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Growth of sulphuric acid nanoparticles under wet and dry conditions

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Abstract

New particle formation, which greatly influences the number concentrations and size distributions of an atmospheric aerosol, is often followed by a rapid growth of freshly formed particles. The initial growth of a newly formed aerosol is the crucial process determining the fraction of nucleated particles growing into cloud condensation nuclei sizes, which have a significant influence on climate. In this study, we report the laboratory observations of the growth of nanoparticles produced by nucleation of H_2SO_4 and water in a laminar flow tube at temperatures of 283, 293 and 303 K, under dry (a relative humidity of 1 %) and wet conditions (relative humidity of 30 %) and residence times of 30, 45, 60 and 90 s. The initial H_2SO_4 concentration spans the range from 2×10^8 to 1.4×10^{10} molecule cm^{-3} and the calculated wall losses of H_2SO_4 were assumed to be diffusion limited. The detected particle number concentrations, measured by the Ultrafine Condensation Particle Counter (UCPC) and Differential Mobility Particle Sizer (DMPS), were found to depend strongly on the residence time. Hygroscopic particle growth, presented by growth factors, was found to be in good agreement with the previously reported studies. The experimental growth rates ranged from 20 nm h^{-1} to 890 nm h^{-1} at RH 1 % and from 7 nm h^{-1} to 980 nm h^{-1} at RH 30 % and were found to increase significantly with the increasing concentration of H_2SO_4. Increases in the nucleation temperature had a slight enhancing effect on the growth rates under dry conditions. The influence of relative humidity on growth was not consistent – at lower H_2SO_4 concentrations, the growth rates were higher under dry conditions while at H_2SO_4 concentrations greater than 1×10^9 molecule cm^{-3} the growth rates were higher under wet conditions. The growth rates show only a weak dependence on the residence time. The experimental observations were compared with predictions made using a numerical model, which investigates the growth of particles with three different extents of neutralization by the ammonia NH_3: (1) pure H_2SO_4 – H_2O particles (2) particles formed by ammonium bisulphate, $(NH_4)HSO_4$ (3) particles formed by ammonium sulphate, $(NH_4)_2SO_4$. The highest growth rates were found for ammonium sulphate particles. Since the model accounting for the initial H_2SO_4 concentration predicted the experimental growth rates correctly, our results suggest that the commonly presumed diffusional wall losses of H_2SO_4 are not so significant. We therefore assume that there are not only losses of H_2SO_4 on the wall but also a flux of H_2SO_4 molecules from the wall into the flow tube, the effect being more profound under dry conditions and at higher temperatures of the tube wall. Based on a comparison with the atmospheric observations, our results indicate that sulphuric acid alone can not explain the growth rates of particles formed in the atmosphere.

1 Introduction

Aerosol particles influence the global radiative balance and climate directly by scattering and absorbing solar radiation and indirectly by acting as condensation cloud nuclei (Charlson et al., 1992). New particle formation through the photochemical reactions of gaseous species significantly influences the number concentrations and size distributions of atmospheric aerosol and also aerosol models suggest that atmospheric nucleation is very likely a major source of aerosol particles in the global atmosphere (Spracklen et al., 2006) and that it is also a significant source of cloud condensation nuclei (Spracklen et al., 2008, Merikanto et al., 2009). Several mechanisms of new particle formation have been proposed, including the binary homogeneous nucleation of water and sulphuric acid (Vehkamäki et al., 2002), ternary homogeneous nucleation of water, sulphuric acid and ammonia or amines (Ball et al., 1999; Korhonen et al., 1999; Benson et al., 2009; Berndt et al., 2010; Kirkby et al., 2011), ion-induced nucleation (Lee et al., 2003; Lovejoy et al., 2004; Yu et al., 2010; Kerminen et al., 2010; Hirsikko et al., 2011) and homogeneous nucleation involving iodine species (Kulmala, 2003). However, it still remains unclear which mechanism is dominant in the atmosphere (Kulmala et al., 2004b), mainly because the preferred new particle formation mechanism depends on the atmospheric conditions and geographical location. Our current inability to quantify new particle formation correctly results in huge uncertainties into the assessment of the direct and indirect effects of aerosols on climate change in the climatic models (Spracklen et al., 2006; Merikanto et al., 2009).

Atmospheric nucleation is often followed by a rapid growth of freshly formed particles. The initial growth of a newly formed aerosol is the crucial process determining the fraction of nucleated particles growing to cloud condensation nuclei sizes (~ 50 nm and larger) and hence subsequently participating in cloud formation processes (Dusek et al., 2006; Andreae and Rosenfeld, 2008; Kulmala and Kerminen, 2008). The majority of particle growth rates observed during atmospheric measurements lies in the range of 1–10 nm h^{-1}, indicating that it takes about 12–72 h before the nucleated particles grow to cloud condensation nuclei sizes (Kulmala and Kerminen, 2008). Many recent studies have suggested that sulphuric acid plays a key role in the atmospheric nucleation and subsequent growth of newly formed particles (Sipillä et al., 2010; Brus et al., 2011; Kirkby et al., 2011). Growth rates based entirely on the condensation of sulphuric acid vapour greatly underestimate the growth rates observed in atmospheric measurements (Sihto et al., 2006; Nieminen et al., 2010), mainly because low-volatile organic species are responsible for up to 90 % of the observed growth (Makëla et al., 2001; Smith et al., 2008). Although the growth of freshly formed particles has been intensively studied for a long time, the exact mechanism is still not well understood.

The processes governing the growth of particles in a nucleation mode size range are condensation, self-coagulation and coagulation scavenging (Leppä et al., 2011). After formation, the particles grow by multiple condensations of different organic and inorganic vapours (Kulmala, 2003). The condensation rate of different chemical species is influenced by the Kelvin effect, which increases the equilibrium vapour pressure with decreasing particle size and increasing molar volume of the condensing compound. According to the Nano-Köhler theory (Kulmala et al., 2004a), the non-volatile or low-volatile compounds are responsible for the initial growth of freshly formed particles and the condensation of more volatile components increases with increasing particle size (Zhang et al., 2004). Self-coagulation – coagulation between particles in the same size mode – increases the mean diameter and decreases the particle number concentration in this mode. Unless the number concentration of freshly formed particles is 1×10^6 cm^{-3} or higher, self-coagulation is only a minor contributor to the initial growth of nucleation mode particles (Kulmala and Kerminen, 2008). The coagulation scavenging of nucleation mode particles with pre-existing larger particles results in a decrease of the total particle number concentration and an increase of the diameter describing the whole aerosol population. The growth of nucleation mode particles due to coagulation scavenging is thus only apparent, because none of the particles in this mode grow larger (Leppä et al., 2011).

There are several methods to determine the particle growth rates from the atmospheric particle size distribution measurements. A data analysis method based on the fitting of the aerosol general dynamic equation to the particle size distributions has recently been introduced (Kuang et al., 2012). This approach enables for the first time the decoupling of the size and time dependence of particle growth rates. The growth rate of sub-3 nm particles can be determined from the time lag between the increase of the concentration of sulphuric acid and the particles in the sub-3 nm size range (Weber et al., 1997; Sihto et al., 2006). The maximum concentration method (Hirsikko et al., 2005) is based on investigating of spectra from air ion spectrometer, in which the timing of maximum concentration in each size fraction is followed. Another method is based on the temporal evolution of the geometric mean diameters of the nucleation mode particles, which are determined by fitting a log-normal function to the obtained particle size distributions. To determine the growth rate, a first-order polynomial is subsequently fitted to the geometric mean diameters of the nucleation mode during the new particle formation event (dal Maso et al., 2005). In laboratory studies, kinetic models or methods based on the temporal evolution of the geometric mean diameters of the measured particle size distributions are mainly used to determine the growth rates of particles formed during nucleation experiments (Young et al., 2008).

