Supplementary material for the manuscript:

# α-pinene secondary organic aerosol yields increase at higher relative humidity and low $NO_x$ conditions

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## 1 Supplementary material for the experimental results

### 1.1 Seed aerosol composition

### 1.1.1 Experiments with hydroscopic seed aerosol (expts. 1-14)

Figure S1 shows the temporal evolution of $NH_4/SO_4$ in (mol $mol^{-1}$). Seen by the different ratios and temporal evolution, the experiments were performed with different seed compositions even when nebulizing always the same concentration (1g $L^{-1}$) of $NH_4HSO_4$ solution in ultrapure milli-Q water.

We estimate that 1 ppbv of gaseous $NH_3$ was needed to neutralize 4 μg $m^{-3}$ $NH_4HSO_4$ to $(NH_4)_2SO_4$ using the following formula:

$$c_{\mathrm{NH_3}} = \frac{m_{\mathrm{SO4}} \times V_{\mathrm{mol}}}{M_{\mathrm{SO4}}} = \frac{4\times10^{-6}\frac{\mathrm{g}}{\mathrm{m^3}} \times 0.024\frac{\mathrm{m^3}}{\mathrm{mol}} \times 10^{9}}{96\ \mathrm{g/mol}} \approx 1\mathrm{ppbv} \qquad \text{(S 1)}$$

where $c_{\mathrm{NH3}}$ is the concentration of $NH_3$, $V_{\mathrm{mol}}$ is the molar volume, $m_{\mathrm{SO4}}$ the mass concentration of $SO_4$ and $M_{\mathrm{SO4}}$ the molar mass of $SO_4$.

During experiments 1-6, the molar ratio between $NH_4$ and $SO_4$ represents an acidic seed condition. We claim that during those experiments the more highly concentrated $H_2SO_4$ solution (0.1 M) in the HONO source was the reason for it. The following calculation shows an estimation of how much $H_2SO_4$ was needed to be added to the SC to form $NH_4HSO_4$ from originally present $(NH_4)_2SO_4$. Assuming the highest seed concentration added to the chamber: 8 μg $m^{-3}$ $(NH_4)_2SO_4$ (= $6 \times 10^{-8}$ mol/m³ $(NH_4)_2SO_4$) yields $1.6 \times 10^{-6}$ mol $(NH_4)_2SO_4$ for the full 27 m³ PSI smog chamber. To form $NH_4HSO_4$ from this, $1.6 \times 10^{-6}$ mol $H_2SO_4$ = $1.6 \times 10^{-4}$ g= 0.16 mg ≈ 0.1 μL $H_2SO_4$

would have to be injected to the chamber. In terms of solution injected this means for the 0.1 M $H_2SO_4$ solution: 1 µL was most probably injected into the chamber.

The neutralization was confirmed by nebulization tests of $(NH_4)_2SO_4$ and $NH_4HSO_4$ resulting in apparent relative ionization efficiencies (RIE) of 1.1 and 0.55 for $SO_4$, respectively, if no chemical transformation is assumed. The RIE is defined as ionization efficiency (IE) of a compound normalized to the IE of $NO_3$ in the HR-ToF-AMS. Because these compounds are both believed to thermally decompose to $NH_3$ and $H_2SO_4/SO_3+H_2O$ prior to ionization, a dependence of the anion RIEs on the parent compound is unlikely. Thus the observed ratios rather indicate neutralization of $NH_4HSO_4$ to $(NH_4)_2SO_4$ between nebulizer and measurement.

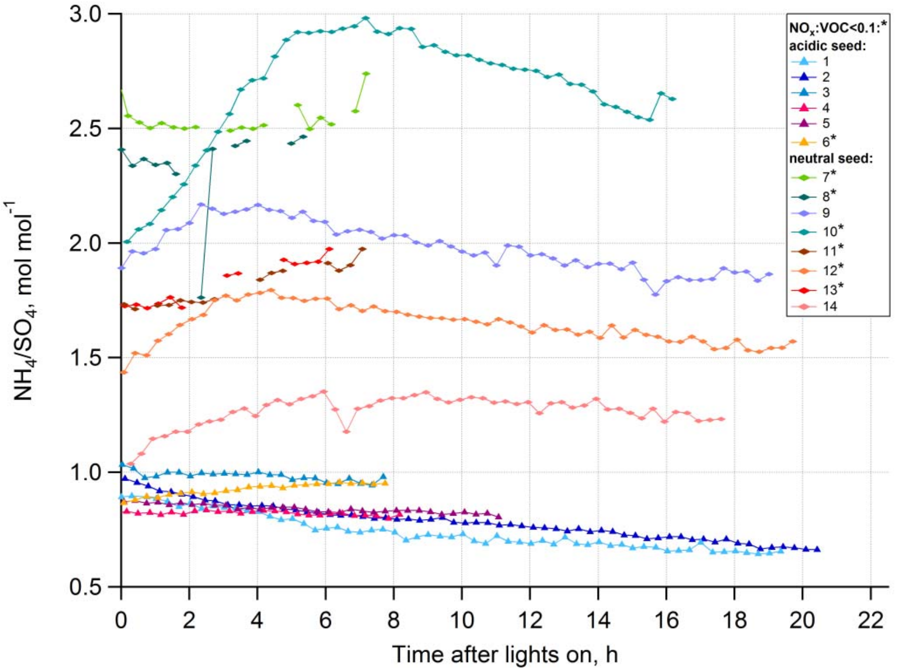


**Figure S1. Molar ratio of ammonium to sulfate (NH4/SO4) as a function of time after lights on. Seed composition during experiments 1–6: SA & AHS due to significant concentration of $H_2SO_4$ added. Note that the ratio of $NH_4/SO_4$ in pure ammonium sulphate injected in the AMS changed in different days by 20%, which would explain some of the scattering in the $NH_4/SO_4$ ratio at the beginning of experiments 7–14. The increase of this ratio during these experiments to values above 2 could not be explained. This increase could not be fully attributed to inorganic nitrate formation (here considered to be more likely organo-nitrate), as the nitrate molar concentrations are one order of magnitude lower than ammonium concentrations (especially under low $NO_X$ conditions). Also, as the aerosol was dried we do not expect interference from water on ammonium concentrations.**

### 1.1.2 Experiments with hydrophobic seed aerosol (expts. 15-17)

Figure S2 shows the distinct mass spectrum (MS) of the fluorinated carbon seed (hydrophobic CF-seed) aerosol. Table S1 lists the corresponding relative intensities compared to $CF_3$ of each major ion. The HR-ToF-AMS high resolution analysis is a good tool to distinguish between α-pinene SOA and the hydrophobic CF-seed ion peaks in the mass spectrum. The decay rate constants of the hydrophobic CF-seed concentration in the smog chamber could thus easily be estimated by fitting the sum of three main ions ($CF_2$, $CF_3$, $C_2F_3O$).

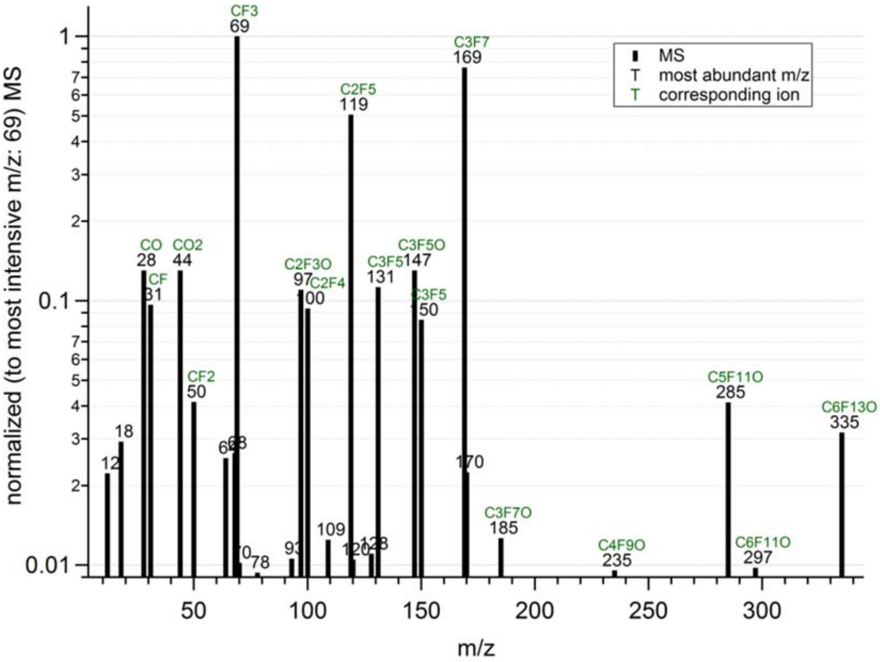


**Figure S2. Mass spectrum of the hydrophobic CF-seed measured with the HR-ToF-AMS normalized to $CF_3$ (the ion with the highest intensity).**

**Table S1. Mass spectrum of the hydrophobic CF-seed measured with HR-ToF-AMS normalized to $CF_3$ (ion with highest intensity).**

| *m/z* | Ion formula | Normalized intensity | *m/z* | Ion formula | Normalized intensity |
|---|---|---|---|---|---|
| 28 | CO | 0.130 | 147 | $C_3F_5O$ | 0.130 |
| 31 | CF | 0.097 | 150 | $C_3F_5$ | 0.085 |
| 44 | $CO_2$ | 0.130 | 169 | $C_3F_7$ | 0.762 |
| 50 | $CF_2$ | 0.041 | 185 | $C_3F_7O$ | 0.013 |
| 69 | $CF_3$ | 1.000 | 235 | $C_4F_9O$ | 0.010 |
| 97 | $C_2F_3O$ | 0.110 | 285 | $C_5F_{11}O$ | 0.041 |
| 100 | $C_2F_4$ | 0.094 | 297 | $C_6F_{11}O$ | 0.010 |
| 119 | $C_2F_5$ | 0.506 | 335 | $C_6F_{13}O$ | 0.032 |
| 131 | $C_3F_5$ | 0.113 | | | |

## 1.2 Transmission and collection efficiency correction of the HR-ToF-AMS

During experiments 9, 10, 12 and 14-17, the transmission efficiency of one of the two $PM_{2.5}$ lenses used in the HR-ToF-AMS was sub-unity for particles up to vacuum aerodynamic diameters ($d_{va}$) of 230 nm, the region where the organic : sulfate ratio is highest. The not-transmitted aerosol was accounted for by means of HR-ToF-AMS and SMPS comparison. The sulfate seed and hydrophobic CF-seed mass distributions were captured well within the measurement region by both, HR-ToF-AMS and SMPS. The seed volume concentration $V_{\mathrm{seed}}$ was determined by applying the loss rate constant of the hydrophobic CF-seed ($k_{\mathrm{CF}}$) or sulfate ($k_{\mathrm{SO4}}$), respectively, to the measured initial SMPS volume concentration $V_{\mathrm{initial}}$. E.g.:

$$V_{\mathrm{seed}} = V_{\mathrm{initial}} \times \exp^{-k_{\mathrm{SO}_4} t}, \tag{S 2}$$

or accordingly with $k_{\mathrm{CF}}$ for the hydrophobic CF-seed. The additionally formed organic volume concentration $\Delta V_{\mathrm{SMPS}}$ was derived from the difference of total and seed volume concentration ($V_{\mathrm{Org,SMPS}} = V_{\mathrm{total}} - V_{\mathrm{seed}}$). The method is displayed in Figure S3. The collection efficiency (*CE*) of organics ($CE_{\mathrm{org}}$) in the HR-ToF-AMS in turn was determined by the ratio of $V_{\mathrm{org,AMS}}$ and $V_{\mathrm{Org,SMPS}}$ shown in Figure S4. HR-ToF-AMS mass concentrations divided by the corresponding densities of the species yielded the HR-ToF-AMS volume. $CE_{\mathrm{org}}$ was ~ 0.55 for experiments 12 and 14 with lower RH and ~ 0.75 for experiments 9 and 10 with higher RH. The hydrophobic CF-seed experiments showed a $CE_{\mathrm{org}}$ of 1. This trend is also size driven, affected by sub-unity particle transmission efficiency for small particles.

The remaining experiments were conducted with the second $PM_{2.5}$ lens, which exhibited good transmission efficiency at lower $d_{\mathrm{va}}$. The SMPS upper diameter cut off for experiments 1–6 was set to 600 nm mobility diameter instead of the standard 1000 nm in this study and thus the HR-ToF-AMS volume exceeded the SMPS volume. Therefore, a $CE_{\mathrm{org}}$ of 1 was assumed for experiments 1–6, in which only liquid-phase particles were expected. The $CE_{\mathrm{org}}$ for experiments 7, 8, 11 and 13 were between 0.7–0.9. All organic mass concentrations and SOA yields given in this study are corrected by dividing the measured values by the collection efficiency, summarized in Table S2.

