Interactive comment on “Heterogeneous uptake of ammonia and dimethylamine into sulfuric and oxalic acid particles” by Sauerwein and Chan

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The authors would like to thank Anonymous Referee #1 for the comments on the manuscript. We respond to the specific comments made by the referee below and identify the changes we have done to the manuscript.

Anonymous Referee #1: The manuscript describes time-dependent measurements of the competitive partitioning of ammonia and dimethylamine to droplets/particles containing sulfuric acid or oxalic acid deposited on a substrate. Although many previous measurements have studied the partitioning of one of these gas phase species, this paper provides insight into the relative abundances of the species in the gas and condensed phase at different gas phase concentrations and relative humidities when acting in competition. The manuscript is helpful in providing a qualitative exploration of the problem although I believe some of the quantitative aspects need to be interpreted with some caution due to experimental uncertainties, particle sizes, etc. The inherently qualitative interpretation of the measurements does limit the more general application of the work (and is sometimes quite hard to follow). However, the insights provided are sufficiently new that the manuscript merits publication - I do suggest the authors respond to the following suggestions before the paper can be accepted.

Page 5, line 40: The authors suggest that re-volatilization occurs at long times with the neutralization ratio decreasing from 1.7 to 1.5. Looking at the data in Figure 1, this seems to me to be over-interpreting the data. Firstly the “noise” in the calculated ratio seems to be larger than the error bars included with the points (e.g. see the fluctuations in the points around 17 hours for the DMA 0.15 ppm measurement at 50 % RH) – I suggest the authors consider again the uncertainties in their measurements. Secondly, how do the authors know that any such small change is not just due to a drift in environmental conditions (e.g. RH or temperature)? In fact, there is very little discussion of experimental errors in the analyses and the magnitude of uncertainties is quite key in verifying the veracity of trends identified in the data. I recommend a fuller discussion of experimental reproducibility and uncertainties.

Response: We thank the anonymous referee #1 for the valuable comment. Uncertainties as indicated by error bars in the figures originate from the analysis of particle composition with ion chromatography analysis, while additional uncertainties that could explain fluctuations in particle phase concentration can only be described qualitatively. Those include:

1. Particle number - Variation in total particle count deposited on the hydrophobic film of 2000±100 droplets can cause a noticeable acceleration (if less particles were deposited) or delay (if more particles were deposited) in neutralization of the total sample including all particles.
2. Uncertainties resulting from variation in DMA/NH3 gas ratios or gas concentration - Gas concentrations were estimated from regular gravimetric measurements of the permeation tubes to determine permeation rates. The small diffusion rates would lead to small changes between successive weight measurements and resulted in a few percent uncertainty. In addition, small variations in temperature (293.3±0.2 K) can cause small fluctuations in permeation rates (see additions made to the supplemental information). Though the uncertainty in gas concentrations was estimated and listed in Table 1, the effect of those uncertainties on the final particle phase concentration could not be quantified. Gas testing procedures and uncertainty estimations were added to the supplementary information.
3. Variations in temperature (296.3±1.0 K) and RH (10%±2% and 50%±3%) within the flow cells may have had small influences on uptake kinetics, and yet those uncertainties could not be further quantified.

In order to address the comments of Referee #1, in addition to the added information the supplement of the manuscript, we have added a qualitative description of the uncertainties into section 2.3, which reads as follows:

“Uncertainties as shown in the figures were calculated based on errors resulting from IC measurements. Additional uncertainties of particle phase DMAH and NH3 resulting from independent parameters such as the variations in total particle count, and uncertainties in generation and determination of gas concentrations also led to some fluctuations beyond the quantified errors.”

The authors further agree with the referee’s argumentation, that the decrease in neutralization ratio towards equilibrium lies within the margin of error if unquantifiable uncertainties are also considered. The paragraphs starting from line 38 - 41 on page 5, the sentence on line 11-13 on page 11, and the sentence in line 25-26 on page 12 were deleted. The subsequent sentence on page 11 line 14 was changed to

“Under amine-free atmosphere, the neutralization ratio of these equilibrated particles decreased to $X_{SO_2} = 1.2±0.2$ at 10% RH and $X_{SO_2} = 1.7±0.2$ at 50% RH, as a result of DMA evaporation (Table 1).

On page 10, under consideration of uncertainties, we changed lines 23-25 to

“DMAH/NH3 ratios (Figure 8b) stayed roughly constant.”

On page 11 line 39-41 was changed to

“Under exposure to N2, DMAH-NH3 mixed particles that were originally in liquid phase state and contained large amounts of DMAH (Fig. 9 h, k) exhibited a decrease in $X$, reflecting that the equilibrium compositions of these droplets were sensitive to changes in DMA and NH3 gas concentrations.”

And the sentence on page 12 line 27 was moved to line 14 and altered as follows:

“When NH3 is present in neutralized, DMAH-rich sulfate droplets, DMA from the surrounding gas phase can displace NH3 from droplets, and prompt additional NH3 to evaporate to form non-neutralized particles.”

Despite the adjustments to more accurately describe the uncertainties of the measurements, we believe that the main conclusions of this work on the roles of particle phase and extent of neutralization in the co-uptake are not affected.

**Anonymous Referee #1:** Pages 6-7: I find the discussion of the change in neutralization and DMAH/NH4 ratios along with the surface acidity quite confusing. Given the large size of the droplets and the long timescales for the measurements, I can’t see that different surface kinetic parameters (uptake coefficients) for the amine and ammonia can govern the change in these ratios. Indeed, I don’t think this is what the authors are saying – if they are, then they need to consider competing rates of gas diffusion limited uptake, diffusional mixing within these liquid droplets, sensitivity of such large droplets to surface kinetics etc. Whichever is correct, the discussions is very confusing. This need for clarity is even more true when the authors then state that Figure 4 confirms that the uptake of DMA and NH3 proceed independently.

**Response:** We thank the anonymous referee #1 for pointing out those ambiguities. As mentioned at the end of section 3.2.1, the comparison of mixed gas with single gas uptake as shown in Figure 4 indicates that the initial NH3 and DMA partitioning into acidic particles happens independently from each other. Thus, using uptake coefficients from earlier studies on single gas uptake to elucidate the mixed gas uptake process seems reasonable. Based on uptake coefficients reported in the literature which are larger for NH3 than for DMA, one would expect the observed trend of the DMAH/NH4 ratio to decrease as uptake proceeds since NH3 uptake is faster than DMA. Yet it is unclear why the initial DMAH/NH3 ratio to decrease as uptake proceeds since NH3 uptake is faster than DMA. Yet it is unclear why the initial DMAH/NH3 ratio decreases as uptake proceeds.

To DMA/NH3 ratios (gas phase). Our discussion of surface acidity pertains to the very initial periods of uptakes. The uptake coefficient describes the overall uptake process. This includes inter-related processes such as gas phase diffusion, immediate reaction of gas molecules colliding with the aerosol surface or adsorption and dissolution, followed by further liquid phase diffusion and proton transfer in the bulk particle.
Judging based on calculated mean thermal velocities $\omega_{\text{NH}_3} = 607 \text{ m s}^{-1}$ and $\omega_{\text{DMA}} = 373 \text{ m s}^{-1}$ (296K) (based on diffusion coefficients of Massman, 1998 and Yaws 1995), NH$_3$ diffuses faster than DMA in gas phase. Yet, DMA possesses a higher gas phase and particle phase basicity than NH$_3$ (Brauman et al., 1971; Parrillo et al., 1993, Ge et al., 2011a) and a higher effective Henry’s law constant than NH$_3$ for uptake into acidic solutions (Ge et al. 2011b) such as the sulfuric acid particles. Surface acidity was consequently considered to be one possible explanation why the stronger basicity of DMA may contribute to the equality of the DMAH/NH$_3$ in fresh particles and DMA/NH$_3$ ratios. This effect, however, diminishes as the particle gets gradually neutralized.

To add clarity to the discussion in section 3.2.1, we have added more description and rearranged paragraphs from lines 7-8 on page 7 as well as lines 34-40 from page 6 as follows:

“Starting from the second measured values, a clear decrease in DMAH/NH$_3$ ratios can be observed. Figure 4 compares the uptake of DMA and NH$_3$ in single and mixed gas experiments. The initial uptake trends of single gas and co-uptake do not deviate noticeably, indicating that DMA and NH$_3$ uptake took place independent of each other. Consequently, earlier reported uptake coefficients from single gas uptake NH$_3$ and DMA into sulfuric acid may be used for co-uptake analysis.”

And “Wang et al. (2010) reported an uptake coefficient ($\gamma_{\text{DMA}}$) of about 0.03 for DMA uptake into concentrated H$_2$SO$_4$ of $\geq 62$ wt% ($\leq 10\%$ RH) at 283 K. The coefficient is noticeably smaller than that of close to unity reported for NH$_3$ uptake into H$_2$SO$_4$ of similar acidity (Swartz et al., 1999). In the current study, NH$_3$ uptake into fresh H$_2$SO$_4$ droplets was not overwhelmingly dominant. However, as the uptake continued, the DMAH/NH$_3$ ratios decreased by 30-40% for all experimental conditions within the first 1-2 hours (Fig. 3 a-d), which indicates a preferential uptake of NH$_3$. Since the gas concentrations of both NH$_3$ and DMA were constant, it is likely that the decreasing particle acidity and increasing neutralization ratio caused this change.”

Anonymous Referee #1: Page 12, lines 30-36: The authors consider the relevance of the high gas phase concentrations studied here when compared to atmospheric concentrations. It seems equally important to consider the importance of the particle size range studied. How do the authors expect their results to impact on our understanding of the much smaller particles that must be considered in the atmosphere? There is a brief comment on this at the very end of the summary section.

When considering the application of the current results to submicron particles, two aspects might be of importance:

1. The overall gas uptake would likely be accelerated. For submicron particles gas phase diffusion limitations would also have to be taken into consideration. Yet, we believe that the major findings in our paper i.e. the initially independent uptake of both gases into acidic particles as well as the roles of phase state and neutralization in DMAH or NH4 competition and displacement is not expected to change.

2. Impact of particle size on crystallization behavior or inhibition of crystallization. DMAH, even if its concentration was low compared to NH$_3$’ (DMAH/NH$_3$ = 0.05), was able to suppress NH3SO$_4$ precipitation. As it is generally easier to induce crystallization in larger particles, we assume that this effect should extend to particles of smaller sizes.

To stronger illustrate these aspects, the following sentence in the Summary and Conclusions section was modified to:

“It should also be mentioned that particle size may affect the gas uptake kinetics, as well as the crystallization behavior of the particle. When applying the results of this study to submicron particles, one may expect a considerably faster uptake and thus changes in DMAH/NH$_3$ ratios in acidic particles. Yet the overall trends of displacement reactions based on phase state and neutralization ratio as well as crystallization inhibition by DMAH are considered applicable to particles of smaller size. Nevertheless,[...]”

