

Effect of addition of four base compounds on sulphuric-acid–water new-particle formation: a laboratory study

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Effect of four different base compounds [ammonia (NH₃), monomethyl- (MMA), dimethyl- (DMA) and trimethylamine (TMA)] on sulphuric-acid–water nucleation was studied using a laminar flow tube. The concentration and size distribution of freshly-formed particles were monitored with an Ultrafine Condensation Particle Counters (UCPC) and a Differential Mobility Particle Sizer (DMPS) system. Two separate experiments were conducted. In the first experiment, the sulphuric acid concentration was measured using a mass spectrometer and the amount of base compound input was determined. In the second experiment, the concentration of base compounds in the flow tube was directly measured with an online ion chromatograph. All experiments were conducted at the constant temperature of 298 K and relative humidity of 30%, as well as constant sulphuric acid concentration. The concentration of the added base compounds was increased stepwise from 27 up to 25 000 pptv. An enhancement of the particle nucleation rate was observed only with TMA, and the maximum enhancement factor (EF) was approximately 5.5 at the TMA concentration of 2500 pptv. The possible nucleation enhancement by the other base substances was most probably saturated due to background contaminant levels of DMA, MMA and NH₃. Detection of the base compounds was discussed, and the results obtained in this study were compared with those from other similar laboratory experiments found in literature.

Introduction

Atmospheric aerosols have potentially large effect on climate and human health (Kappos *et al.* 2004, Feingold and Siebert 2009). Secondary formation from gas to liquid is a widely-accepted source of aerosol particles in the atmosphere worldwide (Weber *et al.* 1996, Kulmala *et al.* 2004, Spracklen *et al.* 2006). Observations and model calculations suggest

that atmospheric new-particle formation may significantly increase the concentration of Cloud Condensation Nuclei (CCN) which consequently may change the lifetime and albedo of clouds (Lihavainen *et al.* 2003, Merikanto *et al.* 2009).

Since sulphuric acid (H₂SO₄) has been suggested to be the key component in atmospheric nucleation (Kulmala *et al.* 2006, Sipilä *et al.* 2010, Brus *et al.* 2011, Kirkby *et al.* 2011), a large number of laboratory experiments have

been conducted to investigate the role of sulphuric acid in the first steps of nucleation (e.g. Benson *et al.* 2008, 2009, 2011, Young *et al.* 2008, Berndt *et al.* 2008, 2010, Brus *et al.* 2010, 2011, Sipilä *et al.* 2010, Kirkby *et al.* 2011, Zollner *et al.* 2012). Although the efforts to reveal the underlying mechanisms in nucleation have been vast, the results obtained in laboratories have not been consistent when considering the relation between sulphuric acid concentration and nucleation rates with each other, or when comparing laboratory experiments with the atmospheric measurements. The power dependency of nucleation rate on the sulphuric acid concentration has been found to be between one and two in the atmosphere, which is far from the values predicted by the classical nucleation theory (CNT) (Reiss 1950, Laaksonen *et al.* 1995, Bein and Wexler 2007): the CNT predicts the power dependency of 10 to 15 for the binary nucleation between H_2SO_4 and H_2O .

Amines are ubiquitous in the atmosphere and they are produced by a large variety of sources (Ge *et al.* 2011). Anthropogenic amine sources include animal husbandry, industry and combustion (O'Neill and Phillips 1992, Ngwabie *et al.* 2007, Rappert and Müller 2005), while natural sources are mainly the oceans (Wang and Lee 1994, Caldéron *et al.* 2007), biomass burning (Lobert *et al.* 1990, Yokelson *et al.* 1997), vegetation (Schade and Crutzen 1995) and geological sources (Schulten and Schnitzer 1998). The most common amines in the atmosphere are those having a low molecular weight with the number of carbon atoms between 1 and 6, such as monomethyl- (MMA), dimethyl- (DMA) and trimethylamine (TMA) (Ge *et al.* 2011). Concentrations of these amines have large variability in the atmosphere, from couple of pptv up to several tens of ppbv depending on the sampling site and distance from the source of these amines (Ge *et al.* 2011).

It is believed that nucleation of sulphuric acid and water alone cannot explain new-particle formation in the atmospheric boundary layer. The recent quantum-chemical calculations (Kurten *et al.* 2008, Loukonen *et al.* 2010, Ortega *et al.* 2012), theoretical works (Ball *et al.* 1999, Korhonen *et al.* 1999, Napari *et al.* 2002) and also observations (Lloyd *et al.* 2009, Bzdek

et al. 2010, Wang *et al.* 2010, Kulmala *et al.* 2013) suggest participation of bases like amines or ammonia in the process of nucleation and growth of the atmospheric particles. Amines most probably form salts under acidic conditions. These salts have a very low vapour pressure, so they form clusters of sizes of a few molecules.

Recent laboratory experiments showed a significant increase in the nucleation rate when amines or ammonia had been introduced into the sulphuric acid–water system (Ball *et al.* 1999, Benson *et al.* 2009, 2011, Berndt *et al.* 2010, Erupe *et al.* 2010, Kirkby *et al.* 2011, Zollner *et al.* 2012, Almeida *et al.* 2013). Here we present results from laminar flow tube experiments involving sulphuric acid, water and four separate base compounds. Two sets of measurements were carried out in order to identify the effect of four base compounds on the new-particle formation of the sulphuric-acid–water system. Our aim was to shed new light on which compounds are likely to be involved in atmospheric nucleation and which concentration range of these compounds is relevant to the nucleation process.

Experimental methods

The measurement setup used here was very similar to that presented in Brus *et al.* (2010), Neitola *et al.* (2013) and Škrabalová *et al.* (2014). Only the main principle and significant modifications are described here. Important changes in the setup were the production of sulphuric-acid vapour with a saturator and addition of the base compounds into the flow tube (Fig. 1).

The sulphuric-acid vapour was produced in a saturator that was thermally controlled with a circulating liquid bath (LAUDA RC 6). The saturator was filled with 150–200 ml of pure sulphuric acid (~97%, Baker analyzed), and the temperature of the saturator was measured with a calibrated PT100 probe (with uncertainty of ± 0.05 K) inserted into the back end of the saturator just above the liquid surface. The saturator itself was a half-meter-long iron cylinder with a PTFE insert covering the inside of the cylinder. A flow of purified, dry, particle-free air was taken through the saturator saturating the flow according to the temperature of the satura-