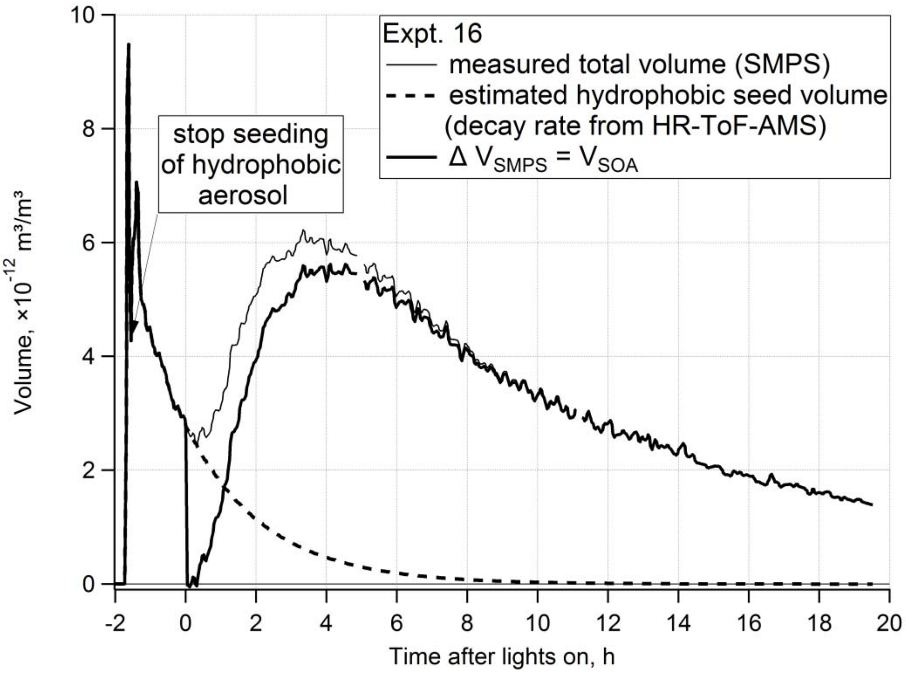


**Figure S3. Measured SMPS total volume concentration, estimated hydrophobic seed volume concentration (with decay rate constant $k_{\mathrm{CF}}$ determined from HR-ToF-AMS data) and the difference of both, $\Delta V_{\mathrm{SMPS}}$, as a function of time after lights on. $\Delta V_{\mathrm{SMPS}}$ corresponds to the secondary organic volume concentration, $V_{\mathrm{SOA}}$, formed.**

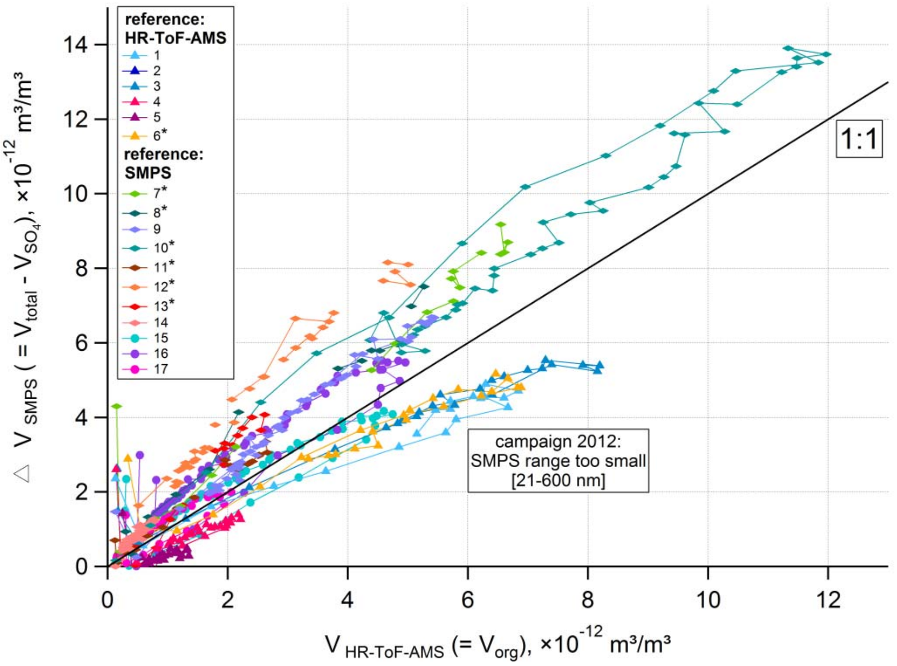


**Figure S4. Comparison of 20-minutes averaged organic volume concentrations derived from the SMPS measurement, Δ$V_{SMPS}$, and the organic compounds derived from the HR-ToF-AMS measurement, $V_{HR\text{-}ToF\text{-}AMS}$ (=$V_{org}$). Δ$V_{SMPS}$ represents the difference between total SMPS volume concentration, $V_{total}$, and the estimated $SO_4$ volume concentration. The legend shows for each experiment, which instrument, HR-ToF-AMS or SMPS, was taken as reference.**

## 1.3 Different $NO^+/NO_2^+$ ratios between calibrating with $NH_4NO_3$ and SC processing phases to underline presence of organonitrates

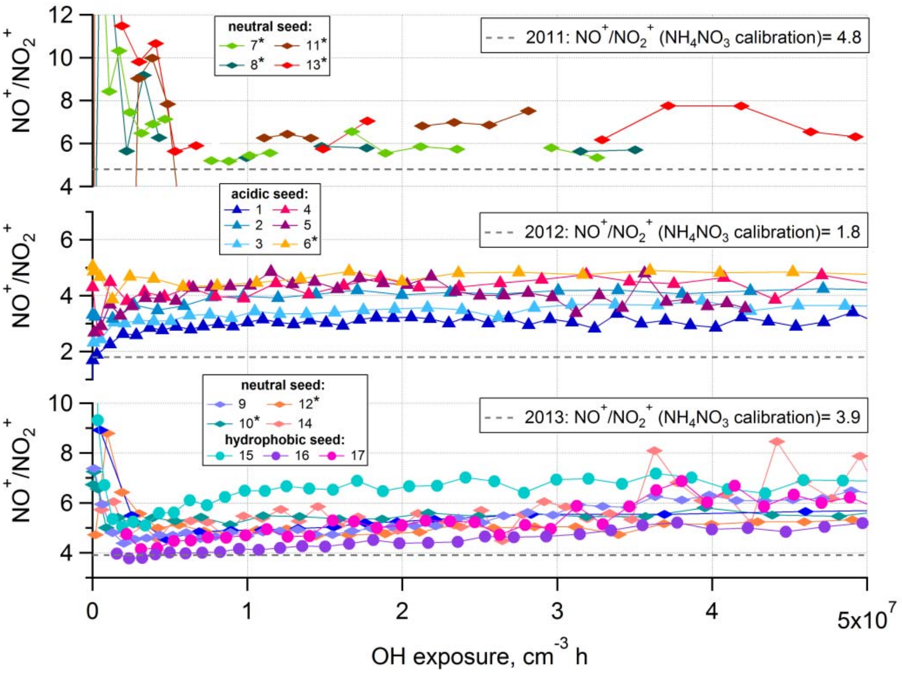


**Figure S5. 20-min averaged $NO^+/NO_2^+$ ratio as a function of OH exposure compared to the measured ratio of $NO^+/NO_2^+$ from calibration data (dashed lines) using $NH_4NO_3$ for each set of experiments. The absolute magnitude of observed $NO^+/NO_2^+$ ratios for $NH_4NO_3$ are affected by instrument temperature, tuning, and vaporizer status (e.g. Pieber et al., submitted), and thus the relative changes between calibration standard and chamber measurement are critical for organonitrate identification (Farmer et al., 2010).**

## 1.4 Determination of wall loss rate constants

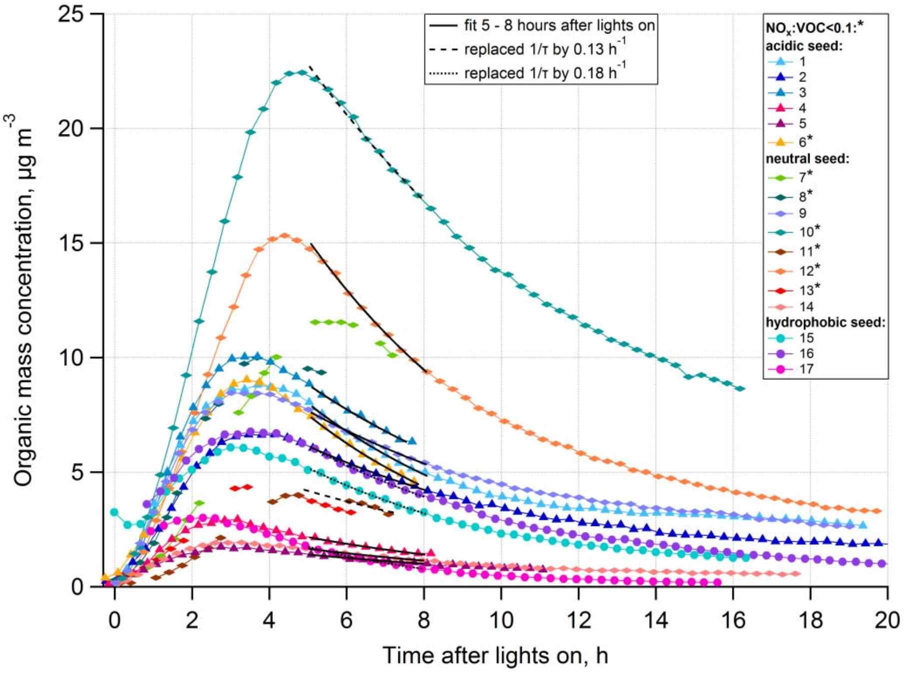
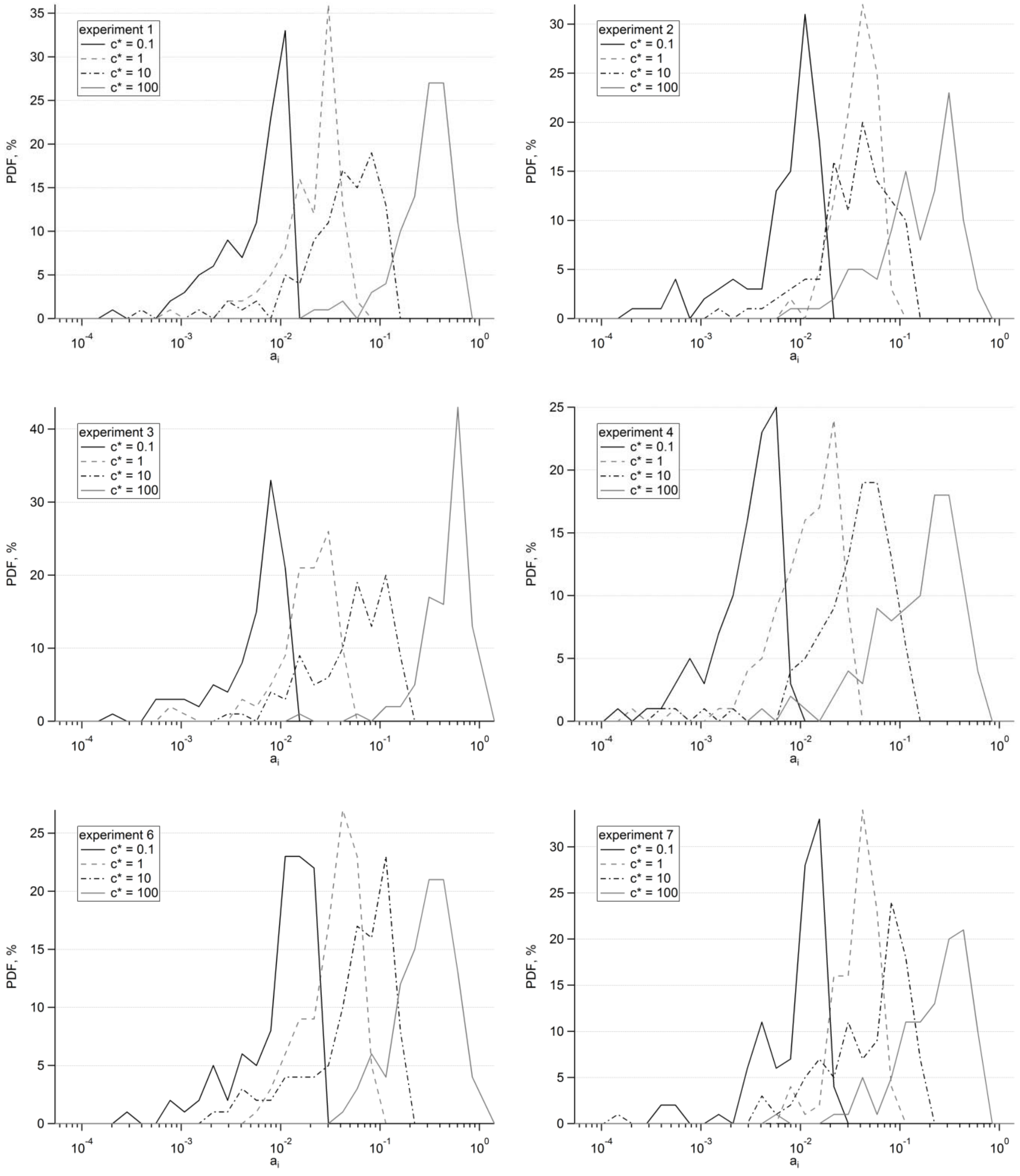


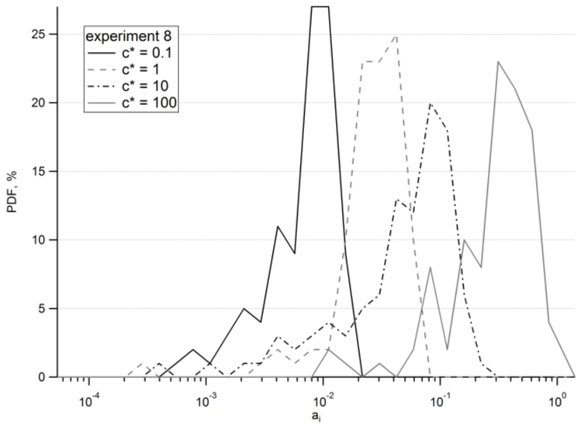
**Figure S6. 20-min-averaged organic mass concentration as a function of time after lights on. Traces were fit with an exponential between 5 and 8 h after lights on to determine the wall loss rate constant. Wall loss decay rate constants for experiments with too short fit period were replaced by the respective mean 1/τ-values of 0.13 h$^{-1}$ (dashed lines) and 0.18 h$^{-1}$ (dotted lines).**

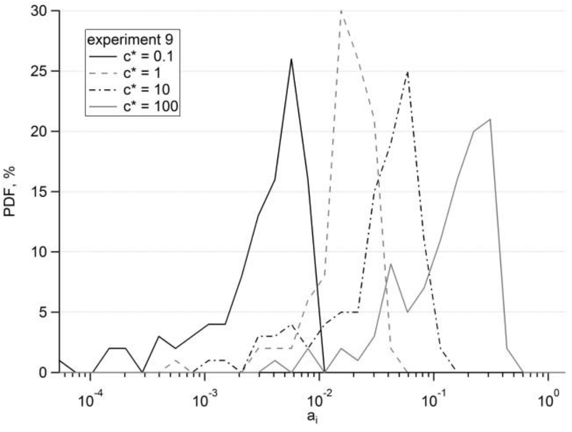
**Table S2. List of wall-loss-correction parameters ($1/\tau$) in $h^{-1}$ and collection efficiencies ($CE_{org}$) applied to each experiment.**