Minor changes/corrections:
Anonymous Referee #1: Page 3, line 20: The method for checking the gas phase ratios is not clearly described. The sentence describing this procedure needs to be expanded on: “To ensure accuracy of the gas ratio, measures were taken including conditioning the setup for a prolonged period, separating RH conditioning cells and reaction cells.”

Response: NH₃ and DMA are both very “sticky” gases (Robacker and Bartelt 1996, Hansen et al. 2013, Dawson et al. 2014), and are prone to adsorb to instrumental surfaces. Yet, the stickiness varies among different amines and ammonia (Namieśnik et al. 2003, Dawson et al. 2014). Measurements of the reestablishment of gas concentrations after the system underwent a cleaning process showed that the time to reach stable gas concentrations at the inlet of the flow cell took up to 4 hours for NH₃ and up to 8 hours for DMA. A much shorter recovery time was observed if only the gas supply was temporarily interrupted (e.g. for weighing permeation tubes, and/or changing the N₂ cylinder). In that case the time for re-establishment of stable concentrations took <1 hour for both gases. Since a drop in the concentration of one or both gases (e.g. due to wall losses) would result in a change of DMA/NH₃ ratio, we allowed 2 h equilibration time when the gas supply was interrupted and about 12 hours for reconditioning after the setup was cleaned. Since flow cells were likewise conditioned with DMA and NH₃ gas, we equilibrated the sulfuric acid or oxalic acid particles to the respective RH of 10% or 50% in separate clean cells.

In order to address the reviewers comment we have clarified the sentence as follows:

“To ensure accuracy of the gas ratio, the system was conditioned for several hours to minimize wall losses either one or both gases prior to the uptake experiment (see supplemental information for detailed descriptions).”

We added more detail on the gas generation system, including the conditioning procedure, into the supplement of the paper.

Anonymous Referee #1: Page 6, line 6: Presumably the authors are referring to Sections 3.3 and 3.4 here?

Response: We thank the referee for this remark, the section numbering has been updated throughout the manuscript.

Anonymous Referee #1: Page 9, line 21: The error bar on this line is 0.00 – this is presumably not correct.

Response: DMAH/NH₃ ratios at the time of neutralization (t_{neutral}) reached 0.032±0.001 for the 0.1_{10\%} condition and 0.19±0.01 for the 0.5_{10\%} condition (Table 2), showing a slight enrichment of NH₃⁺ in the particle over the gas phase.”

References

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The authors would like to thank Anonymous Referee #2 for the comments on the manuscript. We respond to the specific comments made by the referee below and identify the changes we have done to the manuscript.

Anonymous Referee #2: p2, line 10: The phrase “highest in marine particles as well as urban and rural aerosols” is confusing. It is not clear whether the authors are highlighting the importance of alkylaminium ions in marine aerosols, or the 140-560 nm size range.

Response: We thank the anonymous referee #2 for the comment. To improve clarity the sentence was changed to

“In fact, mass loadings of alkylaminium ions (R₃NH⁺) are the highest in particles with a diameter of 140-560 nm, both in urban and rural, as well as in marine aerosols (Müller et al., 2009; VandenBoer et al., 2011; Youn et al., 2015).”

Anonymous Referee #2: p2, line 28: Do the particles actually absorb more water than ammonium sulfate particles across different compositions and sizes? Or are there some limits (e.g., only below the deliquescence point of ammonium sulfate)?

Response: Recent studies on the hygroscopicity of methyl- and ethyl-aminium sulfate salts and their mixtures with sulfuric acid (Chu et al. 2015, Sauerwein et al. 2015, Rovelli et al. 2016) have shown that short-chain alkyl-aminium sulfates are significantly more hygroscopic than ammonium sulfate up to 95% RH, hence beyond the deliquescence point of ammonium sulfate. In all three studies, hygroscopicity of alkyl-aminium sulfates was shown to increase from primary to tertiary aminium sulfate. The difference in hygroscopicity decreases as extent of neutralization decreases to bisulfate composition, where aminium and ammonium bisulfate possess similar hygroscopic properties (Sauerwein et al. 2015).

Anonymous Referee #2: p3, line 30: Are the first experimental parameters for the sulfuric acid particles? If so, may want to specify that.

Response: We agree with anonymous referee #2. To no leave any ambiguity, we added the following for clarification

“Combination of the DMA flow (0.15 or 0.9-1.0 ppm) and the NH₃ flow (1.8-1.9 ppm) resulted in DMA/NH₃ ratios of 0.07±0.01 and 0.46±0.04 at 10% RH, as well as 0.07±0.01 and 0.49±0.02 at 50% RH for experiments with H₂SO₄ (Table 2), and 0.49±0.02 at 10% and 0.52±0.01 at 70% RH for experiments with H₂C₂O₄.”

Further changes were made as suggested by anonymous referee #2 as follows:

Anonymous Referee #2: p6, line 4: Add ‘2’ to SO4 (as appears later in Section 3.2).

Response: Changes were made as follows:
“Figure 2 depicts the temporal profiles of DMAH/\(\text{SO}_4\), NH\(_4\)/\(\text{SO}_4\) and \(X\) at the different gas ratios and RH. At 10% RH particles solidified during the experiment (Fig. 2a and b, indicated by crosshatched areas) and needed 2 to > 18 hours (for 0.5\(10^\%\) and 0.1\(10^\%\), respectively) to completely neutralize sulfate.”

5 **Anonymous Referee #2:** p6, section 3.2: Check section numbers here and throughout.

**Response:** We thank the referee for this comment, the section numbering has been updated throughout the manuscript.

6 **Anonymous Referee #2:** Section3.2: NH\(_3\) displaced DMAH...should this be NH\(_4\)? And then in paragraph below NH\(_4\) displaced by DMA...should be DMAH? Recommended to check throughout.

**Response:** We agree with anonymous referee #2 that the displacement of one alkaline species by another alkaline gas is inseparable connected with the gas absorption and protonation, and hence technically the argumentation, that DMAH\(^+\) is displaced by NH\(_4^+\) is correct. Yet, the authors like to follow the terminology that is commonly used in literature focused on similar kind of displacement reactions such as Qiu et al. 2011.

10 **Anonymous Referee #2:** Also recommended to check notation such as NH\(_4\) vs. NH\(_4^+\), which appears to be used inconsistently.

**Response:** Following the definition in section 2.3, we use DMAH to represent particle phase \(n\text{NH}_2(\text{CH}_3)_2^+ + n\text{NH}(\text{CH}_3)_2\text{H}\), NH\(_4\) to represent \(n\text{NH}_4^+ + n\text{NH}_3\), \(\text{SO}_4\) to indicate total amount of sulfate species = \(n\text{H}_2\text{SO}_4 + n\text{HSO}_4^- + n\text{SO}_4^{2-}\), and \(\text{C}_2\text{O}_4\) to indicated total amount of oxalate species (\(n\) denotes the molar amounts of each compound). The manuscript was reviewed and expressions such as NH\(_4^+\) and NH\(_4\)-species were consistently named as NH\(_4\), the same was done for DMAH.

15 **Anonymous Referee #2:** p8, line 40: “During the”

**Response:** Following the suggestion the sentence was rewritten as:

> “During NH\(_3\)-DMA co-uptake the absorbed DMAH seems to have suppressed the precipitation of NH\(_4\)\(\text{HSO}_4\) in particles with a composition of 1.1 < NH\(_4\)/\(\text{SO}_4\) < 1.5, so that the phase change started only at a NH\(_4\)/\(\text{SO}_4\) around 1.5 (Fig. 5a and b).”

20 **Anonymous Referee #2:** Table 1: The subscript on the \(N\) looks like a superscript.

**Response:** the term \(X_{N2}\) in Table 1 and the table caption have been updated to \(X_N\).

25 **Anonymous Referee #2:** Fig. 2: x-axis font in panel b appears larger than in other panels. Some other inconsistencies between panels-recommended to check closely

**Response:** The figure has been updated as shown below
5 References


Heterogeneous uptake of ammonia and dimethylamine into sulfuric and oxalic acid particles

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Abstract. Heterogeneous uptake is one of the major mechanisms governing the amounts of short-chain alkyl-amines and ammonia (NH₃) gases resident in atmospheric particles. Molar ratios of aminium to ammonium ions detected in ambient aerosols often exceed typical gas phase ratios. The present study investigated the simultaneous uptake of dimethylamine (DMA) and NH₃ into sulfuric and oxalic acid particles at gaseous DMA/NH₃ molar ratios of 0.1 and 0.5 at 10%, 50%, and 70% relative humidity (RH). Single gas uptake and co-uptake were conducted under identical conditions and compared. Results showed that the particulate dimethyl-aminium/ammonium molar ratios (DMAH/NH₄⁺) changed substantially during the uptake process, which was predominantly-severely influenced by the extent of neutralization and the particle phase state. In general, DMA uptake and NH₃ uptake into concentrated H₂SO₄ droplets were initially similarly efficient, yielding DMAH/NH₄⁺ that were similar to DMA/NH₃ ratios. As the co-uptake continued the DMAH/NH₄⁺ gradually dropped due to a preferential uptake of NH₃ into partially neutralized still acidic droplets. At 50% RH, once once the sulfate droplets at 50% RH were neutralized, the stronger base DMA displaced some of the ammonium absorbed earlier, leading to DMAH/NH₄⁺ that waternarios up to four times higher than the corresponding gas phase ratios. However, at 10% RH, crystallization of partially neutralized sulfate particles prevented further DMA uptake, while NH₃ uptake continued, and displaced DMAH⁺ after the solid particles were completely neutralized, forming almost pure ammonium sulfate. Displacement of DMAH⁺ by NH₃ has also been observed in neutralized, solid oxalate particles. The results illustrate why can explain why DMAH/NH₄⁺ ratios in ambient liquid aerosols the DMAH/NH₃ can be larger than DMA/NH₃, despite of an excess of NH₃ in the gas phase. The uptake of DMA to aerosols consisting of crystalline ammonium salts, however, is unlikely, even if the gas concentrations of comparable DMA and NH₃ are of the same magnitude gas phase concentrations.

1. Introduction

NH₃ and short-chain alkyl-amines (R₂N) gases are frequently detected in the atmosphere. Total emissions of NH₃ largely dominate those of R₂N (Schade and Crutzen, 1995). The characteristic ambient mixing ratios of NH₃ and R₂N are in the order of several parts per billion by volume and parts per trillion, respectively (Ge et al., 2011; You et al., 2014; Zheng et al., 2015). Many of the emission sources of R₂N such as agricultural and industrial activities also release NH₃ (Behera et al., 2013). Hence, elevated R₂N gas concentrations are likely accompanied by enhanced concentrations of NH₃ (Schade and Crutzen, 1995; Zheng et al., 2015). Despite the 2-3×two to three orders of magnitude difference in gas phase concentration, particle phase aminium-to-ammonium (R₂N/NH₃) molar ratios of up to 0.2 have been detected. For instance, average R₂NH/NH₃ molar ratios of 0.0045–0.17 were measured in PM₁₅ in urban and rural continental air masses over urban and rural sites in Ontario, Canada (VandenBoer et al., 2011), 0.02 in PM₁₀ in an urban area of Arizona, USA (You et al., 2015) and 0.23 in particles with a vacuum aerodynamic diameter of 50-800 nm in California, USA (Sorooshian et al., 2008).

