

***Interactive comment on* “Case studies of particle formation events observed in boreal forests: implications for nucleation mechanisms” by F. Yu and R. Turco**

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Reply to Referee #1’s comments

The authors thank the referee for the constructive and up to the point comments. Our detailed replies to the referee #1’s comments (in *Italic*) are given below.

Anonymous Referee #1

Major comments:

The main point made by the authors in this paper that the observed overcharging ratios (OR) clearly greater than unity (roughly 80% of the measurement days) are indicative of a "significant" contribution from ion-mediated nucleation and that in only about 20%

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of the nucleation event days an alternative nucleation mechanisms is needed. This statement is backed up by four simulated cases which show that pure ion-mediated nucleation is able to produce many observed features of the events, including the total number concentration of 3-6 nm particles and the values of measure OR above 3 nm. It remains unclear what is meant by the term "significant".

1. By comparing predicted and observed key variables related to nucleation events, we show that ion-mediated nucleation (IMN) appears to be able to fully account (within the range of observational uncertainty) for the observed nucleation rates on four well-defined case study days that exhibited medium to high electrical overcharging of freshly nucleated particles. The observed OR values on about 80% of nucleation event days are within, or exceed, the OR range represented by the four case study days. Since the OR value is a direct indicator of ion-mediated nucleation, as demonstrated quantitatively by the simulations of these events, it is reasonable to infer that IMN is most likely the dominant source of particles on other days with similar OR values. While the specific results therefore indicate a dominant role for IMN, we use the term "significant" to account for the possibility of contributions from other nucleation sources that may not have been identified, or defined in such a way that they can be explicitly modeled on the same molecular basis as IMN. This point, aimed at uncertainty, will be clarified in the revised paper.

We should also note that an alternative nucleation mechanism is not the only possibility for explaining the ~20% of nucleation event days with weak overcharging or weak undercharging. As we show in the paper, the appearance of a weak overcharge or undercharge may be associated with variability in the air mass sampled – which mimics a time dependence in the observed variables even when IMN is contributing substantially to particle formation.

I fully agree that ion-mediated nucleation must explain some fraction of new-particle formation during days with OR greater than unity but I cannot agree that the results presented in the paper demonstrate convincingly that this fraction would be close to

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100%. Below I have listed a few detailed arguments in this regard.

2. We have noted in our paper that the present case studies have uncertainties, both in the model and the measurements used to constrain the simulations. In the last paragraph of the paper, we discuss additional work that may help to reduce these uncertainties. Nevertheless, the simulations presented in the present paper are the most comprehensive, well-constrained, and detailed case studies of atmospheric nucleation processes to date (at least to our knowledge). Considering the nature of the comparisons and the overall agreement among multiple variables, we think that we have made a strong case (beyond a reasonable level of uncertainty) for the dominant role of IMN in at least a large fraction of nucleation events observed during the field campaign in boreal forests. The detailed arguments given below by the referee, when considered with our responses, do not materially change this conclusion.

First, as demonstrated by Laakso et al. (2007, ACP, 1333-1345) and in detail by Kerminen et al. (2007, JGR, D21205), the functional dependence of OR on the particle diameter is highly sensitive to the particle growth rate. The authors assume that only sulfuric acid contributes to the growth of sub-3 nm particles. This assumption results in the smallest possible growth rate for sub-3 nm particles and, more importantly, the smallest possible values of OR above 3 nm. If the authors allowed higher growth rates for sub-3 nm particles, their simulations would predict larger values of OR above 3 nm, which would be inconsistent with the measured values of OR. My point here is that without really knowing the growth rate of sub-3 nm particles, it is impossible to state whether the apparent "consistency" between simulated and observed values of OR is indicative of a dominant contribution from ion-mediated nucleation or whether it simply results from too low growth rates assumed in these simulations.

