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 ΔHvap 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 ΔHvap, hence, sensitivity analysis towards this parameter was included in this section. More discussion on the choice of the specific ΔHvap 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 μg 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 μg 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 μg m^{-3}, and the organic aerosol mass is 1.96 μg 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 nm ±2.9 nm. Therefore the particles were monodisperse within ±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 °C ±2 °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 (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.

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 constrains, 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 ΔH_{vap} is in this work. Is this simply to test the kinetic evaporation model?

Reply: As specified in General comment 1, the C* and ΔH_{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_{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 μg m^{-3} seems very low)? If so, do the authors have any hope of actually constraining the SVOA component? For C* = 10 μg 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 μg 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 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 °C (line 144), why are the initial data points 20 °C, 50 °C, and ~40 °C in these figures? This inconsistency is confusing.

Reply: For ambient measurements, the aerosols were brought to a room at 25 ^{O}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 ^{O}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*- ΔH_{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).

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 ΔH_{vap} the kinetic model results correspond.

Reply: We will add 'ΔH_{vap} = 80 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 ΔH_{vap} = 80 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 $\Delta HVAP$ value of 60-80 kJ/mol represent the boreal forest organic aerosols best.'

Reference:

Asmi, A., Wiedensohler, A., Laj, P., Fjaeraa, A.-M., Sellegri, K., Birmili, W., Weingartner, E., Baltensperger, U., Zdimal, V., Zikova, N., Putaud, J.-P., Marinoni, A., Tunved, P., Hansson, H.-C., Fiebig, M., Kivekäs, N., Lihavainen, H., Asmi, E., Ulevicius, V., Aalto, P. P., Swietlicki, E., Kristensson, A., Mihalopoulos, N., Kalivitis, N., Kalapov, I., Kiss, G., de Leeuw, G., Henzing, B., Harrison, R. M., Beddows, D., O'Dowd, C., Jennings, S. G., Flentje, H., Weinhold, K., Meinhardt, F., Ries, L., and Kulmala, M.: Number size distributions and seasonality of submicron particles in Europe 2008–2009, Atmos. Chem. Phys., 11, 5505-5538, doi:10.5194/acp-11-5505-2011, 2011.

Crippa, M., Canonaco, F., Lanz, V. A., Äijälä, M., Allan, J. D., Carbone, S., Capes, G., Ceburnis, D., Dall'Osto, M., Day, D. A., DeCarlo, P. F., Ehn, M., Eriksson, A., Freney, E., Hildebrandt Ruiz, L., Hillamo, R., Jimenez, J. L., Junninen, H., Kiendler-Scharr, A., Kortelainen, A.-M., Kulmala, M., Laaksonen, A., Mensah, A. A., Mohr, C., Nemitz, E., O'Dowd, C., Ovadnevaite, J., Pandis, S. N., Petäjä, T., Poulain, L., Saarikoski, S., Sellegri, K., Swietlicki, E., Tiitta, P., Worsnop, D. R., Baltensperger, U., and Prévôt, A. S. H.: Organic aerosol components derived from 25 AMS data sets across Europe using a consistent ME-2 based source apportionment approach, Atmos. Chem. Phys., 14, 6159-6176, doi:10.5194/acp-14-6159-2014, 2014.

Ehn, M., Petäjä, T., Birmili, W., Junninen, H., Aalto, P., and Kulmala, M.: Non-volatile residuals of newly formed atmospheric particles in the boreal forest, Atmos. Chem. Phys., 7, 677–684, doi:10.5194/acp-7-677-2007, 2007.

Gysel, M., McFiggans, G. B., Coe, H.: Inversion of tandem differential mobility analyser (TDMA) measurements, J. Aerosol. Sci., 40, 134-151, 2009.

Hong, J., Häkkinen, S. A. K., Paramonov, M., Äijälä, M., Hakala, J., Nieminen, T., Mikkilä, J., Prisle, N. L., Kulmala, M., Riipinen, I., Bilde, M., Kerminen, V.-M., and Petäjä, T.: Hygroscopicity, CCN and volatility properties of submicron atmospheric aerosol in a boreal forest environment during the summer of 2010, Atmos. Chem. Phys., 14, 4733-4748, doi:10.5194/acp-14-4733-2014, 2014.

Huffman, J. A., Docherty, K. S., Aiken, A. C., Cubison, M. J., Ulbrich, I. M., DeCarlo, P. F., Sueper, D., Jayne, J. T., Worsnop, D. R., Ziemann, P. J., and Jimenez, J. L.: Chemically-resolved aerosol volatility measurements from two megacity field studies, Atmos. Chem. Phys., 9, 7161-7182, 2009

Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Chhabra, P. S., Seinfeld, J. H., and Worsnop, D. R.: Changes in organic aerosol composition with aging inferred from aerosol mass spectra, Atmos. Chem. Phys., 11, 6465-6474, doi:10.5194/acp-11-6465-2011, 2011.

Answers to Referee #2

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

Detailed Comments

1) It should be made clear in the abstract, body, and conclusion that this study estimates the effective volatility distribution of SOA after it has formed and undergone aging (particle-phase reactions) and not the volatility distribution of the condensing organic gases that produced the SOA. While the authors do not imply the latter, some readers may inadvertently misinterpret the results and incorrectly apply them for modeling purposes if the caveat is not explicitly stated.

Reply: This is correct, and this issue will be clarified through the whole manuscript.

This then brings up the question of the usefulness of the results. If the estimated volatility distribution of SOA does not represent the volatility distribution of the condensing organics then where and how would one use this information? What is it that we have learned from this exercise that is of value? To drive this point further, it is possible that the semi-volatile fraction of the condensing organics may be more than 40%, such that some then undergoes particle-phase reactions to form low- and extremely low-volatile compounds. Upon heating the SOA in the VTDMA, these newly formed compounds (e.g., dimers, oligomers) may partially decompose back to the original species or may even fragment (especially at higher temperatures) to something completely different before evaporating. However, these processes are not examined in the present study. The evaporation model simply assumes that the three lumped species (with different volatilities) do not chemically interact. Thus, it is difficult to draw any useful or meaningful conclusions out of the present analysis.

Reply: Indeed, the volatility distribution of SOA studied here did not represent the volatility distribution of the condensing organic compounds in the gaseous phase. However, it provides “one side of the story” in the form of insights into the volatility (and hence e.g. the evaporation potential) of the compounds that are present in the particle phase (of course with the caveat of the effects of the elevated temperature). This will be useful input for closure studies combining this information with condensation studies aiming to derive how the aerosol size distributions are affected by given gas-phase species. In fact, we are working on such a closure study for future. Furthermore, the results are useful to compare the volatility of the boreal forest aerosol to similar results from other sites (e.g. Cappa and Jimenez 2010; Cappa and Wilson, 2011; May et al., 2013a). Finally, it also provides insight into the usefulness and applicability (and limitations) of TD setups for inferring information about aerosol volatility. We will add discussion on these issues to the revised manuscript.

2) Furthermore, since the VTDMA experiments were carried out under dry conditions, the boreal forest SOA is expected to be viscous (Virtanen et al. 2010 Nature), especially at 25 C, such that there would be significant particle-phase diffusion limitation for the evaporating species. Perhaps the evidence for this limitation is present in Figure 3, which shows that the model tends to be way more evaporative than observed at the lower temperatures–in fact, the first data point indicates no evaporation (MFR = 1). This can potentially skew the effective volatility distribution estimated by the model quite a bit.

Reply: The referee is right that the kinetics of evaporation of non-liquid particles may be somewhat affected by the diffusion coefficient of a viscous solution (Tong et al., 2011). However, it should be noted that the ambient data were mixtures of organics, water and inorganics, for which it is difficult to quantify the potential diffusivity impacts. We will add brief discussion on this issue to the revised manuscript.

3) It is stated that the residence time inside the thermodenuder was around 2.5 s. Does this mean that the evaporation model was run for just 2.5 s to simulate each data point? Also, does the model assume that the aerosol instantly reaches the targeted temperature the moment it enters the thermodenuder? Can the authors estimate the time it takes the aerosol to reach the target temperature? The model should account for it if it's comparable to the residence time.

Reply: Yes, the evaporation model was run for 2.5s to simulate each data point, since measured evaporation time is 2.5 s in this case. The temperature profile was measured with a temperature sensor (Rotronic HC2-CO4) inside the heating tube at flow rate of 2 L/min with setting temperature at 100 °C (see Fig.1). As shown in Fig. 1, the temperature did not reached the targeted temperature at the moment the aerosols entered the thermodenuder but increased slowly at the entrance of the heating tube and reached the targeted temperature ±5 °C at around 20 cm from the entrance. The temperature stayed at this value before falling near the exit, 45 cm from the entrance of the heating tube. This distance with temperature within ±5 °C of the targeted one was used for calculation the residence time of the heating section. The obtained residence time was then applied in the model analysis. It was assumed that the particles were instantaneously thermally equilibrated with the surrounding gas phase. We think this is a reasonable assumption with respect to the time scales relevant for the evaporation, as the system was in atmospheric pressure

4) Please show error bars on the VTDMA measurements displayed in Figures 2 and 3.

Reply: We will add error bars on the VTDMA measurements data to the revised manuscript.

5) The authors state that the agreement between the VTDMA results and the PMF- derived results as reasonable when it is quite the opposite. The linear correlation coefficient (r) of 0.4 indicates there is not a good correlation between the VTDMA- and PMF-based results (Figure 5c,d). The coefficient of determination (r^2) is only 0.16, which means only 16% of the variation can be explained by the linear relationship between the two methods. It is clear that the comparison of VTDMA and PMF results was not quite successful. I suggest that the authors revise the text at all the appropriate places and describe the results of correlation as they are.

Reply: Thank you for pointing this out, we agree. Consequently, we will make revisions in line 44-47 of the revised manuscript:

‘In general, the best agreement between the VTDMA results and the PMF-derived mass fractions of organics was obtained when $\Delta HVAP = 80$ kJ/mol was set for all organic groups in the model, with a linear correlation coefficient of around 0.4. However, this still indicates that only about 16% (R^2) of the variation can be explained by the linear regression between the results from these two methods.’

Discussion in line 388-400 will be revised as: ‘Using the enthalpy value of 60 kJ/mol for all organic groups, the modeled mass fraction of SVOA was higher than the SVOA from the PMF analysis. The opposite is true for LVOA, while using $\Delta HVAP$ values of 100 kJ/mol for all organic groups, the comparison results differed significantly from the 1:1 line. With enthalpy value of 80 kJ/mol for organics, the VTDMA-based OA composition was approximately equal to the ones from the PMF results, however, with a linear correlation coefficient of only 0.4. This relatively low correlation coefficient suggests that additional information on each of the method is needed to analyze the potential links between the AMS and volatility data. Moreover, Paciga et al. (2016) studied the volatility distribution of the PMF-derived organics and estimated that almost half of the SVOC, which was determined from PMF, is semi-volatile, while 42% is low-volatile and 6% is extremely low-volatile. This suggests that the two PMF-derived organic groups, commonly labeled for their oxidation levels, might not be directly linked to their actual volatilities.

