Supplement of Atmos. Chem. Phys., 20, 10441–10458, 2020
https://doi.org/10.5194/acp-20-10441-2020-supplement

Supplement of

Comparing secondary organic aerosol (SOA) volatility distributions derived from isothermal SOA particle evaporation data and FIGAERO–CIMS measurements

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Supplementary material

FIGAERO-CIMS calibration

Figure S1 shows the results of the T_{max} to P_{sat} calibration measurements done using polyethylene glycols (PEG) solutions in acetonitrile with 5 to 8 glycol units (blue dots). A bivariate linear fit (Pitkänen et al., 2016; York et al., 2004) that takes the uncertainties of the points into account was then applied to normal logarithm of the P_{sat} values as a function of measured T_{max} values. Literature values of P_{sat} with uncertainties were taken from Krieger et al., (2018) and standard deviation of three T_{max} measurements was used as uncertainty for T_{max} values.

References

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Pitkänen, M. R. A., Mikkonen, S., Lehtinen, K. E. J., Lipponen, A. and Arola, A.: Artificial bias typically neglected in comparisons of uncertain atmospheric data, Geophysical Research Letters, 43(18), 10,003-10,011, doi:10.1002/2016GL070852, 2016.

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Table S1: Minimum, mean and maximum time that the particles have evaporated during the FIGAERO sample collection. All times are relative to the start of RTC filling.

Sample	Minimum evaporation time (min)	Mean evaporation time (min)	Maximum evaporation time (min)
Medium O:C high RH fresh	0	15	30
Medium O:C high RH RTC	173	216	259
Medium O:C dry fresh	0	15	30
Medium O:C dry RTC	170	213	256
Low O:C high RH fresh	0	15	30
Low O:C high RH RTC	168	211	254
Low O:C dry fresh	0	15	30
Low O:C dry RTC	152	195	238

Table S2: The best fit C^* values for medium O:C and low O:C high RH experiments when C^* values of PMF factors were optimized with respect to the measured isothermal evaporation. For each experiment three different results are given which correspond to simulations initialized with the PMF mole fraction at the minimum, mean and maximum time that the particles have evaporated during the sample collection (See Table S1). The C^* values are rounded to two significant digits and are in units μgm^{-3}. C^* values below 10^{-3} μgm^{-3} are not reported explicitly since the evapogram fitting method is not sensitive to these values.

	Medium O:C fresh sample min evap. time	Medium O:C fresh sample mean evap. time	Medium O:C fresh sample max evap. time	Medium O:C RTC sample min evap. time	Low O:C fresh sample min evap. time	Low O:C fresh sample mean evap. time	Low O:C fresh sample max evap. time	Low O:C RTC sample min evap. time
Factor M1/L1	3.47	$4.96 \cdot 10^{-1}$	$1.48 \cdot 10^{-1}$	36.10	11.40	$3.06 \cdot 10^{-1}$	$8.91 \cdot 10^{-2}$	$<10^{-3}$
Factor M2/L2	$2.89 \cdot 10^{-1}$	$2.89 \cdot 10^{-1}$	$2.17 \cdot 10^{-1}$	$4.12 \cdot 10^{-1}$	$6.79 \cdot 10^{-1}$	$3.55 \cdot 10^{-1}$	$3.63 \cdot 10^{-1}$	$2.40 \cdot 10^{-2}$
Factor M3/L3	$1.00 \cdot 10^{-2}$	$9.93 \cdot 10^{-3}$	$2.11 \cdot 10^{-3}$	$4.42 \cdot 10^{-3}$	$2.88 \cdot 10^{-2}$	$2.87 \cdot 10^{-2}$	$9.55 \cdot 10^{-3}$	$7.13 \cdot 10^{-3}$
Factor M4/L4	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$1.55 \cdot 10^{-3}$	$1.54 \cdot 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$
Factor M5/L5	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$
Factor D1a	96.63	$7.68 \cdot 10^{-1}$	$9.86 \cdot 10^{-2}$	69.35	133.83	130.03	$3.49 \cdot 10^{-1}$	$1.04 \cdot 10^{-1}$
Factor D1b	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$