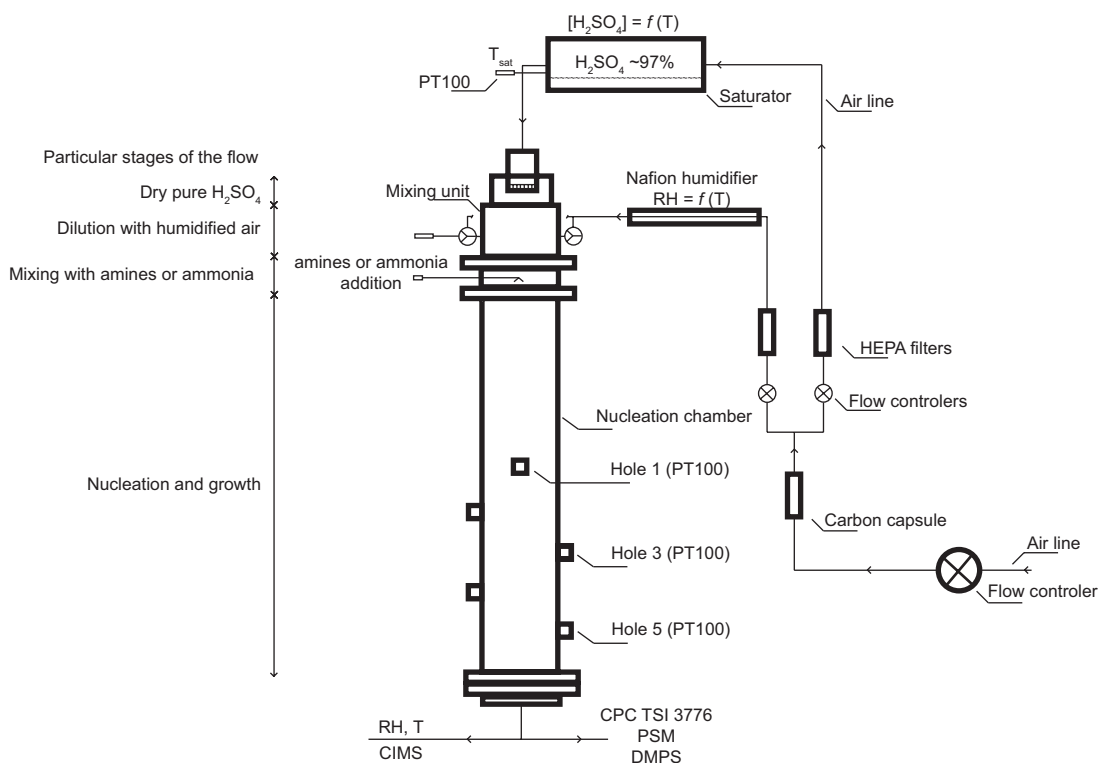


Fig. 1. Schematic layout of the experimental setup.

tor. The temperatures of incoming and outgoing flows were kept at the same level as that in the saturator to prevent saturator warming with incoming flow and condensation after the saturator, before the flow tube.

The flow from the saturator was turbulently mixed with humidified clean, particle-free air in the mixing unit made of PTFE, mounted on top of the flow tube. Immediately after the mixing unit (2 cm downstream), a metal tube (inner diam. 1/8") was inserted with the tip reaching approximately the center axis of the flow tube. The tip of the tube was cut open, so that the flow was directed parallel to the main flow. The base compounds were introduced into the main flow through this metal tube. The residence time between the mixer and the introduction of the base compounds was very short (0.3 s) for forming any particles (excluding clusters of a few molecules), preventing the base compounds simply condensing on the particles and thus, being able to participate in the nucleation process itself. The flow tube consisted of two stain-

less steel cylinders (inner diam. 6 cm, length 100 cm) connected with a 5-cm PTFE piece between the cylinders. The flow tube was positioned vertically and it was thermally controlled with a circulating liquid bath (LAUDA RC 6). The second half of the flow tube had four holes 20 cm from each other, which made it possible to ensure a constant temperature of the flow tube along its axis using PT100 probes. The humidity of the mixing flow was controlled by three Nafion® humidifiers (MD-series, Perma pure, USA). Ultrapure Milli-Q water (Millipore, resistivity 18.2 M Ω .cm @25 °C) was used for the humidification. The relative humidity (RH) and temperature were also measured at the end of the flow tube using Vaisala HMP37E and humidity data processor (Vaisala HMI38). The saturator and mixing flow rates were controlled by mass flow controllers (MKS type 250, $\pm 3\%$). The saturator flow rate was kept between 0.13 and 0.3 lpm and the mixing flow rate was kept at 11 lpm, which resulted in approximately 30-s residence time in the flow tube.

The gas phase base compound was produced using a portable calibration system (Environnement S.A., France, model VE3M). It is a system that uses constant rate permeation tubes in a constant temperature oven. The tube is placed inside the oven ($T = 40 \pm 0.1$ °C), where the compound evaporates through a PTFE membrane at the top of the permeation tube into a carrier gas flow. The base compound concentration was controlled by changing the flow rate through the calibration case. The carrier gas (N_2 , 6.0) was further cleaned with scrubbers inside the calibration case. The concentration in the flow tube was calculated via mixing ratios of the flow from the calibration case and the total flow. The permeation tubes used in this study had permeation rates of $610 \text{ ng min}^{-1} \pm 15\%$, $566 \text{ ng min}^{-1} \pm 15\%$, $482 \text{ ng min}^{-1} \pm 50\%$ and $200 \text{ ng min}^{-1} \pm 25\%$ for TMA, DMA, MMA and NH_3 , respectively.

Two experiments were carried out. In the first one, only sulphuric acid concentration was measured and base concentration input was determined, while in the second one, only the base compound concentration was measured. The two experiments were conducted using the same setup and similar conditions. Base compounds used in the first experiment were TMA, DMA, MMA and NH_3 and DMA, MMA and NH_3 in the second experiment. Experiments were started by measuring the H_2SO_4 - H_2O system without any additional base compounds. When the particle concentration and sulphuric acid concentration in the flow tube stabilized, the base compound was added, starting approximately from 30 pptv. The concentration of the selected base compound was increased stepwise every 6 to 12 hours until the maximum concentration was reached. The maximum concentration was 4000–5000 pptv in the first experiment and up to 25 000 pptv in the second experiment. The sulphuric acid concentration (i.e. saturator temperature) was kept constant. An additional test was done in the first experiment by keeping the amine concentration constant and increasing stepwise the saturator temperature. After reaching the maximum concentration, the feeding of the base compound was cut off and the flow through the saturator was closed. The flow tube was cleaned first by mechanically brushing the walls and rinsing with acetone and deionized water. After mechanical

cleaning, the flow tube was cleaned thermally by heating the walls of the flow tube up to 70 °C with a carrier gas flow on for 12 to 24 hours. After cleaning, the reproducibility of particle production rate in similar conditions was tested, and the next experiment with another base compound was started. If the particle production rate was different, cleaning was done again until the conditions were fulfilled.

Detection of particles, sulphuric acid and the base compounds

The particle number concentration was monitored using an Ultrafine Condensation Particle Counter (UCPC, TSI Inc. model 3776) and Particle Size Magnifier (PSM, Airmodus Ltd., Vanhanen *et al.* 2011) and the particle number size distribution (3–250 nm) was monitored with a Differential Mobility Particle Sizer (DMPS). The DMPS consisted of a bipolar neutralizer (^{63}Ni), a short HAUKE-type Differential Mobility Analyzer (DMA) and an UCPC (TSI Inc. model 3025A).

The gas-phase sulphuric acid concentration was measured using a Chemical Ionization Mass Spectrometer (CIMS, Eisele and Tanner 1993, Mauldin *et al.* 1998, Petäjä *et al.* 2009). In CIMS, sulphuric acid molecules are ionized in the CI inlet via proton transfer with nitrate ions (NO_3^-). The nitrate ions are produced by ionizing nitric acid (HNO_3) with a radioactive source (^{241}Am). The nitrate ions are then mixed in a controlled manner with the sample flow in a drift tube with the help of concentric sheath and sample flow, together with electrostatic lenses. The uncertainty of the measured sulphuric acid concentration is a factor of two (Petäjä *et al.* 2009). CIMS was used with an inlet flow rate of 6 lpm to maintain a sufficient flow rate to the other instruments from the flow tube. Decreasing the inlet flow rate from the nominal 10 lpm does not effectively change the results (Neitola *et al.* 2013). All the presented sulphuric acid monomer concentrations were measured values and not corrected for any losses. To get the concentration at the end of the flow tube, the presented monomer concentrations must be multiplied by a factor of 4.4 which is the loss factor in the used CIMS inlet sampling tube (Brus *et al.* 2011).

