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Supplement of

Retention of α-pinene oxidation products and nitro-aromatic compounds during riming

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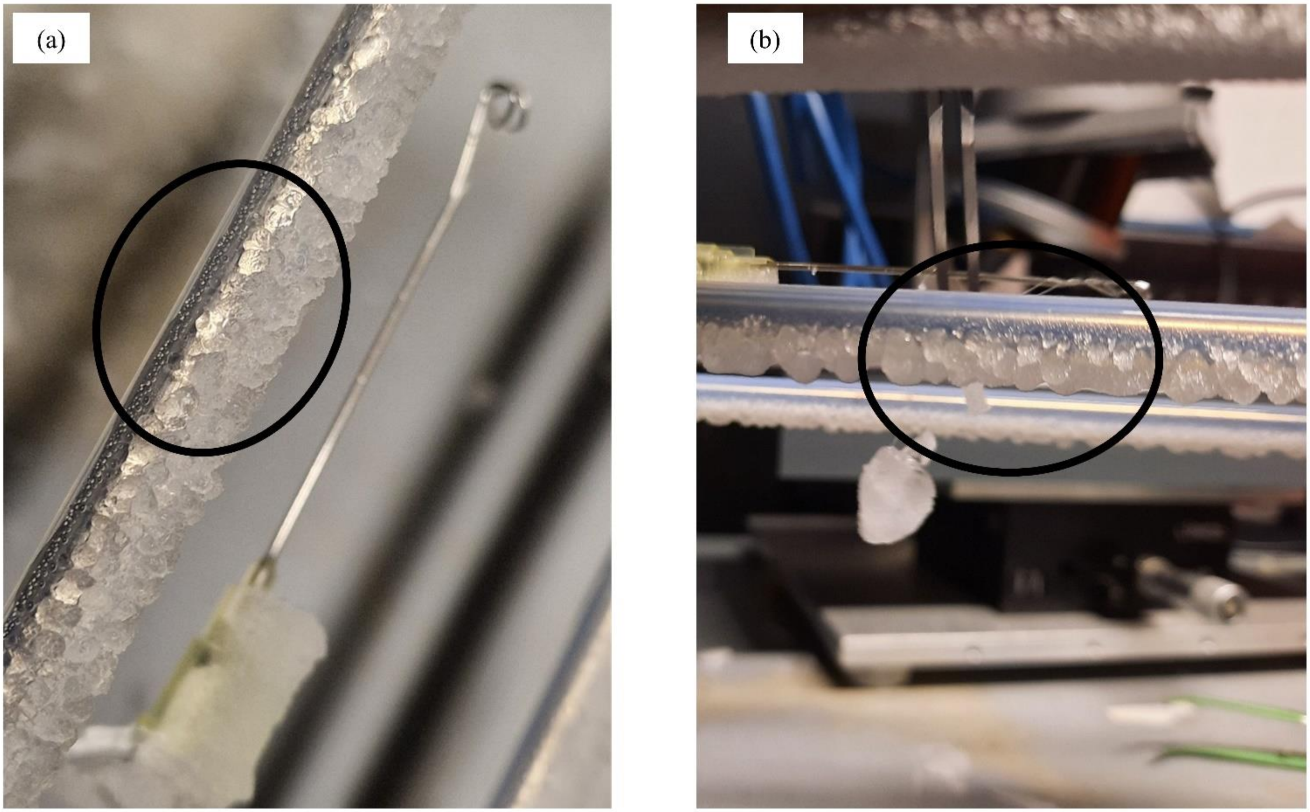

Figure S1: Photo of ice grown under dry (a)) and wet (b)) growth conditions.

