Supplementary information for manuscript

Evaporation of sulphate aerosols at low relative humidity

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S1 AMS measurements

The evaporation of particles based on AMS measurements showed that the particles were composed almost exclusively of sulphuric acid. Calculations of the kappa value κ, based on the AMS measurements, yield a value close to the κ for pure sulphuric acid particles (see Fig. S2).

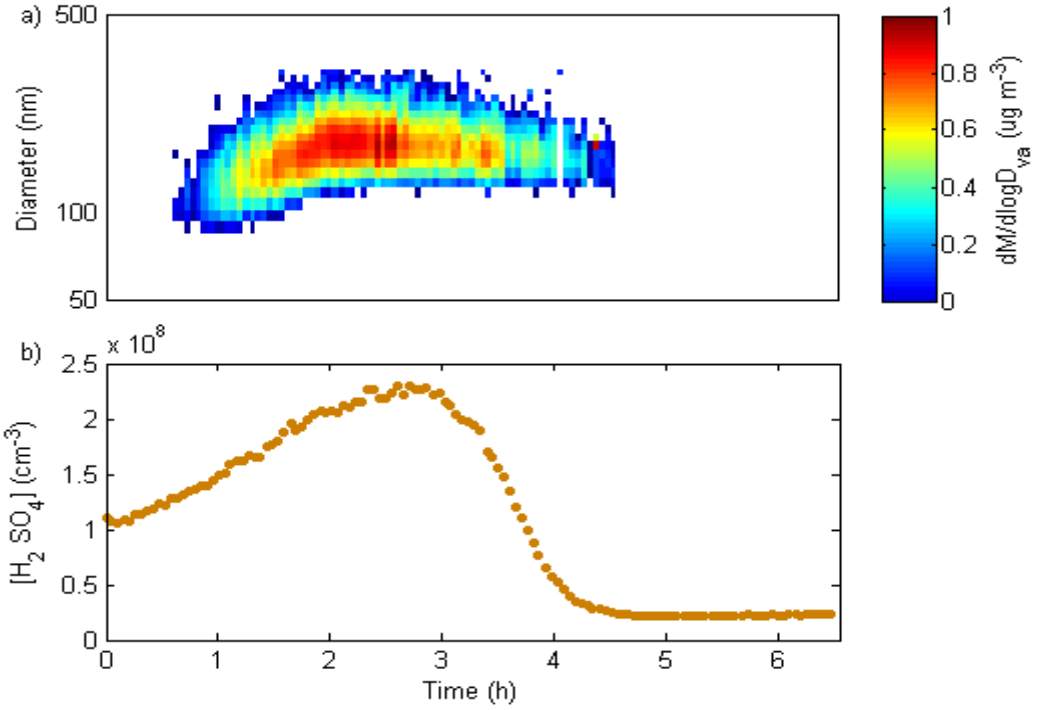

Figure S1. (a) Sulphate mass size distribution ug·m^{-3} (from AMS data) and (b) gas–phase H_2SO_4 concentration (from CIMS data) increases until reaches a peak value during the aerosol particle evaporation experiment 2 performed at *T=288.8 K*.

