

Interactive comment on “Kinetic nucleation and ions in boreal particle formation events” by L. Laakso et al.

Anonymous Referee #1

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In this paper, the authors present and analyze the particle formation measurements obtained during a field campaign (QUEST-2). The presented data on the simultaneous measurements of the evolution of sulfuric acid gas concentration, ion cluster size distributions (diameters range from 0.3 nm to 50 nm), and nanoparticle size distributions (down to 3 nm) are unique and provide useful information to test various nucleation mechanisms. From the observed properties of ion cluster size distributions, the authors conclude that ions are involved in the particle formation. The authors also investigate the possibility of kinetic nucleation to explain the observed evolution of ion size distributions, using an aerosol microphysical model and with various assumptions about nucleation and cluster growth. Based on the model simulations, the authors claim that the relative contribution of ion-based particle formation is smaller than kinetic nucleation of neutral clusters and that their findings corroborate the TSCs hypothesis. Over-

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all, this paper presents some unique and original results that will be of interesting to many researchers in the field. However, this paper has flaws in the interpretation of the observations and some conclusions are not fully justified. I recommend the publication of this paper in ACP after the following comments are addressed properly.

Major comments:

1. About Equation (1) ($J=K C^2$). A significant fraction of the model interpretations presented in this paper are based on the assumptions that ammonia stabilizes all the clusters and the nucleation rate is determined by equation (1) (i.e., the collision rate of sulfuric acid molecules). I have several doubts about the validity of these assumptions.

(a) The authors assume that the formation rate of ammonium bisulphate clusters is limited by sulfuric acid molecules. Does this mean that sulfuric acid molecules, once formed, is converted to ammonium bisulphate quickly? If this is the case, H_2SO_4 should not be able to accumulate to a level above $1E6 \text{ cm}^{-3}$ which is inconsistent with observed H_2SO_4 concentration (ammonium bisulphate can't be detected by CIMS). If H_2SO_4 is converted to ammonium bisulphate slowly, equation (1) may be invalid because sulfuric acid dimer is unstable under the conditions.

(b) While NH_3 can be readily uptaken by sulfuric acid solution and react with H_2SO_4 in the solution, it is not clear how NH_3 will react with gas phase H_2SO_4 molecules and small H_2SO_4 clusters. Theoretical study by Ianni and Bandy (J. Phys. Chem, 103, 2801, 1999) suggests that NH_3 molecule is not able to stabilize the H_2SO_4 hydrates sufficiently to initial aerosol formation.

(c) While there is no doubt that NH_3 can stabilize the H_2SO_4 clusters and enhance the sulfuric acid homogeneous nucleation by some degree, it is unclear how significant that NH_3 may actually enhance the nucleation rates. Theoretical calculations suggest that the enhancement coefficient could be more than 30 orders of magnitude at NH_3 concentration of 15 ppt (Korhonen et al., JGR, 104, 26349, 1999), however, the laboratory study (Ball et al., JGR, 104, 23709, 1999) indicates that the nucleation was only

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enhanced by 1 to 2 orders of magnitude at NH_3 concentration of 80 and 170 ppt.

(d) Equation (1) actually suggests that the nucleation is barrierless, but the authors didn't discuss under what conditions (temperature, relative humidity, NH_3 concentration, H_2SO_4 concentration) that equation (1) is valid. Can equation (1) be applied to predict nucleation in other locations?

In summary, the validity of equation (1) remains to be established. The authors should emphasize this when they make conclusions about the relative importance of ion-induced nucleation and kinetic nucleation. The authors should also discuss how sensitive are the simulated results to the values of K and C used?

2. page 3925, lines 3-5. It is unjustified to say "ion-induced nucleation can not be the only or the main particle formation mechanism". As the authors explained in the lines 16-25, the loss of ion clusters due to nucleation is a minor sink for ion concentrations (the observed nucleation rates were much less than the ionization rates) and the nearly constant ion concentration is expected. The sentence should be changed to something like "The relative constant ion concentration during nucleation events can't tell if ion-induced nucleation is the only or the main particle formation mechanism".

3. page 3923, line 4. The authors pointed out here that "particle formation was relatively weak during the days 85 and 88 which is probably caused by large values of CS ." However, Figure 9 actually indicates that days 85 and 88 had stronger particle formation events than other days (see N_{tot} and 3-5 nm (-1, 0, +1)). Since days 85 and 88 had higher CS , how to explain this? Based on model simulations (Figure 11), the nucleation event on Day 85 is also weak which is in conflict with the observation. Could the difference indicate that the model missed some key microphysics?

4. Figures 7-9 indicate that ions around 1 nm size don't have strong diurnal variations. Since H_2SO_4 gas concentration is much lower during the night, it's interesting to see that ion clusters maintained similar sizes during the night. Another interesting feature is that small positive ions are generally larger than small negative ions. It would be

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useful if the authors could discuss these features and suggest the possible reasons.

5. section 4.2.3. I don't understand why the ion-induced nucleation leads to significantly larger ion concentrations in the diameter range 1.5-3 nm under the conditions studied. The particles nucleated on ions don't carry the charge all the times as a result of neutralization by opposite ions. The lifetime of ion clusters is probably around 1000 s but it may take more than one hour to grow the ion clusters to the size of 1.5-3 nm (depending on precursor concentrations). Thus, for all the particles reaching 1.5-3 nm, only a small fraction may still carry a charge.

Minor comments

1. page 3917, line 6. How is "the corresponding charged particles" decided? Does it actually mean "the corresponding concentration measured with the charger"?
2. page 3923, line 27. You must specify under what conditions negative ions can grow without any energetic barrier. It can't be true under all conditions.
3. page 3924, lines 8-9. It is very hard to see from the color scaled figures about the changes in the size distributions of smallest ions. I would suggest that the authors include a figure of $dN/d\log D_p$ versus D_p (at selected times) to demonstrate the point.
4. page 3925, line 28. What is the physical meaning of the undercharged particles? It's easy to understand that overcharging is probably due to ion nucleation.
5. page 3927, line 1. What does "a net unipolar charge" mean?

Technical corrections:

- (1) page 3917, lines 20-23. Rephrase of the sentences is needed.
- (2) page 3917, line 24. The arrow connecting the equations is missing.
- (3) page 3919, line 23. What does the sentence mean?
- (4) page 3920, line 15, delete "in"

(5) page 3926, lines 17-20. After reading the sentences for several times, I still don't understand what are the points here. Suggest rephrasing the sentences or explaining in a little more detail.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 3911, 2004.

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