In this paper, we present the results of a laboratory study of the growth behaviour of sulphuric acid nanoparticles produced by homogeneous nucleation of H_2SO_4 and water under wet and dry conditions. A variety of experimental conditions have been studied to assess the effect of temperature, relative humidity, residence time and H_2SO_4 concentration on the growth of freshly nucleated particles. The growth of the particles was calculated using a zero dimensional model, which was designed to simulate the processes governing the initial steps of particle growth and accounts for the condensation of sulphuric acid as well as the uptake of water and ammonia by the particles. Furthermore, three different extents of neutralization of the particles by ammonia and their growth were investigated: pure sulphuric acid – water particles, particles corresponding to an ammonium bisulphate solution and particles corresponding to an ammonium sulphate solution. The comparison of the particle growth rates determined from the different modifications of the model, as well as an analysis of the growth rates as a function of different experimental conditions is presented here.

2 Methods

The growth behaviour of sulphuric acid nanoparticles produced by the homogeneous nucleation of sulphuric acid and water vapour was studied. The nucleation experiments were carried out in a laminar flow tube at the Finnish Meteorological Institute, Helsinki, Finland. The detailed description of the flow tube and the operational principle has been presented and discussed in detail by Brus et al. (2010) and Neitola et al. (2013).

2.1 Measurements and experimental setup

Dry and particle-free air served as the carrier gas in this study. Sulphuric acid vapour was produced from a liquid reservoir by passing a stream of carrier gas through a thermally controlled saturator with high purity H_2SO_4 (97 % w.t., Baker analyzed) and another stream of the carrier gas was saturated with water vapour by passing through a set of Nafion humidifiers (MH-050, Permapure, USA). Both streams were introduced into a mixing unit and then the mixed gas stream flowed through the tube, where particles nucleated and grew to detectable sizes. At the outlet of the flow tube, the number concentrations of the produced particles were measured using an ultrafine condensation particle counter (UCPC, Model 3776, TSI Inc., USA). The same modification to UCPC TSI 3776 has been done as described in Brus et al. (2010) to obtain a d_{50}cut-off of 2.25 nm. The saturator temperature was increased from a nominal 39 °C up to 40 °C, the condenser temperature was decreased from a nominal 10 °C down to 8 °C. At these new temperatures no homogenous nucleation was observed inside the counter. Particle size distributions were measured using a differential mobility particle sizer (DMPS) with a short HAUKE-type Differential Mobility Analyzer (DMA), a bipolar radioactive ^{63}Ni neutralizer and UCPC (Model 3025A, TSI Inc., USA).

The measurements were performed at relative humidities of $\sim 1\,\%$ and $\sim 30\,\%$, presented here as dry and wet conditions respectively. The flow tube was kept at constant temperature during the measurements and the nucleation temperatures investigated were 283, 293 and 303 K. The relative humidity was measured by a humidity sensor (Vaisala HMI38) and temperature by a probe (PT100). Both lines of purified and particle free air (saturator and mixing flow) were controlled by a mass flow rate controller to within ±3 % (MKS type) (Brus et al., 2010). The total gas flow inside the tube was maintained to provide four residence times in the tube: 30, 45, 60 and 90 s.

The temperature of the H_2SO_4 saturator was increased stepwise in 7 increments of 5 K during each measurement resulting in a gradually growing concentration of sulphuric acid in the flow tube. In order to determine the number concentration of gas-phase H_2SO_4 in the tube, the saturation vapour pressure of H_2SO_4 in the saturator was calculated first using the following equation (Kulmala and Laaksonen, 1990):

$$\ln p_{\mathrm{SA}} = \ln p_{\mathrm{SA,0}} + \frac{\Delta H_{\mathrm{v}}(T_0)}{R}\left[-\frac{1}{T} + \frac{1}{T_0} + \frac{0,38}{T_{\mathrm{c}} - T_0} \times \left(1 + \ln\frac{T_0}{T} - \frac{T_0}{T}\right)\right], \quad (1)$$

where p_{SA} is the saturation vapour pressure (atm) of H_2SO_4 at a temperature of T (K) $p_{\mathrm{SA,0}}$ is the saturation vapour pressure of H_2SO_4 at the temperature $T_0 = 360$ K (Ayers et al., 1980), ΔH_{v} is the enthalpy of vaporization, T is the temperature of the saturator and T_{c} is the critical temperature ($T_{\mathrm{c}} = 905$ K). The H_2SO_4 vapour concentration in the flow tube was then calculated by applying the mixing law, i.e. dividing the sulphuric acid vapour flux leaving the saturator by the total flow in the laminar flow tube. The initial concentrations of H_2SO_4, at which newly formed particles were detected during the experiments, covered the range from 2×10^8 to 1.4×10^{10} molecule cm^{-3}. The wall losses of H_2SO_4 in the flow tube were assumed to be a diffusion controlled first-order rate process, which can be described by a simple equation given by Hanson and Eisele (2000):

$$[H_2SO_4]_t = [H_2SO_4]_0 e^{-kt} \tag{2}$$

where $[H_2SO_4]_0$ is the initial concentration of H_2SO_4, $[H_2SO_4]_t$ is the concentration after time t and k is the rate constant given by the equation:

$$k = 3.65\frac{D}{r^2} \tag{3}$$

where r is the radius of the flow tube and D is the RH dependent diffusion coefficient of H_2SO_4 (Hanson and Eisele, 2000). In our experiment, k was 0.0381 s^{-1} for dry conditions and k was 0.0323 s^{-1} for wet conditions.

Although no measurement of the NH_3 concentration was done during the experiments, NH_3 is assumed to be present in the system (Brus et al., 2011; Neitola et al., 2013). Since NH_3 and other chemical species are ubiquitous in the ambient environment, the presence of these compounds at low concentrations cannot be excluded in the case of laboratory measurements (e.g. Benson et al., 2011; Kirkby et al., 2011). The nucleated sulphuric acid nanoparticles in our experiments are thus partially neutralized to $(NH_4)_2SO_4$ and $(NH_4)HSO_4$ during the measurements. The extent of the partial neutralization depends on the particle size and relative humidity and is highest for the smallest particles and highest relative humidities (Biskos et al., 2009). In our previous study with similar setup (Neitola et al., 2013), the concentration of ammonia was measured with the MARGA system (instrument for Measuring AeRosols and Gases, ten Brink et al., 2007). The average NH_3 concentrations were 60 pptv under dry conditions and 126 pptv under wet conditions. These concentrations did not change with the increasing temperature of the saturator and thus the NH_3 is assumed to originate from the carrier gas and from the ultrapure water used to humidify the mixing flow.

The DMPS detected particles in the size range from 3 to 200 nm with a time resolution of 12 min. The uncertainties of the measured particle mode diameters were estimated to be 10 % based on a comparison of the DMPS used with a standard one (Wiedensohler et al., 2012). The raw DMPS data were inverted to yield the number size distributions of the formed particles. The charging efficiencies were calculated using the parametrization of Wiedensohler and Fissan (1991). The obtained number size distributions were then fitted with the log-normal distribution and the geometric mean diameter of the nucleation mode was determined. The particle growth rates were then obtained from the change of the modal geometric mean as a function of time.