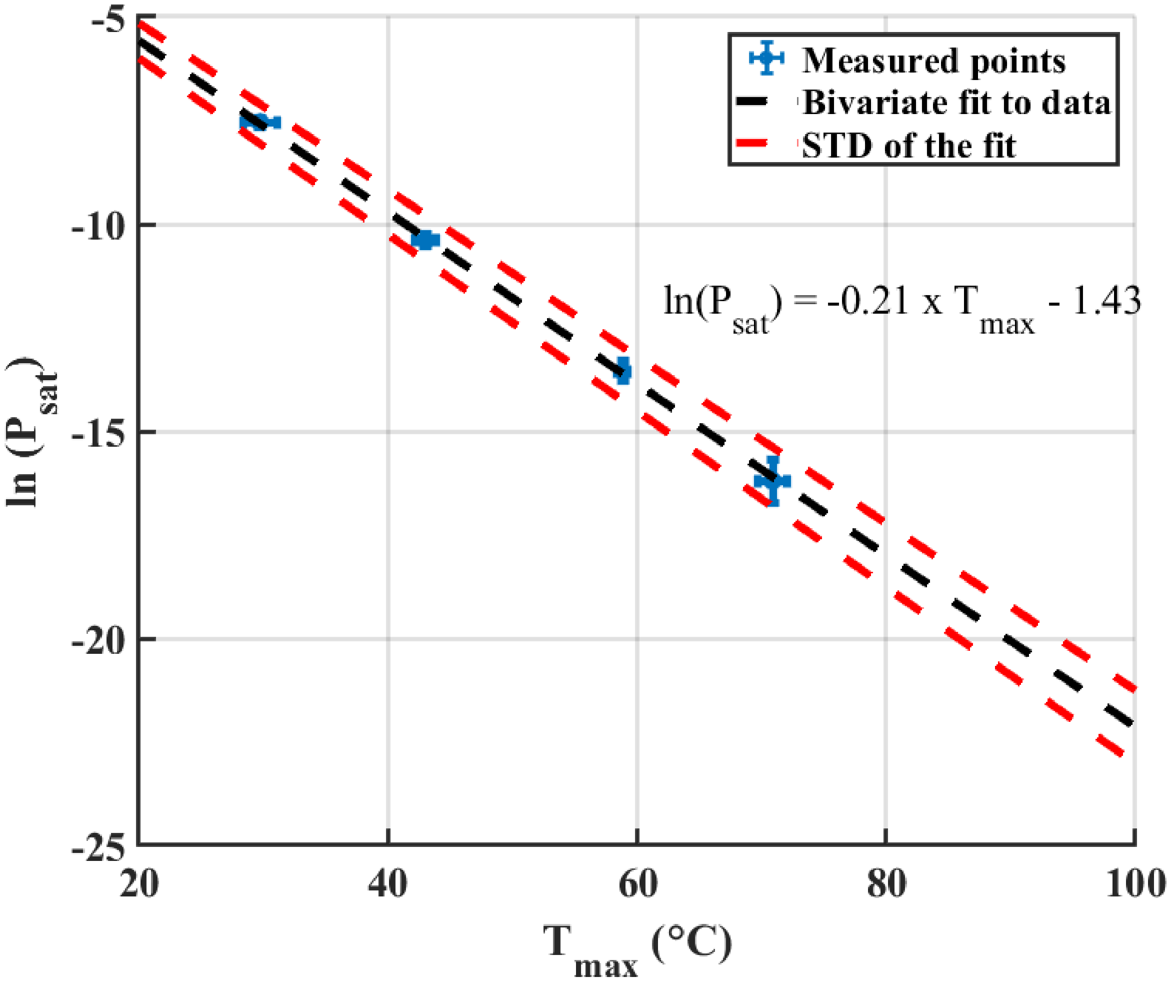

Figure S1: Calibration measurements and fitted parametrization which connects the maximum desorption temperature T_{max} to saturation vapor pressure P_{sat}.

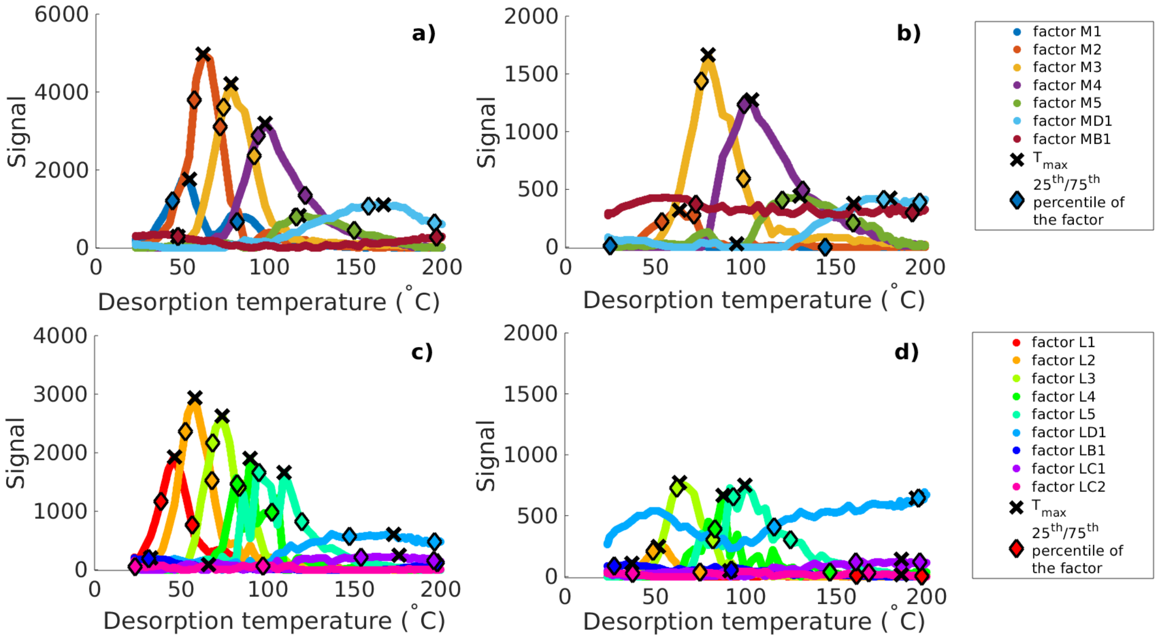

Figure S2: Full positive matrix factorization (PMF) mass loading profiles for thermal desorption of secondary organic aerosol (SOA) from α-pinene at high RH conditions.

a) Fresh sample of medium O:C SOA

b) Residual particles of medium O:C SOA after 173-259 minutes of evaporation in a residence time chamber (RTC), i.e. the RTC sample

c) Fresh sample of low O:C SOA

d) Residual particles of low O:C SOA after 168-254 minutes of evaporation in the RTC, i.e. the RTC sample.

