

## Answers to Referee #1

The authors appreciate the time the reviewer has spent on our manuscript, helping us to produce a higher quality, understandable publication. All the requested corrections and suggestions are addressed and introduced to the revised version of the manuscript.

### 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)?

Reply: Even though there have been several earlier studies (Huffman et al., 2009) reporting the evaporation of ammonium sulfate, the specific  $C^*$  and  $\Delta H_{\text{vap}}$  values are scarce or not available at all. We also wanted to compare results obtained with our technique to previous studies. In Sect. 3.2, the main scope was to evaluate the performance of the model. It is reported that the model is sensitive towards  $\Delta H_{\text{vap}}$ , hence, sensitivity analysis towards this parameter was included in this section. More discussion on the choice of the specific  $\Delta H_{\text{vap}}$  was given in Sect. 3.4.1. We will highlight these aspects in the revised manuscript.

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.

Reply: The information the manuscript gave is perhaps misleading: the average total particle concentration from the dataset used was in fact  $2.90 \mu\text{g m}^{-3}$ , and the organic aerosol mass is  $1.96 \mu\text{g m}^{-3}$ . The value the manuscript reported was the mass concentration of the selected monodisperse aerosol particles (100 nm in diameter). We will clarify this in the revised manuscript.

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)?

Reply: Yes, the values we gave in Fig. 7 in the manuscript were the volatility distributions obtained. The values are the median values of the dataset taken during the whole campaign.

### **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”?

Reply: We agree that the statement here was not written in a clear way. The sentence will be changed as: ‘Typical organic groups determined using the PMF analysis include e.g. hydrocarbon-like OA (HOA), biomass burning OA (BBOA) and cooking OA (COA) or oxygenated OA (OOA).’

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

Reply: We will change this part into: ‘The sensitivity of the kinetic model was tested towards different parameters of organic compounds, including density, molar mass, saturation vapor concentration, and diffusion coefficient.’

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?

Reply: The aerosol flow rate of DMAs in our system was 1 l/min, while the sheath flow of the DMAs was kept at 10 l/min. Such flow configuration is quite commonly utilized in the TDMA community. Applying the Stolzenburg kernels with the selected dry sizes and

these flow rates into the DMA and assuming that full width of the peak width at half maximum (FWHM) describes well the width of the transfer function, the following width was obtained:  $100 \text{ nm} \pm 2.9 \text{ nm}$ . Therefore the particles were monodisperse within  $\pm 3 \%$ . However, this spread was already taken into account in the inversion toolkit by Gysel et al. (2009) in the data analysis.

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

Reply: The total length of the thermodenuder (TD) is 50 cm.

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?

Reply: The major loss processes in the heating tube are caused by thermophoresis and Brownian diffusion. According to Ehn et al. (2007), who used a similar TD as ours, the losses for aerosol particles above 15 nm in diameter were observed to be less than 20% when heated to 280 °C. Due to these losses, we might indeed underestimate the mass concentration of the monodisperse aerosol particles after heating. However, our study was focusing on the change in particle size, which should not be affected very much by the losses. We will add a brief discussion of the losses to the revised manuscript.

6) Equation 1: Is the denominator truly at room temperature (25 °C), or is this really ambient temperature, which could fluctuate drastically?

Reply: Yes, the size of the original particles was selected by the first DMA at room temperature. The room temperature, where the first DMA located was set and maintained at  $25 \text{ °C} \pm 2 \text{ °C}$ .

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.

Reply: We agree. The statement will be corrected as: ‘With  $VFR = 1$  at a given temperature, we consider particles have not evaporated, while with  $VFR = 0$  particles are considered to fully evaporate upon

heating 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.

**Reply: The abbreviation ‘EC’ will be used here instead.**

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 ( $\Delta H_{\text{vap}}$ ) and mass accommodation coefficient ( $\alpha$ ) 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.

**Reply: The *fmincon* function indeed does not guarantee a global minimum. However, this was tested for by changing the initial guesses the function was run with and it was found that the solution we got was dependent on the initial guess we used. To guarantee the uniqueness of the fit, we used only three volatility bins in the fits. Furthermore, the optimization method was constrained with the mass fraction of each organic group and the total measured mass fraction of organics from AMS data. With those constraints, *fmincon* finds the best solution the computer can give and will be quite close to the global minimum.**

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)?