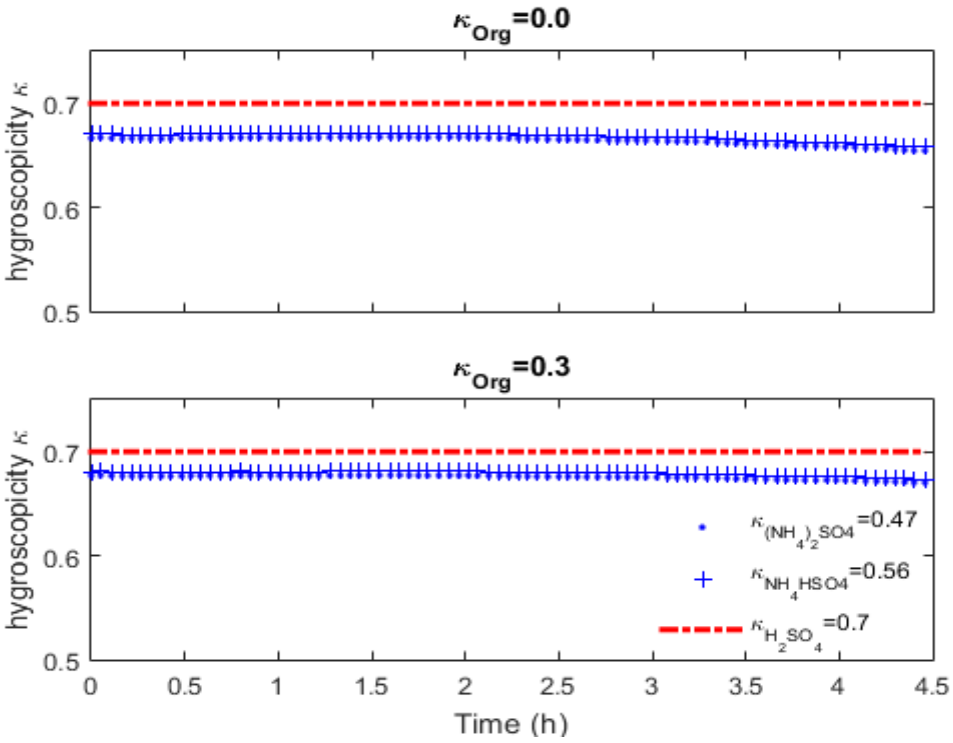

Figure S2. Hygroscopicity kappa (*κ*), based on the AMS measurements, of mixed particles as a function of time for experiment 3. *κ* derived from the hygroscopicities of the components (assumed the lower and higher κ values for bases like ammonium sulphate, $\kappa_{(NH4)2SO4}=0.47$ and ammonium bisulfate, $\kappa_{(NH4)HSO4}=0.56$ (Topping et al., 2005; Petters and Kreidenweis 2007), and organics with *O:C=0*, $\kappa_{Org}=0.0$ and *O:C=1*, $\kappa_{Org}=0.3$ (Massoli et al., 2010)) and their respective volume fractions by applying the Zdanovskii–Stokes–Robinson (ZSR) mixing rule. For the calculation of the volume concentration of each compound assumed liquid phase density of SO_4, NH_4, NO_3, Chl, Org constituents (http://cires1.colorado.edu/jimenez–group/wiki). The difference in percentage of *κ* values calculated for the two extreme cases of $\kappa_{(NH4)2SO4}=0.47$, $\kappa_{(NH4)HSO4}=0.56$ is 0.4 %, while for $\kappa_{Org}=0.0$ and $\kappa_{Org}=0.3$ is 1 %. The result shows a *κ* very close to that of pure sulphuric acid (Sullivan et al., 2010).

S2 Activity coefficients of H_2SO_4 and SO_3 and water activity

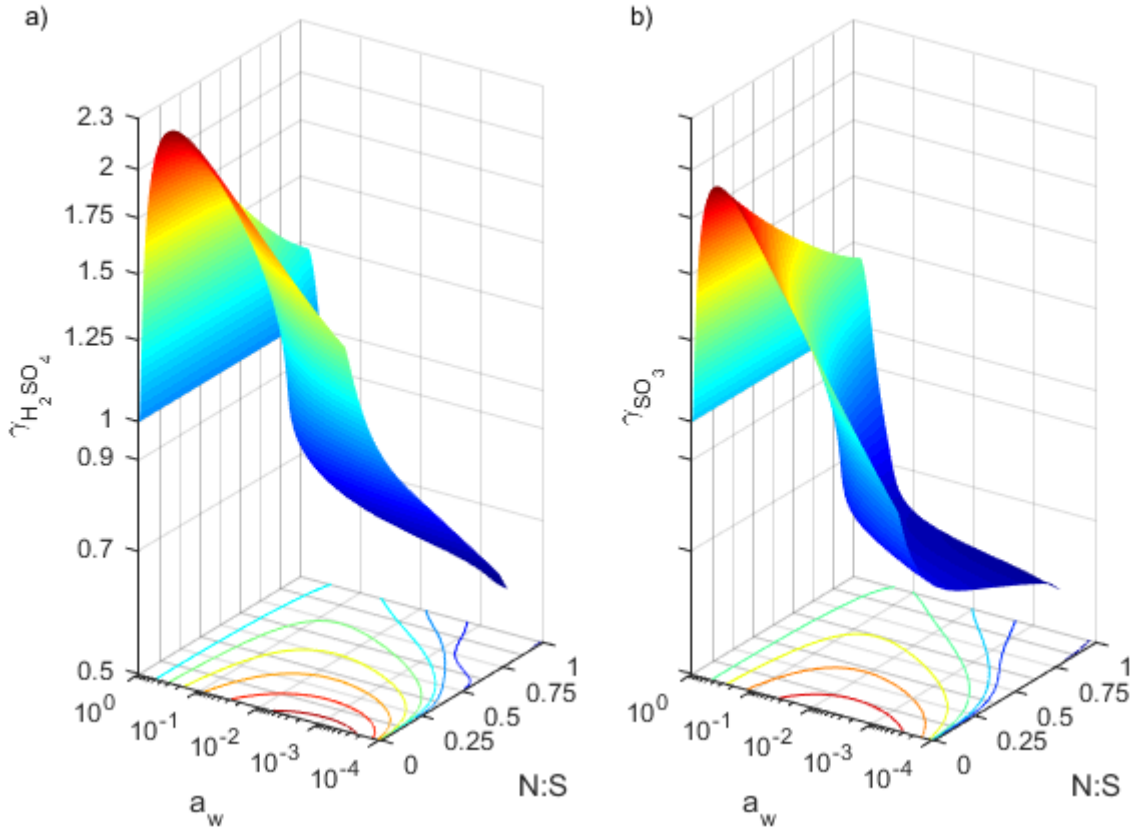

Figure S3. Modelled activity coefficient of (a) H_2SO_4 (γ_{H2SO4}) with equilibrium constant $K_{H2SO4}=2.40\cdot10^9$ $mol\cdot kg^{-1}$, and (b) SO_3 (γ_{SO3}) with equilibrium constant ${}^xK_{SO3}=1.43\cdot10^{10}$, at $T=288.8$ K, as a function of the water activity, a_w, on the y–axis and $N:S$ on the x–axis. The colour coded contours on x–y axes represent constant activity coefficient for a) $\gamma_{H2SO4}=0.8–2.2$ and b) $\gamma_{SO3}=0.8–1.8$.