The black crosses show the peak desorption temperature T_{max} and the diamonds show the 25th and 75th percentiles of the factors area. In medium O:C samples' analysis, factor MB1 is omitted and factor MD1 is divided into a new factors MD1a and MD1b. In low O:C samples' analysis, factors LC1 and LC2 are omitted and factor LD1 is divided into new factors LD1a and LD1b. See Sect. 3.1 in the main text for details.

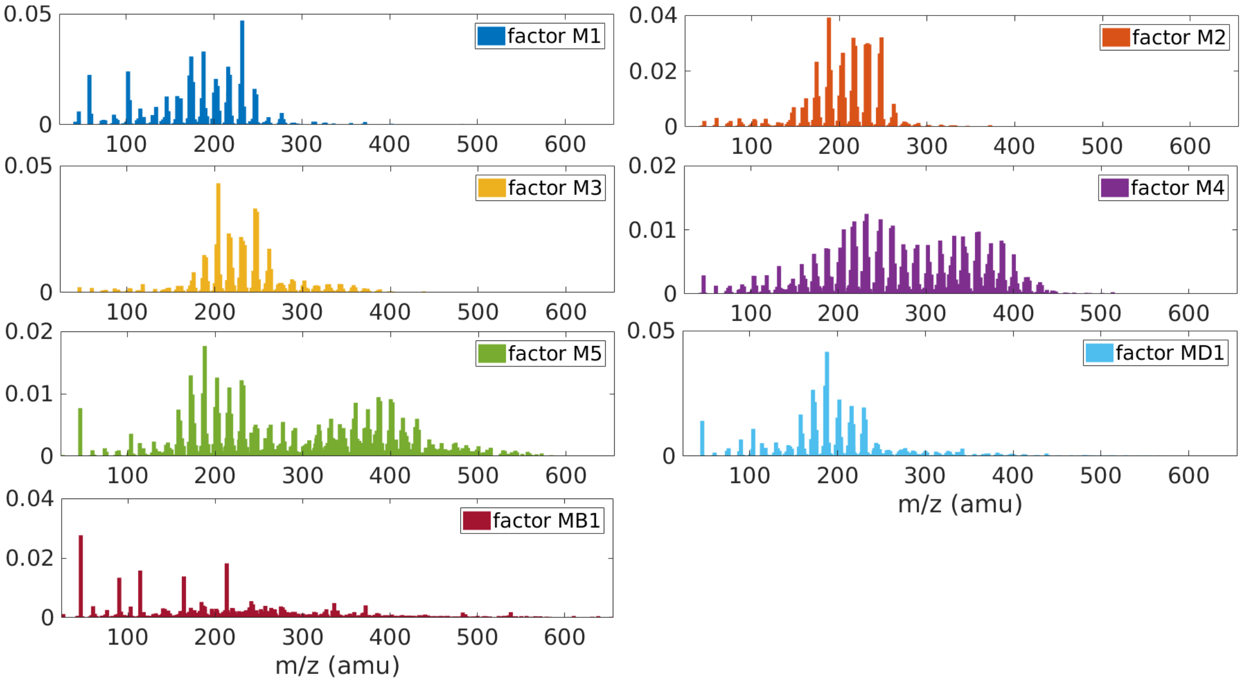

Figure S3: PMF mass spectra for medium O:C samples. These factors correspond to factors shown in Fig. S2.

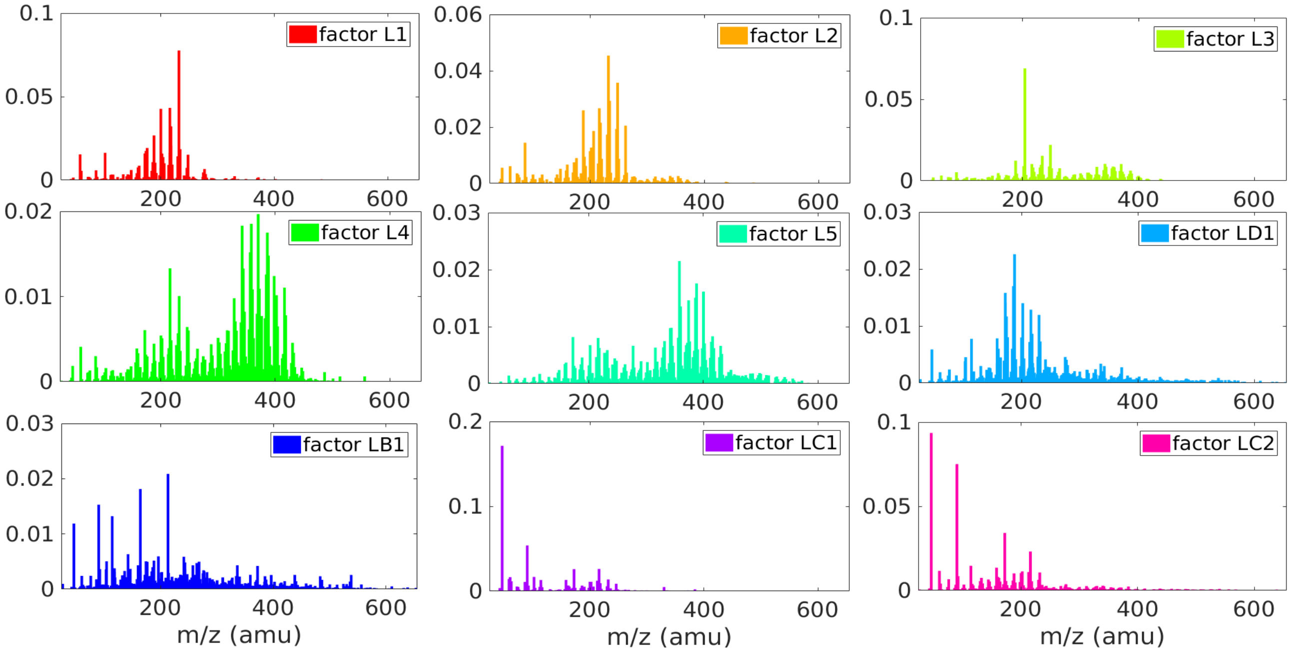

Figure S4: PMF mass spectra for low O:C samples. These factors correspond to factors shown in Fig. S2.