Large R₂NH/NH₃ ratios in particles below 20 nm have been correlated to enhanced particle formation (VandenBoer et al., 2011; Youn et al., 2015). Laboratory studies (Almeida et al., 2013; Jen et al., 2014), field measurements (Mäkelä et al., 2001;
Kulmala et al., 2013), as well as computational methods (Kurtén et al., 2008; Olenius et al., 2013) have indicated that clusters of sulfuric acid (H$_2$SO$_4$) and DMA are more stable than clusters formed from NH$_3$-H$_2$SO$_4$ nucleation, and thus R$_3$N may contribute more to new particle formation than NH$_3$. Furthermore, R$_3$N are able to form sulfuric acid-amine clusters by replacing NH$_3$ from ammonium-sulfuric acid clusters (Bzdek et al., 2010a; Bzdek et al., 2010b) and ammonium nitrate nanoparticles (Lloyd et al., 2009), despite the presence of NH$_3$ in the gas phase (Lloyd et al., 2009). If not directly participating in the formation of particles nucleation of particles, R$_3$N can also efficiently partition into clusters and small particles (Kürten et al., 2016) to promote particle growth.

However, R$_3$N are not only detected in the nucleation mode (Mäkelä et al., 2001; Smith et al., 2008), but also in aerosols exceeding 100 nm in diameter. In fact, mass loadings of alkylammonium ions (R$_3$NH$^+$) are the highest in particles with a diameter of 140-560 nm, both in urban and rural, as well as in marine aerosols are the highest in marine particles as well as urban and rural aerosols with a diameter of 140-560 nm (Müller et al., 2009; VandenBoer et al., 2011; Youn et al., 2015). These ammonium ions were observed to be internally mixed with sulfate, nitrate or organic acids (Sorooshian et al., 2008; Müller et al., 2009; Pratt et al., 2009; Smith et al., 2010; VandenBoer et al., 2011; Healy et al., 2015; Youn et al., 2015), suggesting that heterogeneous reactions forming ammonium salts are an important sink for atmospheric R$_3$N (You et al., 2014; Tao et al., 2016). On the other hand, enhanced NH$_4^+$ concentrations in particles of the accumulation mode typically dominate R$_3$NH$^+$ concentrations, leading to low observed R$_3$NH/NH$_4$ molar ratios. A second peak of R$_3$NH/NH$_4$ in the coarse mode has been reported (VandenBoer et al., 2011; Youn et al., 2015), although the causes of these higher ratios in larger particles are not resolved to date.

Chemical characteristics of R$_3$N and their salts can deviate significantly from those of NH$_3$ and its salts. For instance, due to the electron donor effect of the alkyl groups, the nitrogen atom of R$_3$N molecules is more nucleophilic towards hydronium ions, making them stronger bases than NH$_3$ (Breitmaier and Jung, 2005). Furthermore, short-chain methyl- and ethyl- aminium nitrates, chlorides, and sulfates possess higher osmotic coefficients than their ammonium counterparts (Bonner, 1981; Macaskill and Bates, 1986; Chu et al., 2015; Sauerwein et al., 2015; Rovelli et al., 2016), which increases the aerosol hygroscopicity and liquid water content. Besides, secondary and tertiary aminium sulfates remain in the liquid state even at RH below 3% (Chan and Chan, 2013) and they effectively lower the deliquescence RH of the particles when mixed with ammonium sulfate (Qiu and Zhang, 2012). Particles with a large R$_3$NH/NH$_4$ ratio are consequently less acidic and could absorb more water than ammonium sulfate ((NH$_3$)$_2$SO$_4$) can, even at low RH.

Particulate R$_3$NH$^+$ concentrations in ambient aerosols are positively correlated with particle acidity, liquid water content, and RH (Sorooshian et al., 2008; Rehbein et al., 2011; VandenBoer et al., 2011; Youn et al., 2015). Numerous laboratory uptake experiments of R$_3$N into H$_2$SO$_4$ (Wang et al., 2010), ammonium nitrate, sulfate and bisulfate aerosols have confirmed such correlations (Lloyd et al., 2009; Bzdek et al., 2010b; Qiu et al., 2011; Chan and Chan, 2012, 2013). However, the conditions in those experiments would also promote heterogeneous uptake of NH$_3$ (Swartz et al., 1999). Although there are many studies on the uptake of either NH$_3$ (Huntzicker et al., 1980; McMurry et al., 1983; Daumer et al., 1992; Swartz et al., 1999; Hanson and Kosciuch, 2003; Liggio et al., 2011) or R$_3$N (Bzdek et al., 2010a; Bzdek et al., 2010b; Wang et al., 2010; Bzdek et al., 2011; Qiu et al., 2011; Chan and Chan, 2012) into acidic particles, to date none has been reported on the simultaneous uptake of NH$_3$ and R$_3$N to date.

Barsanti et al. (2009) were the first to model the relative importance of R$_3$N (using DMA as a model compound) and NH$_3$ in gas-particle partitioning. They showed that even when NH$_3$ gas phase concentrations exceeded those of R$_3$N by an order of magnitude, aminium R$_3$NH$^+$ ions can still dominate NH$_4^+$ in the aqueous acetic acid particles, due to their stronger basicity.
Yet, owing to the lack of chemical and physical parameters available, the study relied strongly on estimations of group contributions.

The present study is the first to investigate the simultaneous uptake of R$_3$N and NH$_3$ by acidic particles with analysis of particle phase composition. We explored the temporal changes in R$_3$NH/NH$_3$ molar ratios during the uptake of DMA and NH$_3$ into H$_2$SO$_4$ and oxalic acid (H$_2$C$_2$O$_4$) particles at different DMA/NH$_3$ gas ratios (0.1 and 0.5) and RH (10% and 50% RH). We used supermicron particles because they enabled a longer observation window period and phase state identification, and sufficient mass concentrations for studying the temporal changes in particle composition during the uptake until equilibrium was reached. The results also reveal the influence of the extent of neutralization and the change in phase state on the uptake behavior of both gases. DMA was chosen as the model R$_3$N due to its atmospheric abundance (Müller et al., 2009; Rehbein et al., 2011; Hu et al., 2015; Youn et al., 2015) and unique characteristics, such as forming a non-crystallizing DMAS droplet even at low RH (Chan and Chan, 2013) and its higher hygroscopicity than that of (NH$_4$)$_2$SO$_4$.

2. Methods

Supermicron particles deposited on a hydrophobic substrate were placed in a temperature- and humidity-controlled flow-cell coupled to a Raman microscope setup (Yeung et al., 2009). DMA and NH$_3$ at low ppm levels were generated by directing a humidified N$_2$ carrier flow through permeation tubes holders containing tubes filled with pure liquefied NH$_3$ and DMA at controlled temperatures. The two gases were mixed and introduced to four cells in parallel. Post reaction samples were analyzed by ion chromatography (IC). R$_3$N and NH$_3$ gas molecules and aminium ions in solution tend to adsorb on surfaces (Dawson et al., 2014; Hansen et al., 2013; Robacker and Bartelt, 1996). To ensure accuracy of the gas ratio, measures were taken including conditioning the setup for a prolonged period, separating RH conditioning cells and reaction cells. To ensure accuracy of the gas ratio, the system was conditioned for several hours to minimize wall losses either one or both gases prior to the uptake experiment (see supplemental information for detailed descriptions). A schematic of the experimental setup is shown in the supplemental information Fig. S1.

2.1 Generation and detection of NH$_3$ and DMA gases

A humidified N$_2$ carrier flow was directed into two electronic mass flow controllers (MKS Instruments Inc., GE50A) at 1000 ± 10 cm$^3$ min$^{-1}$ and subsequently introduced into glass permeation tube holders (Fig. S1). The tube holders consisted of a water coated coil and a chamber containing the permeation tubes of either NH$_3$ or DMA (VICI Metronics, Dynacal), as well as a thermocouple to regulate the temperature to 293.3±0.2 K. Permeation rates were determined gravimetrically to calculate the mixing ratio of each gas.

Combination of the DMA flow (0.15 or 0.9-1.0 ppm) and the NH$_3$ flow (1.8-1.9 ppm) resulted in DMA/NH$_3$ ratios of 0.07±0.01 and 0.46±0.04 at 10% RH, as well as 0.07±0.01 and 0.49±0.02 at 50% RH for experiments with H$_2$SO$_4$ (Table 2), and 0.49±0.02 at 10% and 0.52±0.01 at 70% RH for experiments with H$_2$C$_2$O$_4$. We denote these experimental conditions for uptake into H$_2$SO$_4$ by 0.1$_{\text{ox}}$$_{10\%}$, 0.5$_{\text{ox}}$$_{50\%}$, 0.1$_{\text{ox}}$$_{50\%}$, and 0.5$_{\text{ox}}$$_{50\%}$, and for uptake into H$_2$C$_2$O$_4$ by ox0.5$_{10\%}$ and ox0.5$_{70\%}$. For co-uptake gas flows from both permeation devices were mixed and split equally into four custom-made PTFE flow cells. Single gas flows were generated by bypassing one of the permeation tubes. The cells were maintained at 296.3±1.0 K and RH of 10%±2% and 50%±3%. The system including the PTFE cells was equilibrated with the NH$_3$ and/or DMA gas for about 12 h before the start of each experiment. The stability of the generated gas concentrations arriving at the PTFE cells was confirmed by ion-molecule reaction mass spectrometry (IMR-MS, AirSense, V&F Analyse-und Messtechnik GmbH).
2.2 Particle generation

The stock solutions of 30 wt% H$_2$SO$_4$ or highly concentrated saturated H$_2$C$_2$O$_4$ were prepared from ultrapure water (18.2 MΩ) and concentrated H$_2$SO$_4$ (97 wt%, Acros Organics, titrated against standardized NaOH) or H$_2$C$_2$O$_4$ powder (99%, Aldrich). For each experiment, a few mL of the solution were drawn into a piezoelectric particle generator (MicroFab Tech., Inc.). Approximately 2000±100 droplets of 60 μm in diameter were deposited on a hydrophobic film (FEP membranes, YSI Inc.) The sample was then inserted into a clean flow cell connected to humidified high purity N$_2$ (~1000 cm$^3$ min$^{-1}$) to equilibrate to either 10 or 50% RH for 45 min. The sample films were subsequently transferred into the PTFE reaction cells. RH conditioning and transfer of films took place inside a glove bag (GLOVEBAG, Glas Col®) to avoid exposure of the samples to room air and humidity.

