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Supplement of

Assessing the influence of NO_x concentrations and relative humidity on secondary organic aerosol yields from α-pinene photo-oxidation through smog chamber experiments and modelling calculations

Lisa Stirnweis et al.

Correspondence to: Imad El-Haddad (imad.el-haddad@psi.ch) and Urs Baltensperger (urs.baltensperger@psi.ch)

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_{NH3} is the concentration of NH_3, V_{mol} is the molar volume, m_{SO4} the mass concentration of SO_4 and M_{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} $(NH_4)_2SO_4$ (= 6×10^{-8} mol/m³ $(NH_4)_2SO_4$) yields 1.6×10^{-6} mol $(NH_4)_2SO_4$ for the full 27 m³ PSI smog chamber. To form NH_4HSO_4 from this, 1.6×10^{-6} mol H_2SO_4 = 1.6×10^{-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.

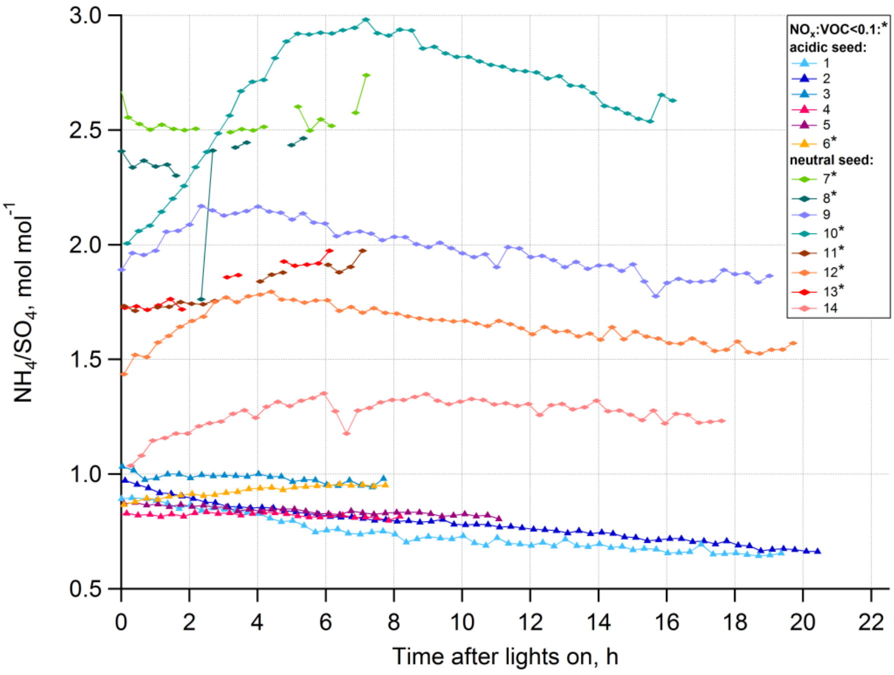


Figure S1. Molar ratio of ammonium to sulfate (NH4/SO4) as a function of time after lights on. Seed composition during experiments 1–6: SA & AHS due to significant concentration of H_2SO_4 added. Note that the ratio of NH_4/SO_4 in pure ammonium sulphate injected in the AMS changed in different days 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).

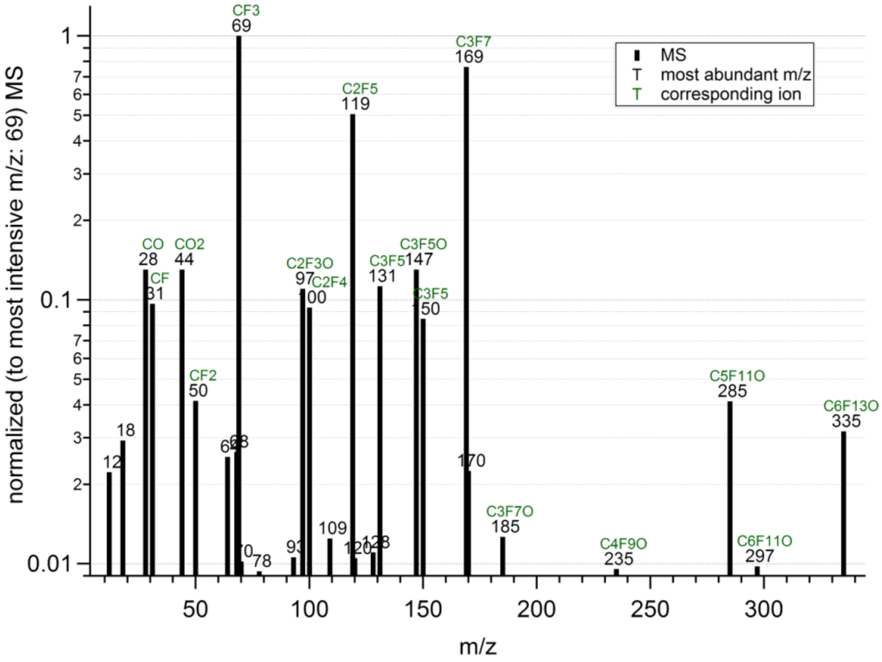


Figure S2. Mass spectrum of the hydrophobic CF-seed measured with the HR-ToF-AMS normalized to CF_3 (the ion with the highest intensity).

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

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_{seed} was determined by applying the loss rate constant of the hydrophobic CF-seed (k_{CF}) or sulfate (k_{SO4}), respectively, to the measured initial SMPS volume concentration V_{initial}. E.g.:

$$V_{\mathrm{seed}} = V_{\mathrm{initial}} \times \exp^{-k_{\mathrm{SO_4}} t}, \tag{S 2}$$

or accordingly with k_{CF} for the hydrophobic CF-seed. The additionally formed organic volume concentration ΔV_{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_{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_{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_{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_{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_{org} of 1 was assumed for experiments 1–6, in which only liquid-phase particles were expected. The CE_{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.

