



**Organic aerosol in the summertime Southeastern United States: Components and their link to volatility distribution, oxidation state and hygroscopicity**

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**Abstract**

The volatility distribution of the organic aerosol (OA) and its sources during the Southern Oxidant and Aerosol Study (SOAS; Centerville, Alabama) was constrained using measurements from an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and a thermodenuder. Positive Matrix Factorization (PMF) analysis was applied on both the ambient and thermodenuded high resolution mass spectra, leading to four factors: more oxidized oxygenated OA (MO-OOA), less oxidized oxygenated OA (LO-OOA), an isoprene epoxydiols (IEPOX) related factor (Isoprene-OA) and biomass burning OA (BBOA). BBOA had the highest mass fraction remaining



(MFR) at 100°C, followed by the isoprene-OA, and the LO-OOA. Surprisingly the MO-OOA evaporated the most in the TD. The estimated effective vaporization enthalpies assuming an evaporation coefficient equal to unity were  $58 \pm 13$  kJ mol<sup>-1</sup> for the LO-OOA,  $89 \pm 10$  kJ mol<sup>-1</sup> for the MO-OOA,  $55 \pm 11$  kJ mol<sup>-1</sup> for the BBOA, and  $63 \pm 15$  kJ mol<sup>-1</sup> for the Isoprene-OA. The estimated volatility distribution of all factors covered a wide range including both semi-volatile and low-volatility components. BBOA had the lowest average volatility of all factors, even though it had the lowest O:C ratio among all factors. LO-OOA was the more volatile factor and its high MFR was due according to the model to its low enthalpy of vaporization. The Isoprene-OA factor had intermediate volatility, quite higher than suggested by a few other studies. The analysis suggests that deducing the volatility of a factor only from its MFR could lead to erroneous conclusions. The oxygen content of the factors can be combined with their estimated volatility and hygroscopicity to provide a better view of their physical properties.

## 1. Introduction

Population exposure to atmospheric particulate matter (PM) increases premature mortality from cardiovascular and respiratory diseases (Pope et al., 2002; IARC, 2013; Cohen et al., 2017). The same particles also modulate the planetary radiative balance and hydrological cycle (IPCC, 2013; NASEM, 2016; Seinfeld et al., 2016). Organic aerosol (OA) constitutes a significant part of submicron aerosol mass (Zhang et al., 2007) and it is characterized by daunting chemical complexity (Kanakidou et al., 2005; Hallquist et al., 2009). OA is directly emitted from anthropogenic and natural sources, but it is also produced by condensation of products formed during the oxidation of gas-phase organic compounds with O<sub>3</sub>, NO<sub>3</sub> and OH radicals (secondary organic aerosol, SOA; Kanakidou et al., 2005). OA formation can be further promoted by the interactions of anthropogenic and biogenic compounds; in the southeastern United States, anthropogenic sulfate enhances OA formation through rapid reactive uptake of IEPOX to particles and aqueous phase reactions (Xu et al., 2015a; Xu et al., 2016a; Budisulistiorini et al., 2017).

Several approaches have been developed to unravel the sources and the degree of atmospheric processing of aerosol sampled by the AMS. These include custom principal component analysis (Zhang et al., 2005), multiple component analysis (Zhang et al.,



2007), PMF (Paatero and Tapper 1994; Lanz et al., 2007) and the multilinear engine (ME-2) (Lanz et al., 2008; Canonaco et al., 2013). Applying the above source apportionment techniques on AMS mass spectra, information about the aerosol sources and the degree of the atmospheric processing can be derived. Important primary components include hydrocarbon-like OA (HOA) (Zhang et al., 2005) and biomass burning OA (BBOA) (Aiken et al., 2009). The most abundant and ubiquitous OA component is the oxygenated OA (OOA), which often consists of a more oxygenated (MO-OOA) and a less oxygenated OA (LO-OOA) factor (Lanz et al., 2007). In the southeastern (SE) United States, MO-OOA and LO-OOA are dominant factors, comprising 47-79% of the total OA (Xu et al., 2015b). Factors related to biogenic secondary OA have been identified in urban, suburban and remote areas (Budisulistiorini et al., 2013; Chen et al., 2015; Kostenidou et al., 2015). In the SE United States, an Isoprene-OA factor linked to IEPOX uptake is present during warm periods, contributing up to 36% of the total OA in the summertime (Xu et al., 2015b).

Central to understanding the atmospheric impacts of OA is constraining its volatility and hygroscopicity (Kanakidou et al., 2005). Volatility measurements are mostly carried out using heated laminar flow reactors, known as thermodenuders (TD) (Burtscher et al., 2001; An et al., 2007) or isothermal dilution (Grieshop et al., 2009). In these systems, changes in OA mass concentration are related to the OA evaporation rate and its volatility can be estimated. The comparison of aerosol evaporation measurements across studies and conditions with TD or isothermal dilution chambers is not straightforward. The established proxy for volatility is the “mass fraction remaining (MFR)”, i.e., the mass of the aerosol remaining after a volatility measurement (Huffman 2009; Cerully et al., 2015; Xu et al., 2016b). MFR has often been used as a relative measure of volatility, as it is assumed that the volatility of particulate matter increases as MFR decreases for particles and TD conditions that are otherwise identical. Although clearly linked to volatility, the MFR depends on the enthalpy of vaporization ( $\Delta H_{\text{vap}}$ ), the aerosol concentration, the heating section residence time, the particle size distribution, and potential particle-to-gas mass transfer resistances. All these parameters therefore complicate the linking of the measured MFR to the volatility. An additional complication is that organic aerosol mixtures are characterized by a distribution of volatilities. A



94 number of studies have attempted to estimate this volatility distribution with appropriate  
95 TD models (Cappa and Jimenez, 2010; Lee et al., 2010; Paciga et al., 2016; Saha and  
96 Grieshop 2016; Louvaris et al., 2017; Saha et al., 2017).

97 Three studies have reported volatility distributions of the isoprene (or IEPOX)  
98 SOA and the total OA for the southeastern United States. Lopez-Hilfiker et al. (2016)  
99 suggested that the IEPOX SOA had a very low saturation concentration with  $C^*=10^{-4} \mu\text{g m}^{-3}$   
100  $\text{m}^{-3}$ , based on the FIGAERO-CIMS signals of  $\text{C}_5\text{H}_{12}\text{O}_4$  and  $\text{C}_5\text{H}_{10}\text{O}_3$ . They assumed that  
101 these signals correspond to 2-methyltetrols and 3-MeTHF-3,4-diols and/or C5 alkene  
102 triols, which are tracers for isoprene SOA. Using the total FIGAERO-CIMS signal  
103 ( $\text{C}_x\text{H}_y\text{O}_z\text{N}_{0-1}$ ) the same authors estimated an extremely low total OA average volatility of  
104  $C^*=3.7 \times 10^{-7} \mu\text{g m}^{-3}$  for the OA with ELVOCs representing 99% of the total. This is the  
105 lowest reported volatility for ambient OA in the literature. Hu et al. (2016) estimated an  
106 average volatility of  $C^*=5.2 \times 10^{-5} \mu\text{g m}^{-3}$  for the IEPOX SOA. Their results were based on  
107 the MFR of the IEPOX SOA (calculated by PMF) using ambient and thermodenuded  
108 AMS measurements. The volatility distribution of IEPOX SOA was estimated applying  
109 the technique of Faulhaber et al. (2009). The corresponding total OA volatility  
110 distribution covered the range from  $C^*=10^{-9}$  to  $1 \mu\text{g m}^{-3}$ . Saha et al. (2017) used an  
111 Aerosol Chemical Speciation Monitor (ACSM) and a thermodenuder to estimate an  
112 average total OA volatility of  $C^*=0.21 \mu\text{g m}^{-3}$  and a vaporization enthalpy of  $100 \text{ kJ mol}^{-1}$ .

113 The two-dimensional volatility basis set (2D-VBS) framework, describing the  
114 OA concentration as a function of its oxygen content and volatility is a promising  
115 approach to describe the partitioning and chemical evolution of the thousands of  
116 compounds present in OA (Donahue et al., 2012). If expanded to include hygroscopicity,  
117 the framework can be strengthened considerably. Several studies have attempted to link  
118 hygroscopicity and volatility (Kuwata et al., 2007; Asa-Awuku et al., 2009; Frosh et al.,  
119 2013) or hygroscopicity and oxidation state (Masoli et al., 2010; Chang et al., 2010;  
120 Lathem et al., 2013; Thalman et al., 2017), however only a few focus on all the properties  
121 combined (Jimenez et al., 2009; Tritscher et al., 2011; Cerully et al., 2015). Jimenez et al.  
122 (2009) combined data from various studies and suggested that hygroscopicity and  
123 oxidation state increase as volatility decreases. The generality of this finding has been  
124 questioned by subsequent studies (Meyer et al., 2009; Tritscher et al., 2011; Lathem et al.,



2013). Recently, Nakao (2017) proposed a theoretical framework, in which the hygroscopicity is explicitly related to oxidation state and volatility. With this approach, each OA “source” can have a unique set of volatility and hygroscopicity parameters that evolve with atmospheric oxidative aging – along a path that requires further constraints from chemistry.