3. It is true that the functional dependence of OR on the particle diameter is highly sensitive to the particle growth rate. It is also true that higher growth rates for sub-3 nm particles would lead to larger values of OR above 3 nm. However, the referee has over-estimated the uncertainty in the growth rate of sub-3 nm particles.

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The growth rate of sub-3 nm particles can be constrained by the time-delay between the increase in $[H_2SO_4]$ and N_{3-6} during the morning hours. We assume that only sulfuric acid contributes to the growth of sub-3 nm particles, not to obtain the smallest possible values of OR above 3 nm, but because the condensation of H_2SO_4 (and associated water uptake) can, roughly speaking, fully explain the initial growth rates of sub-3 nm particles (see Fig. 9 for the time delay between an H_2SO_4 increase and the N_{3-6} increase on the mornings of the days with clear overcharging). Indeed, almost everyone now agrees that the activation size of the initial particle embryos for the condensation of secondary growth materials (e.g., organics, yet to be identified by species) is probably on the order of 3 nm diameter. Smaller values of D_{act} lead to larger growth rates for sub-3 nm particles and shift the simulated increase in N_{3-6} to earlier times, which is less consistent with observations. These arguments are spelled out in the paper on page 5697. Of course, if other condensates on the young embryos are identified, and they change the thermodynamics and growth rates of the embryos substantially, the ORs could be affected accordingly.

While we believe that it is reasonable to assume the dominant contribution of H_2SO_4 (and associated water) to the growth of sub-3 nm particles, we acknowledge that it is quite possible that other materials (e.g., organics) may also contribute to the growth of sub-3 nm particles under some conditions. We carried out sensitivity tests in which we decreased D_{act} from 3 nm to 2.5 nm and then to 2 nm, and thus allowed "organic" condensation above these sizes. A value of D_{act} of 2 nm obviously overestimated the growth rates of sub-3 nm particles because the simulated increases in N_{3-6} clearly preceded those of observed beyond the uncertainty range. Moreover, the average ORs predicted for $D_{act}=2.5$ nm and 2 nm, while higher than those for $D_{act}=3$ nm, still fall within the range of observed average OR values shown in Fig. 11.

Second, neither Laakso et al. (2007) nor this study considers the diurnal variability of the measured values of OR. From Figure 10 it is clear that the simulated values of OR vary diurnally, probably because of the variability of the simulated growth rate of sub-3

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nm particles. Simulated values of OR are usually highest around noon, as one might expect due to the highest sulfuric acid concentrations. Since also nucleation is most active during high sulfuric acid concentrations, the agreement between the simulated and observed values of OR should be best at this time of the day in case one has assumed the correct nucleation mechanism. Again, without knowing observed values of OR around the noontime, great care should be taken before stating anything about the agreement between simulated and observed values of OR.

4. In addition to the growth rates, the difference in the growth rate and stability between charged and neutral clusters/particles also affects the OR values. The diurnal variability of simulated ORs differs for different days (Fig. 10) and it is not true in general, based on our model, that "Simulated values of OR are usually highest around noon". For example, ORs for 3 nm particles are highest during the morning hours on April 18 and May 12 (Fig. 10).

We agree with referee that the comparisons of simulated and observed time-resolved ORs (instead of average values) will add additional insight into the nucleation processes at work, and will further constrain models when these data are available. However, we feel that comparisons of average values are also reasonable and useful at this stage, considering the significant fluctuations in the measured ORs (see Fig. 7 in Laakso et al., 2007) and other uncertainties that exist.

Third, as the authors certainly know, the survival rate of nucleated particles is highly sensitive to both the growth rate of sub-3 nm particles and condensation sink (which determines the scavenging rate of growing clusters). Neither of these two quantities is known very accurately in these simulations. As a result, there is an inherent uncertainty in the production rate of 3-6 nm particles regardless of whether the simulated nucleation rate is correct or not.