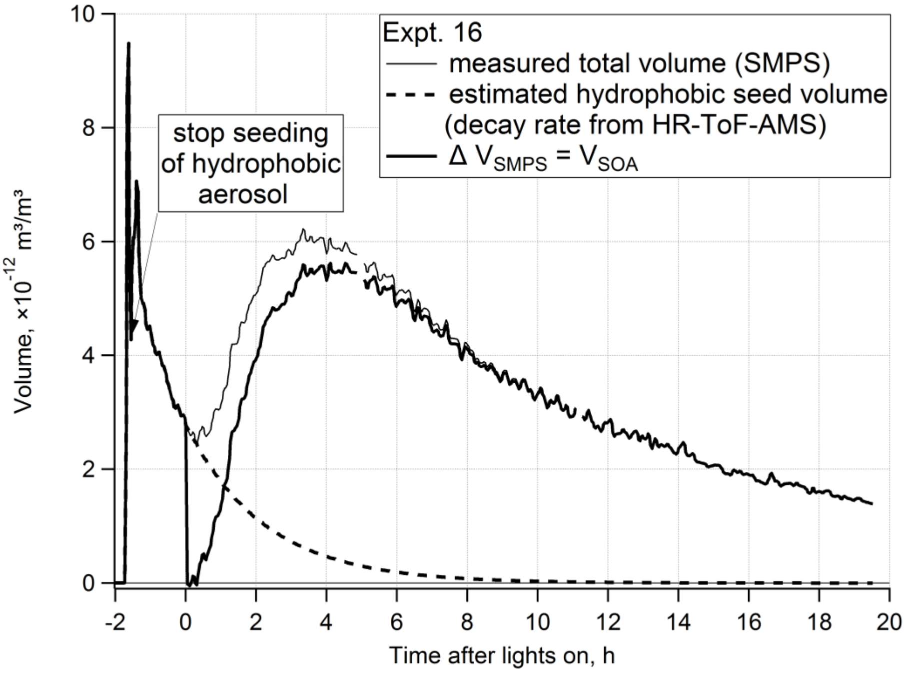


Figure S3. Measured SMPS total volume concentration, estimated hydrophobic seed volume concentration (with decay rate constant k_{CF} determined from HR-ToF-AMS data) and the difference of both, ΔV_{SMPS}, as a function of time after lights on. ΔV_{SMPS} corresponds to the secondary organic volume concentration,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

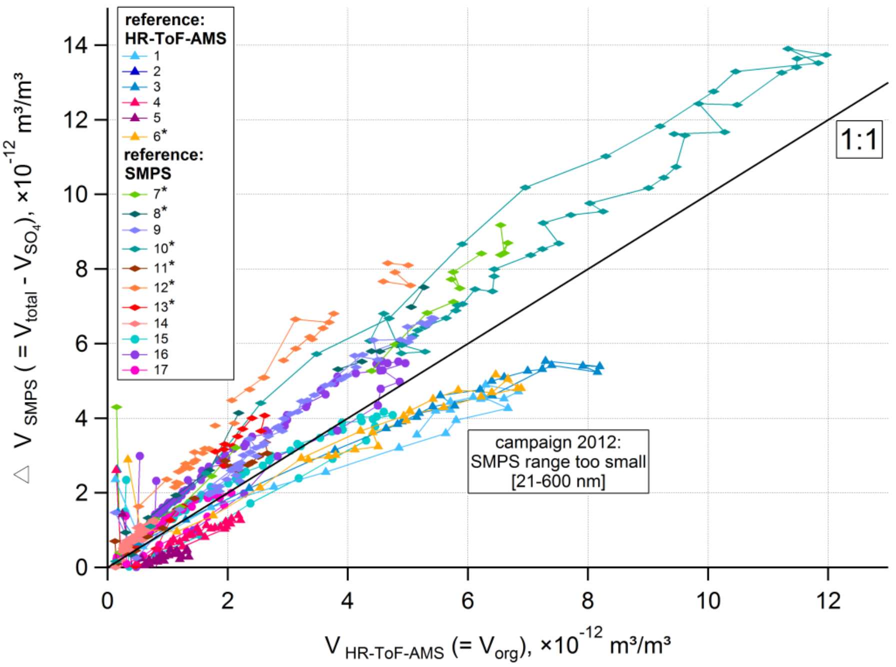


Figure S4. Comparison of 20-minutes averaged organic volume concentrations derived from the SMPS measurement, ΔV_{SMPS}, and the organic compounds derived from the HR-ToF-AMS measurement, $V_{HR\text{-}ToF\text{-}AMS}$ (=V_{org}). ΔV_{SMPS} represents the difference between total SMPS volume concentration, $V_{total,}$ 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

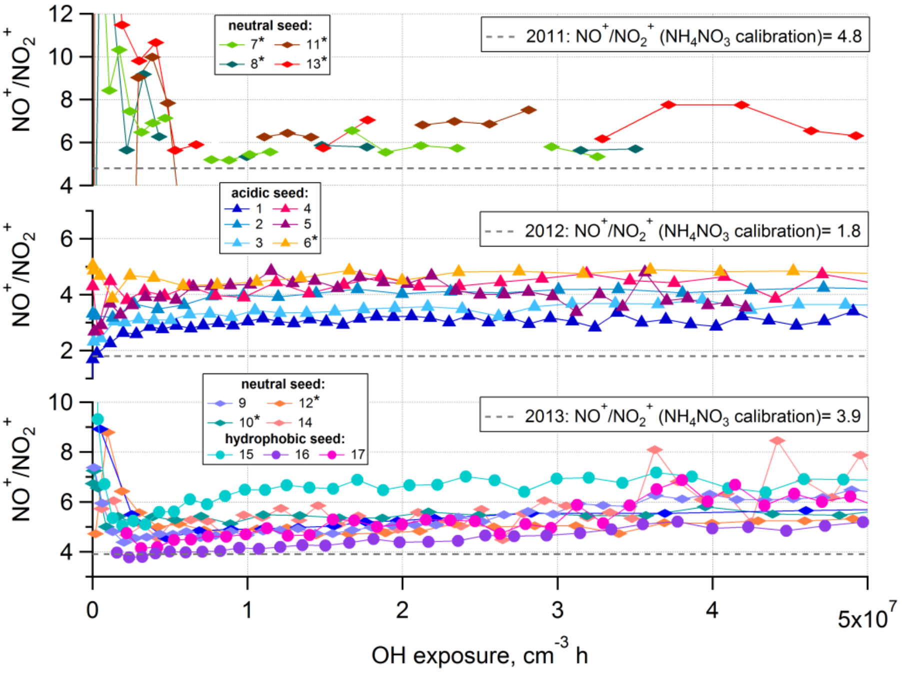


Figure S5. 20-min averaged NO^+/NO_2^+ ratio as a function of OH exposure compared to the measured ratio of NO^+/NO_2^+ from calibration data (dashed lines) using NH_4NO_3 for each set of experiments. The absolute magnitude of observed NO^+/NO_2^+ ratios for NH_4NO_3 are affected by instrument temperature, 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

