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Interactive comment on "Quantifying the volatility of organic aerosol in the southeastern U.S." *by* Provat K. Saha et al.

Anonymous Referee #1

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General Comments:

Saha and co-authors present a well-articulated investigation of the volatility properties of organic aerosol at two sites in the southeast United States. The opportunity at Centerville, AL during SOAS is uniquely favorable since there were so many collocated measurements (of meteorological metrics and AMS factors, for example). The authors do a good job motivating the juxtaposition of these data to other data they have collected in Raleigh, albeit at a different time of year. Overall, I find the goal of the work and its presentation quality to be acceptable for ACP and important for the scientific community. However, I have some concerns about the discussion. For example, I think the issue of solubility, while not specifically addressed by their measurements, should be better woven throughout their discussions in the manuscript to make it clearer that the properties of volatility and solubility simultaneously affect the gas-particle partition-

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ing of organic compounds. I look forward to discussing the following issues with the authors:

Specific Comments:

1. Page 2, Line 15: Although it is well-known that volatility plays a pivotal in gas-particle partitioning, I think it is worth mentioning that solubility will also be critical for this phenomenon, especially in places like the southeast US. Admittedly, solubility is outside the scope of this paper (and the RH of the observations is maintained relatively low at 30-40%). It is of course still vital and useful to gain an in-depth knowledge of the partitioning behavior of compounds to the "dry" organic phase. However, please also be careful throughout the text about statements like in line 17-18: "vapor pressure determines whether an organic compound is found in the particle- or gas-phase" since this is not exactly true for many compounds, which are highly volatile and highly soluble, for example. This should be reworded for completeness.

2. Did the authors size select the particles before entry to the TD units? It does not appear so. Could they comment on their method of incorporating the size distribution information into their model? Did they use a moving sectional, fixed sectional, or a modal algorithm? Or was only a single diameter used as is implied on page 6, line 13? If this is the case, can the authors provide some insight into how the inaccuracies introduced in their model results from the width of the distributions (as seen in Fig. S6c,d)? Are there significant size-dependent particle losses in the system and are these temperature dependent?

3. Page 6, Line 19-21: what is the reason for putting only the fi sets that have been "accepted" against the TS-TD data through the VRT-TD analysis? What sets are undetected by not doing both applications for every set and then taking the best performers? On a related note, what initial fi values were used as input to the solver and how dependent was the "accepted" solution on these values? Were these initial conditions varied at all? Why are the authors confident they have evaluated the entire space of

volatility distributions?

4. Page 7, Line 8-9: How do the enthalpies of vaporization used in this WRF-Chem simulation compare with those derived from the observations here (could they add this to the methods section)? What are the implications of comparing the volatility distribution from a model to observations when they are using different enthalpies? Is this something that other researchers should take seriously when comparing model output to TD data? On Page 15, Lines 20-24, the authors provide some discussion of this issue. However, they seem to be assessing the sensitivity of the enthalpies in the model independently of the mass yields being used. Is this appropriate?

5. Page 9, Line 8-9: I'm not familiar with the term "condensation sink diameter". Could the authors please explain it and potentially provide an equation in the supporting info for this quantity? How is it related to the more common term, condensation sink which is in units of inverse time?

6. Do the authors have an explanation for why the 80-0 and 80-4 cases with evaporation coefficient equal to 0.5 and 1.0 performed acceptably for the Raleigh cases and not for the Centerville cases? How close were they to being accepted with the VRT-TD data? It perhaps appears that they performed better for the TS-TD data at Centerville than they did at Raleigh (or at least the cases around them with discernible colors did).

7. Page 10, Lines 5-10: The low enthalpies used in models are based on observation data (e.g. Offenberg et al. 2006; Pathak et al. 2007; Stanier et al., 2008) of so-called "effective" enthalpies, so please consider mentioning this for completeness; Stanier et al. (2008) were a bit higher than others and in line with the lower bound explored in this study. It has been argued that low enthalpies of vaporization result from describing systems with too few volatility surrogates (Riipinen et al., 2010). Could the authors comment on what they attribute the void between their high enthalpies and historical low enthalpies to? If they run their model with only two surrogates, for example, do they get low enthalpies as well?

8. Can the authors please provide some statistics to go along with the comparison in Fig. 4? For example, it would be useful to have mean bias, correlation coefficient and root mean square error so that future studies would have something succinct to use as a benchmark.