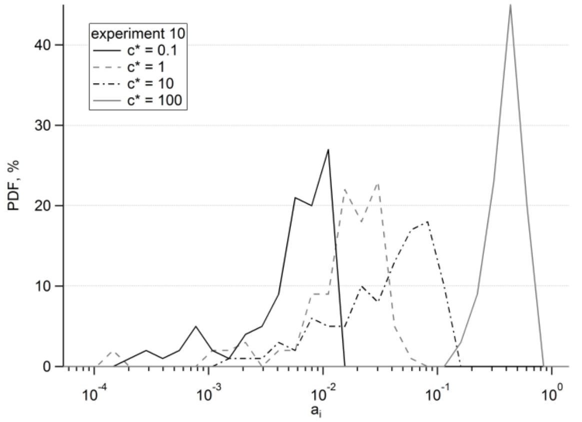
| No | $1/\tau$ $h^{-1}$ | $CE_{org}$ |
|---|---|---|
| 1 | 0.17 | 1.00 |
| 2 | 0.11 | 1.00 |
| 3 | 0.13 | 1.00 |
| 4 | 0.16 | 1.00 |
| 5 | 0.11 | 1.00 |
| 6 | 0.17 | 1.00 |
| 7 | 0.13 | 0.78 |
| 8 | 0.13 | 0.70 |
| 9 | 0.11 | 0.75 |
| 10 | 0.13 | 0.75 |
| 11 | 0.13 | 0.89 |
| 12 | 0.16 | 0.55 |
| 13 | 0.13 | 0.80 |
| 14 | 0.10 | 0.55 |
| 15 | 0.18 | 1.00 |
| 16 | 0.18 | 1.00 |
| 17 | 0.18 | 1.00 |

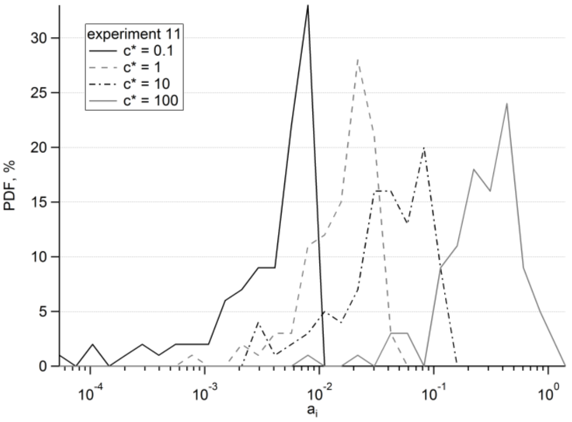
## 1.5 Probability density functions for *a*$_i$ values using parameterized yields as a function of $C_{OA}$ (Fig. 5 in the main text)

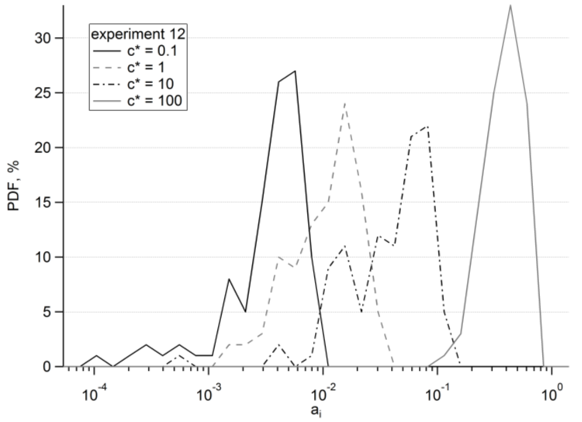


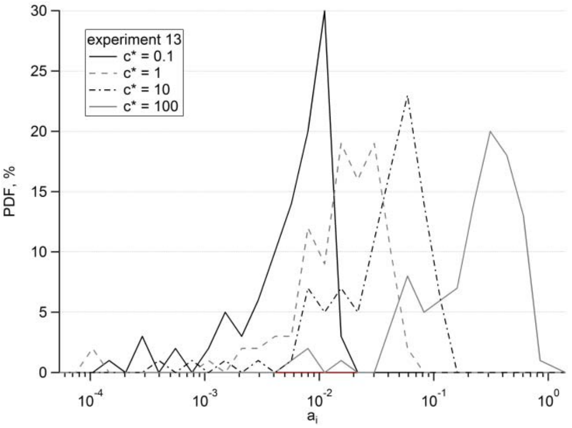

experiment 8
c* = 0.1
c* = 1
c* = 10
c* = 100
PDF, %
0
5
10
15
20
25
$10^{-4}$
$10^{-3}$
$10^{-2}$
$10^{-1}$
$10^{0}$
$a_i$

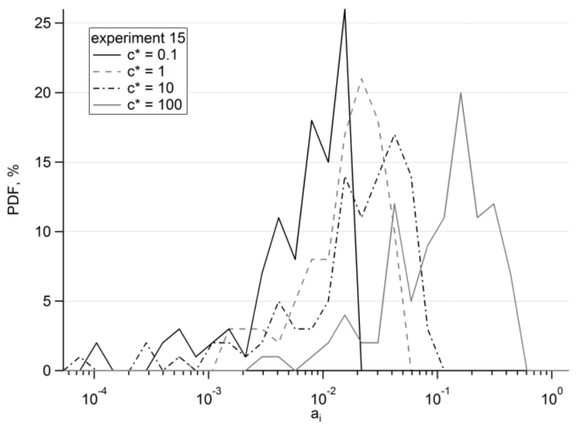

experiment 9
c* = 0.1
c* = 1
c* = 10
c* = 100
PDF, %
0
5
10
15
20
25
30
$10^{-4}$
$10^{-3}$
$10^{-2}$
$10^{-1}$
$10^{0}$
$a_i$

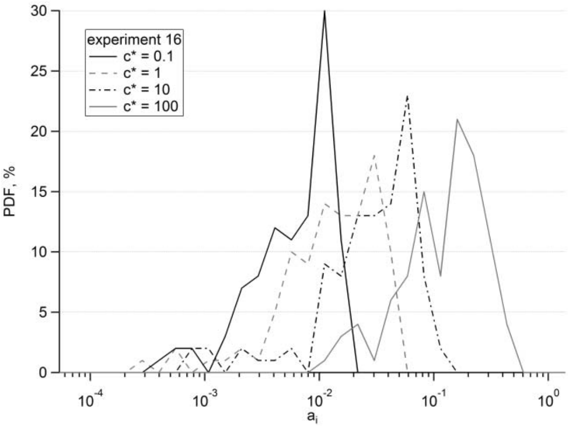

experiment 10
c* = 0.1
c* = 1
c* = 10
c* = 100
PDF, %
0
10
20
30
40
$10^{-4}$
$10^{-3}$
$10^{-2}$
$10^{-1}$
$10^{0}$
$a_i$


experiment 11
c* = 0.1
c* = 1
c* = 10
c* = 100
PDF, %
0
5
10
15
20
25
30
$10^{-4}$
$10^{-3}$
$10^{-2}$
$10^{-1}$
$10^{0}$
$a_i$


experiment 12
c* = 0.1
c* = 1
c* = 10
c* = 100
PDF, %
0
5
10
15
20
25
30
$10^{-4}$
$10^{-3}$
$10^{-2}$
$10^{-1}$
$10^{0}$
$a_i$


experiment 13
c* = 0.1
c* = 1
c* = 10
c* = 100
PDF, %
0
5
10
15
20
25
30
$10^{-4}$
$10^{-3}$
$10^{-2}$
$10^{-1}$
$10^{0}$
$a_i$


experiment 15
c* = 0.1
c* = 1
c* = 10
c* = 100
PDF, %
0
5
10
15
20
25
$10^{-4}$
$10^{-3}$
$10^{-2}$
$10^{-1}$
$10^{0}$
$a_i$


experiment 16
c* = 0.1
c* = 1
c* = 10
c* = 100
PDF, %
0
5
10
15
20
25
30
$10^{-4}$
$10^{-3}$
$10^{-2}$
$10^{-1}$
$10^{0}$
$a_i$

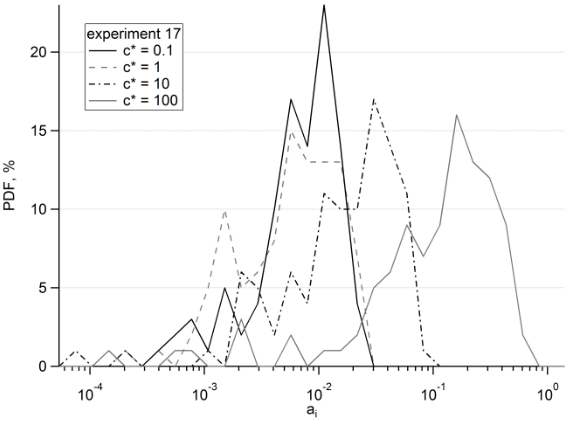


**Figure S7. Probability density functions (PDF) of *ai* values for volatility bins (c*=0.1; 1; 10; 100) to solve Eq. (10) in the main text. The results for experiments 5 and 14 are not shown due to negative solution values.**

## 1.6 Aerosol yield as a function of α-pinene reacted

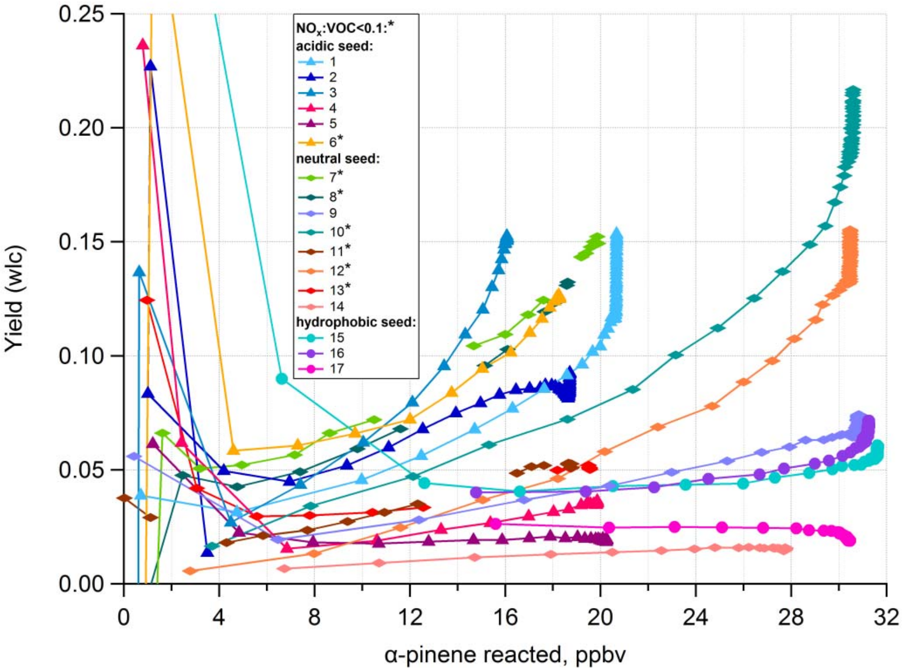


**Figure S8. 20-min-averaged wall-loss-corrected yield as a function of reacted α-pinene. At the same concentration of α-pinene reacted, different yields are obtained due to various $NO_x$/α-pinene ratios, relative humidities and seed compositions. Traces are color coded for each experiment according to Table 1 in the main text. Asterisks indicate low $NO_x$ experiments. This figure is for illustrative purposes showing the different aerosol yields for the same concentration of α-pinene reacted, but different experimental conditions.**

### 1.7 Analysis of the influence of experimental conditions on yields using a multi-linear analysis

The influence of the experimental conditions on the calculated yields was investigated using a multilinear analysis technique. Different models were explored using the following sets of independent variables:

(i) Model 1: α-pinene concentration, RH, seed concentration, and $NO_x$/VOC ratio;

(ii) Model 2: Model 1 + consideration of a first order interaction term between RH and $NO_x$/VOC ratio (i.e. the compounds formed at high and low $NO_x$ interact differently with water).

(iii) Model 3: Model 1 + consideration of the influence of the seed composition. This was achieved either by considering independently the different seeds as fitting variables or by considering the interaction between RH and the seed chemical nature (i.e. SOA compounds interaction with water depends on the seed nature). The seed nature was parameterized using discrete binary values. We did not observe a statistically significant correlation between yields and seed nature, but rather between yields and the first interaction term between RH and seed composition (RH* SeedNature).

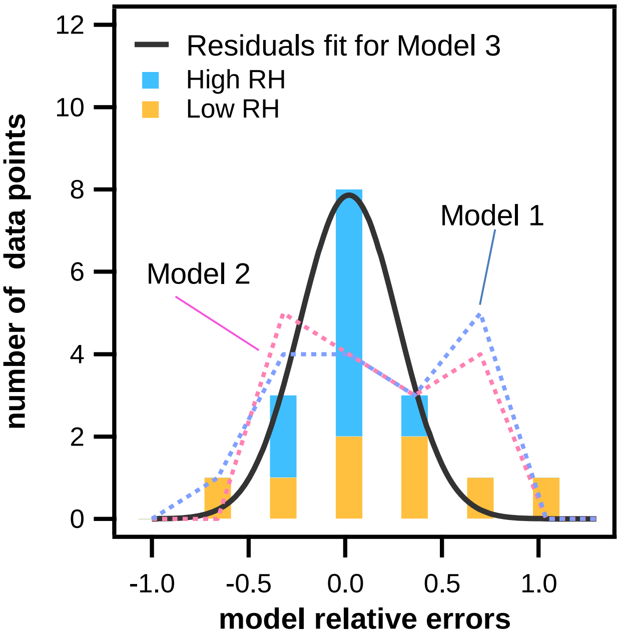


**Figure S9. Residual distributions for the three assumed models, (measured_yield – modelled_yield)/measured_yield.**

The models' residual distributions are examined in Figure S9. The model that represented best the experimental data is model 3, the results of which are reported in Table S3 and discussed in Sect. 3.1 in the main text. For this model, there is not enough evidence showing that the model residuals are not normally distributed (adjusted Jarque-Bera Lagrange multiplier test (Jarque and Bera, 1980), critical value = 2.8), for both low and high RH cases (shown in orange and blue, respectively). The model mean bias is 2% and the estimated error is 25% within the estimated measurement uncertainties, showing that the parameters considered may be sufficient to explain the variability in the data. Model 3 explains the observations significantly better than model 1 and 2 (variance equality F test, $p<0.01$), where standard errors are on average 50% and the mean bias >10%. The multivariate analysis shows that the yields are independent of the seed concentrations, but are a function of α-pinene concentration, RH, seed composition, and $NO_x$/VOC ratio. We did not observe a significant interaction between RH and $NO_x$ (model 2).

