

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.

We would like to thank the referee for the suggestions and careful editorial comments. We reply to the comments item by item below (text in blue):

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=109 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 4.4e-10 cm<sup>3</sup>s<sup>-1</sup>. It follows that for these data, H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub> IIN was observed for L~0.22 but not for L~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-E IIN results shown in Figure 5F.

Indeed, adding the discussion on the parameter L will move the observation towards more quantitative. We have added the following discussion:

“McMurry and coworkers (McMurry et al., 2005) have introduced a parameter L (Eq.3) to quantitatively evaluate the likelihood of NPF, and they found that NPF mostly occurred when L is smaller than 1. A similar result has been reported by Kuang et al., (2010), and a slightly different threshold L value 0.7 was determined.

$$L = \frac{CS}{[H_2SO_4]} \cdot \frac{1}{\beta_{11}} \text{ (Eq.3)}$$

Here, L is dimensionless parameter representing the probability that NPF will not occur, and  $\beta_{11}$  is the collision rate between H<sub>2</sub>SO<sub>4</sub> vapor molecules, which is characterized as 4.4× 10<sup>-10</sup> cm<sup>3</sup>s<sup>-1</sup>. Our results suggest a consistent L that most (75 percentile) S-E cases happen when L is lower than 0.73 and most (75 percentile) S-NE cases are observed when L is larger than 1.54.”

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.

We explicitly mention the maximum number of H<sub>2</sub>SO<sub>4</sub> in the sentence now:

“controlled the appearance of H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub> clusters (3< #S < 13): All such clusters were observed when [HOM]/[H<sub>2</sub>SO<sub>4</sub>] was smaller than 30.”

- 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.

The referee is right that fragmentation is very likely to happen inside the instrument, which has not been well quantified. On the other hand, as we stated in the manuscript, no ionization can be used if we aim to measure these weakly bonded clusters. Under such circumstances, the APi-TOF is very suitable for cluster measurement. As also pointed out by the other referee, we replace "a best instrument" by "a well suited instrument".

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..."

Modified.

- p. 4, lines 111-112: "...often dominates the daytime spectrum in the daytime when it is abundant,..." ???

We removed the "daytime" in the sentence.

- p. 4, line 118: replace "comparing" with "compared"

Modified.

- p. 4, line 127: delete " ;"

Modified.

- p. 5, line 163: delete "In specific,"

Modified.

- p. 11, Figure 3 caption: replace "unclear is IIN..." with "unclear if IIN..."

Modified.

- p. 11, line 285: delete "however" (Alternatively, it could be separated using commas, but this would make for an awkward sentence.)

Modified.

- p. 12, line 309: "this type of days..."

Modified

- p. 12, line 310: "are conducive of IIN events..."

Our original wording seems right.

- p. 12, line 315: "has not been evidenced,..."

Modified

- p. 14, Figure 5: Difficult to distinguish blue from black boxes.

We change the black box to grey in Figure 5.

- p. 14, line 349: "This indicate the..."

Modified.

- p. 15, line 371: "The abundancy and ..."

Modified.

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.

The manuscript analyzes cluster ion data from the SMEAR station in Hyytiälä, Finland, from three springtime measurement periods. Data from anion measurements with an APi-TOF mass spectrometer and an NAIS instrument are analyzed. The focus of the analysis is on H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub> cluster ions in comparison to HOM ions and their relation to aerosol nucleation events. It is found that the ratio between [HOMs] and [H<sub>2</sub>SO<sub>4</sub>] controls the presence of large H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub> clusters. Furthermore, the probability for IIN to occur is largest and reaching almost 100% when clusters containing 6 or more H<sub>2</sub>SO<sub>4</sub> molecules are present. The contribution of IIN to the total nucleation is reported to range between 4 and 45%, with an average of 12% contribution for cases that are dominated by H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub> nucleation and 18% in HOM-driven events. The manuscript is an extension of a series of papers focusing on results from the APi-TOF measurements in Hyytiälä (e.g. Ehn et al., 2010 and 2011, Schobesberger et al., 2013 and 2015; Yan et al., 2016; Bianchi et al., 2017). The previous papers focused mostly on the role of HOMs while this one focuses on the role of H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub> anion clusters, therefore the paper presents sufficient new material to warrant publication in ACP. There is a number of minor points and technical corrections to consider before publication in ACP:

We would like to thank the referee for the helpful and detailed comments and suggestions.