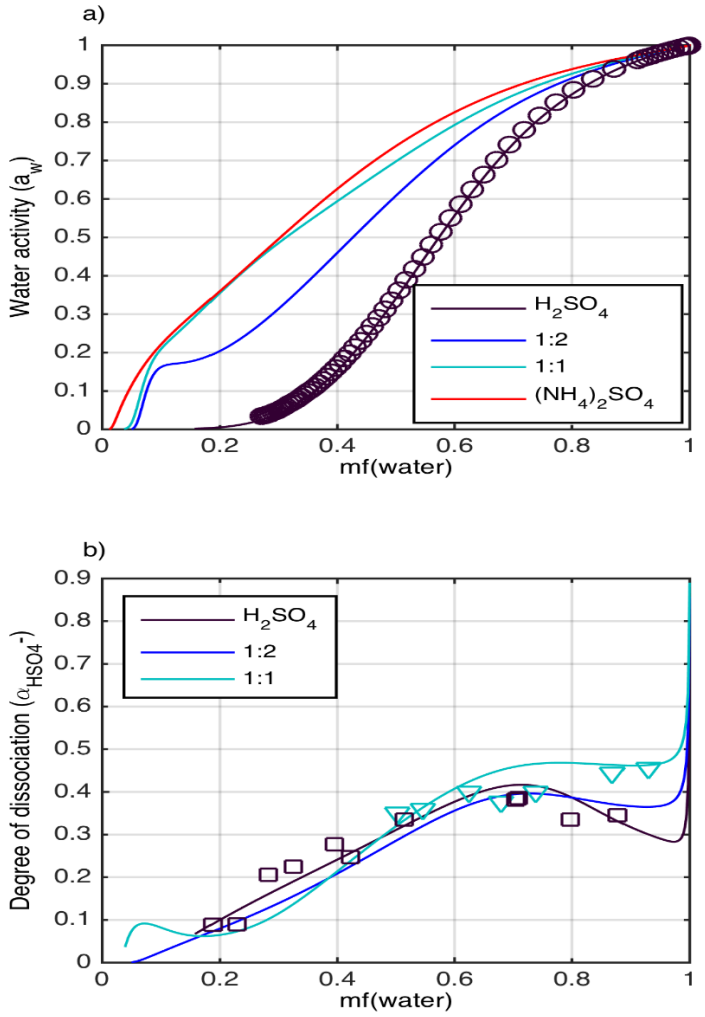

Figure S4. (a) Modelled water activity curves and b) degree of dissociation of HSO_4^- as a function of water mass fraction in aqueous solutions of H_2SO_4 and mixtures of $(NH_4)_2SO_4$ and H_2SO_4. The model simulations and measurements were performed at 298 K. The modelled water activity curves are lines colour coded. The purple curve corresponds to pure sulphuric acid, blue and cyan curves to 1:2 and 1:1 molar ratio of *$(NH_4)_2SO_4$:H_2SO_4* and red curve to pure ammonium sulphate. The measured water activity curve is symbol coded. The purple circle symbol corresponds to $H_2SO_{4(aq)}$ (Staples 1981). (b) the modelled degree of dissociation, α_{HSO4^-}, curves are lines colour coded (corresponding to same aqueous solutions as the curves in Fig. S4.a. The measured degree of dissociation is symbol colour coded (purple squares corresponds to $H_2SO_{4(aq)}$, Myhre et al. (2003), cyan triangles to the 1:1 *$(NH_4)_2SO_4$:H_2SO_4* mixture, Dawson et al. (1986)). The model results can be compared with analogous results in Fig. 10 from Zuend et al., 2011.

