Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-575-RC2, 2016

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

Received and published: 1 September 2016

General Comments:

This manuscripts presents measurements and analysis of the evaporation behavior of organic aerosol (OA) measured at two different locations – one more rural, one more urban, but both influenced by significant concentrations of BVOCs. Measurements were taken with a dual thermodenuder system in which both the temperature and residence time were varied. Main conclusions of the work include that the OA evaporation behavior was fairly similar at the two sites and did not vary much over the course of the measurement campaign, and also that much of the OA is in low-volatility bins which are currently not represented in (most) air-quality models.

The manuscript is well written and generally well argued, and overall the topic and quality of the manuscript makes it suitable for publication in ACP. However, I have a few

concerns about the analysis and interpretation as explained below which I suggest the authors should address before publication.

Major comments:

1. The authors focus on the "best fit solution" and address to some extent the sensitivity of the error (SSR) to changes in dHvap and gamma (e.g. Fig. 3). I request that they also address the sensitivity of the error to changes in the fi. I am particularly worried that the fi in the lower C* bins may not be well constrained by the data.

2. Regarding higher C* bins, on page 6 lines 1-2 the stated reason for not including C*>10 μg/m3 is that less than 5% of the materials would be present in the condensed phase at the average COA of 5 μg/m3. Common VBS bins used range from 0.1 to 100 μg/m3 for ambient OA concentration of $\sim$10 μg/m3. Elevated OA episodes (OA > 10 μg/m3) were observed, especially at the Raleigh site (Figure S7). It would be reasonable to include the 100 μg/m3 bin in the model to account for these episodes. Have the authors investigated the effects of including higher volatility bins on the fitted model parameters? As referee #1 pointed out and according to Riipinen et al. (2010), a two-surrogate product model could lead to very different conclusions about dHvap. How does the inclusion of more and lower volatility bins affect modeled dHvap? In other words, does bin selection introduce bias in to model results (and if so, how much)?

3. Page 6 Line 21-23: Have the authors attempted to apply the two models in a different order (VRT-TD first then TS-TD)? How much does this change the results?

4. Page 13 Line 1-6: mean C* is perhaps not a suitable metric to correlate with the fraction of isoprene OA. If isoprene OA was in fact much less volatile, its overall contribution to mean C* would be minor; the calculated mean C* value would be dominated by fi values of more volatile surrogate compounds. Using Ceff would present similar issues. It seems more appropriate to investigate the correlation between isoprene OA and individual bin fi's.

5. Page 6, line 7: Was a constant collection efficiency of 0.5 also applied to all thermally denuded data? Evaporating part of the organic aerosol (and therefore changing the org/sulfate ratio) could change the collection efficiency, which would bias MFR measurements. The authors could partially address this issue by comparing total SMPS and ACSM measurements (mass), i.e. the ACMS/SMPS ratio in the bypass and after the thermodenuder.

6. Fig S7 seems to assume that all nitrate measured in the ACSM is inorganic. This seems to contradict discussion earlier in the manuscript of the potential importance of organic nitrates. Previous work has shown that the ratio of NO+ to NO2+ fragments measured by AMS or ACSM instruments is quite different for organic nitrates and ammonium nitrate, and that the ratio can be used to estimate the fraction of measured nitrate due to organic nitrates. I suggest the authors use these measurements from the ACSM to estimate how much of the measured nitrate is organic vs. inorganic. Assuming full neutralization of sulfate by ammonium (which is reasonable in the presence of ammonium nitrate) could also be used to calculate the nitrate attributable to ammonium nitrate and, therefore, the nitrate due to organic nitrates.

7. Page 4 Line 12: "All Rts reported here are calculated assuming plug flow at room temperature" This implies that a plug flow (as opposed to parabolic) velocity profile is assumed in the evaporation model. Is this correct? It was suggested by (Cappa, 2010) that assuming plug flow profile would lead to underestimation of dHavp and overestimation of Csat. Have the authors explored different assumptions for gas velocity profile in the model?

Minor comments:

8. Page 5 Line 2: Please expand on what "instrumental inter-calibration factors" entail

9. Page 6 Line 23-24: Please clarify on how variability is calculated. Is it based on measured MFR values or OA measurements? Is it calculated over small intervals or over the entire course of campaign?

10. Page 8 Line 31: Please provide references for previous field studies.

11. Page 10 Line 8-10: Please add discussion on why observed slope may be different from the empirical relation determined by Epstein et al.

12. Page 2 line 6: "...SOA is formed in the atmosphere via condensation of low-volatility products..." This statement is not inclusive enough. Please revise.

References

Cappa, C. D.: A model of aerosol evaporation kinetics in a thermodenuder, Atmos. Meas. Tech., 3(3), 579–592, doi:10.5194/amt-3-579-2010, 2010.

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

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-575, 2016.