Base compound concentrations were measured using an instrument for Measuring AeRosols and Gases (MARGA 2S ADI 2080, Methrom Applikon Analytical BV, Netherlands, ten Brink *et al.* 2007). MARGA is a semi-continuous online ion chromatograph (IC) which is used for measuring several inorganic species from the aerosol (Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ , Na^+ , K^+ , Mg^+ , Ca^{2+}) and the gas phase (HCl , HNO_3 , HONO , NH_3 , SO_2). In this study, we used the MARGA instrument also to measure MMA, DMA and TMA. In MARGA sample air flow (~16.7 lpm) is taken through a Wet Rotating Denuder (WRD) where most of the soluble gases are absorbed. Due to much slower diffusion velocity of the particles, they pass the WRD and enter the Steam-Jet-Aerosol-Collector (SJAC, Slanina *et al.* 2001), where conditions are supersaturated with water vapour, growing the particles until they are collected at the bottom of the SJAC. Sample solutions from the WRD and SJAC are collected in syringes from where samples are injected once an hour to the ion chromatographs to be quantified by conductivity detectors. Detection limits differ from 0.01 to 0.1 $\mu\text{g m}^{-3}$ for the species listed by the manufacturer. MARGA was calibrated for detection of amines by injecting known concentrations as a sample liquid directly in to the column of the IC and identifying the peak forming in to the conductivity spectra. The amines are ionized by protonation resulting in ions of nature of amine- H^+ (for example MMA protonation: $\text{CH}_3\text{NH}_2\text{H}^+$). By calibrating it is possible to identify possible overlapping ions and to measure substances which are not nominally measured with the MARGA system. The calibration does not provide a calibration factor for atmospheric concentration as it is done directly for the column and the penetration efficiency for amines in gas phase or in particles through the sampling lines to the IC is unknown. As stated in Praplan *et al.* (2012), the measurement of amines with an IC is very difficult below 100 pptv levels. ICs have been used for atmospheric measurements for amine concentrations, but MARGA is a semi-continuous instrument, as normally ICs are offline instruments, and the samples are analyzed later in the laboratory. This is the first time when MARGA was used for the detection

of amines in continuous measurements from gas phase and particles. For more details of the instrument, see Makkonen *et al.* (2012).

Results and discussion

Experiments were started by setting the saturator flow rate and temperature (approximately 0.3 lpm and 298 K in the first experiment) so that the desired particle number concentration was achieved inside the flow tube. These concentrations were in the range $4630\text{--}10^4 \text{ cm}^{-3}$ in the first experiment, corresponding to approximately $155\text{--}335 \text{ cm}^{-3} \text{ s}^{-1}$ in the nucleation rate (J_{exp}). The mixing flow rate was kept constant throughout both experiments at 11 lpm, and the conditions were kept constant for several hours to ensure steady-state conditions. After stability was achieved, the base substance was introduced into the main flow. In the first experiment, the average sulphuric acid concentrations were $2.8 \pm 0.14 \times 10^6 \text{ cm}^{-3}$, $6.78 \pm 0.69 \times 10^5 \text{ cm}^{-3}$, $1.61 \pm 0.19 \times 10^6 \text{ cm}^{-3}$ and $1.32 \pm 0.15 \times 10^6 \text{ cm}^{-3}$ for TMA, DMA, MMA and NH_3 , respectively. After each amine addition with constant saturator temperature in the first experiment, a test with stepping the saturator temperature was done. In this experiment, the added amine concentration (0 pptv, ~100 pptv, 1000 pptv and 3000 pptv) was kept constant throughout the whole cycle of stepping the saturator temperature (271 K, 276 K, 281 K, 285 K, 295 K and 300 K). In the second experiment, lower temperature of the saturator ($T_{\text{sat}} = 284 \text{ K}$) and saturator flow rate ($Q_{\text{sat}} = 0.13 \text{ lpm}$) were used. This resulted in the lower particle concentration (approximately $6\text{--}30 \text{ cm}^{-3}$) and the lower nucleation rate $0.2\text{--}1 \text{ cm}^{-3} \text{ s}^{-1}$. The condensation sink was also lower in the second experiment as the particle concentration was significantly lower. This was done to study if the lowered condensation sink affects the base compounds ability to influence the nucleation process.

First experiment

After the initial TMA addition, the original size distribution narrowed, especially for large par-

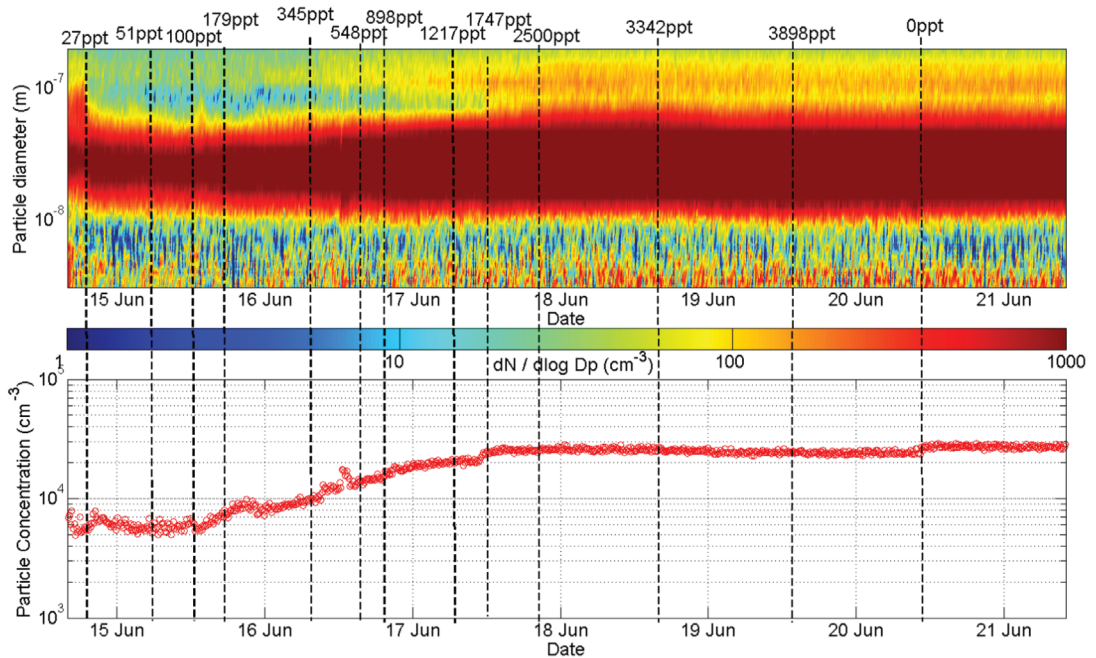


Fig. 2. Evolution of size distribution and total particle concentration during addition of trimethylamine (TMA) measured with the DMPS system. Sulphuric acid concentration was kept constant, $[\text{H}_2\text{SO}_4] = 2.8 \pm 0.14 \times 10^6 \text{ cm}^{-3}$.

particle diameters, suggesting a higher condensation sink as the particle number concentration increased. The increased condensation sink decreased the amount of condensable vapours available. The mode peak remained at the particle diameter of about 30 nm. The particle number size distributions for each TMA addition are presented in the Appendix with extensive discussion on the particles size and their growth. The UCPC and PSM showed similar particle concentrations as the particle diameter was well above the cut-off diameter of both instruments (3 nm, for TSI model 3776, 1.5 nm for PSM). The total particle number concentration started to increase from 4630 cm^{-3} (Fig. 2). After each step of increasing the TMA concentration, the total particle number concentration increased until the TMA concentration reached approximately 2500 pptv when the system became saturated. The maximum particle number concentration at the saturation level of base concentration was approximately $25\,500 \text{ cm}^{-3}$. During the addition, another mode of particles appeared in the size distribution with a mode peak approximately at 100 nm (Fig. 2, upper panel). This mode was intensified until the saturation point was reached at the TMA concen-

tration of 2500 pptv. Heterogeneous reaction of amines with sulphuric acid increases the growth of particles at these sizes (Wang *et al.* 2010). Studies by Lloyd *et al.* (2009) and Bzdek *et al.* (2010) give further support for the growth by the reactive uptake of TMA into ammonium nitrate particles and exchange of amine into bisulfate and nitrate nuclei. A further increase of the TMA concentration did not affect the particle size distribution or number concentration. When the feeding of TMA into the system was stopped, the particle number size distribution and concentration remained unaltered, suggesting that a decent amount of TMA had deposited onto the walls of the flow tube during the experiment and continued to evaporate to the flow.