S3 Ssaturation vapour pressure parameterizations

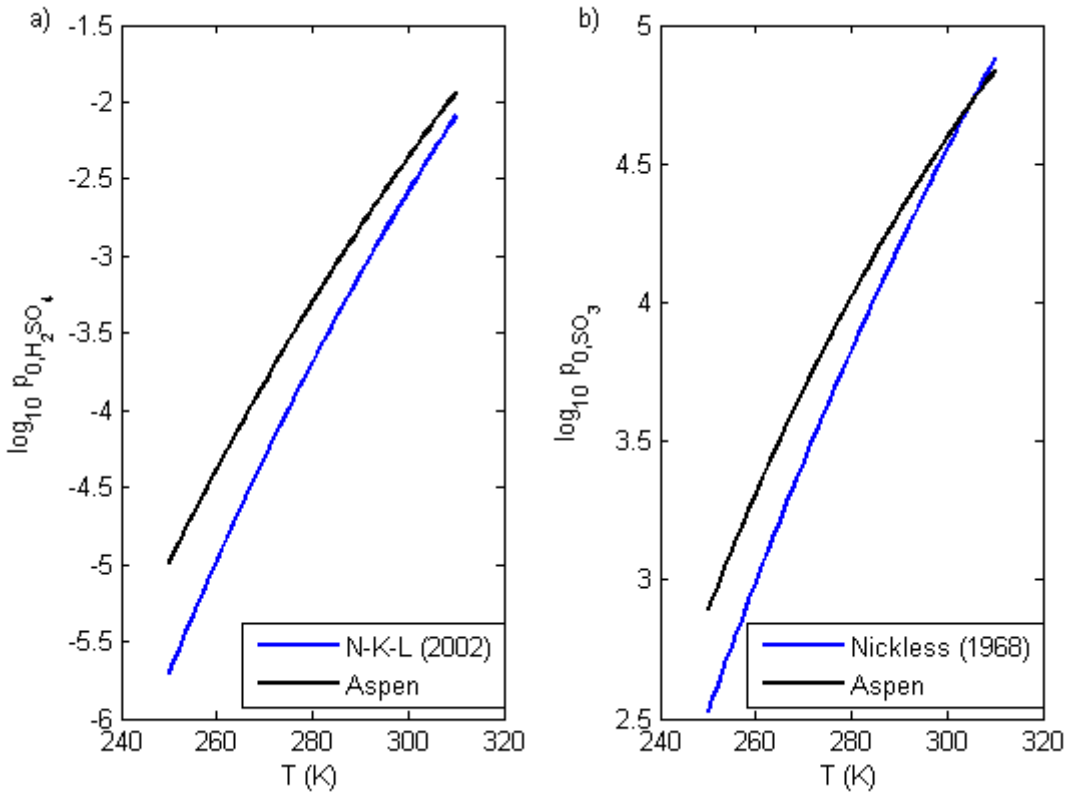

Figure S5. Saturation vapour pressures for H_2SO_4 and SO_3. Comparison among two different pure liquid saturation vapour pressure parameterizations (a) for H_2SO_4 and (b) for SO_3. In panel (a) the blue curve corresponds to the parameterization from the work of Kulmala and Laaksonen (1990), which was optimized by Noppel et al., 2002 (N–K–L). The black curve corresponds to the parameterization from Que et al., 2011 (original Aspen Plus Databank). In panel (b) the blue curve corresponds to the parameterization from the work of Nickless (1968) and the black curve to the parameterization from Que et al., 2011 (original Aspen Plus Databank).