2.3 Particle analysis

For each condition, the experiment was repeated in different time intervals to complete one time series. The samples were removed from the cell and submerged in ~12 mL of ultrapure water for extraction and subsequent chemical analysis. Both cation and anion contents were measured by IC (Metrohm, 881 compact IC Pro) as described by Sauerwein et al. (2015). IC yields total values for DMA and NH$_3$ species, and hence the distribution between molecules and ions in the samples could not be determined. In the following we use DMAH to represent $n$NH$_2$(CH$_3$)$_2$$^+$ + $n$NH(CH$_3$)$_2$$_{aq}$ and NH$_4$ to represent $n$NH$_4$ + $n$NH$_3$$_{aq}$ in the particles, where $n$ denotes the molar amounts of each compound. The same is true for the distribution between acidic species. Hereafter the molar amount of the total sulfate is indicated by SO$_4$ = $n$H$_2$SO$_4$ + $n$HSO$_4$ - + $n$SO$_4$$_{2-}$, and the total oxalate is indicated by C$_2$O$_4$. Molar ratios in the particle phase are accordingly denoted by DMAH/NH$_4$, DMAH/SO$_4$, and NH$_4$/SO$_4$, while gaseous molar ratios are denoted by DMA/NH$_3$.

DMAH concentrations of the first measurement points for particles in the 0.110% and 0.130% conditions lay at the lower end of the IC calibration range. A conservative estimation of up to 15% uncertainty for these values would decrease the DMAH/NH$_4$ ratio by 0.02, which has negligible impacts on the observed trends and values (see Fig.3). Uncertainties as shown in the figures were calculated based on errors resulting from IC measurements. Additional uncertainties of particle phase DMAH and NH$_4$ resulting from independent parameters such as the variations in total particle count, and uncertainties in generation and determination of gas concentrations also led to some fluctuations beyond the quantified errors.

After 35-38 hours, samples showed no significant changes in particle composition and were thus considered to be in equilibrium. Equilibrated samples were divided into two groups, with one directly undergoing IC analysis and the other placed in clean cells under an N$_2$ atmosphere for > 5 hours prior to IC analysis to further investigate their compositional stability in an amine- and ammonia-free environment.

Furthermore, uptake experiments at 0.510% and of NH$_3$ at 10% RH were repeated with particles of 60-200 μm in size in flow cells equipped with a quartz window to track alterations in chemical composition and concurrent morphological changes with a Raman microscope (Renishaw RM series) as described by Yeung et al. (2009) and Chu et al. (2015). A 20 mW Argon ion laser (514.5 nm) was deployed for sample excitation and a 1800 g mm$^{-1}$ grating was selected to obtain spectra in the range of 200 to 4000 cm$^{-1}$ with a resolution of 1.4 cm$^{-1}$.
3. Results and discussion

Uptake of NH$_3$, DMA and their mixtures into H$_2$SO$_4$ particles were conducted at 10% and 50% RH. Single component uptake served as the base case for comparison. Additional experiments with H$_2$C$_2$O$_4$ at 10 and 70% RH were conducted at a gas ratio of 0.5 only and are discussed in Sect. 3.3. A summary of all the experimental conditions is given in Table 1.

The uptake of alkaline gases into acidic droplets involves a series of inter-related processes including gas phase diffusion, immediate reaction of gas molecules colliding with the aerosol surface (Eq. 1a and b) or adsorption and dissolution (Eq. 2a and b), followed by further liquid phase diffusion and proton transfer in the bulk particle (Eq. 3a and b) (Swartz et al., 1999; Kulmala and Wagner, 2001; Davidovits et al., 2006; Pöschl et al., 2007; Kolb et al., 2010).

The above equations and related reaction steps indicate a strong acidity dependence, thus with increasing neutralization, the scope extent of DMA and NH$_3$ uptake may change. Here, the extent of (stoichiometric) neutralization of the particles is defined as the number of moles of alkaline species over moles of acidic species, $X = (\text{DMAH}+\text{NH}_3)/\text{SO}_4$ or $X = (\text{DMAH}+\text{NH}_3)/\text{C}_2\text{O}_4$ and is hereafter referred to as the neutralization ratio. In the course of the uptake experiments, the neutralization ratio ranged from highly acidic ($X = 0$) to neutral ($X = 2$). However, not all equilibrated particles were completely neutralized, as will be further discussed in Sect. 3.4.

3.1 Single gas uptake

At 50% RH, the uptake of NH$_3$ fully neutralized the H$_2$SO$_4$ droplets within 2 hours, forming aqueous (NH$_3$)$_2$SO$_4$ droplets (Fig. 1, grey diamonds). At 10% RH, NH$_3$ uptake (Fig. 1, open diamonds) was similar to that at 50% RH initially, until $X$ exceeded 1.1, where crystallization significantly retarded the subsequent uptake. The continued increase in particulate NH$_3$ even after crystallization indicates that crystalline acidic particles were still susceptible to uptake, but imposed bulk diffusion limitations that retarded the uptake. Neutralization was not complete within the measured period of 15 hours.

Uptake of DMA at the mixing ratio of 0.15 ppm (Fig. 1, triangles) was significantly slower than that at 1 ppm (Fig. 1, squares). Like the initial uptake of NH$_3$, DMA uptake did not differ significantly between 10% and 50% RH, until approaching equilibrium at DMAH/SO$_4$ ratios of 1.5±0.1 at 10% RH, and 1.7±0.1 (DMA$_{0.15\text{ppm}}$) and 1.9±0.1 (DMA$_{1\text{ppm}}$) at 50% RH (Table 1, $X_{\text{eqal}}$). There was no indication of phase change in these particles even at 10% RH. This is consistent with earlier studies, where secondary and tertiary methyl and ethyl-aminium sulfates were described as hygroscopic, non-crystallizing salts at RH ≤ 10% (Qiu and Zhang, 2012; Chan and Chan, 2013; Chu et al., 2015). Furthermore, these studies showed that upon drying of synthesized DMAS droplets (DMAH/SO$_4$ ratios = 2) with amine-free air, DMA evaporated from the particles, leading to a final DMAH/SO$_4$ ratio of 1.5 at < 3% RH (Chan and Chan, 2013; Chu et al., 2015). In our experiment, the same equilibrium DMAH/SO$_4$ ratio of 1.5 was established at 10% RH, despite a continuous supply of DMA gas.
Particles exposed to 1 ppm of DMA at 10% RH were more neutralized initially with $X_{\text{DMA}} = 1.7\pm 0.1$ (Table 1) and then equilibrated to lower $X_{\text{DMA}}$ of 1.5±0.1 (Table 1). Some of the initially absorbed DMA molecules had re-partitioned into the gas phase despite the presence of DMA gas in the surrounding atmosphere. The phenomenon of re-volatilization is further discussed in Sect. 4.

3.2 DMA-NH$_3$ co-uptake

Figure 2 depicts the temporal profiles of DMAH/SO$_4$, NH$_3$/SO$_4$ and X at the different gas ratios and RH. At 10% RH particles solidified during the experiment (Fig. 2a and b, indicated by crosshatched areas) and needed 2 to > 18 hours (for 0.5$_{10\%}$ and 0.1$_{10\%}$, respectively) to completely neutralize sulfate. Upon reaching neutralization, NH$_3$ had almost completely displaced the DMAH absorbed earlier from the solid particles. The phase transition and DMAH displacement at 10% RH will be further discussed in Sect. 3.2.3 and 3.2.4.

At 50% RH SO$_4^{2-}$ was completely neutralized (Fig. 2c and d) within 1-2 hours. Neutralization in droplets was followed by a partial displacement of NH$_3$ by DMA, reaching a final equilibrium composition enriched in DMAH (Sect. 3.2.2). The results show that the DMAH/NH$_3$ ratios varied substantially during uptake before stable compositions were reached. In the following, we will discuss the dependence of gas uptake on the phase state and neutralization ratio of the particles.

3.2.1 Uptake into liquid acidic droplets

Figure 3 displays the changes in the DMAH/NH$_3$ ratios as a function of time for the four co-uptake experiments. For the first measurement point under each condition, the DMAH/NH$_3$ ratio (Table 2, $t_{\text{initial}}$) was close to the gas phase DMA/NH$_3$ ratio (indicated by grey bands in Fig. 3), implying that initially both gases partitioned equally effectively into highly concentrated H$_2$SO$_4$. For instance, in panels a and b the DMAH/NH$_3$ ratios in the acidic droplets were 0.07±0.01 and 0.43±0.04, comparable to gaseous DMA/NH$_3$ ratios of 0.07 and 0.46, respectively. Starting from the second measured values, a clear decrease in DMAH/NH$_3$ ratios can be observed. Figure 4 compares the uptake of DMA and NH$_3$ in single and mixed gas experiments. The initial uptake trends of single gas and co-uptake did not deviate noticeably, confirming indicating that DMA and NH$_3$ uptake took place independent of each other. Consequently, earlier reported uptake coefficients from single gas uptake NH$_3$ and DMA into sulfuric acid may be used for co-uptake analysis.

Swartz et al. (1999) measured the heterogeneous uptake of NH$_3$ into a chain of 70 wt% and 40 wt% H$_2$SO$_4$ droplets (equilibrated at 10% and 50% RH, respectively), and obtained gas phase diffusion-corrected uptake coefficients ($\gamma_{\text{NH}_3}$) of 0.8 and 1.0, respectively. The highly effective uptake into concentrated H$_2$SO$_4$ at pH < 0 was attributed to surface reactions, i.e., NH$_3$ molecules reacting with interfacial hydronium ions (H$_3$O$^+$) without prior solvation (Swartz et al., 1999). As H$_2$SO$_4$ droplets in the present study have a solution pH ≤ -0.9 (Wexler and Clegg, 2002) at both 50% RH (43 wt% H$_2$SO$_4$) and 10% RH (64 wt% H$_2$SO$_4$), protonation without prior dissolution may take place for NH$_3$ in the first few minutes of uptake when pH is very low.

Wang et al. (2010) reported an uptake coefficient ($\gamma_{\text{DMA}}$) of about 0.03 for DMA uptake into concentrated H$_2$SO$_4$ of ≥ 62 wt% (< 10% RH) at 283 K. The coefficient is noticeably smaller than that of close to unity reported for NH$_3$ uptake into H$_2$SO$_4$ of similar acidity (Swartz et al., 1999). In the current study, NH$_3$ uptake into fresh H$_2$SO$_4$ droplets was not overwhelmingly dominant. However, as the uptake continued, the DMAH/NH$_3$ ratios decreased by 30-40% for all experimental conditions within the first 1-2 hours (Fig. 3 a-d), which indicates a preferential uptake of NH$_3$. Since the gas concentrations of both NH$_3$ and DMA were constant, it is likely that the decreasing particle acidity and increasing neutralization ratio caused this change.
To date no systematic study on the relevance of surface protonation has been conducted for DMA uptake. However the gas phase basicity of NH$_3$ and its derivatives (such as R,N) have been shown to correlate well with the differential heats of chemisorption on acidic (zeolite) surfaces (Parrillo et al., 1993). Since DMA possesses a slightly higher gas phase basicity than NH$_3$ (Brauman et al., 1971; Parrillo et al., 1993), DMA gas molecules might, similar to NH$_3$, have a high affinity to interfacial H$_3$O$^+$. Surface protonation on fresh H$_2$SO$_4$ particles may thus be important for the initial uptake of both NH$_3$ and DMA, which could explain why the initial particle phase ratio is equal to the gas phase ratio.