**Table S3. Multilinear analysis results for model 3 showing the relationship between the observed yields (%) and the different experimental parameters investigated (independent variables), including α-pinene concentration (ppbv), $NO_x$/VOC ratio (ppbv $ppbv^{-1}$), seed initial concentration (µg $m^{-3}$) and RH (%) for different seed composition. The coefficients relating the yields to the independent variables are shown together with the corresponding uncertainties (1sd) estimated through the least-squares calculation. The significance of the overall fit is assessed using an F test analysis, showing that closure is achieved (F significance = $1.1\times10^{-7}$). The statistical significance of the individual parameters is represented by the t-statistics (t Stat) and the P-value. The parameter statistically not significant ($p>0.05$) is highlighted in grey.**

| Independent variables | Coefficients | t Stat | P-value |
|---|---|---|---|
| RH*AS&AHS | 0.21±0.03 | 8.0 | $3.8\times10^{-6}$ |
| RH*AHS&SA | 0.15±0.03 | 4.5 | $6.9\times10^{-4}$ |
| RH*CF | 0.09±0.04 | 2.0 | $5.0\times10^{-2}$ |
| $[seed]_0$ | -0.03±0.13 | -0.25 | $8.1\times10^{-1}$ |
| $NO_x$/VOC | -3.3±0.06 | -5.6 | $1.1\times10^{-3}$ |
| [α-pinene] | 0.21±0.06 | 3.5 | $4.1\times10^{-3}$ |

## 1.8 Additional supplementary figures

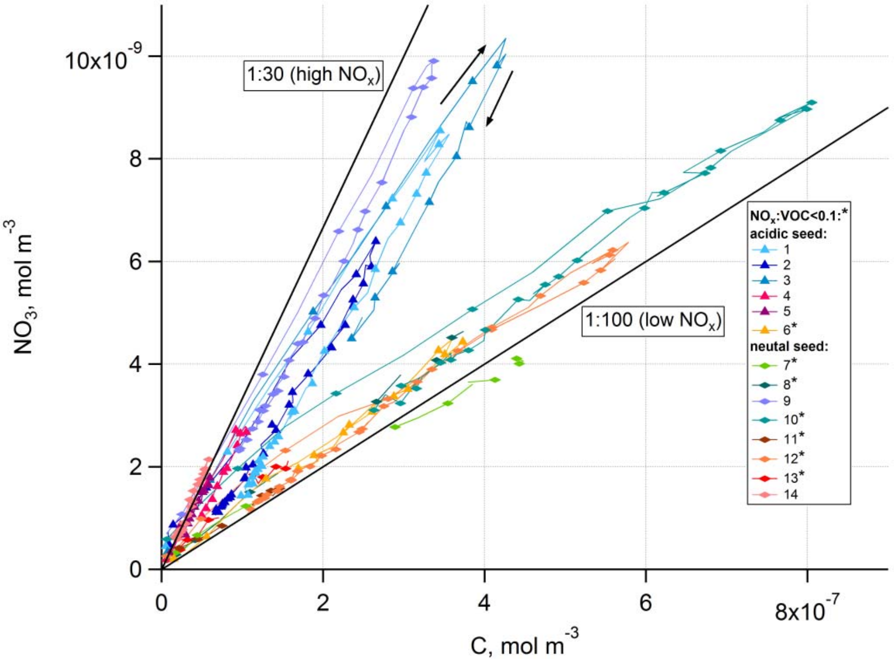


**Figure S10. Molar concentrations of nitrate ($NO_3$) as a function of molar concentration of carbon (C) for all experiments with hygroscopic seed. High $NO_x$ experiments follow a ratio of approximately 1:30, low $NO_x$ experiments a ratio of approximately 1:100. The two arrows indicate that $NO_3$:C ratio slightly decreases when the initially high $NO_x$ concentration decayed to low values in the end of high $NO_x$ experiments 1, 2 and 3, although the ratio remains much higher than that observed at low $NO_x$ conditions. This indicates that $NO_3$-containing compounds are lost at faster rate than other compounds.**

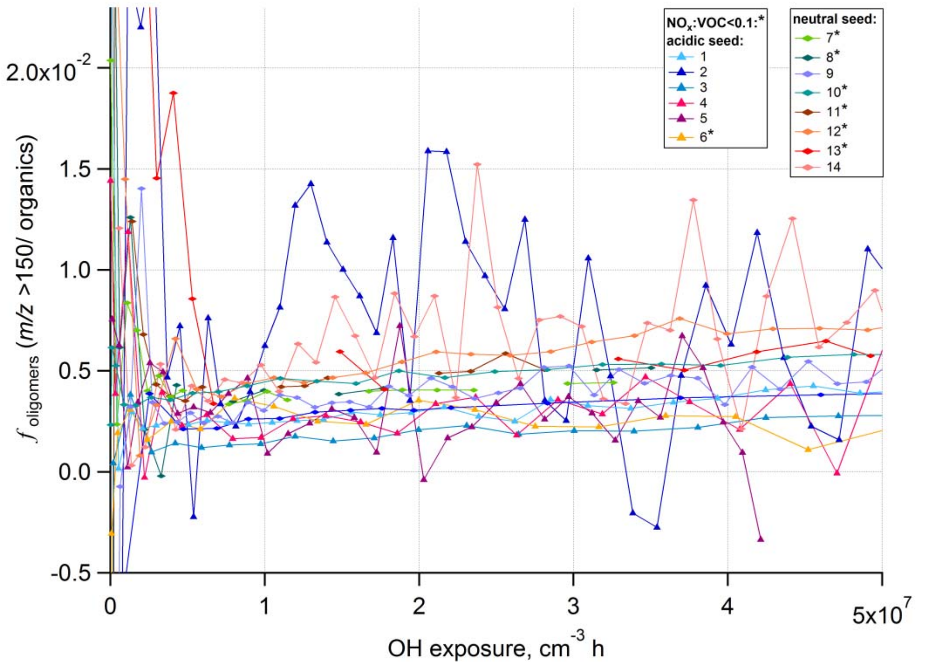


**Figure S11. 20-min-averaged mass fraction of organics with m/z > 150 (e.g. oligomers) of the total organic mass concentration as a function of OH exposure. Symbols indicate the seed composition, colors indicate the respective experiment as given in the legend.**

## 1.9 Evolution of aerosol size distributions and total particle number concentration

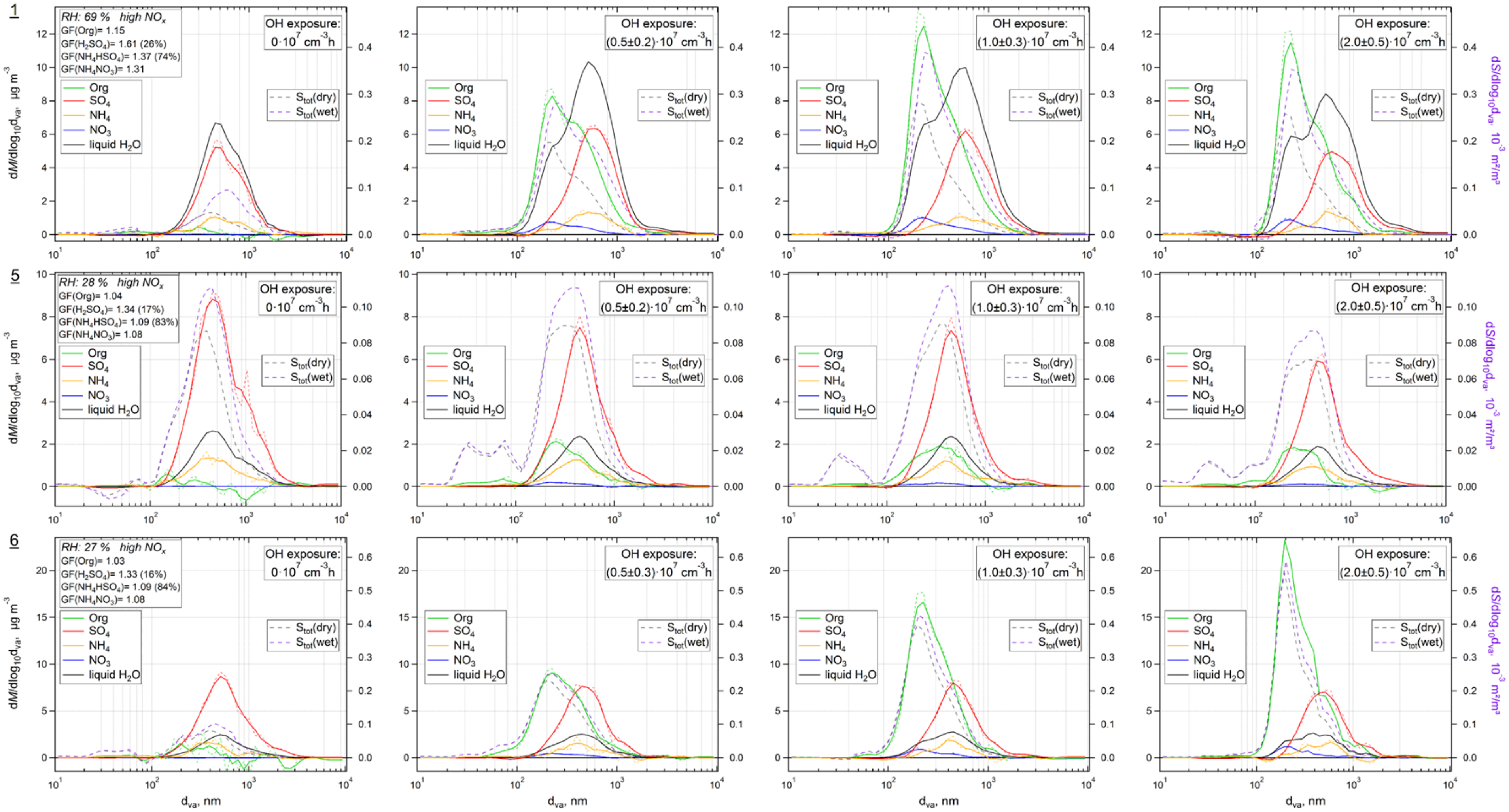


**Figure S12.** Evolution of size distributions. Measured organic, SO4, NH4, NO3 mass distributions for OH exposures of 0×, (0.5 ± 0.2)×, (1.0 ± 0.3)× and (2.0 ± 0.5) × $10^7$ $cm^{-3}$ h. Black lines represent estimated liquid water content (RH and individual GFs given for each experiment, method described in main text). The calculated dry and wet surface distributions are shown on the right axes. Number of each experiment is given on the left edge (1, 5, 6).

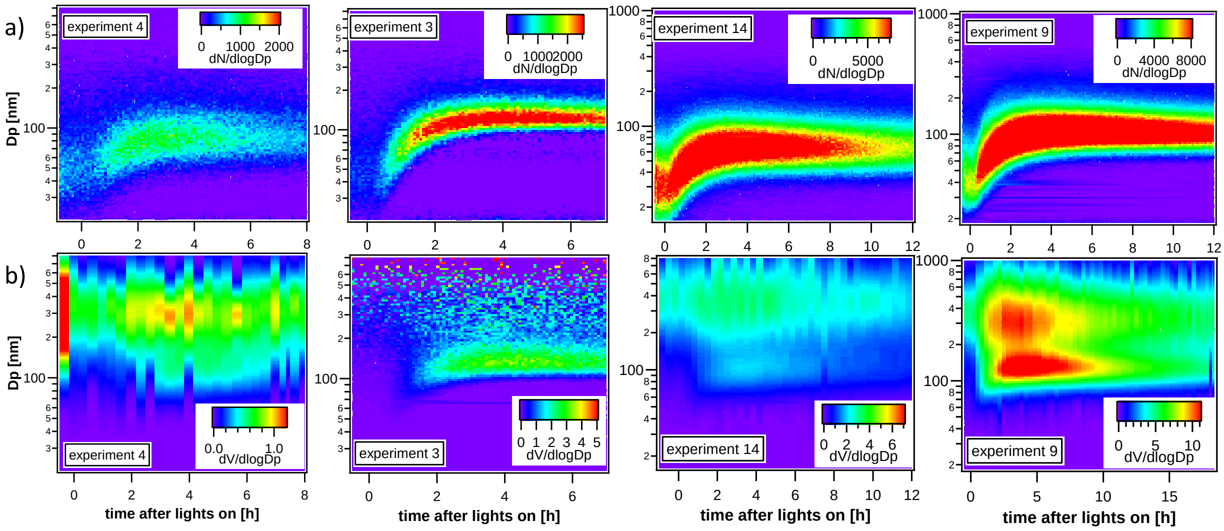


**Figure S13. 3-dimensional time dependent (a) number and (b) volume size distributions for experiments 4, 3, 14 and 9, measured by the SMPS.**

