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

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Anonymous Referee #2 General Comments: R2.0. This manuscript 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

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explained below which I suggest the authors should address before publication.

A2.0. We thank the reviewer for his/her review and useful comments. We address the specific comments below.

Major comments:

R2.1. 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.

AR2.1. For solving a fi distribution, we have used a non-linear constrained optimization solver (fmincon in Matlab). We provided constraint for the lower (fi minimum = 0.02) and upper (fi maximum = 0.4) boundary for a fi value in each C* bin. This choice of a wide solution space for solving a fi value in each C* bin should address any sensitivity of the error to an optimum solution of fi. As we discussed in our manuscript that our selected C* bin range was based on our measurement conditions; specifically, the highest TD operating temperature and the average ambient OA loading provide limitations on the lower and upper C* bins we consider, respectively. Page 6, Lines 5-6, “With the above C* bin limits, materials having C* < 10-4 μg m-3 are lumped into the lowest bin. . .. . . .”. Bins lower than ∼10ˆ-4 are not constrained in our data set because maximum TD operating temperature was 180°C. Materials those survived at 180 °C may well be even lower volatility, but we need to see it evaporate to be able to say anything quantitative about volatility. The key point is that within this predefined range, our approach provides an empirical OA volatility distribution that explains the observed evaporation of bulk OA in our dual-TD system.

R2.2. Regarding higher C* bins, on page 6 lines 1-2 the stated reason for not including C*>10 _g/m3 is that less than 5% of the materials would be present in the condensed phase at the average COA of 5 _g/m3. Common VBS bins used range from 0.1 to 100 _g/m3 for ambient OA concentration of _10 _g/m3. Elevated OA episodes (OA

> 10 _g/m3) were observed, especially at the Raleigh site (Figure S7). It would be reasonable to include the 100 _g/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)?

AR2.2. As noted in the manuscript that the selection of C* bin range in our fitting was based on our measurement conditions, specifically the highest TD operating temperature and average ambient OA loading. We performed sensitivity analysis on the selection of C* bin range. Fig. AR.3 shows an example result showing the comparison between fits with ranges of C*= [10ˆ-4 to 10 μg m-3] (base case used in our paper) versus C*= [10ˆ-3 to 10ˆ2 μg m-3] of the Raleigh campaign average TD observations. Results indicate that C*= [10ˆ-3 to 10ˆ2 μg m 3] fails to recreate the observed evaporations at higher TD temperature and that there is an indistinguishable change at lower temperature conditions (where the C* = 10ˆ2 μg m-3 would have any influence on the fit).

The reviewer correctly pointed out that there were a few elevated COA episodes ($\geq$ 10 μg m-3) during the Raleigh campaign. However, these episodes were for a relatively short period of time (2-3 hours) and the time required for collecting a complete set of thermograms using our TD setup was $\sim$ 4-5 hours, we were not been able to capture a complete set of data under a consistently elevated COA which could be fitted to constrain higher volatility bins.

As we discussed earlier in response to reviewer #1 (AR1.7) Comment, by reducing the number of surrogate compounds, the system representation would potentially move further away from realistic enthalpies. Therefore, we focused to describe the aerosol using the VBS representation with a commonly-used number of bins. We have not tested the dependence of the apparent ΔHvap values on the number of surrogate compounds. Our goal of this study was to describe ambient OA within this pre-defined framework. In our fitting, we represented ΔHvap as a function of C* bin (ΔHvap = intercept-slope (log10C*)) and found that a relatively 'shallow' logC* dependence (slope $\sim$ 0, 4) better explain the observed temperature sensitivity of bulk OA in TDs. This suggests that an effective ΔHvap required to explain the observed temperature sensitivity of bulk OA would be less sensitive to an inclusion of higher/lower C* bins within a realistic range. However, we do recommend that further work explores the sensitivity of the apparent ΔHvap to the number of surrogate bins in future studies considering the use of basis sets with fewer bins.

R2.3. 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?

AR2.3. The order of model application has no effect on derived parameters. We have used the same model for fitting data from TS-TD and VRT-TD. For a given input temperature (T) and residence time (Rt), the evaporation kinetics model predicts a mass fraction remaining; MFR (T, Rt). In our method, the fitting can be done in one step (fitting all data from TS-TD and VRT-TD together) or two steps. We have found that the two-step fitting approach gives identical results to fitting all data simultaneously. We, therefore, elected to use a two-step fitting approach because it narrows down the parameter space substantially in the first step, which reduces the computational requirements substantially. An additional advantage to applying the 'two-step' approach in this work is that it distinctly demonstrates the benefit of the additional dimension (Rt) we have added to the traditional TD measurement space (T) via goodness of fit quantification across the [γe, ΔHvap] space at each step (Fig. 3).

R2.4. 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.