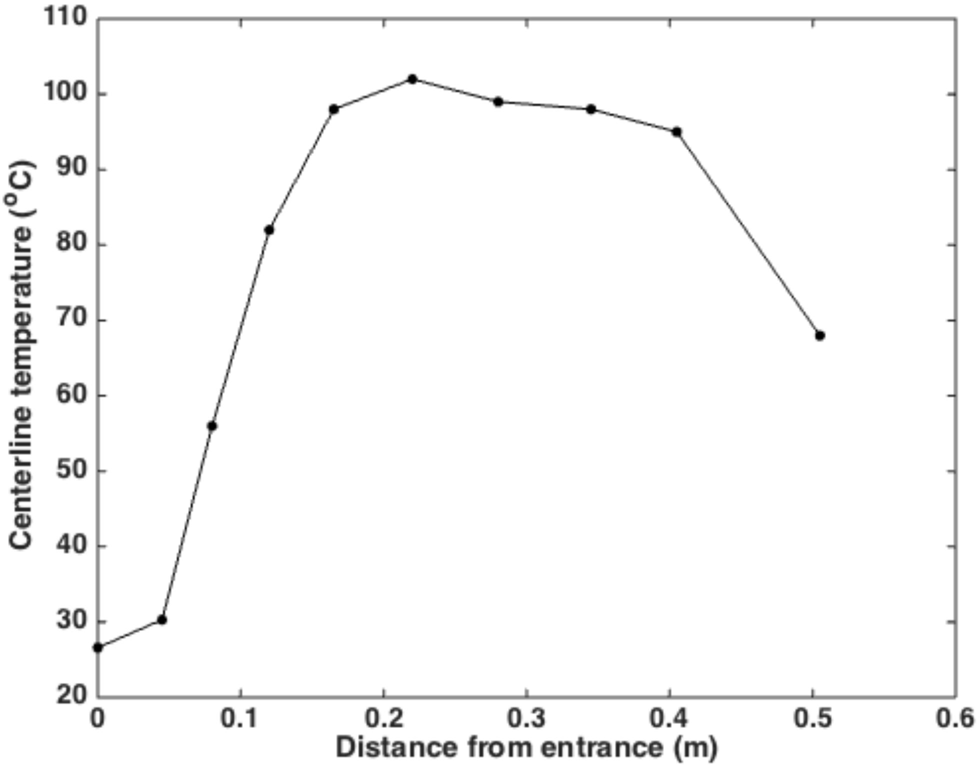

Fig.1. Temperature profile along the axis of the heating section at a flow rate of 2 L/min.

Reference:

Cappa, C. D., and Jimenez, J. L.: Quantitative estimate of the volatility of ambient organic aerosol, Atmos. Chem. Phys., 10, 5409-5424, doi:10.5194/acp-10-5409-2010, 2010.

Cappa, C. D., and Wilson, K. R.: Evolution of organic aerosol mass spectra upon heating: implications for OA phase and partitioning behavior, Atmos. Chem. Phys., 11, 1895-1911, doi:10.5194/acp-11-1895-2011, 2011.

May, A. A., Levin, E. J. T., Hennigan, C. J., Riipinen, I., Lee, T., Collett, J. L., Jimenez, J. L., Kreidenweis, S. M. and Robinson, A. L.: Gas-particle partitioning of primary organic aerosol emissions: 3. Biomass burning, J. Geophys. Res. Atmos., 118(19), 11,327-11,338, doi:10.1002/jgrd.50828, 2013a.

Paciga, A., Karnezi, E., Kostenidou, E., Hildebrandt, L., Psichoudaki, M., Engelhart, G. J., Lee, B.-H., Crippa, M., Prevot, A. S. H., Baltensperger, U., and Pandis, S. N.: Volatility of organic aerosol and its components in the megacity of Paris, Atmos, Chem. Phys., 16, 2013-2023, doi:10.5194/acp-16-2013-2016, 2016.

Tong, H.-J., Reid, J. P., Bones, D. L., Luo, B. P., and Krieger, U. K.: Measurements of the timescales for the mass transfer of water in glassy aerosol at low relative humidity and ambient temperature, Atmos. Chem. Phys., 11, 4739–4754, doi:10.5194/acp-11-4739- 2011, 2011.

List of changes:

Page 1, line 25-28: Text was changed to 'The volatility distribution of secondary organic aerosols formed and undergone aging, i.e. the particle mass fractions of semi-volatile, low-volatility and extremely low-volatility organic compounds in the particle phase was characterized in a boreal forest environment of Hyytiälä, Southern Finland.'

Page 1-2, line 47-51: Text was changed to: 'In general, the best agreement between the VTDMA results and the PMF-derived mass fractions of organics was obtained when ΔH_{VAP} = 80 kJ/mol was set for all organic groups in the model, with a linear correlation coefficient of around 0.4. However, this still indicates that only about 16% (R^2) of the variation can be explained by the linear regression between the results from these two methods.'

Page 2-3, line 91-99: Text was added as: 'Here, it needs to be noted that the volatility distribution of ambient aerosols does not represent the volatility distribution of the condensing organic compounds in the gaseous phase. However, it provides insights into the evaporation potentials of the compounds that are present in the particle phase. Furthermore, it will be useful for closure studies combining this information with condensation studies aiming to derive how the aerosol size distributions are affected by given gaseous species. Finally, measuring the evaporation of aerosols is also essential for testing the applicability and limitations of TD setups for inferring the volatility of aerosols.'

Page 3, line 105-108: Text was changed to: '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).'

Page 3, line 120-125: Text was changed to: '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).'

Page 4, line 157-159: Text was added as: 'The spread of the number size distribution of the aerosol was taken into account in the data inversion using the piecewise linear inversion approach (Gysel et al., 2009).'

Page 4, line 163-165: Text was added as: 'It was assumed that the particles were instantaneously thermally equilibrated with the surrounding gas phase, as the system was under atmospheric pressure.'

Page 4, line 167-175: Text was added as: 'The major particle losses during the heating process are from thermophoresis and Brownian diffusion (Wehner et al., 2002; Häkkinen et al., 2012). According to Ehn et al. (2007), who used a similar TD, 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, the VTDMA-measured data underestimates the mass concentration of the monodisperse aerosol particles after heating. However, this study was focusing on the change in particle size, which should not be affected very much by the losses. Hence, the effect of the particle losses on the study results can be considered negligible.'

Page 4, line 182-184: Text was changed to: 'With VFR = 1 at a given temperature, particles are considered to not evaporate, while with VFR = 0 particles fully evaporate upon heating at that temperature.'

Page 6, line 260, line 262, 'Elemental carbon' was changed to 'EC'

Page 6, line 270-274, Text was changed to: 'This optimization method was constrained by setting the sum of mass fraction of organics from the model be equal to the mass fraction of OA measured by HR-AMS, and the mass fraction of each individual organic group to be larger than zero but lower than the total measured mass fraction of OA.'

Page 7, line 293-295, Text was changed to: 'This vaporization enthalpy (ΔH_{VAP}) of Epstein et al. (2010) (Eq. 3) was also tested in the model calculations.'

Page 7, line 327-328, 'C^* dependent enthalpy' was changed to 'the ΔH_{VAP} of Epstein et al. (2010) '

Page 7, line 330-334: Text was changed to: 'In short, even though there have been afore-mentioned earlier studies reporting the C^* and ΔH_{VAP} of AN and AS, we selected the ones shown by the red curves in Fig. 3 from our VTDMA technique for the model input to simulate the evaporation of ambient aerosols.'

Page 8, line 347-349: Text was added as: 'The different simulated evaporation behavior indicates that the model is sensitive towards ΔH_{VAP} values. '

Page 8, line 350-351: 'C^* dependent enthalpy' was changed to 'the ΔH_{VAP} of Epstein et al. (2010) '

Page 8, line 359-361: Text was changed to: 'By using the other vaporization enthalpy values (e.g. Combinations 1 to 8 in Table 2), better agreement between the fitted and observed thermograms (Fig. 3) was obtained. '

Page 8, line 365-368: Text was changed to: 'According to the performance of the model to TD data, the model was observed to be sensitive towards ΔH_{VAP} values. Low ΔH_{VAP} values (i.e., ΔH_{VAP} = 60-80 kJ/mol) are suggested to be used in the model in order to reproduce the measured thermograms.'

Page 8, line 378-380: Text was changed to: 'Since this study focuses on the volatility distribution of organics using a complex kinetic model, we chose to limit the PMF OA components to the main ones clearly connected with oxidation state.'

Page 9-10, line 421-434: Text was changed to: 'Using the enthalpy value of 60 kJ/mol for all organic groups, the modeled mass fraction of SVOA was higher than the SVOA from the PMF analysis. The opposite was true for LVOA, while using ΔH_{VAP} values of 100 kJ/mol for all organic groups, the comparison results differed significantly from the 1:1 line. With the enthalpy value of 80 kJ/mol for organics, the VTDMA-based OA composition was approximately equal to the ones from the PMF results, however, with a linear correlation coefficient of only 0.4. This relatively low correlation coefficient suggests that additional information on each of the method is needed for analyzing the potential links between the AMS and volatility data. Moreover, Paciga et al. (2016) studied the volatility distribution of the PMF-derived organics and estimated that almost half of the SVOC, which was determined from PMF, is semi-volatile, while 42% is low-volatile and 6% is extremely low-volatile. This suggests that the two PMF-derived organic groups, commonly labeled for their oxidation levels, might not be directly linked to their actual volatilities.'

Page 10, line 455: 'C^* dependent enthalpy' was changed to 'the ΔH_{VAP} of Epstein et al. (2010)'

Page 10, line 470-476: Text was added as: 'Tong et al. (2011) concluded that the diffusion coefficient of a viscous solution might affect the kinetics of evaporation of non-liquid particles, as aerosol particles in boreal forest environment are expected to be viscous according to Virtanen et al. (2010). Hence, also non-unity mass accommodation coefficients of a mixture and the particle-phase diffusion limitation on evaporation can add uncertainties to the interpretation of the TD data.'

Page 11, line 509-512: Text was changed to: 'Conclusively, these two case studies suggest that an effective ΔH_{VAP} value of 60-80 kJ/mol represent the boreal forest organic aerosols best and this effective ΔH_{VAP} value should be assumed in the model when comparing with the PMF results.'