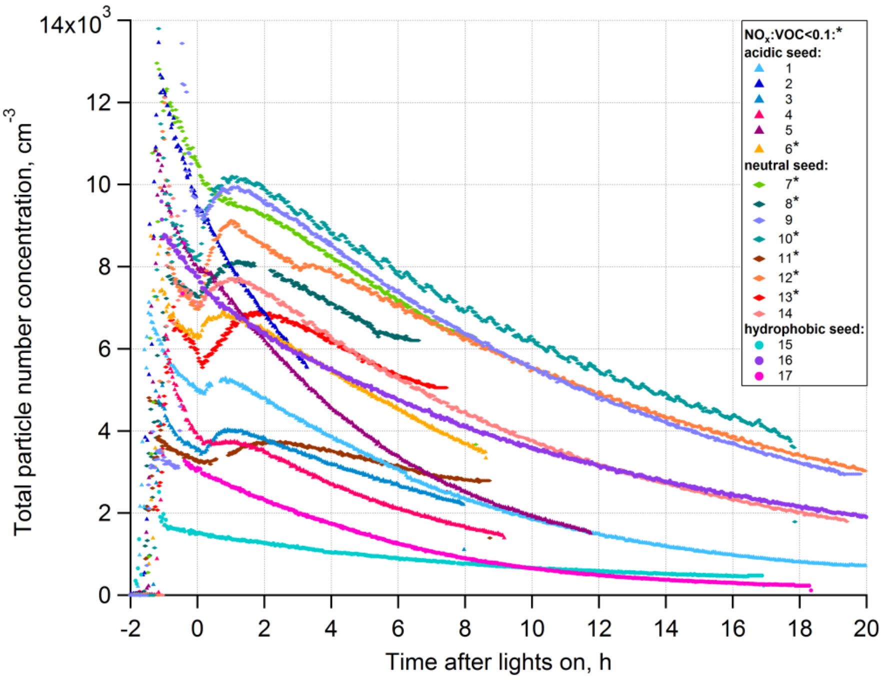
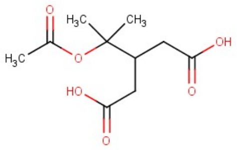
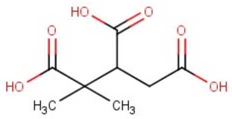
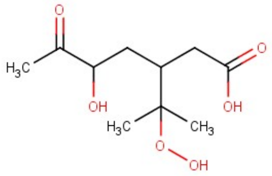
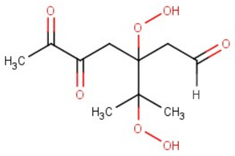
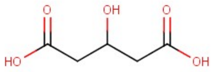
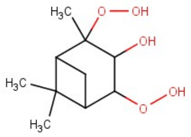
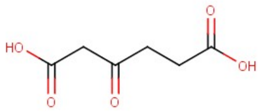
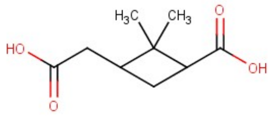
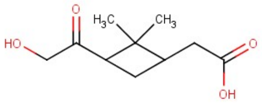
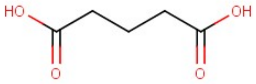
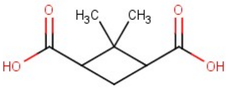
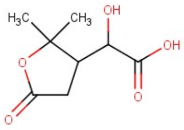
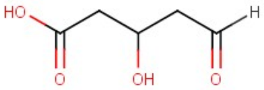
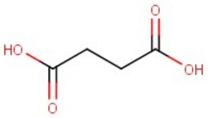
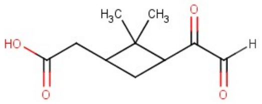
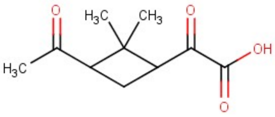
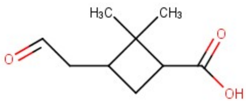
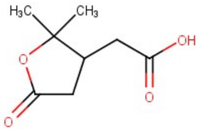


**Figure S14. Total particle number concentration as a function of time after lights on.**

## 2 Supplementary material for the phase partitioning calculations

**Table S 4. Characterization of the model compounds: molecular weight MW, O:C ratio, vapor pressure from EVAPORATION, assignment to volatility bin based on C$^0$, molecular structure, reference stating the compound as product of α-pinene photooxidation.**

| *Name* | *MW (g/mole)* | *O:C* | *Vapor pressure (Pa, 298 K)* | *Volatility bin: C* (μg m$^{-3}$)* | *Molecular structure* | *Reference* |
|---|---|---|---|---|---|---|
| Diaterpenylic acid acetate | 232 | 0.6 | $1.009 \times 10^{-6}$ | 0.01 $(\alpha_1)$ |  | Eddingsaas et al., 2012 |
| 3-MBTCA | 204 | 0.75 | $7.281 \times 10^{-9}$ | 0.01 $(\alpha_1)$ |  | Eddingsaas et al., 2012 |
| ValT4N9 | 234 | 0.6 | $4.048 \times 10^{-7}$ | 0.01 $(\alpha_1)$ |  | Valorso et al., 2011 |
| ValT4N10 | 248 | 0.7 | $1.472\times 10^{-6}$ | 0. 1 $(\alpha_2)$ |  | Valorso et al., 2011 |
| 3-hydroxy-glutaric acid | 148 | 1 | $5.167\times 10^{-6}$ | 0. 1 $(\alpha_2)$ |  | Kleindienst et al., 2007 |
| ValT4N3 | 218 | 0.5 | $1.416 \times 10^{-6}$ | 0. 1 $(\alpha_2)$ |  | Valorso et al., 2011 |
| 3-oxoadipic acid | 160 | 0.833 | $2.129 \times 10^{-5}$ | 1 $(\alpha_3)$ |  | - |
| Pinic acid | 186 | 0.444 | $4.622 \times 10^{-5}$ | 1 $(\alpha_3)$ |  | Eddingsaas et al., 2012 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Hopinonic acid | 200 | 0.4 | $7.650 \times 10^{-5}$ | $1\ (\alpha_3)$ |  | Eddingsaas et al., 2012 |
| Glutaric acid | 132 | 0.8 | $1.020 \times 10^{-5}$ | $10\ (\alpha_4)$ |  | - |
| Norpinic acid | 172 | 0.5 | $1.443 \times 10^{-4}$ | $10\ (\alpha_4)$ |  | Jaoui et al., 2001 |
| 2-hydroxy-terpenylic acid | 188 | 0.625 | $7.148 \times 10^{-4}$ | $10\ (\alpha_4)$ |  | Eddingsaas et al., 2012 |
| 5-COOH-3-OH-pentanal | 132 | 0.8 | $5.834 \times 10^{-3}$ | $100\ (\alpha_5)$ |  | - |
| Succinic acid | 118 | 1 | $3.121 \times 10^{-3}$ | $100\ (\alpha_5)$ |  | - |
| 10-oxopinonic acid | 198 | 0.4 | $7.535 \times 10^{-3}$ | $100\ (\alpha_5)$ |  | Jaoui et al., 2001 |
| 4-oxopinonic acid | 198 | 0.4 | $4.790 \times 10^{-3}$ | $100\ (\alpha_5)$ |  | Jaoui et al., 2001 |
| Pinalic acid | 170 | 0.33 | $4.688 \times 10^{-2}$ | $100\ (\alpha_5)$ |  | Jaoui et al., 2001 |
| Terpenylic acid | 172 | 0.5 | $9.306 \times 10^{-2}$ | $100\ (\alpha_5)$ |  | Eddingsaas et al., 2012 |

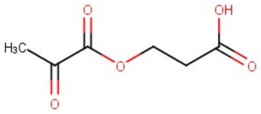
|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| 3-(2-oxopropanyloxy) propanoic acid | 160 | 0.83 | $4.953 \times 10^{-2}$ | 100 ($\alpha_5$) |  | Altieri et al., 2008 |

**Table S 5. Average $\alpha_i$-parameters and range (in brackets) of the volatility bins with $C^*$ = 0.1-100 µg m$^{-3}$ for 10 selected volatility distributions.**

|  | $\alpha_2$ | $\alpha_3$ | $\alpha_4$ | $\alpha_5$ |
|---|---|---|---|---|
| Exp 1 | 0.0061 (0.0023-0.0119) | 0.0223 (0.0114-0.0308) | 0.0577 (0.0315-0.0894) | 0.3279 (0.1374-0.5020) |
| Exp 2 | 0.0102 (0.0063-0.0138) | 0.0289 (0.0204-0.0521) | 0.0504 (0.0248-0.0781) | 0.2201 (0.0453-0.3784) |
| Exp 3 | 0.0073 (0.0031-0.0112) | 0.0216 (0.0065-0.0347) | 0.0650 (0.0156-0.1275) | 0.4929 (0.3765-0.6219) |
| Exp 4 | 0.0038 (0.0023-0.0051) | 0.0116 (0.0046-0.0224) | 0.0502 (0.0217-0.0757) | 0.2244 (0.0757-0.3235) |
| Exp 7 | 0.0100 (0.0041-0.0151) | 0.0431 (0.0246-0.0592) | 0.0725 (0.0271-0.1214) | 0.2314 (0.0938-0.4741) |
| Exp 8 | 0.0070 (0.0040-0.0123) | 0.0326 (0.0160-0.0595) | 0.0570 (0.0099-0.1272) | 0.3580 (0.1329-0.5688) |
| Exp 9 | 0.0037 (0.0023-0.0056) | 0.0167 (0.0089-0.0245) | 0.0501 (0.0252-0.0644) | 0.1512 (0.0388-0.3063) |
| Exp 10 | 0.0074 (0.0048-0.0096) | 0.0168 (0.0047-0.0309) | 0.0504 (0.0115-0.0868) | 0.4044 (0.2623-0.5743) |
| Exp 11 | 0.0047 (0.0012-0.0085) | 0.0191 (0.0082-0.0310) | 0.0450 (0.0266-0.0788) | 0.3122 (0.1662-0.4873) |
| Exp 12 | 0.0032 (0.0016-0.0049) | 0.0126 (0.0037-0.0212) | 0.0459 (0.0112-0.0863) | 0.4037 (0.2522-0.5725) |
| Exp 13 | 0.0069 (0.0018-0.0098) | 0.0185 (0.0073-0.0307) | 0.0476 (0.0122-0.0833) | 0.2946 (0.0591-0.5217) |

**Table S 6. Contributions of model compounds *j* to volatility bins $C_i$* ($\chi_{j,i}$ values) for cases org, id, and sd. Minimal contribution of model compounds is 0.01.**

| $C_i$* ($\mu g\ m^{-3}$) | *Exp No* | *1* | *2* | *3* | *4* | *7* | *8* | *9* | *10* | *11* | *12* | *13* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.1 | ValT4N10 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.5 | 0.1 | 0.1 | 0.1 | 0.1 | 0.5 |
| | 3-hydroxyglutaric acid | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.5 | 0.9 | 0.9 | 0.9 | 0.9 | 0.5 |
| 1 | Pinic acid | 0.9 | 0.1 | 0.9 | 0.9 | 0.3 | 0.5 | 0.1 | 0.9 | 0.9 | 0.9 | 0.5 |
| | Hopinonic acid | 0.1 | 0.9 | 0.1 | 0.1 | 0.7 | 0.5 | 0.9 | 0.1 | 0.1 | 0.1 | 0.5 |
| 10 | Norpinic acid | 0.5 | 0.5 | 0.5 | 0.6 | 0.5 | 0.5 | 0.5 | 0.99 | 0.5 | 0.99 | 0.5 |
| | 2-hydroxy-terpenylic acid | 0.5 | 0.5 | 0.5 | 0.4 | 0.5 | 0.5 | 0.5 | 0.01 | 0.5 | 0.01 | 0.5 |
| 100 | 10-Oxopinonic acid | 0.2 | 0.9 | 0.1 | 0.1 | 0.7 | 0.5 | 0.9 | 0.01 | 0.1 | 0.01 | 0.5 |
| | 4-Oxopinonic acid | 0.8 | 0.1 | 0.9 | 0.9 | 0.3 | 0.5 | 0.1 | 0.99 | 0.9 | 0.99 | 0.5 |

**Table S 7. Contributions of model compounds *j* to volatility bins $C_i$* ($\chi_{j,i}$ values) for case sdfr. Minimal contribution of model compounds is 0.01.**

| $C_i$* ($\mu g\ m^{-3}$) | *Exp No* | *1* | *2* | *3* | *4* | *7* | *8* | *9* | *10* | *11* | *12* | *13* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.1 | ValT4N10 | 0.09 | 0.09 | 0.1 | 0.1 | 0.1 | 0.1 | 0.09 | 0.01 | 0.1 | 0.01 | 0.1 |
| | 3-hydroxyglutaric acid | 0.01 | 0.01 | 0.1 | 0.1 | 0.1 | 0.1 | 0.01 | 0.01 | 0.1 | 0.01 | 0.1 |
| | ValT4N3 | 0.9 | 0.9 | 0.8 | 0.8 | 0.8 | 0.8 | 0.9 | 0.98 | 0.8 | 0.98 | 0.8 |
| 1 | 3-oxoadipic acid | 0.02 | 0.02 | 0.05 | 0.1 | 0.02 | 0.1 | 0.02 | 0.01 | 0.1 | 0.01 | 0.1 |
| | Pinic acid | 0.02 | 0.02 | 0.05 | 0.1 | 0.02 | 0.1 | 0.02 | 01 | 0.2 | 0.2 | 0.2 |
| | Hopinonic acid | 0.96 | 0.96 | 0.9 | 0.8 | 0.96 | 0.8 | 0.96 | 0.98 | 0.7 | 0.79 | 0.7 |
| 10 | Glutaric acid | 0.59 | 0.59 | 0.05 | 0.96 | 0.68 | 0.1 | 0.59 | 0.01 | 0.4 | 0.01 | 0.15 |
| | Norpinic acid | 0.01 | 0.01 | 0.05 | 002 | 0.02 | 0.1 | 0.01 | 0.88 | 0.5 | 0.98 | 0.75 |
| | 2-hydroxy-terpenylic acid | 0.4 | 0.4 | 0.9 | 0.02 | 0.3 | 0.8 | 0.4 | 0.11 | 0.1 | 0.01 | 0.1 |
| 100 | 5-COOH-3-OH-pentanal | 0.97 | 0.97 | 0.67 | 0.76 | 0.65 | 0.69 | 0.97 | 0.29 | 0.72 | 0.08 | 0.79 |
| | Succinic acid | 0.01 | 0.01 | 0.1 | 0.2 | 0.25 | 0.01 | 0.01 | 0.24 | 0.18 | 0.32 | 0.01 |
| | 10-Oxopinonic acid | 0.01 | 0.01 | 0.18 | 0.02 | 0.05 | 0.15 | 0.01 | 0.46 | 0.05 | 0.1 | 0.1 |
| | 4-Oxopinonic acid | 0.01 | 0.01 | 0.05 | 0.02 | 0.05 | 0.15 | 0.01 | 0.01 | 0.05 | 0.5 | 0.1 |