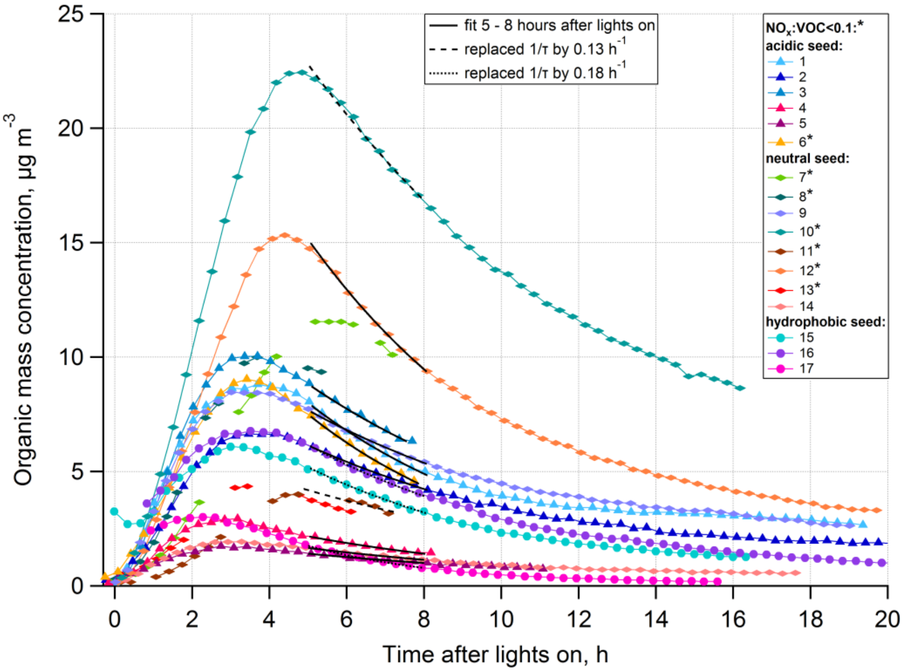
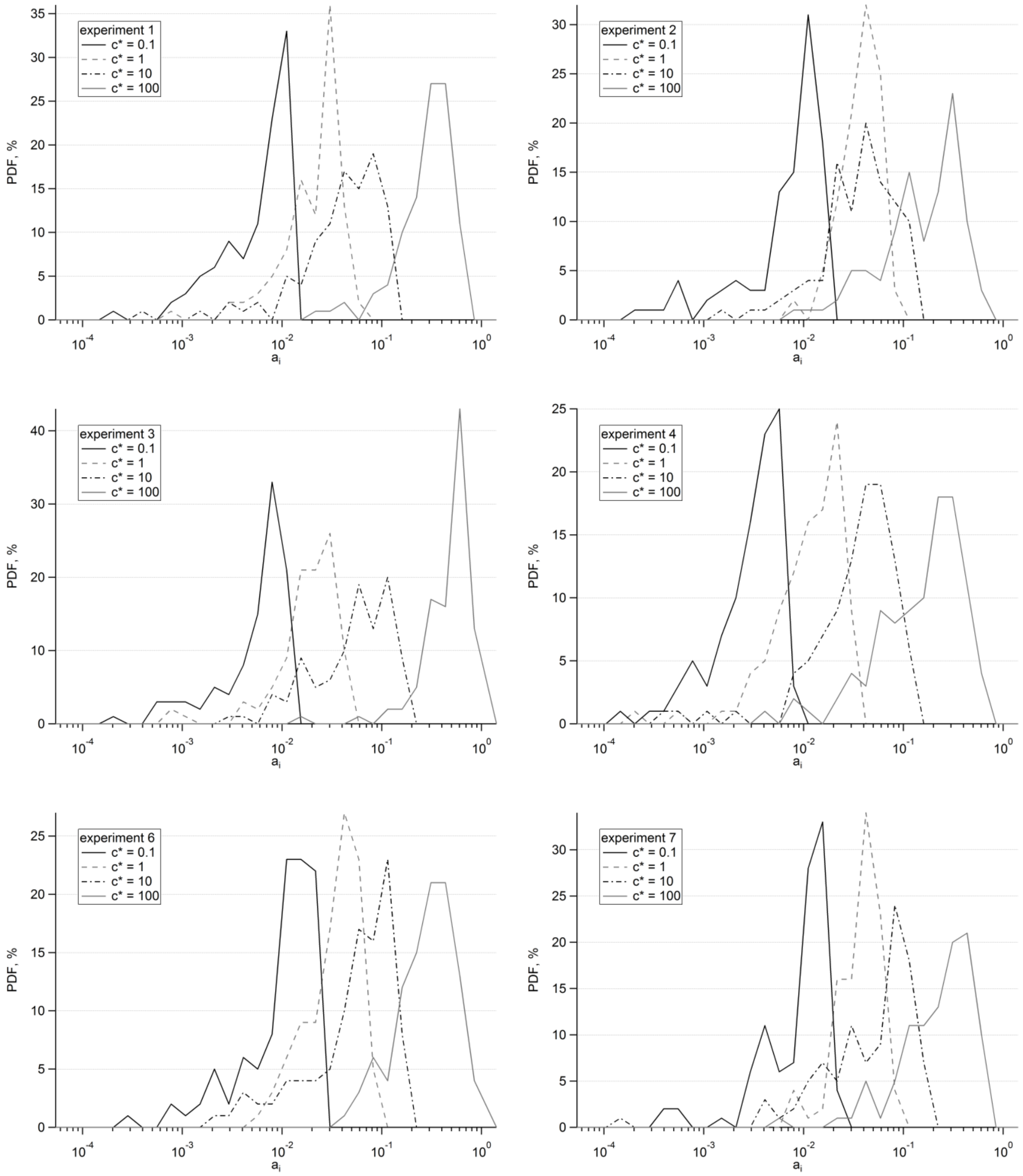


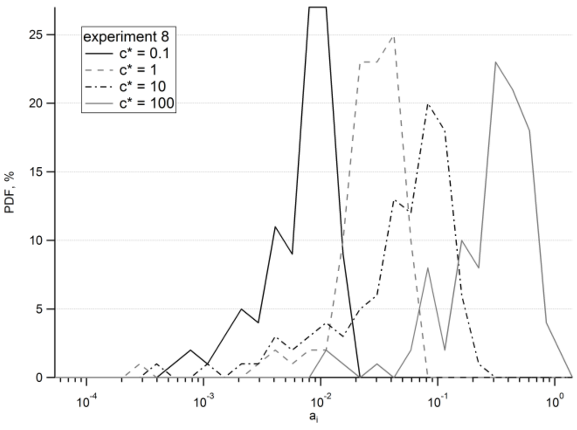
Figure S6. 20-min-averaged organic mass concentration as a function of time after lights on. Traces were fit with an exponential between 5 and 8 h after lights on to determine the wall loss rate constant. Wall loss decay rate constants for experiments with too short fit period were replaced by the respective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

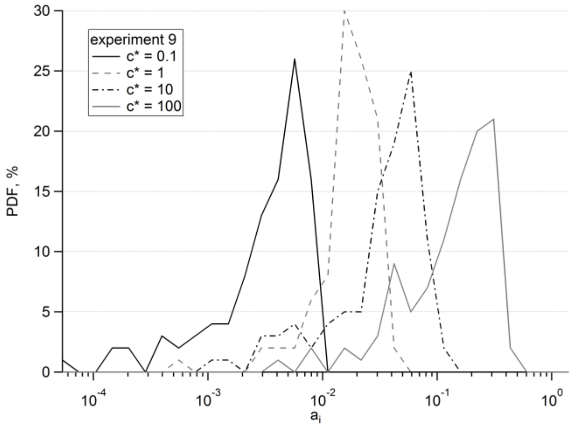
Table S2. List of wall-loss-correction parameters (1/τ) in h^{-1} and collection efficiencies ($CE_{org)}$ applied to each experiment.

