

Interactive comment on “Is Mass Transfer in Secondary Organic Aerosol Particles Intrinsically Slow? Equilibration Timescales of Engine Exhaust and α -Pinene SOA Under Dry and Humid Conditions” by Khairallah Atwi et al.

Anonymous Referee #1

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Review of “Is mass transfer in secondary organic aerosol particles intrinsically slow? Equilibration timescales of engine exhaust and α -pinene soa under dry and humid conditions” by Atwi et al.

The authors present observations of the extent of evaporation for SOA formed either from alpha-pinene photooxidation or from exhaust from a small engine, after dilution from relatively high concentrations (100's of micrograms/m³) to relatively low concentrations (~5 micrograms/m³). They observe the particles to shrink by a small amount, typically ~5-10%, to a new, relatively constant value on a timescale of ~1 h. The

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experiments appear to be of good quality.

They interpret these observations in terms of a single-component evaporation model from which they deduce the effective saturation concentration and evaporation coefficient. I have substantial concerns regarding the interpretation. There is a fundamental limitation from the outset, namely that the authors assume that the particles are made of one compound and thus the evaporation can be characterized through a single value of the effective saturation concentration and evaporation coefficient. It is now well-established that SOA is composed of many, many compounds, not one compound, and that treatments of SOA as if made of one component are too simple and can yield results that are not linked to true physical properties. (Think of the two-product model, for example.) This fundamental assumption dictates the entire analysis and the results and inferences that can possibly result. The team has previously published results using similar methods and with the same core assumption. I believe that this work should not be published because it perpetuates what I believe to be an overly simplified analysis framework. I strongly encourage the authors to expand the scope of their model to treat the SOA in a more physical manner, at minimum as if composed of a distribution of compounds with varying volatilities. This would not get at issues of oligomerization (mentioned by the authors as potentially important) and how this might impact their interpretation. But it would at least move it in the right direction in terms of using a more realistic representation of the physical properties. That said, I suspect that the authors will quickly find that if they expand their modeling framework they will end up with many unknown model parameters and many degenerate solutions, greatly complicating interpretation. I wish I could see a more favorable outcome for this work, but unless the core assumption underlying the analysis is changed I do not see a path to publication of this work.

Below I provide specific comments on the manuscript, and further discussion of my core concern regarding the analysis/interpretation framework.

Abstract: it is by now well-established that SOA comprises a variety of compounds with

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a distribution of vapor pressures. Given this, it is now unclear what it means to have an “effective thermodynamic saturation concentration” of a single value.

P2/L17: There are many models that use a kinetic approach to partitioning. The complexity of the process representation may be limited, but kinetic partitioning is nonetheless used in numerous atmospheric models. “Some” models assume instantaneous equilibrium.

P3/L13: The effective evaporation coefficients determined by Saleh/Saha et al. are not necessarily the same as those reported in the previous paragraph. The determination and reporting of an evaporation coefficient is highly dependent upon assumptions made in the interpretation. There is a direct link between the assumed volatility distribution and the obtained evaporation coefficient. The comparison here does not recognize sufficiently this complexity. This is noted two paragraphs later, but the nuance is lost in this paragraph. I suggest bringing these together to minimize misunderstanding.

P3/L25: better as “estimated by traditional interpretation of smog chamber experiments.”

P3/L26: Even non “aged” SOA may have oligomers.

P3/L31: When the components that are very low volatility, and thus evaporate only a little bit upon e.g. dilution, the evaporation experiments mentioned are not able to establish the evaporation coefficients of these components. A noticeable change in particle size/mass must be observed for an evaporation coefficient to be determined. Thus, the cited studies determined evaporation coefficients for the components that contributed most to the mass change. This issue needs to be recognized throughout the manuscript. The authors can only determine evaporation coefficients for components that evaporate non-negligibly and that comprise a notable fraction of the volume.

P3/L33: There are a multitude of studies that have studied SOA from anthropogenic precursors. I do not understand what the authors mean here in saying that lab studies

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focus exclusively on biogenic SOA. This is simply incorrect.

