Atmos. Chem. Phys. Discuss., 8, S2741–S2745, 2008
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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 #2**

Received and published: 16 May 2008

This manuscript discusses an important topic, the contribution of ion-induced nucleation on atmospheric new particle formation. It is well-written, and in its current form, discreet, compared to the original manuscript. It is certainly worth of publication in ACP after some improvements.

However, in my opinion, the main problem in this article is the black-and-white attempt to explain all NPF by ion-induced nucleation by choosing days supporting this idea, explaining the days which do not support the idea out and then generalizing the results.

Some general comments:

"Out of roughly 30 nucleation event days sampled during the campaign, four were initially selected on the basis of indications that the observed air masses were relatively homogeneous." ...

"However, to extend the scope of the study, one case of weak electrical overcharging and one of clear undercharging, of the nucleated particles were also selected."

Altogether six days were analyzed, and out of the six, two days were clearly undercharged. These undercharged days, which were added because of the recommendation from the referees, gave results that show minor importance from ion-induced nucleation. The authors explain the minor contribution of ion-induced nucleation by non-uniform air masses.

I can not agree with this statement, as we may look the days used in this study in more detail, see http://www.atm.helsinki.fi/~junninen/.

The fact that two "minor contribution days" do not significantly differ from the "good days" can be easily seen from the data figures, and the air mass trajectories.

Another argument against this conclusion is shown in a recent publication,

"Analysis of one year of Ion-DMPS data from the SMEAR II station, Finland" By STÉPHANIE GAGNÉ, LAURI LAAKSO, TUUKKA PETÄJÄ, VELI-MATTI KERMINEN and MARKKU KULMALA, Published article online: 14-Apr-2008 doi: 10.1111/j.1600-0889.2008.00347.x http://www.blackwell-synergy.com/doi/pdf/10.1111/j.1600-0889.2008.00347.x

Here, a significant fraction (~20-25%) of new particle formation days is undercharged or in steady-state, and not all of these days can be explained by non-uniform air masses.

The article by Gagné et al., 2008, however, shows clearly that ions are indeed involved in the nucleation process. The main question is whether the ions are the main (or "significant") contributor to the NPF or if they produce only a fraction of particles, and whether the results from few days during the spring period can be generalized for the



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whole year.

Another example with clear contribution from ions AND some other mechanism is given by e.g.

Laakso, L., Grönholm, T., Kulmala, L., Haapanala, S., Hirsikko, A., Lovejoy, E. R., Kazil, J., Kurtén, T., Boy, M., Nilsson, E. D., Sogachev, A., Riipinen, I., Stratmann, F. & Kulmala, M. 2007: Hot-air balloon as a platform for boundary layer profile measurements during particle formation. Boreal Env. Res. 12: 279–294. http://www.borenv.net/BER/pdfs/ber12/ber12-279.pdf (Figures 3 and 4)

As clearly seen in this article, the behavior of negative and positive ions differ from each other, most of the time pro-negative ions. Looking the Figures 3-9 in the current manuscript, positive ions seem to be more important in the nucleation which is in contrast with the observations. This is an indication that the nucleation mechanism, or at least the chemical compounds used in the model are not necessarily the ones responsible for atmospheric particle formation.

The more pronounced effect of negative ions is also discussed in the following articles:

Hirsikko, A., Bergman, T., Laakso, L., Dal Maso, M., Riipinen, I., Hõrrak, U., and Kulmala, M.: Identification and classification of the formation of intermediate ions measured in boreal forest, Atmos. Chem. Phys., 7, 201-210, 2007.

Hirsikko, A., Laakso, L, Hõrrak, U., Aalto, P. P., Kerminen, V.-M. & Kulmala, M. 2005: Annual and size dependent variation of growth rates and ion concentrations in boreal forest. Boreal Env. Res. 10: 357–369.

Laakso L., Anttila T., Lehtinen K.E.J., Aalto P.P., Kulmala, M., Hõrrak U., Paatero J., Hanke M. & Arnold F. 2004. Kinetic nucleation and ions in boreal particle formation events. Atmos. Chem. Phys. 4: 2353–2366 (Figure 7).

Some more specific comments



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1. Introduction

"An analysis by Laakso et al. (2007) of these measurements concluded that ion nucleation processes make a relatively small contribution to new particle formation (under the conditions sampled)."

One potential reason which can explain part of the discrepancy is the contribution of ion-ion recombination which can not be treated by the method used by Laakso et al., 2007. Laakso et al. describe ion-induced nucleation as charged nucleation whereas the approach by Yu and Turco also incorporates growing recombination products to ion-induced nucleation.

"...as none of the existing theories for binary and ternary homogeneous nucleation provide a quantitative explanation for most of the observations (e.g., Yu, 2006b, 2007)."

The problem in existing theories is not necessarily related to problems in theories themselves, but the chemistry - most of the theories are using only H2SO4, H2O and NH3. Also the chemistry in this paper is based on H2SO4 and H2O only, with additional condensing organic vapor.

2. The kinetic IMN...

Page 5688, line 2. Please add reference (Laakso et al., 2007)

General question: what are the ion-aerosol attachment coefficients between e.g. 2 nm particles and cluster ions used? What is the ion-ion recombination coefficient used?

Page 5691, line 2: "In these cases, the data sequence for the event-day was used without adjustment, and the previous caveats regarding these inhomogeneous event-days are emphasized in the discussion"

What does this sentence mean in practice?

Figure 3-8: please correct the units of "dN/dlogdp"



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Figure 9: Figure shows the charged fractions obtained from the charging states in Laakso et al., 2007. In this manuscript, the charged fractions are given for 2 and 3 nm, whereas in original manuscript for 1, 1.5 and 2 nm. How and why is such diameter conversion made?

Charging state tells how many times more charges there are in equilibrium. In aim to get the charged particle fraction, one has to multiply this number with equilibrium charged fraction. In this manuscript, how this has been calculated, and what is the equilibrium charged fraction for 2 and 3 nm particles used?

The original article only provides charging states @2nm and @1.5nm, and for some days, data is not available for both polarities. Please add correct reference for 27 April 2005, negative particles. Also, there is data available for positive particles on 3 May 2005. Please add this data to figure 10 (c1).

Recommendations:

This article can be published, after the following points are addressed:

- The discrepancy between negative and positive particles is discussed

- The questions related to calculations of charged fraction and its determination answered

- Data for 3 May 2005, positive CF added.

- Some more care taken in the generalization of the results.

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