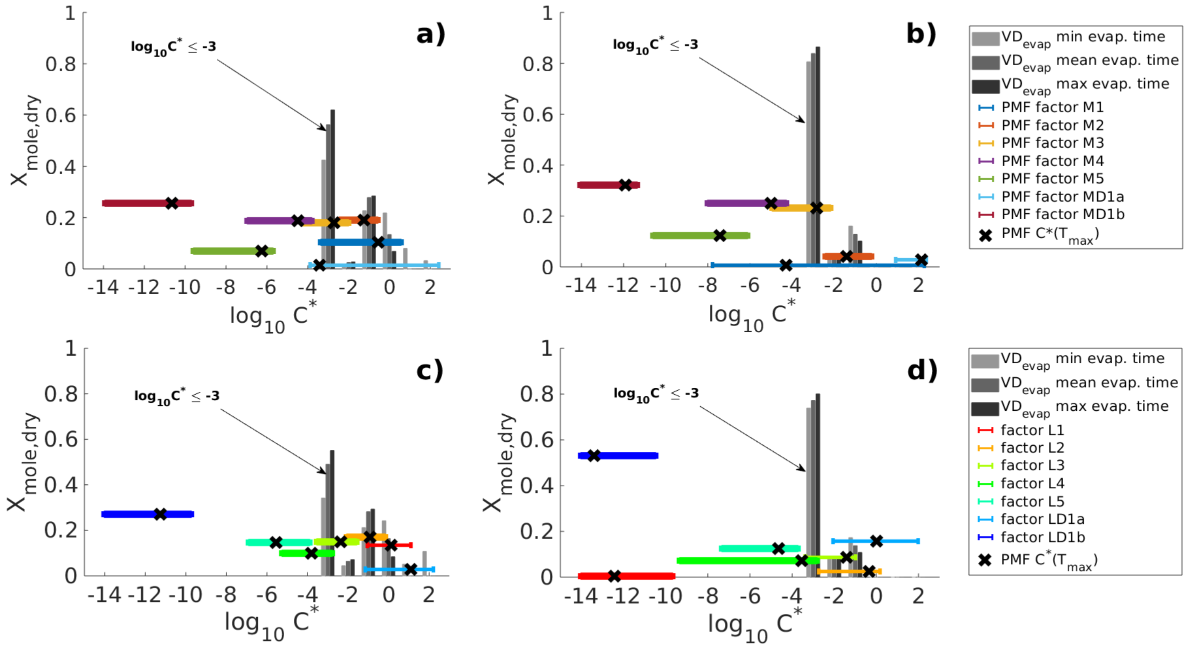

Figure S5: Volatility distributions in high RH experiments determined from model fitting of evapogram data (VD_{evap}) and PMF analysis of FIGAERO-CIMS data (VD_{PMF}) for the same four cases shown in Fig. S2

a) Fresh sample of medium O:C SOA

b) Residual particles of medium O:C SOA (the RTC sample)

c) Fresh sample of low O:C SOA

d) Residual particles of low O:C SOA (the RTC sample).

VD_{evap} is shown for the best fit simulation (grey bars). The different grey shades show the VD_{evap} in the simulation at minimum, mean and maximum time that the particles have evaporated when the FIGAERO sample was collected (see Table S1). Black crosses show the $\log_{10}(C^*)$ calculated for each PMF factor from the peak desorption temperature T_{max}. The horizontal colored lines show the range of $\log_{10}(C^*)$ calculated from the 25th and 75th percentiles of each PMF factors mass loading profile.