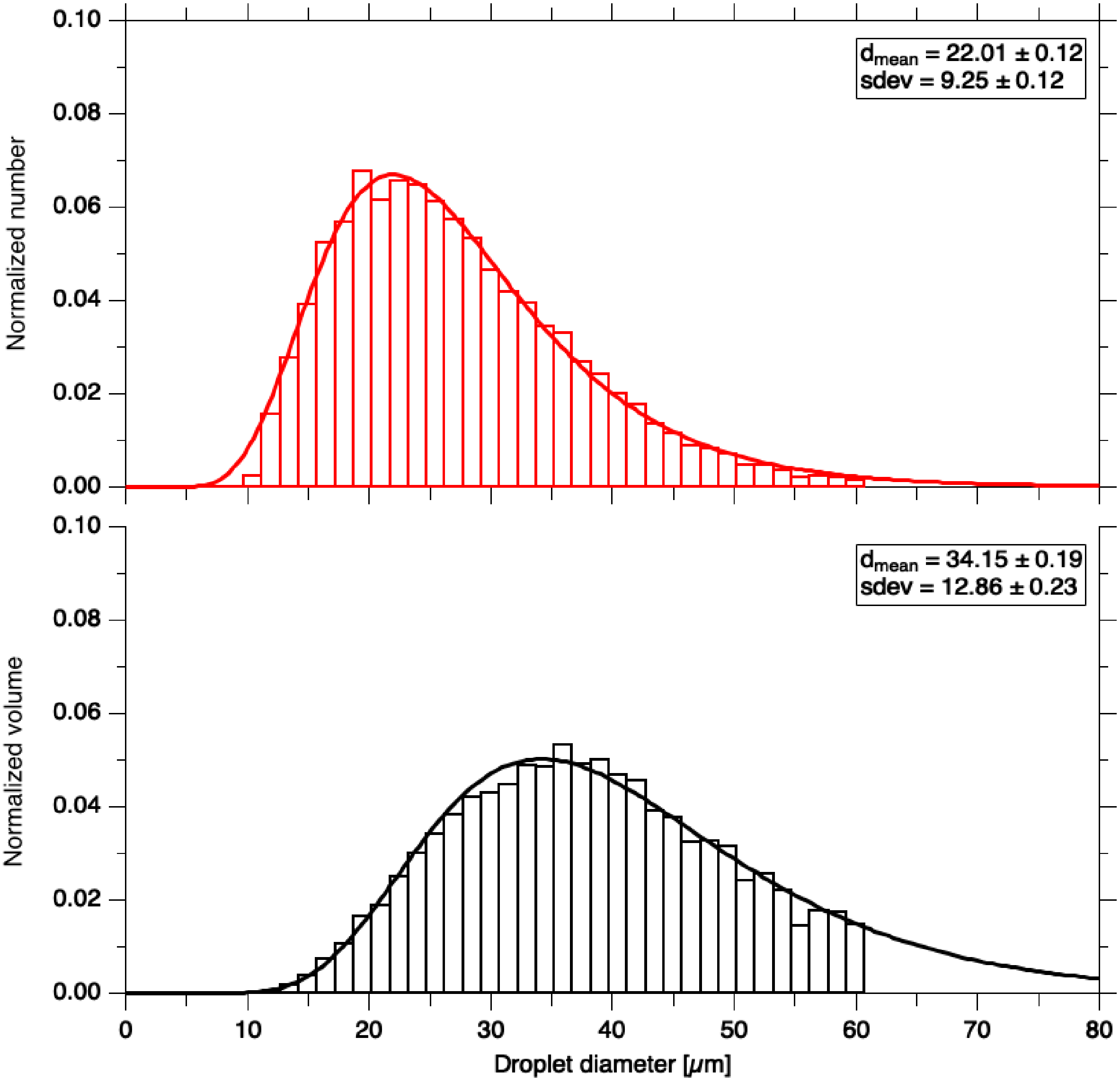

Figure S2: Normalized droplet number (a) and volume distribution (b) of the supercooled droplets generated using four spraying nozzles. The lines represent the log-normal fit functions.

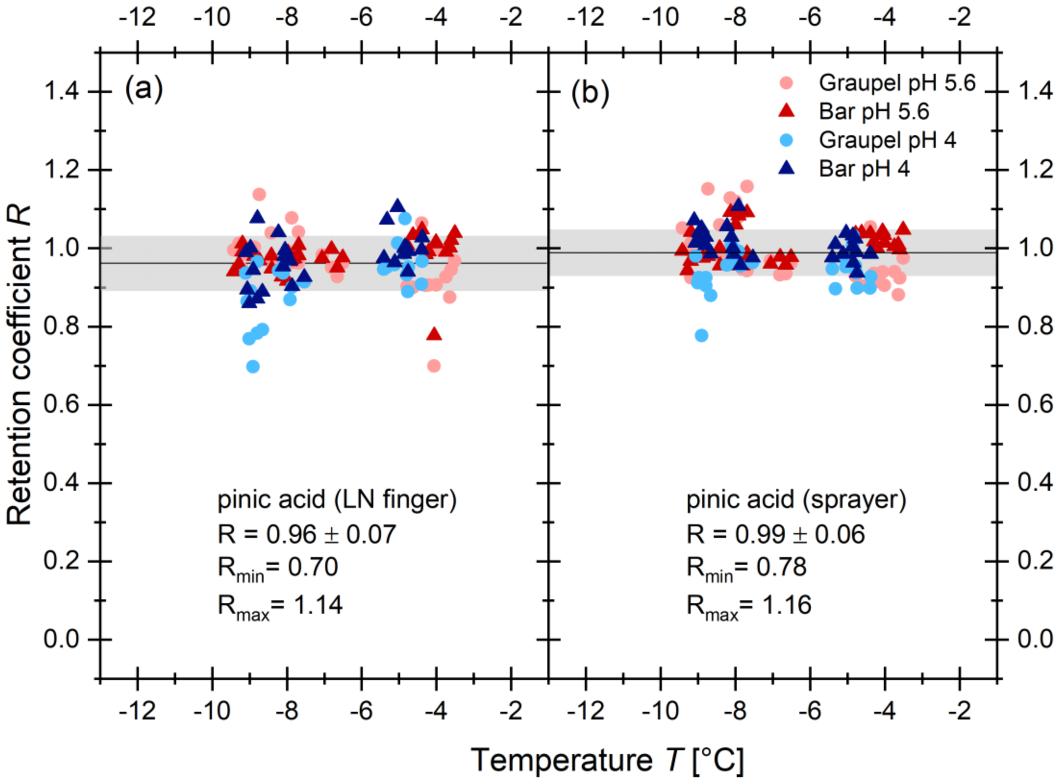

Figure S3: Experimentally determined retention coefficients of pinic acid using (a) the LN finger and (b) the sprayer solution as a function of the temperature during the experiment for different rime collectors. The circles represent the graupel samples and the triangles those of the Teflon-coated bars. For the blue symbols, the pH was adjusted to 4 by adding HCl (30 %), the red symbols are without adding HCl. The solid black line represents the mean of all measurements, and the grey area represents one standard deviation.