Page 11, line 516-518: Text was changed to: 'The volatility of ambient aerosol particles formed and undergone aging was studied with a Volatility Tandem Differential Mobility Analyzer (VTDMA) in a boreal forest environment in Hyytiälä from April to May of 2014.'

Page 11, line 528-533: Text was changed to: 'The best correlation between the VTDMA results and the PMF-derived mass fractions of organics was obtained when ΔH_{VAP} = 80 kJ/mol was assumed for all organic groups in the model, with a linear correlation coefficient of around 0.4. This relatively low correlation coefficient indicates that we need to acquire additional information on each of the method to address the potential relation between the AMS and volatility data.'

Page 19: line 825-827: Text was added as: 'b: The particle mass concentration in particle size bin of 90-110 nm from DMPS is used to represent the particle mass concentration of the monodisperse aerosols (i.e. D_P = 100 nm).'

Page 22: Axis was changed accordingly. Errorbar was added into the measurement dot.

Page 23: Measurement curve was changed to dot, while model result curves were changed to lines. Figure caption was changed to: ‘Figure 3: An example of measured (black dots) vs. modeled (green, magenta and red lines) thermograms assuming different vaporization enthalpies of the organics.‘

Page 25, line 916-918: Text was added as: ‘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).‘

Page 26: Figure 6 in previous manuscript was moved to supplement, while previous figure 7 was changed to Fig. 6. Line 934: text was added as: ‘ΔH_{vap} = 80 kJ/mol was used in the kinetic evaporation model.‘ Legend of the figure was changed to: ‘Kinetic model results’ on the left, ‘Statistical model results (PMF) on the right‘.

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Estimates of the organic aerosol volatility in a boreal forest using two independent methods

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Abstract

The volatility distribution of secondary organic aerosols formed and undergone aging, i.e. the particle mass fractions of semi-volatile, low-volatility and extremely low-volatility organic compounds in the particle phase was characterized in a boreal forest environment of Hyytiälä, Southern Finland. This was done by interpreting field measurements using a Volatility Tandem Differential Mobility Analyzer (VTDMA) with a kinetic evaporation model. The field measurements were performed during April and May of 2014. On average, 40 % of organics in particles was semi-volatile; 34 % low-volatility organics and 26 % extremely low-volatility organics. The model was, however, very sensitive towards the vaporization enthalpies assumed for the organics (ΔH_{VAP}). The best agreement between the observed and modeled temperature-dependence of the evaporation was obtained when effective vaporization enthalpy values of 80 kJ/mol were assumed. The low effective enthalpy value might result from several potential reasons, including molecular decomposition or dissociation that might occur in the particle phase upon heating, mixture effects and compound-dependent uncertainties in the mass accommodation coefficient. In addition to the VTDMA-based analysis, semi-volatile and low-volatile organic mass fractions were independently determined by applying Positive Matrix Factorization (PMF) to High-Resolution Aerosol Mass Spectrometer (HR-AMS) data. The factor separation was based on the oxygenation levels of organics, specifically the relative abundance of mass ions at *m/z* 43 (*f43*) and *m/z* 44 (*f44*). The mass fractions of these two organic groups were compared against the VTDMA-based

results. In general, the best agreement between the VTDMA results and the PMF-derived mass fractions of organics was obtained when ΔH_{VAP} = 80 kJ/mol was set for all organic groups in the model, with a linear correlation coefficient of around 0.4. However, this still indicates that only about 16% (R^2) of the variation can be explained by the linear regression between the results from these two methods. The prospect of determining of extremely low volatile organic aerosols (ELVOA) from AMS data using the PMF analysis should be assessed in future studies.

1 Introduction

Atmospheric aerosols influence the Earth's climate both directly and indirectly through affecting the radiation balance, and altering the albedo, lifetime and precipitation patterns of clouds (IPCC, 2013). However, uncertainty in the spatial and temporal variability of the aerosol size distribution, chemical composition and physicochemical properties make it difficult to quantify the aerosol climate effects. The physicochemical properties of atmospheric aerosol populations vary (e.g. Jimenez et al., 2009). In terms of aerosol chemical composition measurements, one of the greatest challenges is the presence of a vast number of different organic components in the particles (Kanakidou et al., 2005; Goldstein et al., 2007; Kroll et al., 2011; Donahue et al., 2013). Understanding of the chemical and physical properties of these organic compounds remains incomplete (Hallquist et al., 2009).

One of the key physicochemical properties of atmospheric organic compounds is their volatility, which determines their partitioning between the gas and particle phase (Pankow et al., 1994; Bilde et al., 2015). Atmospheric aerosol particles are mixtures of organic and inorganic compounds having different volatilities. Volatilities of the common inorganic species are relatively well known, while information on the volatility of organic species, especially on extremely low-volatile organics (Ehn et al., 2014; Bilde et al., 2015), is still incomplete.

Different compounds evaporate differently at different temperatures depending on their volatilities, described with saturation vapor concentrations and enthalpies of vaporization (Kreidenweis et al., 1998). Therefore, measuring the evaporation of particles at different temperatures provides indirect information on the volatility of particles. Thermodenuders (TD) where particle populations are heated, often coupled with a Tandem Differential Mobility Analyzer (TDMA), are often used to obtain volatility information on particles. More quantitative information on the volatility distribution can be further obtained by coupling the measurement data with a kinetic evaporation model (e.g. Riipinen et al., 2010; Cappa et al., 2010) that describes the evaporation rate of aerosols inside the TD. While the combination of different TD-setups has been applied to quantify the volatility of laboratory-generated aerosol particles (e.g. Häkkinen et al., 2014) as well as field observations (e.g. Lee et al., 2010; Cappa et al., 2010; Häkkinen et al., 2012), it has not been utilized to determine the volatility distribution of ambient organic aerosol in a boreal environment. Here, it needs to be noted that the volatility distribution of ambient aerosols does not represent the volatility distribution of the condensing organic compounds in the gaseous phase. However, it provides insights into the evaporation potentials of the compounds that are present in the particle phase. Furthermore, it will be useful for closure studies combining this information with condensation studies aiming to derive how the aerosol size distributions are affected by given gaseous species. Finally, measuring the evaporation of aerosols is also essential for testing the applicability and limitations of TD setups for inferring the volatility of aerosols.

Positive Matrix Factorization (PMF) is one of the widely used factor analysis techniques for environmental applications. PMF allows separating organic aerosol (OA) mass spectra into individual groups based on their bulk chemical characteristics, providing information on the OA sources and atmospheric processing (Lanz et al., 2007; Huffman et al., 2009; Zhang et al., 2011). 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). OOA can be further separated into low volatility OOA (LV-OOA) and semi-volatile OOA (SV-OOA). Even though there have been multiple studies using PMF to identify different organic OA groups from ambient data (Ulbrich et al., 2009; Hildebrandt et al., 2010; Ng et al., 2010), especially the SV-OOA and LV-OOA groups, to our knowledge there are only few studies (Cappa and Jimenez, 2010; Paciga et al., 2016) attempting to directly connect the oxygenation levels from these two OOA groups with the volatility of OA obtained by other methods. Comparing the volatility distribution obtained using a mass transfer model and VTDMA data to the oxidation level derived from the AMS data using PMF can help in quantifying the volatilities of SV-OOA and LV-OOA.

In this study, we provide quantitative information on volatility distributions of organic species of ambient aerosol in a boreal forest environment. The sensitivity of the kinetic model was tested towards different parameters of organic compounds, including density, molar mass, saturation vapor concentration, diffusion coefficient and vaporization enthalpy values. More specifically, the sensitivity result to assumed vaporization enthalpy values of organics is discussed. The VTDMA-derived volatility distributions are compared with the ones obtained from the statistical analysis of the AMS.

2 Methods

2.1 Measurements site

The measurements were performed at the Hyytiälä SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations II) between 14 April and 31May 2014. The SMEAR II station, located in Southern Finland, is surrounded by a 54-year-old pine forest. The closest large city is Tampere with a population of around 213 000 and about 48 km to the South-West of the measurement station.

A series of ambient parameters, e.g., particle number size distribution of 3-1000 nm particles (Aalto et al., 2001), ambient meteorological conditions such as temperature, relative humidity, solar radiation, wind speed and wind direction as well as gas phase concentrations of e.g. SO_2, O_3, NO_X, are continuously measured at the station.

2.2 Particle Volatility

The evaporation behavior of submicron aerosols was investigated using a Volatility Tandem Differential Mobility Analyzer (VTDMA), which is part of a Volatility-Hygroscopicity Tandem Differential Mobility Analyzer (VH-TDMA) system (Hong et al., 2014). A brief schematic view of the VTDMA is shown in Fig. 1. In brief, a monodisperse aerosol population (particle diameter of 30, 60, 100 and 145 nm; RH < 10%) was selected by a Hauke-type Differential Mobility Analyzer (DMA; Winklmayr et al., 1991). The aerosol flow was then heated by a thermodenuder at a set temperature, after which the remaining aerosol material was introduced into a second DMA followed by a condensation particle counter (CPC, TSI 3010 & TSI 3772), where the number size distribution of the aerosol after heating was measured. The spread of the number size distribution of the aerosol was taken into account in the data inversion using the piecewise linear inversion approach (Gysel et al., 2009). The thermodenuder is a 50-cm stainless steel tube. No adsorptive material for removing the gas phase was used after the heating section. The residence time inside the thermodenuder was around 2.5 s. The heating temperature of the setup ramped from 25 °C to 280 °C with a time resolution of about an hour. It was assumed that the particles were instantaneously thermally equilibrated with the surrounding gas phase, as the system was under atmospheric pressure.

The major particle losses during the heating process are from thermophoresis and Brownian diffusion (Wehner et al., 2002; Häkkinen et al., 2012). According to Ehn et al. (2007), who used a similar TD, 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, the VTDMA-measured data underestimates the mass concentration of the monodisperse aerosol particles after heating. However, this study was focusing on the change in particle size, which should not be affected very much by the losses. Hence, the effect of the particle losses on the study results can be considered negligible.

The VTDMA measures the particle diameter (and concentration) after heating at each temperature for particles of certain initial size. From this information volume fraction remaining (VFR) after the heating of particles of diameter D_P can be defined as follows

$$VFR(D_P) = \frac{D_p{}^3(T)}{D_p{}^3(T_{room})} = GF_V^3(T). \tag{1}$$

GF_V describes how much of the particles shrink in size upon heating. With VFR = 1 at a given temperature, particles are considered to not evaporate, while with VFR = 0 particles fully evaporate upon heating at that temperature. The mass fraction remaining (MFR) after the heating was assumed to be equivalent to VFR assuming that particle density was constant upon heating (Häkkinen et al., 2012).

Data during a running time window (5 hours) was inserted into the model with a time resolution of half an hour to make sure a full thermogram, i.e. the VFR or

MFR as a function of temperature, could be obtained. The corresponding results represented the conditions (VFR or MFR) at the median time of the 5-hour time window.