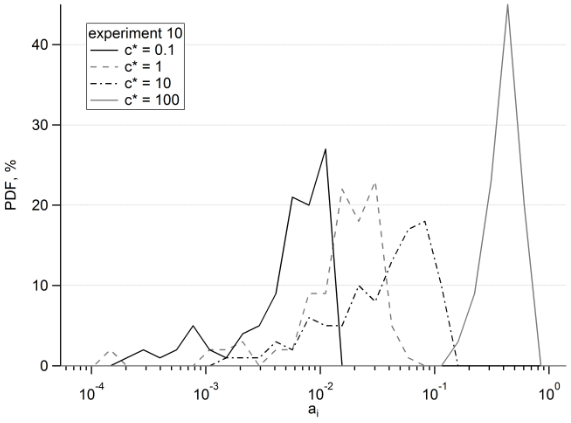
No	1/τ h^{-1}	CE_{org}
1	0.17	1.00
2	0.11	1.00
3	0.13	1.00
4	0.16	1.00
5	0.11	1.00
6	0.17	1.00
7	0.13	0.78
8	0.13	0.70
9	0.11	0.75
10	0.13	0.75
11	0.13	0.89
12	0.16	0.55
13	0.13	0.80
14	0.10	0.55
15	0.18	1.00
16	0.18	1.00
17	0.18	1.00

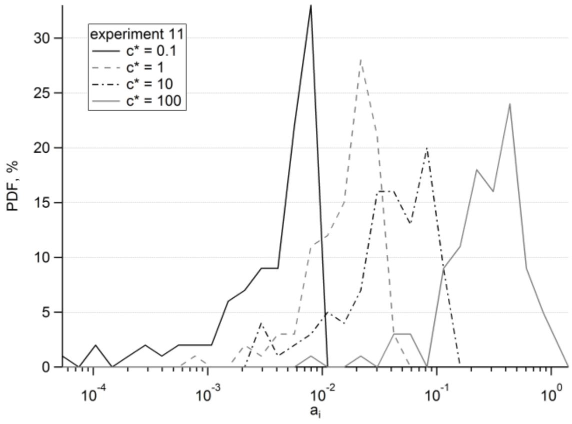
1.5 Probability density functions for *a*$_i$ values using parameterized yields as a function of C_{OA} (Fig. 5 in the main text)

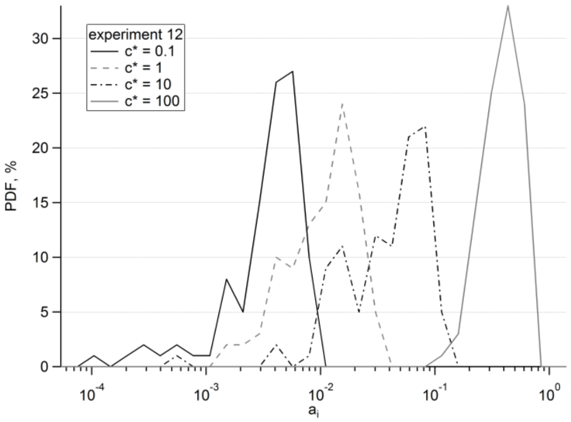


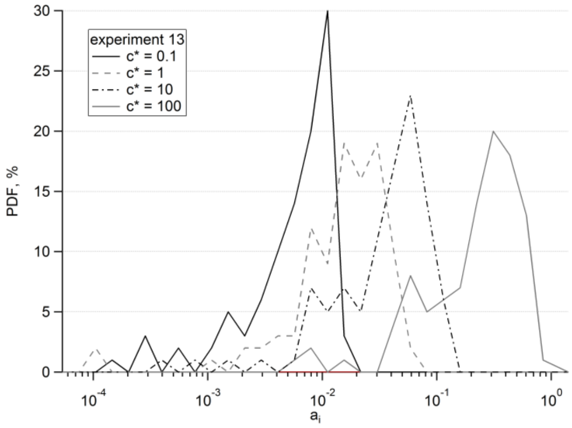

experiment 8
c* = 0.1
c* = 1
c* = 10
c* = 100
PDF, %
0
5
10
15
20
25
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
a_i

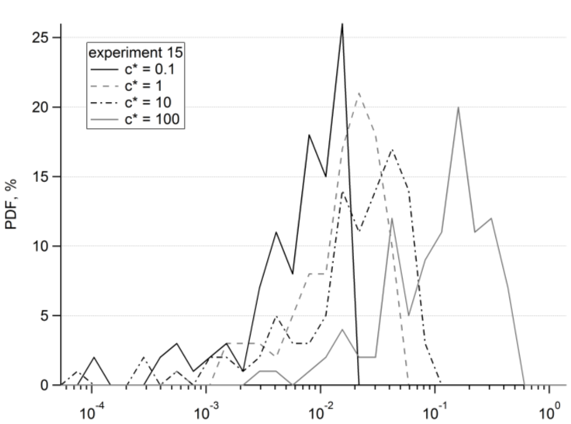

experiment 9
c* = 0.1
c* = 1
c* = 10
c* = 100
PDF, %
0
5
10
15
20
25
30
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
a_i

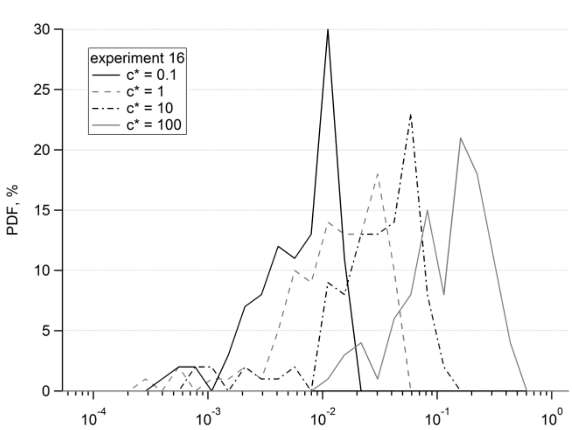

experiment 10
c* = 0.1
c* = 1
c* = 10
c* = 100
PDF, %
0
10
20
30
40
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
a_i


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

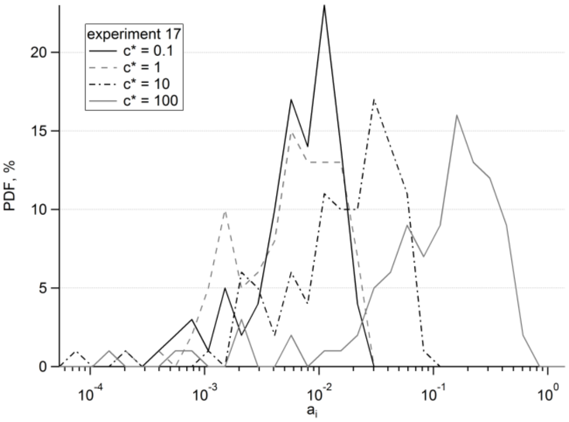


Figure S7. Probability density functions (PDF) of *ai* values for volatility bins (c*=0.1; 1; 10; 100) to solve Eq. (10) in the main text. The results for experiments 5 and 14 are not shown due to negative solution values.