In this study we build upon the work of Xu et al. (2015a) and Cerully et al. (2015) and attempt to constrain the volatility distributions and effective vaporization enthalpy of each PMF factor of OA sampled during the SOAS field campaign at Centreville, Alabama. We then proceed to associate the hygroscopicity parameters estimated by Cerully et al. (2015) with the volatility distributions and test their consistency with the Nakao (2017) theoretical framework.

## 2. Experimental

### 2.1 Measurement site and campaign

The measurements were performed in Centreville, Alabama, (32°54'11.81"N, 87°14'59"W). The station was located in an area significantly influenced by biogenic emissions (Liao et al., 2007; Spracklen et al., 2011). Anthropogenic emissions also affect the site. The measurements were conducted during the Southern Oxidant and Aerosol Study (SOAS), which was part of the Southern Atmosphere Study (SAS; <http://www.eol.ucar.edu/projects/sas>) from June 1 to July 15 2013. A summary of important findings can be found in Carleton et al. (2017), while additional results relevant for our study can be found in Xu et al. (2015a), Cerully et al. (2015), Guo et al. (2015) and Saha et al. (2017).

### 2.2 Instrumentation

The aim of the specific measurements was to characterize both the ambient and the water soluble fraction of the non-thermally and thermally-denuded PM<sub>1</sub>. For the vaporization a thermodenuder, TD, (Cerully et al., 2014) was used. A particle-into-liquid sampler (PILS) (Weber et al., 2001) was used to collect the water soluble aerosol components and then the solution was nebulized. The aerosol passed every 12 or 15 min through four lines: ambient bypass, ambient TD, PILS bypass and PILS TD. In this work



156 we used the ambient denuded measurements only. Details about the experimental set up  
157 can be found in Cerully et al. (2015).

158 The sampling instrumentation included an Aerodyne HR-AMS, a Scanning  
159 Mobility Particle Sizer (SMPS, Classifier model 3080, DMA model 3081, CPC model  
160 3022A, TSI), a Cloud Condensation Nuclei counter (CCNc, Droplet Measurement  
161 Technologies). The TD used in this campaign has been characterized by Cerully et al.  
162 (2014). Briefly, the TD consisted of a heating and a cooling section. The first part was a  
163 stainless steel tube 30 with in length and 0.68 in inner diameter. The cooling section was  
164 removed during this campaign, as the re-condensation of the vapors is minimal when the  
165 ambient mass concentration is low, which was the case for this campaign (Cappa et al.,  
166 2010; Saleh et al., 2011; Cerully et al., 2014). The temperature in the TD was 60, 80 and  
167 100°C. The total flow rate passing through the TD was 1.5 L min<sup>-1</sup> and so the average TD  
168 residence time was approximately 7 s.

169

### 170 3. Data Analysis

#### 171 3.1 PMF and elemental ratios

172 PMF (Lanz et al., 2007) was applied to both ambient bypass and TD HR organic  
173 mass spectra according to the procedure of Ulbrich et al. (2009). Details about the PMF  
174 solution are provided in the SI (Figures S1 and S2). The O:C and H:C elemental ratios  
175 were estimated using the approach of Canagaratna et al. (2015). Xu et al. (2015a) also  
176 used the Canagaratna et al. (2015) O:C approach, however Cerully et al. (2015) applied  
177 the older algorithm of Aiken et al. (2008). For any comparisons between this work and  
178 previous studies we converted the old O:C to the new O:C ratios using the corresponding  
179  $f_{44}$  fraction according to the equation:  $O:C = 0.079 + 4.31 f_{44}$  (Canagaratna et al., 2015).

180

#### 181 3.2 Collection efficiency (CE)

182 Xu et al. (2015a) estimated the AMS CE using the composition-dependent  
183 approach of Middlebrook et al. (2012). The average bypass CE was estimated to be  
184  $0.65 \pm 0.12$ , while the average TD CE was slightly higher  $0.7 \pm 0.11$ . The difference was  
185 statistically significant with a  $p$  value less than 0.0001. These estimates can be more



uncertain than their variability suggests, due to their sensitivity to aerosol ammonium and neutralization. The sensitivity of our results is discussed in Section 5.3.

### 3.3 TD losses

The thermodenuded OA was corrected for particle losses due to sedimentation, diffusion and thermophoresis inside the thermodenuder. More details about the thermodenuder characterization are provided by Cerully et al. (2014).

### 3.4 MFR

For the MFR calculations only data with ambient OA concentration higher than  $0.2 \mu\text{g m}^{-3}$  were used in order to avoid extreme variations of the MFR. For such low concentrations the corresponding TD concentrations can be very low introducing significant error in the MFR calculation. The fractions of the data for each factor above the threshold of  $0.2 \mu\text{g m}^{-3}$  are given in Table 1. For the total OA, MO-OOA and LO-OOA this fraction was above 92% but for the Isoprene-OA and BBOA was lower (76% and 42% respectively). The four (or five) consecutive ambient and TD measurements during each hour were averaged. The variability of the four (or five) averaged values was 4-16%.

### 3.5 Volatility distribution estimation

The dynamic mass transfer model of Riipinen et al. (2010) was used to estimate the OA volatility distributions. The model simulates the particle evaporation inside the thermodenuder solving the corresponding system of differential equations describing the mass transfer between the particle and gas phases:

$$\frac{dm_p}{dt} = -\sum_{i=1}^n I_i \quad (1)$$

$$\frac{dC_i}{dt} = I_i N_{tot} \quad (2)$$

where  $m_p$  is the organic particle mass,  $C_i$  is the gas-phase concentration of compound  $i$ ,  $N_{tot}$  is the total number concentration of the particles,  $n$  is the number of the assumed



214 organic aerosol components, and  $I_i$  the mass flux of the compound  $i$  given by the Vesala  
215 et al. (1997) equation:

$$216 \quad I_i = \frac{2\pi d_p p M_i D_i \beta_{mi}}{RT_{TD}} \ln \left[ \frac{1 - \frac{p_i}{p}}{1 - \frac{p_i^0}{p}} \right] \quad (3)$$

217 where  $d_p$  is the particle diameter,  $R$  the molar gas constant,  $M_i$  and  $D_i$  the molar mass and  
218 the diffusion coefficient of compound  $i$  at temperature  $T_{TD}$ . The diffusion coefficient ( $D_i$ )  
219 depends on the temperature and is calculated according to Chen and Othmer (1962) and  
220  $\beta_{mi}$  is the correction factor given by Fuchs and Sutugin (1970).  $p$  is the total gas pressure,  
221 while  $p_i$  and  $p_i^0$  are the partial vapor pressures of the compound  $i$  at the particle surface  
222 and far away from the particle respectively.  $p_i^0$  is given by:

$$223 \quad p_i^0 = x_i \gamma_i p_{sat,i} \exp\left(\frac{4M_i \sigma}{RT_p \rho d_p}\right) = x_{mi} \frac{C_i^* RT_{TD}}{M_i} \exp\left(\frac{4M_i \sigma}{RT_p \rho d_p}\right) \quad (4)$$

224 where  $x_i$  is the mole fraction of  $i$ ,  $\gamma_i$  the activity coefficient of  $i$  in the particle,  $p_{sat,i}$  the  
225 pure component vapor pressure of  $i$  over a flat surface,  $T_p$  the particle temperature (we  
226 assume that  $T_p = T_{TD}$ ),  $x_{mi}$  the mass fraction of  $i$  in the particle,  $\rho$  the particle density and  $\sigma$   
227 the particle surface tension.  $C_i^*$  is the effective saturation concentration of  $i$  at 298 K.

228 The change of the vapor pressure with temperature is calculated by the Clausius-  
229 Clapeyron equation:

$$230 \quad C_i^*(T_{TD}) = C_i^*(298\text{ K}) \exp\left[\frac{\Delta H_{vap,i}}{R} \left(\frac{1}{298} - \frac{1}{T_{TD}}\right)\right] \frac{298}{T_{TD}} \quad (5)$$

231 where  $\Delta H_{vap}$  is the vaporization enthalpy of component  $i$ .

