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# MODELLING OF SULFURIC ACID NANOPARTICLES GROWTH

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## INTRODUCTION

Aerosol particles influence global radiative balance and climate directly through scattering and absorbing solar radiation and indirectly by acting as condensation cloud nuclei. The atmospheric nucleation is often followed by a rapid growth of freshly formed particles. The initial growth of aerosol is the crucial process determining the fraction of nucleated particles growing into cloud condensation nuclei sizes (~ 50 nm and larger). The subject of this study is modelling of growth behaviour of sulfuric acid nanoparticles produced by nucleation of water and sulfuric acid under wet and dry conditions.

## METHODS

The nucleation experiments were carried out in a laminar flow tube at the Finnish Meteorological Institute, Helsinki. The sulfuric acid nanoparticles were produced by nucleation of sulfuric acid and water under different conditions: RH 1% and 30%, T 283, 293 and 303 K, 4 residence times – 30, 45, 60 and 90 s and at initial  $[H_2SO_4]$  from  $2 \times 10^8$  to  $1.4 \times 10^{10}$  molecule  $cm^{-3}$ . The particle number concentrations were measured by UCPC and particle size distributions by DMPS. The obtained number size distributions were fitted with the log-normal distribution and the geometric mean diameter of the nucleation mode was determined. The particle growth rates were obtained from the change of the modal geometric mean as a function of time. The experimental observations were then compared with predictions made using a numerical model. The particle growth was modelled dynamically by calculating the mass transfer rate of sulfuric acid onto the particles using the Fuchs-sutugin equation:

$$I_{SA} = 2\pi dp D_{SA} FS(\alpha, Kn)(C_{SA} - C_{SA, sat})$$

$$FS(\alpha, Kn) = \frac{1 + Kn}{1 + 0.337 Kn + \left(\frac{1.33}{\alpha}\right)(1 + Kn)Kn}$$

$$Kn = \frac{6D_{SA}}{c_{SA} dp}$$

Here  $d_p$  is the particle diameter (m),  $D_{SA}$  is the diffusion coefficient ( $m^2 s^{-1}$ ),  $\alpha$  is the mass accommodation coefficient of sulphuric acid,  $C_{SA}$  is the gas phase concentration of sulphuric acid

(molecule cm<sup>-3</sup>) and  $C_{SA,sat}$  is the number concentration of sulphuric acid at the saturation vapour pressure (molecule cm<sup>-3</sup>). Moreover,  $FS(\alpha, Kn)$  is the so-called Fuchs-Sutugin correction factor which accounts for non-continuum effects in the mass transfer and  $c_{SA}$  (m s<sup>-1</sup>) is the mean molecular speed of sulphuric acid molecules in the gas phase. Here the value of  $C_{SA}$  was taken from the measurements, and  $C_{SA,sat}$  was set as equal to zero corresponding to the assumption that sulphuric acid behaves as a non-volatile vapour. Finally, the value of  $\alpha$  was set as equal to unity based on the measurements conducted by Hanson (2005). The diffusional wall losses of sulfuric acid were calculated according to Hanson and Eisele (2005). Due to anticipated presence of ammonia in the system, the freshly formed particles were partially neutralized. Therefore the model considered 3 different ammonium to sulphate ratios: 1) pure H<sub>2</sub>SO<sub>4</sub> - H<sub>2</sub>O particles 2) particles formed by ammonium bisulphate (NH<sub>4</sub>)HSO<sub>4</sub> 3) particles formed by ammonium sulphate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The “effective” growth rate of particles over the experiment, GR, was calculated as follows:

$$GR = \frac{d_p - d_{init}}{t_{exp}},$$

where  $d_p$  is the particle diameter at the end of the experiment, and  $t_{exp}$  is the residence time in the laminar flow tube. The applied time step was 0.1 seconds in all of the performed calculations.