S4 The Kelvin effect

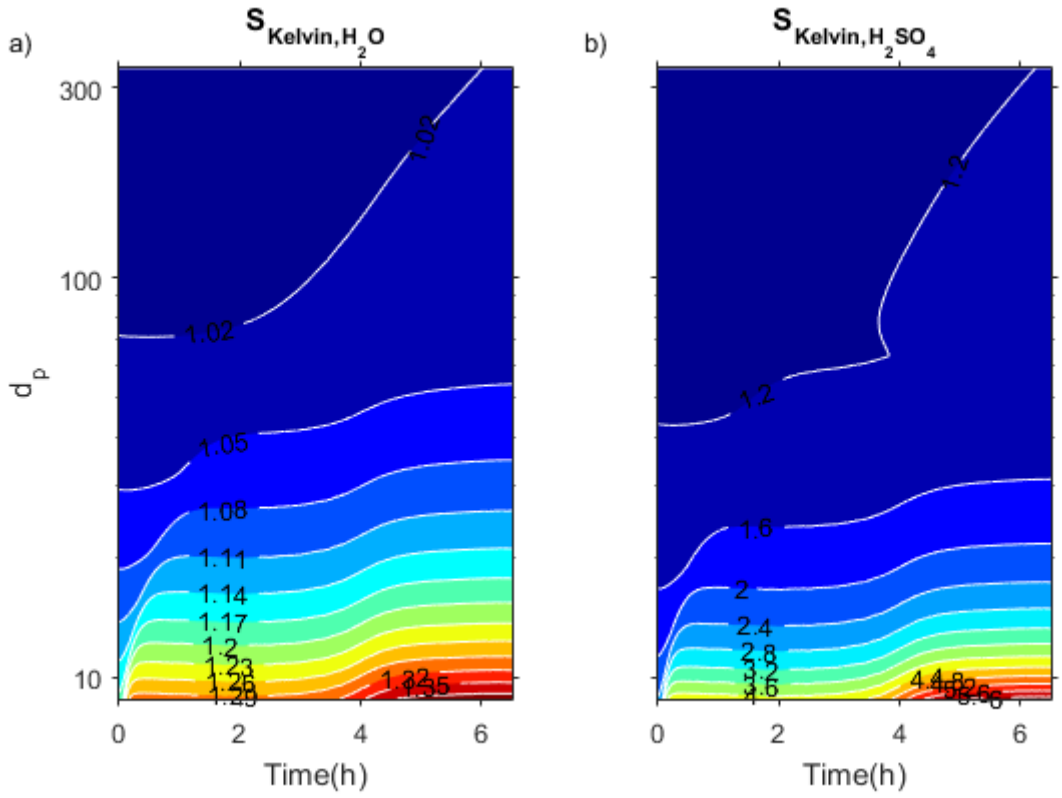

Figure S6. The Kelvin effect for experiment 2 at *T=288.8 K* for Case 2a ($K_{H2SO4}=2.40\cdot10^9$ *mol·kg*$^{-1}$ and $^xK_{SO3}=1.43\cdot10^{10}$) illustrates the increase in (a) the water (white contours correspond to $S_{Kelvin,H2O}=1.02–1.38$) and (b) the H_2SO_4 (white contours represent the Kelvin terms $S_{Kelvin,H2SO4}=1.2–6.0$) saturation vapour pressure. The minimum particle size for experiment 2 is ~40 nm, so the maximum value of the Kelvin term is ~1.44 for sulphuric acid.

S5 Saturation concentration of H_2SO_4 and SO_3

We can calculate the saturation concentration of H_2SO_4 ($C_{H2SO4,S}$, Eq.S1) and SO_3 ($C_{SO3,S}$, Eq.S2) in $\mu g \cdot m^{-3}$ (supplement Fig. S7) with the H_2SO_4 dissociation equilibrium coefficients**,** $K_{H2SO4}=2.4 \cdot 10^9\ mol \cdot kg^{-1}$, and ${}^xK_{SO3}=1.43 \cdot 10^{10}$, based on the mole fractions (Fig. 2), the modelled activity coefficients (Fig. S3), the pure liquid saturation vapours pressure parameterizations (Eq. 10 and 11), and the Kelvin effect (Eq. 13).

$$C_{H_2SO_4,S} = \frac{p_{0,H_2SO_4} \cdot x_{H_2SO_4} \cdot \gamma_{H_2SO_4} \cdot C_{k,H_2SO_4}}{R \cdot T \cdot M_{H_2SO_4}} \quad \text{(S1)}$$

$$C_{SO_3,S} = \frac{p_{0,SO_3} \cdot x_{SO_3} \cdot \gamma_{SO_3} \cdot C_{k,SO_3}}{R \cdot T \cdot M_{SO_3}} \quad \text{(S2)}$$

For almost dry conditions ($a_w=3.7 \cdot 10^{-4}$) and $N:S=0$, $C_{H2SO4,S} \approx 2.6\ \mu g \cdot m^{-3}$ and $C_{SO3,S} \approx 8.8\ \mu g \cdot m^{-3}$. However, as long as a_w is larger than $1.3 \cdot 10^{-3}$, $C_{H2SO4,S}$ becomes larger than $C_{SO3,S}$. Thus, for the conditions during the experiments ($RH>0.3$ %) this thermodynamic setup can be categorized as Case 2a.

With the Aspen Plus Databank pure–liquid saturation vapour pressure parameterization and $K_{H2SO4}=4.00 \cdot 10^9\ mol \cdot kg^{-1}$ and ${}^xK_{SO3}=4.55 \cdot 10^{10}$ $C_{H2SO4,S}$ is always higher than $C_{SO3,S}$ ($C_{H2SO4,S}=3.33\ \mu g \cdot m^{-3}$ and $C_{SO3,S}=2.28\ \mu g \cdot m^{-3}$ at $a_w=2 \cdot 10^{-4}$ and $N:S=0$) (Fig. S7). Thus, this model setup can be also classified as Case 2a.

