assumed here, and of the influence of particle phase on evaporation." We believe that this succinctly captures the important issues raised by the reviewer.

Comment by Referee 11) P10017, L16-21: "*Simulations using the dimer-decomposition model with different starting particle sizes show some dependence on particle size (d_p = 90, 180 and 360 nm), with larger particles having smaller MFRs at a given time (**Error! Reference source not found.**a). However, the overall differences are relatively small and reasonably consistent with the observations given that the observations have typically considered a narrower size range than examined here.*"

I still think that the differences between the different particle sizes in Fig 7a is relatively large and it shows that something is missing in the model in order to explain the nearly size independent evaporation rates reported by e.g. Vaden et al. (2011). As mentioned previously several studies (e.g. Virtanen et al., 2010; Abramson et al., 2013 and Zhou et al., 2013) have shown that SOA particles are not liquid-like but viscous tar or even solid-like. I think it would be appropriate to mention that the mass transfer limited diffusion within the particle-phase will also influence the isothermal evaporation but that this was not considered. What was the RH in the flow tube?

Reply: *We have added a statement that mass transfer limitations within the particle phase have not been accounted for here, but can influence evaporation dynamics (see above). Regarding the question about RH, the RH was not directly measured in the flow tube, but was ~30% for all experiments as "house" air was used and this is the typical value. We have added the following sentence:*

"The relative humidity of the air stream was ~30% for all experiments."

Comment by Referee 12) P10020, L13-16: "*If the particles were primarily semi-volatile monomers for which evaporation were limited by diffusion in the particle phase, then changes in* *viscosity would lead to substantial increases in the observed evaporation rate (Zaveri et al., 2014)"*

Do you mean:

If the particles were primarily semi-volatile monomers for which evaporation were limited by diffusion in the particle phase, then changes in viscosity would lead to substantial increases in the observed evaporation rate (Zaveri et al., 2014)

This we also showed in Roldin et al. (2014) (Fig 5c)

Yes, and the additional citation was added.

Comment by Referee 13) P100, L19-22: "Thus, it seems that a hybrid model where the particles are composed of a substantial fraction of dimers (or oligomers) and some smaller fraction of low-volatility compounds may ultimately provide a more complete description."

I fully agree.

We thank the reviewer for this confirmation.

I suggest that you add the evaporation curves from Vaden et al. (2011) to Fig. 4b and Fig. 7.

These have been added to the figures.

References

Cappa, C. D., and Wilson, K. R.: Evolution of organic aerosol mass spectra upon heating: implications for OA phase and partitioning behavior, Atmospheric Chemistry and Physics, 11, 1895-1911, 10.5194/acp-11-1895-2011, 2011.

Grieshop, A. P., Donahue, N. M., and Robinson, A. L.: Is the gas-particle partitioning in alpha-pinene secondary organic aerosol reversible?, Geophysical Research Letters, 34, L14810 10.1029/2007gl029987, 2007.

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