

## Review of

The role of H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub> anion clusters in ion-induced aerosol nucleation mechanisms in the boreal forest

by

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This paper analyzes data from springtime observations at the Hyytiälä observatory carried out in 2011, 2012, and 2013. Measurements of ion chemical composition were made using the Atmospheric Pressure interface Time of Flight Mass Spectrometer (APi-TOF), while measurements of precursor vapor concentrations (H<sub>2</sub>SO<sub>4</sub>, and HOM) were measured by chemical ionization mass spectrometry. NH<sub>3</sub> was also measured. In addition, a DMPS system was used to measure aerosol size distributions (3-990 nm), and neutral particle (2.5-42 nm) and ion (0.8-42 nm) number distributions were measured with the NAIS. These data were used to calculate particle growth rates and ion induced and neutral particle nucleation rates. Some evidence for ion induced nucleation (IIN) was found on about 50% of measurement days, although IIN rates were less than neutral particle nucleation rates. When IIN was observed, anions comprised of H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub> were dominant on about 50% of the time. However, when [HOM]/[H<sub>2</sub>SO<sub>4</sub>] exceeded 30, the dominant IIN pathway appeared to involve HOM. This is a nice study that provides valuable new insights into the chemical processes that lead to IIN at this location. It is significant work based on excellent observational results. The paper is concise and clearly written. I recommend publication in ACP, and offer a few suggestions for the authors to consider.

### Suggestion:

On p. 11 the authors point out that the likelihood of H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub> IIN depends strongly on [H<sub>2</sub>SO<sub>4</sub>]/CS. When this ratio equaled about 10<sup>10</sup> cm<sup>-3</sup>s, IIN was observed, while IIN was far less likely when [H<sub>2</sub>SO<sub>4</sub>]/CS=10<sup>9</sup> cm<sup>-3</sup>s. McMurry and coworkers (McMurry et al. 2005) argued that the likelihood that nucleated clusters will grow into new particles decreases rapidly when the dimensionless parameter,  $L$ , exceeds a value on the order of 1. Kuang and coworkers (Kuang et al. 2010) showed that new particle formation was rarely observed when  $L > 0.7$ . From equations [A3] and [A5] of McMurry et al (2005), it is straightforward to show that:

$$L = \frac{CS}{[H_2SO_4]} \cdot \frac{1}{\beta_{11}}$$

where  $\beta_{11}$  is the collision rate between H<sub>2</sub>SO<sub>4</sub> vapor molecules. A characteristic value for  $\beta_{11}$  is  $4.4 \times 10^{-10}$  cm<sup>3</sup>s<sup>-1</sup>. It follows then for these data, H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub> IIN was observed for  $L \sim 0.22$  but not for  $L \sim 2.2$ . This is consistent with theoretical expectations and prior work, and would move the authors closer to providing a quantitative theoretical explanation for the S IIN results shown in Figure 5F.

### Points that should be clarified.

- Line 26, p. 1: “All such clusters were observed...” In the context of this sentence, this implies that all clusters from #S=3 to infinity were observed. This is obviously not what is intended.
- p. 4, line 120: “...a best instrument...” The previous sentence acknowledges that some fragmentation occurs. It might also be mentioned that the extent of fragmentation is not quantitatively understood. Have the authors confirmed that the API-TOF produces less fragmentation than other mass spectrometers with different interface designs? I don’t think so.

Minor editorial corrections:

The paper contains numerous minor, distracting language errors, which I illustrate with the following examples. The text should be thoroughly edited by a native English speaker.

- p. 2, line 57: should be “as ion-induced...”
- p. 4, lines 111-112: “..often dominates the daytime spectrum in the daytime when it is abundant...” ???
- p. 4, line 118: replace “comparing” with “compared”
- p. 4, line 127: delete “,”
- p. 5, line 163: delete “In specific,”
- p. 11, Figure 3 caption: replace “unclear is IIN...” with “unclear if IIN...”
- p. 11, line 285: delete “however” (Alternatively, it could be separated using commas, but this would make for an awkward sentence.)
- p. 12, line 309: “this type of days...”
- p. 12, line 310: “are conducive of IIN events...”
- p. 12, line 315: “has not been evidenced,...”
- p. 14, Figure 5: Difficult to distinguish blue from black boxes.
- p. 14, line 349: “This indicate the...”
- p. 15, line 371: “The abundancy and ...”

Kuang, C., I. Riipinen, T. Yli-Juuti, M. Kulmala, A. V. McCormick and P. H. McMurry (2010). "An improved criterion for new particle formation in diverse atmospheric environments." *Atmospheric Chemistry and Physics* **10**: 1-12. doi: 10.5194/acp-10-1-2010.

McMurry, P. H., M. A. Fink, H. Sakurai, M. R. Stolzenburg, L. Mauldin, K. Moore, J. N. Smith, F. L. Eisele, S. Sjostedt, D. Tanner, L. G. Huey, J. B. Nowak, E. Edgerton and D. Voisin (2005). "A Criterion for New Particle Formation in the Sulfur-Rich Atlanta Atmosphere." *Journal of Geophysical Research - Atmospheres* **110**: D22S02. doi: 10.1029/2005JD005901.