Wang et al. (2010) reported an uptake coefficient ($\gamma_{\text{NH}_3}$) of about 0.03 for DMA uptake into concentrated H$_2$SO$_4$ of ≥ 62 wt% (≤ 10% RH) at 283 K, which is noticeably smaller than the coefficient of close to unity reported for NH$_3$ uptake into H$_2$SO$_4$ of similar acidity (Swartz et al., 1999). In the current study, NH$_3$ uptake into fresh H$_2$SO$_4$ droplets was not overwhelmingly dominant. However, as the uptake continued, the DMA/NH$_3$ ratios dropped by 30-40% for all experimental conditions within the first 1-2 hours (Fig. 3a-d), which indicates a preferential uptake of NH$_3$. Since the gas concentrations of both NH$_3$ and DMA were constant, it is likely that the decreasing particle acidity and increasing neutralization ratio caused this change. Swartz et al. (1999) reported a threshold pH ≤ 0 for surface protonation to occur and a drop in $\gamma_{\text{NH}_3}$ by one order of magnitude when the pH was increased to above zero. Hanson and Kosciuch (2003) observed a similar drop in $\gamma_{\text{NH}_3}$ during the uptake of NH$_3$ into H$_2$SO$_4$, when the solution approached ammonium bisulfate (NH$_4$HSO$_4$) composition. Using the E-AIM model (Wexler and Clegg, 2002, www.aim.env.uea.ac.uk/aim) we estimated that NH$_3$O$^+$ decreased by about 40% as the neutralization ratio increased from $X = 0$ (H$_2$SO$_4$ droplets) to 0.5. Once the particles were half neutralized ($X = 1$, bisulfate stoichiometry), the solution pH were estimated to exceed zero. Hence if we assume a similar threshold as reported by Swartz et al. (1999), surface protonation (Eq. 1a and b), which can explain the comparable initial uptake of DMA and NH$_3$, may no longer be relevant when particles approached bisulfate composition.

Figure 4 compares the uptake of DMA and NH$_3$ in single and mixed gas experiments. The uptake trends of single gas and co-uptake did not deviate noticeably, confirming that DMA and NH$_3$ uptake took place independent of each other. Despite the increase in pH when neutralization ratios exceeded unity ($X = 1$), there were sufficient amounts of H$_3$O$^+$ to support the uptake of both gases. Hence, the presence of NH$_3$ gas molecules at 14 times higher concentration than DMA had little effect on the uptake of DMA into acidic particles. The same can be said for DMA, which seemed not to have influenced NH$_3$ partitioning into acidic droplets. This finding clearly differentiates the group of hydrophilic R,N from more hydrophobic organics such as hexadecane, hexadecanol (Daumer et al., 1992) or typical atmospheric organic vapor (Liglio et al., 2011), which form an organic film that limits the access of NH$_3$ to the inorganic core.

The independent uptake of DMA and NH$_3$ at 10% RH prevailed until the particles underwent phase change (Fig. 4a and c, dotted lines). Once particles effloresced, a preferential uptake of NH$_3$ was observed, which resulted in a significant drop in DMAH/NH$_3$ (Fig. 3a and b), as discussed in Sect. 2.3.2. At 50% RH the co-uptake of DMA and NH$_3$ was independent from each other until the particles reached complete neutralization ($X = 2.0$) (Fig. 4b and d, solid lines). Once neutralized, only DMA uptake continued (Fig. 4b) with concurrent displacement of NH$_3$ (Fig. 4d) as discussed hereafter.

### 3.2.2 Displacement of NH$_3$ from neutralized droplets

When approaching full neutralization, where both gases started to compete for limited available H$_3$O$^+$ ions, the DMAH/NH$_3$ ratios in droplets of the 0.1% and 0.5% experiments started to increase (Fig. 3c and d, solid line). In solution DMA (pK_a = 10.64; Hall, 1957) is a stronger base than NH$_3$ (pK_a = 9.21), consequently it has a higher affinity for H$_3$O$^+$ than NH$_3$ does. Thus, while the fraction of DMA species gradually increased, some of the NH$_3$$^+$ dissociated (Eq. 3a, reverse reaction) and NH$_3$ was released back to the gas phase (Eq. 2a, reverse reaction).
Similar displacement of NH$_4^+$ by alkyl-amines has been reported for aqueous particles of ammonium bisulfate, chloride, oxalate and sulfate at 50 and 75% RH (Chan and Chan, 2012, 2013) and nitrate at 20% RH (Lloyd et al., 2009). Similarly, Lloyd et al. (2009) observed the displacement of NH$_4^+$ by trimethylamine (TMA) from water-coated NH$_4$NO$_3$ nanoparticles despite an excess of NH$_3$ gas ($n$TMA$_{1000}$/$n$NH$_3$$_{10}$ = 0.1), although they did not report the quantity percentage of NH$_4^+$ displaced. Their gas phase conditions were comparable to our experiment at 0.15% RH. In our experiment DMA was able to displace about 9% of the initially absorbed NH$_4^+$ (Table 2, $\chi_{(NH_4)}$). The equilibrium DMAH/NH$_4$ ratio in the 0.15% RH condition experiment was 0.18±0.02 (Table 2, $t_{equil}$), which indicates an enhancement of DMA by a factor of 2.3 in the particle phase compared to the gas phase. Particles under the 0.5% RH conditions experiment equilibrated at a DMAH/NH$_4$ ratio of 1.77±0.13, hence 3-4 times higher than the gas ratio, by the time a stable particle composition was established, with 50% of the initially absorbed NH$_4^+$ was displaced (Table 2). Yet it should be noted that equilibrated particles at 0.5% RH possessed a neutralization ratio of only $X = 1.8±0.1$, hence the particle was incompletely neutralized (see Sect. 3.4) despite the presence of 1.9 ppm NH$_3$ and 0.9 ppm DMA in the surrounding gas phase.

The experimental equilibrium DMA/NH$_3$ and DMAH/NH$_4$ ratios (Table 2, $t_{equil}$) were compared with calculations using the E-AIM Model (Model II, 296 ± 1 K, no solid formation; Wexler and Clegg, 2002). Measured equilibrium DMAH/SO$_4$$_{2}$, NH$_4$/SO$_4$ were used as input parameters. The E-AIM predicted DMA/NH$_3$ gas ratios that would equilibrate over particles lay in our experiments with DMA/NH$_3$ often bare 0.14 and 0.01, and hence below the experimental DMA/NH$_3$ gas ratios of 0.49 and 0.07. Considering the entire uptake process, the modelled result would These results imply that E-AIM would predict DMAH/NH$_4$ even larger than our reserved ratios simply a more intensive displacement of NH$_4^+$ by DMA and stronger enrichment of DMA relative to NH$_3$ species in the particle phase compared to the gas phase. Yet, the experimental findings They are also qualitatively consistent with the E-AIM predicted values and consistent with earlier simulations by Barsanti et al., (2009), who reported that DMAH/NH$_4$ in submicron acetic acid droplets can be significantly larger than their gas phase ratio, even if gas concentrations of NH$_3$ dominated DMA by one to three orders of magnitudes.

Thus, in the current study we provide Our measurements are experimental evidence that DMA preferentially partitions into neutralized liquid sulfate particles over NH$_3$, due to its stronger basicity. DMA then partially displaces NH$_4^+$ from neutralized aqueous particles even when the NH$_3$ gas concentration is one order of magnitude greater than the DMA gas concentration.

### 3.2.3 Phase transition and uptake into solid acidic particles

NH$_3$ (single gas) uptake into H$_2$SO$_4$ at 10% RH decelerated noticeably when the NH$_4$/SO$_4$ ratio exceeded 1.1 (Fig. 5, filled triangles). A comparable retardation occurred in the co-uptake experiments 0.11% and 0.51%, but at NH$_4$/SO$_4$ ratios of about 1.5 (Fig. 5a and b, open triangles).

We used Raman microscopy (Chu et al., 2015) to further investigate the slowdown retardation of the reactions and possible changes in the physical state for the single uptake of NH$_3$ (Fig. 6) and the co-uptake experiment 0.51% (Fig. 7). Note that each sample was composed of several hundreds of closely packed deposited droplets deposited on a substrate. The droplets were not expected to reach the same cation-to-sulfate stoichiometry, nor exhibit phase transitions at the exact same time. For the acquisition of in-situ Raman signals, we selected individual particles just before and right after phase transition, and in crystalline state, to represent the phase change process.

During the single gas uptake of NH$_3$ into H$_2$SO$_4$ droplets at 10% RH, crystallization occurred within the first 60 min. As shown in Fig. 6, during efflorescence of acidic droplets (Fig. 6, spectra 2 and 3) the HSO$_4^-$ characteristic bands at 590 cm$^{-1}$ and...
1035 cm$^{-1}$ (Dawson et al., 1986; Lund Myhre et al., 2003) transformed to doublets at 579/609 cm$^{-1}$ and 1013/1043 cm$^{-1}$ of solid particles (Fig. 6, spectra 2 and 3), suggesting the formation of crystalline NH$_4$HSO$_4$ (Dawson et al., 1986; Colberg et al., 2004). As uptake continued, a gradual shift towards (NH$_2$)$_2$SO$_4$ was indicated by an increase in the SO$_4^{2-}$ stretching mode 975 cm$^{-1}$ and a decrease in the HSO$_4^-$ band at 579 cm$^{-1}$ (Fig. 6, spectrum 4). The retarded diffusion of NH$_3$ from the surface to the interior of the crystals is likely to have limited the uptake, explaining why the spectra did not fully resemble (NH$_2$)$_2$SO$_4$ (Fig. 6, spectrum 5) within the measured period.

Efflorescence was also observed for the co-uptake of NH$_3$ and DMA at 10% RH. Under 0.5$_{10\%}$ conditions, most particles experienced the first morphological change after 40–60 min of uptake, forming fairly spherical solids with long lined patterns (Fig. 7, yellow rectangular). Raman spectral analysis of particles that had only just transitioned from liquid to solid phase state (Fig. 7, spectrum 3) showed an emerging SO$_4^{2-}$ band at 984 cm$^{-1}$. Meanwhile the HSO$_4^-$ frequencies near 590 cm$^{-1}$ and 1030 cm$^{-1}$ in the droplet (Fig. 7, spectrum 2) shifted towards 597 cm$^{-1}$ and 1043 cm$^{-1}$ in the solid particle (Fig. 7, spectrum 3) but both remained single broad peaks, without signs of scissoring as observed for bisulfate from NH$_3$ single gas uptake (Fig. 6, spectra 3 and 4). The observed features more closely resemble the spectral characteristics of leutovicite (NH$_4$)$_2$H(SO$_4$)$_2$ (Colberg et al., 2004) than those of NH$_4$HSO$_4$ or (NH$_2$)$_2$SO$_4$.