In the following, we reply to the referee's comments item by item.

Minor points

line 43: The paper by Dunne et al., Science, 2016 should be referenced here as well.

Agreed. The paper is referenced

136: quantification of the APi-TOF results. Was the transmission of the APi-TOF characterized as described by Heinritzi et al., AMT, 2016? Can you be sure that the transmission did not change due to the changes in tuning (l 139)?

First, we believe the question is about quantification with CI-APi-TOF.

The data used here were not corrected for transmission calibration, as this instrumental fact was not recognized back to the years when the measurement was done. On the other hand, to obtain a systematic dataset of sulfuric acid and HOM concentration, the voltage tuning of the instrument was not very different between years included in this work. We attached a year-distinguished figure using the same data as in Figure 2B, in which we can see data from different years are well-mixed.

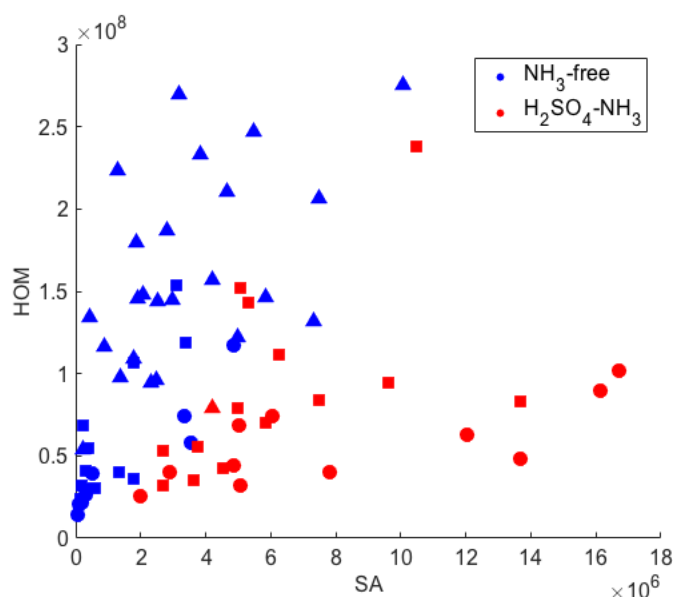


Figure R1. The effect of concentration of HOMs and H<sub>2</sub>SO<sub>4</sub> on the appearance of H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub> clusters. Symbols represent data from different years, circles for 2011, squares for 2012 and triangles for 2013.

181: What about recombination with ions larger than 3.5 nm?

In our calculation: the loss term of ions in the J<sub>IIN</sub> equation are divided into two terms:

1 – Ion-Ion recombination: the ions in the size bin (2.5-3.5 nm) become neutrals however stay in the size bin itself, since they recombine with < 3.5 nm ions (4<sup>th</sup> term in Eq 2).

2 – Coagulation sink: Ion loss term to coagulation which is the loss of ions to bigger sized particles or ions (>3.5 nm), leading to their loss outside of the size bin (2<sup>nd</sup> term in Eq 2).

Figure 2: panel B is as important as panel A. Why is B just shown as a small inset? Please show B as a separate panel of the same size as A, or even as a separate Figure.

Agreed. The Figure 2B was made in parallel with Figure 2A.

347: Please explain in detail how J<sub>IIN</sub> for 2.5 nm particles was calculated (here, or in Section 2).

Formation rates of 2.5 nm particles (J<sub>2.5</sub>) and ions (J<sub>IIN 2.5</sub>) are calculated using equations Eq (1) and (2) in section 2 lines 176 and 184, respectively.

404-575: Please check all references carefully: In many cases there are co-authors missing (and no “et al.” is included), e.g. Bianchi et al., 2017, Dada et al., 2017, Ehn et al., 2010, Ehn et al., 2011, Kulmala et al., 2004, Schobesberger et al., 2013 and 2015, and even in Yan et al., 2016, and many others.

Modified.