2.2 Model description

The particle growth inside the laminar flow tube was simulated with a zero dimensional model that accounts for the condensation of sulphuric acid as well as uptake of water and ammonia by the particles. The former process was modelled dynamically by calculating the mass transfer rate of sulphuric acid onto the particles, I_{SA} (molecule s^{-1}), using the Fuchs-Sutugin equation (Fuchs and Sutugin, 1970):

$$I_{SA} = 2\pi d_p D_{SA} \mathrm{FS}(\alpha, Kn)(C_{SA} - C_{SA,sat}) \tag{4}$$

$$\mathrm{FS}(\alpha, Kn) = \frac{1 + Kn}{1 + 0.337Kn + \left(\frac{1.33}{\alpha}\right)(1 + Kn)\,Kn} \tag{5}$$

$$Kn = \frac{6D_{SA}}{c_{SA} d_p} \tag{6}$$

Here d_p is the particle diameter (m), D_{SA} is the diffusion coefficient ($m^2 s^{-1}$), α is the mass accommodation coefficient of sulphuric acid, C_{SA} is the gas phase concentration of sulphuric acid (molecule cm^{-3}) and $C_{SA,sat}$ is the number concentration of sulphuric acid at the saturation vapour pressure (molecule cm^{-3}). Moreover, FS(α, Kn) is the so-called Fuchs-Sutugin correction factor which accounts for non-continuum effects in the mass transfer and c_{SA} (ms^{-1}) 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. This assumption is reasonable for systems that contain ammonia (e.g. Kulmala et al., 2000). Finally, the value of α was set as equal to unity based on the measurements conducted by Hanson (2005).

The uptake of the considered semi-volatile compounds, ammonia and water, was modelled as follows. First, since there were no direct measurements of the ammonia concentration levels in the system, we applied three different degrees of particle neutralization: (1) no ammonia was assumed to be taken up by the aerosols, (2) ammonia was assumed to condense along with sulphuric acid so that a 1 : 1 molar ratio was maintained between ammonia and sulphuric acid, corresponding thus to an ammonium bisulphate solution, and (3) two ammonia molecules were assumed to condense for each acid molecule which corresponds to an ammonium sulphate solution. The particles were assumed to be aqueous regardless of the relative humidity and the particle water content was calculated as a function of the water activity (a_w) using the appropriate molality data found in the literature (Staples, 1981, for sulphuric acid, and Tang and Munkelwitz, 1994, for ammonium-bisulphate and -sulphate). Here the water activity a_w was calculated according to the relation a_w = RH/Ke where RH is the relative humidity in the instrument and Ke is the Kelvin term (Seinfeld and Pandis, 1998). Finally, the particle surface tension and density were calculated using the model presented by Hyvärinen et al. (2005).

The initial particle diameter d_{init} was taken from the measurements at the lowest temperature of the saturator and the initial chemical composition was set so that the particles were in equilibrium with respect to water and ammonia. The increase of the particle diameter as a function of the increasing sulphuric acid concentration (temperature of the saturator) was then simulated. Also, the particle size was increased after each time step by first converting the total particle mass (obtained as described above) to a corresponding volume and further to a diameter d_p by assuming that the particles are spherical. At the end of the simulation, the "effective" growth rate of particles over the experiment, GR, was calculated as follows:

$$\mathrm{GR} = \frac{d_\mathrm{p} - d_\mathrm{init}}{t_\mathrm{exp}}, \tag{7}$$

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 s in all of the performed calculations.

3 Results and discussion

3.1 Reproducibility of the measurements

The reproducibility of the performed measurements is illustrated in Fig. 1a and b, which show the results of experiments at a temperature of 283 K, a residence time of 60 s and under dry conditions (RH ~ 1 %) taken one day apart. The total particle concentrations as a function of the H_2SO_4 concentration measured by DMPS for both experiments are presented in Fig. 1a. Except the first points, which show larger scatter and with a ratio of these concentrations of 1 : 1.17, the ratios of the remaining concentrations range from 1 : 1.01 to 1 : 1.07. The observed variation of the median particle diameters as a function of the initial H_2SO_4 concentrations with standard deviations as error bars is shown in Fig. 1B. At the same temperature, relative humidity, residence time and comparable H_2SO_4 concentrations, the maximum difference of single median particle diameters determined from both experiments was 0.6 nm with most diameters varying by 0.3 or 0.4 nm. These results show that the measurements of the particle diameters and particle number concentrations were very reproducible.

3.2 Variation of particle number concentrations and particle size distributions

During each experiment, the temperature of the saturator was increased in seven consecutive steps of 5 K every two hours, resulting in a distinct increase of the H_2SO_4 concentration in the gas phase and a subsequent significant rise of the particle number concentration. The stability of particle production was not achieved immediately; it took approximately 30 min to obtain a steady particle production. The first 30 minutes of every period of constant saturator temperature were therefore excluded from the analysis. The data from the DMPS were then averaged over the whole period analysed to receive a single data point characterizing each saturator temperature and the data from the UCPC were averaged over two equal periods of 45 min to receive two data points.

The determined curves of the particle number concentration as a function of the initial H_2SO_4 concentration measured by both DMPS and UCPC at $T = 293$ K, RH ∼ 30 % and at residence times of 45, 60 and 90 s are presented in Fig. 2. The total number concentrations determined from both instruments were found to be strongly dependent on the residence time of the gaseous mixture in the flow tube. The significance of residence time in nucleation measurements has been discussed in previous studies (Sipilä et al., 2010; Berndt et al., 2010). The results clearly show that the observed total number concentration is influenced by the growth process and the longer the residence time, the larger the fraction of nucleated particles grows beyond the detection limits of the UCPC and DMPS. For example, during the experiment performed at $T = 293$ K and RH ∼ 30 %, at a H_2SO_4 concentration of 6.5×10^8 molecule cm^{-3}, the particle number concentration increases about one order of magnitude from $3.2 \times 10^3 \pm 0.15 \times 10^3$ cm^{-3} at a residence time of 45 s to $3 \times 10^4 \pm 1.1 \times 10^3$ cm^{-3} at a residence time of 90 s. Absolutely no particles were detected during experiments performed at a residence time of 30 s indicating that the nucleated particles were not able to grow to detectable sizes during the first 30 s of the experiments. The particle number concentrations at all residence times were rather stable at any H_2SO_4 concentration (see Fig. 2). The total particle concentrations obtained from the DMPS measurements were slightly lower than the values detected with the stand-alone UCPC, due to the lower cut-off diameter (d_{50} = 2.25 nm) of the stand-alone UCPC (Brus et al., 2010) and the upper limit (200 nm) of the DMPS which undercounts at higher sulphuric acid concentrations (Fig. 2). By a comparison of the measurements from both instruments, we received an almost linear relationship between the concentrations in most cases, which can be seen in Fig. 3. A visible decrease of the particle concentration at the temperature of the saturator 295 K corresponding to the H_2SO_4 concentration of $\sim 3.5 \times 10^9$ molecule cm^{-3} recorded by UCPC can be seen in Fig. 2. This artefact of the experimental setup was observed when the temperature of the acid saturator was close to the temperature of the mixing unit (~ 293 K) and this behaviour was also reported in our previous study with a very similar setup (Neitola et al., 2013).