Desorption correction procedure

2-nitrophenol has the lowest effective Henry’s law constant and therefore possesses the highest probability of transition from the droplet phase to the gas phase, resulting in a high gas phase concentration in the wind tunnel. For such a substance the measurement technique using the liquid nitrogen finger collection is not reliable since the gas molecules might adsorb on the liquid nitrogen cooled ice and thereby bias the retention value. Also, there is currently no other reliable measurement technique for measuring the desorption of a highly volatile substance right at the point where the retention measurements were carried out. Therefore, the desorption coefficient valid for the retention measurement was estimated based on a two step temperature and exposure time correction outlined in detail in the following.

First step: desorption measurements

The same solution (see Table 1) used for the retention measurements, containing 2-nitrophenol and NaBr as internal standard (IS), was nebulized and the droplets were transported downstream in the wind tunnel. The droplets were sampled in a vial in the lower horizontal part of the tunnel after a residence time of approximately 1 s (point A in figure S4). The solution was then collected and measured by UHPLC-HRMS. Desorption measurements were carried out at different temperatures (between 0 °C and 19 °C) to obtain a temperature dependency.

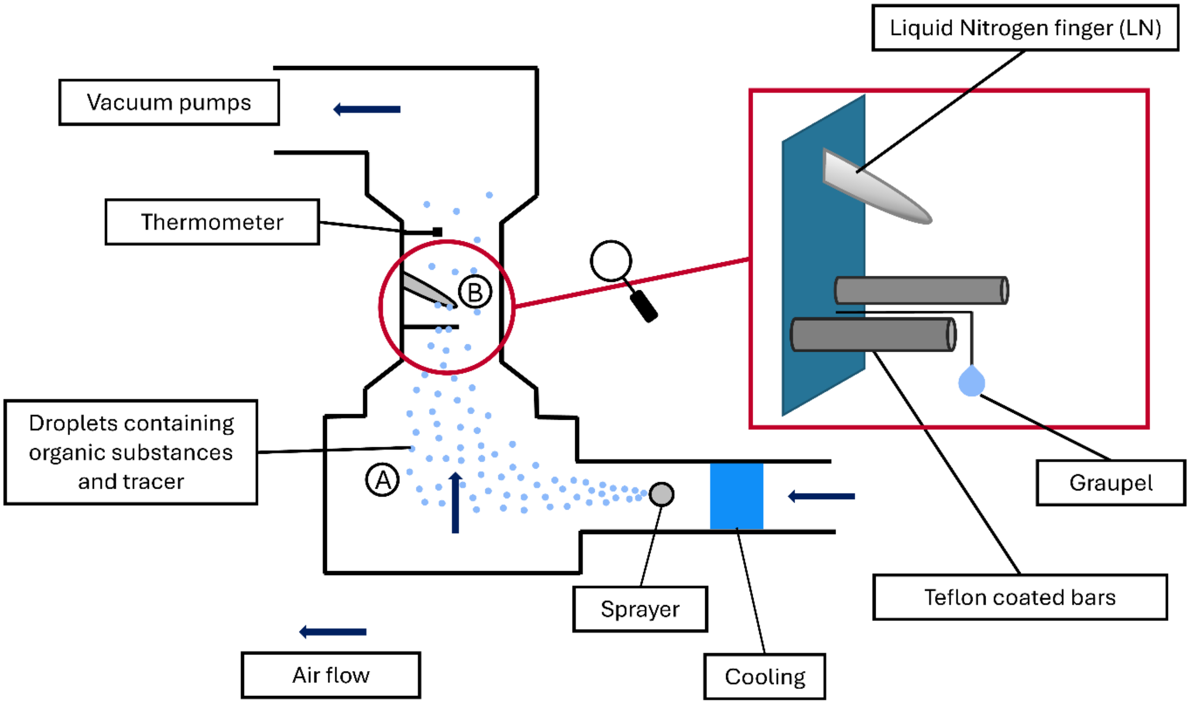

Figure S4: Schematic of the wind tunnel. Cooled air transported the generated water droplets containing the compounds into the experimental region (red circle). Red rectangle: The enlarged experimental area shows the three surfaces on which the riming took place: Graupel, liquid nitrogen finger and Teflon-coated bars. Desorption measurements were performed at point A and retention measurements were performed at point B.

The definition of the desorption coefficient is shown in Eq. (S1). The numerator describes the ratio of the compound remaining in the sample (droplets sampled in a vial) to a reference sample, which is in this case the sprayer solution, which is the solution immediately before droplet formation, takes place $(c^{\text{vial}}_{\text{compound}}/c^{\text{sprayer}}_{\text{compound}})$. The denominator describes the same ratio but for the IS $\left(c^{\text{vial}}_{\text{IS}}/c^{\text{sprayer}}_{\text{IS}}\right)$:

$$D_{\text{compound}} = \frac{c^{\text{vial}}_{\text{compound}}/c^{\text{sprayer}}_{\text{compound}}}{c^{\text{vial}}_{\text{IS}}/c^{\text{sprayer}}_{\text{IS}}} \tag{S1}$$

Figure S5 shows the desorption coefficient as a function of the temperature as measured in the lower part of the wind tunnel. Obvious from Fig. S5 is a strong dependence of the desorption coefficient of 2-nitrophenol on temperature, indicating less desorption at lower temperatures. This is expected since the mass transfer rate of a dissolved compound to the environment decreases for decreasing temperatures. The reason for this is that the mass transfer depends, among others on the temperature-dependent parameters like gas- and aqueous-phase diffusivities and the effective Henry's law constant. The observed variations in the values are greater than those expected due to analytical measurement error. These variations are likely attributable to fluctuations in the conditions within the wind tunnel, which were expected to be also present during the retention measurements.