232 The model inputs include the loss corrected MFRs, the thermodenuder  
233 temperature and residence time, the bypass average particle size and the OA  
234 concentration. The output of the model is the OA volatility distribution in terms of  
235 effective saturation concentrations ( $C^*$ ) at 298 K, in combination with its effective  
236 vaporization enthalpy ( $\Delta H_{vap}$ ) and the mass accommodation (evaporation) coefficient  
237 ( $a_m$ ). We fit the measured thermograms using a consecutive 3-bin  $C^*$  distribution, with  
238 varying mass fraction in each bin. The bins corresponded to saturation concentrations of  
239 0.1, 1, and 10  $\mu\text{g m}^{-3}$  at 298K. The enthalpy of vaporization ( $\Delta H_{vap}$ ) was also estimated,





while the accommodation coefficient was assumed to be equal to unity. The best (optimum) solutions and the corresponding uncertainties are calculated using the approach of Karnezi et al. (2014). For each solution the average mass fraction in each bin and its corresponding standard deviation, was estimated using the top 2% of the mass fraction combinations with the lowest error. In this study for the comparison between volatilities we will use the average volatility based on mass fraction weighted  $\log_{10}C^*$ .

### 3.6 Hygroscopicity

Details about the hygroscopicity analysis of the corresponding data can be found in Cerully et al. (2015). Using a CCNc Cerully et al. (2015) estimated the hygroscopicity parameter  $\kappa$  of the total and water soluble ambient and thermodenuded  $PM_{10}$  OA. The same authors performed linear regression of the ambient water soluble  $\kappa_{org}$  with the PMF factors of the ambient water soluble OA. During the periods of the water solubility measurements the BBOA concentration was too low to allow the separation of the factor, so its hygroscopicity was not determined. The PMF results of the ambient total and the ambient water soluble data were practically the same.

## 4. Results and Discussion

### 4.1 Volatility of organic aerosol

The average OA mass concentration was  $5 \mu\text{g m}^{-3}$ . The loss-corrected OA MFR is depicted in Figure 1a. Half of the total OA evaporated at  $100^\circ\text{C}$  ( $T_{50}=100^\circ\text{C}$ ). The estimated volatility distribution (Figure 1b) indicates that 46% of the organic aerosol was semivolatile organic compounds (SVOCs) (compounds with  $1 \leq C^* \leq 100 \mu\text{g m}^{-3}$ ) and 54% was low volatility organic compounds (LVOCs) ( $0.001 \leq C^* \leq 0.1 \mu\text{g m}^{-3}$ ). Part of the material assigned to the  $0.1 \mu\text{g m}^{-3}$  bin has volatility less than this value. The fact that there were no measurements above  $100^\circ\text{C}$  does not allow us to constrain further the contributions of the LVOCs and ELVOCs. The average volatility based on mass fraction weighted  $\log_{10}C^*$  values was  $C^*=0.55\pm0.29 \mu\text{g m}^{-3}$ . Please note that this value is useful only for comparisons of volatility distributions in the same VBS volatility range. The mass fraction of each volatility bin is provided in Table S1. The effective vaporization enthalpy of the total OA was  $86\pm9 \text{ kJ mol}^{-1}$ .



## 4.2 Volatility of OA components

The PMF analysis using both the ambient and TD measurements suggested four factors. The OA consisted of 43% more oxidized OOA (MO-OOA), 29% less oxidized OOA (LO-OOA), 19% Isoprene-OA and 9% biomass burning OA (BBOA). The same four factors and OA composition were obtained by Xu et al. (2015a) using only the ambient AMS HR mass spectra (Table 2). Details about their characteristics, correlation with external tracers and justification of their names are provided by Xu et al. (2015a). The ambient OA factor time series were practically the same in the two analyses with  $R^2 > 0.93$ , the mass spectra were also similar with angle  $\theta$  equal to 3–4 degrees for LO-OOA, MO-OOA and Isoprene-OA and 12 degrees for the BBOA factor (Figure S3). Thus, our PMF results are robust and quite consistent with the previous analysis.

The loss-corrected MFRs of the four factors are depicted in Figure 2. BBOA evaporated less, as its MFR was close to unity at all temperatures. The BBOA factor was quite oxygenated with an O:C of 0.58 compared to previous studies (e.g., Crippa et al., 2013; Florou et al., 2017). The corresponding BBOA could be chemically aged or PMF may be mixing the BBOA with aged background OA. Even though BBOA and Isoprene-OA had similar O:C ratios (0.58 and 0.59 correspondingly), the Isoprene-OA MFR was lower. Surprisingly the MFR of MO-OOA was lower than that of LO-OOA, even though MO-OOA had a higher O:C ratio (0.99) than LO-OOA (0.63). Relying only on MFR one would reach the conclusion that MO-OOA was more volatile than LO-OOA.

The predicted thermograms for each factor are also depicted in Figure 2 and the resulting volatility distributions are shown in Figures 3a–3d. Figures 3e and 3f show the comparison of the volatility compositions and the vaporization enthalpies between the four OA factors. The mass fractions of each volatility bin (in the aerosol phase), average volatility ( $C^*$ ) and the vaporization enthalpy of each factor are given in Table S1.

The average LO-OOA mass concentration was  $1.66 \mu\text{g m}^{-3}$  and this factor based on the model was composed of 73% SVOCs and 27% LVOCs. Its average volatility was  $C^* = 1.88 \pm 0.32 \mu\text{g m}^{-3}$  and its effective vaporization enthalpy  $58 \pm 13 \text{ kJ mol}^{-1}$ . The average MO-OOA mass concentration was  $1.96 \mu\text{g m}^{-3}$ . According to its volatility distribution 56% of the MO-OOA was SVOCs and 44% was LVOCs. Its effective vaporization



enthalpy was  $89 \pm 10 \text{ kJ mol}^{-1}$  and its average volatility  $0.95 \pm 0.31 \mu\text{g m}^{-3}$ . According at least to the model the MO-OOA was less volatile on average than the LO-OOA even if it evaporated more in the TD. This counterintuitive behavior is explained by the TD model by the higher effective vaporization enthalpy of the MO-OOA, probably due to the contribution of dicarboxylic and tricarboxylic acids which have vaporization enthalpies higher than  $100 \text{ kJ mol}^{-1}$  (e.g., Saleh et al., 2008; 2010; Kostenidou et al., submitted) Our results suggest that deducing the volatility of a component using only its MFR or its O:C ratio may lead to incorrect conclusions This finding is also supported by Xu et al. (2016b), where they suggest that different O:C distributions could result in the same bulk O:C but different volatility distributions, which may lead to particles with the same O:C but different MFR.

BBOA was the less abundant factor with average mass concentration equal to  $0.5 \mu\text{g m}^{-3}$ . According to the TD model, 53% of the BBOA consisted of SVOCs and the other 47% was LVOCs. Its average volatility was  $C^* = 0.59 \pm 0.22 \mu\text{g m}^{-3}$  and its effective vaporization enthalpy was  $55 \pm 11 \text{ kJ mol}^{-1}$ . Finally, the average Isoprene-OA mass concentration was  $0.9 \pm 0.5 \mu\text{g m}^{-3}$  and composed of 59% SVOCs and 41% LVOCs. Its estimated average volatility was  $C^* = 1.05 \pm 0.30 \mu\text{g m}^{-3}$  and its vaporization enthalpy  $63 \pm 15 \text{ kJ mol}^{-1}$ .

These results suggest that all factors contained components with a wide range of volatilities. Based on their average volatility BBOA was the least volatile, followed by MO-OOA, Isoprene-OA and finally LO-OOA was the more volatile OA component. The availability of measurements at only three temperatures introduces uncertainty in the above results. A detailed sensitivity analysis is presented in Section 5.

## 5. Sensitivity analysis

### 5.1 Effective enthalpy of vaporization ( $\Delta H_{\text{vap}}$ )

We estimated the volatility distributions for three fixed vaporization enthalpies: 50, 80 and  $100 \text{ kJ mol}^{-1}$  for all factors (Table S2). While the corresponding thermograms do not reproduce as well the corresponding measurements, it is instructive to examine the corresponding volatility distributions taking into account this time the measurement uncertainties.



The 80 and 100 kJ mol<sup>-1</sup> values lead to thermograms for MO-OOA consistent with the measurements given the uncertainty of the latter (Figure A1, Appendix). The resulting MO-OOA volatility distributions (Figure A2, Appendix) are within the uncertainty range of the distributions shown in Figure 3. The LVOC content of the factor varies from 35% to 60% as the  $\Delta H_{\text{vap}}$  varies from 80 to 100 kJ mol<sup>-1</sup>. The optimum (base case) solution suggested a 44% LVOC content.

The situation is a little more complex for LO-OOA due to the higher variability of the corresponding MFR measurements. All three  $\Delta H_{\text{vap}}$  values lead to solutions that are consistent with the observations within experimental uncertainty. This results in a wide range of volatility distributions with the LVOC content varying from 25% to 90% (Figure A2). The best (base case) solution suggested 27% LVOCs, so the sensitivity analysis suggests that the LO-OOA may have been significantly less volatile.

Only the 50 and 80 kJ mol<sup>-1</sup> values lead to acceptable thermograms for the Isoprene OA (Figure A1). The LVOCs are predicted to contribute to the factor from 35 to 75% (Figure A2) as the assumed  $\Delta H_{\text{vap}}$  varies from 50 to 80 kJ mol<sup>-1</sup>. The optimum (base case) solution corresponded to 41% LVOCs.