The observed variation in the particle size distributions obtained from the inversion of the raw DMPS data from a single experiment – a measurement performed at a constant nucleation temperature of $T = 283$ K, a residence time of 60 s, a RH of ~ 30 % and at different H_2SO_4 concentrations – is presented in Fig. 4. The increasing total particle concentration and particle median diameter correspond with the increasing H_2SO_4 concentration in the gaseous mixture. The values of the total number concentrations during all of the measurements ranged from $1.1 \times 10^3 \pm 0.17 \times 10^3$ cm^{-3} to $4.7 \times 10^4 \pm 1.2 \times 10^3$ cm^{-3} and were generally higher during experiments performed at RH of ~ 30 % and nucleation temperature of 303 K. The values of the median particle diameter ranged from 14.4 ± 0.1 nm to 39.8 ± 1.6 nm and particles grew larger at a RH of ~ 30 % and at high H_2SO_4 concentrations.

3.3 Growth of the particles under dry and wet conditions

The H_2SO_4-H_2O nucleation was affected by the presence of impurities originating from ultrapure water and carrier gas. The enhancing effect of NH_3 on nucleation was observed in the laboratory experiments and was found to be stronger at low relative humidities (Berndt et al., 2010; Benson et al., 2011). The freshly formed H_2SO_4 particles are partially neutralized to ammonium bisulphate, $(NH_4)HSO_4$, and ammonium sulphate, $(NH_4)_2SO_4$. For a fixed relative humidity, the hygroscopic growth of these particles was found to decrease with decreasing particle size owing to a greater degree of neutralization, since $(NH_4)_2SO_4$ is less hygroscopic than H_2SO_4 (Biskos et al., 2009). When considering the effect of water vapour on the particle growth, the hydration of H_2SO_4 should be taken into account. The number of water molecules attached to an H_2SO_4 molecule increases significantly with the growing relative humidity and the higher the relative humidity, the higher the growth rate due to the condensation of H_2O on the particles (Nieminen at al., 2010).

The variation of the particle diameters has the same pattern under both wet and dry conditions, which is illustrated in Fig. 5. Hygrospcopic growth behaviour can be described with the so-called hygroscopic growth factor GF:

$$\mathrm{GF} = \frac{D_\mathrm{p}\,(\mathrm{wet})}{D_\mathrm{p}\,(\mathrm{dry})}$$

In this study, the dry diameter D_p(dry) corresponds to the median particle diameters obtained from measurements performed at a RH of ~ 1 % and the wet diameters D_p(wet) to the median particle diameters obtained from measurements at a RH of ~ 30 %. Hygroscopic growth factors determined from measurements performed at $T = 293$ K ranged from 1.05 to 1.35 and at $T = 303$ K the values covered the range from 1.1 to 1.42. Our findings were then compared with the results from Biskos et al. (2010), who measured the hygroscopic growth of acidic sulphate nanoparticles over a wide range of relative humidities using the tandem DMA technique. At a relative humidity of ~ 30 %, Biskos et al. (2010) report for dry diameters from 7.5 nm to 36.1 nm, which are comparable with this study, growth factors from 1.18 to 1.3. The best agreement with our study was found for $T = 303\,\text{K}$, since most GF values determined at this temperature were close to 1.25, which is illustrated in Fig. 6. At $T = 293\,\text{K}$, most GFs were around 1.1 and reached values above 1.2 only at a residence time of 90 s and for H_2SO_4 concentrations of 5×10^9 molecule cm^{-3} and higher (Fig. 6). The hygroscopic growth factors were not determined for $T = 283\,\text{K}$, since the differences in the determined median particle diameters from measurements under wet and dry conditions at all residence times were so small that in most cases they fall within the uncertainity range of the measurements. A clear dependence of GFs on H_2SO_4 concentration can be seen in Fig. 6. At lower H_2SO_4 concentrations, the GFs slightly decrease and at a H_2SO_4 concentration of $\sim 3 \times 10^9$ molecule cm^{-3} they start to increase. However, the GFs calculated from our model were not in good agreement with the experimental values. For this reason, it could not be explained if the trends in the GFs behaviour are real or spurious.

3.4 Wall losses of sulphuric acid

The initial concentrations of H_2SO_4, at which newly formed particles were detected during the experiments, covered the range from 1.8×10^8 to 1.4×10^{10} molecule cm^{-3}. Previous nucleation experiments, conducted with H_2SO_4 produced from a liquid reservoir, reported that nucleation occurred at an H_2SO_4 concentration of $\sim 10^9$ molecule cm^{-3} and higher (Wyslouzil et al., 1991; Viisanen et al., 1997; Ball et al., 1999; Zhang et al., 2004). The H_2SO_4 molecules can attach to the inner surfaces of the flow tube during experiments and in order to determine the residual concentration of H_2SO_4 the corrections of the initial concentrations are necessary. The wall loss factor characterizing the diffusion losses of sulphuric acid on the walls of the tube is defined as:

$$\text{WLF} = \frac{[H_2SO_4]_0}{[H_2SO_4]_t}$$

where $[H_2SO_4]_0$ is the initial concentration of sulphuric acid in the flow tube determined from Eq. (1) and $[H_2SO_4]_t$ is the concentration of sulphuric acid after time t. In this study, the time t was set as equal to half of the residence time of the gaseous mixture in the flow tube and thus the concentration $[H_2SO_4]_t$ corresponds approximately to the H_2SO_4 concentration in the middle of the flow tube. This assumption was based on our previous studies where the nucleation zone was determined experimentally (Brus et al., 2010) and also verified by the CFD model (Herrmann et al., 2010). The estimated wall loss factors span the range from 1.9 to 4.8 under wet conditions and from 2.2 to 6.2 under dry conditions for a t from 22 s to 45 s calculated as half of the initial residence times.

However, when using the calculated H_2SO_4 concentrations corrected by WLFs as an input parameter into our model, the experimental values did not agree with the theoretical predictions. This can be seen from Fig. 7, which illustrates the variation of both the measured and calculated median particle diameters at a RH of ~ 30 % with $T = 283$ K and a residence time of 60 s. 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 with high H_2SO_4 concentrations. These results suggest that the H_2SO_4 concentration corresponding to the middle of the flow tube is too low and does not describe the growth behaviour of the particles correctly. For this reason, the initial H_2SO_4 concentration corresponding to the H_2SO_4 concentration at the beginning of the flow tube was used as the input parameter for all the model calculations in the further analysis.

3.5 The particle growth rates and model evaluation

The growth of freshly formed particles was calculated using the numerical model described in Sect. 2.2. By including the initial H_2SO_4 concentration determined from Eq. (1) into the model, we gained much better agreement with the experimental data as compared to the results based on the H_2SO_4 concentrations corrected for wall losses (Hanson and Eisele, 2000). A comparison of the experimental and numerical results is illustrated in Fig. 8, which shows the experiment conducted at $T = 283\,\mathrm{K}$, a RH of ~30 % and a residence time of 60 s (compare with Fig. 7). As can be seen there, the calculations agree very well with the experimental data, despite the fact that the model slightly overestimates the growth rates at a residence time of 90 s at all temperatures and under both wet and dry conditions (Fig. 9). It should be noted that the model accounts only for H_2SO_4, water and ammonia while different impurities may have been present in our system in trace concentrations. Such compounds might have influenced the nucleation process and the subsequent growth of the freshly formed particles.