DMA, MMA and NH_3 did not affect the total particle number concentration throughout the addition of these base substances (Figs. 3–5). This indicates that the system was already saturated with respect to these substances. The saturation levels of these compounds was expected to arise from the carrier gas and the water used for humidification of the mixing flow. The saturation levels reported in literature are approximately 35 pptv for MMA (Zollner *et al.* 2012) and from

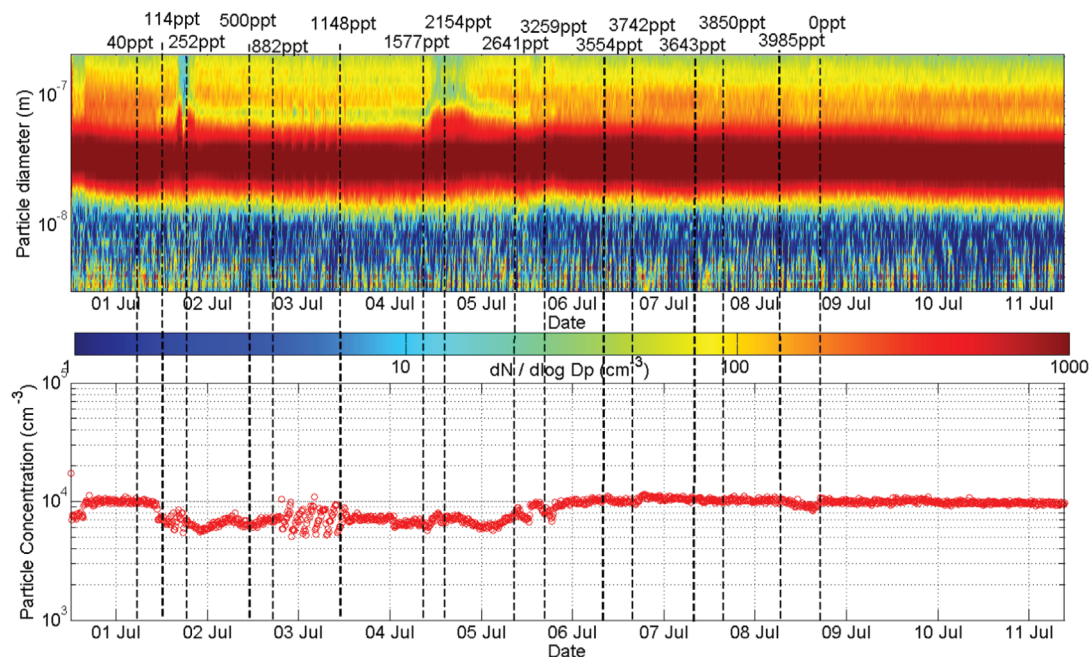


Fig. 3. Evolution of size distribution and total particle concentration during addition of dimethylamine (DMA) measured with the DMPS system. Sulphuric acid concentration was kept constant, $[H_2SO_4] = 6.78 \pm 0.69 \times 10^5 \text{ cm}^{-3}$.

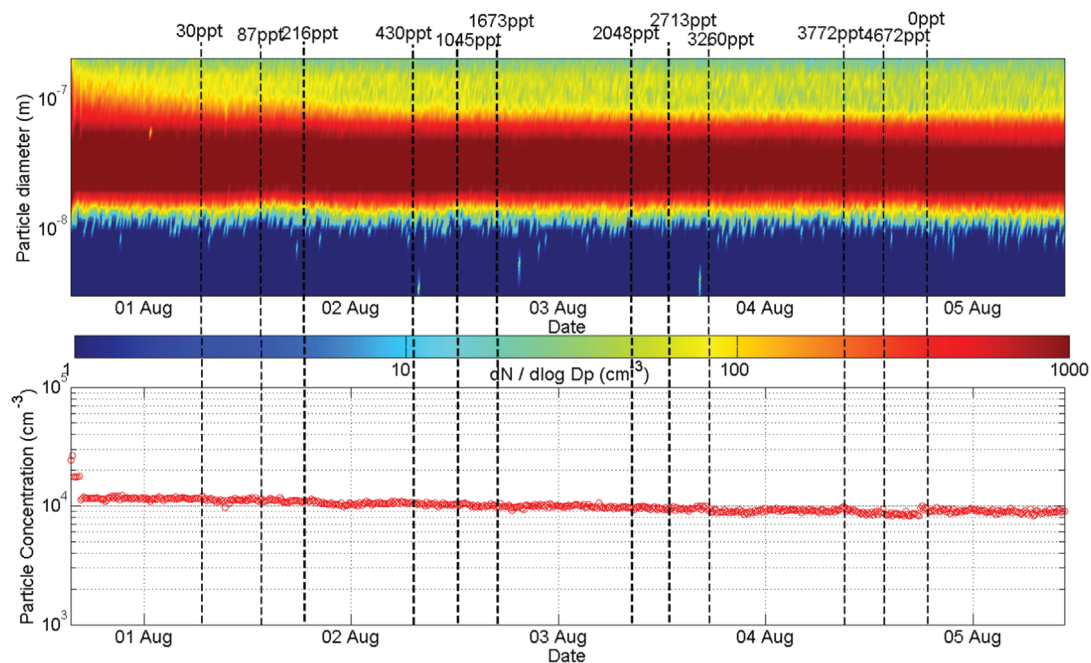


Fig. 4. Evolution of size distribution and total particle concentration during addition of monomethylamine (MMA) measured with the DMPS system. Sulphuric acid concentration was kept constant, $[H_2SO_4] = 1.61 \pm 0.19 \times 10^6 \text{ cm}^{-3}$.

45 pptv (Zollner *et al.* 2012) up to 1220 pptv (benson *et al.* 2011) for NH_3 . For DMA, saturation

levels according to Almeida *et al.* (2013) are above 5 pptv and the largest enhancement

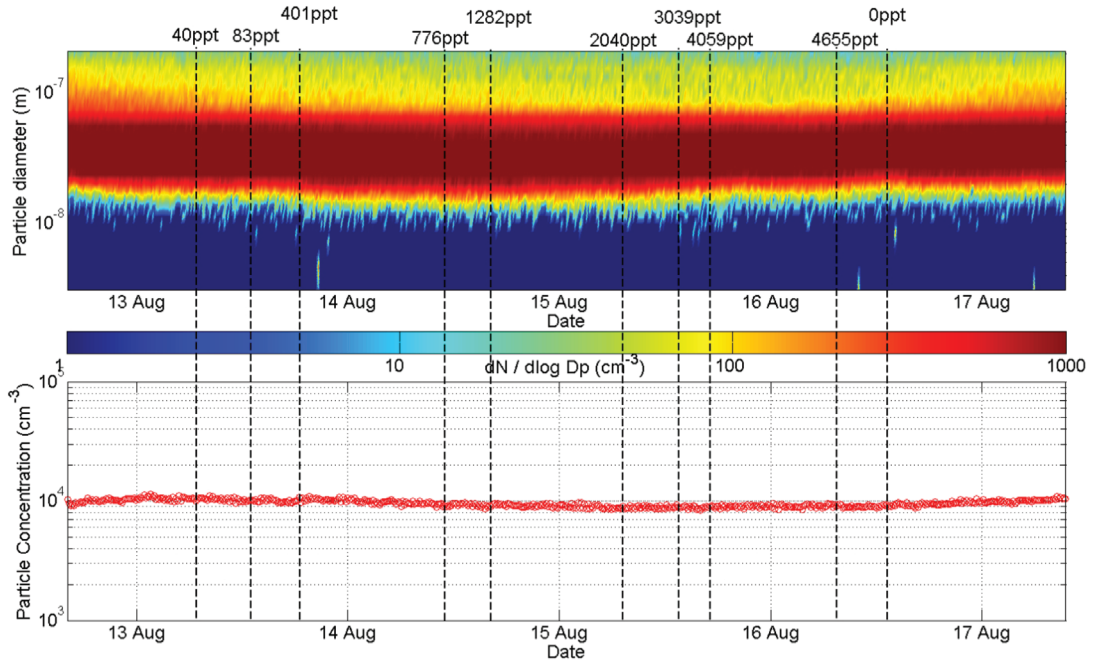


Fig. 5. Evolution of size distribution and total particle concentration during addition of ammonia (NH_3) measured with the DMPS system. Sulphuric acid concentration was kept constant, $[\text{H}_2\text{SO}_4] = 1.32 \pm 0.15 \times 10^6 \text{ cm}^{-3}$.

was observed with the addition of 0.1–5 pptv of DMA (Almeida *et al.* 2013). These saturation levels were taken from the above articles corresponding to the conditions (RH, nucleation temperature, etc.) closest to the experiments presented here. The saturation levels depend on the conditions of the measurements (nucleation temperature, RH, H_2SO_4 concentration, background levels of contaminants). In the case of MMA (Fig. 4), the size distribution narrowed in the similar manner as with TMA (Fig. 2). Small, temporary changes in the particle size distribution and total particle concentration after adding DMA (Fig. 3) were most probably due to small changes in the flow rates.