**Table S 8. Contributions of model compounds *j* to volatility bins $C_i$* ($\chi_{j,i}$ values) for case orgfr. Minimal contribution of model compounds is 0.01.**

| $C_i^*$ ($\mu g\ m^{-3}$) | *Exp No* | *1* | *2* | *3* | *4* | *7* | *8* | *9* | *10* | *11* | *12* | *13* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.1 | ValT4N10 | 0.09 | 0.09 | 0.05 | 0.03 | 0.05 | 0.1 | 0.1 | 0.01 | 0.01 | 0.01 | 0.1 |
| | 3-hydroxyglutaric acid | 0.01 | 0.01 | 0.9 | 0.94 | 0.9 | 0.1 | 0.1 | 0.01 | 0.01 | 0.98 | 0.1 |
| | ValT4N3 | 0.9 | 0.9 | 0.05 | 0.03 | 0.05 | 0.8 | 0.8 | 0.98 | 0.98 | 0.01 | 0.8 |
| 1 | 3-oxoadipic acid | 0.02 | 0.02 | 0.05 | 0.21 | 0.02 | 0.1 | 0.02 | 0.05 | 0.01 | 0.05 | 0.1 |
| | Pinic acid | 0.02 | 0.02 | 0.05 | 0.01 | 0.02 | 0.1 | 0.02 | 0.9 | 0.01 | 0.9 | 0.2 |
| | Hopinonic acid | 0.96 | 0.96 | 0.9 | 0.78 | 0.96 | 0.8 | 0.96 | 0.05 | 0.98 | 0.05 | 0.7 |
| 10 | Glutaric acid | 0.98 | 0.98 | 0.05 | 0.02 | 0.98 | 0.1 | 0.98 | 0.01 | 0.01 | 0.01 | 0.15 |
| | Norpinic acid | 0.01 | 0.01 | 0.35 | 0.49 | 0.01 | 0.1 | 0.01 | 0.98 | 0.77 | 0.98 | 0.75 |
| | 2-hydroxy-terpenylic acid | 0.01 | 0.01 | 0.6 | 0.49 | 0.01 | 0.8 | 0.01 | 0.01 | 0.22 | 0.01 | 0. 1 |
| 100 | 5-COOH-3-OH-pentanal | 0.9 | 0.8 | 0.7 | 0.01 | 0.8 | 0.4 | 0.58 | 0.01 | 0.01 | 0.01 | 0.3 |
| | Succinic acid | 0.08 | 0.18 | 0.89 | 0.9 | 0.18 | 0.3 | 0.4 | 0.44 | 0.79 | 0.44 | 0.6 |
| | 10-Oxopinonic acid | 0.01 | 0.01 | 0.01 | 0.02 | 0.01 | 0.15 | 0.01 | 0.35 | 0.01 | 0.01 | 0.05 |
| | 4-Oxopinonic acid | 0.01 | 0.01 | 0.09 | 0.02 | 0.01 | 0.15 | 0.01 | 0.2 | 0.19 | 0.54 | 0.05 |

**Table S 9. Experimental organic yields and O:C ratios compared with calculated average organic yield, water content, and O:C ratio for the different cases. The first column gives the experiment number and relative humidity of the calculated case. Experimental conditions marked with "c" refer to the corresponding experiment.**

| *Expt No* | | *Experiment* | *Calculations* | | | | |
|---|---|---|---|---|---|---|---|
| | | | Case org | Case id | Case sd | Case sdfr | Case orgfr |
| Expt 1 | org yield (µg m$^{-3}$) | $2.1^{c}$ | 8.58 | 7.94 | 8.29 | 4.67 | 3.23 |
| 28% RH | water (µg m$^{-3}$) | | 0.351 | 0.307 | – | – | 0.126 |
| | O:C | $0.72^{c}$ | 0.509 | 0.512 | 0.517 | 0.561 | 0.547 |
| Expt1 | org yield (µg m$^{-3}$) | 13.4 | 13.83 | 15.88 | 12.70 | 19.46 | 13.71 |
| 69% RH | water (µg m$^{-3}$) | | 1.822 | 3.431 | – | – | 3.153 |
| | O:C | 0.62 | 0.492 | 0.483 | 0.489 | 0.685 | 0.694 |
| Expt 2 | org yield (µg m$^{-3}$) | $2.1^{c}$ | 6.56 | 6.40 | 6.76 | 4.44 | 4.03 |
| 28% RH | water (µg m$^{-3}$) | | 0.293 | 0.249 | – | – | 0.140 |
| | O:C | $0.72^{c}$ | 0.536 | 0.536 | 0.539 | 0.518 | 0.526 |
| Expt 2 | org yield (µg m$^{-3}$) | 8.6 | 9.30 | 10.23 | 8.89 | 11.80 | 8.82 |
| 67% RH | water (µg m$^{-3}$) | | 1.279 | 2.041 | – | – | 1.505 |
| | O:C | 0.62 | 0.519 | 0.510 | 0.521 | 0.604 | 0.617 |
| Expt 3 | org yield (µg m$^{-3}$) | $3.9^{c}$ | 7.69 | 6.99 | 7.93 | 3.81 | 4.31 |
| 29% RH | water (µg m$^{-3}$) | | 0.329 | 0.286 | – | – | 0.239 |
| | O:C | $0.66^{c}$ | 0.509 | 0.513 | 0.512 | 0.570 | 0.621 |
| Expt 3 | org yield (µg m$^{-3}$) | 12.6 | 12.74 | 14.41 | 12.45 | 13.82 | 13.25 |
| 66% RH | water (µg m$^{-3}$) | | 1.504 | 2.707 | – | – | 2.724 |
| | O:C | 0.62 | 0.489 | 0.479 | 0.490 | 0.666 | 0.691 |
| Expt 4 | org yield (µg m$^{-3}$) | 3.9 | 4.22 | 3.79 | 4.65 | 4.45 | 3.84 |
| 29% RH | water (µg m$^{-3}$) | | 0.186 | 0.158 | – | – | 0.223 |
| | O:C | 0.66 | 0.521 | 0.526 | 0.523 | 0.678 | 0.651 |
| Expt 4 | org yield (µg m$^{-3}$) | $12.6^{c}$ | 7.48 | 7.99 | 7.39 | 11.23 | 12.32 |
| 66% RH | water (µg m$^{-3}$) | | 0.944 | 1.541 | – | – | 2.776 |
| | O:C | $0.62^{c}$ | 0.503 | 0.499 | 0.505 | 0.757 | 0.733 |
| Expt 7 | org yield (µg m$^{-3}$) | $5.5^{c}$ | 12.16 | 11.73 | 12.68 | 8.45 | 7.37 |
| 26 %RH | water (µg m$^{-3}$) | | 0.465 | 0.408 | – | – | 0.357 |
| | O:C | $0.60^{c}$ | 0.508 | 0.508 | 0.510 | 0.523 | 0.602 |
| Expt 7 | org yield (µg m$^{-3}$) | 16.2 | 16.36 | 17.71 | 16.20 | 17.35 | 16.54 |
| 67 %RH | water (µg m$^{-3}$) | | 1.874 | 3.505 | – | – | 3.588 |
| | O:C | 0.64 | 0.502 | 0.495 | 0.502 | 0.596 | 0.678 |
| Expt 11 | org yield (µg m$^{-3}$) | 5.5 | 4.88 | 4.46 | 5.18 | 5.36 | 5.21 |
| 26%RH | water (µg m$^{-3}$) | | 0.188 | 0.155 | – | – | 0.205 |
| | O:C | 0.60 | 0.513 | 0.517 | 0.516 | 0.579 | 0.551 |
| Exp 11 | org yield (µg m$^{-3}$) | $16.2^{c}$ | 8.65 | 9.62 | 8.51 | 14.34 | 16.57 |
| 67%RH | water (µg m$^{-3}$) | | 1.092 | 1.910 | – | – | 3.589 |
| | O:C | $0.64^{c}$ | 0.493 | 0.486 | 0.494 | 0.678 | 0.691 |
| Expt 8 | org yield (µg m$^{-3}$) | $5.3^{c}$ | 8.35 | 7.90 | 8.84 | 5.27 | 5.04 |
| 25 %RH | water (µg m$^{-3}$) | | 0.252 | 0.254 | – | – | 0.192 |
| | O:C | $0.57^{c}$ | 0.494 | 0.495 | 0.496 | 0.563 | 0.563 |
| Expt 8 | org yield (µg m$^{-3}$) | 12.3 | 11.93 | 12.70 | 12.00 | 13.33 | 11.88 |
| 60 %RH | water (µg m$^{-3}$) | | 1.180 | 1.826 | – | – | 1.741 |
| | O:C | 0.62 | 0.485 | 0.480 | 0.484 | 0.626 | 0.640 |
| Expt 13 | org yield (µg m$^{-3}$) | 5.3 | 5.10 | 4.77 | 5.53 | 5.32 | 5.45 |
| 25 %RH | water (µg m$^{-3}$) | | 0.179 | 0.153 | – | – | 0.211 |
| | O:C | 0.57 | 0.526 | 0.524 | 0.523 | 0.558 | 0.576 |
| Expt 13 | org yield (µg m$^{-3}$) | $12.3^{c}$ | 7.83 | 8.25 | 7.78 | 12.61 | 12.80 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 60 %RH | water (µg m$^{-3}$) | | 0.805 | 1.197 | – | – | 2.125 |
| | O:C | 0.62[c] | 0.505 | 0.499 | 0.508 | 0.626 | 0.673 |
| Expt 9 | org yield (µg m$^{-3}$) | 2.4[c] | 7.61 | 7.15 | 8.31 | 5.07 | 3.95 |
| 23 % | water (µg m$^{-3}$) | | 0.254 | 0.212 | – | – | 0.138 |
| | O:C | 0.61[c] | 0.509 | 0.509 | 0.511 | 0.551 | 0.569 |
| Expt 9 | org yield (µg m$^{-3}$) | 11.1 | 10.82 | 11.06 | 10.98 | 12.18 | 10.52 |
| 56 %RH | water (µg m$^{-3}$) | | 1.042 | 1.384 | – | – | 1.564 |
| | O:C | 0.75 | 0.504 | 0.501 | 0.505 | 0.620 | 0.673 |
| Expt 10 | org yield (µg m$^{-3}$) | 20.3[c] | 21.42 | 19.67 | 21.06 | 21.36 | 19.75 |
| 26 %RH | water (µg m$^{-3}$) | | 0.700 | 0.689 | – | | 0.815 |
| | O:C | 0.56[c] | 0.479 | 0.484 | 0.481 | 0.583 | 0.562 |
| Expt 10 | org yield (µg m$^{-3}$) | 29.6 | 27.33 | 27.01 | 26.74 | 28.47 | 30.08 |
| 50 %RH | water (µg m$^{-3}$) | | 1.889 | 2.650 | – | | 3.140 |
| | O:C | 0.64 | 0.467 | 0.468 | 0.467 | 0.643 | 0.606 |
| Expt 12 | org yield (µg m$^{-3}$) | 20.3 | 16.37 | 14.77 | 16.45 | 20.35 | 18.50 |
| 26 %RH | water (µg m$^{-3}$) | | 0.574 | 0.300 | – | | 0.754 |
| | O:C | 0.56 | 0.468 | 0.473 | 0.469 | 0.590 | 0.578 |
| Expt 12 | org yield (µg m$^{-3}$) | 29.6[c] | 21.51 | 21.31 | 21.49 | 28.75 | 30.79 |
| 50 %RH | water (µg m$^{-3}$) | | 1.610 | 1.320 | – | | 3.029 |
| | O:C | 0.64[c] | 0.456 | 0.456 | 0.457 | 0.639 | 0.611 |

**Table S 10. Details of the calculations performed for experiment 4, volatility distributions #2 and #93 at low (29 %) and high (66 %) RH for cases org, id, sd, sdfr, and orgfr: mass fraction of products ($\alpha_2$-$\alpha_5$) in volatility bins with $C^*$ = 0. 1 - 100 µg m$^{-3}$, organic yield, and O:C ratio obtained for the volatility distribution; gas-particle partitioning (g/p) and electrolyte phase / organic-rich phase partitioning (ep/op) of each component.**

| | | *Expt 4, vd #2* | | | | *Expt 4, vd #93* | | | |
|---|---|---|---|---|---|---|---|---|---|
| Volatility bins | $C^* = 0.1$ µg m$^{-3}$ | $\alpha_2 = 0.00229$ | | | | $\alpha_2 = 0.00511$ | | | |
| | $C^* = 1$ µg m$^{-3}$ | $\alpha_3 = 0.01454$ | | | | $\alpha_3 = 0.01760$ | | | |
| | $C^* = 10$ µg m$^{-3}$ | $\alpha_4 = 0.04447$ | | | | $\alpha_4 = 0.02998$ | | | |
| | $C^* = 100$ µg m$^{-3}$ | $\alpha_5 = 0.32354$ | | | | $\alpha_5 = 0.20232$ | | | |
| ***Case org*** | *RH* | *29 %* | | *66 %* | | *29 %* | | *66 %* | |
| | Org yield, µg m$^{-3}$ | 4.48 | | 8.28 | | 3.80 | | 6.02 | |
| | O:C ratio | 0.490 | | 0.478 | | 0.530 | | 0.507 | |
| | *Model compound ratio* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* |
| | Diaterpenylic acid acetate | 0.003 | - | 0.000 | - | 0.012 | - | 0.004 | - |
| | 3-MBTCA | 0.000 | - | 0.000 | - | 0.000 | - | 0.000 | - |
| | ValT4N9 | 0.010 | - | 0.003 | - | 0.003 | - | 0.001 | - |
| | ValT4N10 | 0.009 | - | 0.004 | - | 0.010 | - | 0.005 | - |
| | 3-Hydroxyglutaric acid | 0.075 | - | 0.014 | - | 0.076 | - | 0.017 | - |
| | Pinic acid | 0.548 | - | 0.171 | - | 0.663 | - | 0.241 | - |
| | Hopinonic acid | 0.801 | - | 0.269 | - | 0.905 | - | 0.350 | - |
| | Norpinic acid | 1.555 | - | 0.460 | - | 1.844 | - | 0.639 | - |
| | 2-Hydroxyterpenylic acid | 7.321 | - | 2.172 | - | 8.057 | - | 2.808 | - |
| | 10-Oxopinonic acid | 91.10 | - | 32.35 | - | 106.3 | - | 43.79 | - |
| | 4-Oxopinonic acid | 46.54 | - | 16.31 | - | 53.72 | - | 21.50 | - |
| | Sum | 0.003 | - | 0.000 | - | 7.88 | - | 0.004 | - |
| ***Case id*** | *RH* | *29 %* | | *66 %* | | *29 %* | | *66 %* | |
| | Org yield, µg m$^{-3}$ | 3.92 | | 9.07 | | 3.59 | | 6.39 | |
| | O:C ratio | 0.495 | | 0.473 | | 0.534 | | 0.502 | |
| | *Model compound ratio* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* |
| | Diaterpenylic acid acetate | 0.005 | - | 0.001 | - | 0.014 | - | 0.004 | - |
| | 3-MBTCA | 0.000 | - | 0.000 | - | 0.000 | - | 0.000 | - |
| | ValT4N9 | 0.013 | - | 0.003 | - | 0.006 | - | 0.002 | - |
| | ValT4N10 | 0.019 | - | 0.004 | - | 0.021 | - | 0.006 | - |
| | 3-Hydroxyglutaric acid | 0.068 | - | 0.014 | - | 0.073 | - | 0.020 | - |
| | Pinic acid | 0.626 | - | 0.132 | - | 0.671 | - | 0.184 | - |
| | Hopinonic acid | 1.011 | - | 0.214 | - | 1.084 | - | 0.298 | - |
| | Norpinic acid | 1.912 | - | 0.405 | - | 2.051 | - | 0.563 | - |
| | 2-Hydroxyterpenylic acid | 9.447 | - | 1.998 | - | 10.13 | - | 2.780 | - |
| | 10-Oxopinonic acid | 99.59 | - | 21.07 | - | 106.8 | - | 29.30 | - |
| | 4-Oxopinonic acid | 63.31 | - | 13.39 | - | 67.90 | - | 18.63 | - |
| | Sum | 12.38 | - | 4.91 | - | 0.014 | - | 0.004 | - |
| ***Case sd*** | *RH* | *29 %* | | *66 %* | | *29 %* | | *66 %* | |
| | Org yield, µg m$^{-3}$ | 4.86 | | 8.24 | | 3.99 | | 5.79 | |
| | O:C ratio | 0.492 | | 0.478 | | 0.532 | | 0.509 | |
| | *Model compound ratio* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* |