An indirect way to determine the H_2SO_4 concentration in experimental devices is based on the measured growth rates of the freshly formed particles. The H_2SO_4 concentrations in our study derived solely from the growth rates determined experimentally and verified in our model indicate that the commonly assumed wall losses of H_2SO_4 on the inner surfaces calculated from Eq. (2) are not as significant as previously believed. We therefore speculate that the wall is not an infinite sink for H_2SO_4, but that there is also a flux of H_2SO_4 from the wall to the flow tube. For example in the study by Hanson and Eisele (2000), the wall of a laminar flow tube was found to be a significant source of H_2SO_4 at a RH of $< 0.5\,\%$ and the concentration of H_2SO_4 from the wall reached up to $3 \times 10^8\,\mathrm{molecule\,cm^{-3}}$. Another possible explanation for the discrepancy between the H_2SO_4 concentrations calculated from Eq. (2) and that derived from our experimental growth rates might be the limited adsorption capacity of the wall. The wall becomes saturated with H_2SO_4 during experiments and therefore further adsorption of H_2SO_4 molecules might be hindered after a certain time period. We estimated the “real” wall losses of H_2SO_4 by matching the predicted and observed growth rates through tuning the initial H_2SO_4 concentration in the model. Although the estimated wall losses were slightly scattered for different experimental conditions (RH, temperature and residence time), a reasonable agreement found for the experimental and modelled data yields an estimation of the wall losses to be ~10 % for a residence time of 45 s, ~15 % for a residence time of 60 s and ~25 % for a residence time of 90 s, corresponding to WLFs of 1.11, 1.18 and 1.33, respectively.

The experimental growth rates, determined from Eq. (7), range from 20 nm h^{-1} to 890 nm h^{-1} under dry conditions and from 7 nm h^{-1} to 980 nm h^{-1} under wet conditions. When analyzing the dependence on the experimental conditions, the measured growth rates were found to increase with growing H_2SO_4 concentration and increased almost linearly with increasing particle size. Also increases in the nucleation temperature were found to have a slight enhancing effect on particle growth rates under dry conditions. At a very low RH, the wall is a source of H_2SO_4 molecules and the flux is proportional to the H_2SO_4 vapour pressure, which increases with rising temperature. The influence of the RH is not consistent – at lower H_2SO_4 concentrations the growth rates were higher under dry conditions, at H_2SO_4 concentrations of $\sim 1\times 10^9$ molecule cm^{-3} and above the growth rates were higher under wet conditions. The residence time was found to have a negligible effect on the measured growth rates.

The predicted growth rates, calculated from the model with the initial H_2SO_4 concentration using Eq. (7), range from 7 nm h^{-1} to 1100 nm h^{-1} under dry conditions and from 15 nm h^{-1} to 1300 nm h^{-1} under wet conditions. Growth rates over 1000 nm h^{-1} were reached only at very high H_2SO_4 concentrations of 8×10^9 molecule cm^{-3} and higher and at a residence time of 90 s. Most growth rates span the range from ~ 10 nm h^{-1} to ~ 500 nm h^{-1} under dry conditions and from ~ 15 nm h^{-1} to ~ 400 nm h^{-1} under wet conditions. Our model considered 3 different numbers of NH_3 molecules taken up by each molecule of H_2SO_4 during particle formation. All three tested degrees of neutralization provided results that are in good agreement with the experimental data and all of them capture the trends in the growth rate values in a similar manner (see Fig. 8). The highest growth rates were achieved for ammonium sulphate particles. The numerical results indicate that the presence of NH_3 enhances the growth of a freshly formed aerosol.

Figure 10 depicts the experimental growth rates under wet conditions, at a residence time of 90 s and at three nucleation temperatures 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 during 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 sulphate particles under wet conditions (RH = 30 %) is also depicted. The best agreement with our data was found for sulphuric acid-driven growth rates from a study by Stolzenburg et al. (2005), who investigated the growth of particles containing ammonium sulphate, which is consistent with the chemical compositions of particles in our study. Most observed atmospheric growth rates correspond to substantially lower H_2SO_4 concentrations and our results thus show that in most cases sulphuric acid alone cannot explain the growth rates observed in the atmosphere. H_2SO_4 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'Down et al., 2002; Kulmala et al., 2013).

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_2SO_4 and water at $T = 288$ K, RH from 11 % to 23 % and at initial H_2SO_4 concentrations from 10^8 to 10^{10} molecule cm^{-3}. The observed particle growth rates in their experiment ranged from 95 nm h^{-1} to 500 nm h^{-1}. Benson et al. (2008) measured the binary nucleation of H_2SO_4 and water at $T = 288$ K, at RH from 10 % to 55 % and at H_2SO_4 concentrations from 10^8 to 10^9 molecule cm^{-3}. The particle growth rates estimated from their measurements were roughly from 160 to 490 nm 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. 11.

4 Conclusions

The results of an experimental study of sulphuric acid nanoparticle growth under different conditions are presented here. The measurements were performed in a laminar flow tube at temperatures of 283, 293 K and 303 K, at RHs of 1 % and 30 %, an initial H_2SO_4 concentration from 2×10^8 to 1.4×10^{10} molecule cm^{-3} and at four different residence times. The number concentrations and size distributions of the newly formed particles were measured with a UCPC and a DMPS. The obtained size distributions were fitted with a log-normal distribution in order to determine the median particle diameter and the temporal variation of the median diameter was used to calculate the growth rate of the nucleation mode. The variation of the growth rates and their dependence on the experimental conditions were analysed. A comparison of the experimental values with the theoretical ones predicted from a model considering the growth of particles with three different ammonia to sulphate ratios was made.

It was shown that our system can produce very reproducible results. A strong dependence of the number concentrations of newly formed particles on residence time was observed. The obtained growth rates were found to increase significantly with increasing H_2SO_4 concentration. A slightly enhancing effect of increased RH on growth rates was observed at higher H_2SO_4 concentrations and a clear dependence of the growth rates on increasing nucleation temperature was recorded under dry conditions. The residence time was found to have a negligible effect on the growth rates. The modelled growth rates were highest for ammonium sulphate particles indicating that NH_3 promotes particle growth under both wet and dry conditions. A comparison of our data with atmospheric measurements shows that growth rates based solely on the condensation of H_2SO_4 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.

The wall losses of H_2SO_4 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_2SO_4 are not as great 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_2SO_4 molecules, but that there is also a flux of H_2SO_4 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_2SO_4 from the wall may cause a significant underestimation of the residual H_2SO_4 concentration. More detailed measurements are needed to gain a better understanding of the processes influencing the H_2SO_4 concentration in experimental devices and the role of sulphuric acid in the early stages of particle growth.

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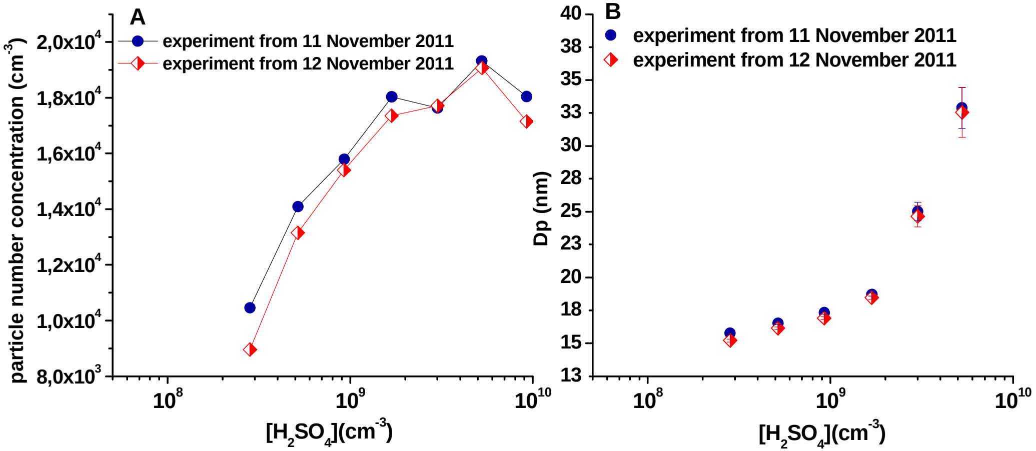

Fig. 1. (A) The variation of the total particle concentrations determined from a DMPS from measurements performed at $T = 283$ K, with a RH of $\sim 1\,\%$ and a residence time of 60 s taken one day apart. **(B)** The median particle diameters determined from measurements performed at $T = 283$ K, with a RH of $\sim 1\,\%$ and a residence time of 60 s taken one day apart. The standard deviations of the median particle diameters are depicted as error bars.