P4/L27: An explicit assumption of the model is that the system can be modeled using a single vapor pressure. As noted above, it is well established that SOA is a distribution of species of differing volatility. Thus, the single-volatility approximation used here is limited in terms of its physical realism. While it does not “require a priori knowledge about aerosol volatility,” it does a priori assume that SOA is describable by a single volatility. This substantial limitation should be noted. Moreover, the limitations of this fundamental assumption should be assessed. What if the authors assumed that the particles were composed of two compounds with volatilities that differed by one order of magnitude and existed in proportions that allowed for the average volume loss observed? Or of one higher volatility and one non-volatile component? Would the time-dependent trajectory (i.e. equilibration) differ from the single-component model, or is the trajectory completely independent of the assumption of a single-component system? This can be theoretically explored by the authors via minimal modification of their modeling framework. It will, however, introduce further unknowns. Thus, they might consider a systematic exploration of the assumption. To me, this foundational model assumption is the fundamental limitation of this entire study.

P6/L6: It is stated that C_{sat} and α are the “unknowns” since the other parameters can be estimated. But it is unclear how the wall term ω is known. Bounds can be established (zero to one), but it is not known. This should be discussed.

P7/L16: mlpm is non-standard.

Fig. 2: I find the schematic unclear. It appears that 25 lpm is going in to the chamber but only 1 lpm is coming out. Is this correct? The authors also use a lot of symbols in the figure that could benefit from a legend. And some flows are labeled, others are not. Consistency in labeling would be helpful.

Fig. 3: What is “POA” in this figure? This typically means “primary organic aerosol.” How is the OA concentration zero when there is POA around?

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Fig. 3: Is there no black carbon for the engine emissions? The authors seem to assume that all mass is OA. Has this been confirmed?

Fig. 6: Would surface area distributions be more appropriate, since the condensational sink is what matters?

Fig. 6 vs. Fig. 7: I do not understand the relationship between these figures. The peak in the number distribution for, for example, the dry Engine SOA case, is near 100 nm. So how is the diameter for the condensation sink only 67 nm?

Fig. 8 and P10/L6: The nature of the “low” versus “high” loading conditions is unclear. This is not discussed in the methods. How were these conditions obtained? Are these just random differences between experiments? Or some systematic examination of loading? And what is “high” and what is “low.” This doesn’t appear to be stated clearly. I find this discussion unclear, including the extrapolation to the particles having sufficient volatile material had it evaporated.

P10/L17: The statement that “humidity was a significant factor” is sufficiently imprecise to be incorrect. This was only found to be the case for one of the two systems considered. So for one it is not a factor, the other it is.

P11/L16: The authors again frame these literature studies in contrast to the current study as fundamentally different. They simply, as the authors note, build from different assumptions but are, as least in theory, reconcilable. This is already known, and even mentioned by some of the studies cited (and some that are not cited). It is suggested that the authors reframe this to indicate that their study is further support for the idea that the evaporation coefficient cannot be determined without clear understanding of the underlying volatility distribution. Also, at the end of this paragraph the authors appear to link lower volatility to slower evaporation, which is fine, but in the context of evaporation coefficients this is inconsequential.

P11/L30: The authors observed that the particles stopped shrinking (after wall correc-

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tion) in a noticeable way after ~100 mins up to a total time of 300 mins. From this they are concluding that the particles have reached equilibrium. How do they know? What if there is a fraction of the particle that evaporates rapidly and a fraction that evaporates/equilibrates slowly? Much slower than the timeframe experimentally covered here? How can the authors rule out the possibility that, had they looked over even longer timescales they would not have observed a continued evolution of the system? This comes back to the fundamental assumption that the authors interpret everything within a single-component framework. I believe that the authors need to push beyond this single-component framework to consider the implications, at the minimum, of what would happen if they took a fuller approach.

P12/L2: I find this a bit unconvincing for the following reason. The authors have not done a sufficient job of examining the loading dependence. They have examined exactly two concentrations that differ by only a factor of two, not performed a systematic exploration. And, in the example shown in Fig. 8, this is not representative of the average results (deduced from table 3), which show much smaller differences, on average, between the two loading cases. Further, as with the entire study, this interpretation is very much limited by the fundamental assumption of a single-component aerosol.

P12/L10: I find the statement regarding timescales of chemical transformations unclear. Chemical transformations occur on time scales ranging from seconds (or much, much less) to much longer. Chemical transformations, like partitioning, occur on a continuum of timescales. The authors cite Seinfeld and Pandis here (which is missing from the reference list). I ask them to point to the page where this range of timescales is given for “chemical transformations.”

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