1.6 Aerosol yield as a function of α-pinene reacted

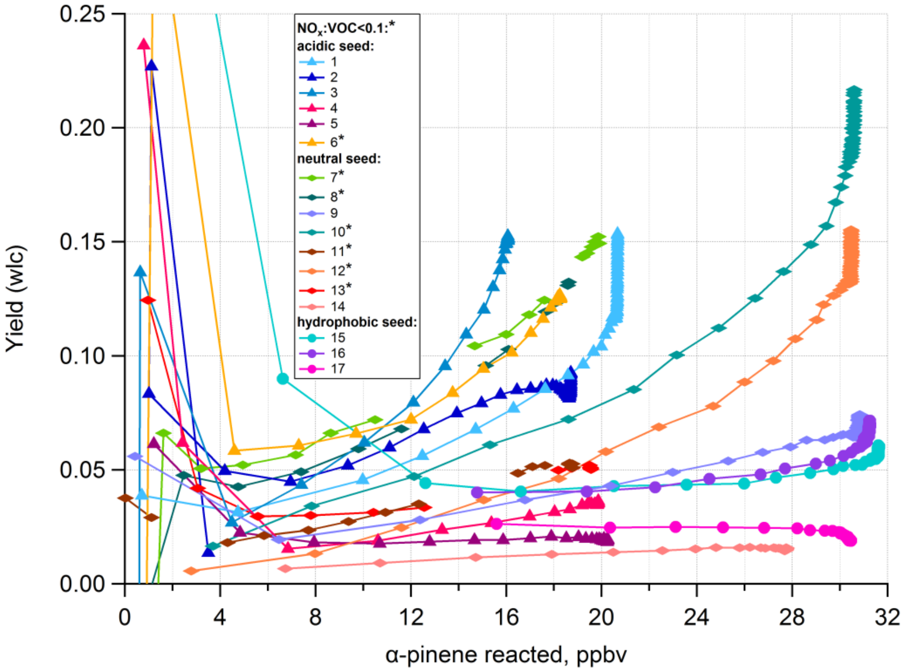


Figure S8. 20-min-averaged wall-loss-corrected yield as a function of reacted α-pinene. At the same concentration of α-pinene reacted, different yields are obtained due to various NO_x/α-pinene ratios, relative humidities and seed compositions. Traces are color coded for each experiment according to 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).

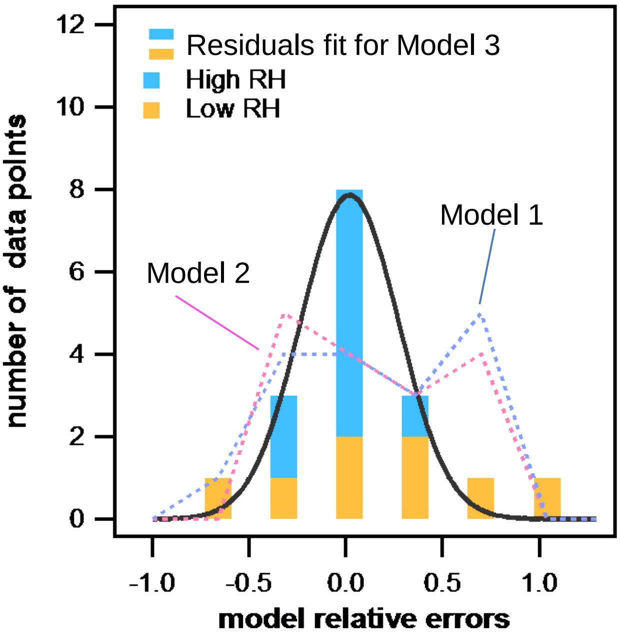


Figure S9. Residual distributions for the three assumed models, (measured_yield – modelled_yield)/measured_yield.

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 = 1.1×10^{-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	3.8×10^{-6}
RH*AHS&SA	0.15±0.03	4.5	6.9×10^{-4}
RH*CF	0.09±0.04	2.0	5.0×10^{-2}
$[\text{seed}]_0$	-0.03±0.13	-0.25	8.1×10^{-1}
NO_x/VOC	-3.3±0.06	-5.6	1.1×10^{-3}
[α-pinene]	0.21±0.06	3.5	4.1×10^{-3}

1.8 Additional supplementary figures

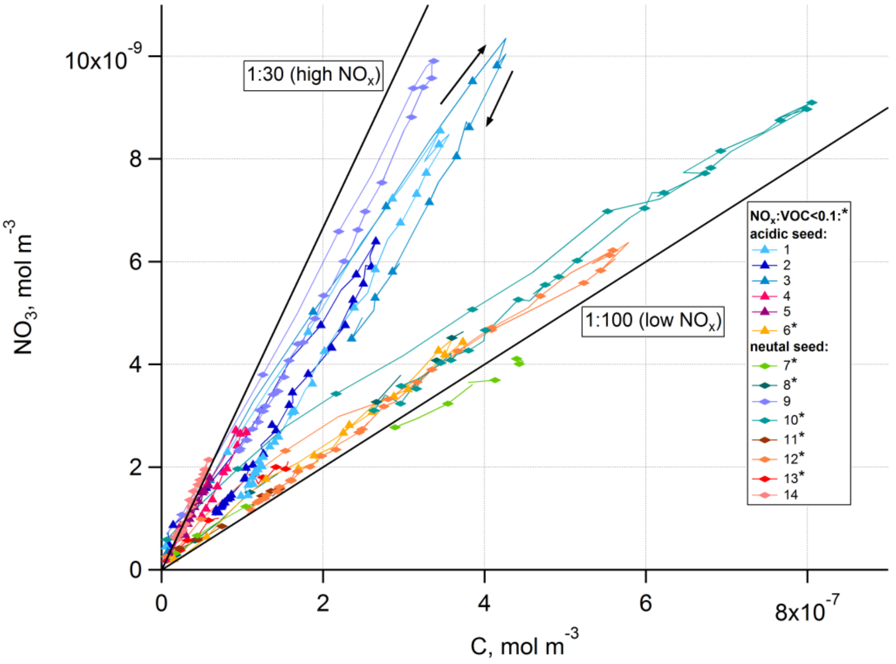


Figure S10. Molar concentrations of nitrate (NO_3) as a function of molar concentration of carbon (C) for all experiments with hygroscopic seed. High NO_x experiments follow a ratio of approximately 1:30, low NO_x experiments a ratio of approximately 1:100. The two arrows indicate that NO_3:C ratio slightly 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.