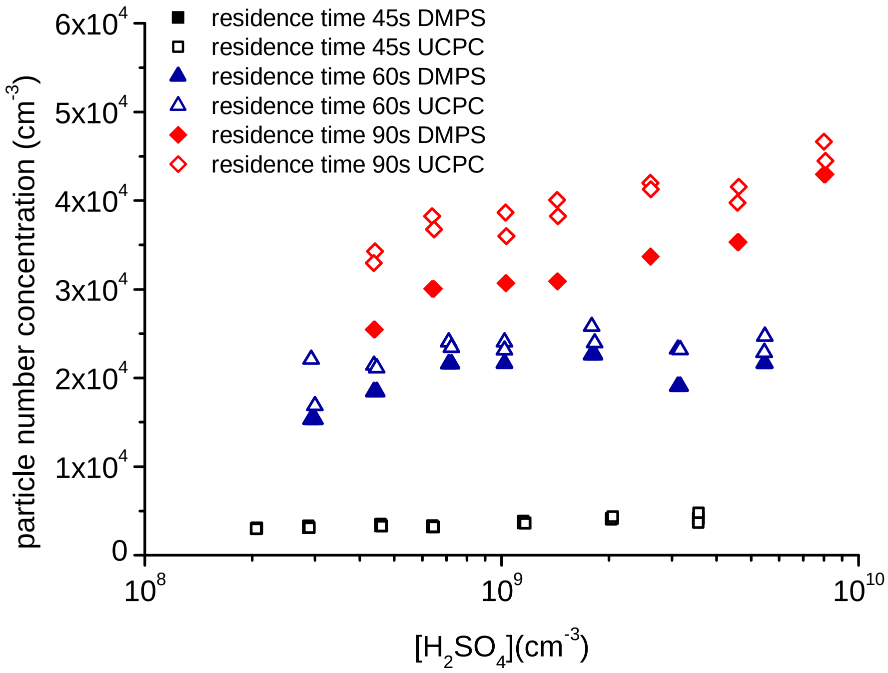

Fig. 2. The observed particle number concentrations at different residence times at *T* = 293 K and with a RH of ~30 %. The solid symbols present the number concentrations determined by a DMPS and the open symbols are number concentrations determined by a UCPC.

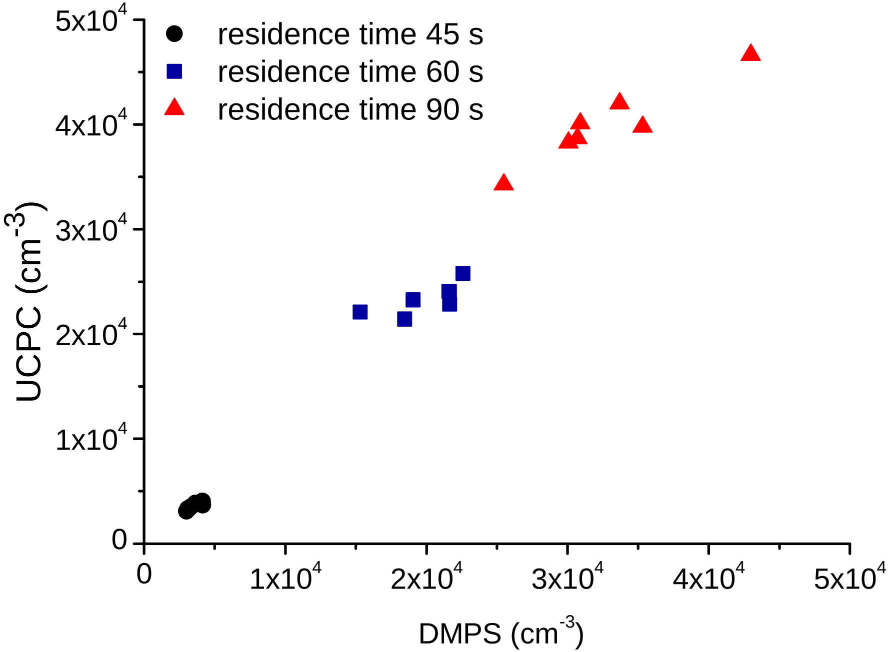

Fig. 3. An almost linear relationship was reached by a comparison of the particle number concentrations determined from a DMPS and a UCPC at different residence times at $T = 293$ K and with the RH set at 30 %.

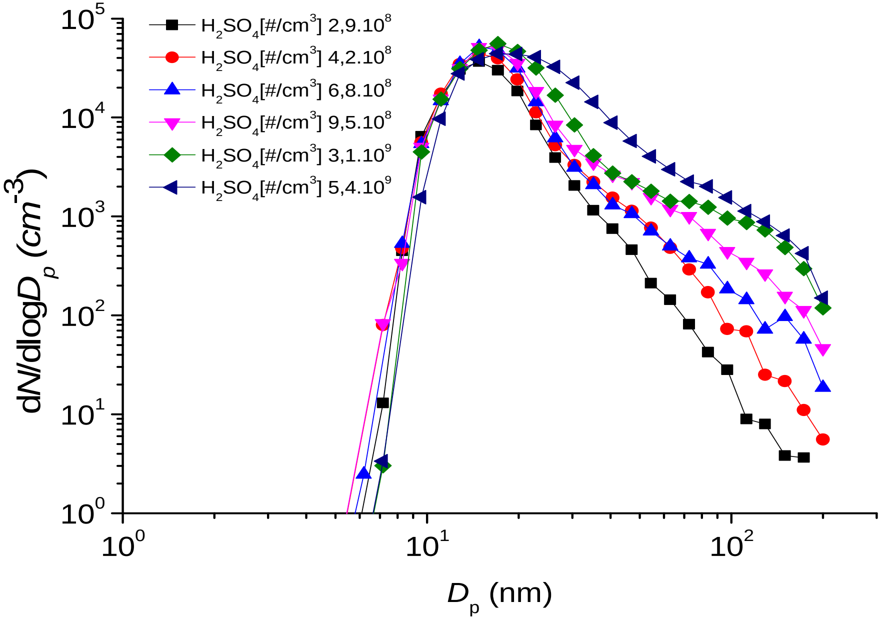

Fig. 4. The variation in the median particle diameters at different H_2SO_4 concentrations at T = 283 K, with the RH set at 30 % and a residence time of 60 s.