Finally, for the BBOA as the  $\Delta H_{\text{vap}}$  varies from 50 to 80 kJ mol<sup>-1</sup> (the 100 kJ mol<sup>-1</sup> value does not lead to acceptable solutions) the LVOC content increases from 65 to 87% (Figure A2), values that are higher than the estimated 47% LVOCs in the optimum (base case) solution.

## 5.2 Accommodation coefficient

It has been assumed in the analysis so far that there were no resistances to the evaporation of the OA in the TD and that the accommodation coefficient,  $a_m$ , was equal to one. We performed two sensitivity tests using accommodation coefficients of one and two orders of magnitude lower (0.1, 0.01). The volatility distributions, the average volatility  $C^*$  and the vaporization enthalpy of each factor are given in Table S1. The corresponding MFRs are illustrated in Figure A3 and the volatility distributions in Figure A4.

A value of  $a_m$  equal to 0.01 is inconsistent with the measured thermograms of MO-OOA, Isoprene-OA and total OA (Figure A3). For LO-OOA and BBOA the



predicted thermograms are within the experimental error of the measured values and the resulting volatility distributions are quite close to those of the base case. For example, for LO-OOA the LVOC content is 40% (Figure A4) compared to 27% in the optimum solution. This rather surprising insensitivity of the volatility distribution is that the model balances the effects of the lower  $a_m$  with an increase of the predicted  $\Delta H_{\text{vap}}$ . In the case of the LO-OOA the estimated enthalpy of vaporization increases to  $121 \text{ kJ mol}^{-1}$ .

The intermediate value of  $a_m=0.1$  leads to predicted MFR values within the experimental error for LO-OOA, Isoprene-OA and BBOA, but not for MO-OOA or total OA (Figure A3). For the acceptable cases the average volatility of the OA components decreases by a factor of 2-3 and the effective  $\Delta H_{\text{vap}}$  increases by  $30\text{--}40 \text{ kJ mol}^{-1}$ . The LVOC content of LO-OOA increases from 27% to 52%, while the increase of the Isoprene-OA and BBOA LVOCs is small (from 41 to 47% and from 60 to 64%) respectively (Figure A4).

For the MO-OOA and the total OA only the  $a_m=1$  simulations provided acceptable results.

The above analysis suggests that the estimated volatility distributions have a surprisingly low sensitivity to the assumed evaporation coefficient, but the  $\Delta H_{\text{vap}}$  is quite sensitive to this value. This result is quite different from other studies (e.g., Lee et al., 2010; Cappa and Jimenez 2010; Riipinen et al., 2010) and is due to the limited temperature range of the measurements in the present work.

### 5.3 TD collection efficiency

In this case we repeated the calculations assuming a lower AMS CE for the aerosol that passed through the TD. Assuming a 10% lower CE in the TD, the volatility distribution of MO-OOA and Isoprene-OA changed by less than 10% (Table S1). However, the volatility distribution of LO-OOA and BBOA shifted towards lower values with the average volatility decreasing by around a factor of 2. The reasons for this behavior could be the high LO-OOA MFR uncertainty and the low mass concentration of the BBOA. The corresponding thermograms and volatility distribution are shown in Figures S4 and S5.



## 6. Comparisons with other studies

**MO-OOA and LO-OOA:** The volatility distributions of the MO-OOA and LO-OOA were similar to those of the aged aerosol in Finokalia (FAME-08) (Lee et al., 2010) in which the SVOCs accounted for 60% and LVOCs for 40% of the OA using an  $a_m=0.05$  and  $\Delta H_{\text{vap}}=80 \text{ kJ mol}^{-1}$  (Figure S7). The SOAS LO-OOA appears to be a little more volatile than the summertime SV-OOA in Paris (Paciga et al., 2016) and Mexico City (Cappa et al., 2010), while the MO-OOA is a lot more volatile than the LV-OOA in these locations. These summertime OOA components in SOAS were more volatile compared to the wintertime OOA in Paris and Athens (Louvaris et al., 2017), which had a lower SVOC content (45% for Paris and 31% in Athens).

**BBOA:** Figure S6b illustrates the volatility comparisons between the BBOA factor and the BBOA factors from Mexico City, Paris (winter) and Athens (winter). The estimated SVOC content of all four BBOA factors was surprisingly similar around 50% with the Mexico City BBOA having the higher fraction (70%). The differences in LVOCs and ELVOCs are at least partially due to the temperature ranges used in the corresponding measurements. The corresponding O:C ratios of the factors were quite different, 0.58 for SOAS, 0.4 for Mexico City, 0.29 for Paris, and 0.23 for Athens (all estimated using the Canagaratha et al. (2015) approach). Part of the reason of the discrepancy may be hidden in the least volatile components of BBOA that were not examined in the present study.

**Isoprene-OA:** Lopez-Hilfiker et al. (2016) suggested that the IEPOX SOA had much lower saturation concentration,  $C^*=10^{-4} \mu\text{g m}^{-3}$ , compared to the volatility of the Isoprene-OA estimated here. Potential reasons for the discrepancy may include the fact that their conclusion was based on major components of IEPOX SOA and not all the products, the fact that Isoprene-OA factor may not be entirely composed of IEPOX, potential interactions of these components with the substrate used in FIGAERO-CIMS, the role of the vaporization enthalpy in the thermal behavior of these compounds, etc. As a consistency test, we used the volatility distribution of Lopez-Hilfiker et al. (2016) as input to the code of Riipinen et al. (2010) varying the enthalpy of vaporization. The best result was obtained for an abnormally high value of  $\Delta H_{\text{vap}}=208 \text{ kJ mol}^{-1}$  and even then the



model underestimates the observed evaporation of Isoprene-OA (Figure S7). Using more reasonable values of  $\Delta H_{\text{vap}}$  for such compounds the discrepancies between our measurements and the predictions are even larger, suggesting that the Lopez-Hilfiker et al. (2016) volatility estimates are not consistent with our results and appear not to represent the full volatility range of Isoprene-OA.

A similar discrepancy exists with the low estimated volatility for the IEPOX SOA by Hu et al. (2016) which is even lower than that of Lopez-Hilfiker et al. (2016) (Figure S6c). One reason for the discrepancy is that their estimate was based on the empirical method of Faulhaber et al. (2009) which has been calibrated using the TD behavior of 5 known compounds and neglecting potential differences in  $\Delta H_{\text{vap}}$ .

These discrepancies clearly show that there is need for additional investigation of the volatility of the various components of the isoprene SOA in the atmosphere.

**Total OA:** Figure S6d compares the total OA volatility estimated in this study to those of Lopez-Hilfiker et al. (2016), Hu et al. (2016), and Saha et al. (2017) for the same location (Centreville) and period. To facilitate the comparison, given that different temperature ranges were used in the above studies, the  $C^*=0.1 \mu\text{g m}^{-3}$  bin is used to represent compounds of even lower volatility than this value. Our results are quite consistent with those of Saha et al. (2017) especially considering the differences in both the TD design and modeling of the results. On the other hand, the Hu et al. (2016) and Lopez-Hilfiker et al. (2016) results suggest an OA with much lower volatility that is inconsistent with our TD measurements.

## 7. Link to the 2D-VBS framework

Figure 4 shows the location of our factors in the 2D-VBS framework of Donahue et al. (2012). The PMF sources locations in the 2D-VBS were estimated using the elemental ratios derived by the method of Aiken et al. (2008) for consistency with the original figure. The O:C of the MO-OOA, LO-OOA, Isoprene-OA and BBOA factors was 0.8, 0.46, 0.44 and 0.46 correspondingly. The MO-OOA factor is in the proposed LV-OOA area but it includes a SVOC component that does not exist in the original 2D-VBS. The LO-OOA factor is quite consistent with the proposed SV-OOA area. The





Isoprene-OA is also located in the SV-OOA area based on our results. Finally, the BBOA factor has the expected volatility range, but is in the upper border of the 2D-VBS BBOA area due to its high oxidation state observed during SOAS.

## 8. Linking the hygroscopicity of OA components to their O:C ratio and volatility

Cerrully et al. (2015) estimated the hygroscopicity  $\kappa$  parameter for each factor for the SOAS campaign for supersaturation  $s=0.4\%$  using PMF analysis on the PILS aerosol. The resulting values were:  $\kappa_{\text{MO-OOA}}=0.16\pm0.02$ ,  $\kappa_{\text{LO-OOA}}=0.08\pm0.02$  and  $\kappa_{\text{Isoprene-OA}}=0.20\pm0.02$ . During the periods of the PILS measurements the BBOA contribution was very low and PMF could not resolve this factor. The Isoprene-OA factor had a higher  $\kappa$  than MO-OOA, but its O:C ratio was lower (0.62) than MO-OOA (1.02). This contradicts Jimenez et al. (2009) which proposed that the hygroscopicity increases linearly as the O:C ratio increases and the recent study of Thalman et al. (2017) which suggested that for OOA factors the relationship between the hygroscopicity and the O:C is linear.