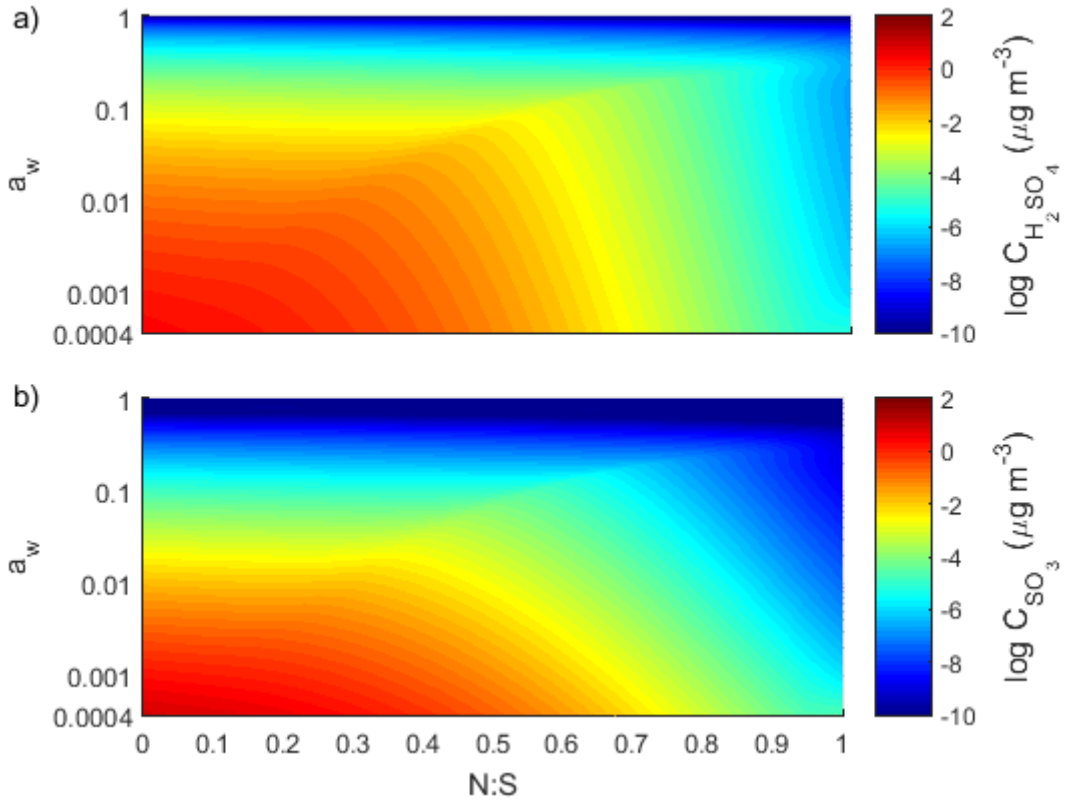

Figure S7.I. (a) The saturation concentration of H_2SO_4 ($C_{H2SO4,S}$) and (b) SO_3 ($C_{SO3,S}$) in $\mu g \cdot m^{-3}$ as a function of a_w and $N:S$ at $T=288.8$ K. The H_2SO_4 dissociation equilibrium coefficients are $K_{H2SO4}=2.4 \cdot 10^9$ $mol \cdot kg^{-1}$, and ${}^xK_{SO3}=1.43 \cdot 10^{10}$. For the pure liquid saturation vapour pressures used the N–K–L and Nickless parameterisations.

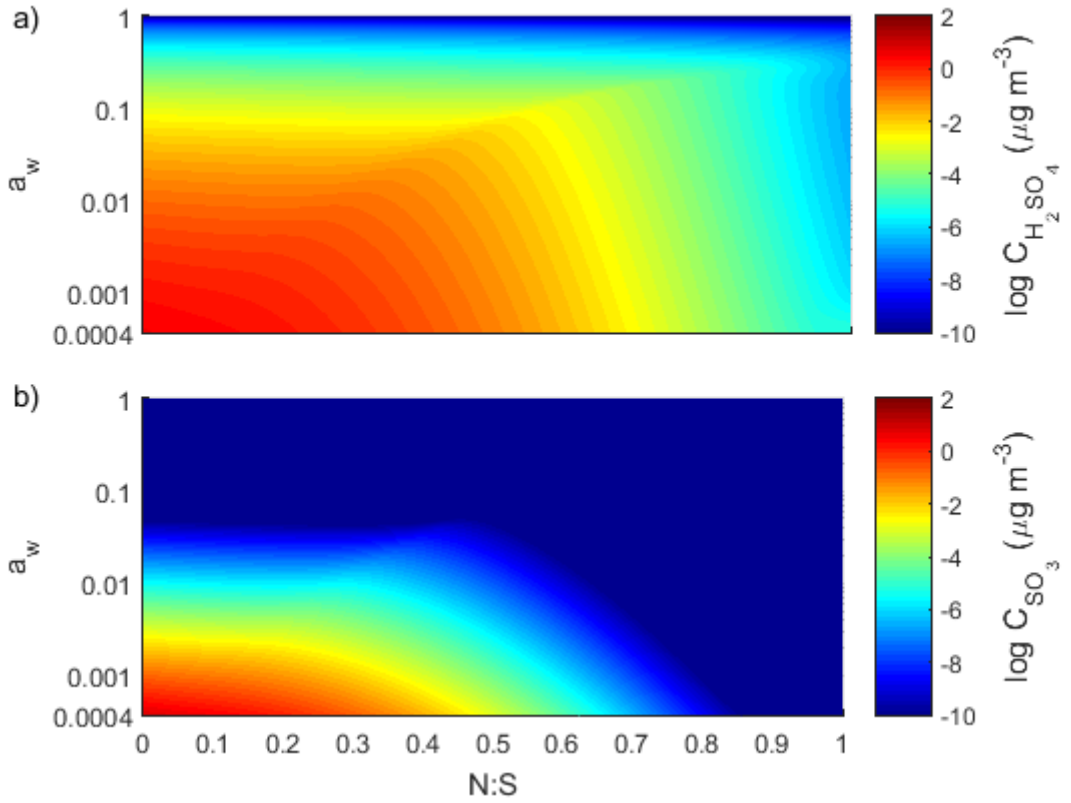

Figure S7.II. (a) The saturation concentration of H_2SO_4 ($C_{H2SO4,S}$) and (b) SO_3 ($C_{SO3,S}$) in $\mu g \cdot m^{-3}$ as a function of a_w and $N:S$ at $T=288.8$ K. The H_2SO_4 dissociation equilibrium coefficients are $K_{H2SO4}=4.00 \cdot 10^9$ mol kg^{-1}, and ${}^{x}K_{SO3}=4.55 \cdot 10^{10}$. For the pure liquid saturation vapour pressures used the parameterisations from Aspen Plus Databank.

