

Review of acp-2016-774

Hong et al. "Estimates of organic aerosol volatility in a boreal forest using two independent methods"

Overview:

The authors present a nice manuscript utilizing two methods to interpret field measurement data using a kinetic evaporation model and a statistical model. I recommend that their submission be accepted as a paper in *Atmospheric Chemistry and Physics*, after they address the following comments.

General Comments:

1) Sections 3.1 and 3.2 appear to be very light on the "discussion" aspect of these "Results and Discussions". What do these results (and their associated figures) provide, beyond a bunch of entries in a table (i.e., what are the implications)?

2) Regarding the authors' identification of the two-factor solution as SVOA and LVOA and the fact that the authors report that the particle concentration was $0.1 \mu\text{g m}^{-3}$, it seems to me that it is more likely that the reported two-factor solution from PMF is LVOA and ELVOA. Relating to Specific Comment 15 below, I have serious doubts that a compound having $C^* = 10 \mu\text{g m}^{-3}$ can be reliably constrained using the kinetic evaporation model.

3) What are the volatility distributions that were derived? I understand that this is not a generalizable outcome, but perhaps a table summarizing the outcomes from the authors work (including AS, AN, and EC) would clarify this for the reader. This is typically done in the literature, including some of the authors' cited references (e.g., Cappa and Jimenez, 2010; Grieshop et al., 2009; Kuwayama et al., 2015; Lee et al., 2010; May et al., 2013a, 2013b, 2013c; Paciga et al., 2016). Are these the values that the authors are reporting in lines 29-34 in the abstract (this is only obvious in the text of the manuscript in the description of Figure 7)?

Specific Comments:

1) Line 95: As written, it almost appears as if the authors are referring to the BBOA factor as a secondary source. Perhaps, a better descriptor for HOA would be "from fossil fuel combustion"?

2) Lines 108-110: In my opinion, the authors should explicitly state that this sensitivity is tested with the kinetic model.

3) Lines 131-134: What are the DMA flow rates, and are the authors concerned with how monodisperse the aerosol population may be given the resulting resolution due to these flows?

4) Line 141: What is the length of the thermodenuder (TD)?

5) Line 141: What kinds of particle losses might be expected in the TD, how significant might they be, and how might these losses, if neglected/uncorrected for, bias the study results?

6) Equation 1: Is the denominator truly at room temperature ($25 \text{ }^\circ\text{C}$), or is this really ambient temperature which could fluctuate drastically?

7) Lines 152-154: I recommend that the authors clarify that if $VFR = 1$ at a given temperature, this implies that they have not evaporated, rather than stating they are non-volatile. Similarly, for $VFR = 0$, this implies that the particles have fully evaporated at that temperature.

8) Lines 226-227 and 229: The authors have already stated that elemental carbon is abbreviated as "EC" in line 171, so repeating this twice more in these two lines is not necessary.

9) Lines 235-237: I am unfamiliar with the Matlab canned routine *fmincon*, but I am curious if this guarantees a global minimum or if the solver could find local minima instead? For example, due to the uniqueness issue posed by Cappa and Jimenez (2010), May et al. (2013a) utilized a brute-force forward approach to investigate the volatility distribution along with enthalpy of vaporization (ΔH_{vap}) and mass accommodation coefficient (α) to determine the global minimum within their solution space using the Riipinen et al. (2010), while Paciga et al. (2016) employ the error minimization approach of Karnezi et al. (2014) to improve the reliability of their solution, also using the Riipinen et al. (2010) model. In my opinion, the authors should comment on their choice of optimization approach and how this could potentially bias their outcomes, if *fmincon* does not guarantee a global minimum in its solution.

10) Lines 244-247: While I understand why the authors are selecting 100 nm as the size to focus on for their analysis, I am curious as to what the overall size distribution of the particles is. Will “arbitrarily” (probably not the right word) selecting a single size bias the outcomes if, for example, the geometric mean diameter of all particles in the sample is 300 nm (since evaporation rates are size dependent)?

11) Lines 266-299: The authors claim that the “volatilities of common inorganic species are relatively well known” in the Introduction (line 69). Therefore, I am wondering what the purpose of going through the process of fitting the saturation concentration (C^*) and ΔH_{vap} is in this work. Is this simply to test the kinetic evaporation model?

12) Lines 319-320: I am curious as to why the authors consider Combinations 4-8 to be “ C^* -independent” even though H_{vap} is different for each C^* for these cases.

13) Lines 335-339: There are a number of studies that characterize the volatility of organic aerosol from individual emission sources, including one by one of the co-authors (May et al., 2013a), so I would argue that this statement is not strictly true as written.

14) Lines 344-346: The authors appear to be implying that $C_3H_7^+$ is negligible at m/z 43. Is this true?

15) Table 1: where does the value of “particle total mass” come from? And is this really the total mass concentration ($0.1 \mu\text{g m}^{-3}$ seems very low)? If so, do the authors have any hope of actually constraining the SVOA component? For $C^* = 10 \mu\text{g m}^{-3}$, the predicted mass fraction in the particle phase is 1%, following Donahue et al. (2006). If truly only 1% of the SVOA mass is in the particle phase, how much certainty do the authors have in their analysis?

16) Figures 2-3: If the initial temperature set point in the TD is 25 °C (line 144), why are the initial data points 20 °C, 50 °C, and ~40 °C in these figures? This inconsistency is confusing.

17) Figures 2-3: This appears to be a little messy with marker-and-line combinations representing both experimental data and model outputs. I recommend, for example, changing the data to markers and the predictions to lines.

18) Figure 5: First, I would recommend that the authors clarify that the y-axis represents interpretation using the kinetic model and that the x-axis represents interpretation using the statistical model (PMF). Second, something that I find curious is that the slopes of both columns are identical, but the offsets are different. Does this indicate a systematic bias or is this an artifact of there only being two factors in the comparison?

19) Figure 6: The Epstein et al. (2010) $C^* - \Delta H_{\text{vap}}$ has been trashed relentlessly in studies probing ΔH_{vap} because it is based on pure components, and the relationship clearly doesn't work for mixtures. I don't think that we as a community need yet another figure demonstrating this (but having some discussion of this in the text is fine).

20) Figure 7: First, both pie charts are derived from models, so I suggest that the labels are changed to say something like "Kinetic model results" for the left and "Statistical model results (PMF)" for the right.

Second, in the caption, it would be useful for the reader if the authors state to which value of ΔH_{vap} the kinetic model results correspond.

Third, if this is indeed really LVOA and ELVOA that is being identified in PMF (see General Comment #3 above), then the kinetic model outcome is biased by the authors' assumed definitions of the PMF model results. This potential bias should be resolved either explicitly or implicitly as the authors respond to General Comment #3 and Specific Comment #15.

21) Figures 8-9: What are the implications here? Is, for example, an effective $\Delta H_{\text{vap}} = 80 \text{ kJ mol}^{-1}$ the optimum value that is representative of ambient organic aerosol at the sampling site? I'm not really sure how to interpret these figures without some additional context, either in the captions or in the body of the manuscript itself.

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