**The 4**During NH$_3$–DMA co-uptake the absorbed DMAH$^+$ seems to have suppressed the precipitation of NH$_4$HSO$_4$ precipitation in particles with a composition of 1.1 $<$ NH$_4$/SO$_4$ $< 1.5$, so that the phase change started only at a NH$_4$/SO$_4$ around 1.5 (Fig. 5a and b). It can be seen from the 0.1$_{10\%}$ experiment (Fig. 5a) that this suppression of NH$_4$HSO$_4$ precipitation also even occurred if the DMAH/NH$_3$ at the time of phase change was as low as 0.05 at the time of phase change (Table 2, t$_{pc}$), hence even if the concentration of DMA species was low compared to the amount of NH$_3$species present in the particle). Since R$_3$NH/NH$_3$ ratios in ambient samples near emission sites can be up to 0.23 (Sorooshian et al. 2008). Since and with DMAH$^+$ as-is the most frequently detected aminium ion in aerosols (Müller et al., 2009; Rehbein et al., 2011; Hu et al., 2015; Youn et al., 2015). DMAH/NH$_3$ ratios in aerosols can possibly reach $\geq 0.05$ and thus could change thus DMA can affect the crystallization behavior of NH$_3$–H–SO$_4$–salts in atmospheric particles. Furthermore, by by retaining the particles of a composition of 1.1 $< \text{NH}_4/\text{SO}_4 < 1.5$ at 10% RH in liquid phase, the presence of DMA species accelerated the uptake of NH$_3$ compared to single gas NH$_3$ uptake where crystallization retarded the uptake into particles with NH$_4$/SO$_4 > 1.1$.

After the NH$_3$–DMAH–mixed particles crystallized, the uptake of NH$_3$ continued at a slower pace (Figure 5a and b), while DMA was no longer absorbed and the DMAH/NH$_3$ ratio started to decrease (Fig. 3a). In earlier reports of single gas R$_3$N uptake (where R$_3$N might be methylamine, DMA, TMA or triethylamine), R$_3$N (in the absence of NH$_3$) were observed to effectively adsorb onto NH$_4$HSO$_4$ surfaces in a coated flow reactor (Qiu et al., 2011). In the presence of NH$_3$ in our experiments, however, DMA was not taken up by acidic crystalline particles. Liu et al. (2012) reported steric effects to influence the uptake effectiveness of primary, secondary and tertiary methyl-amines into solid citric and humic acid measured in a Knudsen cell reactor, where smaller R$_3$N molecules are more effectively absorbed than larger ones. A similar effect of steric hindrance may have caused the preferential uptake of the smaller NH$_3$ molecules over DMA in our experiments. Besides steric reasons, the release of more lattice enthalpy during the formation of (NH$_4$)$_2$H(SO$_4$)$_2$ and (NH$_2$)$_2$SO$_4$ may have made the uptake of NH$_3$ also thermodynamically favorable.

DMAH/NH$_3$ ratios at the time of neutralization ($t_{\text{neutral}}$) reached 0.03$\pm$0.001 for the 0.1$_{10\%}$ condition and 0.19$\pm$0.01 for the 0.5$_{10\%}$ condition (Table 2), showing a slight enrichment of NH$_3$ in the particle over the gas phase.
3.2.4 Displacement of DMAH\(^+\) from solid neutralized particles

After reaching full neutralization, both Raman spectral analysis and IC results of solid particles indicated a gradual reduction of DMAH\(^+\)-DMA species and increase of NH\(_3\)-NH\(_4\)\(^+\) species in the particle phase, which is also reflected in decreasing DMAH/NH\(_4\) ratios in Fig. 3a and b.

At 10–20 minutes after the phase transition, DMAH\(^+\)-NH\(_4\)\(^-\)-mixed particles experienced a second morphological change to a polycrystalline structure (Fig. 7, grey rectangular, spectrum 4). Raman spectra of these particles showed a slowly vanishing HSO\(_4\) band at 1043 cm\(^{-1}\), and however, a significant decrease in the full width at half maximum (FWHM) of the increase in the SO\(_4^2\) band at 980 cm\(^{-1}\), which indicates the (full) crystallization of sulfate (Lee et al., 2008), was only observed hours after the morphology change (Fig. 7, spectrum 4). We suspect that the observed morphological changes are related to the formation of a (NH\(_2\)\(_2\))SO\(_4\) shell structure due to DMAH\(^+\) displacement by NH\(_3\). DMAH\(^+\) was subsequently slowly displaced from the particle core, which eventually led to the formation of crystalline (NH\(_2\)\(_2\))SO\(_4\) with only traces of DMAH\(^+\) left inside the particles, as revealed by IC analysis.

It is interesting to note that the DMAH/NH\(_4\) ratios of equilibrated particles for 0.5\(^\text{10%}\) and 0.1\(^\text{10%}\) were both 0.02 (Table 2). Even if the NH\(_3\) gas concentration is only twice of that of DMA, NH\(_3\) can almost completely displace DMAH\(^+\) from the solid particle.

Since different gas mixtures resulted in similar particle composition, calculations by \textit{E-AIM} based on these equilibrated particle compositions yielded similar gas phase DMA/NH\(_3\) ratios for the 0.1\(^\text{10%}\) and 0.5\(^\text{10%}\) experiments of 0.57 and 0.32, with an uncertainty of up to 40% due to strong temperature sensitivity. The modelled results are qualitatively in agreement with the experimental results, confirming that despite considerable amounts of DMA in the gas phase, the equilibrated solid sulfate particle would predominantly contain NH\(_4\)\(^+\)species.

Overall it can be concluded that, for DMA-NH\(_3\) co-uptake, NH\(_3\) is favorably absorbed into acidic liquid particles, except for very concentrated H\(_2\)SO\(_4\), where DMA and NH\(_3\) seem to partition similarly effectively. Unless the particles either crystallize or are close to full neutralization, DMA and NH\(_3\) in general do not influence each other’s uptake and act as if they were the only gas present.

For uptake into neutralized particles, DMA is favorably absorbed into liquid neutral particles due to its stronger basicity leading to partial NH\(_4\)\(^+\) displacement depending on gas phase NH\(_3\) concentrations. NH\(_3\) is favorably taken up into solid neutral particles and can almost completely displace DMAH\(^+\) due to the thermodynamically favorable formation of (NH\(_2\)\(_2\))SO\(_4\) crystals and steric reasons.

3.3 Uptake into oxalic acid particles

We performed additional experiments with H\(_2\)C\(_2\)O\(_4\) to further elucidate the influence of phase state on the co-uptake process. H\(_2\)C\(_2\)O\(_4\) is a model organic acid frequently detected in ambient aerosols (Kawamura and Ikushima, 1993; Decesari et al., 2000; Yao et al., 2003; Yu et al., 2005; Müller et al., 2009). Efflorescence of aqueous supermicron H\(_2\)C\(_2\)O\(_4\) particles occurs at 51.8\(^\text{-}\)56.7\(^\%\) RH, forming anhydrous solids (Peng et al., 2001). We chose to examine the co-uptake of DMA and NH\(_3\) into initially solid and initially liquid particles, respectively, at 10\(^\%\) and 70\(^\%\) RH, respectively.

Figure 8 compares the co-uptake into H\(_2\)C\(_2\)O\(_4\) and H\(_2\)SO\(_4\) particles at DMA/NH\(_3\) = 0.5. Within the first hour of uptake into solid H\(_2\)C\(_2\)O\(_4\) particles at 10\(^\%\) RH (Fig. 8a, inverted triangles), the neutralization ratio increased to X = 0.3. In the subsequent 15 hours, no further major increase was not observed, suggesting that the gas uptake into anhydrous H\(_2\)C\(_2\)O\(_4\) particles
was incomplete and may have been limited to adsorption on the surface and outer layers of the particles. DMAH/NH$_4$ ratios (Figure 8b) stayed roughly constant decreased from initially 0.26±0.05 during the first four hours of uptake to 0.17±0.04 after 14-15 h (Table 2), despite a relatively constant overall neutralization ratio (X = 0.3). Some of the initially ad-/absorbed DMA molecules were displaced by NH$_2$.

The uptake at 70% RH starting with H$_2$C$_2$O$_4$ droplets was monitored under the microscope for subsequent phase changes (Fig. S2). Within 15 minutes of uptake, liquid particles transformed into round, irregularly patterned solids, suggesting that the uptake of even small amounts of gas caused a phase change in these H$_2$C$_2$O$_4$ particles. The formation of ammonium salts via the uptake of NH$_3$ has earlier been shown to decrease the hygroscopicity of H$_2$C$_2$O$_4$ particles and influence change their phase state (Peng and Chan, 2001; Ma et al., 2013). We found that prior to phase change, a ring of small satellites formed around the droplets. This observation can be most plausibly explained by the pinning effect caused by the fast evaporation of the solvent from a droplet deposited on a substrate (Deegan et al., 1997). Similar halo formation has been described for other atmospheric particles (Hamacher-Barth et al., 2016) but yet, we believe that this effect does not have a significant impact on the general uptake observations here. The co-uptake trends into solidified H$_2$C$_2$O$_4$ particles at the ox0.5% conditions experiments were comparable to those of 0.51% and 0.5% into H$_2$SO$_4$ (Fig. 8b), indicating that the solids formed during phase change (dashed lines, Fig. 8) did not retard the uptake and that diffusion inside the particle bulk was not a limiting factor of the uptake. In fact, the particles were almost completely neutralized within the first hour of reaction. Similar observations have been reported by Li et al. (2015), who investigated NH$_3$ uptake into submicron organic particles produced from oxidation of isoprene, a precursor gas of H$_2$C$_2$O$_4$ (Ervens et al., 2014). Li et al. (2015) showed that even at RH down to <5%, NH$_3$ uptake was not restricted by diffusion. Unlike the co-uptake into partially neutralized H$_2$SO$_4$ particles at 10% RH, where DMA uptake discontinued once the particles formed solids, uptake of DMA into solid, partially neutralized H$_2$C$_2$O$_4$ particles remained effective.

Within two hours of uptake, the solid particles of ox0.5% experienced a morphological change and transformed into crystals (Fig. S2). Concurrently, the DMAH/NH$_4$ ratios dropped from 0.34 to <0.1 (Table 2, t$_{equil}$), showing that NH$_3$ can displace DMAH$^+$ from neutralized oxalate particles, which may trigger the transformation to a crystalline morphology. Final particle morphologies show a centered-particle with a monoclinic or orthorhombic crystal structure, a shape typical of ammonium oxalate (Blake and Clegg, 2009), and surrounded by small residuals of the satellite particles (Fig. S2).