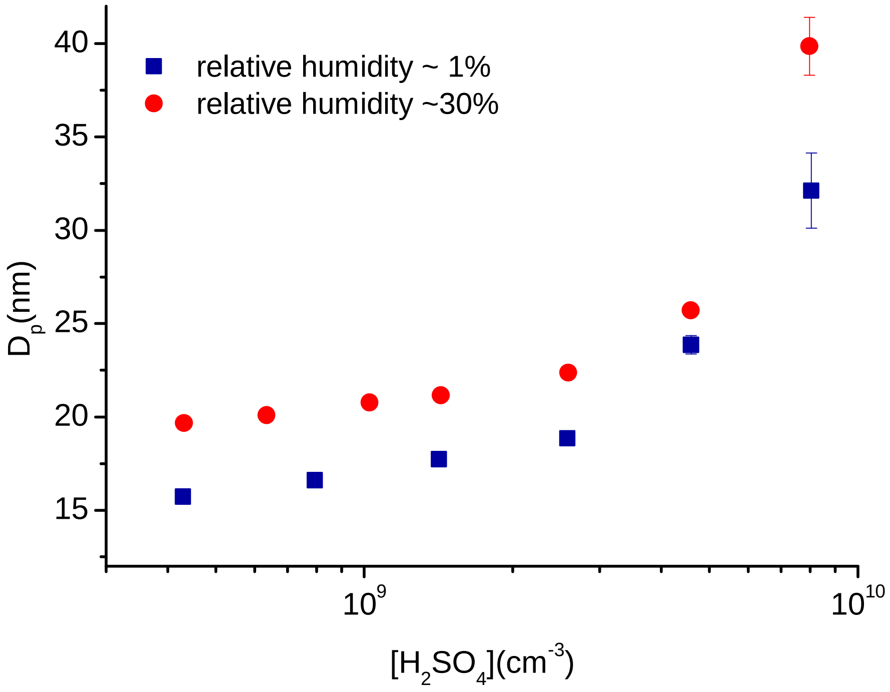

Fig. 5. The variation in the median particle diameters determined from measurements performed at $T = 303$ K, with a residence time of 60 s and at different RHs. The standard deviations of the median particle diameters are depicted as error bars.

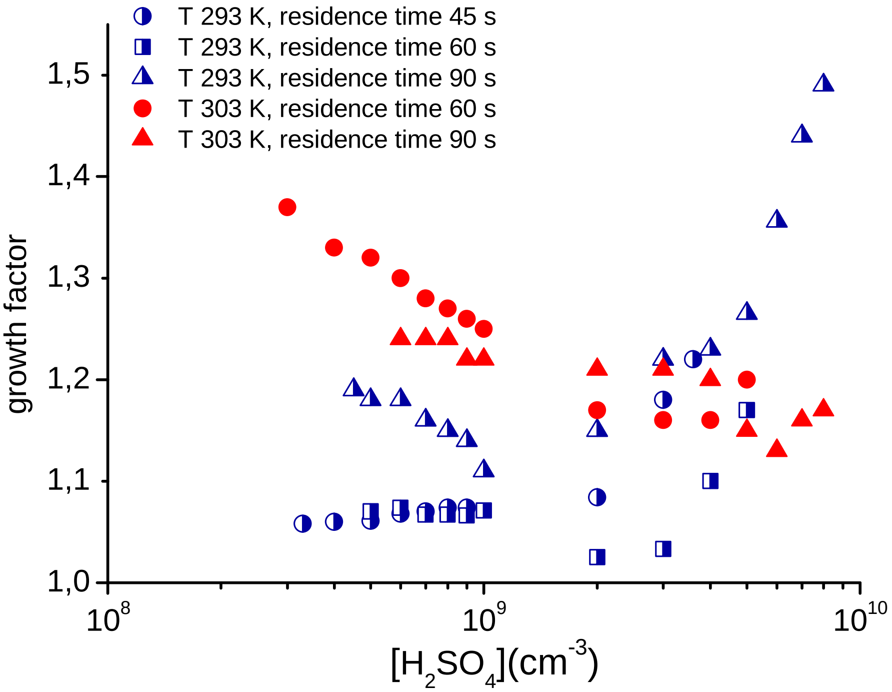

Fig. 6. The growth factors as a function of the H_2SO_4 concentration at T = 293 and T = 303 K at different residence times.

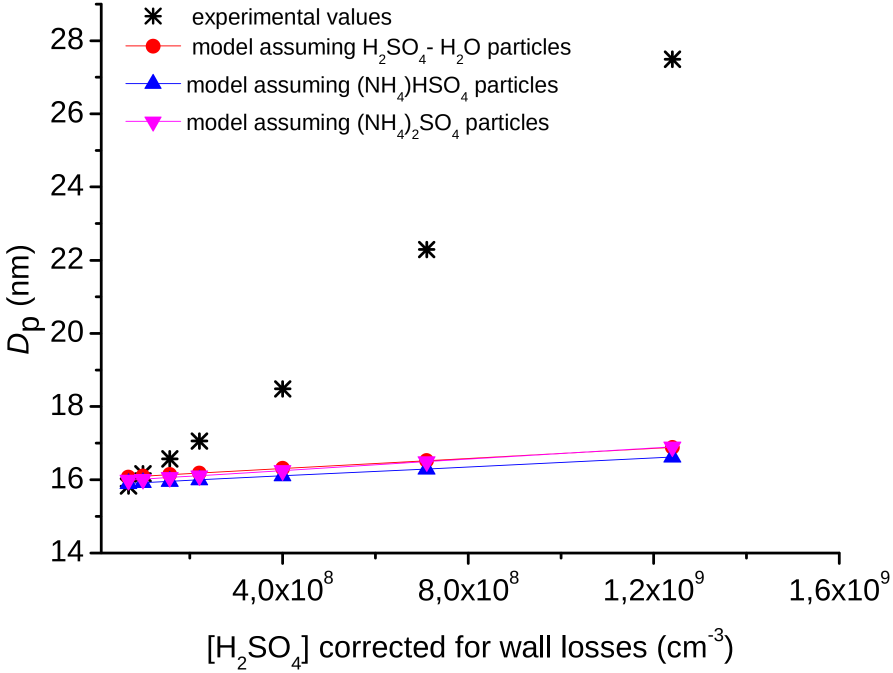

Fig. 7. The comparison of the experimental median particle diameters from a measurement conducted at T = 283 K, with a RH of ~ 30 % and a residence time of 60 s and values predicted theoretically from a model using the H_2SO_4 concentration corrected for wall losses, determined according to Hanson and Eisele (2000).

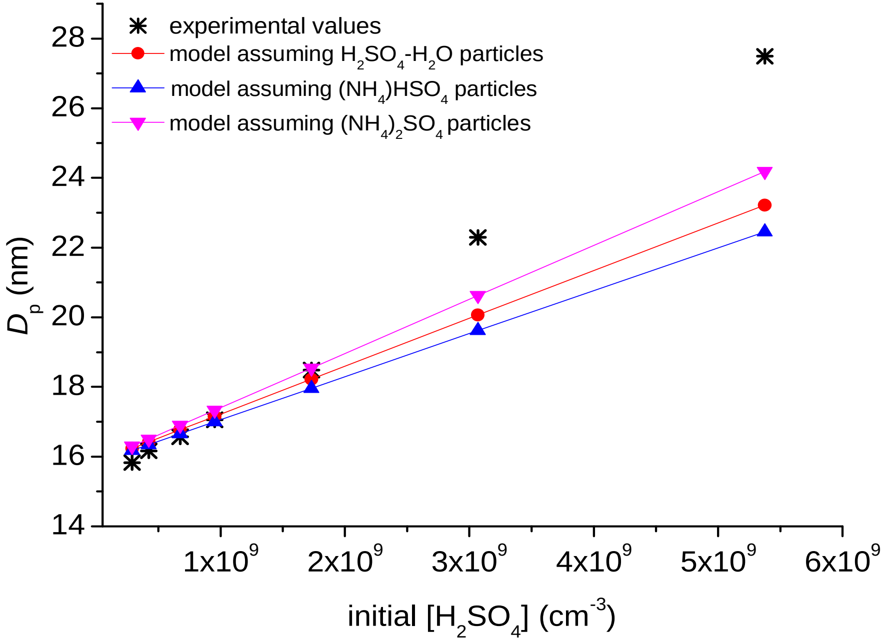

Fig. 8. The comparison of the experimental median particle diameters from a measurement conducted at $T = 283$ K, with a RH of ~30% and a residence time of 60 s and the values predicted theoretically from a model using the initial H_2SO_4 concentration without a correction for wall losses.

