

Review of Li and Shiraiwa “Timescales of Secondary Organic Aerosol to Reach Equilibrium at Various Temperatures and Relative Humidities”

General Comments

In this manuscript, the authors use simulations to calculate the gas/particle equilibration time for secondary organic aerosol as a function of temperature, relative humidity, and SOA microphysical properties. The topic of SOA partitioning, equilibration, and phase state are highly relevant in atmospheric chemistry, the topic is timely, and will be of interest to the readers of ACP.

This work is a logical extension of the previous work done by the PI. It essentially combines work in predicting the phase state of particles as a function of atmospheric conditions with work on calculating gas/particle equilibration times (Shiraiwa et al., 2017; Shiraiwa and Seinfeld, 2012). Based on past results from the PI on these topics, the present results are not particularly surprising, but I think there is enough new material here to warrant publication. This publication essentially closes the loop between predicting phase state and calculating the gas/particle equilibration time.

With that said, there are a few areas that could be improved before publication. The authors could do a better job of calling out, in the manuscript, what is new unique about this manuscript relative to the previous publications by the PI. A few of the conclusions reached in this work also seem to contradict the PI's previous publications and the authors should clear this up. The authors could help readers put this work into context if they explain why they make certain assumptions in their model (i.e., a closed system), offer some insights into how realistic these assumptions are relative to the ambient atmosphere, and explain how their conclusions would be different if/when the assumptions are not atmospherically representative. While the manuscript is generally well written and clear, there was one section that was somewhat confusing and should be clarified before publication. With that said, there are no major shortcomings with the manuscript and, providing the authors make some revisions, I have no reservations about recommending this manuscript for publication in ACP.

Major Specific Comments

Lines 23-25, Figure A1, and elsewhere. In the present manuscript the authors conclude that the equilibration timescale for low volatile compounds is shorter than for semi-volatile compounds when other conditions are equal. However, Shiraiwa and Seinfeld 2012 report the opposite (see for example Figure 2), with ELVOC's having longer equilibration times than SVOCs (Shiraiwa and Seinfeld, 2012). The authors should comment in the text on why these studies reach opposite conclusions.

Lines 115-123. I understand that the authors need to make some assumptions or approximations in their model/calculations. I am trying to understand how atmospherically realistic these

assumptions are. The two main assumptions in the present model are of a closed system and that the condensation of molecule Z does not alter the composition and microphysical properties of the pre-existing particles.

It is clear that the real atmosphere isn't a closed system. The argument could be made that on seconds-to-minutes timescales, it may approximate a closed system, but the processes that authors are modeling are sometimes occurring on timescales of hours or even days. In addition, one of the author's major conclusions is that low volatility material reaches equilibrium more slowly than higher volatility material. I understand why this is the case in a closed system, but would this conclusion also hold in an open system like in the atmosphere with a constant dilution and/or loss of gas-phase molecules? A plume transported from the surface to the upper troposphere would experience an evaporative driving force where this model seems focused on cases where the driving force is toward the particle phase (condensation).

With respect to a single compound (Z) changing the composition and microphysical properties, it may be true that a single molecule or even a few molecules rarely make up the bulk of the SOA mass. However, in the real atmosphere, particles obviously grow and their composition and microphysical properties change as SOA condenses. The PI of this manuscript has previously used kinetic modeling to reproduce particle growth, so I'm not really clear on why these assumptions needed to be made (Shiraiwa et al., 2013).

In the both cases, I think it is important that the authors explain: why they chose to make these assumptions, how likely it is that these assumptions are representative of the atmosphere, and how their conclusions would likely be different if the assumptions are not correct.

Lines 276-292 and Figure 5. This figure and associated text was confusing. The figure was confusing because particle diameter and total mass loading are typically not independent of one another in a model or in the atmosphere. I eventually understood the point the authors were trying to make. Perhaps providing some context by pointing out where different atmospheric regimes lie (i.e., remote, typical continental, polluted) in the figure would help. The associated text is also confusing; it wasn't clear what point the authors were trying to make here. They seem to postulate several different processes which could determine particle equilibration timescales (e.g., bulk diffusion, gas-diffusion). Can't the KM-GAP model be used to clear this up? Overall, I'm not sure what message the authors are trying to convey here.

Minor Comments and Technical Corrections

Line 89. It is a little confusing here about what temperature was used in the calculations. I wasn't clear whether 273.15 K was used (the most common definition of standard temperature), or if the temperature was variable as a function of pressure altitude. Adding to the confusion, Table S2 lists standard temperature as 288.15 K. Please clarify.

Lines 108-110. An assumption here is that the organic and aqueous phases are not phase separated. The authors point out later in the manuscript that phase separations may occur, but I suggest also briefly mentioning that phase separation has been observed for laboratory generated SOA (You et al., 2012) here, since it is very relevant to their modeling results.

Lines 144 and elsewhere. I found the use of C_0 as an abbreviation more confusing than necessary. It seems C_0 is identical to the much more commonly used C^* . Why not use the commonly accepted C^* ? The authors also use $C_{p,0}$ and $C_{g,0}$, which have a different meaning and cause some confusion with C_0 . Whatever symbol the author use for the saturation vapor pressure please define it the first time it is used.

Figures 4, A1, A2. The labels on different contours were illegible on the printed document.

References

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Shiraiwa, M., Li, Y., Tsimpidi, A. P., Karydis, V. A., Berkemeier, T., Pandis, S. N., Lelieveld, J., Koop, T., and Pöschl, U.: Global distribution of particle phase state in atmospheric secondary organic aerosols, *Nature Communications*, 8, 15002, 10.1038/ncomms15002 <https://www.nature.com/articles/ncomms15002#supplementary-information>, 2017.

You, Y., Renbaum-Wolff, L., Carreras-Sospedra, M., Hanna, S. J., Hiranuma, N., Kamal, S., Smith, M. L., Zhang, X., Weber, R. J., Shilling, J. E., Dabdub, D., Martin, S. T., and Bertram, A. K.: Images reveal that atmospheric particles can undergo liquid-liquid phase separations, *Proceedings of the National Academy of Sciences of the United States of America*, 109, 13188-13193, 10.1073/pnas.1206414109, 2012.