## RESULTS

When using the calculated H<sub>2</sub>SO<sub>4</sub> concentrations corrected for wall losses as an input parameter into our model, the experimental values did not agree with the theoretical predictions (Fig. 1). The model fails to capture the observed growth rates in all cases since it predicts significantly lower particle growth than that observed in experiments and the deviations are more profound at a RH of ~1% and at high H<sub>2</sub>SO<sub>4</sub> concentrations. By including the initial H<sub>2</sub>SO<sub>4</sub> concentration into the model, we gained much better agreement with the experimental data as compared to the results based on the H<sub>2</sub>SO<sub>4</sub> concentrations corrected for wall losses. The calculations agree very well with the experimental data (Fig. 2). Fig. 3 depicts the experimental growth rates under wet conditions, at a residence time of 90 s and at nucleation temperatures 283, 293 and 303 K and the atmospheric growth rates, obtained in Heidelberg and Hyytiälä during the QUEST project (Fiedler et al., 2005), data obtained in Atlanta during the ANARChE study (Stolzenburg et al., 2005), data from Beijing the CAREBeijing-2008 campaign (Yue et al., 2010), data from Mace Head during the PARFORCE campaign (O’Dowd et al., 2002) and data from Kent, Ohio (Erupe et al., 2010) are depicted for comparison. A trend line which presents the theoretical predictions of the growth of ammonium sulfate particles under wet conditions (RH=30%) is also depicted. Most observed atmospheric growth rates correspond to substantially lower H<sub>2</sub>SO<sub>4</sub> concentrations and our results thus show, that in most cases sulfuric acid alone cannot explain the growth rates observed in the atmosphere. H<sub>2</sub>SO<sub>4</sub> is the main condensing vapour responsible for particle growth only in large urban areas, where it can contribute up to 60 % to the growth (Stolzenburg et al., 2005, Yue et al., 2010). In order to explain the atmospheric growth rates, the condensation of additional chemical species is assumed, mainly organic compounds (Erupe et al., 2010, Fiedler et al., 2010) and iodine species (O’Dowd et al., 2002). There are only a few previously reported values of particle growth rates from nucleation experiments. Young et al. (2008) have studied the binary nucleation of H<sub>2</sub>SO<sub>4</sub> and water at T=288 K, RH from 11% to 23% and at initial H<sub>2</sub>SO<sub>4</sub> concentrations from 10<sup>8</sup> to 10<sup>10</sup> molecule cm<sup>-3</sup>. The observed particle growth rates in their experiment ranged from 95 nm h<sup>-1</sup> to 500 nm h<sup>-1</sup>. Benson et al. (2008) measured the binary nucleation of H<sub>2</sub>SO<sub>4</sub> and water at T=288 K,

at RH from 10% to 55% and at  $\text{H}_2\text{SO}_4$  concentrations from  $10^8$  to  $10^9$  molecule  $\text{cm}^{-3}$ . The particle growth rates estimated from their measurements were roughly from 160 to 490 nm  $\text{h}^{-1}$ . The results of these studies are in good agreement with the growth rates determined from our experiments, as can be seen in Fig. 4.

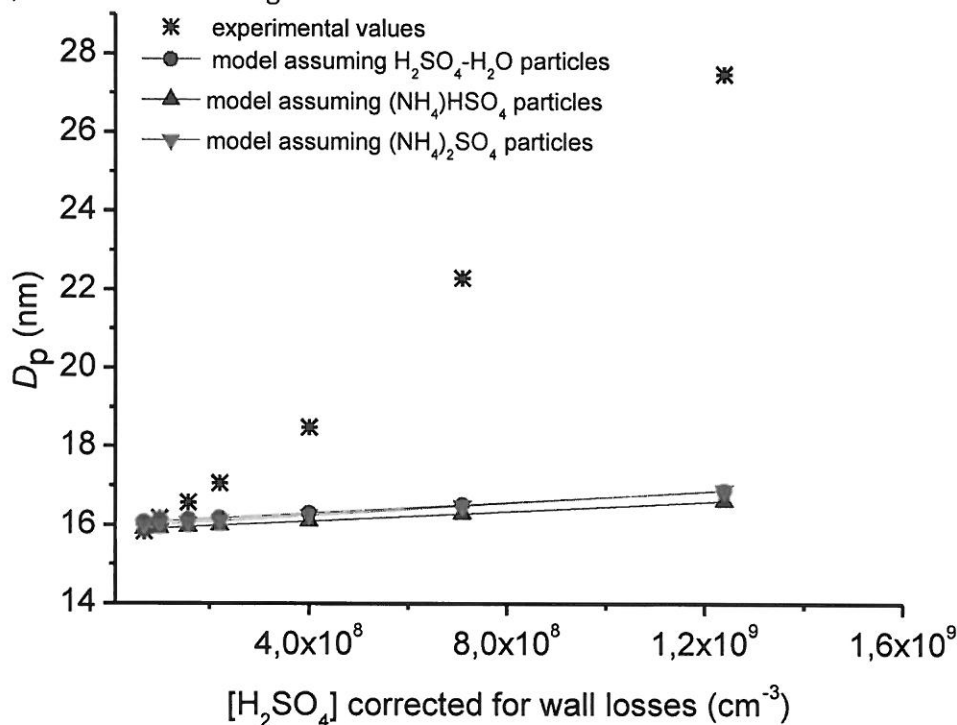


Fig. 1: The comparison of the experimental median particle diameters ( $T=283\text{K}$ ,  $\text{RH}=30\%$ , residence time 60s) and values predicted theoretically from a model using the  $\text{H}_2\text{SO}_4$  concentration corrected for wall losses as an input parameter