2.3 Particle chemical composition

A High-Resolution Aerosol Mass Spectrometer (HR-AMS, Aerodyne Research Inc., Billerica, USA) was used to determine the chemical composition of aerosol particles during the experimental period. Detailed description of the instrument, measurement and data processing can be found in other publications (DeCarlo et al., 2006; Canagaratna et al., 2007). A Sunset semi-continuous OC/EC analyzer was deployed to determine the mass concentrations of organic carbon (OC) and elemental carbon (EC) concentrations in aerosols using a thermal-optical protocol (Bauer et al., 2009).

2.3.1 Pairing of inorganic species

The neutral inorganic salts were calculated from the molar concentration of all ions measured by the HR-AMS based on ion-pairing schemes introduced by Reilly and Wood (1969) and Gysel et al. (2007). SO_4^{2-} was first neutralized by NH_4^+, and the excess of NH_4^+ was then used to neutralize NO_3^-. The simplified ion-paring scheme was introduced as below:

$$\begin{aligned}
n_{H_2SO_4} &= max\left(0, n_{SO_4^{2-}} - n_{NH_4^+}\right),\\
n_{NH_4HSO_4} &= min\left(\, 2n_{SO_4^{2-}} - n_{NH_4^+}, n_{NH_4^+}\right),\\
n_{(NH_4)_2SO_4} &= \ min(max\left(\, n_{NH_4^+} - n_{SO_4^{2-}}, 0\right),\ n_{SO_4^{2-}}),\\
n_{NH_4NO_3} &= min\ (max\left(\, n_{NH_4^+} - 2n_{SO_4^{2-}}, 0\ \right),\ n_{NO_3^-}),
\end{aligned} \qquad (2)$$

where *n* denotes the number of moles. This should naturally be treated only as a rough estimation, as the scheme assumes perfectly internally mixed particles, and the competing bonding of NH_4^+ between SO_4^{2-} and NO_3^- in particle phase is not fully described.

2.3.2 Positive matrix factorization (PMF) of organic aerosol composition

Factor analysis is commonly used to de-convolve the time-dependent OA concentrations and mass spectra into their basic components, based on a linear algebraic model explaining the observed variance. The resulting components, i.e. factors, are interpretable as separate organic sub-groups. The sum of these organic groups' concentrations should closely match the measured organic aerosol mass. Positive Matrix Factorization (Paatero et al., 1997) is one of these component analysis techniques, constrained so that only positive concentration and mass spectra are obtained. In this study, PMF was applied by using the PMF2 algorithm implemented with the user-interface Sofi by Canonaco et al. (2013) to the organic aerosol data measured by the HR-AMS.

2.4 Kinetic evaporation model

A time-dependent evaporation model (Riipinen et al., 2010) was used to simulate the evaporation of a monodisperse aerosol population in a heated flow tube by solving the relevant mass transfer equations. The TD temperature profile, residence time, initial particle size and the thermophysical properties of the aerosol particles were used as input to the model. The volatility of the aerosol constituents was described by the effective saturation concentration, C^*, at standard conditions.

According to Donahue et al. (2013) and Murphy et al. (2014), compounds with different effective saturation vapor concentrations can be classified into extremely low volatile (ELVOC; $C^* < 10^{-4}$ μg/m^3), low volatile (LVOC; 10^{-3} μg/m^3 $< C^* < 10^{-1}$ μg/m^3), semi-volatile (SVOC; $10^{-0.5}$ μg/m^3 $< C^* < 10^{2.5}$ μg/m^3) and intermediate volatile (IVOC; $10^{2.5}$ μg/m^3 $< C^* < 10^{6.5}$ μg/m^3) organic compounds. In the model, we assume the OA to consist of three organic groups with their individual characteristic saturation concentration of 10^{-5} (ELVOA), 10^{-2} (LVOA) and 10 μg/m^3 (SVOA), corresponding to 10^{-10}, 10^{-7}, 10^{-5} Pa, or 10^4, 10^7, 10^{10} molec/cm^3: the aim being to obtain the particle mass fractions of each of the organic group. The ambient particles were assumed to be a mixture of six species, including the afore mentioned organic groups and three inorganic components, namely ammonium nitrate (AN), ammonium sulfate (AS) and EC. AN and AS were assigned with their own characteristic effective saturation vapor concentration and effective vaporization enthalpies obtained from laboratory measurements (see Table 1). EC was assumed to be non-volatile in the temperature range used in this study (assuming C^* of 10^{-30} μg/m^3). As a result, the corresponding average volatility distribution of the ambient aerosol was obtained by letting the difference between the measured and modeled evaporation of the ambient aerosol to reach a minimum with a certain pair of mass fractions of these three organic groups together with known mass fractions of AS, AN and EC from HR-AMS and OC/EC measurements. The MATLAB optimization function *fmincon* with constrains was used to obtain the optimal fit between the measured and modeled thermograms. This optimization method was constrained by setting the sum of mass fraction of organics from the model be equal to the mass fraction of OA measured by HR-AMS, and the mass fraction of each individual organic group to be larger than zero but lower than the total measured mass fraction of OA.

The input parameters, including the physicochemical properties of the six components used for the model as well as particle properties, are summarized in Table 1. Specifically, a mass accommodation coefficient of unity was used along the whole study, thus yielding the maximum estimates for C^*s. To best match the overlapping size ranges of the instruments (VTDMA 30-145 nm and HR-AMS 60-1000 nm), in this study we focus on modeling the evaporation of 100 nm particles.

Lee et al. (2010) reported that the modeled MFR is likely to depend strongly on the vaporization enthalpy values. Hence, sensitivity tests towards this variable were performed. In the sensitivity analysis the vaporization enthalpy values of organics with different volatilities were either assumed to be the same or varied for the different organics, e.g. [100 80 60] kJ/mol. Epstein et al. (2010) fitted the average ΔH_{VAP} as a function of $\log_{10}C^*$ to a set of surrogate organic compounds and obtained the following relationship:

$$\Delta H_{VAP} = -11 * log_{10}C^* + 129. \tag{3}$$

where ΔH_{VAP} and C^* are in the units kJ/mol and μg/m^3, respectively. This vaporization enthalpy (ΔH_{VAP}) of Epstein et al. (2010) (Eq. 3) was also tested in the model calculations. The combinations of enthalpy values of all these three organic groups used in this study are summarized in Table 2.

3 Results and discussion

3.1 Inorganic volatility

Figure 2 illustrates the measured and model-interpreted thermograms (i.e. MFR as a function of the heating temperature) of ammonium nitrate and ammonium sulfate. Vallina et al. (2007) reported that for 150 nm AN and AS particles, the volatilization temperatures (temperature of full particle evaporation) are around 60 °C and 180 °C, respectively, by using a similar VTDMA system with a residence time of around one second. According to the experimental curves (black line) in Fig. 2, AN and AS evaporated completely at around 45 °C and 180 °C, respectively. These results are close to those of Vallina et al. (2007), when the effect of faster evaporation for smaller particles and longer residence time of this study are taken into account.

Modeled thermograms for both AN and AS were obtained by treating the saturation vapor pressures and enthalpy of vaporization as fitting parameters. The optimum C^*-ΔH_{VAP} pair was obtained by minimizing the difference between the measured and model-interpreted thermograms (red lines in Fig. 2). The measured evaporation of AN was reproduced using C^* and ΔH_{VAP} of 76 μg/m^3 (corresponding to $2.6 \cdot 10^{-3}$ Pa) and 152 kJ/mol, respectively. The obtained ΔH_{VAP} is 1.5 times higher than reported previously (Brandner et al., 1962; Hildenbrand et al, 2010; Salo et al., 2011), and the saturation vapor concentration of the same magnitude as in previous studies (Brandner et al., 1962; Chien et al., 2010). For AS, C^* and ΔH_{VAP} of $2 \cdot 10^{-3}$ μg/m^3 and ΔH_{VAP} of 94 kJ/mol reproduced the measurements best. Chien et al. (2010) reported an observation of AN partially decomposing to NH_3 and HNO_3 upon heating. Huffman et al. (2009) similarly suggested that AS might decompose to ammonium bisulfate and ammonia when heating to around 90-140 °C. The evaporation mechanisms of these inorganics might be different from the evaporation of organics, where the ΔH_{VAP} of Epstein et al. (2010) was obtained, since besides sublimation, decomposition might also occur during the evaporation of inorganics. Hence, the vaporization enthalpy from Eq. 3 is not used for the simulation of the evaporation of inorganics. In short, even though there have been afore-mentioned earlier studies reporting the C^* and ΔH_{VAP} of AN and AS, we selected the ones shown by the red curves in Fig. 3 from our VTDMA technique for the model input to simulate the evaporation of ambient aerosols. Moreover, according to the saturation vapor concentration obtained for AN and AS in this study, we can conclude that AN and AS can be considered as semi-volatile and low-volatility compounds, respectively.

The measured thermogram and corresponding evaporation mechanism of ammonium bisulfate (NH_4HSO_4) are not available at present. In order to neglect the effect of ammonium bisulfate on particle evaporation behavior, only data with the mass fraction of ammonium bisulfate less than 10% of total aerosol mass (calculated from Eq. 2) was analyzed.

3.2 Performance of the model for TD data on the organic mixtures

Figure 3 shows example fits to the observed thermograms using different combinations of organic vaporization enthalpies (Table 2). The different simulated evaporation behavior indicates that the model is sensitive towards ΔH_{VAP} values. The median norm of residuals, which describes the difference between the fit and observed thermograms, was the largest when the ΔH_{VAP} of Epstein et al. (2010) (e.g. Combinations 9 in Table 2) for organics were applied in the model. As ΔH_{VAP} increases, the sensitivity of C^* to temperature changes also increases, requiring also lower C^* values to match observations (see the red curve in Fig. 3). This is also in line with Cappa & Jimenez (2010) who suggested that value of C^* as low as 10^{-15} μg/m^3 for extremely low volatility material is required to match the observations when C^*-dependent vaporization enthalpy values of Epstein et al. (2010) are used.

By using the other vaporization enthalpy values (e.g. Combinations 1 to 8 in Table 2), better agreement between the fitted and observed thermograms (Fig. 3) was obtained. Donahue et al. (2006) pointed out that artificially low ΔH_{VAP} values are expected when we present the complex organic mixture aerosol with one single organic compound or of very few components. The artificially low ΔH_{VAP} values should thus be rather referred to effective enthalpy of vaporization (see e.g. Offenberg et al., 2006). According to the performance of the model to TD data, the model was observed to be sensitive towards ΔH_{VAP} values. Low ΔH_{VAP} values (i.e., ΔH_{VAP} = 60-80 kJ/mol) are suggested to be used in the model in order to reproduce the measured thermograms.

