

Interactive  
Comment

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

**F. Yu and R. Turco**

Received and published: 18 May 2008

The authors thank the referee for the constructive and helpful comments. Our detailed replies to the referee 2's comments (in *Italic*) are given below.

Anonymous Referee 2

*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*

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



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.

I. This appears to be a misunderstanding. We selected the case study days not because they support the ion nucleation, but, as pointed out clearly in the paper, based on indications that the observed air masses were relatively homogeneous (in term of relatively smooth diurnal changes in observed [H<sub>2</sub>SO<sub>4</sub>] and N<sub>3-6</sub>). We have emphasized in the paper that air mass homogeneity is essential for reasonable or meaningful point-site analysis. One can take a look at the Fig. 1b of Riipinen et al. (2007) where observed [H<sub>2</sub>SO<sub>4</sub>] and N<sub>3-6</sub> are given, it is clear that the days selected for case study in this paper are the best in term of the completeness and smoothness in [H<sub>2</sub>SO<sub>4</sub>] and N<sub>3-6</sub> data. Other well-defined nucleation days were not selected because of either incompleteness in [H<sub>2</sub>SO<sub>4</sub>] and N<sub>3-6</sub> time series or relatively large scattering in the data (around earlier morning and noon time). This point will be clarified in the revised paper.

We believe that the case study days we selected are representative (in terms of meteorology conditions and the ranges of [H<sub>2</sub>SO<sub>4</sub>], N<sub>3-6</sub>, charging ratios, etc.), and we generalize our results based on the comparison of the average overcharge ratios on the case study days with those of others (i.e., Figure 11). It should be noted that we offer two explanations for the around 20% of nucleation event days with weak overcharging or weak undercharging: (1) an alternative (yet to be identified) nucleation mechanism, and (2) variability in the air mass sampled. See below for more discussions.

*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 under-*

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

*charged. 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.*

II. First, we don't claim that non-uniformity in the air masses sampled is the only explanation for the days with weak overcharging and clear undercharging. It has been clearly stated in the paper that "An alternative explanation is the involvement of species other than sulfuric acid in nucleation and growth of sub-3 nm particles on that day and such species remain to be identified."

Second, in our original manuscript submitted to ACPD, we aimed to focus on around 80% of nucleation event days showing clear overcharging. However, we did point out in the original manuscript that neutral nucleation may be responsible for the relatively few "undercharged" nucleation event days. Under the recommendation of the referee, we looked into two events days with weak overcharging or clear undercharge (April 13 and May 2). Our careful analysis suggests that, in addition to the neutral nucleation, significant variability in the sampled air masses many also contribute to the observed undercharge in the 3-5 nm particles (see page 5698).

Third, when we talk about air mass variability, we refer to the local inhomogeneity in the air masses and we are not sure if the air mass trajectories are good indications. As far as nucleation is concerned, local air mass inhomogeneity can be clearly seen in the fluctuations in measured [H<sub>2</sub>SO<sub>4</sub>], N<sub>3-6</sub>, and particle size distributions (see our discussions on page 5698). Airborne measurements of nucleation mode aerosol concentrations during nucleation events over the boreal forest clearly show significant vari-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

ability in nucleated particles, which has been attributed to variability in land coverage between forests and lakes (O'Dowd et al., ACPD, 8, 2821, 2008).

Finally, it remains to be investigated how and to what degree air mass variability may lead to undercharge of 3-5 nm particles. One possible scenario is that many sub-3 nm particles nucleation in the locations favorable for nucleation but unfavorable for growth (relatively low T, high RH, low organics, such as over lakes) may be in equilibrium with ambient ions. When these sub-3 nm particles transport to location favorable for growth (high condensable precursor gases, such as over forests), they may experience enhanced growth rate which may lead to the undercharge of 3-5 nm particles. Clearly more research is needed in this regard.

We will make above points clear in the revised paper.

*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*

*Here, a significant fraction (around 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 whole year.*

III. The one year of ion-DMPS data summarized in Figure 6 of Gagné et al. (2008) are in general consistent with 7-week ion-DMPS data shown in Figure 8 of Laakso et al. (2007). Both Gagné et al. (2008) and Laakso et al. (2007) show that a large fraction of (around 80%) of nucleation event days have clear overcharging in 3- 5 nm particles.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

We agree with the referee that "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". To answer this question is one of main objective of the present study. The comprehensive and well-constrained nucleation case studies presented here clearly show that the ion-mediated nucleation not only can account for the observed N3-6 but also is generally consistent with measured average overcharging ratios of 3-5 nm particles for major fraction of nucleation events.