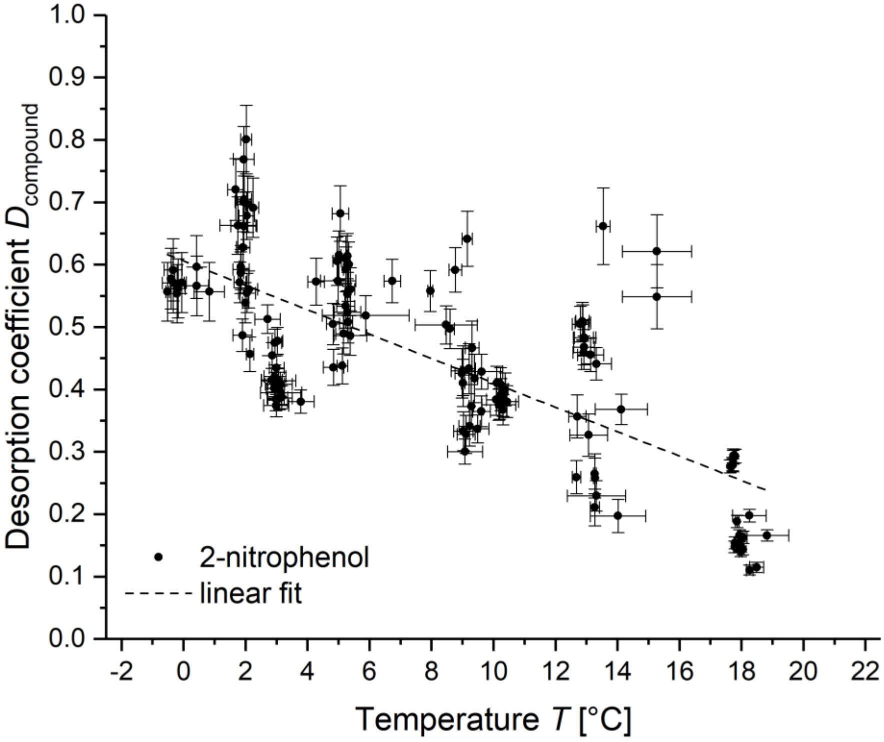

Figure S5: Desorption coefficient for 2-nitrophenol. The errors correspond to the error of the analytical measurement (y-axis) or the standard deviation of the temperature measurement during the collection time of each sample (x-axis). The dashed line represents a linear regression.

A statistically significant linear trend is visible in the measurement series. A linear regression with the equation $D_{\text{compound}} = a_{\text{D}} \cdot x \cdot [°C]^{-1} + b_{\text{D}}$ was performed to extrapolate the desorption to the temperatures present during the experiments. This leads to the following equation, S2, for the fit function.

$$D_{\text{compound}} = (-0.020 \pm 0.002) \cdot x \cdot [°C]^{-1} + (0.606 \pm 0.015) \qquad \text{(S2)}$$

Extrapolating the results to the experimental conditions (e.g. -10 °C and -4 °C) yields $D_{\text{compound}} = 0.81$ and $D_{\text{compound}} = 0.67$ for typical dry and wet growth conditions respectively.

Second step: semi-empirical exposure time correction

The exposure time in the tunnel from the point of the desorption (point A in figure S4) to the retention measurements (point B in figure S4) is another 3 s (overall 4 s) which introduced another source of uncertainty. Thus, the measured *D* after one second of exposure had to be corrected for this time effect. This was done by a semi-empirical approach using theory and the results of the first step introduced above. From the convective diffusion equation assuming a well-mixed droplet, Pruppacher and Klett (2010, p. 775, Eq. 17-144) showed that the desorption of a dissociating gas with the initial condition of zero gas phase concentration follows a $1/t$ law. This functional relationship was used to fit the data from the first step to get a time dependence correction of the desorption coefficient. More specifically the following fit function was utilized:

$$D(T, L, t) = c(T, L) + \left(\frac{a(T,L)}{1+a(T,L)b(T,L)t}\right) \qquad \text{Eq (S3)}$$

Here $D(T, L, t)$ is the temperature (T), liquid water content (L), and time (t) dependent desorption correction coefficient which asymptotically approaches the equilibrium value at a given temperature and liquid water content $c(T, L)$. That is, when t tends towards infinity Eq. (S3) approaches $c(T, L)$. This coefficient describes the fraction of 2-nitrophenol in the liquid phase in equilibrium with its gas phase. It was derived from the assumption of the equilibrium gas/liquid partitioning in a confined system consisting of a single gas (2-nitrophenol) and a given amount of liquid water (1 and 2 g/m^3) (Seinfeld and Pandis 2006, p.290, Eq. 7.9). In the referenced Eq. 7.9 from Seinfeld and Pandis (2006) the temperature dependent Henry's law constant was calculated according to Guo and Brimblecombe (2007) for the temperatures used during the retention measurements. The results are shown in Fig. (S6).

