

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

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Interactive comment on “Kinetic nucleation and ions in boreal particle formation events” by L. Laakso et al. Anonymous Referee #1 Received and published: 24 August 2004

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

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the relative contribution of ion-based particle formation is smaller than kinetic nucleation of neutral clusters and that their findings corroborate the TSC's hypothesis.

Overall, 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.

Comment: In addition to comments below, also the language was checked and revised.

Major comments: 1. About Equation (1)($J=K C_1^2$). 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.

Comment: This article investigates the effects of kinetic nucleation on cluster, ion and particle concentrations and charging states. It does not take any strict opinion on chemistry. That task is remained for the nucleation scientists. However, discussion related to this important comment is added.

(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 $1E6$ 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.

Comment: According to the knowledge I have (personal communication with two MS-chemists), it is possible, that mass spectrometer actually break ammonium bisulphate clusters and observes sulphuric acid even the actual compound in the atmosphere is

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ammonium bisulphate.

It is also possible, that instead of ammonium bisulphate we have a combination of organic vapours and sulphuric acid (see e.g. R. Zhang and I. Suh and J. Zhao and D. Zhang and E. C. Fortner and X. Tie and L. T. Molina and M. J. Molina, 2004, Atmospheric new particle formation enhanced by organic acids, *Science*, 304, 1487-1489).

However, we are not so much interested in chemistry but our main focus is on kinetics and dynamic behavior of the clusters. Actually, the latest results of Vehkamäki et al. 2004 (Hanna Vehkamäki, Ismo Napari, Markku Kulmala and Madis Noppel Stable ammonium bisulphate clusters in the atmosphere. Accepted for publication in *Phys. Rev. Letters*, 2004) indicate, that ammonium bisulphate clusters may prevent nucleation. So, main attention should be put on kinetics and dynamic behavior, not on detailed chemistry.

(b) While NH₃ can be readily uptaken by sulfuric acid solution and react with H₂SO₄ in the solution, it is not clear how NH₃ will react with gas phase H₂SO₄ molecules and small H₂SO₄ clusters. Theoretical study by Lanni and Bandy (*J. Phys. Chem.*, 103, 2801, 1999) suggests that NH₃ molecule is not able to stabilize the H₂SO₄ hydrates sufficiently to initial aerosol formation.

Comment: This comment is relevant and important. A more comprehensive discussion is given by Vehkamäki et al., (2004). We also added the following text to the article:

“In this study, we have used ammonia as a stabilizing compound in kinetic nucleation. However, it is possible that instead of ammonia, sulphuric acid is stabilized by some other compound like organics which concentration is high enough (Zhang et al., 2004). If the stabilizing agent is different from ammonia, the results may slightly change in numbers, but the qualitative conclusions remain the same.”

(c) While there is no doubt that NH₃ can stabilize the H₂SO₄ clusters and enhance the sulfuric acid homogeneous nucleation by some degree, it is unclear how significant

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that NH₃ may actually enhance the nucleation rates. Theoretical calculations suggest that the enhancement coefficient could be more than 30 orders of magnitude at NH₃ 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 enhanced by 1 to 2 orders of magnitude at NH₃ concentration of 80 and 170 ppt.

Comment: Our model does not use that ternary parameterization. Ammonia concentration do not affect kinetic nucleation, if the concentration is sufficiently high.

A good paper discussing such experiments is written by Kim et al., (1998) (Kim, T.O. and Ishida, T. and Adachi, M. and Okuyama, K. and Seinfeld, J.H., 1998, Nanometer sized particle formation from NH₃/SO₂/H₂O/Air mixtures by ionizing irradiation, *Aerosol Science and Tehcnology*, 29, 111-125)

(d) Equation (1) actually suggests that the nucleation is barrierless, but the authors didn't discuss under what conditions (temperature, relative humidity, NH₃ concentration, H₂SO₄ concentration) that equation (1) is valid. Can equation (1) be applied to predict nucleation in other locations?

Comment: This comment is relevant and important. According to Vehkamäki et al., 2004, this assumption is valid at least in temperature range 248–298K at RH 90% and ammonia concentrations between 0.1–100 ppt. Decreasing RH does not change the conclusions.

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?

Comment: This is a useful comment. We are now preparing a new manuscript where we simulate 18 months of measurements and in this paper a sensitivity study is carried out. We have used in our studies Fuchs theory which is quite well founded, even there

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has been some discussion how well that theory can be used. Smaller value of K leads to smaller particle formation rates and vice versa. If the value is significantly lower, the relative contribution of ion based nucleation may increase. Since C is simply the measured sulphuric acid concentration, it is not as important to vary it.

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".