S6 Geometrical mean diameter

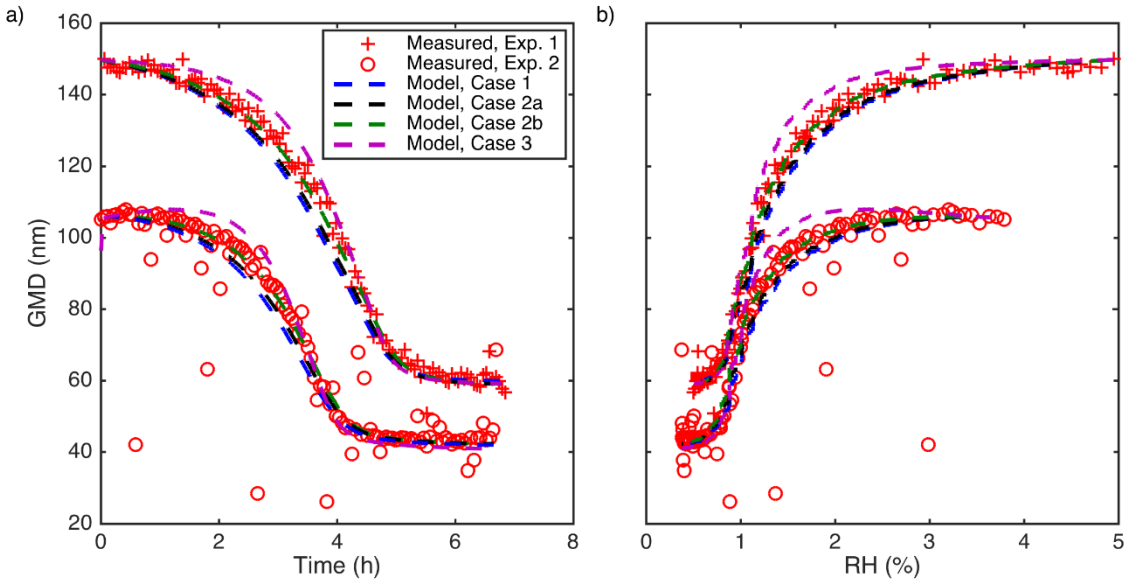

Figure S8. Modelled and measured GMD evolution as a function of (a) time and (b) RH for experiments 1 and 2 performed at *T=288.8 K*. The model results are from simulations 8–11 and 20–23 with NH_3 as a particle phase contaminant listed in Table 2 (Case 1 ($K_{H2SO4}=3.80\cdot10^9$ *mol·kg*$^{-1}$), Case 2a ($K_{H2SO4}=4.00\cdot10^9$ *mol·kg*$^{-1}$ and ${}^xK_{SO3}=4.55\cdot10^{10}$), Case 2b ($K_{H2SO4}=5.00\cdot10^9$ *mol·kg*$^{-1}$ and ${}^xK_{SO3}=5.00\cdot10^9$) and Case 3 ($K_{H2SO4}=1.00\cdot10^{11}$ *mol·kg*$^{-1}$ and ${}^xK_{SO3}=5.00\cdot10^7$)). The pure liquid saturation vapour pressures of H_2SO_4 and SO_3 are calculated with the parameterizations from Que *et al*. (2011) (originally from the Aspen Plus Databank).