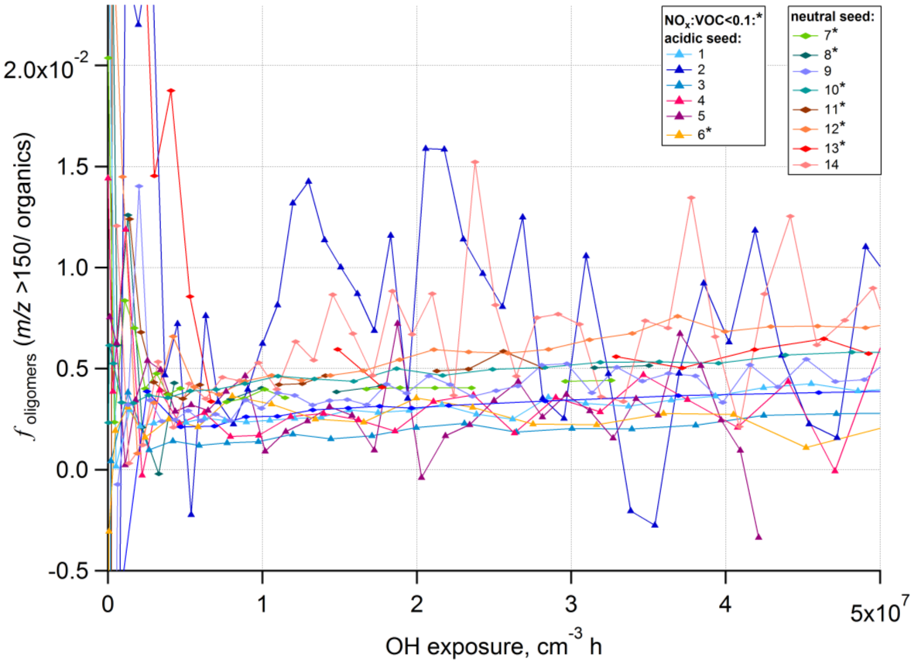


Figure S11. 20-min-averaged mass fraction of organics with m/z > 150 (e.g. oligomers) of the total organic mass concentration as a function of OH exposure. Symbols indicate the seed composition, colors indicate the respective experiment as given in the legend.

1.9 Evolution of aerosol size distributions and total particle number concentration

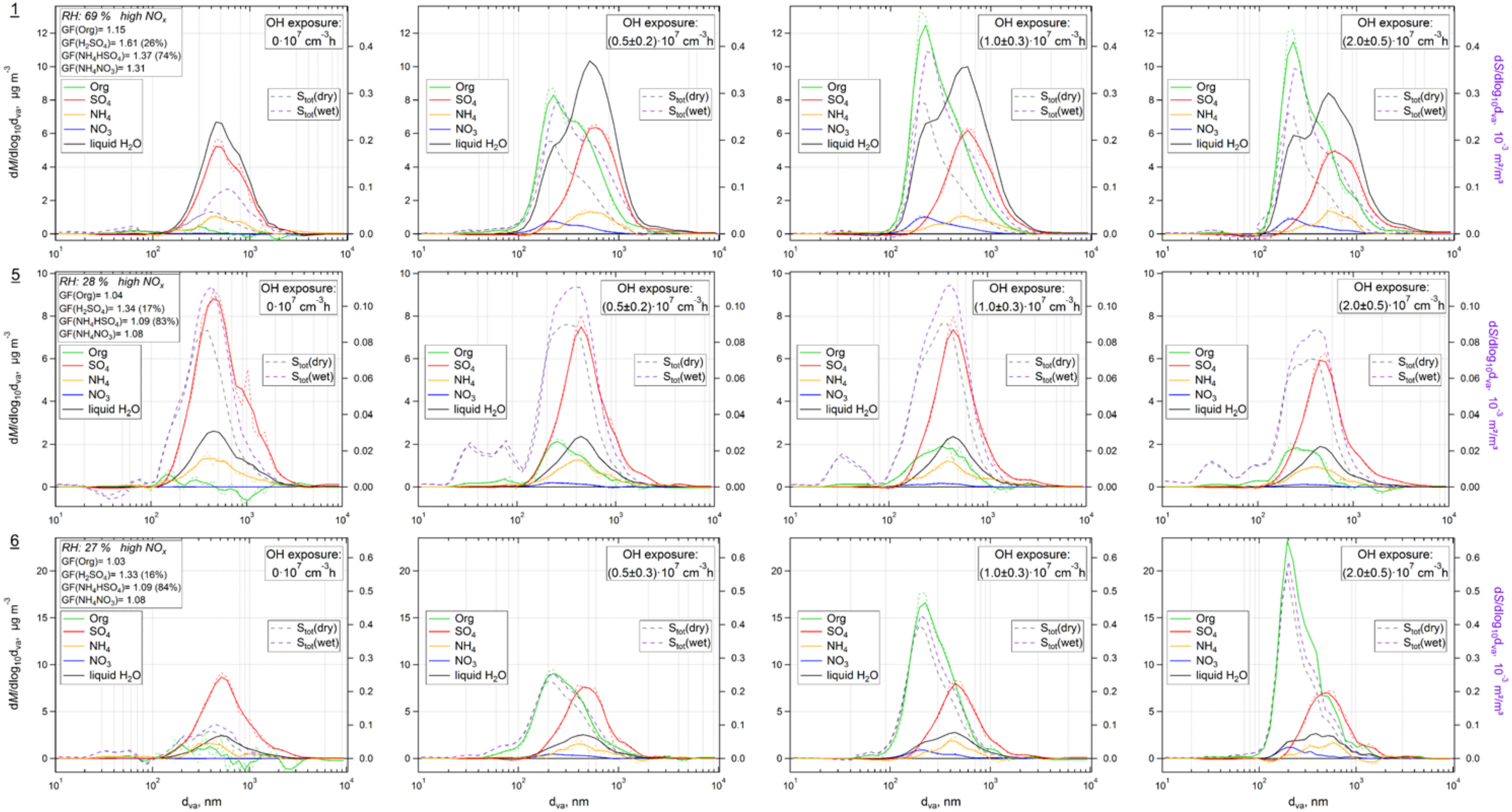


Figure S12. Evolution of size distributions. Measured organic, SO4, NH4, NO3 mass distributions for OH exposures of 0×, (0.5 ± 0.2)×, (1.0 ± 0.3)× and (2.0 ± 0.5) × 10^7 cm^{-3} h. Black lines represent estimated liquid water content (RH and individual GFs given for each experiment, method described 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).