|  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | Diaterpenylic acid acetate | 0.007 | 0 | 0.003 | $5\cdot10^{-5}$ | 0.008 | 0 | 0.004 | $2\cdot10^{-4}$ |
|  | 3-MBTCA | 0.000 | $3\cdot10^{-11}$ | 0.000 | 0.019 | 0.000 | $3\cdot10^{-11}$ | 0.000 | 0.052 |
|  | ValT4N9 | 0.002 | 0 | 0.001 | $4\cdot10^{-6}$ | 0.003 | 0 | 0.001 | $2\cdot10^{-5}$ |
|  | ValT4N10 | 0.009 | 0 | 0.004 | $2\cdot10^{-7}$ | 0.012 | 0 | 0.005 | $1\cdot10^{-6}$ |
|  | 3-Hydroxyglutaric acid | 0.039 | $3\cdot10^{-5}$ | 0.008 | 0.671 | 0.035 | $1\cdot10^{-5}$ | 0.008 | 1.301 |
|  | Pinic acid | 0.455 | 0 | 0.168 | $5\cdot10^{-5}$ | 0.578 | 0 | 0.257 | $2\cdot10^{-4}$ |
|  | Hopinonic acid | 0.801 | 0 | 0.278 | $1\cdot10^{-6}$ | 1.046 | 0 | 0.400 | $6\cdot10^{-6}$ |
|  | Norpinic acid | 1.210 | 0 | 0.447 | $4\cdot10^{-4}$ | 1.465 | 0 | 0.677 | $1\cdot10^{-3}$ |
|  | 2-Hydroxyterpenylic acid | 5.381 | 0 | 2.101 | $2\cdot10^{-4}$ | 6.041 | 0 | 3.013 | $8\cdot10^{-4}$ |
|  | 10-Oxopinonic acid | 89.04 | 0 | 33.28 | $1\cdot10^{-6}$ | 118.5 | 0 | 49.58 | $7\cdot10^{-6}$ |
|  | 4-Oxopinonic acid | 48.73 | 0 | 16.90 | $1\cdot10^{-6}$ | 66.23 | 0 | 24.61 | $7\cdot10^{-6}$ |
|  | AS | 0.00 | 13.76 | 0.00 | 44.53 | 0.00 | 11.19 | 0.00 | 49.41 |
|  | Organic sum | 9.788 | $2\cdot10^{-6}$ | 5.473 | 0.019 | 7.423 | $6\cdot10^{-6}$ | 7.305 | 0.073 |
| ***Case sdfr*** | *RH* | *29 %* |  | *66 %* |  | *29 %* |  | *66 %* |  |
|  | Org yield, µg $m^{-3}$ | 6.21 |  | 15.77 |  | 2.45 |  | 7.8 |  |
|  | O:C ratio | 0.755 |  | 0.806 |  | 0.576 |  | 0.69 |  |
|  | *Model compound ratio* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* |
|  | Diaterpenylic acid acetate | 0.010 | 0 | 0.003 | - | 0.012 | 0 | 0.006 | 0.159 |
|  | 3-MBTCA | $1\cdot10^{-5}$ | $5\cdot10^{-12}$ | 0.000 | - | 0.000 | $5\cdot10^{-11}$ | $7\cdot10^{-6}$ | 2.223 |
|  | ValT4N9 | 0.007 | 0 | 0.001 | - | 0.005 | 0 | 0.002 | 0.067 |
|  | ValT4N10 | 0.067 | 0 | 0.013 | - | 0.028 | 0 | 0.014 | 0.020 |
|  | 3-Hydroxyglutaric acid | 0.005 | $2\cdot10^{-6}$ | 0.001 | - | 0.049 | $5\cdot10^{-5}$ | 0.002 | 10.17 |
|  | ValT4N3 | 0.219 | 0 | 0.051 | - | 0.036 | 0 | 0.021 | 0.005 |
|  | 3-Oxoadipic acid | 0.053 | $1\cdot10^{-9}$ | 0.012 | - | 0.267 | $2\cdot10^{-8}$ | 0.031 | 3.083 |
|  | Pinic acid | 1.090 | 0 | 0.247 | - | 0.847 | 0 | 0.393 | 0.126 |
|  | Hopinonic acid | 4.625 | 0 | 0.712 | - | 1.701 | 0 | 0.752 | 0.030 |
|  | Glutaric acid | 1.817 | $2\cdot10^{-7}$ | 0.513 | - | 9.423 | $3\cdot10^{-6}$ | 1.066 | 3.881 |
|  | Norpinic acid | 1.754 | 0 | 0.405 | - | 2.132 | 0 | 0.864 | 0.290 |
|  | 2-Hydroxyterpenylic acid | 6.079 | 0 | 1.518 | - | 8.949 | 0 | 3.824 | 0.281 |
|  | 5-COOH-3-OH-pentanal | 18.23 | $1\cdot10^{-10}$ | 3.80 | - | 86.76 | $1\cdot10^{-9}$ | 10.73 | 3.076 |
|  | Succinic acid | 3.405 | $4\cdot10^{-4}$ | 0.980 | - | 27.41 | $7\cdot10^{-3}$ | 1.538 | 8.926 |
|  | 10-Oxopinonic acid | 500.4 | 0 | 87.75 | - | 188.7 | 0 | 93.89 | 0.033 |
|  | 4-Oxopinonic acid | 320.5 | 0 | 47.70 | - | 121.2 | 0 | 53.65 | 0.033 |
|  | AS | 0 | 0.718 | 0 | - | 0 | 7.212 | 0 | 78.55 |
|  | Organic sum | 6.805 | $1\cdot10^{-4}$ | 2.063 | - | 15.96 | $8\cdot10^{-4}$ | 3.450 | 2.256 |
| ***Case orgfr*** | *RH* | *29 %* |  | *66 %* |  | *29 %* |  | *66 %* |  |
|  | Org yield, µg $m^{-3}$ | 4.29 |  | 17.53 |  | 3.56 |  | 9.05 |  |
|  | O:C ratio | 0.659 |  | 0.798 |  | 0.661 |  | 0.730 |  |
|  | *Model compound ratio* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* |
|  | Diaterpenylic acid acetate | 0.009 | - | 0.001 | - | 0.012 | - | 0.002 | - |
|  | 3-MBTCA | $5\cdot10^{-5}$ | - | $3\cdot10^{-6}$ | - | $6\cdot10^{-5}$ | - | $7\cdot10^{-6}$ | - |
|  | ValT4N9 | 0.002 | - | $3\cdot10^{-4}$ | - | 0.003 | - | 0.001 | - |
|  | ValT4N10 | 0.007 | - | 0.001 | - | 0.010 | - | 0.002 | - |
|  | 3-Hydroxyglutaric acid | 0.046 | - | 0.002 | - | 0.055 | - | 0.006 | - |
|  | ValT4N3 | 0.063 | - | 0.020 | - | 0.090 | - | 0.036 | - |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 3-Oxoadipic acid | 0.192 | - | 0.014 | - | 0.240 | - | 0.031 | - |
| Pinic acid | 0.600 | - | 0.098 | - | 0.763 | - | 0.183 | - |
| Hopinonic acid | 0.743 | - | 0.116 | - | 0.992 | - | 0.229 | - |
| Glutaric acid | 8.667 | - | 0.841 | - | 10.47 | - | 1.717 | - |
| Norpinic acid | 1.575 | - | 0.224 | - | 1.972 | - | 0.428 | - |
| 2-Hydroxyterpenylic acid | 5.884 | - | 0.692 | - | 7.573 | - | 1.444 | - |
| 5-COOH-3-OH-pentanal | 64.61 | - | 4.85 | - | 77.04 | - | 10.65 | - |
| Succinic acid | 26.48 | - | 2.234 | - | 31.50 | - | 4.687 | - |
| 10-Oxopinonic acid | 87.93 | - | 15.22 | - | 116.2 | - | 29.68 | - |
| 4-Oxopinonic acid | 42.36 | - | 6.48 | - | 58.94 | - | 13.32 | - |
| AS | - | - | - | - | - | - | - | - |
| Organic sum | 12.31 | - | 1.853 | - | 10.22 | - | 3.02 | - |

**Table S 11. Details of the calculations performed for experiment 8, volatility distribution #11 and experiment 13, volatility distribution #45 at low (25 %) and high (60 %) RH for cases org, id, sd, sdfr, and orgfr: mass fraction of products ($\alpha_2$-$\alpha_5$) in volatility bins with $C^*$ = 0. 1 - 100 µg m$^{-3}$, organic yield, and O:C ratio obtained for the volatility distribution; gas-particle partitioning (g/p) and electrolyte phase/ organic-rich phase partitioning (ep/op) of each component.**

| | | *Expt 8, vd #11* | | | | *Expt 13, vd #45* | | | |
|---|---|---|---|---|---|---|---|---|---|
| Volatility bins | $C^*$ = 0. 1 µg m$^{-3}$: $\alpha_2$ | 0.00406 | | | | 0.00780 | | | |
| | $C^*$ = 1 µg m$^{-3}$: $\alpha_3$ | 0.03478 | | | | 0.01355 | | | |
| | $C^*$ = 10 µg m$^{-3}$: $\alpha_4$ | 0.06248 | | | | 0.05476 | | | |
| | $C^*$ = 100 µg m$^{-3}$: $\alpha_5$ | 0.36049 | | | | 0.30196 | | | |
| ***Case org*** | *RH* | *25 %* | | *60 %* | | *25 %* | | *60 %* | |
| | Org yield, µg m$^{-3}$ | 8.59 | | 12.54 | | 5.11 | | 8.09 | |
| | O:C ratio | 0.479 | | 0.475 | | 0.536 | | 0.516 | |
| | *Model compound ratio* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* |
| | Diaterpenylic acid acetate | 0.006 | - | 0.002 | - | 0.009 | - | 0.003 | - |
| | 3-MBTCA | 0.000 | - | 0.000 | - | 0.000 | - | 0.000 | - |
| | ValT4N9 | 0.002 | - | 0.001 | - | 0.003 | - | 0.001 | - |
| | ValT4N10 | 0.006 | - | 0.003 | - | 0.010 | - | 0.004 | - |
| | 3-Hydroxyglutaric acid | 0.044 | - | 0.011 | - | 0.063 | - | 0.016 | - |
| | Pinic acid | 0.300 | - | 0.124 | - | 0.516 | - | 0.196 | - |
| | Hopinonic acid | 0.467 | - | 0.199 | - | 0.801 | - | 0.311 | - |
| | Norpinic acid | 0.854 | - | 0.338 | - | 1.431 | - | 0.522 | - |
| | 2-Hydroxyterpenylic acid | 4.266 | - | 1.658 | - | 6.695 | - | 2.440 | - |
| | 10-Oxopinonic acid | 51.91 | - | 23.65 | - | 88.43 | - | 36.90 | - |
| | 4-Oxopinonic acid | 28.46 | - | 12.47 | - | 48.78 | - | 19.33 | - |
| | Sum | 6.182 | - | 3.938 | - | 9.141 | - | 5.421 | - |
| ***Case id*** | *RH* | *25 %* | | *60 %* | | *25 %* | | *60 %* | |
| | Org yield, µg m$^{-3}$ | 8.03 | | 13.23 | | 4.74 | | 8.48 | |
| | O:C ratio | 0.479 | | 0.471 | | 0.539 | | 0.509 | |
| | *Model compound ratio* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* |
| | Diaterpenylic acid acetate | 0.007 | - | 0.001 | - | 0.012 | - | 0.004 | - |
| | 3-MBTCA | 0.000 | - | 0.000 | - | 0.000 | - | 0.000 | - |
| | ValT4N9 | 0.003 | - | 0.003 | - | 0.005 | - | 0.001 | - |
| | ValT4N10 | 0.010 | - | 0.003 | - | 0.017 | - | 0.005 | - |
| | 3-Hydroxyglutaric acid | 0.036 | - | 0.012 | - | 0.061 | - | 0.018 | - |
| | Pinic acid | 0.333 | - | 0.108 | - | 0.559 | - | 0.167 | - |
| | Hopinonic acid | 0.538 | - | 0.175 | - | 0.903 | - | 0.270 | - |
| | Norpinic acid | 1.017 | - | 0.331 | - | 1.708 | - | 0.511 | - |
| | 2-Hydroxyterpenylic acid | 5.025 | - | 1.638 | - | 8.439 | - | 2.526 | - |
| | 10-Oxopinonic acid | 52.97 | - | 17.26 | - | 88.96 | - | 26.63 | - |
| | 4-Oxopinonic acid | 33.67 | - | 10.97 | - | 56.55 | - | 16.93 | - |
| | Sum | 6.678 | - | 3.692 | - | 9.944 | - | 5.142 | - |
| ***Case sd*** | *RH* | *25 %* | | *60 %* | | *25 %* | | *60 %* | |
| | Org yield, µg m$^{-3}$ | 9.11 | | 12.66 | | 5.57 | | 8.03 | |
| | O:C ratio | 0.480 | | 0.476 | | 0.537 | | 0.520 | |
| | *Model compound ratio* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* |
| | Diaterpenylic acid acetate | 0.004 | 0.0 | 0.002 | $3\cdot10^{-6}$ | 0.003 | $3\cdot10^{-5}$ | 0.003 | $2\cdot10^{-5}$ |
| | 3-MBTCA | 0.000 | 0.0 | 0.000 | 0.003 | 0.000 | 0.018 | 0.000 | 0.013 |
| | ValT4N9 | 0.002 | 0.0 | 0.001 | $1\cdot10^{-7}$ | 0.001 | $1\cdot10^{-6}$ | 0.001 | $8\cdot10^{-7}$ |
| | ValT4N10 | 0.006 | 0.0 | 0.003 | $4\cdot10^{-9}$ | 0.006 | $5\cdot10^{-8}$ | 0.005 | $3\cdot10^{-8}$ |