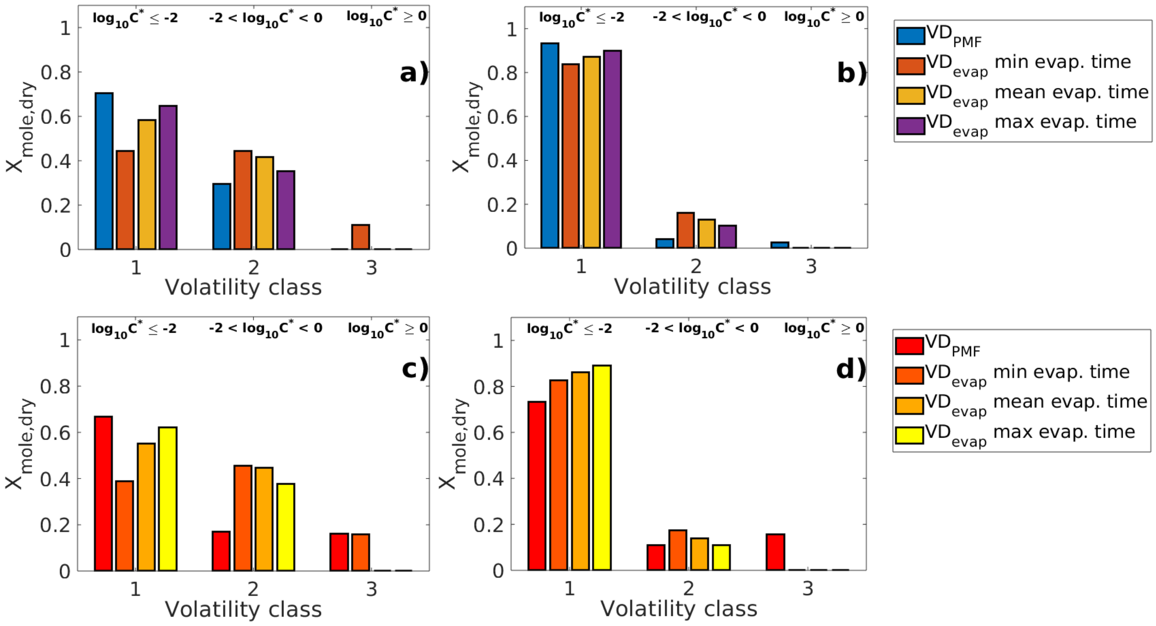

Figure S6: Comparison of VD_{PMF} and VD_{evap} in high RH experiments for the same four cases shown in Fig. S2.
a) Fresh sample of medium O:C SOA
b) Residual particles of medium O:C SOA (the RTC sample)
c) Fresh sample of low O:C SOA
d) Residual particles of low O:C SOA (the RTC sample).
The VD compounds are grouped into three different volatility classes. Min, mean and max evaporation time refer to the FIGAERO sample collection times presented in Table S1. The VD compounds shown in Fig. S5 are grouped into three different volatility classes based on their evaporation tendency with respect to the measurement time scale and particle size. The limits for each volatility class are shown at the top and are the same for each subfigure.

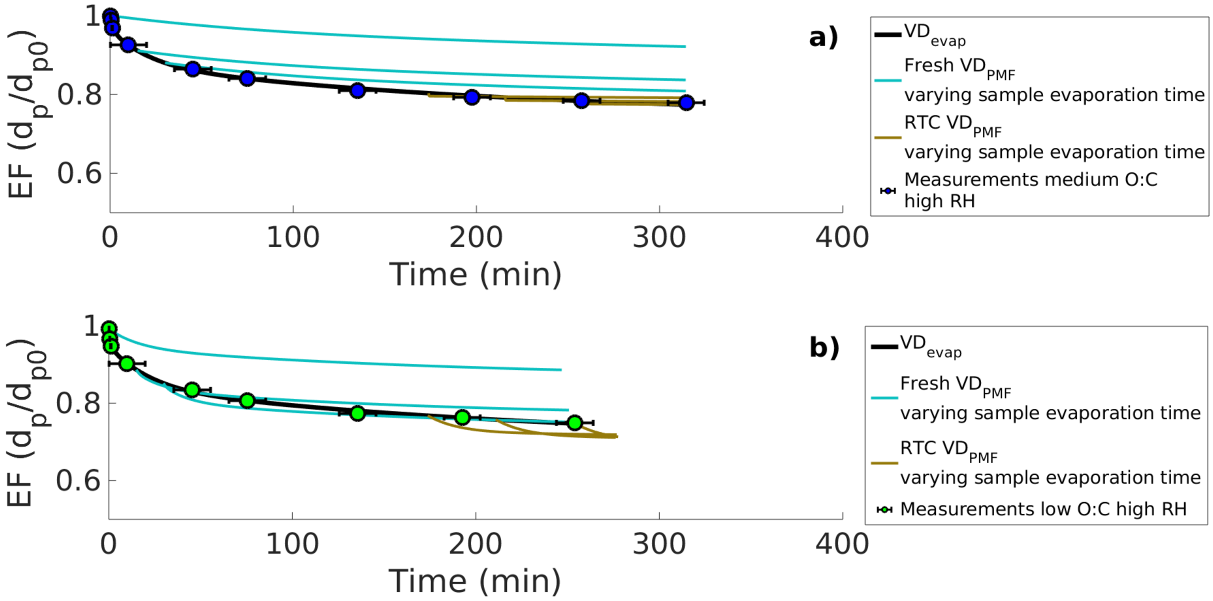

Figure S7: Evapograms of high RH experiments showing the measured evaporation factors (remaining fraction of initial particle diameter; circles) and their uncertainty in time for a) medium O:C SOA and b) low O:C SOA, LLEVAP simulated evapograms calculated using the best fit VD_{evap} (black solid lines) and LLEVAP simulated evapograms calculated with VD_{PMF} (turquoise solid lines for VD_{PMF} of fresh samples and light brown solid lines for VD_{PMF} of the RTC samples). The three turquoise and brown lines present model simulations where the fresh and RTC sample, respectively, were assumed to represent the particle composition at the minimum, mean or maximum evaporation time of the sample (see Table S1).