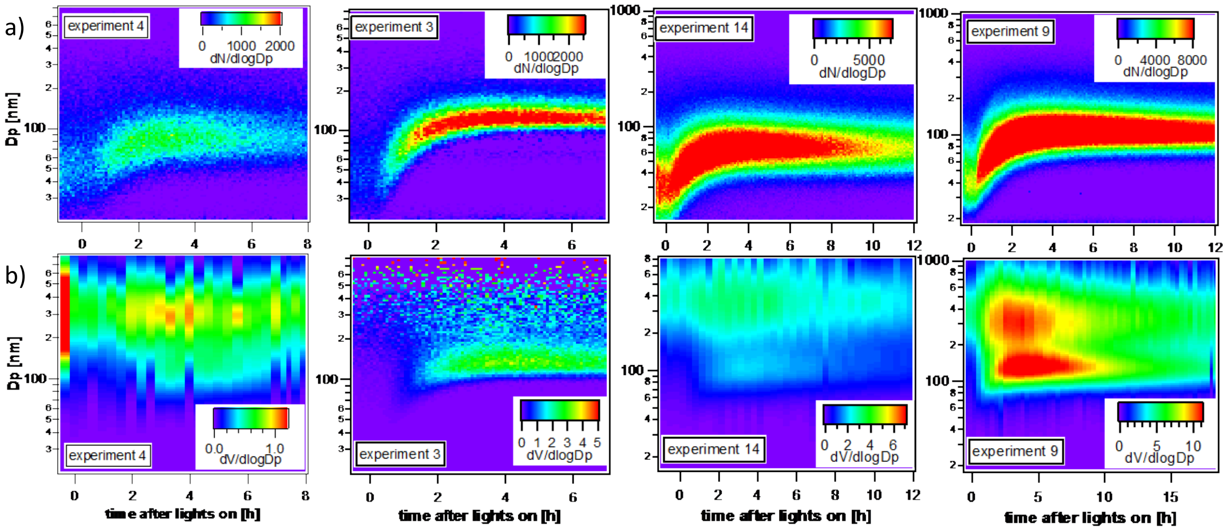


Figure S13. 3-dimensional time dependent (a) number and (b) volume size distributions for experiments 4, 3, 14 and 9, measured by the SMPS.

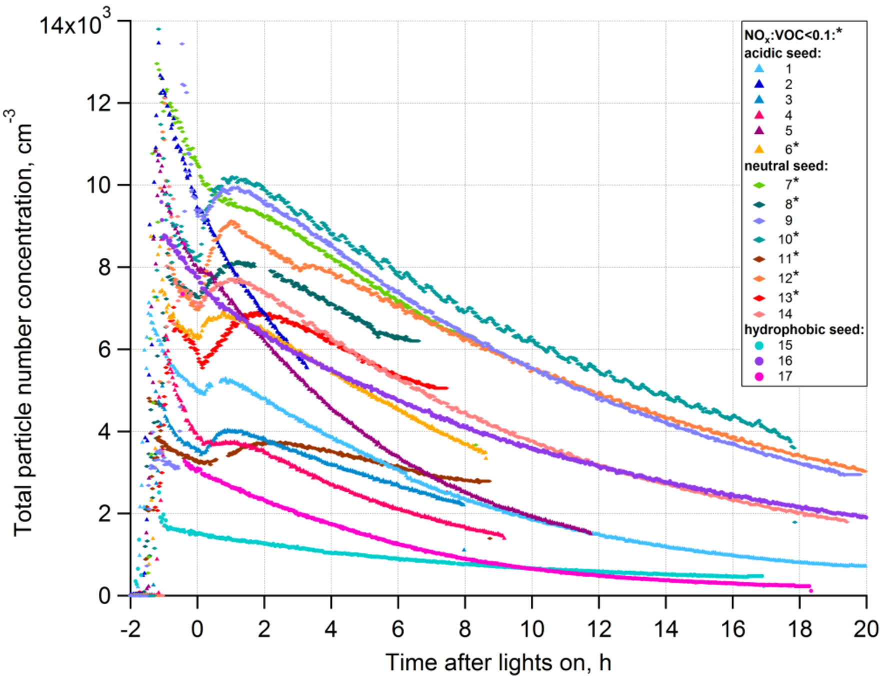
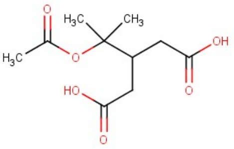
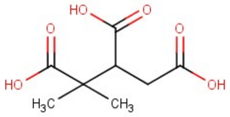
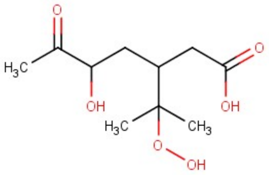
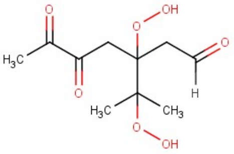
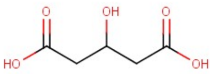
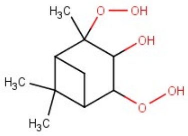
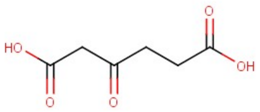
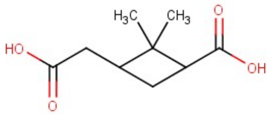
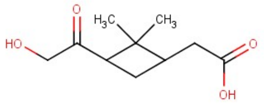
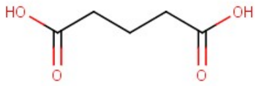
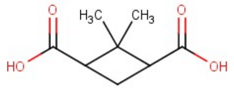
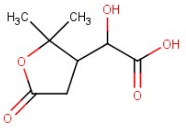
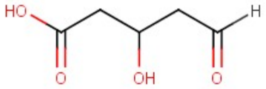
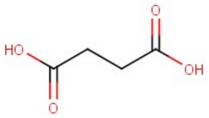
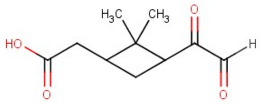
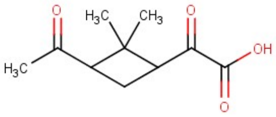
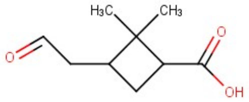
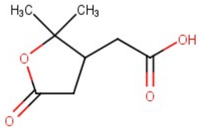


Figure S14. Total particle number concentration as a function of time after lights on.