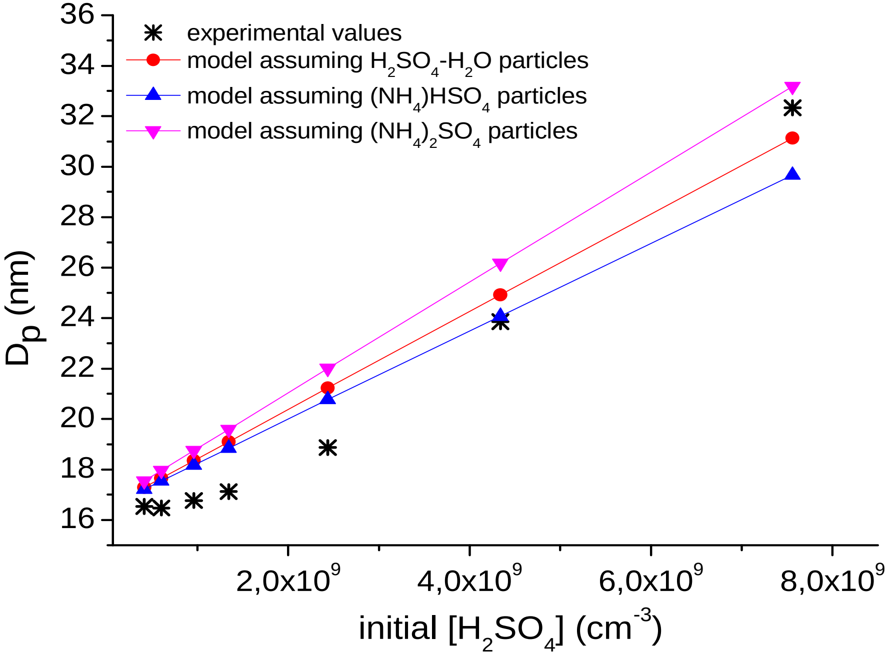

Fig. 9. The comparison of the experimental median particle diameters determined from a measurement conducted at $T = 283$ K, with a RH of ∼ 30 % and a residence time of 90 s and the values predicted theoretically from a model using the initial H_2SO_4 concentration without a correction for wall losses. As can be seen, the model overestimates the growth rates slightly in the case of experiments conducted at a residence time of 90 s.

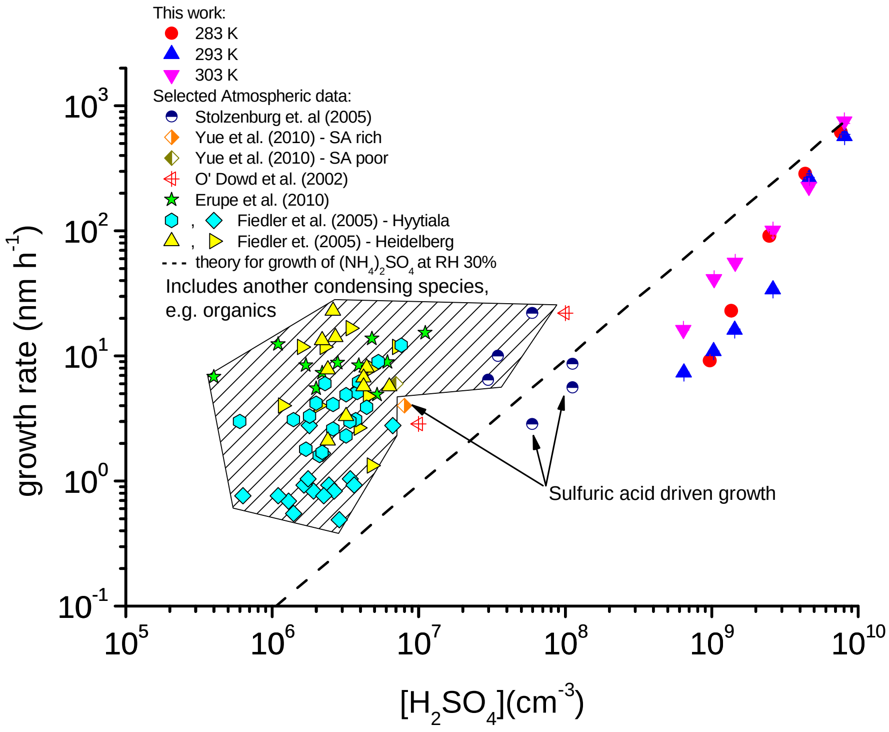

Fig. 10. The experimental growth rates obtained under wet conditions (RH = 30 %), with a residence time of 90 s and three nucleation temperatures of 283, 293 and 303 K. The atmospheric growth rates, obtained in Heidelberg and Hyytiälä during the QUEST project (Fiedler et al., 2005), data obtained in Atlanta during the ANARChE study (Stolzenburg et al., 2005), data from Beijing during 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. The line presents the theoretical predictions of the growth of ammonium sulphate particles at a RH of 30 %.

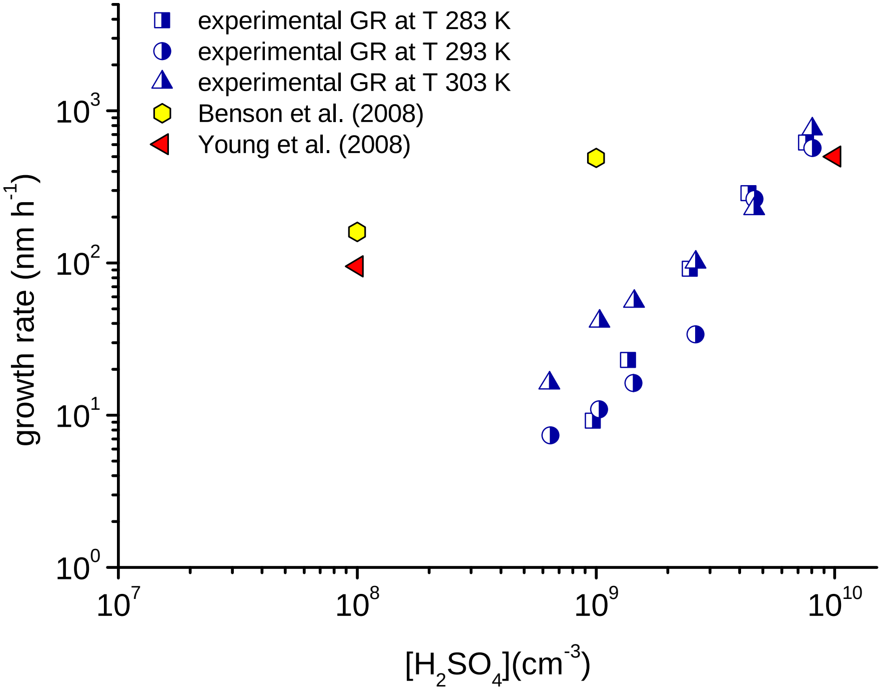

Fig. 11. The experimental growth rates determined from measurements conducted at a RH of 30 %, a residence time of 90 s and three nucleation temperatures are compared with the particle growth rates measured in the nucleation experiments made by Benson et al. (2008) at *T* = 288 K and Young et al. (2008) at *T* = 288 K.