A recent study by Nakao (2017) proposed a theoretical description for the linkage between the O:C ratio, volatility and hygroscopicity. Figure S8 illustrates the experimental saturation concentrations and  $\kappa$  parameters for known compounds found in the literature (Table S3 and S4) together with the Nakao (2017) estimations. The isolines in this figure represent the intrinsic  $\kappa$  which corresponds to the upper limit of  $\kappa$  assuming that the organic species are entirely soluble. The location of the selected known compounds was generally in agreement with the suggested by Nakao (2017) intrinsic  $\kappa$  isolines for  $\kappa$  higher than 0.1. For  $\kappa$  lower than 0.1 the experimental values were underestimated compared to the theoretical  $\kappa$ . This discrepancy could be due to the fact that the compounds in the area with  $\kappa$  above 0.1 are more water soluble than those in the area with  $\kappa$  below 0.1. For example, the solubility of malonic acid is  $1161 \text{ g L}^{-1}$  (Saxena and Hildemann 1996), while the water solubility of suberic acid is  $2.46 \text{ g L}^{-1}$  (Bretti et al., 2006).

Xu et al. (2017) calculated the water solubility of the MO-OOA, LO-OOA and Isoprene-OA in Centreville during the SOAS campaign and found it 100%, 47% and 83% correspondingly. Thus, the intrinsic  $\kappa$  of MO-OOA, LO-OOA and Isoprene-OA is correspondingly  $0.16\pm0.02$ ,  $0.17\pm0.04$  and  $0.24\pm0.03$ . Figure 5 shows the intrinsic  $\kappa$





values of our factors in the 2D-VBS and the Nakao (2017) frameworks. The MO-OOA and LO-OOA values are close to the Nakao (2017) proposed intrinsic  $\kappa$  isolines. However, the Isoprene-OA experimental intrinsic  $\kappa$  (0.24) is higher than the theoretical (0.13). One reason for this disagreement could be the O:C estimate by the AMS. Canagaratna et al. (2015) measured the O:C ratio of a racemic mixture of  $\delta$ -Isoprene epoxydiols ( $C_5H_{10}O_3$ ) and found it around 0.4, which is 1.5 times lower than the theoretical (0.6). If the Isoprene-OA factor behaves similarly to the racemic mixture, its O:C may in fact be as high as 0.9, corresponding to a higher theoretical (Nakao 2017) intrinsic  $\kappa=0.19$ , which is closer to the experimental value (0.24). Although our results cannot be fully explained by the theoretical framework of (Nakao 2017), they denote that the relationship between hygroscopicity, volatility and O:C ratio is rather complicated. The model of Nakao (2017) is based on numerous assumptions that may not always be valid and which could introduce errors in the  $\kappa$  isolines estimation. Recently, Rastak et al. (2017) concluded that the hygroscopicity should be described using more than a single parameter. In addition, Kerrigan and Pandis (2017) suggested that the hygroscopicity could exhibit a maximum at intermediate volatilities.

## 9. Conclusions

The volatility distribution of the OA factors found during the SOAS campaign was estimated using measurements by a thermodenuder coupled with a HR-AMS. Using both the ambient and the thermodenuder data the same four sources were identified compared to the ambient only PMF analysis. The four sources were attributed to MO-OOA, LO-OOA, Isoprene-OA and BBOA. The contribution, the times series and the mass spectra of each factor were similar to the case of the ambient-only PMF. Using the MFRs and the thermodenuder model of Riipinen et al. (2010) the volatility distribution and the vaporization enthalpy of each factor was estimated assuming an accommodation coefficient of unity.

MO-OOA was significantly more oxygenated than LO-OOA, but in contrast with previous studies, its MFR was much lower. According to the model, the MO-OOA was less volatile than the LO-OOA and the implausible behavior of the measured MFR was due to their different effective enthalpies of evaporation:  $89\pm 10$  kJ mol<sup>-1</sup> for the MO-



519 OOA and  $58 \pm 13$  kJ mol<sup>-1</sup> for the LO-OOA. Isoprene-OA had a similar volatility  
520 distribution with MO-OOA, but its vaporization enthalpy was lower at  $63 \pm 15$  kJ mol<sup>-1</sup>.  
521 BBOA had the lowest O:C ratio but it was the least volatile OA component with a  
522 vaporization enthalpy of  $55 \pm 11$  kJ mol<sup>-1</sup>. All factors, included components with a wide  
523 range of volatilities, both semi-volatile and low volatility. The use of a relatively modest  
524 highest temperature (100°C) did not allow the characterization of the least volatile  
525 components of the various factors. The above results suggest that variations in the  
526 enthalpy of vaporization can introduce significant variability in the links between the  
527 measured MFR and the estimated volatility.

528 The contradicting result of the higher MFR of the MO-OOA compared to that of  
529 LO-OOA denotes that depending on the study the behavior of the OOA factors can be  
530 quite variable. It shows that OOA factors are composed of organic compounds with a  
531 wide range of volatility distributions, which may overlap a lot each other. One possible  
532 reason could be the existence of small highly oxygenated molecules. The direct  
533 comparison of the MFR of OOA factors from different or even from the same study is  
534 risky since MFR depends on the TD operation and characteristics, the aerosol size  
535 distribution, the volatility, etc.

536 The counterintuitive finding of Cerully et al. (2015), that Isoprene-OA was more  
537 hygroscopic than MO-OOA even though it had a lower O:C ratio, but similar volatility  
538 distribution, are close but not fully explained by the framework proposed by Nakao  
539 (2017). Future studies are necessary for a comprehensive understanding of the  
540 relationship between the hygroscopicity, volatility and O:C ratio.

541

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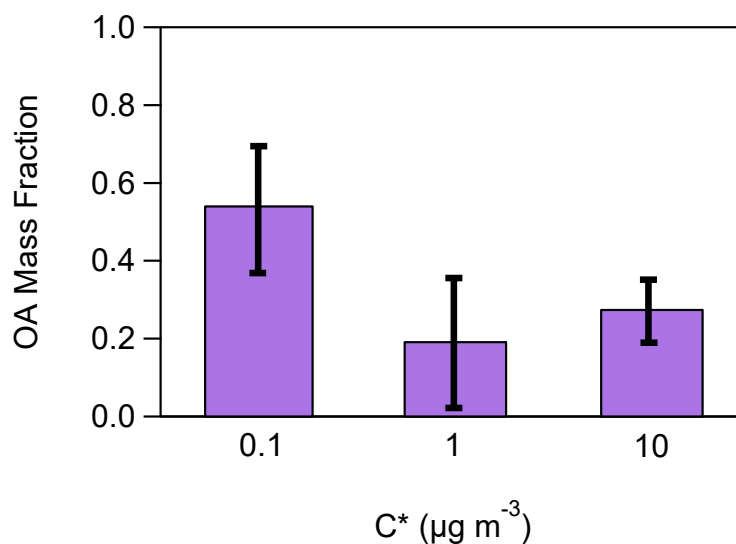
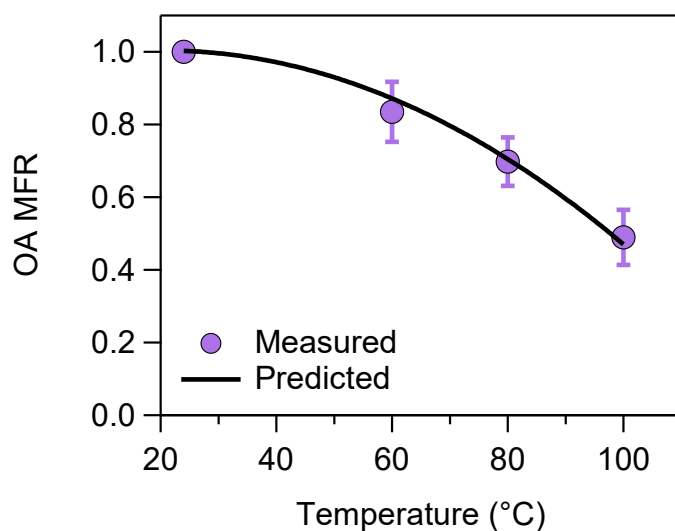
**Table 1.** Average ambient concentration of each factor and total OA, and the corresponding fraction of the data above the threshold ( $0.2 \mu\text{g m}^{-3}$ ).