3.3 AMS-derived volatility distribution using PMF

Two organic aerosol groups (SVOA and LVOA) with different volatilities were separated from the AMS data using the PMF method (Sec. 2.3.2). This common two-factor separation is driven by the relative fractions of *m/z* 44 (*f44*) and *m/z* 43 (*f43*), connected to the oxidation state (e.g. Aiken et al., 2008). Higher factor solutions associated with other organic groups, commonly determined by PMF analysis, such as biomass burning organic aerosol or hydrocarbon-like organic aerosol, were not pursued. Since this study focuses on the volatility distribution of organics using a complex kinetic model, we chose to limit the PMF OA components to the main ones clearly connected with oxidation state.

The mass spectra of the two organic groups are shown in Fig. 4. The LVOA mass spectrum shows a highly abundant *m/z* 44 signal, which mostly corresponds to the CO_2^+ ion (Aiken et al., 2008). The mass fraction of *m/z* 44 shows a good correlation with the O:C ratio in the organic aerosols (Aiken et al., 2008). The SVOA mass spectrum has a high signal at *m/z* 43, corresponding to $C_2H_3O^+$ ion, which is often considered as a proxy for less oxidized organic aerosol. Hence, the relative abundances of ions at *m/z* 43 (*f43*) and *m/z* 44 (*f44*) are our main indicators to separate these two organic groups with different volatilities arising from their different degrees of oxygenation.

Paciga et al. (2016) studied the volatility distribution of an LVOA factor determined by the PMF analysis, and found that a significant amount of the LVOA mass was attributable to ELVOCs with effective saturation concentrations $\leq 10^{-3}$ $\mu g/m^3$. Hence, probably further advances in the PMF analysis would be needed to assign more than two groups of OA. We tested a three-factor application of PMF, based on the ratio of masses of ions between *m/z* 44 and *m/z* 43, and compared the resulting three organics factors with the mass fractions of different organics from the VTDMA data. There was no correlation (R=0.02) between the mass fraction of LVOA from the model and any of PMF three factors. We are not confident to explain, the reason behind this, but it seems possible that the mass spectral statistics based on the PMF classification does not match with the actual volatility grouping. The following discussion thus only focuses on the well-established two-factor PMF solution (SVOA, LVOA) for the organic components.

3.4 Comparison between organic aerosol volatility from VTDMA and PMF analysis

3.4.1 General results

In Fig. 5, we compare the organic volatility distributions obtained from the VTDMA data using constant ΔH_{VAP} values (Combination 1 to 3 in Table 2) with PMF analysis results. Since we used PMF-derived 2-factor results, we summed up the mass fractions of LVOA and ELVOA from the VTDMA for the comparison. The correlation coefficients for the two data sets were relatively similar with ΔH_{VAP} values of 60 kJ/mol (R=0.48) and 80 kJ/mol assumed for all organic groups (R=0.41). Using ΔH_{VAP} of 100 kJ/mol for all organic groups leads to a clearly worse correlation (R=0.25) and the model interpreted that the particles were solely consisting of low volatility organics besides the inorganic species. Using the enthalpy value of 60 kJ/mol for all organic groups, the modeled mass fraction of SVOA was higher than the SVOA from the PMF analysis. The opposite was true for LVOA, while using ΔH_{VAP} values of 100 kJ/mol for all organic groups, the comparison results differed significantly from the 1:1 line. With the enthalpy value of 80 kJ/mol for organics, the VTDMA-based OA composition was approximately equal to the ones from the PMF results, however, with a linear correlation coefficient of only 0.4. This relatively low correlation coefficient suggests that additional information on each of the method is needed for analyzing the potential links between the AMS and volatility data. Moreover, Paciga et al. (2016) studied the volatility distribution of the PMF-derived organics and estimated that almost half of the SVOC, which was determined from PMF, is semi-volatile, while 42% is low-volatile and 6% is extremely low-volatile. This suggests that the two PMF-derived organic groups, commonly labeled for their oxidation levels, might not be directly linked to their actual volatilities.

The agreement between the VTDMA- and PMF-based OA volatility distributions depends on the inorganic mass fractions. The agreement tended to be somewhat better when the inorganic mass fraction was lower (see Fig. S1). Interestingly, when the inorganic mass fraction was lower than 0.3, the modeled results correlated well with the PMF results, with ΔH_{VAP} values of 100 kJ/mol used in the model. Results of Häkkinen et al. (2014) suggested that relatively more particle phase processing, i.e. condensed phase reactions, take place within organic-inorganic aerosol mixtures having a higher aerosol inorganic mass fraction – which could be consistent with our results as well.

The use of varying ΔH_{VAP} values for ELVOA, LVOA and SVOA did not improve the correlation with the PMF results (see Figs. S2 and S3). Specifically, using ΔH_{VAP} values from Eq. 3 would result in particles exclusively consisting of low-volatility organics besides the inorganic species. Lee et al. (2010) reached a similar conclusion. A single effective ΔH_{VAP} value can thus well represent the OA mixture. Cappa and Wilson (2011) studied the volatility of secondary organic aerosol from the oxidation of α-pinene and reached a similar conclusion: α-pinene SOA behaved as if it was comprised of a single ”meta-compound”.

As discussed in Sect. 3.1 we would expect the ΔH_{VAP} of Epstein et al. (2010) to be the physically most correct of the alternatives tested – at least when it comes to simple reversible evaporation. However, if there are other processes in addition to evaporation taking place in the particle phase upon heating, such as the molecular decomposition or dissociation of unstable functional groups, the model might not be able to capture the measured thermogram using Eq. 3. In this case we might end up with an overestimate in the mass fraction of extremely low-volatility organics. Donahue et al. (2006) and Riipinen et al. (2010) also discussed that the evaporation of a mixture is best approximated with considerably lower effective vaporization enthalpy than the one of a pure component aerosol. For VTDMA measurements of ambient aerosols with various compositions and external conditions, the relation between the C* and vaporization enthalpy values might be non-linear, species- and/or system-dependent. Moreover, Saleh et al. (2013) reported that the evaporation of particles in laboratory experiments could be simulated using a mass accommodation coefficient much less than one. Tong et al. (2011) concluded that the diffusion coefficient of a viscous solution might affect the kinetics of evaporation of non-liquid particles, as aerosol particles in boreal forest environment are expected to be viscous according to Virtanen et al. (2010). Hence, also non-unity mass accommodation coefficients of a mixture and the particle-phase diffusion limitation on evaporation can add uncertainties to the interpretation of the TD data.

Finally, we compared the median volatility distributions of the organics during the whole campaign using the two methods (Fig. 6). A constant ΔH_{VAP} value of 80 kJ/mol for all organics was chosen here as the kinetic model input. According to the PMF results, the SVOA contribution to the total organic aerosol mass was around 30%, which is somewhat lower than the SVOA contribution (approximately 40%) obtained based on the VTDMA results. The model estimated that the mass fractions of LVOA and ELVOA of the total OA mass were 34% and 26%, respectively.

3.4.2 Time-dependent case studies

Figures 7 and 8 show two case studies for 21 April and 1 May 2014. Time series of mass fractions of the particle constituents from HR-AMS, organic mass fractions from the VTDMA (using Combination 1-3 in Table 2) and PMF analysis are shown.

When the ambient aerosol was dominated by organics (Fig. 7), the modeled SVOA mass fraction followed the temporal pattern of the one determined from PMF analysis. The elevated SVOA mass fraction in the early morning is probably due to the condensation of SVOC onto the particles when temperature was still low, and the following decrease in SVOA after the early morning could be caused by the evaporation of SVOA after the ambient temperature increased. The model-interpreted SVOA mass fraction using ΔH_{VAP} values of 80 kJ/mol seemed to have somewhat time-delayed effect compared with the one from the PMF analysis.

When the inorganic species dominated the ambient aerosol mass (Fig. 8), a clear diurnal pattern could also be seen from for both the VTDMA and the PMF-derived SVOA and LVOA mass fractions. However, the VTDMA-based mass fraction followed the PMF-derived ones better when using ΔH_{VAP} values of 60 and 80 kJ/mol compared the one using ΔH_{VAP} values of 100 kJ/mol (see also Fig. 5). The relative amount of inorganic species in the particle phase might thus affect the particle phase processing. Conclusively, these two case studies suggest that an effective ΔH_{VAP} value of 60-80 kJ/mol represent the boreal forest organic aerosols best and this effective ΔH_{VAP} value should be assumed in the model when comparing with the PMF results.

4 Summary and conclusions

The volatility of ambient aerosol particles formed and undergone aging was studied with a Volatility Tandem Differential Mobility Analyzer (VTDMA) in a boreal forest environment in Hyytiälä from April to May of 2014. A kinetic evaporation model was used to further interpret the results and quantify the mass fraction of organics with different volatilities.

When testing the performance of the model against the experimental volatility data, the model was observed to be sensitive to the vaporization enthalpy values of the organics. C^*-dependent vaporization enthalpies based on a semi-empirical formula by Epstein et al., 2010 were applied, but the modeled thermograms failed to reproduce the measurements in this case.

The best correlation between the VTDMA results and the PMF-derived mass fractions of organics was obtained when ΔH_{VAP} = 80 kJ/mol was assumed for all organic groups in the model, with a linear correlation coefficient of around 0.4. This relatively low correlation coefficient indicates that we need to acquire additional information on each of the method to address the potential relation between the AMS and volatility data.

The use of a considerably lower enthalpy value (80kJ/mol) than the semi-empirical ones, the model can best approximate the VTDMA data and the PMF results. Potential explanations to why artificially low vaporization enthalpy values provide the best approximation include thermal decomposition process in addition to evaporation in the particle phase, mixture effects and different mass accommodation coefficients for aerosol mixtures rather than for a pure component system (Riipinen et al., 2010). The interpretation of the VTDMA data using the kinetic evaporation model cannot provide an accurate, definitive volatility distribution for boreal forest aerosols due to the uncertainties in ΔH_{VAP} and other potential issues mentioned above. However, using a proper effective ΔH_{VAP} value for OA, the VTDMA-model results nevertheless, for the first time, provide a rough estimate of the volatility for boreal forest aerosols, approximating that around 26% of the monodisperse (100 nm) OA mass is extremely low volatile.

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Table 1: Properties of six particle components used as input for the evaporation model.

