Author Comments to Anonymous Referee #1

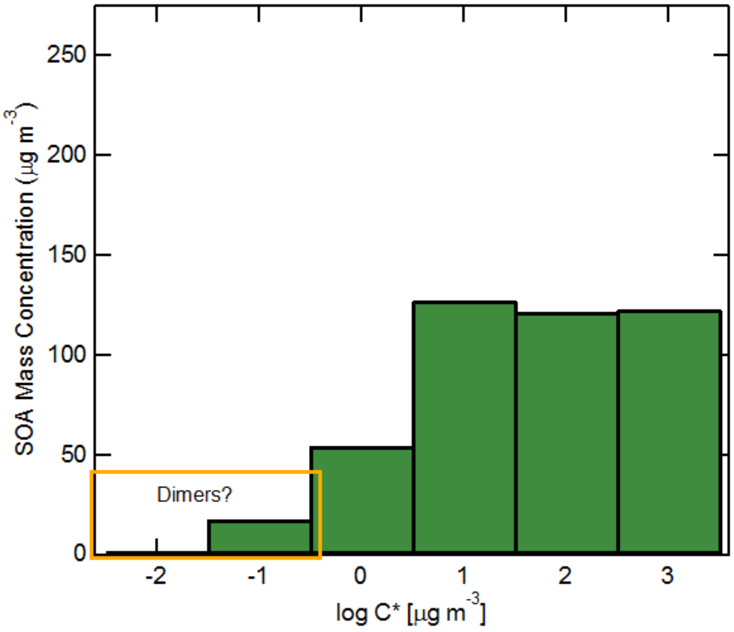
We thank the referee for the very thoughtful and valuable comments which we have addressed below.

Comment by Referee 1) The conclusion of dimer formation being important relies on the kinetic modelling with dimers included in the model. This requires an assumption of initial particle composition which in this work is approximated by first calculating the particle composition based on partitioning theory and previously measured VBS and then calculating the monomer/dimer equilibrium (p. 10006, l. 16-21). However, if the SOA contains dimers, these compounds would be accounted for in the lower volatility bins when VBS was determined from the growth experiments, not by the VBS bins corresponding to the SVOC monomers. The authors estimate the dimer formation time scale to be only a fraction of a second (p. 10014, l. 4-5) which would suggest that the dimers would have been formed also in the growth experiments where VBS was determined and would therefore contribute to the lowest VBS bins. As most of the particle mass is estimated to consist of dimers (p. 10013, l. 8) the way the dimers are treated in the calculation of initial composition could make a large difference on results. Could the authors comment on how big error this could cause on their results and what would be the possible consequences of this regarding their conclusions?

Reply: *The reviewer is correct in that the initial assumption of particle composition is based on a traditional VBS distribution. Although the VBS parameters are influenced to some small amount by dimer formation during the SOA formation process, it has been shown by Cappa and Wilson (2011) that fits to such growth experiments are not particularly sensitive to condensed-phase reactions through the application of their modified VBS model, termed in that paper the sequential equilibrium partitioning model. This is because traditional SOA growth experiments are most sensitive to production of new material from the continuing gas-phase reaction, which is unaffected by reactions in the condensed phase. In other words, it is not correct that dimer/oligomer formation necessarily shows up as an increase in yield in the lower volatility bins of the VBS at the expense of higher volatility bins, and the point is that simple parameterizations based on growth experiments do not provide clear information on the contribution of dimerization, etc..*

The reviewer also makes the observation that the way dimers are treated in the calculation of the initial composition could make a large difference in the results. We have considered the potential influence of the lower volatility bins from the VBS distribution being dimers. As we do not know which VBS bins the reviewer suspects are particularly reflective of dimers, we will make an assumption that those with C = 0.01 and 0.1 ug/m3 are "dimers" and those with higher C* values are monomers. (Note: C* = 0.01 ug/m3 is the lowest bin considered in the VBS parameterization we have used). In this case, a relatively small amount of the total mass would be in the form of dimers to begin with, but would not have zero vapor pressure (as we assumed in our case study). These species would thus be subject to direct evaporation as well as thermal decomposition. As the C* values are relatively "high" from the perspective of evaporation in a TD, these species would tend to contribute to evaporation at lower temperatures. This would in turn lead to an adjustment in the kf, kr and Ea values that would be needed to fit the observations, most likely with a somewhat lower Ea to slow down evaporation from the "non-*

volatile" dimers at these same temperatures. An additional consideration is the amount of mass that is found in what might be considered "dimer" bins. In the figure below, we show the distribution of particulate mass at 500 ug/m3 total OA mass for the VBS distribution we have used (Pathak et al., 2007). The amount of mass that is in these bins is very small, and thus they would not have a controlling effect on the evaporation behavior in the simulations. Thus, even if these bins were reflective of the influence of dimers, they would not strongly affect our measurements.