The effect of the added amines was similar when the amine concentration was kept constant and the saturator temperature was increased stepwise. The hourly-averaged experimental nucleation rates, J_{exp} , as a function of the saturator temperature, T_{sat} , showed that MMA and DMA did not affect the measured nucleation rates (Fig. 6). In the case of TMA, increasing the amine concentration increased the nucleation rates more at lower saturator temperatures. The measured nucleation rates coincided with all

TMA concentrations at the saturator temperature of 295 K and 300 K (Fig. 6).

Adding large amounts of base compounds into the flow may decrease the free sulphuric acid vapour concentration, as the sulphuric acid molecules are bound to the base molecules. It has been calculated that some fraction of sulphuric acid–amine clusters might not get charged in the CI-inlet of CIMS, but this fraction was reported to be in order of 10% or less (Kurten *et al.* 2011). Murphy *et al.* (2007) reported an increase in sulphate concentration when adding MMA into chamber experiment with Secondary Organic Aerosol (SOA) study. To check whether amines actually inhibited the charging of the sulphuric acid clusters, or whether the sulphate concentration increased when base substance was added into the flow tube, the hourly-averaged sulphuric acid monomer and total sulphate concentrations were calculated during the base compound addition. The sulphuric acid monomer (Fig. 7a) and total sulphate (Fig. 7b) concentrations were averaged as a function of the added base concentration for each compound. Standard deviations were a lot smaller than the uncertainty in the sulphuric acid concentration measured by CIMS

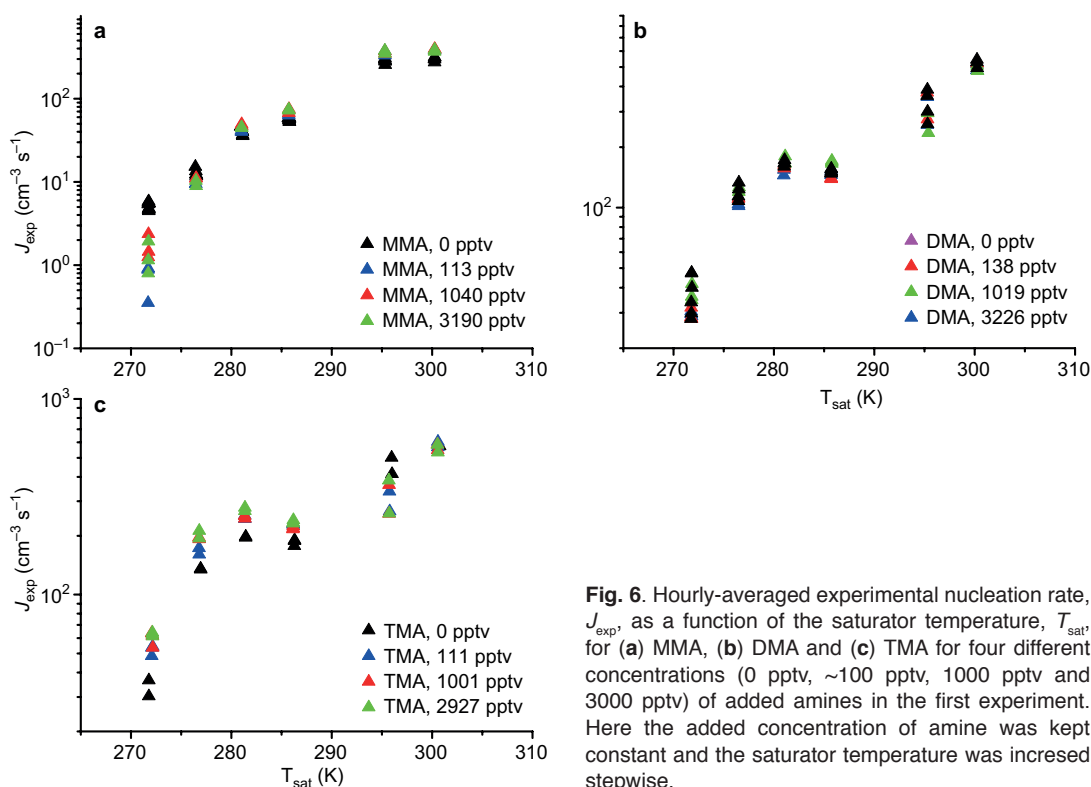
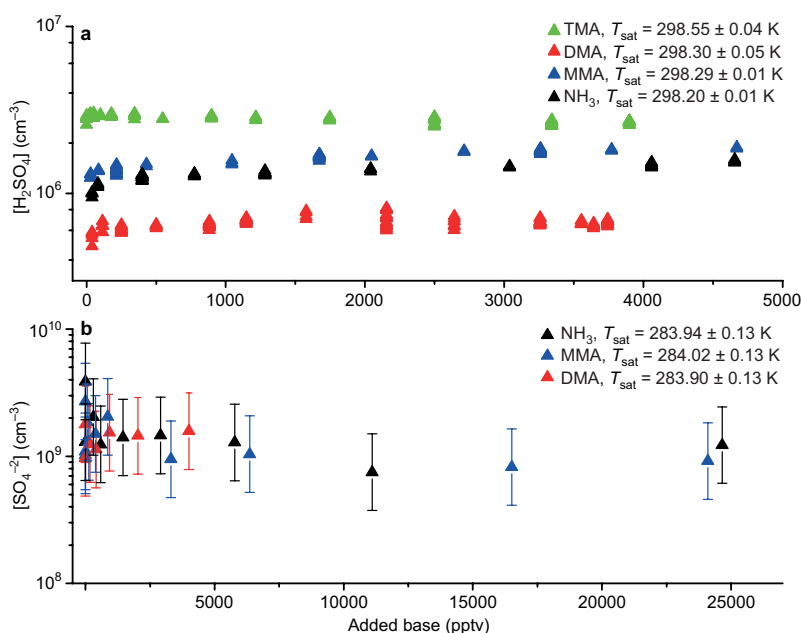


Fig. 6. Hourly-averaged experimental nucleation rate, J_{exp} , as a function of the saturator temperature, T_{sat} , for (a) MMA, (b) DMA and (c) TMA for four different concentrations (0 pptv, ~100 pptv, 1000 pptv and 3000 pptv) of added amines in the first experiment. Here the added concentration of amine was kept constant and the saturator temperature was increased stepwise.

Fig. 7. Measured sulphuric acid concentration (monomer in a, total sulphate in b) as a function of added base concentration for each added base compound. The error bars in b show standard deviations. The saturator temperature was kept constant, at approximately 298 K (in a) for the experiment with mass spectrometers and 284 K (in b) for the experiment with MARGA.



(a factor of two). The temperatures of the saturator were also presented (Fig. 7). Adding the base compounds did not change the measured

sulphuric acid monomer or total sulphate concentrations, and sulphuric acid concentrations were very stable throughout the addition process.