9. In Fig. 4a, is the COA that of the ambient (unheated) sample? There does appear to be systematic overprediction for low COA cases compared to high COA cases. Is this true? Could the authors provide some statistics stratified by COA to assess this? If there is a relationship, could they comment on why it emerges from their approach?

10. Page 13, Line 8: Please avoid using the word “relatively” and opt instead for a quantification of the difference between the afternoon and early morning.

11. Sections 3.4-3.5: The authors have defined both mean(C*) and C*eff and chose the former for their analysis of time series and diurnal profiles. I think this may have been an unfortunate choice. This value, as they say, accounts for both particle- and gas-phase compounds. It is not very surprising to me that it would be a more stable quantity, throughout the SOAS campaign at least. I wonder if they would capture the trends they are after better by using the C*eff which just accounts for the particle-phase material. This at least would seem to make more sense for correlating with AMS factors (Isoprene-OA, LO-OOA, and MO-OOA) since those apply just to the particle phase and not the total organic burden. Using this alternative approach would theoretically introduce a temperature and dilution dependence that might result in a more striking and meaningful variability. Of course, it may on the other hand yield a rather invariant trend similar to what they have already shown.

Minor Changes/Typos:

Pg 1, Line 11: Consider mentioning solubility as well. “quantitative estimates of the thermodynamic (volatility, water solubility, etc)”

Pg 1, Line 14: “one at a biogenic. . .”

Pg 2, Line 6-7: Of course SOA has also been shown to be introduced from oxidation of primary SVOCs and IVOCs followed by condensation and aqueous phase reactions of high soluble compounds. Depending on your definition of “secondary”, it is also formed by heterogeneous oxidation of POA without evaporation. Please mention these here or don’t be so specific about the VOCs role.

Pg 5, Line 16-17: The VBS approach does not assume unity activity coefficients. Instead the activity coefficient are assumed to be lumped into the Cvap, making it C*. And so the activity coefficients have a value, but that value is assumed not to change from the lab or field to other mixtures or conditions.

Page 6, Line 10: I disagree that the model is applied in an “inverse sense”, as it appears that the authors are solving the evaporation problem in the forward way, brute-force, for all of their free parameter combinations and then comparing output to the observations. This could perhaps be labelled reverse engineering, but I think associating it with inverse modeling is inaccurate.

Page 6, Line 27: “common means to improve the performance of OA prediction in chemical transport models”

Fig. 2b,c: There is no explanation or legend for the colors of the trends. The text claims they distinguish different residence times but isn’t this described by the x-axis? Please clarify this point.

Page 9, Line 14: Just write “volatility”. Having the “/C*” is unnecessary. Page 15, Line 7 as well.

Page 9 and Fig. 3: Neither the description in the text nor the figure caption should claim that the figure depicts the fi values. As far as I can tell, it does not.

Page 9, Line 18: Please indicate here, and throughout the text, that this C* is at Tref (presumably 298 or 300 K). This should especially be made clear for any references to mean C*.

Page 10 and Fig. 2: The notation for Ceff is not consistent with Csat_eff.

Page 13, Line 26-27: You do not really need this final sentence since the section you refer to comes directly next.

Page 16, Line 16: Please be quantitative rather than saying “Relatively less volatile”.

Page 16, Line 30: Murphy et al. (2011) compared predictions with the 2D-VBS in a Lagrangian column CTM against the FAME data reported by Lee et al.

References Murphy, B. N., Donahue, N. M., Fountoukis, C., and Pandis, S. N. (2011): Simulating the oxygen content of ambient organic aerosol with the 2D volatility basis set, Atmos. Chem. Phys., 11, 7859-7873, doi:10.5194/acp-11-7859-2011.

Offenberg, J. H., T. E. Kleindienst, M. Jaoui, M. Lewandowski, and E. O. Edney (2006), Thermal properties of secondary organic aerosols, Geophys. Res. Lett., 33, L03816, doi:10.1029/2005GL024623.

Riipinen, I, Pierce, J, Donahue, N, and Pandis, S (2010): Equilibration time scales of organic aerosol inside thermodenuders: Evaporation kinetics versus thermodynamics. Atmos. Environ., 44, 5, 597-607, doi:10.1016/j.atmosenv.2009.11.022

Stanier, Donahue, and Pandis (2008), Parameterization of secondary organic aerosol mass fractions from smog chamber data, Atmos. Environ. 42, 10, 2276-2299, doi:10.1016/j.atmosenv.2007.12.042.

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