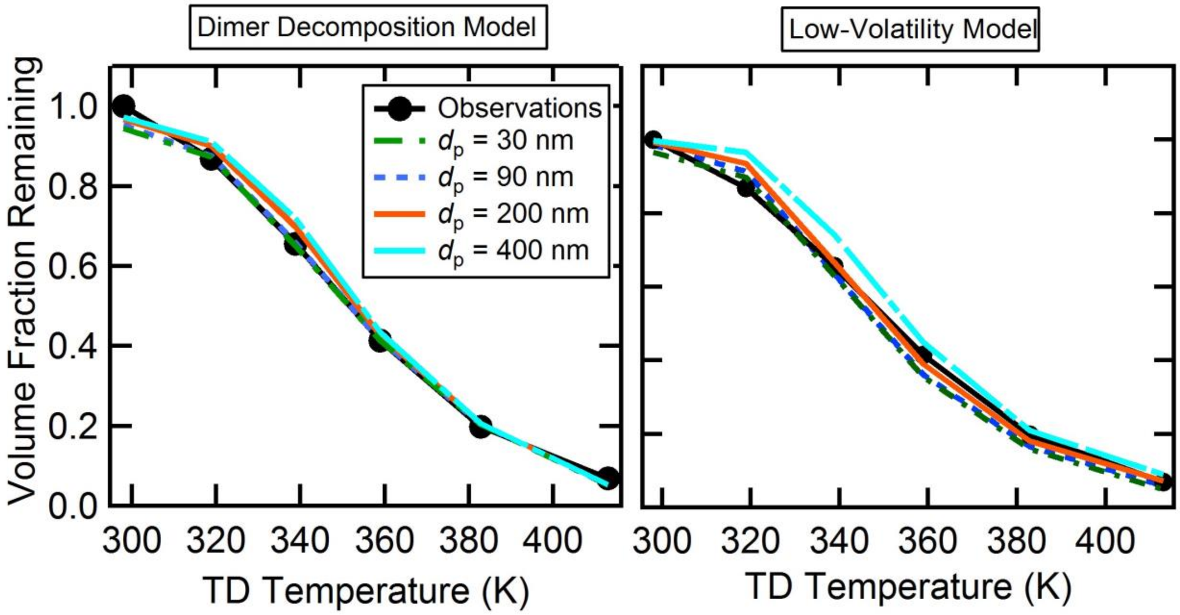


Comment by Referee 2) It is said that the dimers were assumed non-volatile. Were all the VBS bins treated the same way regarding dimer formation? Is it justified to assume that the dimers formed from the compounds in the most volatile VBS bin would also be non-volatile? How would it change the results if the dimers formed from the most volatile SVOCs would evaporate (even though much slower than the monomers)?

Reply: *Yes, all of the VBS bins were treated the same way regarding dimer formation i.e. they all had the same kf, kr and ΔEa. The reviewer raises a good point that the dimers formed from the most volatile SVOCs might evaporate directly more readily than dimers formed from less volatile monomers. The assumption built into the dimer decomposition model is that each bin of dimers will thermally decompose before they would evaporate directly. This thus represents a limiting case. However, we have also presented an alternative model (the low-volatility compound model), in which the volatilities of the compounds comprising the SOA are determined by data fitting and it is assumed that all of these compounds can directly evaporate. This is in effect a second limiting case. The model scenario suggested by the reviewer is a combination of the two models. It is reasonable to think that reality exists somewhere in between these two limiting cases, and is something which we will certainly be exploring in future work. However, to the reviewers more specific question of how it would influence the results, the answer is that it would* *depend on exactly how the vapor pressures of the dimers were specified as we do not know this a priori. Direct evaporation of dimers would compete with decomposition+evaporation, and lead to different fit parameters. Most likely, the decomposition rate at a given temperature would end up decreasing because of the increase in net evaporation from direct dimer evaporation. This would translate to a decrease in ΔEa or an adjustment in the kf/kr values.*

Comment by Referee 3) p. 10004, eq. 2: The VFR was calculated based on volume-weighted average diameters. However, based on Fig. 1 the size distributions were rather wide. Did the model consider polydisperse particle population or did it assume monodisperse population? How large uncertainty does the use of average diameter for VFR cause in respect the comparison of measurement and model?

Reply: *The reviewer is correct in pointing out that by treating the model SOA as monodisperse while the experimental SOA is polydisperse is not a perfect comparison. However, over the range of Dp = 30 to 400 nm the maximum difference between the two predicted curves for the dimer decomposition model is VFR = 0.07 (See accompanying figure). Although all of the model predictions using the same kr, kf, Keqm and deltaEa while varying the particle diameter agree reasonably well with the experimental observations and with each other, a unique set of fit parameters could equally be determined for the different sized particles. The maximum difference between particles of different varying diameter for the low volatility scenario is also small (VFR = 0.11) and the low-volatility product distribution could be further adjusted to provide better model/observation agreement for each particle size. Regardless, the common feature amongst all of the thermodenuder model scenarios is that the particle evaporation can be explained assuming that the particles are either composed of a large fraction of dimers that thermally decompose or of low-volatility compounds that evaporate directly (or some combination thereof).*



Comment by Referee 4) p. 10010, l. 2-6: Evaporation upon isothermal dilution can be rapid for the most volatile SVOCs. Therefore, the composition of diluted SOA can be different, especially if large fraction of initial mass was of the most volatile SVOCs.