Model input parameter	**ELVOA**	**LVOA**	**SVOA**	**Ammonium nitrate (AN)**	**Ammonium sulfate (AS)**	**Elemental carbon (EC)**
Molar mass, M_W (g/mol)	300	200	150	80	132	280
Density, ρ (kg/m^3)	1900	1700	1400	1720	1770	1900
Surface tension, σ (N/m)	0.05	0.05	0.05	0.05	0.05	0.05
Diffusion coefficient, D (10^{-6} m^2/s)	5	5	5	5	5	5
Temperature-dependent factor for D, μ	1.75	1.75	1.75	1.75	1.75	1.75
Saturation vapor concentration, C^* (μg/m^3)	1E-5	1E-2	10	76	2.0E-3	1E-30
Enthalpy of vaporization, ΔH_{VAP} (kJ/mol)	-[a]	-[a]	-[a]	152	94	100
Mass accommodation coefficient, α_m	1	1	1	1	1	1
Activity coefficient, γ	1	1	1	1	1	1
Particle mass for the monodisperse aerosols, m_P (μg/m^3)[b]	0.1					
Particle mobility diameter, D_P (nm)	100					

a: The chosen of enthalpy values of three groups of organics are summarized in Table 2. b: The particle mass concentration in particle size bin of 90-110 nm from DMPS is used to represent the particle mass concentration of the monodisperse aerosols (i.e. D_P = 100 nm).

Table 2: The combinations of vaporization enthalpy values used as an input for the evaporation model.

	ELVOA	LVOA	SVOA
Combination 1.	60	60	60
Combination 2.	80	80	80
Combination 3.	100	100	100
Combination 4.	100	80	60
Combination 5.	120	100	80
Combination 6.	130	110	80
Combination 7.	160	130	80
Combination 8.	140	125	100
Combination 9.	Eq. 3	Eq. 3	Eq. 3

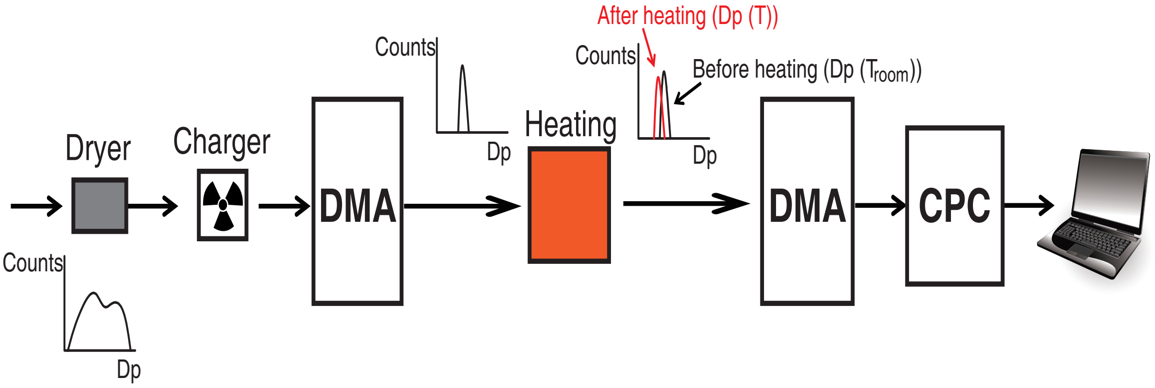


Figure 1: Schematic view of VTDMA system.

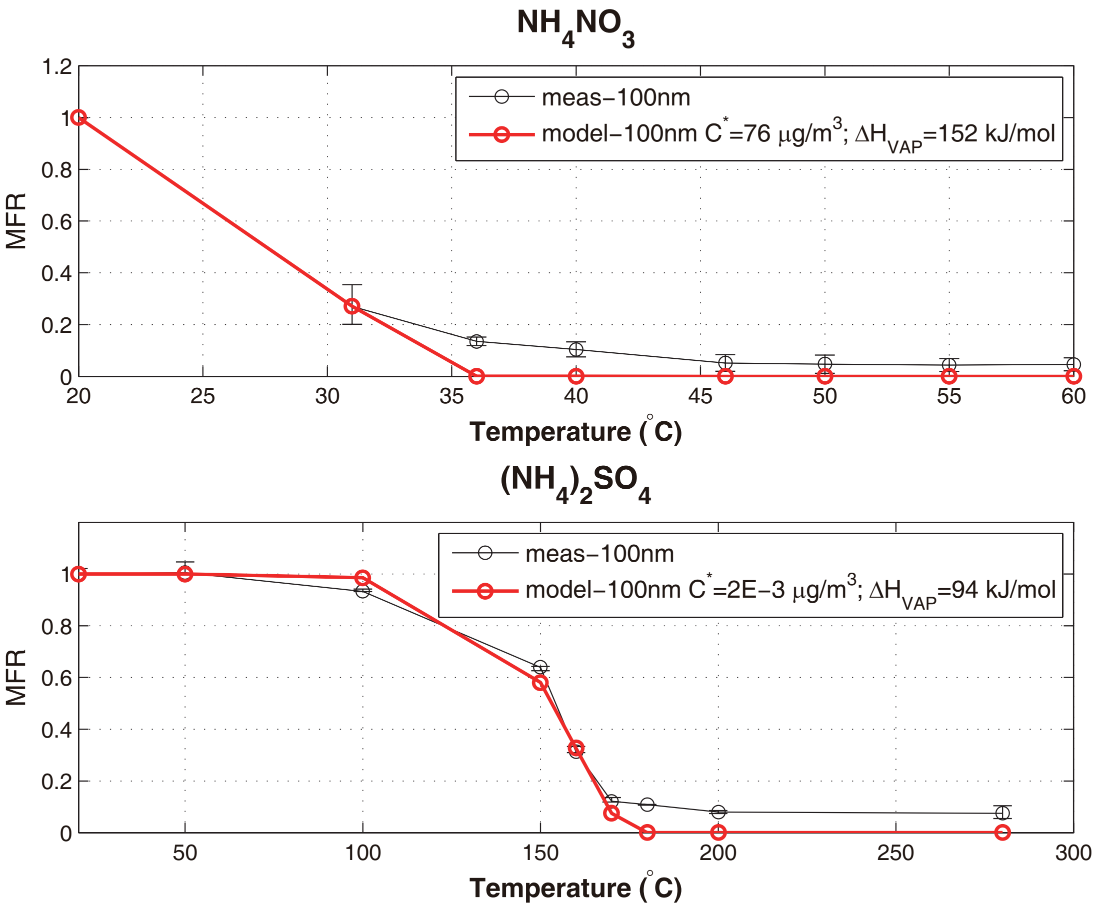


Figure 2: Thermograms of ammonium nitrate and ammonium sulfate using the VTDMA (black lines) and the modeled evaporation using saturation vapor pressures and enthalpies of vaporization corresponding to the best fit with the experimental data (red lines).

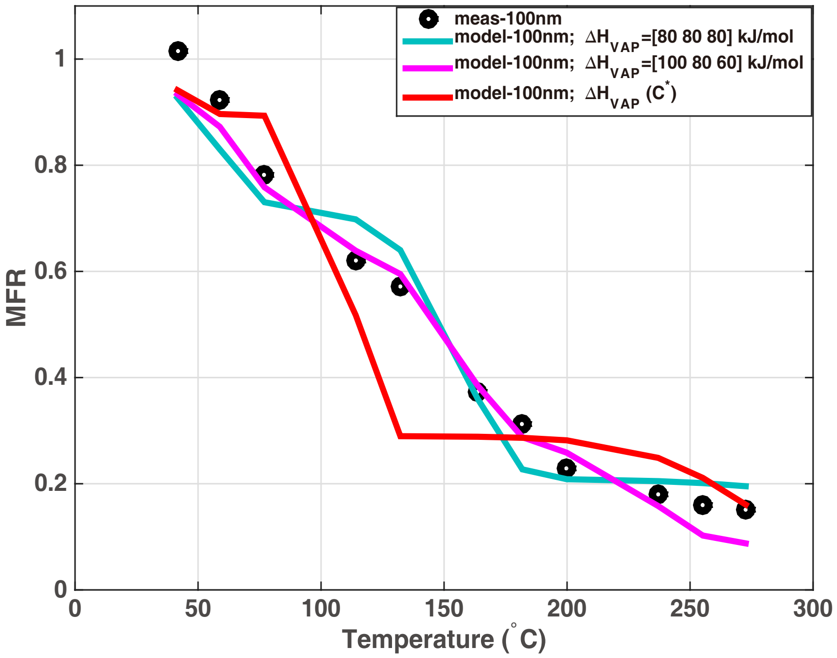


Figure 3: An example of measured (black dots) vs. modeled (green, magenta and red lines) thermograms assuming different vaporization enthalpies of the organics.

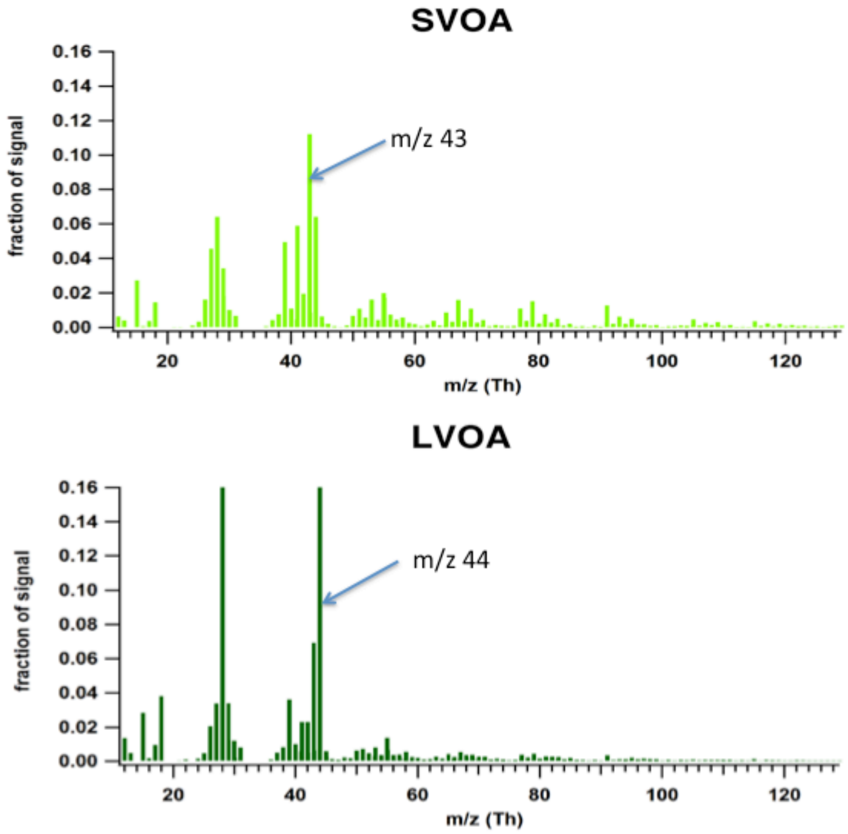


Figure 4: Mass spectrum of SVOA and LVOA obtained from the PMF analysis (two factor solution).