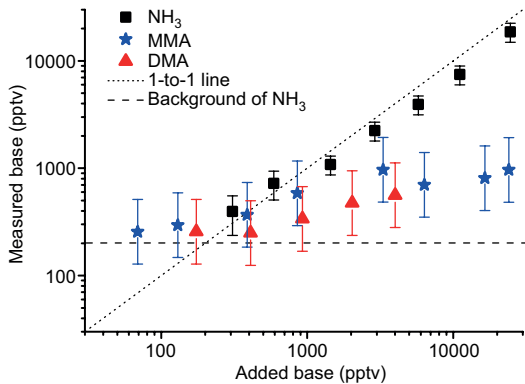


Fig. 8. MARGA measured base concentration as a function of added base concentration from the second experiment. Background concentration of ammonia and 1-to-1 lines are also presented. The error bars represent the uncertainty of MARGA which is dependent on the concentration (from a factor of two to 20%).

In the second experiment, only NH_3 and MMA concentrations were increased to very high concentrations (up to 25 000 pptv) but no change in the total sulphate concentration was observed.

Second experiment

The second experiment was carried out similarly to the first one, except that the saturator flow rate and temperature were decreased and, thereby, the initial particle number concentration was lower (about 6–30 cm^{-3}). This was done in order to investigate whether the decreased condensation sink affects the ability of a base compound to enhance the nucleation process. A dilution flow (half of the sample flow rate of MARGA) was used to meet the inlet flow of MARGA. Only three base compounds (NH_3 , MMA and DMA) were used in this experiment due to the limited instrumental time. The base compound concentrations were measured with MARGA. The NH_3 and MMA concentrations were increased up to 25 000 pptv in order to test the detection range of MARGA. No effect on J_{exp} was observed when adding any of the bases. We expect that the behavior of the TMA addition would have been similar as in the first experiment, as everything was done similarly, except for the lower initial particle concentration. The measured particle concentrations were stable throughout the exper-

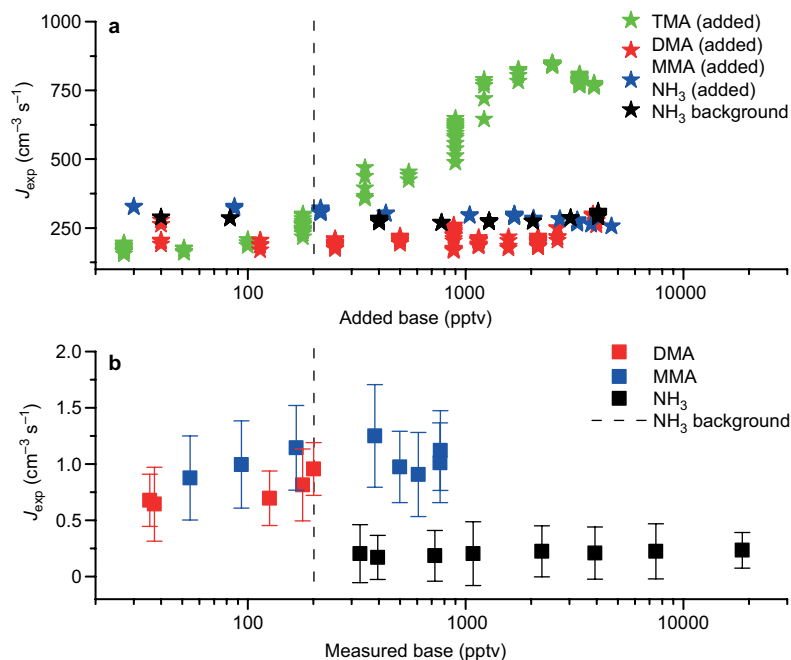
iments, with mean values \pm standard deviations of $6.2 \pm 6.7 \text{ cm}^{-3}$, $31.1 \pm 11.2 \text{ cm}^{-3}$ and $22.7 \pm 8.1 \text{ cm}^{-3}$ for NH_3 , MMA and DMA, respectively. The results were the same as in the first experiment as the particle concentration remained unaltered when adding these three base substances.

The detection limits of MARGA were determined in an independent experiment for each base compounds used in this study by injecting known amount of the substance into the liquid sample solution for the ion chromatograph. The detection limits were found to be 66 pptv for NH_3 , 72 pptv for MMA, 149 pptv for DMA and 294 pptv for TMA. The detection limits were calculated at the STP conditions. Base substance concentrations as a function of the added base concentrations were experimentally determined for the second experiment (Fig. 8). The uncertainties in the MARGA measurements decreased with increasing concentrations (from a factor of two to 20%; see error bars in Fig. 8). The background level of ammonia was determined by measuring six hours from the flow tube by MARGA before any addition of ammonia. The averaged background level of ammonia was found to be 201 pptv. The background levels of other base substances were below the detection limits of MARGA and hence, could not be determined reliably.

The response of MARGA to the ammonia addition was linear as expected. The measured concentrations of DMA and MMA increased very slowly as a function of the corresponding added concentrations, resulting in an increasing deviation from the 1-to-1 line between these two quantities. Reasons for the nonlinear response in the measured concentration of DMA and MMA as compared with that of the added concentration could not be oxidation to some other substance (for example imines or amides), since the system was not expected to have any significant amounts of oxidants in it and the residence time in the flow tube was only 30 s, which is not long enough for oxidation of most of the base compound.

Wall losses of the base substances were not directly measured, but the wall loss factors (WLF) were calculated assuming that they were diffusion-limited, following the method reported in Hanson and Eisele (2000). The dif-

Fig. 9. Experimentally-determined nucleation rates, J_{exp} , in (a) the first and (b) second experiments as a function of the added base concentration. Error bars in **b** show standard deviations. The background level of ammonia is indicated with a vertical dashed line. The scales of the y-axes differ as the initial particle concentration (and thus, nucleation rate) in the second experiment was lower.



fusion coefficients for the base compounds in air were calculated using the Fullers method (Reid *et al.* 1987) with the approximation of binary system at $T = 298$ K. The calculated diffusion coefficients, D , were $0.269 \text{ cm}^2 \text{ s}^{-1}$, $0.162 \text{ cm}^2 \text{ s}^{-1}$, $0.124 \text{ cm}^2 \text{ s}^{-1}$ and $0.094 \text{ cm}^2 \text{ s}^{-1}$ for NH_3 , MMA, DMA and TMA, respectively. The method by Hanson and Eisele (2000) was followed to get the first order rate constant, k :

$$k = 3.65 \frac{D}{r^2}, \quad (1)$$

where r is the radius of the flow tube. The concentration of sulphuric acid in the flow tube at time t , $[\text{H}_2\text{SO}_4]_t$, can be calculated from

$$[\text{H}_2\text{SO}_4]_t = [\text{H}_2\text{SO}_4]_0 \exp(-kt), \quad (2)$$

where $[\text{H}_2\text{SO}_4]_0$ is the sulphuric acid concentration at time zero. The WLF is defined as

$$\text{WLF} = \frac{[\text{H}_2\text{SO}_4]_0}{[\text{H}_2\text{SO}_4]_t}. \quad (3)$$

By using the residence time $t = 30$ s, the WLFs can be calculated using Eq. 3. The kinetically-limited WLFs were 26.3, 7.2, 4.5 and 3.1 for NH_3 , MMA, DMA and TMA, respectively. The diffusion-limited wall loss is a very simpli-

fied version of real loss processes in the system and cannot explain the discrepancy between the added and measured DMA and MMA concentrations. Also, with a steady-state measurements lasting several hours, the walls of the flow tube will be saturated with the base substances resulting continuous evaporation from the walls, which further complicates the loss process analysis. As stated earlier, the losses of amines inside MARGA are unknown at the moment and there is no literature providing information on MARGA calibration for amines from the sample flow, i.e. in the gas phase and particles.