Reply: *The reviewer points out that when OA is composed of a large fraction of SVOCs then there will be rapid evaporation of these compounds upon isothermal dilution which will likely lead to changes in particle composition. However, for α-pinene+*O_3 *SOA, this and other studies have measured both directly and indirectly that rapid dilution does not induce instantaneous evaporation; instead, it takes minutes for the particles to respond to any significant extent. We note that this behavior for SOA is very different than it is for particles made of lubricating oil. Lubricating oil particles exhibit near instantaneous evaporation in response to dilution or vapor stripping. Given that we observe no mass loss upon rapid dilution, the composition of the SOA formed at high* C_{OA} *should not change upon rapid dilution as it would for a semi-volatile aerosol such as lubricating oil.*

Comment by Referee 5) The assumption of initial composition of particles determines to a large extend the modeled mass thermograms. In the low-volatility version of the model the total concentration of each compound C_i,tot was calculated with the exponential equation (p. 10018, l. 11). Could the authors clarify the use of this equation a bit? It is not clear why such exponential equation is used and if it is physically justified. Did the a1, a2, a3 and a4 have same values for each C*? It is said (p. 10018, l. 12-16) that the a values were determined for one certain C_OA value, however later the same set of a values is used for varying C_OA values. Is this consistent use of the a values and the equation for C_i,tot.

Reply: *The functional form used here is entirely empirical, based of that used in (Cappa et Jimenez, 2010). To quote them: "This form was chosen in part because it is generally consistent with observations of the volatility distributions determined for laboratory secondary OA (Presto et Donahue, 2006)and for OA from diesel and woodsmoke emissions (Robinson et al., 2007), but more importantly because it was found to provide generally good agreement between the model and observations." Regarding the question "Did the a1, a2, a3 and a4 have same values for each C*" we wish to clarify that the parameters determine the distribution of mass with respect to C* through the relationship given in the text: (*$C_{i,tot} = a1+a2*\exp(a3*(\log C^*)-a4)$*). In other words, C* does not depend on the 'a' values. It is the* $C_{i,OA}$ *values that depend on the a values (and C*). . To the question regarding the use of the same values for multiple* C_{OA}*'s, we should clarify that the shape of the* $C_{i,tot}$ *curve was determined using the same set of parameters at each* C_{OA} *(with those parameters determined from fitting the observations for one particular* C_{OA}*, as discussed in the manuscript). However, the absolute values of* $C_{i,tot}$ *were scaled using a constant multiplicative factor for each* C_{OA} *such that the absolute model* C_{OA} *matched the observed* C_{OA} *to which it was compared. Given the functional form used (*$C_{i,tot} = a1+a2*\exp(a3*(\log C^*)-a4)$*), this amounts to scaling the parameters and a1 and a2 by a C_OA specific constant. In other words,* $C_{i,tot}(C_{OA}) = b*C_{i,tot}(\text{reference case}) = b*(a1+a2*\exp(a3*\log C^*)-a4)))$ *where b is set for each* C_{OA} *value but is independent of C*. This will be clarified in the revised manuscript, although it should be noted that it has no material impact on the observations given that the functional form is somewhat (although not entirely) arbitrary in the first place.*

Technical comments:
p. 10009, l. 23: There should probably be ‘high’ before ‘C_OA’.
This has been fixed.

Figure 1: I find the x-axis numbers confusing as one would by quickly looking think that the average diameter was 2-4 nm, instead of 20-40 nm. I would thus recommend modifying the x-axis.

The figure has been updated.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 9997, 2015.
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References

Cappa, C. D., and Jimenez, J. L.: Quantitative estimates of the volatility of ambient organic aerosol, Atmospheric Chemistry and Physics, 10, 5409-5424, 10.5194/acp-10-5409-2010, 2010

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.

Pathak, R. K., Presto, A. A., Lane, T. E., Stanier, C. O., Donahue, N. M., and Pandis, S. N.: Ozonolysis of alpha-pinene: parameterization of secondary organic aerosol mass fraction, Atmospheric Chemistry and Physics, 7, 3811-3821, 2007.

Presto, A. A., and Donahue, N. M.: Investigation of alpha-pinene plus ozone secondary organic aerosol formation at low total aerosol mass, Environmental Science & Technology, 40, 3536-3543, 10.1021/es052203z, 2006.

Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N.: Rethinking organic aerosols: Semivolatile emissions and photochemical aging, Science, 315, 1259-1262, 10.1126/science.1133061, 2007.