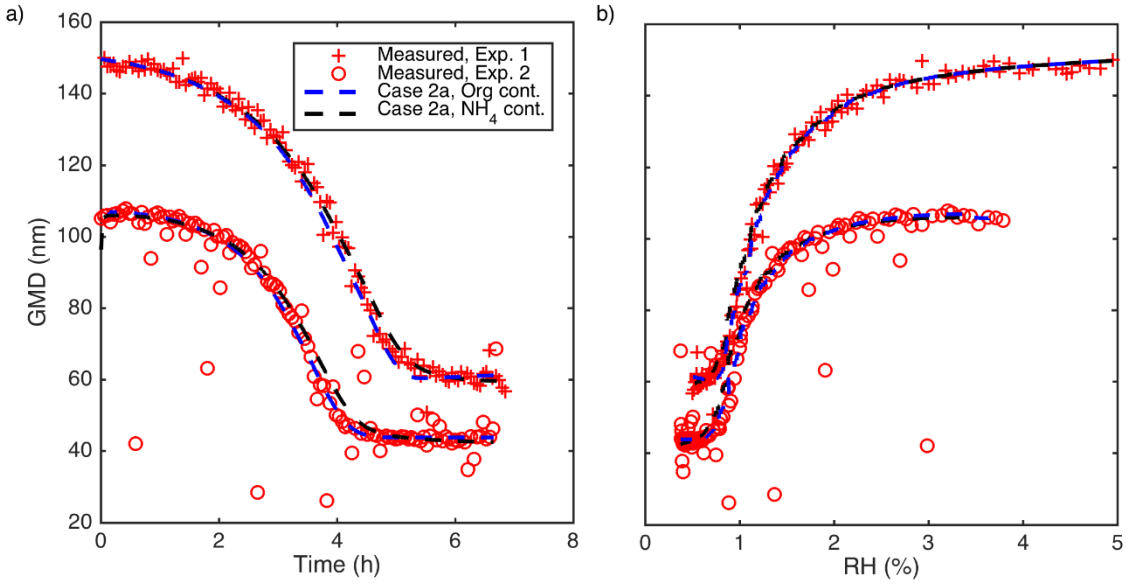

Figure S9. Modelled and measured GMD evolution as a function of (a) time and (b) RH for experiments 1 and 2 performed at *T=288.8 K*. The model results presented are from simulation 2, 6, 14 and 17 listed in Table 2 (Case 2a, $K_{H2SO4}=2.40\cdot10^{9}$ $mol\cdot kg^{-1}$ and $^{x}K_{SO3}=1.43\cdot10^{10}$). The pure liquid saturation vapour pressures of H_2SO_4 and SO_3 are taken from Kulmala and Laaksonen (1990) (Eq. 10) and Nickless (1968) (Eq. 11), respectively. The only difference between the model simulations is the assumed particle contaminant (NH_3 or non–volatile and non–water–soluble organics).

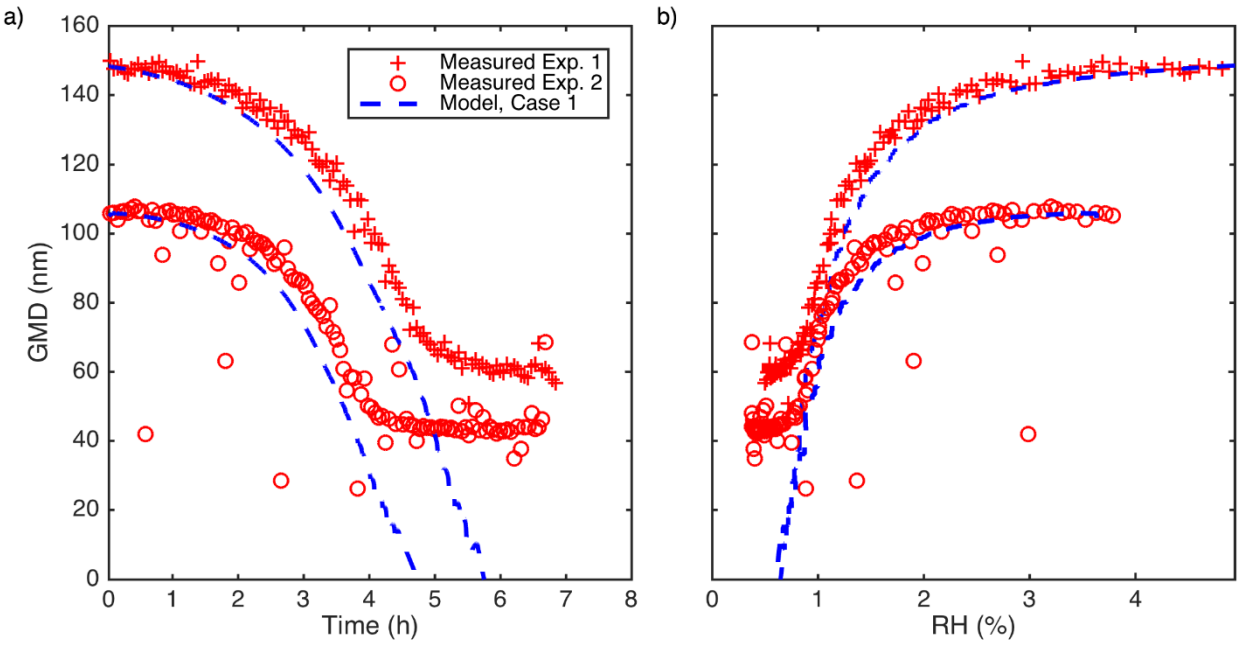

Figure S10. Modelled and measured GMD evolution as a function of (a) time and (b) RH for experiments 1 and 2 performed at *T=288.8 K*. The model results presented arise from Case 1 simulations ($K_{H2SO4}=2.00\cdot10^{9}$ *mol·kg*$^{-1}$) without any particle phase contaminant. The pure liquid saturation vapour pressures of H_2SO_4 was calculated with Eq. 10, N–K–L parameterisation, (Kulmala and Laaksonen (1990) and Noppel et al., 2002).

Supplementary references

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