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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

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General:

In this manuscript, kinetic model simulating ion-mediated nucleation is tested against field data obtained during a number of selected measurement days in the SMEARII station in Hyytiala, Finland. The results are then discussed with respect to other potential nucleation routes and compared with predictions obtained from another model simulating ion-induced nucleation. In principle, this kind of exercise is extremely useful in testing the overall performance of alternative nucleation theories and in filling our gaps in understanding this phenomenon. There are, however, a few issues that should be addressed more carefully before the paper can be accepted for publication in ACP.

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Discussion Paper

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% 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". I fully agree that ion-mediated nucleation explain must 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 100%. Below I have listed a few detailed arguments in this regard.

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.

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.

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.

Finally, on the bottom of page 5700 the authors state that "The large variations in the observed OR values for particles at give 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 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.

Other comments:

The authors should be very careful in what the 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. 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. Third, the fact that the observed particle formation rates do not seem to correlate

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with ammonia levels does 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 condensation sink).

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

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