Comment: Several studies concentrating on nucleation rates have been published, for review, see (Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, *J. Aerosol Sci.*, 35, 143-176, 2004) According to that study: "We conclude that the formation rate of 3-nm particles is often in the range 0.01-10 cm⁻³s⁻¹ in the boundary layer". In Hyttiälä it is typically about 1 cm⁻³s⁻¹ (at 3 nm). Due to the time needed for the growth, nucleation rate at about 1 nm is many times higher (5-100). Since ion-production rate is only 4-5 cm⁻³s⁻¹ and we do not see significant decrease in cluster ion concentration, all particles can not be formed on ions. This is also investigated using the model: if we e.g. assume, that 50% of cluster ions act as cores for ion-induced nucleation, the concentration of 1.5-3 nm ions is many times higher than observed. Since coagulation is scaled to realistic values and theoretical values of ion-aerosol particle attachment coefficients are realistic, discharging events of charged clusters can not explain the small number of ions at size-range 1.5-3 nm.

However, the contribution of ion-induced nucleation in observed particle formation events is an important question we hope we are able to answer next spring when we have complete our data-analysis. So the authors agree with referee that the exact

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contribution of ion-induced nucleation is not known, but that disagree with suggested change for the reasons given above. Based on this comment, the abstract and conclusions were slightly softened.

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 Ntot 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?

Comment: Good point. At least during the day 85 particles are clearly undercharged. Also, the concentrations of 3-5 nm ions are equal during the days 85 and 88 in contrast to days 83, 84, 86 and 87. We don't know the reason for that.

These two days are not simple days with nice continuous particle growth. It is possible, that the effect on observed distributions is due to advection. The problem with box models is that they do not take properly into account e.g. boundary layer evolution and advection. So for sure the model is missing some important parts. Also the chemistry is far from the realistic. We dropped this sentence out as it is possibly unjustified.

4. Figures 7-9 indicate that ions around 1 nm size don't have strong diurnal variations. Since H₂SO₄ 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 useful if the authors could discuss these features and suggest the possible reasons.

Comment: The first comment: this is true. More about this topic can be found from the PhD thesis of Urmas Hõrrak (<http://ael.physic.ut.ee/KF.Private/Urmas.Hõrrak/PhDVeeb/PhD-UH.htm>). Dr. U Hõrrak has also analyzed this phenomena in his recent articles.

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The second phenomenon mentioned has been known for decades. It is related to different proton affinities of different compound that lead to different chemical composition (and thus size) of positive and negative ions. More details can be found from e.g.

Luts, A., J. Salm, Chemical composition of small atmospheric ions near the ground, *J. Geophys. Res.*, 99(D5), 10781-10786, 10.1029/93JD03225, 1994.

Hörrak, U., H. Iher, A. Luts, J. Salm, H. Tammet, Mobility spectrum of air ions at Takhuse Observatory, *J. Geophys. Res.*, 99(D5), 10697-10700, 10.1029/93JD02291, 1994.

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.

Comment: This argument is based on model calculations. We made similar calculations assuming that all or part of the particles formed charged. As a result, we found that the concentration of 1.5-3 nm ions was up to an order of magnitude higher than that of observed. Since we used coagulation coefficients scaled to ion-ion recombination coefficients and measured values for ion properties in the calculations of ion-aerosol attachment coefficients, the effect of discharging is taken into account and this justifies our argument.

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"?

Comment: Yes it does. This is now corrected.

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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.

Comment: This problem is discussed in article by Lovejoy et al., 2004 (Figure 5). Their results suggest barrierless negative ion-induced nucleation with concentration of 107 cm⁻³ H₂SO₄ and RH 80% at temperature of about 270 K. This is not far from our conditions because it is reasonable to assume, that adiabatic decrease of temperature in boundary layer may be 10-30 degrees. This discussion is also included in text now.

Lovejoy E. R., J. Curtius, K. D. Froyd (2004), Atmospheric ion-induced nucleation of sulfuric acid and water, *J. Geophys. Res.*, 109, D08204, doi:10.1029/2003JD004460.

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/dlogD_p versus D_p (at selected times) to demonstrate the point.

Comment: This is so wide article with so many figures already, that we are not willing to include more figures.

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.

Comment: The answer is pretty simple: neutral nucleation. If the particles are formed neutral, it takes time until they get charged.

5. page 3927, line 1. What does "a net unipolar charge" mean? At that size-range the concentration of negative clusters was significantly higher than that of positive (which is a sign of contribution of ion-induced nucleation).

Technical corrections: (1) page 3917, lines 20-23. Rephrase of the sentences is needed.

Comment: Done

(2) page 3917, line 24. The arrow connecting the equations is missing.

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Comment: Done

(3) page 3919, line 23. What does the sentence mean?

Comment: We decided not to repeat all details in this article so reader is referred to an older article. However, a new citation was added here to make the article more user-friendly.

(4) page 3920, line 15, delete "in"

Comment: Done

(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.

Comment: Dropped away. This was one phenomenon which reasons were not fully understood.

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

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