### 3.4 Stability of reaction products and re-volatilization of NH$_3$ and DMA

As shown in Sect. 3.1, single gas DMA uptake into H$_2$SO$_4$ equilibrated with at incompletely neutralized droplets at both 10% and 50% RH with X$_{equil}$ between 1.5 and 1.9 (Table 1). Temporal profiles of the DMA uptake of 1ppm at 10% RH show that DMAH/SO$_4$ ratios peaked after 4.5 hours (Fig. 1), reaching X$_{equil}$ maxima of 1.7±0.1 before DMA partially re-volatilized and particles equilibrated with a more acidic composition of X$_{equil}$=1.5±0.1 (Table 1). When placing equilibrated samples into an amine-free atmosphere, the neutralization ratio of these equilibrated particles decreased further to X$_{eq}=1.2±0.2$ at 10% RH and X$_{eq}=1.7±0.2$ at 50% RH, as a result of DMA evaporation from these particles (Table 1). Similar degassing of methyl and ethyl-amines from synthesized salts has been reported in earlier studies (Chan and Chan, 2013; Chu et al., 2015; Lavi et al., 2015).

To examine the influence of NH$_3$ on the volatilization of DMA from particles and the formation of partially neutralized equilibrated droplets, we compared co-uptake experiments 0.5% and 0.5% to single gas uptake DMA$_{1ppm10%}$, DMA$_{1ppm50%}$. Figure 9 illustrates the maximum neutralization, equilibrium and composition of particles exposed to RH-conditioned N$_2$ atmosphere for the four mentioned experiments.
Particles in In co-uptake experiments, particles reached full neutralization (Fig. 9d and j). The total cation content in particles at 10% RH at the time of neutralization was comprised of >80% NH₄⁺ (Fig. 9d). When approaching equilibrium, DMAH⁺ was displaced by NH₃ and the NH₄⁺ content increased to 98% (Fig. 9e). Although the cation composition had changed, no decrease in X beyond the margin of error was observed (Fig. 9d to e). When even when the particles were exposed to pure N₂ (Fig. 9f), the particle composition did not change due to the formation of a stable crystal. At 50% RH, DMA partially displaced NH₄⁺ from neutralized particles, with an increase in DMAH/SO₄ from 0.7 at the point of maximum neutralization (Fig. 9j) to 1.3 at equilibrium (Fig. 9k). Accompanying the increase in DMAH⁺ was a drop decrease in the total neutralization ratio from X = 2 to about X = 1.8 (Fig. 9j to k), indicating that more NH₃ has degassed than was replaced by DMA. Hence while re-volatilization of DMA was responsible for the decrease in X under for DMA/NH₃ conditions, degassing of NH₃ could be responsible for the decrease in X neutralization ratios in co-uptake experiments. Once exposed to N₂, even more NH₃ evaporated from DMAH-NH₃ mixed particles (Fig. 9k to l), which further increased the acidity of these particles.

It should be noted, that the degassing of NH₃ was negligible for particles of the 0.1 50% condition (Fig. 2c). At the point of maximum neutralization they contained large amounts of NH₄⁺ and a DMAH/NH₃ ratio below 0.1, which seems to have prevented re-volatilization.

Under exposure to N₂, X decreased in DMAH-NH₃ mixed particles that were originally in liquid phase state and contained large amounts of DMAH⁺ (Fig. 9b, h, k). exhibited a decrease in X reflecting that the equilibrium compositions of these droplets were sensitive to changes in DMA and NH₃ gas concentrations.

4. Summary and Conclusions

The co-uptake of DMA and NH₃ into H₂SO₄ and H₂C₂O₄ particles was investigated at different RH and DMA/NH₃ gas ratios. The stoichiometric neutralization ratio and physical state of the particles were the two major factors influencing DMA and NH₃ uptake.

In the uptake into fresh, very acidic H₂SO₄ droplets at 10% and 50% RH, both DMA and NH₃ partitioned effectively, leading to a DMAH/NH₃ ratio comparable to the DMA/NH₃ gas ratio. Subsequently, the DMAH/NH₃ ratio decreased as NH₃ uptake was faster. The uptake of DMA and that of NH₃ were independent of each other because of the availability of abundant acids, as long as the particles did not reach neutralization nor undergo phase change. This result may explain why the highest particulate R₂NH⁺ mass concentrations are detected in acidic aerosols with at low NH₃/SO₄ ratios (Youn et al., 2015).

In fully neutralized droplets at 50% RH, the limited availability of H₂O⁺ ions for acid-base reactions led to a partial displacement of NH₄⁺ by the stronger base DMA. This process yielded equilibrium particle compositions enriched in DMAH⁺ by up to four times the gas phase ratio. It also potentially explains DMA partitioning into the neutralized condensed phase despite excess NH₃ (Sorooshian et al., 2008; Lloyd et al., 2009; Rehbein et al., 2011; VandenBoer et al., 2011). When NH₄⁺ is present in neutralized DMAH-rich sulfate droplets, DMA from the gas phase can displace NH₃ from droplets, and prompt additional NH₃ to evaporate to form non-neutralized particles. Hence, the presence of DMAH can prevent aqueous sulfate particles from full neutralization. In our experiments NH₃ re-volatilization happened at DMAH/NH₃ ratio of above 0.5, which is at the upper end of DMAH/NH₃ measured in atmospheric particles (Sorooshian et al., 2008; VandenBoer et al., 2011; Youn et al., 2015).
At 10% RH, the phase changed from liquid to solid during uptake. This instantly inhibited further DMA uptake, while NH$_3$ uptake continued. Once the particles were fully neutralized, NH$_3$ displaced DMAH$^+$ from crystal structures and finally formed (NH$_3$)$_2$SO$_4$ with little residual NH$_3$DMAH$^+$, regardless of the DMA gas concentrations in the surrounding.

H$_2$C$_2$O$_4$ particles at 70% RH were initially liquid, but transformed into non-crystalline solids after absorbing small amounts of DMA and NH$_3$. Subsequent uptake was similar to that of liquid sulfate particles. The formation of solid, partially neutralized H$_2$C$_2$O$_4$ particles did not hinder DMA uptake. Fully neutralized oxalate particles then crystallized upon displacement of DMAH$^+$ by NH$_3$, similar to the displacement of DMAH$^+$ from crystalline sulfate particles. Anhydrous H$_2$C$_2$O$_4$ at 10% RH was rather inert and took up small amounts of DMA and NH$_3$ presumably by adsorption only.

In solid neutralized particles, NH$_3$ uptake is sterically and thermodynamically favored to form (NH$_3$)$_2$SO$_4$ or ammonium oxalate crystals by displacing DMAH$^+$. Hence, once ambient aerosols are in solid state, they are unlikely to take up R$_3$N, even when R$_3$N and NH$_3$ gas concentrations are of the same magnitude.

In the absence of NH$_3^+$, DMA partially evaporated from DMAH$^+$-rich sulfate droplets. However, in the more common scenarios where NH$_3^+$ is present, DMA can displace NH$_3^+$ from neutral droplets, and cause additional NH$_3$ to evaporate and form non-neutralized particles. Hence, the presence of DMAH$^+$ can prevent aqueous sulfate particles from full neutralization. In our experiments, NH$_3$ re-volatilization required DMAH/NH$_3$ ratios of about 0.5, which is at the upper end of DMAH/NH$_3$ measured in atmospheric particles (Sorooshian et al., 2008; VandenBoer et al., 2011; Youn et al., 2015).

The DMA and NH$_3$ gas concentrations and sulfate neutralization ratios used in the present study are high and are only likely in the vicinity of emission sources or in emission plumes (Sorooshian et al., 2008; Ge et al., 2011). Under such conditions, particle neutralization ratios are likely to be high (Sorooshian et al., 2008), and NH$_3$ and amines compete for particulate H$_3$O$^+$ ions, where DMA can displace NH$_3^+$ in liquid and NH$_3$ can displace DMAH$^+$ in solid particles. Although laboratory experiments have shown that in the absence of NH$_3$, DMA could partially displace NH$_3^+$ from solid ammonium salts including (NH$_3$)$_2$SO$_4$ and NH$_4$NO$_3$ (Lloyd et al., 2009; Qiu and Zhang, 2012; Chan and Chan, 2012, 2013), this scenario is unlikely under atmospheric conditions with abundant NH$_3$.

In this study, we used DMA as a proxy for atmospherically relevant R$_3$N. As different R$_3$N and their sulfate and oxalate salts possess different hygroscopic and crystallization properties (Qiu and Zhang, 2012; Clegg et al., 2013; Chan and Chan, 2013; Chu et al., 2015; Sauerwein et al., 2015) which can all influence uptake behavior, the findings here obtained may not be generalizable to all short-chain aliphatic amine compounds. It should also be mentioned that particle size may affect the particle composition as a result of the uptake, as well as the crystallization of the particle. It should also be mentioned that particle size may affect the gas uptake kinetics, as well as the crystallization behavior of the particle. When applying the results of this study to submicron particles, one may expect a considerably faster uptake and thus changes in DMAH/NH$_3$ ratios in acidic particles. Yet the overall trends of displacement reactions based on phase state and neutralization ratio as well as crystallization inhibition by DMA are considered applicable to particles of smaller size. Nevertheless, the observed results may be most relevant to aerosols larger than 1 µm, which were found in the atmosphere to have the highest R$_3$NH/NH$_3$ ratio (VandenBoer et al., 2011; Youn et al., 2015). To improve our understanding of the mechanisms governing the simultaneous exchange of NH$_3$ and R$_3$N between the gas and particle phases, particle size dependence should be investigated in the future.
Acknowledgements