5. With regard to the growth rate of sub-3 nm particles, please refer to point 3 above. As we discuss in the paper, both the condensation sink and the concentration of condens-

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able organics affect the simulated N_{3-6} , and there exist uncertainties in both terms. However, the values of these parameters used in our simulations were chosen carefully based on the information available in the relevant literature, and we think that these chosen values are representative of the conditions that prevailed during the experiments under investigation.

For the type of study presented here, some level of uncertainty is unavoidable, of course. As we mentioned previously, the case studies are perhaps the most constrained simulations of specific atmospheric nucleation events to date. We certainly agree, and state in the paper, that further research is needed to reduce uncertainties. However, it is also reasonable to conclude, based on the overall comparisons among multiple variables in the present work, that IMN seems to be able to account for many, if not most, of the nucleation events observed in boreal forests, as described in various publications.

Finally, on the bottom of page 5700 the authors state that "The large variations in the observed OR values for particles at given sizes (3, 4, 5 nm) on different days are likely to be associated with variations in the concentrations of the key precursor cases...". I fully agree that these things cause variability in observed OR. However, based on the above, I do not think that the authors can use the term "likely" in this context without considering the other likely reason for the observed variability, which would be that the contribution of ion-mediated nucleation has varied from day to day.

6. We disagree that the variations in observed OR values at particle sizes of 3, 4, and 5 nm on different days can be specifically connected with changes in the relative contribution of IMN. As can be seen from the four simulated curves in Fig. 11, simulated ORs at different sizes predicted by the IMN model vary significantly on different days because of differences in precursor concentrations and other environmental parameters. In other words, the variations in OR are directly connected to variability in other constrained parameters, quantitatively, and in a physically consistent way as represented by the model thermodynamics and kinetics. Nevertheless, as we point out in

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the paper, other (yet to be identified) nucleation mechanisms may need to be invoked in particle formation on days with weak overcharge or clear undercharge. Unfortunately, there are no quantitative mechanisms available at this time that we can include to represent these possibly significant, but more speculative, processes. We will modify the text of the paper to reflect this argument.

Other comments:

The authors should be very careful in what they say about the potential role of ternary sulfuric acid-ammonia water nucleation in these events. First, none of the existing ternary nucleation theories have really been tested properly in their overall performance.

But we do know that, based on laboratory studies, sulfuric acid concentrations exceeding $\sim 10^9 \text{ cm}^{-3}$ are needed to initiate $\text{H}_2\text{SO}_4 - \text{H}_2\text{O} - \text{NH}_3$ ternary homogeneous nucleation (THN) under boundary layer conditions. While not shown in Fig. 12, the calculated THN rates for all six case study days are negligible (well below $10^{-5} \text{ cm}^{-3} \text{ s}^{-1}$ based on both the revised classical THN model of Merikanto et al. (JGR, D15207, 2007) and the kinetic THN model of Yu (JGR, D01204, 2006). We will clearly state these modeling results in the revised paper.

Second, statements like "ammonia would enhance binary water-sulfuric acid nucleation by only 1-2 orders of magnitude" may not be true for atmospheric conditions.

The referee is technically correct, although the laboratory evidence points in this direction. We will alter the text accordingly to be more specific here.

Third, the fact that the observed particle formation rates do not seem to correlate with ammonia levels is not evidence that ammonia is not participating in new particle formation. It could be possible that the nucleation rate is not very sensitive to the exact ammonia concentration at those concentration levels, or that days with higher ammonia concentrations are not as favorable to nucleation for other reasons (such as higher

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condensation sink).

Based on the THN theory, the nucleation rate should be sensitive to ammonia concentrations at the measured levels. We merely note the observed lack of a correlation, which seems inconsistent with THN theory. On the other hand, the referee is speculating on matters for which there is no evidence as far as we know.

The authors should avoid using "grey literature", such as referee or author comments related to ACPD papers, in their text.

We cite the ACPD comments to point out the unresolved arguments about the role of ions in atmospheric nucleation, as one of the main motivations for the present paper. Nevertheless, to address the referee's concern, we will remove the reference to previous ACPD comments.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 5683, 2008.

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