Reply: The average geometric mean dry diameter of the overall size distribution of boreal forest aerosols was 60-200 nm if two-mode fit was applied to the measured number size distribution data (Asmi et al., 2011). We therefore expect that the 100 nm particles were relatively representative of the typical size distributions at the studied site. According to Hong et al. (2014), we observed a size-dependent evaporation between the nucleation mode and accumulation mode particles using similar VTDMA setup, however, size-dependent chemical composition information of aerosol mass is also needed to give conclusive statement regarding to their volatility distribution.

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  $\Delta H_{\text{vap}}$  is in this work. Is this simply to test the kinetic evaporation model?

Reply: As specified in General comment 1, the  $C^*$  and  $\Delta H_{\text{vap}}$  values were inferred to evaluate our approach. These parameters were also used for the model input to simulate the evaporation of ambient aerosols.

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

Reply: The reviewer is correct. We will revise the wording in the manuscript accordingly.

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.

Reply: The statement here was indeed not clear and we will remove it from the revised manuscript.

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

Reply: Ng et al. (2011) stated that "The m/z 43 fragment is mainly  $C_2H_3O^+$  for the OOA component, and  $C_3H_7^+$  for the HOA component." and according to Crippa et al. (2014), the HOA contribution in Hyytiälä is low (6-7%) compared to the oxidized species with significant m/z 43 contribution, SV-OOA (34-37%). Hence, we believe  $C_2H_3O^+$  is the dominant ion at m/z 43 over  $C_3H_7^+$ . Moreover, as both of the ions are indicative of low oxidation level species (Ng et al., 2011), the exact molecular composition of m/z 43 "tracer" signal does not matter either.

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?

Reply: See the answer to General comments #2. The value of  $0.1 \mu\text{g}$  is the mass concentration of the monodisperse aerosol particles (100 nm in diameter), which was calculated from DMPS data. This was done by integrating the particle number size concentration within 90-110 nm multiplying a constant particle density of  $1.2 \text{ kg/m}^3$ , and represented this value as the monodisperse aerosol mass concentration.

16) Figures 2-3: If the initial temperature set point in the TD is  $25^\circ\text{C}$  (line 144), why are the initial data points  $20^\circ\text{C}$ ,  $50^\circ\text{C}$ , and  $\sim 40^\circ\text{C}$  in these figures? This inconsistency is confusing.

Reply: For ambient measurements, the aerosols were brought to a room at  $25^\circ\text{C}$ . For AN and AS, the evaporation measurements were performed in laboratory conditions, where lower temperatures can be achieved, since AN might already evaporate below  $25^\circ\text{C}$ . We will modify the figure and its caption in the revised manuscript to avoid the confusion.

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.

Reply: We will change the figure as suggested in the revised manuscript.

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?

Reply: We will clarify the axes more clearly in the manuscript. From line 827, we will add the following statement: ‘Here, the Y-axis represents the VTDMA results interpretation using the kinetic model and the X-axis represents the AMS results interpretation using the statistical model (PMF)’. The different intercepts are more likely related to the fact that there were only two volatility classes that the particles were assumed to consist of.

19) Figure 6: The Epstein et al. (2010)  $C^* - \Delta H_{\text{vap}}$  has been trashed relentlessly in studies probing  $\Delta H_{\text{vap}}$  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).

Reply: We agree and will move Fig.6 to the supplement.

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.

Reply: The legend of Fig. 7 in the manuscript will be changed as: ‘Kinetic model results’ on the left and ‘Statistical model results (PMF)’ on the right.

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

Reply: We will add ' $\Delta H_{\text{vap}} = 80 \text{ kJ/mol}$  was used in the kinetic evaporation model' in the figure caption.

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.

Reply: This issue was answered both in 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.

Reply: We will modify line 471 as 'These two case studies suggest that an effective  $\Delta H_{\text{VAP}}$  value of 60-80 kJ/mol represent the boreal forest organic aerosols best.'

#### Reference:

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