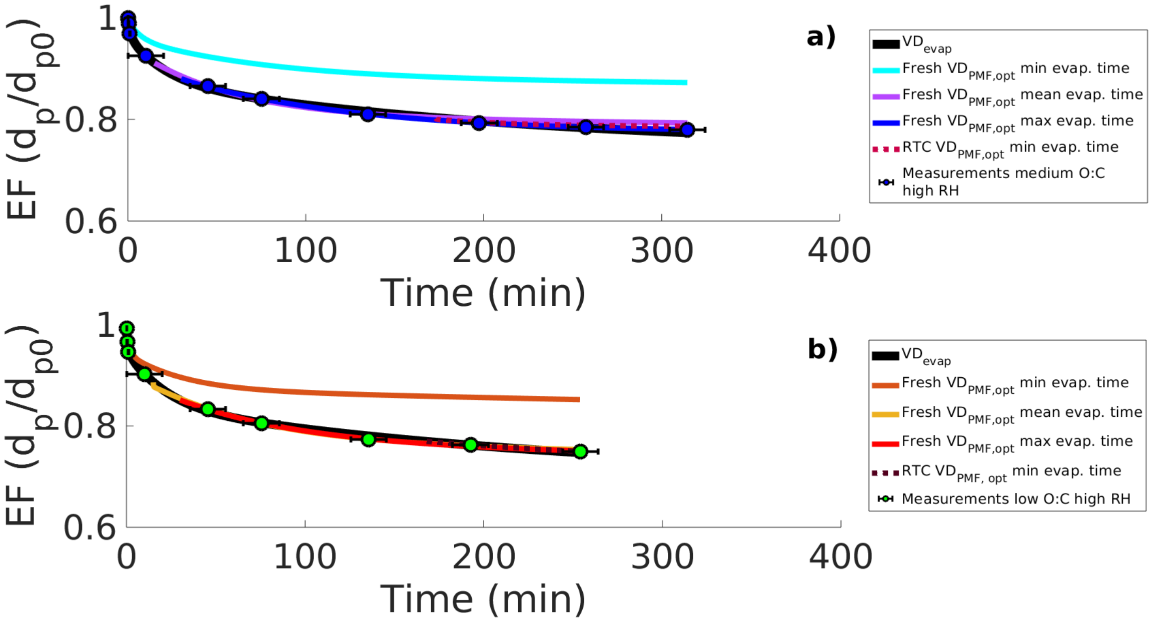

Figure S8: Evapograms of high RH experiments showing the measured evaporation factors (circles) and their uncertainty in time (black whiskers), the best fit simulated evapogram calculated with VD_{evap} (black solid line) and the best fit simulated evapograms calculated with the volatility distribution where the effective saturation concentration (C^*) of each PMF factors are fitted to the measurements ($VD_{PMF,opt}$).

a) Medium O:C SOA

b) Low O:C SOA.

The colored solid lines are for the fresh SOA with varying starting time of the simulation. These simulations assumed that the fresh sample represented the particle composition at the minimum, mean or maximum evaporation time of the fresh FIGAERO-CIMS sample. The dashed lines are showing the simulations based on the SOA collected from the RTC after 173-259 minutes and 168-254 minutes of evaporation for medium O:C and low O:C SOA, respectively. For these residual particle samples, the FIGAERO-CIMS sample was assumed to represent the minimum evaporation time of the sample (see Sect. 3.2 in the main text). For fitting, the C^* of each PMF factor were allowed values from their respective 25th and 75th percentile desorption temperature shown in Fig. S5.

The simulations of the fresh samples that start at the mean or maximum evaporation time resemble the measured evaporation and the evaporation simulations calculated with the VD_{evap}. The simulation of the fresh sample that starts from the minimun evaporation time does not produce evaporation curve similar to the measurements. The results highlight the fact that it is not likely that the fresh sample consists of particles that have just entered the residence time chamber.

