

# 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 #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 alkylammonium 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 alkylammonium ions ( $R_3NH^+$ ) 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-ammonium 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-ammonium 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-ammonium sulfates was shown to increase from primary to tertiary ammonium sulfate. The difference in hygroscopicity decreases as extent of neutralization decreases to bisulfate composition, where ammonium 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 NH<sub>3</sub> flow (1.8-1.9 ppm) resulted in DMA/NH<sub>3</sub> 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<sub>2</sub>SO<sub>4</sub> (Table 2), and 0.49±0.02 at 10% and 0.52±0.01 at 70% RH for experiments with H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.”

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/SO<sub>4</sub>, NH<sub>4</sub>/SO<sub>4</sub> 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<sub>10%</sub> and 0.1<sub>10%</sub>, respectively) to completely neutralize sulfate.”

*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.

*Anonymous Referee #2: Section3.2: NH<sub>3</sub> displaced DMAH...should this be NH<sub>4</sub>? And then in paragraph below NH<sub>4</sub> 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<sup>+</sup> is displaced by NH<sub>4</sub><sup>+</sup> 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.

*Anonymous Referee #2: Also recommended to check notation such as NH4 vs. NH4+, which appears to be used inconsistently.*

**Response:** Following the definition in section 2.3, we use DMAH to represent particle phase  $n\text{NH}_2(\text{CH}_3)_2^+ + n\text{NH}(\text{CH}_3)_2$ , NH<sub>4</sub> to represent  $n\text{NH}_4^+ + n\text{NH}_3$ , SO<sub>4</sub> to indicate total amount of sulfate species =  $n\text{H}_2\text{SO}_4 + n\text{HSO}_4^- + n\text{SO}_4^{2-}$ , and C<sub>2</sub>O<sub>4</sub> to indicated total amount of oxalate species (*n* denotes the molar amounts of each compound). The manuscript was reviewed and expressions such as NH<sub>4</sub><sup>+</sup> and NH<sub>4</sub>-species were consistently named as NH<sub>4</sub>, the same was done for DMAH.

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

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

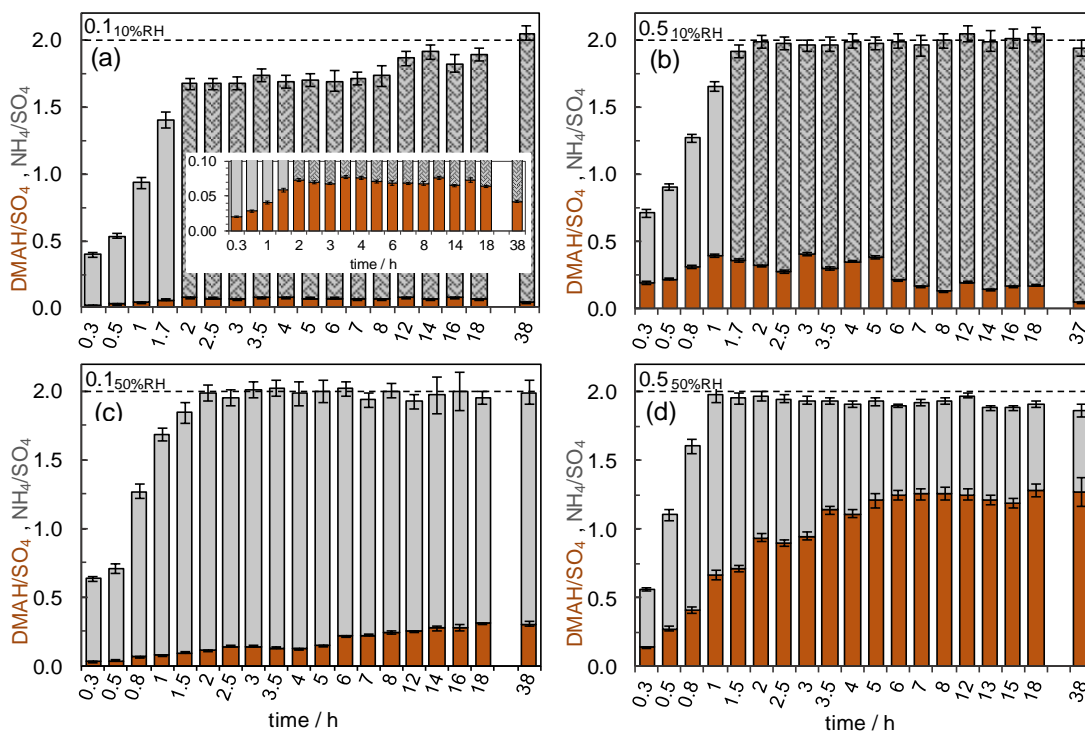
“During  $\text{NH}_3$ -DMA co-uptake the absorbed DMAH seems to have suppressed the precipitation of  $\text{NH}_4\text{HSO}_4$  in particles with a composition of  $1.1 < \text{NH}_4/\text{SO}_4 < 1.5$ , so that the phase change started only at a  $\text{NH}_4/\text{SO}_4$  around 1.5 (Fig. 5a and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

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

**Response:** the term  $X_{\text{N}_2}$  in Table 1 and the table caption have been updated to  $X_{\text{N}_2}$ .

*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



## References

- Chu, Y., Sauerwein, M., and Chan, C. K.: Hygroscopic and phase transition properties of alkyl aminium sulfates at low relative humidities, *Phys. Chem. Chem. Phys.*, 17, 19789–19796, 2015.
- Qiu, C., Wang, L., Lal, V., Khalizov, A. F., and Zhang, R.: Heterogeneous reactions of alkylamines with ammonium sulfate and ammonium bisulfate, *Environ. Sci. Technol.*, 45, 4748–4755, 2011.

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Sauerwein, M., Clegg, S. L., and Chan, C. K.: Water Activities and Osmotic Coefficients of Aqueous Solutions of Five Alkylaminium Sulfates and Their Mixtures with H<sub>2</sub>SO<sub>4</sub> at 25°C, *Aerosol Sci. Tech.*, 49, 566–579, 2015.