Factor	Average Ambient Concentration ( $\mu\text{g m}^{-3}$ )	% of Measurements above the Threshold
MO-OOA	1.96	92
LO-OOA	1.66	96
Isoprene-OA	0.9	76
BBOA	0.5	42
Total OA	5.02	99



**Table 2.** OA mass fractions of the ambient and ambient+TD PMF factors.

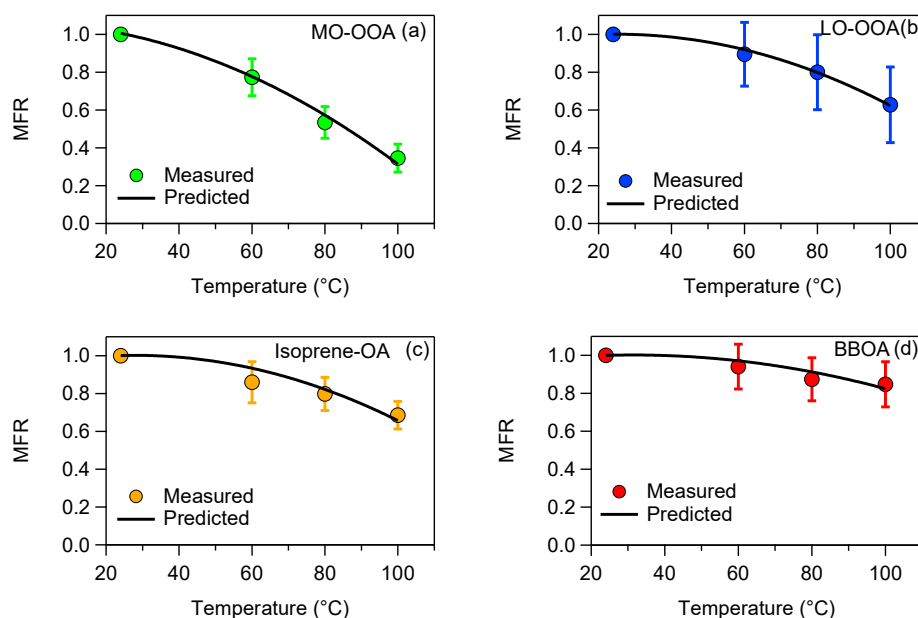
<b>Data Used</b>	<b>MO-OOA</b> (%)	<b>LO-OOA</b> (%)	<b>Isoprene-OA</b> (%)	<b>BBOA</b> (%)
Ambient only	39	32	18	10
Ambient+TD	43	29	19	9



**Figure 1.** (a) Loss-corrected MFR of the total OA. The purple circles correspond to the measurements and the uncertainties to one standard deviation of the mean. It is assumed that MFR=1 at T=24°C. The black line is the model fit estimated using the approach of

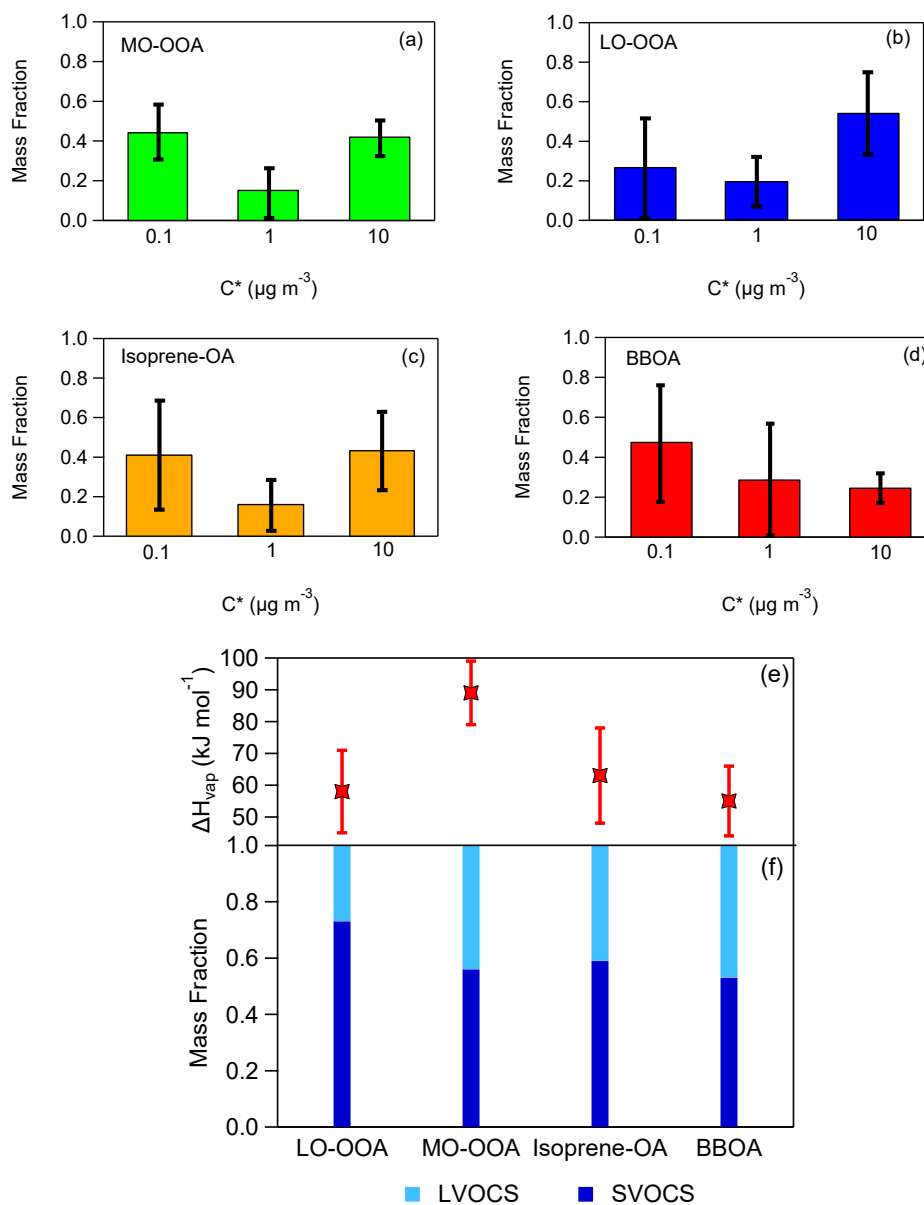


909 Karnezi et al. (2014). (b) The total OA volatility distribution. The uncertainties have been  
 910 estimated according to the algorithm of Karnezi et al. (2014).  
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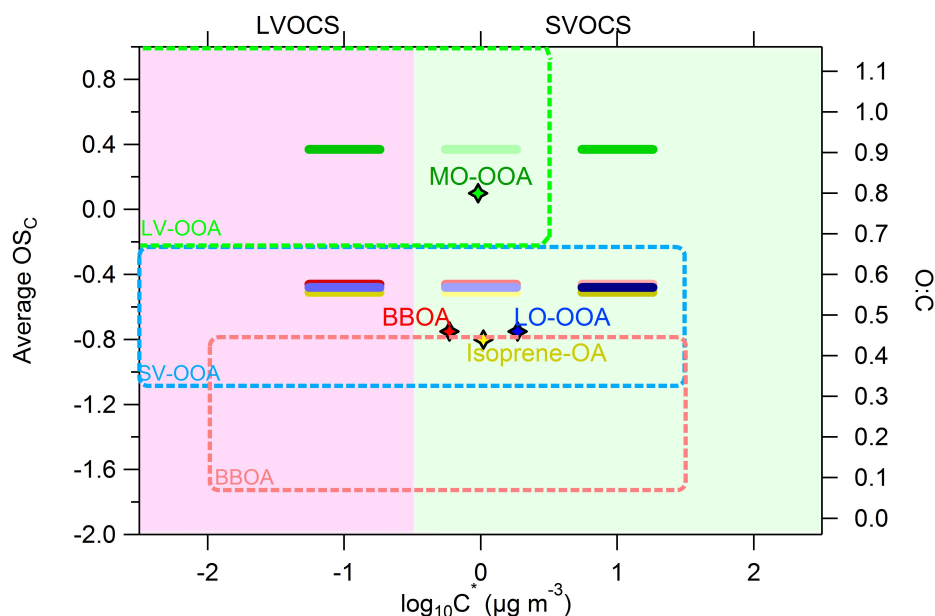
913  
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 915 **Figure 2.** MFRs of the loss-corrected PMF OA factors. The circles represent the  
 916 measurements with the one standard deviation of the mean. The black line corresponds to  
 917 the best predicted MFR using the algorithm of Karnezi et al. (2014).