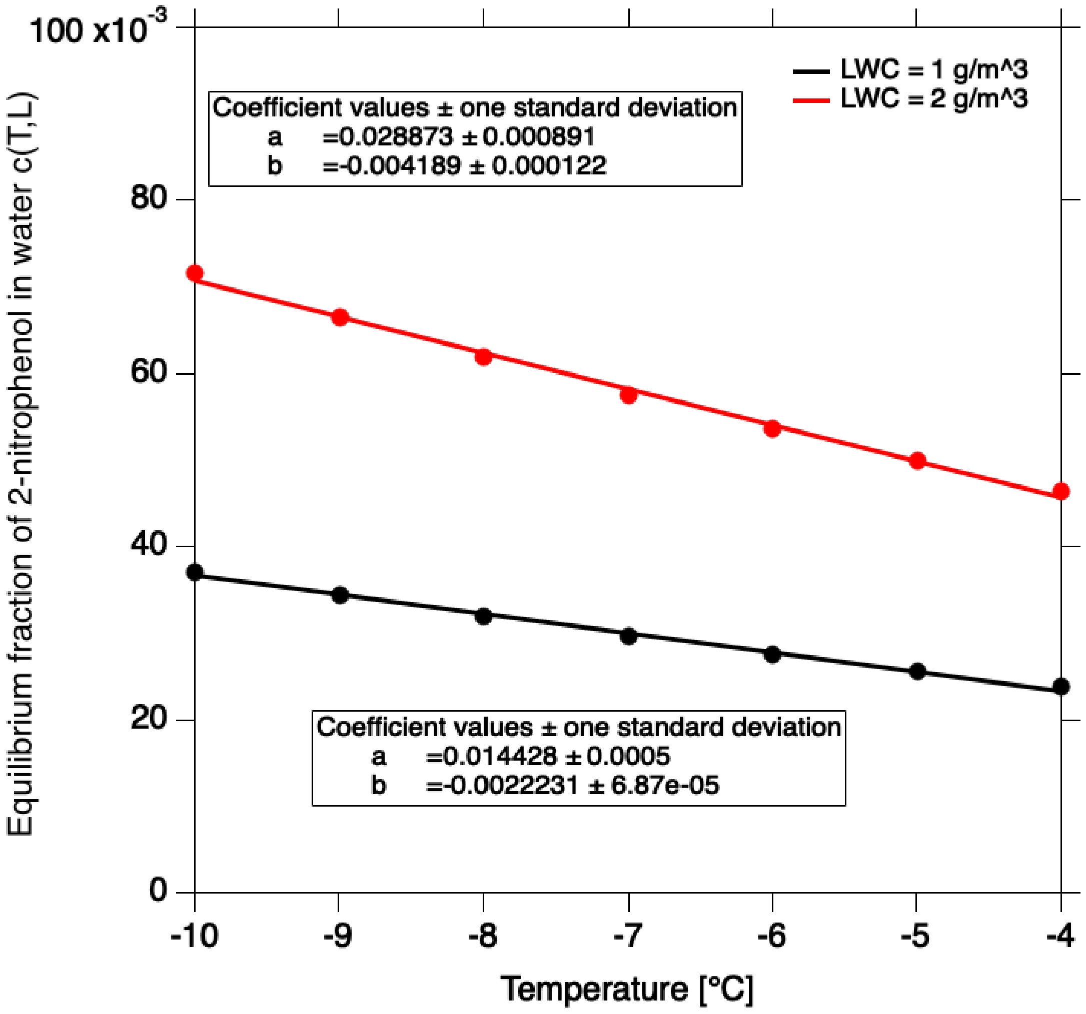

Figure S6: Equilibrium fraction of 2-nitrophenol in water as a function of temperature and liquid water content. Coefficients a and b represent the fit values of the intercept and slope of the linear regressions. Black: LWC = 1 g/m^3. Red: LWC = 2 g/m^3.

When t approaches zero Eq. (S3) yields $c(T,L)$ + $a(T,L)$= 1, which yields $a(T,L)$=1$-c(T,L)$. Hence, the only unknown in Eq. (S3) is coefficient $b(T,L)$ which was used as a fit parameter and thereby parameterized as a function of T and L. Accordingly Eq. (S3) was used along with the extrapolated desorption values to the temperatures prevailed during the retention and the equilibrium fractions (Fig. S6) to derive a parameterization of D which depends on temperature, liquid water content and time.