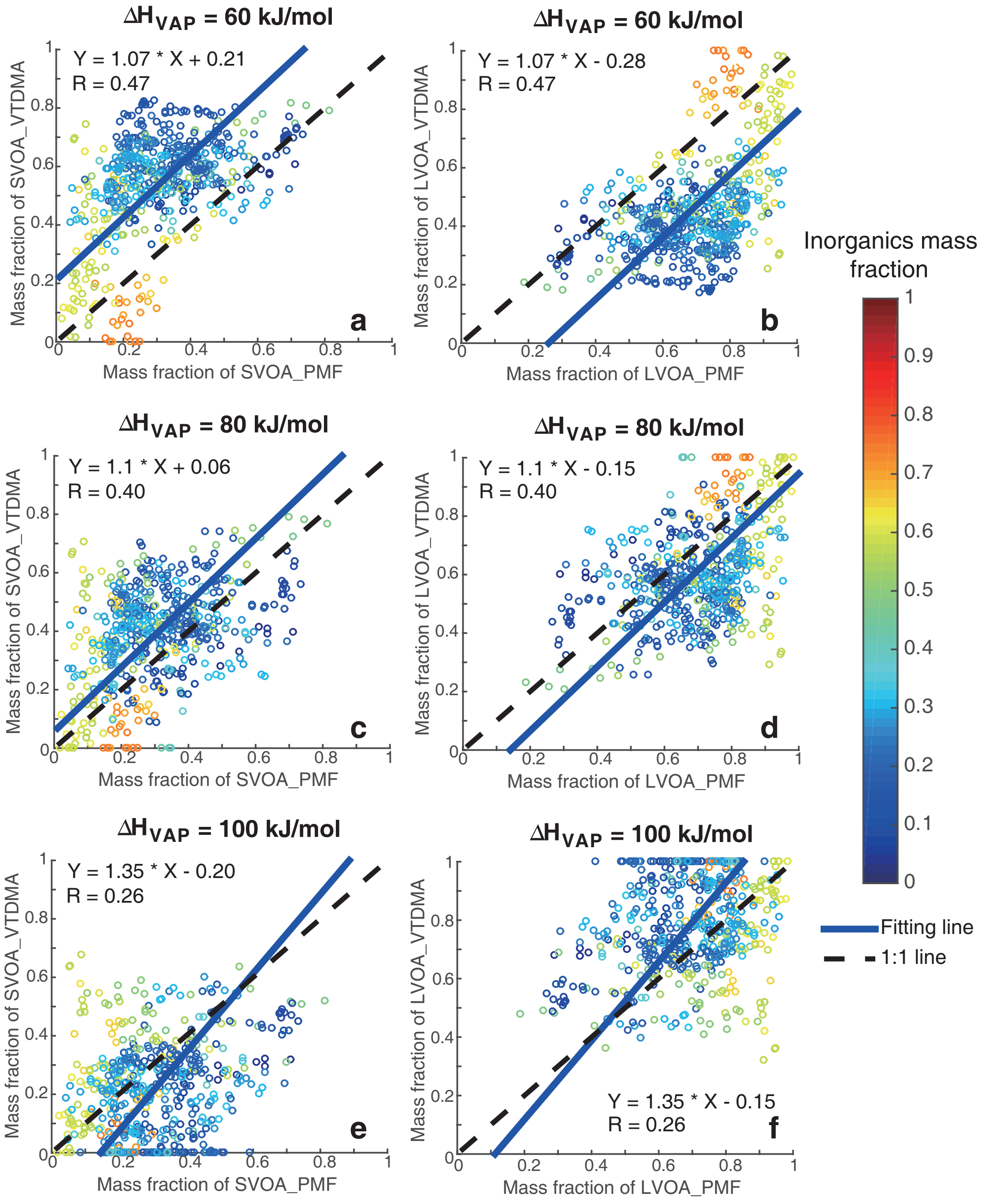
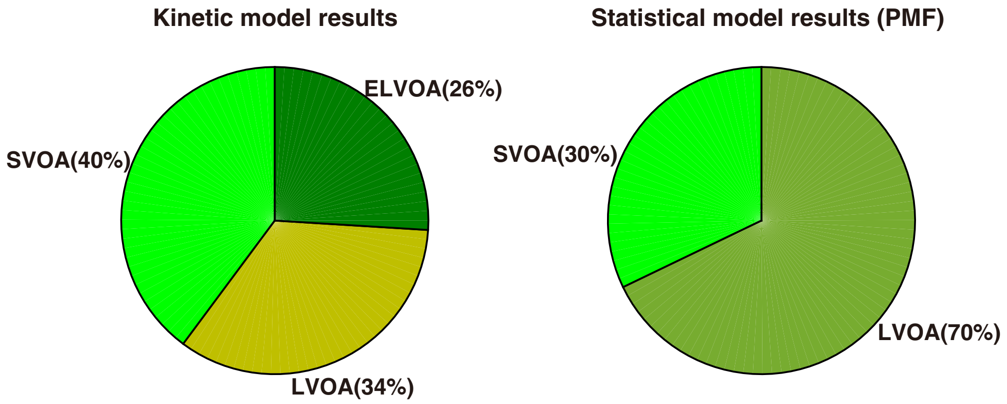


Figure 5: Mass fractions of SVOA and LVOA of the total organic mass obtained from VTDMA data vs. the ones from the PMF analysis. Here, the Y-axis represents the VTDMA results interpretation using the kinetic model and the X-axis represents the AMS results interpretation using the statistical model (PMF). Model results were obtained by using a constant enthalpy value for all organics, corresponding to Combination 1 (a and b), Combination 2 (c and d) and Combination 3 (e and f) in Table 2. The LVOA_VTDMA here is the sum of LVOA and ELVOA mass fractions. The colors of the data points illustrate the inorganic mass fraction in the particles. Correlation coefficient and equation for the line fitted to the data points are given in the legends.



Kinetic model results

Statistical model results (PMF)

Figure 6: Median organic volatility distribution of the ambient aerosols of this study obtained from the VTDMA data interpreted by the kinetic evaporation model (Riipinen et al., 2010) and the AMS data derived from the PMF analysis. ΔH_{vap} = 80 kJ/mol was used in the kinetic evaporation model.

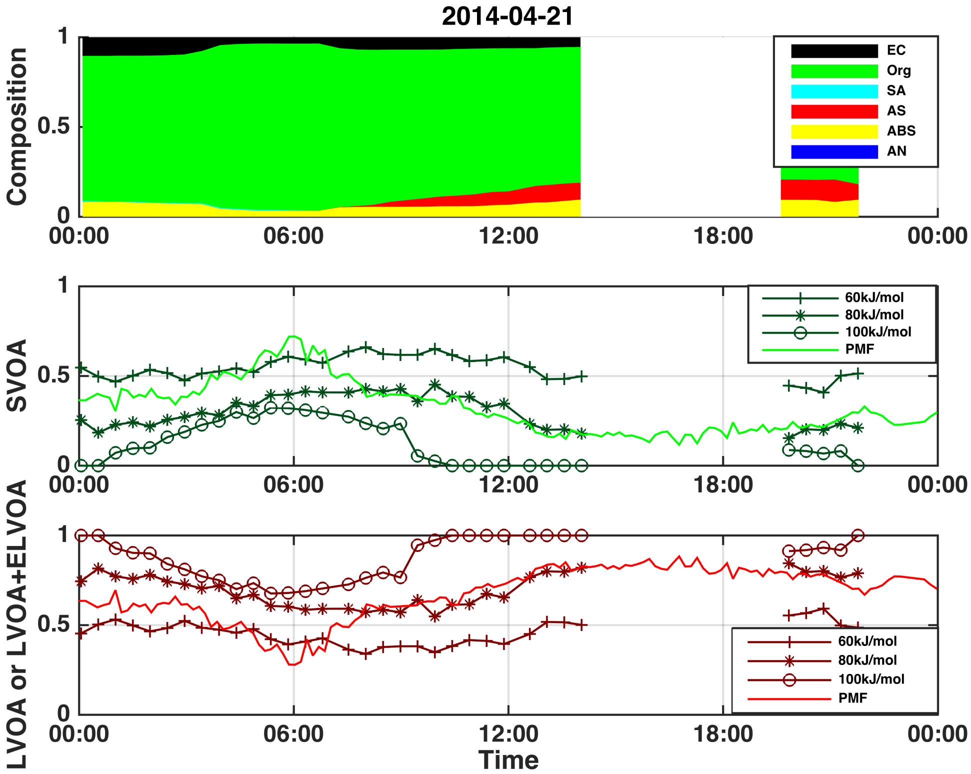


Figure 7: Time series of particle chemical composition obtained from HR-AMS (top), and mass fractions of VTDMA- (the sum of LVOA+ELVOA) and PMF derived SVOA (middle) and LVOA (bottom) on 21 April 2014.

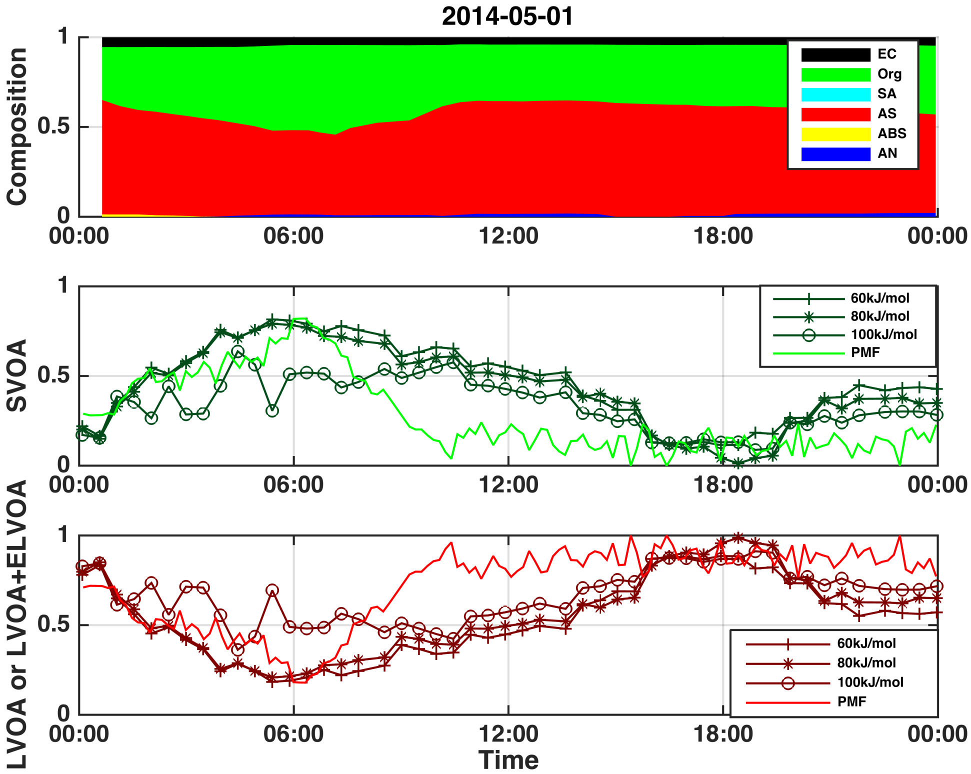


Figure 8: Time series of particle chemical composition obtained from HR-AMS (top), and mass fractions of VTDMA- (the sum of LVOA+ELVOA) and PMF-derived SVOA (middle) and LVOA (bottom) on 01 May 2014.