The experimentally determined values of J_{exp} as a function of added or measured base concentration were compared between the two experiments (Fig. 9). Of the added bases, only TMA enhanced nucleation: the nucleation rates increased from approximately 155 to $845 \text{ cm}^{-3} \text{ s}^{-1}$ corresponding to a maximum enhancement factor (EF) of about 5.5. The maximum EF was calculated by dividing the nucleation rate at the saturation concentration of the base substance with the initial nucleation rate. The background level of ammonia was 201 pptv (dashed, vertical line in Fig. 9). The background ammonia originated from the water used for humidifying the flow and from air used as a car-

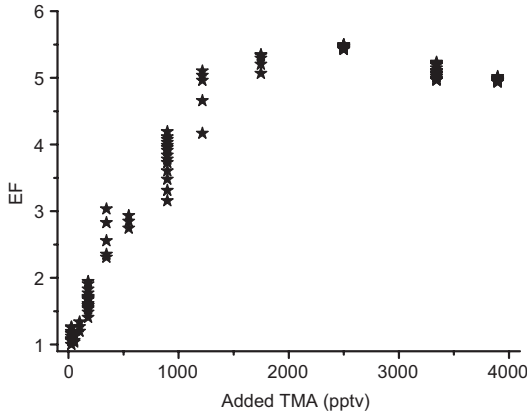


Fig. 10. Enhancement factor (EF) as a function of added TMA concentration in the first experiment. Maximum EF of ~ 5.5 was found with TMA concentration of 2500 pptv. Zero value on the x-axis should be interpreted as zero addition of TMA, while the system still has contaminant levels of TMA.

rier gas. The EF as a function of added TMA concentration illustrates the progress of the EF as TMA was added into the system (Fig. 10).

Comparison with other experiments

There have been numerous laboratory studies of the enhancement of sulphuric-acid–water nucle-

ation by base compounds in various conditions (Table 1). The EF values presented in Table 1 were selected to represent conditions (i.e. RH, nucleation temperature) closest to our study, so they are not necessarily the highest ones reported in the original studies. Only one study was found where the influence of TMA addition on nucleation rate was investigated (Erupe *et al.* 2011), and those results are very similar to ours. The maximum EF was found to be approximately 8 at the TMA concentration of 1350 pptv in similar conditions (RH = 25%, $T_{\text{nuc1}} = 288$ K, $[\text{H}_2\text{SO}_4] = 10^7 \text{ cm}^{-3}$) as in our study. Erupe *et al.* (2011) stated that the EF is inversely proportional to RH and sulphuric acid concentration. In our study, the EF was 5.5 (RH 30%, $T_{\text{nuc1}} = 298$ K, $[\text{H}_2\text{SO}_4] = 2.8 \times 10^6 \text{ cm}^{-3}$) at $[\text{TMA}] = 2500$ pptv, which is lower than the value reported by Erupe *et al.* (2011). This is most likely due to slightly different conditions, as especially the nucleation temperature might play a significant role.

There are several studies using NH_3 which report different values of the maximum EF (Ball *et al.* 1999, Berndt *et al.* 2010, Benson *et al.* 2011, Kirkby *et al.* 2011, Zollner *et al.* 2012). The nucleation temperatures in those studies were very similar (288–296 K), but all the other conditions were different. The NH_3 concentration ranged from 45 pptv (Zollner *et al.* 2012)

Table 1. Information collected from earlier studies of base substances enhancing sulphuric-acid–water nucleation. Listed are the base substance used, relative humidity (RH), nucleation temperature (T_{nuc1}), sulphuric acid concentration $[\text{H}_2\text{SO}_4]$, base concentration [base], enhancement factor (EF) and the carrier gas used. The EF values were either taken from the text of the original papers, or evaluated from the figures if not mentioned in the text. The chosen EF values are the maxima, which means that the base substance concentration can be interpreted as a saturation level concentration.

Study	Substance	RH (%)	T_{nuc1} (K)	$[\text{H}_2\text{SO}_4]$ (cm^{-3})	[base] (pptv)	EF	Carrier gas
Ball <i>et al.</i> (1999)	NH_3	15	295	3×10^9	80	10	N_2
Berndt <i>et al.</i> (2010)	NH_3	41	293	10^7	44635	5	Synth. air
Benson <i>et al.</i> (2011)	NH_3	13–16	288	5×10^6	1220	1–1.5	N_2
Kirkby <i>et al.</i> (2011)	NH_3	38	292	1.5×10^8	100	100	Synth. air
Zollner <i>et al.</i> (2012)	NH_3	27	296	3×10^9	45	1.4×10^5	N_2
Zollner <i>et al.</i> (2012)	MMA	27	296	3×10^9	35	2×10^6	N_2
Almeida <i>et al.</i> (2013)	DMA	38	278	10^7	0.1–5*	10^6	Synth. air
Almeida <i>et al.</i> (2013)	DMA	38	278	2×10^6	13–140**	100	Synth. air
Erupe <i>et al.</i> (2011)	TMA	25	288	10^7	1350	8	N_2
This study	TMA	30	298	2.8×10^6	2500	5.5	Air

* Introducing 0.1–5 pptv of DMA into the system resulted in the EF of 106.

** Introducing 13–140 pptv of DMA into the system resulted in an additional EF of 100 (compared with the case with 0.1–5 pptv of DMA).

to 44 635 pptv (Berndt *et al.* 2010), and the H_2SO_4 concentration ranged from $5 \times 10^6 \text{ cm}^{-3}$ (Benson *et al.* 2011) up to $3 \times 10^9 \text{ cm}^{-3}$ (Ball *et al.* 1999, Zollner *et al.* 2012). As a result of such high variability in conditions, the maximum EF values varied from as low as 1 (Benson *et al.* 2011) to 140 000 (Zollner *et al.* 2012). The effect of NH_3 was probably saturated in our study, since the concentration of background NH_3 (201 pptv) was high, and especially higher than the NH_3 concentrations used in most other studies. Enhancement of nucleation by NH_3 with higher concentrations than the background level of our study was observed in only two studies (Berndt *et al.* 2010, Benson *et al.* 2011). The value of EF in Benson *et al.* (2011) was very low (1 to 1.5), while that found by Berndt *et al.* (2010) was 5 under conditions very similar to those in our study.

In the study by Zollner *et al.* (2012), also MMA was introduced into the flow. They observed an enhancement of six orders of magnitude in the nucleation rates when the MMA concentration was 35 pptv. Since the detection limit of MARGA for MMA was higher (90 pptv) than the concentration used by Zollner *et al.* (2012), we conclude that the effect of MMA addition was already saturated in our system before the addition.

The effect of DMA was also saturated in our study. Almeida *et al.* (2013) reported the EF of 10^6 with the DMA concentration of 0.1–5 pptv. Increasing the DMA concentration to 13–140 pptv resulted in an additional EF of 100. They did not report whether the effect of DMA was saturated or not. Nevertheless, the highest concentration used by Almeida *et al.* (2013) was lower than the detection limit of MARGA (149 pptv). Almeida *et al.* (2013) also conducted their study at a nucleation temperature 20 K lower than in our study.

Summary and conclusions

The effect of four base compounds (TMA, DMA, MMA and NH_3) on sulphuric-acid–water nucleation was investigated in this study. An enhancement of nucleation rates was observed only with TMA, with a maximum enhancement factor

(EF) of 5.5 at the TMA concentration of 2500 pptv. Other base compounds were found not to enhance the nucleation process, so we conclude that the background concentrations of these base substances were high enough already before any addition, i.e. our system was already saturated with respect to these compounds. A decreased initial particle concentration, i.e. decreased condensational sink, did not change the effect of the three base substances (DMA, MMA and NH_3) tested in the second experiment.