General comment on choice of cited references: There is no doubt that the Kulmala group has produced lots of important research with respect to ground-based cluster ion composition measurements with the APi-TOF in Hyytiälä, and it is therefore ok to reference the previous work of your own group frequently. Nevertheless, there have been various contributions to the field of H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub>-IIN by other groups and the choice of references discussed for example in the introduction seems somewhat unbalanced. Out of the 34 references listed in the references section, 29 are from the Kulmala group or co-authored by the Kulmala group (and the 5 remaining references are mainly general ones such as reviews or the IPCC report). It is expected in scientific publications to give reference also to the previous work by others that is relevant for your work. Therefore I suggest to mention/discuss also work from other groups, e.g. Eisele et al., JGR, 2006; Iida et al., JGR 2006, Tammet et al., Atm. Res. 2014; Rose et al., ACP, 2013; Boulon et al., ACP 2010; Kurten et al., JGR, 2016; Froyd and Lovejoy, JPC, 2011, etc. to give some credit also to the rest of the scientific world that performed measurements of H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub> ion induced nucleation and other ion clusters. Also Bianchi et al., Science, 2016; Dunne et al., Science, 2016, and Wagner et al., ACP, 2018, should be included and discussed in the context of this paper (I recognize that these are also coauthored/authored by the Helsinki group).

The reviewer is right that some previous work about IIN should also be referenced. According to their relevance to this work, we have added Eisele et al., 2006; Iida et al., 2006; Kurten et al., 2016, Lovejoy et al., 2004; Wagner et al., 2017; Dunne et al., 2016 into the reference list.

Technical corrections:

line 65 and 67. Bianchi et al. is referenced twice, one time within a sentence is sufficient.modified  
Modified.

75: understandings to understanding

Modified.

92: insert space between semicolon and Ehn, as well as between semicolon and Yan

Modified.

111: “daytime spectrum in the daytime...” avoid duplication

Modified by removing “daytime”

113: “of an ion in the APi-TOF...”

Modified.

115: “note that the APi-TOF...”

Modified.

119: “instruments” to “instrument”

Modified.

120: “is a best instrument” to “is a good...” or “is a well-suited...”

We replace “a best” to “a well-suited”.

127: not the same in the three years...

Modified.

129: “clusters contained 6 clusters” to “clusters contained 6 SA molecules”

Modified.

130: “in the clusters were observed” to were observed in the clusters

Modified.

131: larger than 700 Th for the measurements in 2011.

Modified.

133: Figure 3 is called here before Figure 2 is called. Change order of Figures 2 and 3.

We feel the logic flow goes better with the current figure order. Instead, we avoid calling Figure 3 by rephrasing the sentence to

“because clusters consisting of 6 H<sub>2</sub>SO<sub>4</sub> molecules had little difference from larger clusters in affecting the IIN in terms of occurrence probability (see more details in Sect. 3.3.1).”

139: tunings of CI-APi-TOF → tuning of the CI-APi-TOF

Modified.

181, 184: “Eq. S2” → change numbering of the Equation to “Eq. 2”

Modified.

197: A similar approach

Modified.

204: measurements → measurement

Modified.

204: dependant → dependent

Modified.

242: prevents → suppresses

Modified.

261: “by observing an increase...” (delete “of”)

Modified.

262: “sub-2nm ions”, I think you mean “ions larger than 2 nm” here?

We meant the total signal of ions up to 2 nm. We rephrase this sentence to “... by observing an increase in the total concentration of sub-2 nm ions”

279: "...unclear is IIN occurred was counted..." → "...unclear if IIN occurred were counted..."  
Modified.

289: permanence → continuity  
Modified.

319 and 324: the other type of events  
Modified.

321: less → lower  
Modified.

322: clusters at high temperatures that can evaporate NH<sub>3</sub> back to the atmosphere.  
Modified.

340: Figure 5, panel B: "cloudiness parameter" should probably be "clear-sky parameter", or it should be explained that 1 = clear-sky = 0% cloudiness; and 0 = 100% cloudiness  
We agree that the terminology is a bit confusing. For consistency, we do not change it, but instead, we add the definition in the text:  
"The clear-sky parameter (100% = clear sky and 0% = cloudiness) shows a noticeably higher value during both event types compared to the non-event cases (Fig. 5B)"

349: This indicates  
Modified.

361: Figure 6, panels B and C could be depicted with identical y-range (e.g. 10<sup>-2</sup> to 20), then a comparison would be easier. At least some tick marks should be added to panels B and C.  
Modified. The color for "O-E" is changed to blue in order to be consistent with Figure 5.

368 "Summary and Conclusions" → "Summary" (there are no new conclusions, it is just a summary of the findings presented previously)  
Modified.

380: from → for  
Modified.

382: on other days  
Modified.

385: a mechanism  
Modified.

385: at least responsible for → responsible for at least  
Modified.

404: Reference → References  
Modified.