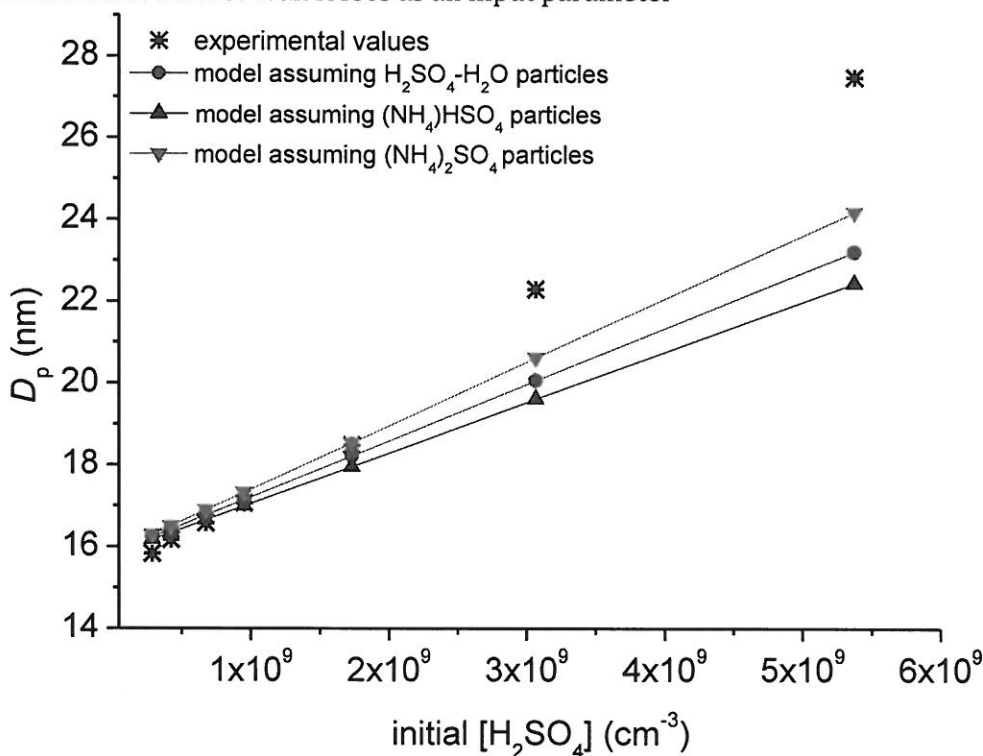


Fig. 2: The comparison of the experimental median particle diameters ( $T=283\text{K}$ ,  $\text{RH}=30\%$ , residence time 60s) and values predicted theoretically from a model using the  $\text{H}_2\text{SO}_4$  concentration without a correction for wall losses

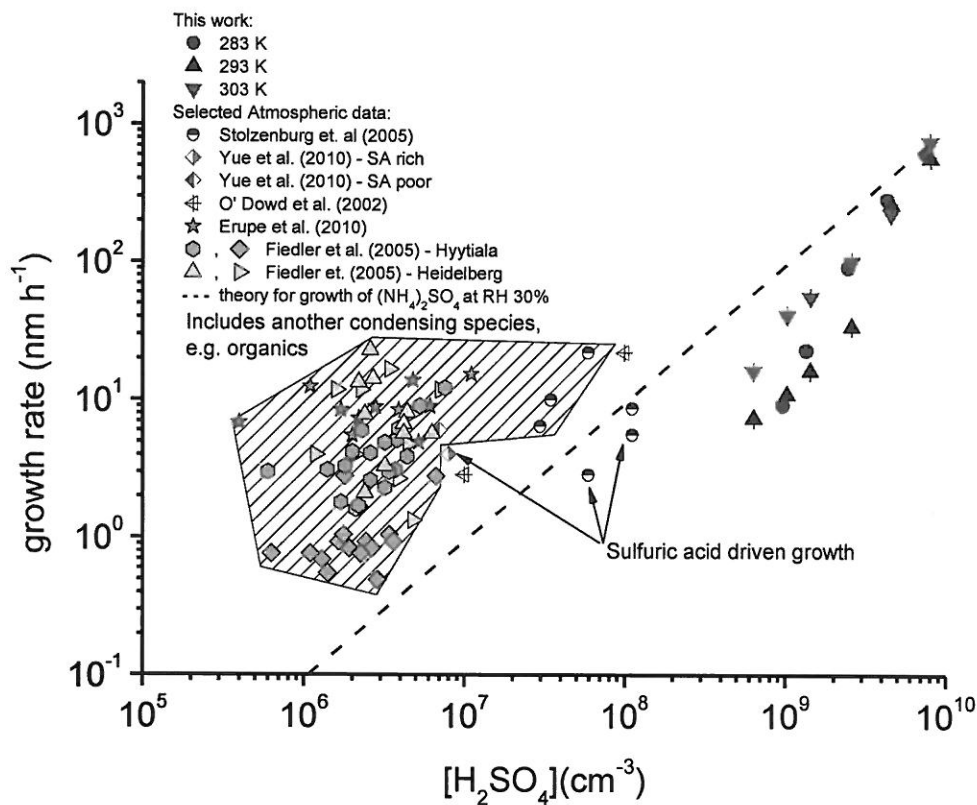


Fig. 3: The experimental growth rates obtained under RH=30%, residence time of 90 s and T of 283, 293 and 303 K. The atmospheric growth rates, obtained at different locations are depicted for comparison. The line presents the theoretical predictions of the growth of ammonium sulphate particles at a RH of 30%.