Base concentrations were measured with MARGA. The background concentration of NH_3 was determined to be 201 pptv. The background concentrations of the amines used in this study could not be determined reliably, as their concentrations were lower than the detection limits of MARGA. The response to the addition of NH_3 was linear and expected, but the measured MMA and DMA concentrations were much lower than the determined input values. The non-linear response of MMA and DMA could not be caused by oxidation because there should not be large amounts of oxidants in the system. It is evident that the amines entered the system, as TMA enhanced nucleation and slightly modified particle number size distributions (*see* Appendix). Diffusion-limited values of WLF were calculated using the Fullers method with the binary system approximation, resulting in WLFs of 26.3, 7.2, 4.5 and 3.1 for NH_3 , MMA, DMA and TMA respectively. The base substance losses in the system were not a first-order process because the losses increased with increasing base concentrations, so wall losses cannot explain the discrepancy between the measured and added base concentrations. MARGA is continuous IC system and by default not designed for measuring amines. According to our knowledge, there is no existing literature on the calibration of MARGA system with amines within the actual flow (gas phase and/or in the particles), and no such information was presented in this study. Currently, it is unknown how large fraction of the amines will actually be detected from the real-sample air flow. Defining the losses of amines within the whole MARGA flow system is a very demanding task and beyond the scope of this study. However, some attempts to define the losses exist for non-continuous IC systems (Praplan *et al.* 2012).

The background ammonia originating from the carrier gas and especially from the water used for humidification is virtually impossible to prevent entering the system. The water used for humidification was the purest available, and changing the carrier gas to e.g. bottled high-quality nitrogen would be impractical as the aim of our study was to have steady-state continuous measurements running for tens of hours. The inlet flow rates of the instruments (16.7 lpm for MARGA, 10 lpm for CIMS and 1.5 lpm for DMPS) demand a high flow rate in the flow tube, which would consume bottled carrier gas very fast, thereby disallowing long lasting steady-state measurements.

The added base did not influence the measured sulphuric acid monomer or total sulphate concentration. The background base concentration was higher than the initial sulphuric acid concentration, and the binding process of sulphuric acid by base substances had already been taken place before adding any bases. Further increase of the base concentration did not affect the measured sulphuric acid monomer concentration as the system was already saturated. The total sulphate concentrations measured by MARGA were approximately two orders of magnitude higher than the sulphuric acid monomer concentration measured with CIMS, even though the conditions (flow rate and temperature of the saturator) were not similar and the two experiments were, therefore, not directly comparable. These findings are in agreement with our previous results (Neitola *et al.* 2013).

Results from this study were compared with similar experiments found in the literature. One study (Erupe *et al.* 2011) using TMA was found. They reported the EF of approximately 8 at a TMA concentration of 1350 pptv, as in this study the EF was approximately 5.5 at a TMA concentration 2500 pptv. Sulphuric acid concentration and relative humidity were similar in both studies and the difference in the EF is most likely rising from the different nucleation temperature used in the studies ($T_{\text{nucl}} = 288$ K and $T_{\text{nucl}} = 298$ K, in Erupe *et al.* (2011) and this study, respectively). In contrast to the present study, other studies showed enhancement with ammonia, monomethylamine and dimethylamine. The saturation-level base concentrations

reported in most of these studies were lower than our experimentally-determined detection limits of the MARGA, which supports our conclusions that our system was already saturated before the addition in respect to these substances.

The wide variety of nucleation conditions (temperature, RH, H_2SO_4 and base concentrations) applied in the studies found in the literature produces a vast variety of EFs and may cause enhancement of nucleation in one study but not in another with similar base compounds concentrations. Also, the different carrier gases (air and N_2 , see Table 1) tend to have different amounts of contaminants. When humidifying the flows, the contaminant levels will significantly increase as water is always a source of ammonia. This implicitly suggests that impurity-free experiments are virtually impossible to conduct. The enhancement factor will then be always dependent on the initial levels of impurities in the system. There are also technical difficulties to measure such low concentrations of any compounds, even though experimental instrumentation has been developing in recent years. Nevertheless, according to this study, the concentration levels where amines effectively affect the nucleation process can be determined to range from only a couple of pptv up tens of pptv for MMA and DMA, and up to approximately 2500 pptv for TMA.

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Appendix

Number size distributions measured with the DMPS were examined more closely when adding the TMA to make sure that the base substances also participate in the nucleation processes and not only condense onto the particles. The shape of the averaged number size distributions and the mean size of the particles change very slightly for each of the TMA addition (Fig. A1). The mode is widening from the right-hand side slightly but main difference is the increasing concentration.

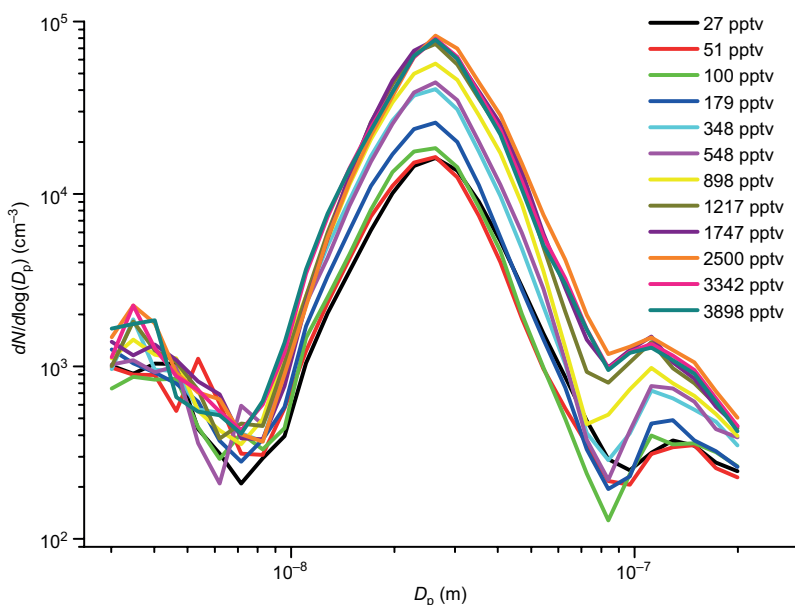


Fig. A1. Mean number size distributions for each of the amine additions. Adding the amine increases the number and growth of the particles.

The information on amines and their ability to grow particles is very scarce in the literature. The few papers found report different mechanisms for the growth, with no consensus regarding the final results. Some suggest amine ability to grow the particles at low relative humidity (10%) by heterogeneous reaction with acidic substances (Murphy *et al.* 2007, Qiu *et al.* 2012).

The particles growth rates are not explicitly calculated but they are within the same range as reported in Škrabalová (2014). From the studies cited in Table 1, only Zollner *et al.* (2012) and Ball *et al.* (1999) used a similar method to produce the sulphuric acid vapour from a saturator. In other studies (see Table 1) sulphuric acid was produced *in situ* by oxidation of SO₂ with OH produced with UV light. In the supplementary material of Zollner *et al.* (2012), the number size distributions show that the mean particle diameter is between 6 and 7.7 nm, with the distribution reaching to 20 nm. The residence time in their study was approximately 12 s. Short calculation gives approximately 20 nm for

mean particle diameter for Zollner *et al.* (2012) if using residence time of 30 s. Similarly to Ball *et al.* (1999), their residence time was 15 s, and mean particle diameters around 5 nm, with a lower relative humidity of 15%. With a higher RH, Ball *et al.*'s (1999) results would most probably be in the same order as Zollner *et al.*'s (2012) and ours. The concentration of sulphuric-acid vapour produced from the saturator follows the basic principle of saturation vapour pressure, which yields much higher sulphuric acid concentrations than what is measured by CIMS, which is concentration of sulphuric acid monomer (Neitola *et al.* 2013). The growth rates in the system like this are very high (Škrabalová *et al.* 2014). Producing sulphuric acid *in situ* would most probably produce significantly lower amount of sulphuric acid, even though the CIMS measured monomer concentrations are in the same range. The different production mechanisms would result in completely different growth rates, and finally diameters of the particles in similar conditions.