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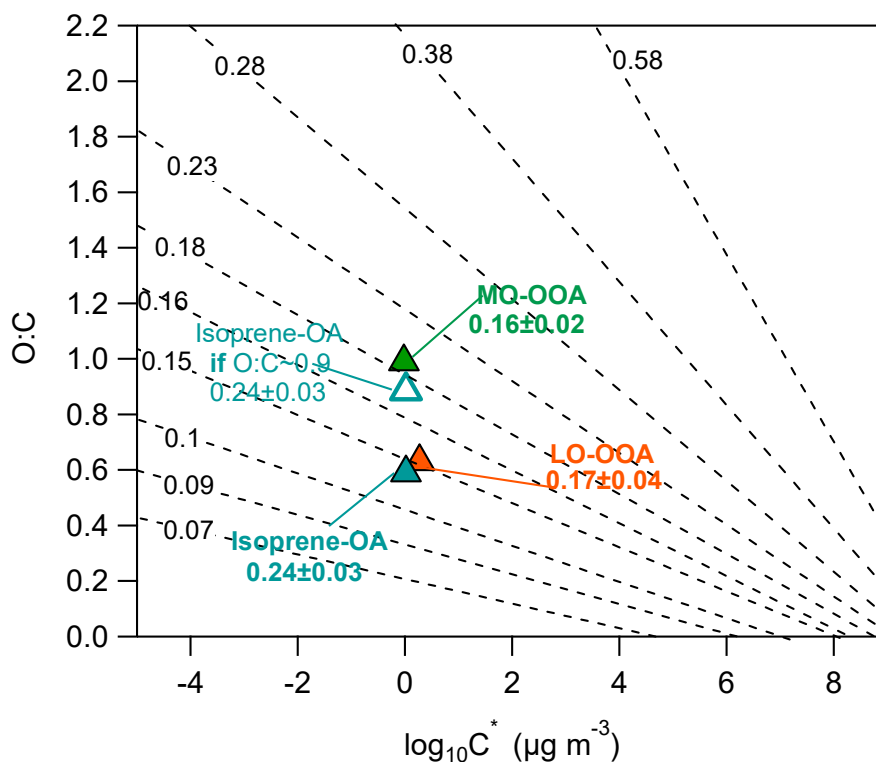


**Figure 3.** (a)-(d) Predicted volatility distributions of the OA PMF factors. The error bars correspond to the uncertainties derived using the approach of Karnezi et al. (2014), (e) vaporization enthalpies comparison between the four OA factors and (f) volatility compositions comparison between the four OA factors.





**Figure 4.** Average carbon oxidation state  $OS_C$  (left y axis) and O:C ratio (right axis) versus the saturation concentration in terms of  $\log_{10} C^*$ . The horizontal bars are the volatility distributions of the SOAS PMF factors: MO-OOA (green), LO-OOA (blue), Isoprene-OA (yellow) and BBOA (red). The darker the color of the horizontal bars the higher the mass fractional contribution for the corresponding  $C^*$  bin. The diamonds represent the average  $\log_{10} C^*$  value for a given PMF factor. The green, light blue and pink dashed areas are the locations of the LV-OOA, SV-OOA and BBOA PMF factors as proposed by Donahue et al. (2012).



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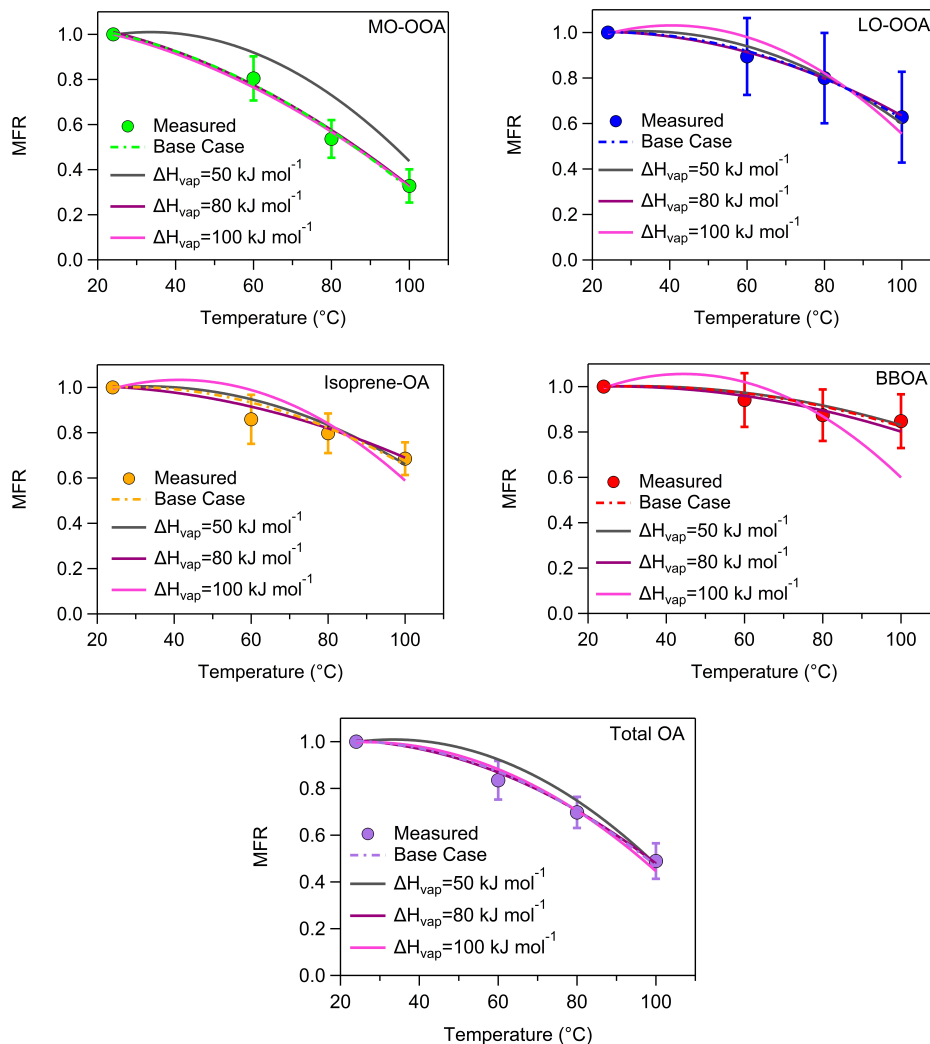
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950 **Figure 5.** O:C ratios versus the average volatility as  $\log_{10}C^*$ . The black isolines  
 951 correspond to the theoretically intrinsic  $\kappa$  suggested by Nakao et al. (2017). The triangles  
 952 denote the SOAS PMF factors. The hygroscopicity of the SOAS PMF factors has been  
 953 transformed into the intrinsic  $\kappa$ , using the water solubility results of Xu et al. (2017). The  
 954 open cyan triangle corresponds to the Isoprene-OA with a hypothetical O:C=0.9.