A2.4. We thank the reviewer for this suggestion. We have performed this additional analysis and a summary result is shown below (Pearson R value between Isoprene-OA fraction and fi's): C* bin = [10ˆ-4 10ˆ -3 10ˆ-2 10ˆ-1 1 10 mean C* C*_eff]; Pearson R value = [0.02 0.29 -0.07 -0.06 -0.14 0.04 -0.06 0.19]

Based on our analysis we did not find any statistically significant relationship between isoprene-OA fraction and fi's in any individual C* bin. This result is consistent with our original observation of no correlation between mean C* of bulk OA and the fractional contribution of isoprene-OA to COA. This new result is included in Table S2 and discussed on Page 13, Lines 29-30: "Neither were statistically significant relationships found between the isoprene-OA fraction and fi's in any particular C* bin (see Table S2)."

R2.5. 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.

AR2.5. Yes, we have analyzed both the bypass and heated (TD) ACSM data using a constant collection efficiency (CE) of 0.5. A comparison of ACSM/SMPS ratio in the bypass (slope = 0.95±0.006) and after the TD (slope = 0.91±0.009) data is shown in panels c and d in Fig S1. A slightly lower slope for the heated measurements suggests that CE could be ∼4-8 % lower for the aerosol that passes through the TD. We did not attempt to use a different CE value for the thermodenuded aerosol based on this analysis because the SMPS measurement also could be affected by a potential change in particle morphology and shape upon heating. However, the bottom line is that the potential uncertainty that may arise from using a constant CE would be very low compared to the overall observed variability in measurements.

R2.6. 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.

AR2.6. The Nitrate measured by an ACSM would be a combination of both organic and inorganic nitrate. We changed the axis label for panel (b and d) of Fig.S7 from ‘inorganic’ to ‘SO4, NO3, NH4’. We explored the NO+ to NO2+ ratio from our ACSM measurements as suggested by the reviewer. A summary of NO+ to NO2+ ratio (campaign average $\pm$ 1 SD) is given below:

Centreville: 10.02 $\pm$ 3.47; Raleigh: 5.93 $\pm$ 1.96; Pure ammonium nitrate (Cal aerosol):3.58 $\pm$ 0.84

The NO+: NO2+ ratios in both campaigns were significantly higher than that of pure ammonium nitrate aerosol in our instrument. This is consistent with a substantial contribution from organic nitrate and with our discussion of the potential importance of organic nitrates. However, an absolute quantification of organic nitrate is not critical for our analysis, as our paper focuses on the volatility of bulk OA as identified by the ACSM/AMS.

R2.7. 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

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and overestimation of Csat. Have the authors explored different assumptions for gas velocity profile in the model?

A2.7. The Cappa (2010) paper discussed the effect of the laminar vs. plug flow assumptions on the derived saturation vapor pressure and enthalpy of vaporization of a single component aerosol. The author notes that the effect of this assumption changes with the compound saturation vapor pressure. It is not clear what effect this assumption would have if a multi-component aerosol is considered. It should be noticed that a plug flow approximation is widely used (Lee et al., 2010; Riipinen et al., 2010; Saleh et al., 2008), with the residence time and non-uniform temperature effects on derived quantities being relatively small (Park et al., 2013). Based on the sensitivity analysis result presented in our earlier dual-TD method characterization paper (Saha et al., 2015) and a detailed two-dimensional laminar flow modeling effort in Park et al. (2013), this plug-flow assumption has relatively smaller influences on evaporation in a TD relative to values of (C*, ΔHvap, and γe).

Minor comments: R2.8. Page 5 Line 2: Please expand on what “instrumental inter-calibration factors” entail

AR2.8.To get directly comparable SMPS concentration data from 3 SMPSs running in parallel with our dual TD system, we ran them periodically in parallel to determine an inter-calibration factor. The inter-calibration factor is determined from a scatter plot of SMPS inter-comparison data collected by running 3 SMPSs in parallel on the bypass line. Among the 3 SMPS, we chose one as a reference upon which all corrections were based. The reference SMPS system was selected based on which yielded counts most consistent with the median of those measured during a group SMPS inter-comparison test of 8 systems from different laboratories during the SOAS field campaign. We added this discussion briefly in the paper: “To get directly comparable SMPS concentration data from 3 SMPSs running in parallel with our dual TD system, we ran them periodically in parallel on the bypass line to determine inter-calibration factors. Further details on SMPS inter-comparison are discussed in Saha et al (2015).”

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R2.9. 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?

AR2.9. We added this discussion to the paper: “Variability is based on measured MFR data. Raw data at each (T, Rt) condition were averaged over 20-30 minutes. At given TD operating conditions (T, Rt), we defined ± 1 standard deviation of MFR data (20-30 minute resolution) from the whole campaign as an indicator of observed variability.”

R2.10. Page 8 Line 31: Please provide references for previous field studies.