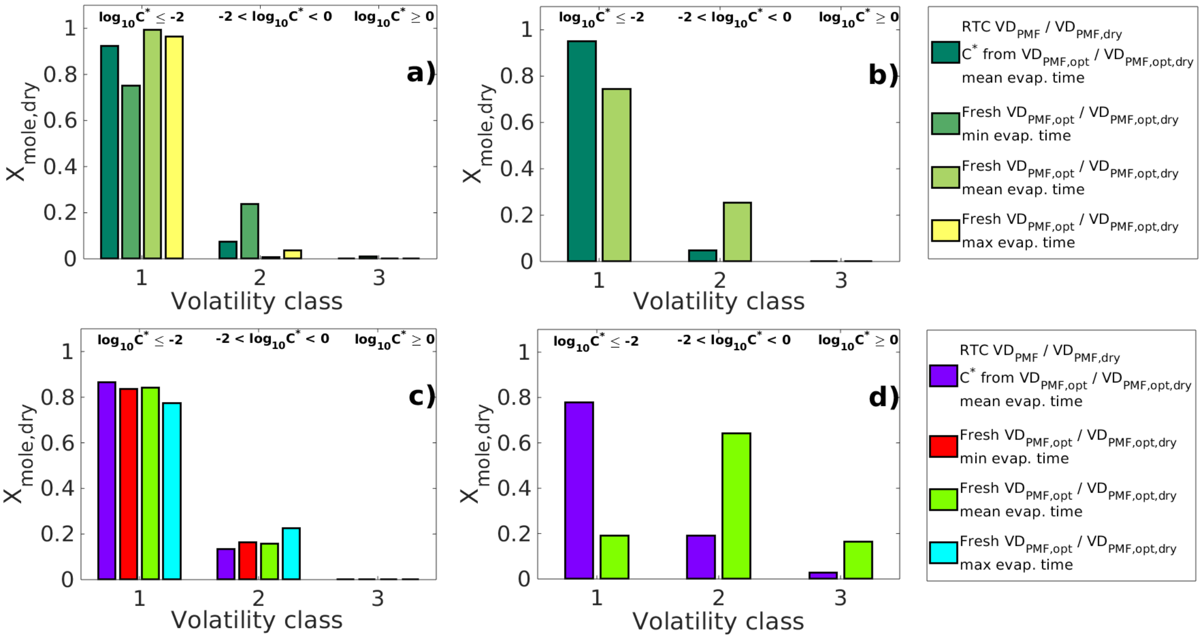

Figure S9: Comparison of the simulated particle composition ($\mathrm{VD}_{\mathrm{PMF,opt}}$, $\mathrm{VD}_{\mathrm{PMF,opt,dry}}$) at varying assumed sample evaporation times to the particle composition determined for SOA collected from the RTC ($\mathrm{VD}_{\mathrm{PMF}}$/$\mathrm{VD}_{\mathrm{PMF,dry}}$) after 173-259 minutes and 168-254 minutes of evaporation for medium O:C and low O:C SOA, respectively. The simulated compositions ($\mathrm{VD}_{\mathrm{PMF,opt}}$ in a and c, $\mathrm{VD}_{\mathrm{PMF,opt,dry}}$ in b and d) are taken from the best fit simulated evapogram obtained from the optimization of the C^* values of fresh sample PMF factors to measured evapogram. The volatility of individual VD compounds are grouped into three volatility classes similar to Fig. S6. The limits for each class are shown at the top and are the same for each subfigure. The C^* values from $\mathrm{VD}_{\mathrm{PMF,opt}}$/$\mathrm{VD}_{\mathrm{PMF,opt,dry}}$ at the mean evaporation time were used for corresponding $\mathrm{VD}_{\mathrm{PMF}}$/$\mathrm{VD}_{\mathrm{PMF,dry}}$ when the volatility grouping was calculated in order to ensure the comparability.
a) Medium O:C SOA in high RH experiment
b) Medium O:C SOA in low RH experiment
c) Low O:C SOA in high RH experiment
d) Low O:C SOA in low RH experiment.
The results of medium O:C SOA in high RH experiments show that the $\mathrm{VD}_{\mathrm{PMF}}$ best resembles the $\mathrm{VD}_{\mathrm{PMF,opt}}$ of the maximum evaporation time, although the difference to the mean evaporation time is not significant. For low O:C SOA in high RH experiments, the results show that the $\mathrm{VD}_{\mathrm{PMF}}$ best resembles the $\mathrm{VD}_{\mathrm{PMF,opt}}$ of the mean evaporation time.

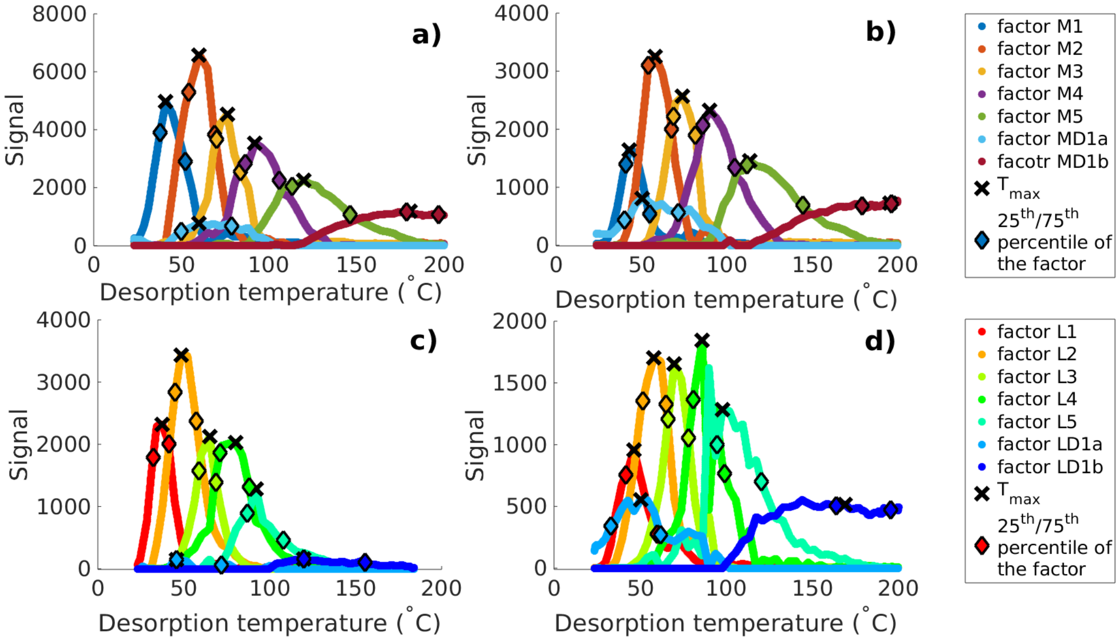

Figure S10: Main PMF mass loading profiles from experiments done in dry conditions.
a) Fresh sample of medium O:C SOA
b) Residual particles of medium O:C SOA after 170-256 minutes of evaporation in a residence time chamber (RTC), i.e. the RTC sample
c) Fresh sample of low O:C SOA
d) Residual particles of low O:C SOA after 152-238 minutes of evaporation in the RTC. The black crosses show the peak desorption temperature T_{max} and the diamonds show the 25th and 75th percentiles of the factors area.