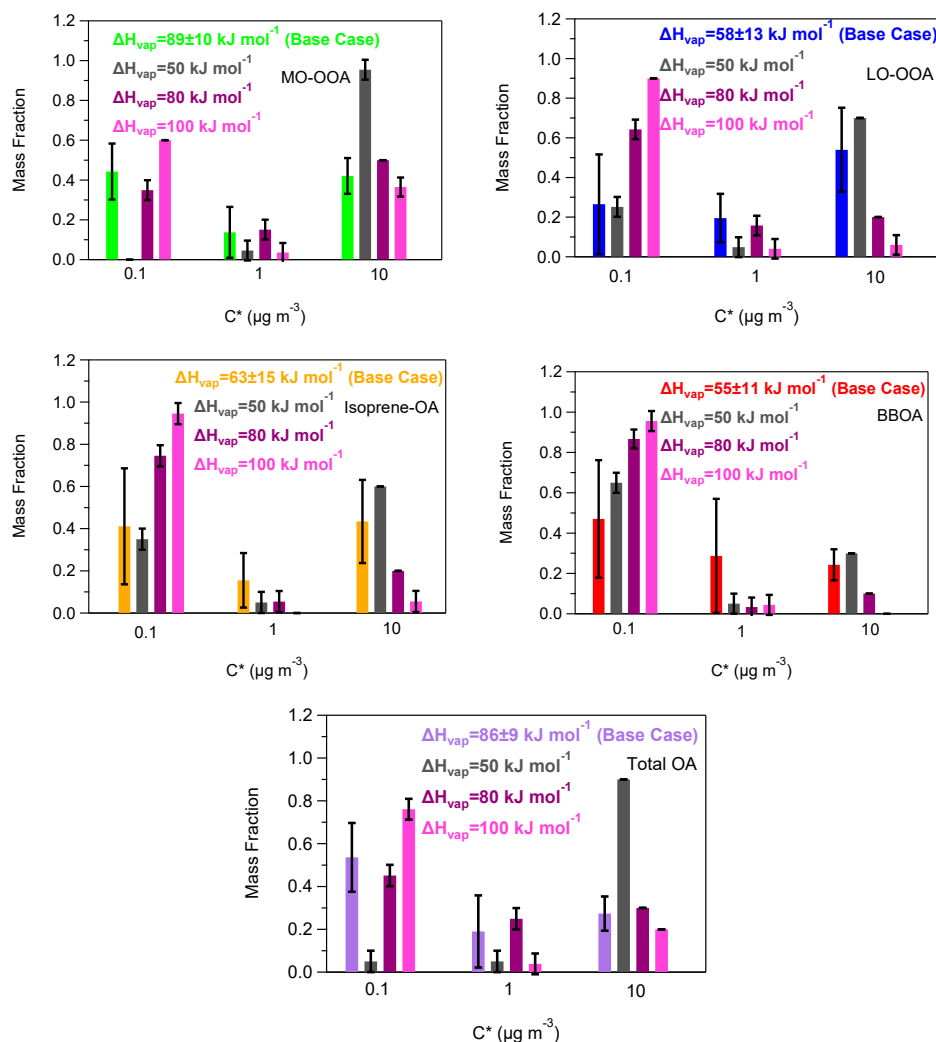
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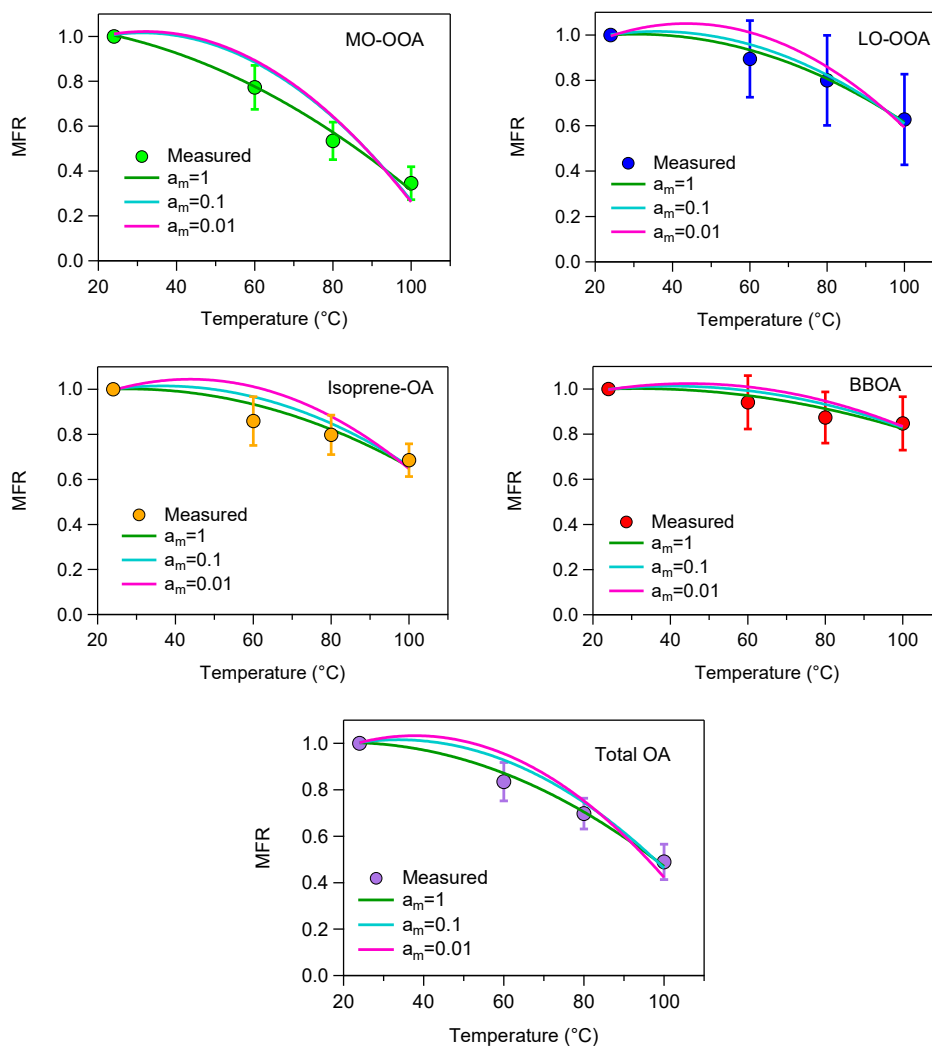
## Appendix



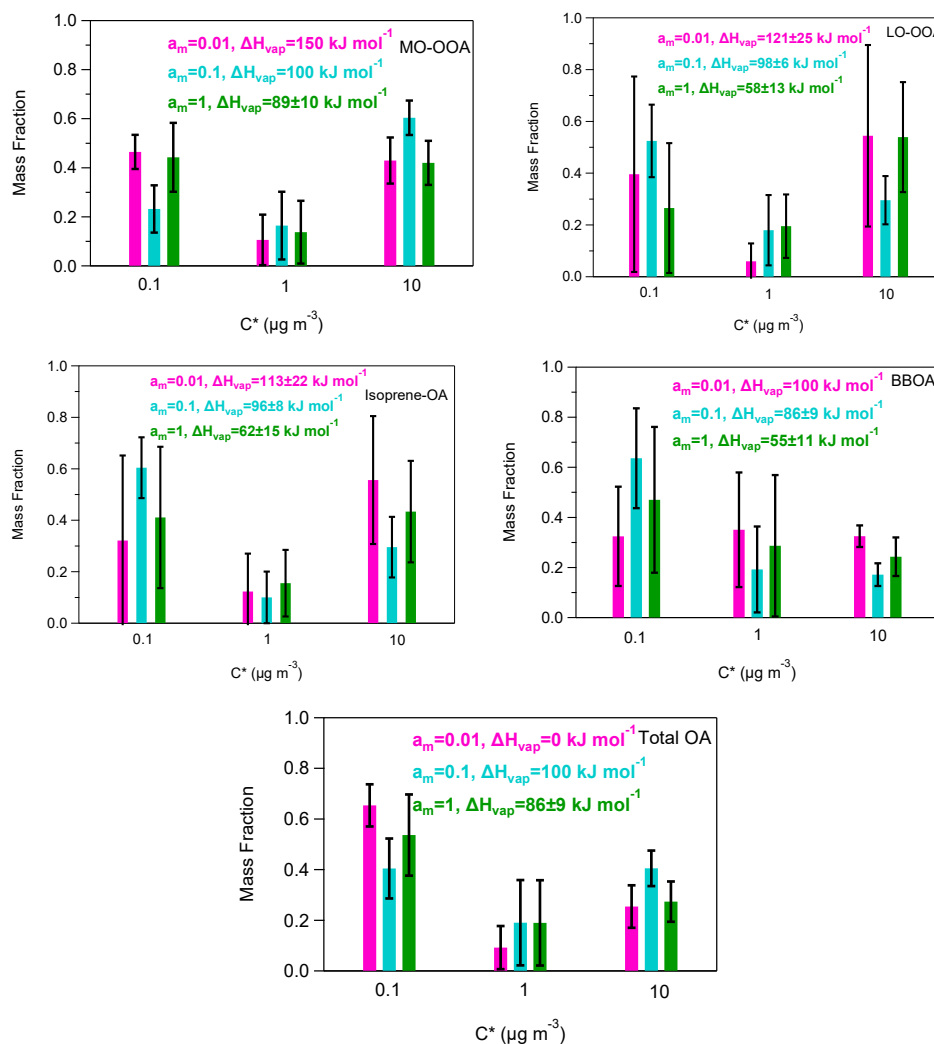
**Figure A1.** MFRs of the loss-corrected PMF OA factors and total OA for fixed values of the vaporization enthalpy. The circles denote the measurements with the one standard deviation of the mean, the dash lines correspond to the base case, the grey lines represent the case of a constant  $\Delta H_{\text{vap}}$  of 50 kJ mol<sup>-1</sup>, the magenta lines stand for the case of a constant  $\Delta H_{\text{vap}}$  of 80 kJ mol<sup>-1</sup> and the pink lines correspond to the case of a constant  $\Delta H_{\text{vap}}$  of 100 kJ mol<sup>-1</sup>.



**Figure A2.** Predicted volatility distributions of the OA PMF factors and total OA for fixed vaporization enthalpy. The error bars are estimated using the approach of Karnezi et al. (2014). The grey bars represent the results of a constant  $\Delta H_{\text{vap}}$  of 50 kJ mol<sup>-1</sup>, the magenta bars correspond to the solution of a constant  $\Delta H_{\text{vap}}$  of 80 kJ mol<sup>-1</sup>, while and the pink bars are the results for the case of a constant  $\Delta H_{\text{vap}}$  of 100 kJ mol<sup>-1</sup>. The green, blue, orange, red and purple bars stand for the base case solutions of MO-OOA, LO-OOA, Isoprene-OA, BBOA and total OA.



**Figure A3.** MFRs of the loss-corrected PMF OA factors and total OA. The circles denote the measurements with the one standard deviation of the mean, the green lines represent the best predicted MFR for  $a_m=1$  (base case), the cyan lines correspond to the best predicted MFR for  $a_m=0.1$ , while the pink lines stand for the predicted MFR for  $a_m=0.01$ .



**Figure A4.** Predicted volatility distributions of the OA PMF factors and total OA. The error bars are estimated using the approach of Karnezis et al. (2014). The green bars represent the results for  $a_m = 1$  (base case), the cyan bars correspond to the solution for  $a_m = 0.1$ , while and the pink bars are the results for  $a_m = 0.01$ .