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	1.009×10^{-6}	0.01 (α_1)		Eddingsaas et al., 2012
3-MBTCA	204	0.75	7.281×10^{-9}	0.01 (α_1)		Eddingsaas et al., 2012
ValT4N9	234	0.6	4.048×10^{-7}	0.01 (α_1)		Valorso et al., 2011
ValT4N10	248	0.7	1.472×10^{-6}	0. 1 (α_2)		Valorso et al., 2011
3-hydroxy-glutaric acid	148	1	5.167×10^{-6}	0. 1 (α_2)		Kleindienst et al., 2007
ValT4N3	218	0.5	1.416×10^{-6}	0. 1 (α_2)		Valorso et al., 2011
3-oxoadipic acid	160	0.833	2.129×10^{-5}	1 (α_3)		-
Pinic acid	186	0.444	4.622×10^{-5}	1 (α_3)		Eddingsaas et al., 2012

Hopinonic acid	200	0.4	7.650×10^{-5}	1 (α_3)		Eddingsaas et al., 2012
Glutaric acid	132	0.8	1.020×10^{-5}	10 (α_4)		-
Norpinic acid	172	0.5	1.443×10^{-4}	10 (α_4)		Jaoui et al., 2001
2-hydroxy-terpenylic acid	188	0.625	7.148×10^{-4}	10 (α_4)		Eddingsaas et al., 2012
5-COOH-3-OH-pentanal	132	0.8	5.834×10^{-3}	100 (α_5)		-
Succinic acid	118	1	3.121×10^{-3}	100 (α_5)		-
10-oxopinonic acid	198	0.4	7.535×10^{-3}	100 (α_5)		Jaoui et al., 2001
4-oxopinonic acid	198	0.4	4.790×10^{-3}	100 (α_5)		Jaoui et al., 2001
Pinalic acid	170	0.33	4.688×10^{-2}	100 (α_5)		Jaoui et al., 2001
Terpenylic acid	172	0.5	9.306×10^{-2}	100 (α_5)		Eddingsaas et al., 2012

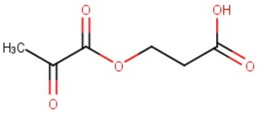
3-(2-oxopropanyloxy) propanoic acid	160	0.83	4.953×10^{-2}	100 (α_5)		Altieri et al., 2008

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

	α_2	α_3	α_4	α_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 (α_2-α_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}	α_2 = 0.00229				α_2 = 0.00511			
	C^* = 1 μg m^{-3}	α_3 = 0.01454				α_3 = 0.01760			
	C^* = 10 μg m^{-3}	α_4 = 0.04447				α_4 = 0.02998			
	C^* = 100 μg m^{-3}	α_5 = 0.32354				α_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 (α_2-α_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}: α_2	0.00406				0.00780			
	C^* = 1 µg m^{-3}: α_3	0.03478				0.01355			
	C^* = 10 µg m^{-3}: α_4	0.06248				0.05476			
	C^* = 100 µg m^{-3}: α_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	$3 \cdot 10^{-6}$	0.003	$3 \cdot 10^{-5}$	0.003	$2 \cdot 10^{-5}$
	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	$1 \cdot 10^{-7}$	0.001	$1 \cdot 10^{-6}$	0.001	$8 \cdot 10^{-7}$
	ValT4N10	0.006	0.0	0.003	$4 \cdot 10^{-9}$	0.006	$5 \cdot 10^{-8}$	0.005	$3 \cdot 10^{-8}$

	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	-

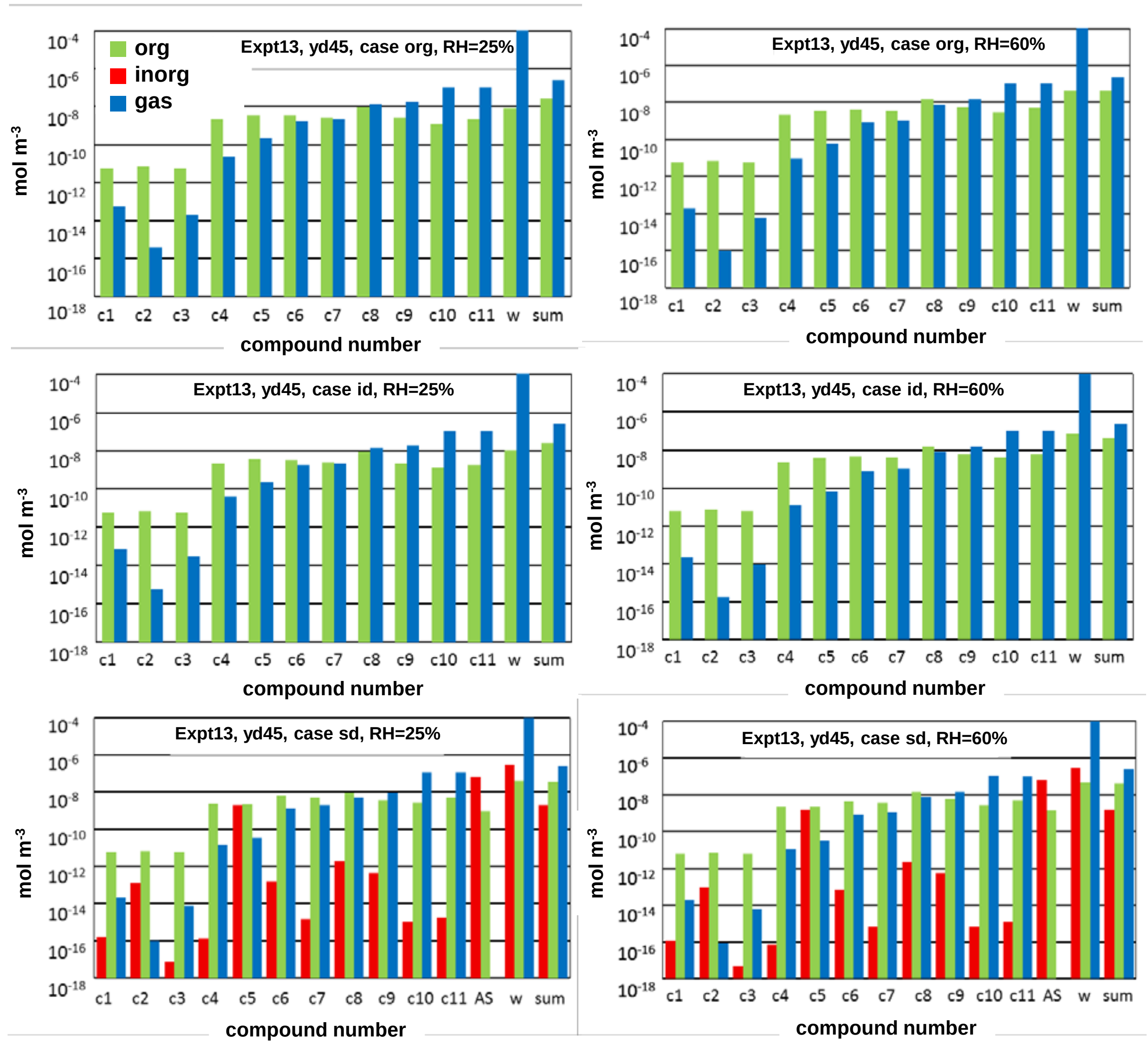


Figure S15. Equilibrium phase partitioning for cases org, id and sd between gas phase (blue), organic-rich phase (green) and electrolyte phase (red) at low (25 %) and high (60 %) RH for experiment 13, volatility distribution #45. c1: diaterpenylic acid acetate; c2: 3-MBTCA, c3: ValT4N9, c4: ValT4N10, 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).

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