|  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | 3-Hydroxyglutaric acid | 0.025 | $2\cdot10^{-7}$ | 0.008 | 0.202 | 0.009 | 0.898 | 0.008 | 0.697 |
|  | Pinic acid | 0.253 | 0.0 | 0.119 | $3\cdot10^{-6}$ | 0.210 | $2\cdot10^{-5}$ | 0.194 | $2\cdot10^{-5}$ |
|  | Hopinonic acid | 0.460 | 0.0 | 0.201 | $2\cdot10^{-8}$ | 0.368 | $3\cdot10^{-7}$ | 0.332 | $2\cdot10^{-7}$ |
|  | Norpinic acid | 0.684 | 0.0 | 0.318 | $3\cdot10^{-5}$ | 0.556 | $2\cdot10^{-4}$ | 0.509 | $2\cdot10^{-4}$ |
|  | 2-Hydroxyterpenylic acid | 3.246 | 0.0 | 1.538 | $2\cdot10^{-5}$ | 2.667 | $1\cdot10^{-4}$ | 2.369 | $9\cdot10^{-5}$ |
|  | 10-Oxopinonic acid | 49.85 | 0.0 | 23.67 | $4\cdot10^{-8}$ | 42.99 | $4\cdot10^{-7}$ | 39.01 | $3\cdot10^{-7}$ |
|  | 4-Oxopinonic acid | 28.85 | 0.0 | 12.60 | $3\cdot10^{-8}$ | 23.35 | $4\cdot10^{-7}$ | 20.75 | $2\cdot10^{-7}$ |
|  | AS | 0 | 1.599 | 0 | 2.099 | 0 | 7.492 | 0 | 6.402 |
|  | Organic sum | 5.752 | $8\cdot10^{-9}$ | 3.889 | 0.005 | 6.510 | 0.052 | 5.460 | 0.037 |
| ***Case sdfr*** | *RH* | *25 %* |  | *60 %* |  | *25 %* |  | *60 %* |  |
|  | Org yield, µg m$^{-3}$ | 5.10 |  | 12.96 |  | 5.22 |  | 12.32 |  |
|  | O:C ratio | 0.566 |  | 0.627 |  | 0.566 |  | 0.623 |  |
|  | *Model compound ratio* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* |
|  | Diaterpenylic acid acetate | 0.007 | 0.0 | 0.002 | $3\cdot10^{-6}$ | 0.006 | 0.0 | 0.002 | $2\cdot10^{-6}$ |
|  | 3-MBTCA | 0.000 | 0.0 | $4\cdot10^{-6}$ | 0.001 | 0.000 | 0.0 | $4\cdot10^{-6}$ | 0.003 |
|  | ValT4N9 | 0.003 | 0.0 | 0.001 | $1\cdot10^{-7}$ | 0.002 | 0.0 | 0.001 | $2\cdot10^{-7}$ |
|  | ValT4N10 | 0.013 | 0.0 | 0.005 | $5\cdot10^{-9}$ | 0.011 | 0.0 | 0.005 | $1\cdot10^{-8}$ |
|  | 3-Hydroxyglutaric acid | 0.023 | $2\cdot10^{-7}$ | 0.003 | 0.041 | 0.024 | $4\cdot10^{-7}$ | 0.002 | 0.094 |
|  | ValT4N3 | 0.018 | 0.0 | 0.011 | $1\cdot10^{-9}$ | 0.015 | 0.0 | 0.012 | $3\cdot10^{-9}$ |
|  | 3-Oxoadipic acid | 0.130 | $8\cdot10^{-12}$ | 0.020 | 0.003 | 0.133 | $2\cdot10^{-11}$ | 0.021 | 0.008 |
|  | Pinic acid | 0.468 | 0.0 | 0.148 | $3\cdot10^{-6}$ | 0.444 | 0.0 | 0.161 | $7\cdot10^{-6}$ |
|  | Hopinonic acid | 0.957 | 0.0 | 0.304 | $3\cdot10^{-8}$ | 0.831 | 0.0 | 0.321 | $7\cdot10^{-8}$ |
|  | Glutaric acid | 4.659 | $7\cdot10^{-9}$ | 0.878 | 0.014 | 4.807 | $2\cdot10^{-8}$ | 0.887 | 0.034 |
|  | Norpinic acid | 1.142 | 0.0 | 0.314 | $2\cdot10^{-5}$ | 1.112 | 0.0 | 0.339 | $6\cdot10^{-5}$ |
|  | 2-Hydroxyterpenylic acid | 4.897 | 0.0 | 1.271 | $1\cdot10^{-5}$ | 4.403 | 0.0 | 1.268 | $2\cdot10^{-5}$ |
|  | 5-COOH-3-OH-pentanal | 40.84 | $2\cdot10^{-13}$ | 6.567 | 0.002 | 42.49 | $5\cdot10^{-13}$ | 6.614 | 0.005 |
|  | Succinic acid | 13.22 | $2\cdot10^{-4}$ | 1.980 | 0.113 | 14.00 | $4\cdot10^{-7}$ | 1.770 | 0.271 |
|  | 10-Oxopinonic acid | 102.8 | 0.0 | 36.67 | $4\cdot10^{-8}$ | 93.99 | 0.0 | 40.07 | $1\cdot10^{-7}$ |
|  | 4-Oxopinonic acid | 67.59 | 0.0 | 21.47 | $4\cdot10^{-8}$ | 57.70 | 0.0 | 22.66 | $1\cdot10^{-7}$ |
|  | AS | 0.0 | 6.708 | 0.0 | 1.777 | 0.00 | 12.79 | 0.00 | 3.725 |
|  | Organic sum | 14.35 | $1\cdot10^{-6}$ | 4.493 | 0.003 | 12.75 | $2\cdot10^{-6}$ | 4.25 | 0.008 |
| ***Case orgfr*** | *RH* | *25 %* |  | *60 %* |  | *25 %* |  | *60 %* |  |
|  | Org yield, µg m$^{-3}$ | 4.94 |  | 12.04 |  | 5.34 |  | 12.59 |  |
|  | O:C ratio | 0.513 |  | 0.640 |  | 0.578 |  | 0.679 |  |
|  | *Model compound ratio* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* | *g/p* | *ep/op* |
|  | Diaterpenylic acid acetate | 0.003 | - | 0.002 | - | 0.008 | - | 0.002 | - |
|  | 3-MBTCA | $5\cdot10^{-5}$ | - | $7\cdot10^{-6}$ | - | $5\cdot10^{-5}$ | - | $7\cdot10^{-6}$ | - |
|  | ValT4N9 | 0.003 | - | 0.001 | - | 0.002 | - | $1\cdot10^{-3}$ | - |
|  | ValT4N10 | 0.011 | - | 0.003 | - | 0.008 | - | 0.002 | - |
|  | 3-Hydroxyglutaric acid | 0.053 | - | 0.006 | - | 0.053 | - | 0.006 | - |
|  | ValT4N3 | 0.012 | - | 0.005 | - | 0.008 | - | 0.004 | - |
|  | 3-Oxoadipic acid | 0.227 | - | 0.033 | - | 0.215 | - | 0.029 | - |
|  | Pinic acid | 0.519 | - | 0.141 | - | 0.465 | - | 0.133 | - |
|  | Hopinonic acid | 0.812 | - | 0.205 | - | 0.634 | - | 0.163 | - |
|  | Glutaric acid | 8.306 | - | 1.560 | - | 8.253 | - | 1.491 | - |
|  | Norpinic acid | 1.404 | - | 0.346 | - | 1.297 | - | 0.327 | - |
|  | 2-Hydroxyterpenylic acid | 6.511 | - | 1.396 | - | 5.377 | - | 1.113 | - |
|  | 5-COOH-3-OH-pentanal | 71.61 | - | 11.04 | - | 71.22 | - | 9.737 | - |
|  | Succinic acid | 26.15 | - | 4.444 | - | 26.78 | - | 4.272 | - |
|  | 10-Oxopinonic acid | 89.92 | - | 25.25 | - | 74.86 | - | 21.33 | - |
|  | 4-Oxopinonic acid | 52.82 | - | 13.11 | - | 39.21 | - | 9.85 | - |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| AS | - | - | - | - | | - | | - |
| Organic sum | 14.20 | - | 4.677 | - | 11.15 | - | 3.56 | - |

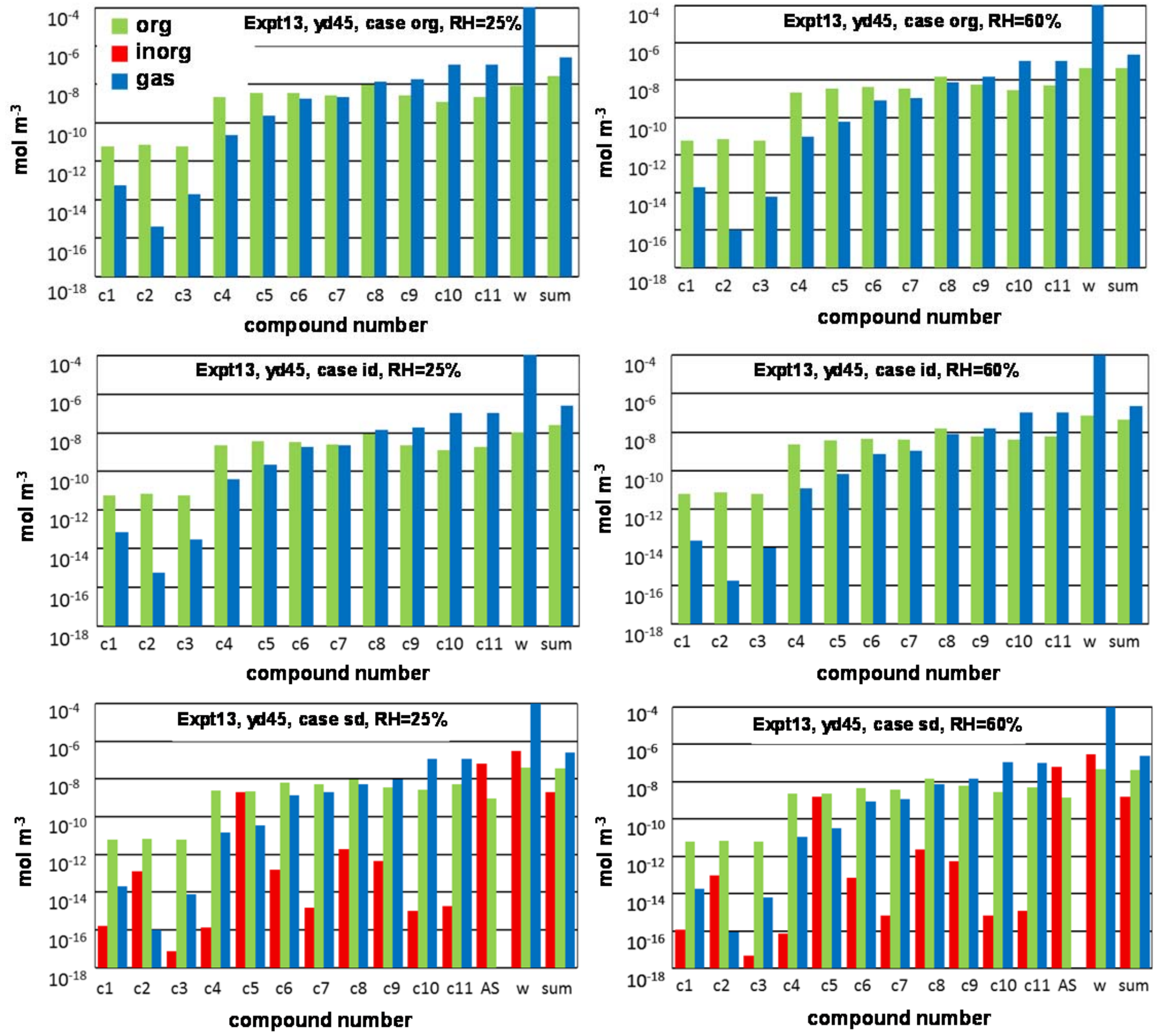


**Figure S15. Equilibrium phase partitioning for cases org, id and sd between gas phase (blue), organic-rich phase (green) and electrolyte phase (red) at low (25 %) and high (60 %) RH for experiment 13, volatility distribution #45. c1: diaterpenylic acid acetate; c2: 3-MBTCA, c3: ValT4N9, c4: ValT4N10, c5: 3-hydroxyglutaric acid, c6: pinic acid, c7: hopinonic acid, c8: norpinic acid, c9: 2-hydroxyterpenylic acid, c10: 10-oxopinonic acid, c11: 4-oxopinonic acid, ammonium sulfate (AS), water (w), and the sum (c1-c11).**

## 3 References

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