AR2.10. Page 9; Line 12-13: References to field studies (“Häkkinen et al., 2012; Huffman et al., 2009; Lee et al., 2010; Paciga et al., 2015; Xu et al., 2016”) are added.

R2.11. Page 10 Line 8-10: Please add discussion on why observed slope may be different from the empirical relation determined by Epstein et al.

AR2.11. The Epstein et al. correlation was determined from range of compounds with known ΔHvap. However, it has been found that for this and other complex OA systems, a correlation other than the Epstein correlation better explains observations. For example, Ranjan et al.(2012) reported dHvap = 85-11logC* for gas–particle partitioning of POA emissions from diesel engine; May et al.(2013) reported dHvap = 85-4logC* for biomass burning POA emission. A key point is that like results from Ranjan et al. (2012), May et al. (2013) and many others, our estimated dHvap correlation for ambient OA is an empirical estimate, which explain our observations better than the Epstein correlation. We added this discussion in the paper. Page10, Line 28-33: “The Epstein et al. correlation was determined from range of compounds with known ΔHvap. Several recent studies of complex OA systems (May et al., 2013; Ranjan et al., 2012) have found that a correlation other than that from Epstein et al. better explains observations. For example, Ranjan et al.(2012) reported ΔHvap = 85-11logC* for gas–particle partitioning of POA emissions from a diesel engine; May et al.(2013) reported ΔHvap = 85-4logC* for biomass burning POA emissions. Similar to these and other studies, our ∆Hvap correlation for ambient OA is an empirical estimate which best explains our observations."

R2.12. Page 2 line 6: ": : :SOA is formed in the atmosphere via condensation of low volatility products: : :" This statement is not inclusive enough. Please revise.

AR2.12. We revised the text. Page 2; Line 5-6: "Secondary OA (SOA) is formed in the atmosphere via oxidation reactions of gas-phase organic species; it may also be formed by reactions in the particle (condensed) phase."

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Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/acp-2016-575/acp-2016-575-AC2-supplement.pdf

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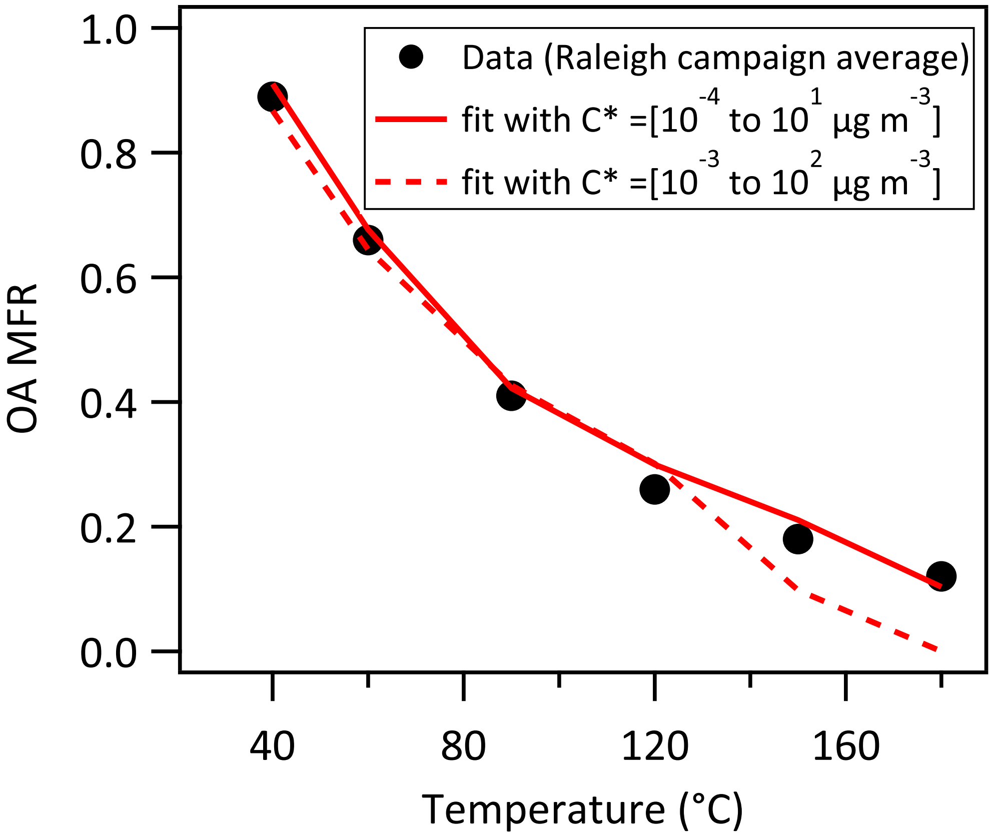

Fig. 1. (Fig.AR.3) Sensitivity of C* bin range in fitting TD data using an evaporation kinetic model. The best fitted curves with (ΔHvap = 100 kj mol-1 and γe = 0.5) are shown.