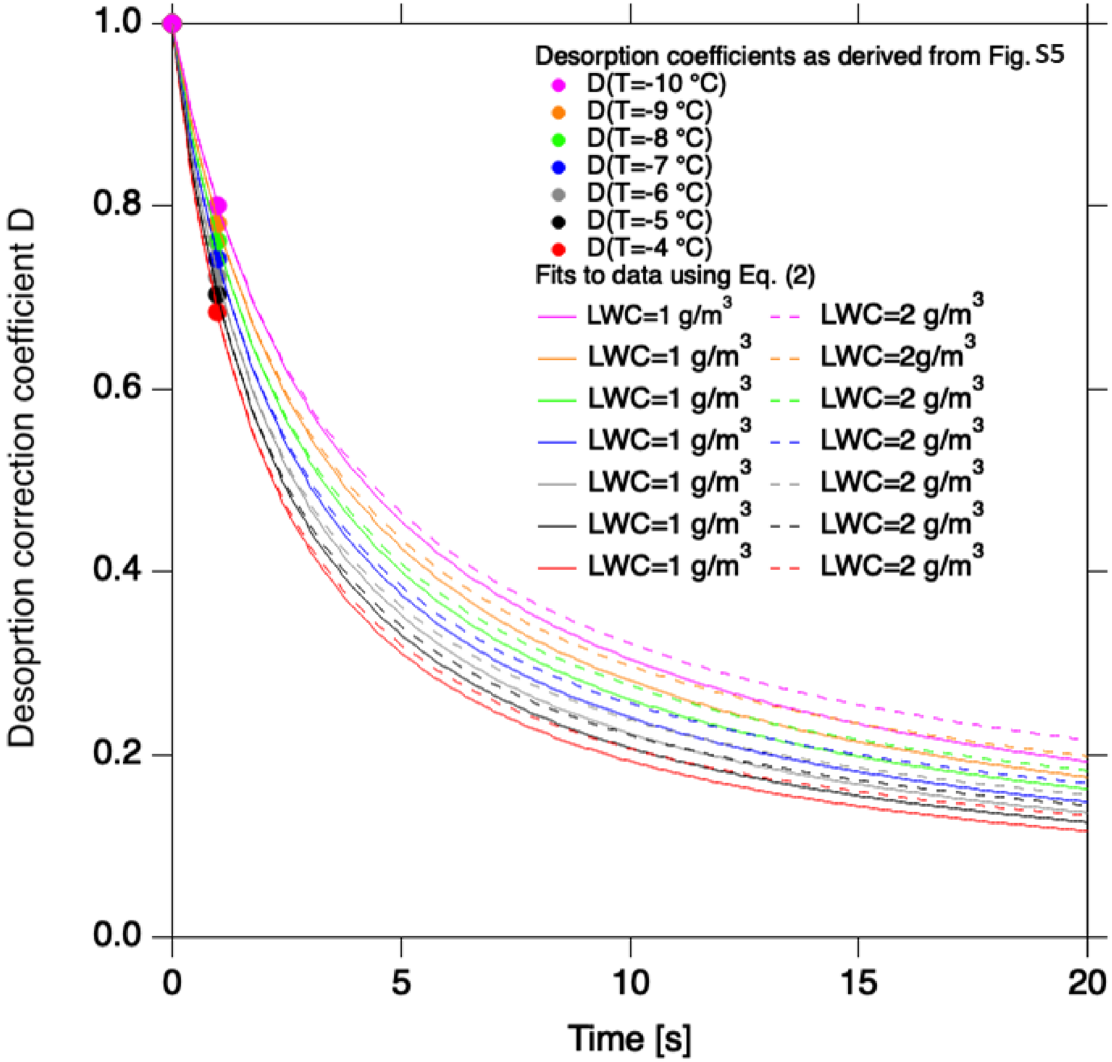

Figure S7: Desorption correction coefficient as a function of time for different temperatures and liquid water contents obtained from Eq. (S3). Solid lines: LWC = 1 g/m^3. Dashed lines LWC = 2 g/m^3. The data points were calculated from Eq. (S2).

From the results shown in Fig. S7 it is obvious that a significant part (37 %) of 2-nitrophenol desorb from the droplets from the point between the desorption and retention measurements (Point A and B in Figure S4). For example at -10 °C the desorption between Point A and B decreases from 0.81 to 0.51. For each curve in Fig. S7 a fit coefficient *b(T, L)* was obtained corresponding to a certain temperature and liquid water content. By plotting these as a function of temperature (Fig. S8) a linear relationship of *b(T, L)* on the temperature and liquid water content was derived.