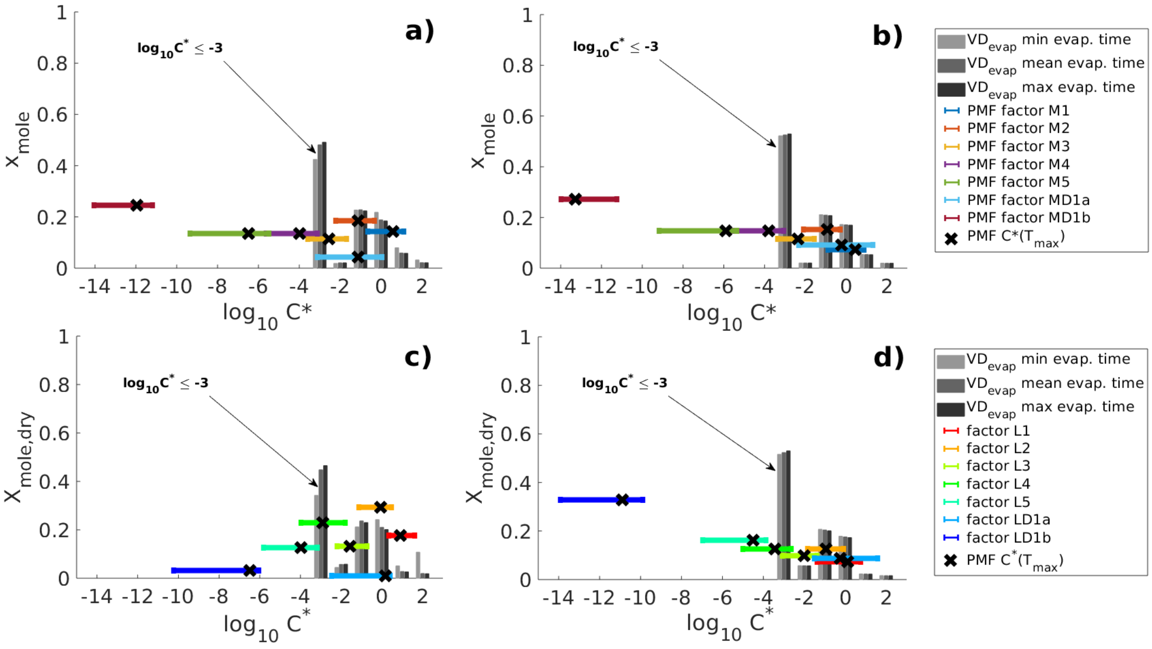

Figure S11: Volatility distributions in dry condition experiments determined from model fitting to the evapogram data (VD_{evap}) and PMF analysis of FIGAERO-CIMS data (VD_{PMF}) for the same four cases shown in Fig. S10.
a) Fresh sample of medium O:C SOA
b) Residual particles of medium O:C SOA (the RTC sample)
c) Fresh sample of low O:C SOA
d) Residual particles of low O:C SOA (the RTC sample).
VD_{evap} is shown for the best fit simulation (grey bars). The different grey shades show the VD_{evap} in the simulation at minimum, mean and maximum time that the particles have evaporated when the FIGAERO sample was collected (see Table S1). Black crosses show the $\log_{10}(C^*)$ calculated for each PMF factor from the peak desorption temperature T_{max}. The horizontal colored lines show the range of $\log_{10}(C^*)$ calculated from the 25th and 75th percentiles of each PMF factors mass loading profile.

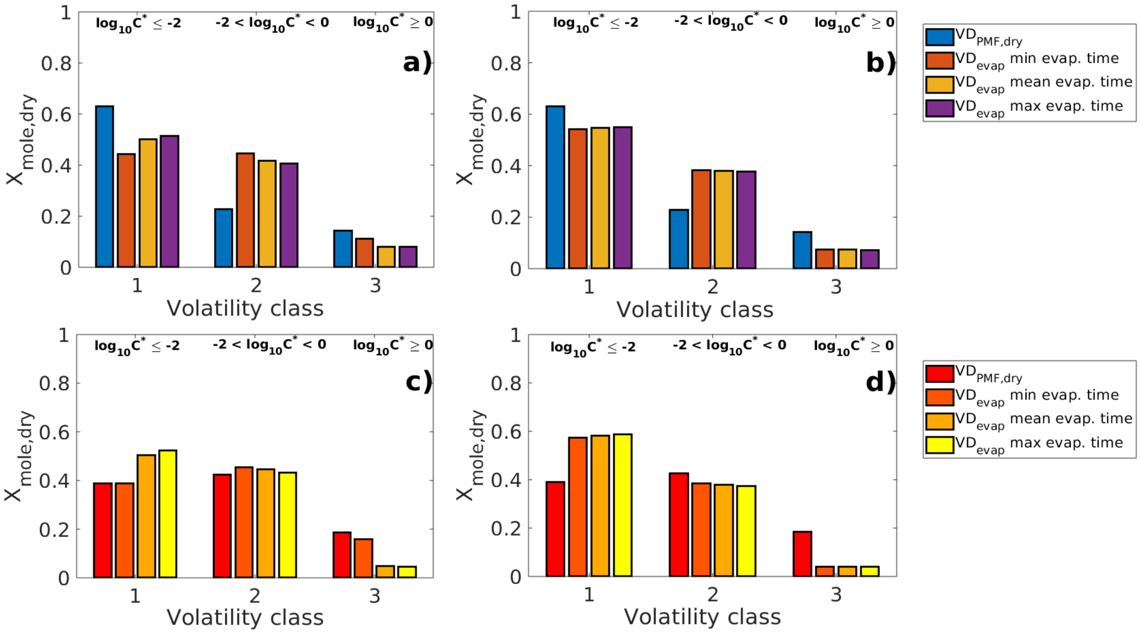

Figure S12: Comparison of $VD_{PMF,dry}$ (volatility distribution where C^* is calculated from T_{max} of each PMF factor) and VD_{evap} (volatility distribution determined by fitting LLEVAP model to measured evapogram) at varying sample evaporation times in dry condition experiments. The VD compounds are grouped into three different volatility classes similar to Fig. S6. The limits for each volatility class are shown at the top and are the same for each subfigure.

a) Fresh sample of medium O:C SOA

b) Residual particle of medium O:C SOA after 170-256 minutes of evaporation (the RTC sample)

c) Fresh sample of low O:C SOA

d) Residual particles of low O:C SOA after 152-238 minutes of evaporation (the RTC sample).