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References


Table 1: Experimental conditions including relative humidity (RH), gas mixing ratios, the maximum neutralization ratios ($X_{\text{max neutral}}$) and neutralization ratios of equilibrated particles ($X_{\text{equil}}$), and the neutralization ratios of equilibrated particles exposed to $N_2$ for about 5 hours ($X_{N_2N_2}$).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Particle composition</th>
<th>RH (%)</th>
<th>[DMA] (ppm)</th>
<th>[NH₃] (ppm)</th>
<th>Neutralization ratio $^a$</th>
<th>$X_{\text{max neutral}}^b$</th>
<th>$X_{\text{equil}}$</th>
<th>$X_{N_2N_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃, 1.9 ppm, 10%</td>
<td>H₂SO₄(aq)</td>
<td>10</td>
<td>1.94 ± 0.13</td>
<td></td>
<td></td>
<td>2.0 ± 0.1</td>
<td>2.0 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>NH₃, 1.9 ppm, 50%</td>
<td>H₂SO₄(aq)</td>
<td>50</td>
<td>1.93 ± 0.12</td>
<td></td>
<td></td>
<td>1.5 ± 0.1</td>
<td>1.5 ± 0.1</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>DMA, 0.15 ppm, 10%</td>
<td>H₂SO₄(aq)</td>
<td>10</td>
<td>0.16 ± 0.02</td>
<td></td>
<td></td>
<td>1.7 ± 0.1</td>
<td>1.7 ± 0.1</td>
<td>1.7 ± 0.2</td>
</tr>
<tr>
<td>DMA, 0.15 ppm, 50%</td>
<td>H₂SO₄(aq)</td>
<td>50</td>
<td>0.16 ± 0.02</td>
<td></td>
<td></td>
<td>1.7 ± 0.1</td>
<td>1.5 ± 0.1</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td>DMA, 1 ppm, 10%</td>
<td>H₂SO₄(aq)</td>
<td>10</td>
<td>1.00 ± 0.11</td>
<td></td>
<td></td>
<td>1.7 ± 0.1</td>
<td>1.7 ± 0.1</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td>DMA, 1 ppm, 50%</td>
<td>H₂SO₄(aq)</td>
<td>50</td>
<td>1.00 ± 0.11</td>
<td></td>
<td></td>
<td>1.9 ± 0.1</td>
<td>1.9 ± 0.1</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>0.1 ppm, 10%</td>
<td>H₂SO₄(aq)</td>
<td>10</td>
<td>0.14 ± 0.01</td>
<td>1.89 ± 0.04</td>
<td></td>
<td>2.0 ± 0.1</td>
<td>2.0 ± 0.2</td>
<td>2.0 ± 0.4</td>
</tr>
<tr>
<td>0.1 ppm, 50%</td>
<td>H₂SO₄(aq)</td>
<td>50</td>
<td>0.14 ± 0.01</td>
<td>1.89 ± 0.04</td>
<td></td>
<td>2.0 ± 0.1</td>
<td>2.0 ± 0.2</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td>0.5 ppm, 10%</td>
<td>H₂SO₄(aq)</td>
<td>10</td>
<td>0.89 ± 0.03</td>
<td>1.93 ± 0.13</td>
<td></td>
<td>2.0 ± 0.1</td>
<td>1.9 ± 0.2</td>
<td>1.9 ± 0.2</td>
</tr>
<tr>
<td>0.5 ppm, 50%</td>
<td>H₂SO₄(aq)</td>
<td>50</td>
<td>0.89 ± 0.04</td>
<td>1.83 ± 0.04</td>
<td></td>
<td>2.0 ± 0.1</td>
<td>1.8 ± 0.1</td>
<td>1.7 ± 0.2</td>
</tr>
<tr>
<td>ox0.5 ppm, 10%</td>
<td>H₂C₂O₄(s)</td>
<td>10</td>
<td>0.89 ± 0.04</td>
<td>1.82 ± 0.03</td>
<td></td>
<td>0.3 ± 0.1</td>
<td>0.3 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>ox0.5 ppm, 50%</td>
<td>H₂C₂O₄(aq)</td>
<td>70</td>
<td>0.96 ± 0.00</td>
<td>1.86 ± 0.01</td>
<td></td>
<td>1.9 ± 0.2</td>
<td>1.9 ± 0.2</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The neutralization ratio is defined as the number of moles of alkaline species over moles of acidic species, $X = (\text{DMAH}+\text{NH}_4)/\text{SO}_4$ or $X = (\text{DMAH}+\text{NH}_3)/\text{C}_2\text{O}_4$. $^b$ For co-uptake experiments $X_{\text{max neutral}}$ describes the maximum neutralization ratio of particles before reaching equilibrium.
Table 2: Comparison of DMA/NH$_3$ (gas) molar ratios at different RH and DMAH/NH$_4$ (particle) ratios at different times (t), as well as the displacement percentage (χ) for DMAH$^+$ (10% RH) and NH$_4^+$ (50% RH) are given.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>RH</th>
<th>DMA/ NH$_3$</th>
<th>DMAH/NH$_4$</th>
<th>Displacement percentage$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>$t_{\text{initial}}^a$</td>
<td>$t_{\text{pc}}^b$</td>
<td>$t_{\text{neutral}}^c$</td>
</tr>
<tr>
<td>0.10%</td>
<td>10</td>
<td>0.07 ± 0.01</td>
<td>0.07 ± 0.01</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>0.50%</td>
<td>50</td>
<td>0.07 ± 0.01</td>
<td>0.08 ± 0.01</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>0.50%</td>
<td>10</td>
<td>0.46 ± 0.04</td>
<td>0.43 ± 0.04</td>
<td>0.27 ± 0.01</td>
</tr>
<tr>
<td>ox0.5%</td>
<td>50</td>
<td>0.49 ± 0.02</td>
<td>0.34 ± 0.02</td>
<td>0.51 ± 0.04</td>
</tr>
<tr>
<td>ox0.5%</td>
<td>70</td>
<td>0.52 ± 0.52</td>
<td>0.34 ± 0.02</td>
<td>0.34 ± 0.02</td>
</tr>
</tbody>
</table>

$^a$ $t_{\text{initial}}$ indicates the time of the first measurement (10-15 min); $^b$ $t_{\text{pc}}$ indicates the time when the majority of particles changed from liquid to solid phase, $^c$ $t_{\text{neutral}}$ indicates the time when particles reached (maximum) neutralization, $^d$ $t_{\text{equil}}$ indicates the time when the particle composition reached equilibrium, $^e$ The displacement percentage $\chi_{\text{DMAH}^+}$ denotes nDMAH$^+$ per particle at time $t_{\text{pc}}$ over time $t_{\text{equil}}$; $\chi_{\text{NH}_4^+}$ denotes nNH$_4^+$ per particle at time $t_{\text{neutral}}$ over $t_{\text{equil}}$. 
Figure 1: Single gas uptake of NH$_3$ (1.9 ppm) and DMA (1 ppm and 0.15 ppm) into H$_2$SO$_4$, at 10% and 50% RH. NH$_4$/SO$_4$ and DMAH/SO$_4$ denote molar ratios of NH$_3$ or DMA species to total sulfate species in the particle.
Figure 2: DMA- NH₃ co-uptake of DMA and NH₃ into H₂SO₄ as a function of time: a) DMA/NH₃ = 0.07 at 10% RH (0.1% H₂SO₄), b) DMA/NH₃ = 0.46 at 10% RH (0.5% H₂SO₄), c) DMA/NH₃ = 0.07 at 50% RH (0.1% H₂SO₄), and d) DMA/NH₃ = 0.49 at 50% RH (0.5% H₂SO₄). A value of two indicates complete neutralization of H₂SO₄. Contributions of DMAH⁺ (brown) and NH₄⁺ (grey) to the neutralization are shown as molar ratios (DMAH⁺/SO₄ and NH₄⁺/SO₄). Crosshatched NH₄⁺ bars indicate that the majority of particles underwent phase transition from liquid to solid. The inner graph in Fig. 2a is a magnified view of the DMAH⁻ fraction.
Figure 3: Particulate DMAH/NH$_4$ molar ratios as a function of time for DMA- NH$_3$ co-uptake at a) DMA/NH$_3$ = 0.07 at 10% RH (0.1$_{10\%}$), b) DMA/NH$_3$ = 0.46 at 10% RH (0.5$_{10\%}$), c) DMA/NH$_3$ = 0.07 at 50% RH (0.1$_{50\%}$), and d) DMA/NH$_3$ = 0.49 at 50% RH (0.5$_{50\%}$). DMA/NH$_3$ gas molar ratios (including uncertainties) are indicated by the grey bands. Dashed vertical lines indicate that the majority of particles underwent phase transition from liquid to solid. Solid vertical lines indicate that particles reached a neutralization ratio of two. Uncertainties from ion chromatography analysis are displayed on the vertical axis unless they are smaller than the symbols.
Figure 4: Comparison of particulate DMAH/\text{SO}_4 (a, b) and NH_4/\text{SO}_4 (c, d) in single gas uptake (line) vs. DMA-NH_3 co-uptake (symbols) into H_2\text{SO}_4 at 10\% RH (a,c) and 50\% RH (b, d), in the first 8 hours of reaction. Dashed vertical lines indicate phase transition of the majority of particles. Solid vertical lines indicate that particles reached a neutralization ratio of two. Uncertainties from ion chromatography analysis are displayed on the vertical axis unless they are smaller than the symbols.
Figure 5: Comparison of particulate NH₄/SO₄ in single gas uptake (filled triangles) vs. DMA–NH₃ co-uptake (open triangles) experiments at 10% RH into H₂SO₄: a) DMA/NH₃ = 0.07, and b) DMA/NH₃ = 0.46. Diamonds denote the net-uptake neutralization ratio (X) in co-uptake experiments. Error bars are omitted for clarity.
Figure 6: Raman spectra of selected particles representing different phase states during uptake of NH$_3$ into H$_2$SO$_4$ at 10% RH. A spectrum of crystalline (NH$_4$)$_2$SO$_4$ is added for reference. Sketches indicate the cation composition range (as inferred from IC measurements) of particles when the spectra were recorded; grey denotes NH$_4^+$ and blue denotes H$_3$O$^+$ (HSO$_4^-$).
Figure 7: Raman spectra and morphological changes of selected particles during DMA - NH$_3$ co-uptake into H$_2$SO$_4$ at 10% RH at a DMA/NH$_3$ molar ratio of 0.46 (0.510%). Sketches indicate the cation composition range (as inferred from IC measurements) of particles when the spectra were recorded. Orange denotes DMAH$^+$, grey denotes NH$_4^+$, and blue denotes H$_3$O$^+$ (HSO$_4^-$).
Figure 8: DMA–NH₃ co-uptake at DMA/NH₃ gas molar ratios of 0.5 (given in Table 1) into sulfuric and oxalic acid particles at 10%, 50% and 70% RH. a) Neutralization ratios as a function of time. The vertical dotted line indicates that the majority of oxalic acid particles at 70% RH underwent phase transition from liquid to solid; the vertical solid line indicates the morphological transformation of oxalic acid particles from a non-crystalline to a crystalline morphology at 70% RH. b) DMAH/NH₄ ratios as a function of particle neutralization ratio; the shaded area indicates the gas phase molar ratio of DMA/NH₃ (including uncertainties).
Figure 9: Particle neutralization ratios and the proportion of each cation at maximum neutralization (first column), equilibrium (second column), and after exposure of equilibrated particles to \( \text{N}_2 \) gas (third column). Color scheme: orange represents DMAH\(^+\), grey represents \( \text{NH}_4^+ \), shaded areas indicate uncertainty of the respective species, and blue represents \( \text{H}_3\text{O}^+ \) (HSO\(_4^-\)). Stars around pie charts indicate that particles were crystalline solids. Concentrations of DMA and \( \text{NH}_3 \) are shown in Table 1.