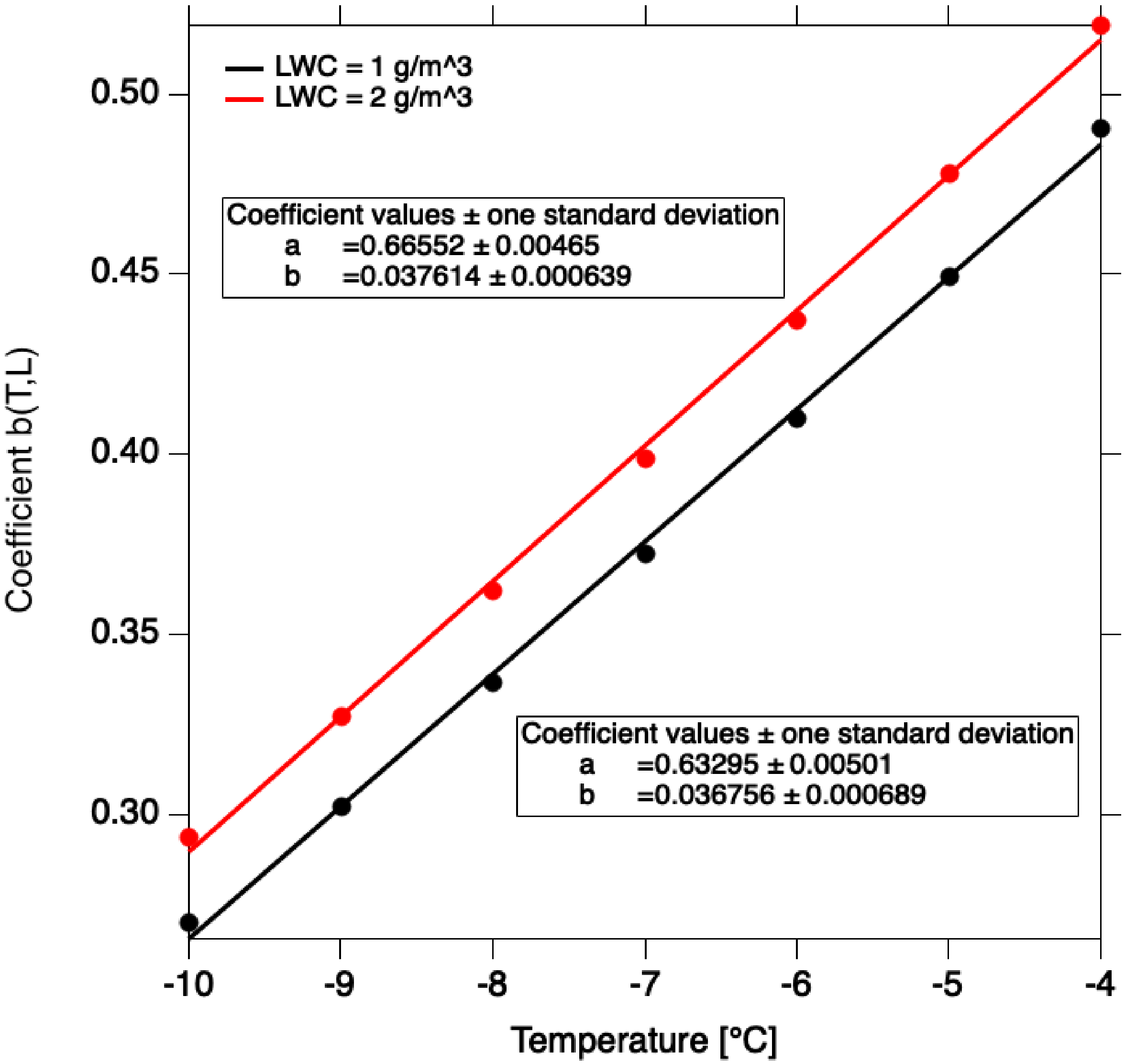

Figure S8: Dependency of the fit parameter *b(T,L)* on the temperature and liquid water content as derived from Fig. S7. Red and black points: values for LWC's of 1 and 2. Red and black lines: fit to the data. Coefficients a and b represent the intercepts and the slopes of the linear regressions.

A close glance at Fig. S7 reveals that the difference between 1 and 2 g/m3 is below 1 %. Thus, the final desorption correction function that was used to correct the retention values for 2-nitrophenol at a given temperature and at the location of the retention measurements is given by Eq. (S3) which was evaluated at *t* = 4 s and LWC=L= 1 g/m^3. The used parameters were:

$$c(T, L = 1) = 0.0144 - 0.0022\,T\ [°\mathrm{C}]$$

$$a(T, L = 1) = 1 - c(T, L)$$

$$b(T, L = 1) = 0.6330 + 0.0368\,T\ [°\mathrm{C}]$$

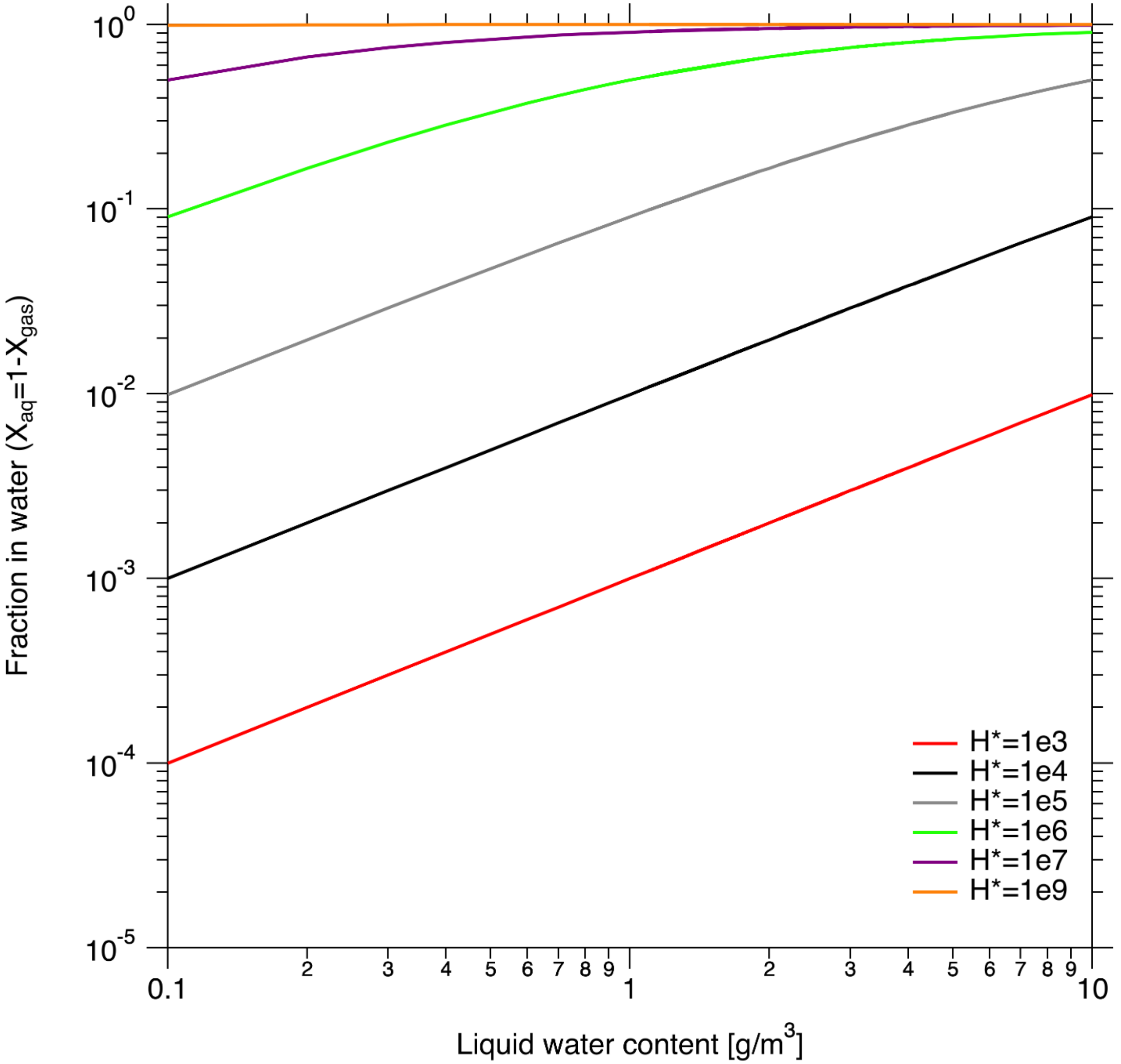

Figure S9: Equilibrium distribution of species between the liquid and gas phase in a confined system as function of the LWC. Figure according to Seinfeld and Pandis (2006).

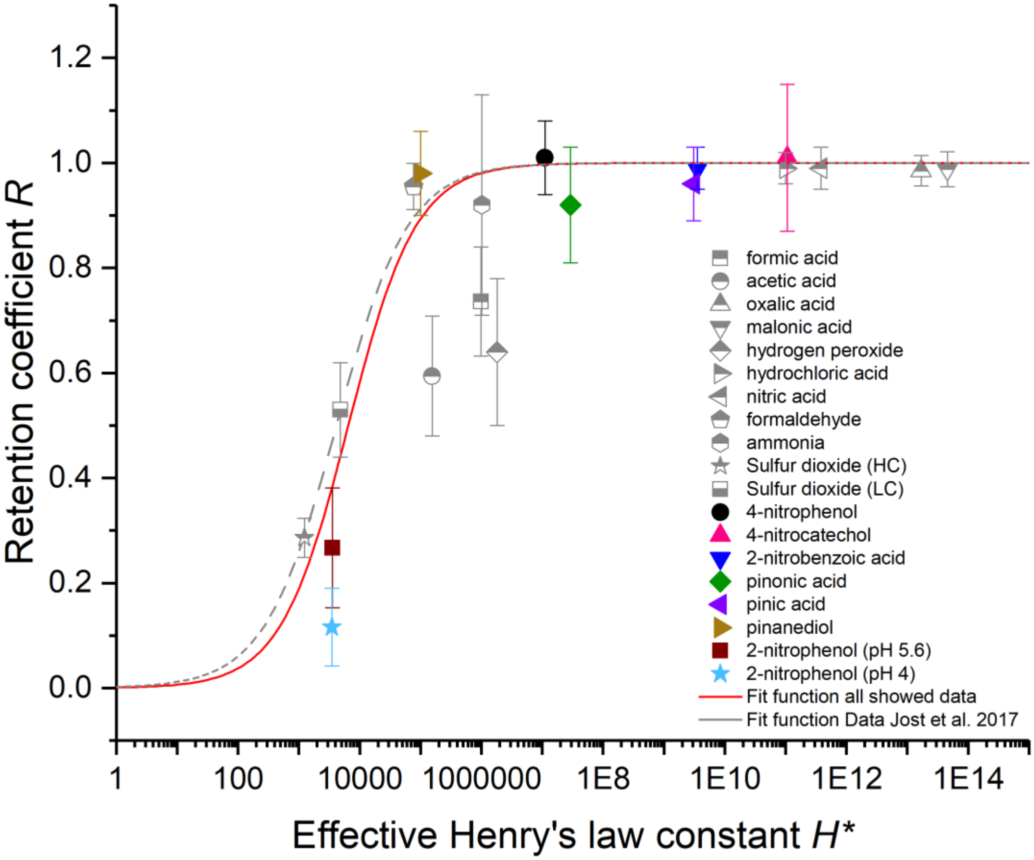

Figure S10: Retention coefficient as a function of H^*. Colorful filled symbols: substances investigated in the present study. Grey symbols: wind tunnel data from earlier studies (Jost et al., 2017; v. Blohn et al., 2013; 2011). Fit function: $R_{H^*} = \left(1 + (a\ /\ H^*)^b\right)^{-1}$. Red solid line: new fit to wind tunnel data with all substances ($a_{\mathrm{red}} = (6.51 \pm 2.01) \cdot 10^3$ and $b_{\mathrm{red}} = 0.78 \pm 0.16$). Grey dashed line: fit of only the grey data points $a_{\mathrm{grey}} = (4.15 \pm 1.47) \cdot 10^3$ and $b_{\mathrm{grey}} = 0.74 \pm 0.18$.

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