Supplementary materials:

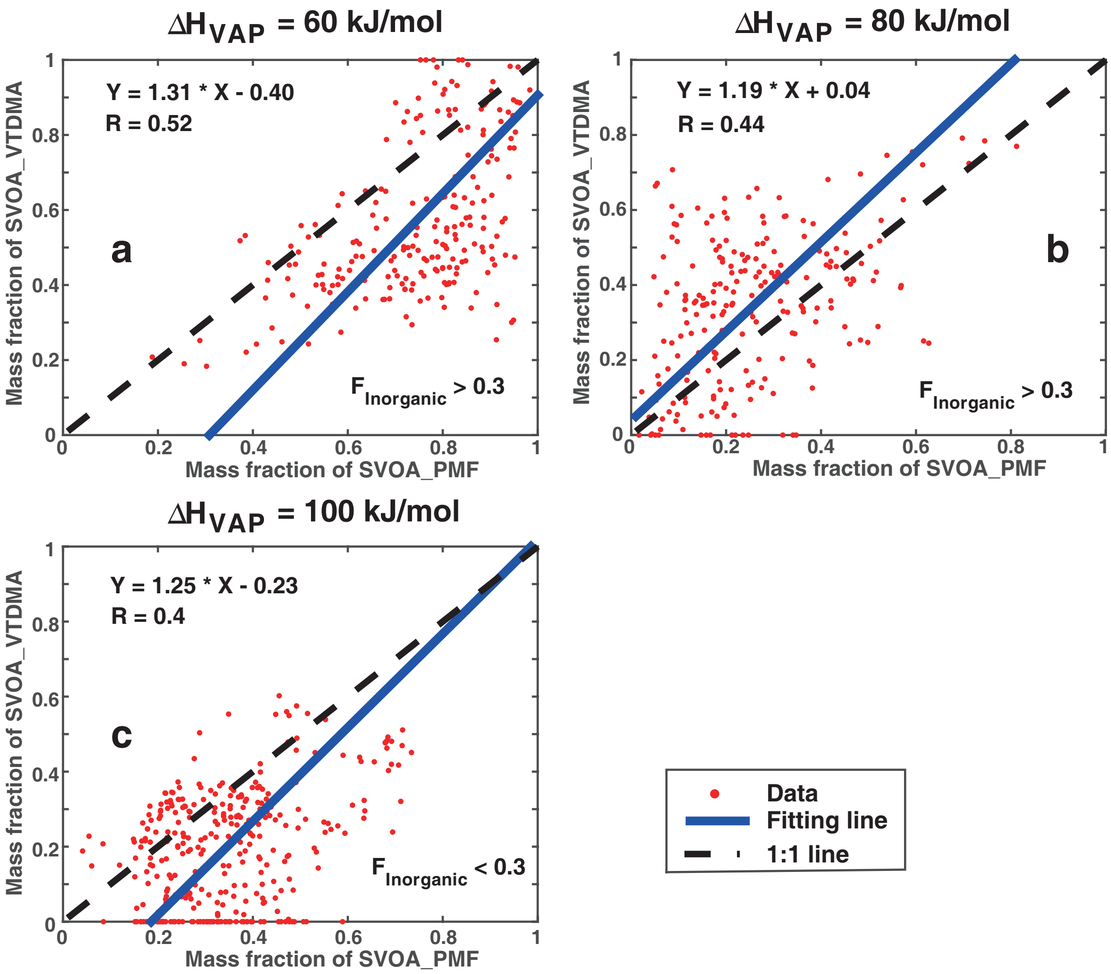


Figure S1: Mass fraction of semi-volatile organics obtained from VTDMA vs. the PMF analysis for different inorganic mass fractions. Modeled results were obtained by using a constant enthalpy value for all organics. Enthalpy values were set as 60, 80 and 100 kJ/mol, respectively. In panel a and b (ΔH_{vap} of [60 60 60] and [80 80 80] kJ/mol for organic groups with different volatilities, respectively) only the data points with particle inorganic mass fraction higher than 0.3 are shown. In panel c (ΔH_{vap} of [100 100 100] kJ/mol for organic groups with different volatilities) only the data points with inorganic particle mass fraction of less than 0.3 are shown.

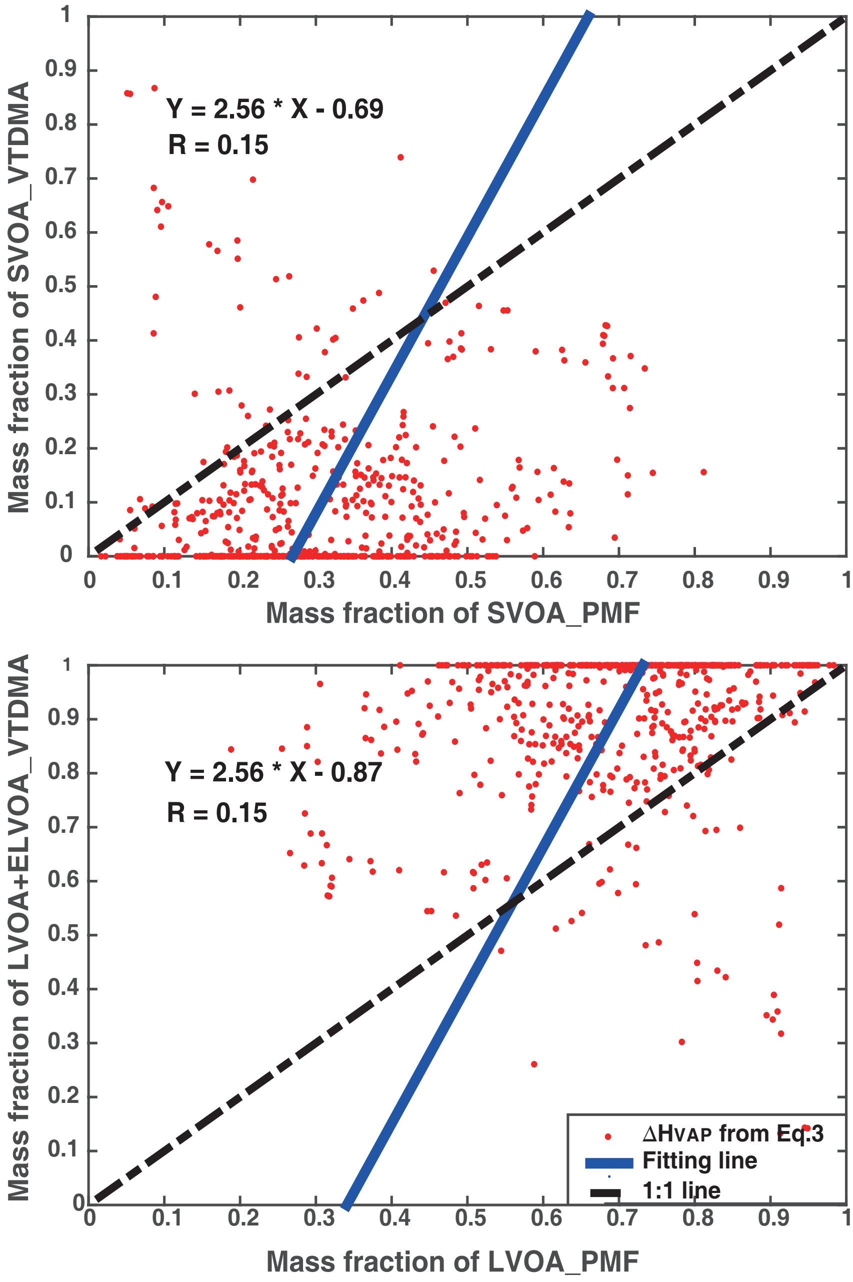


Figure S2: Mass fractions of SVOA and LVOA of the total organic mass obtained from VTDMA data vs. the ones from the PMF analysis. C*-dependent ΔH_{vap} values based on Eq. 3 were used as the input for the kinetic model. Correlation coefficient and equation for the line fitted to the data points to describe the agreement between the VTDMA- and PMF-derived organic mass fractions are also given.

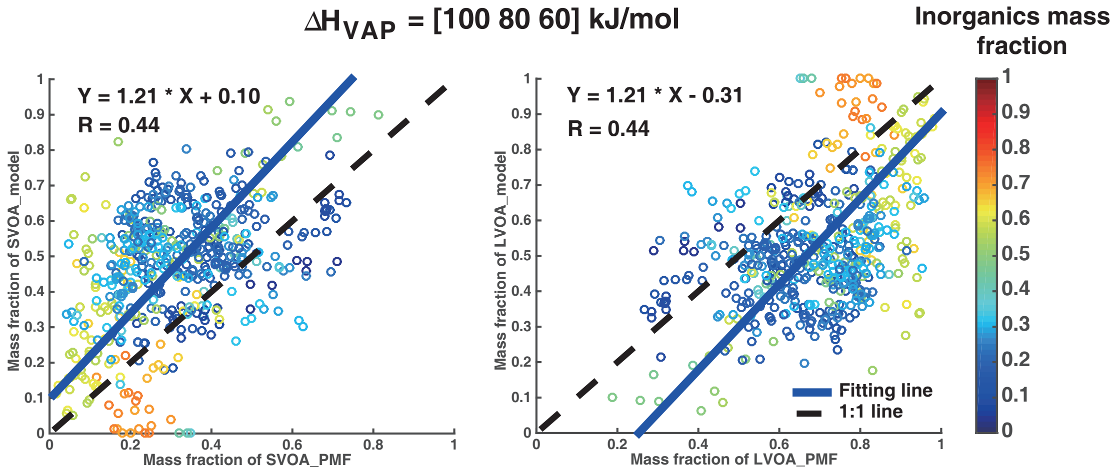


Figure S3: Mass fractions of SVOA and LVOA of the total organic mass obtained from VTDMA vs. the PMF analysis. Model results were obtained by using ΔH_{VAP} values as [100 80 60] KJ/mol (Table 2). Note that mass fraction of LVOA_model means here the sum of LVOA and ELVOA mass fractions obtained from the VTDMA data. The colors of the data points illustrate the particle inorganic mass fraction. Correlation coefficient and equation for the line fitted to the data points are also given.