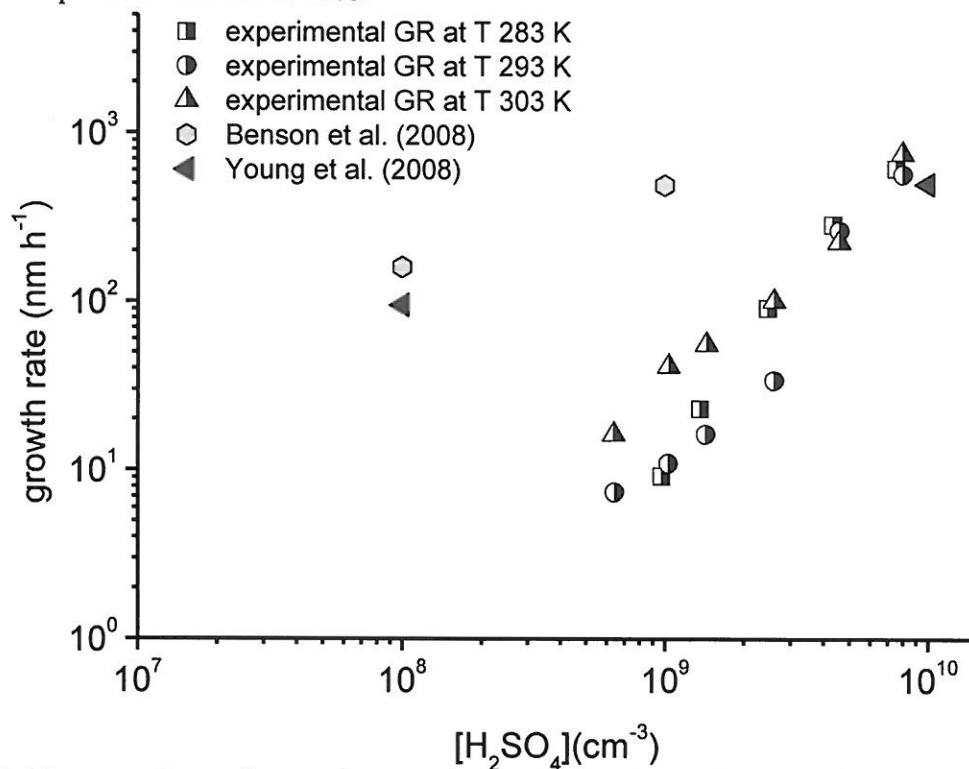


Fig. 4: The experimental growth rates determined at RH=30%, a residence time of 90 s and T 283, 293 and 303 K are compared with the particle growth rates measured in the nucleation experiments made by Benson et al. (2008) at T=288 K and Young et al. (2008) at T=288 K

## CONCLUSIONS

The results of an experimental study of sulphuric acid nanoparticle growth under different conditions and subsequent modelling of particle growth is presented here. The wall losses of H<sub>2</sub>SO<sub>4</sub> derived from experimental growth rates were found to be substantially lower than the diffusion limited values calculated according to Hanson and Eisele (2000). Our results indicate that the wall losses of H<sub>2</sub>SO<sub>4</sub> are not as high as is commonly presumed. Due to long lasting experiments, the measurements are believed to be performed under wall-equilibrium conditions. We therefore speculate that the wall of the flow tube is not an infinite sink for H<sub>2</sub>SO<sub>4</sub> molecules, but that there is also a flux of H<sub>2</sub>SO<sub>4</sub> from the wall into the tube, being more profound under dry conditions. The correct determination of the sulphuric acid concentration in nucleation measurements is a crucial factor for subsequent analysis and data interpretation. Our results show that neglecting the flux of H<sub>2</sub>SO<sub>4</sub> from the wall may cause a significant underestimation of the residual H<sub>2</sub>SO<sub>4</sub> concentration. A comparison of our data with atmospheric measurements shows that growth rates based solely on the condensation of H<sub>2</sub>SO<sub>4</sub> significantly underestimate the growth rates observed in the atmosphere. A satisfactory agreement of our data with the growth rates determined from previous laboratory experimental studies was found.

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