The similar level and frequency of overcharging in other seasons (Gagné et al., 2008) may actually indicate that ion-mediated nucleation is significant in other seasons as well. More well-constrained case studies for other seasons similar to the ones presented here are clearly needed.

*Another example with clear contribution from ions AND some other mechanism is given by e.g. Laakso, L., et. al., 2007: Hot-air balloon as a platform for boundary layer profile measurements during particle formation. Boreal Env. Res. 12: 279-294. (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., et al.: Identification and classification of the formation of intermediate ions measured in boreal forest, Atmos. Chem. Phys., 7, 201-210, 2007. Hirsikko, A., et al.: Annual and size dependent variation of growth rates and ion concentrations in boreal forest. Boreal Env. Res. 10: 357-369. Laakso L., et al.: Kinetic nucleation and ions in boreal particle formation events. Atmos. Chem. Phys. 4: 2353-2366 (Figure 7).*

IV. The nucleation sign preference is an interesting topic that requires further investiga-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

tion. In Yu (ACP, 6, 5193, 2006), the possible reason of sign preference is briefly discussed. The differences in the compositions and thermodynamic properties of positive and negative pre-nucleation clusters are considered in our kinetic model (Yu, 2006). For the four clearly overcharging event days studied, our model predicts more negative ion nucleation on April 27 and May 3, and similar negative and positive ion nucleation on April 18 and May 12 (in term of average overcharging ratios for 3 nm particles, see Fig. 11).

We are aware that the above mentioned references concluded more pronounced effect of negative ions. However, the difference in the negative and positive ion nucleation is not as big as the referee implied here. For example, Hirsikko et al. (2007) showed that, based on three years of measured size distributions of air ions (0.42–7.5 nm in diameter), negative ions and positive ions are clearly involved in total 270 (26% of the analyzed days) and 226 (22% of the analyzed days) of particle formation days, respectively. Based on the 7-week data reported in Laakso et al. (2007, Fig. 8) and one-year data reported in Gagné et al. (2008, Fig. 6), there exist no significant difference between positive and negative overcharging ratios for 3–5 nm particles, although negative overcharging ratios are much higher on a few days. It should be pointed out that in Fig. 7 of Laakso et al. (2007), while the charging ratios for negative and positive 5 nm particles are close, negative 3 nm particles have a very high charging ratios but there is no data for positive 3 nm particles. It is not clear how the difference in the detect efficiency for positive and negative ions may affect the interpretation.

In summary, long-term measurements indicate that both negative and positive ions are involved in the nucleation in boreal forests although nucleation on negative ions is slightly preferred on average. Thus, these observations are generally consistent with our model predictions. Of course, as we pointed out in the paper, our model has uncertainties. More detailed case study, especially with regard to time-dependence variations of both positive and negative charging ratios, could identify and reduce the uncertainties.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

*Some more specific comments 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.*

Agree. Actually this is the point emphasized in the paper as we show most of particles crossing 3 nm grow from neutral sub-3 nm particles resulted from ion-ion recombination.

*"...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 H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O and NH<sub>3</sub>. Also the chemistry in this paper is based on H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O only, with additional condensing organic vapor.*

We just state the fact that the existing theories can't explain the observed nucleation rates, thus implying other nucleation mechanisms (i.e., involving other species).

*2. The kinetic IMN... Page 5688, line 2. Please add reference (Laakso et al., 2007)*

Yes, will do.

*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?*

The recombination coefficients ( $\alpha$ ) and ion-aerosol attachment coefficients ( $\beta$ ) depend mainly on the sizes of ion clusters and particles. The  $\beta$  values for attachment of 0.5 nm and 1.0 nm ions to 2 nm neutral particles are around  $1\text{E-}8\text{ cm}^3/\text{s}$  and  $6\text{E-}9\text{ cm}^3/\text{s}$ , respectively. The  $\alpha$  values for recombination of 0.5 nm and 1.0 nm

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

ions with 2 nm oppositely charged particles are around  $2E-6$  cm<sup>3</sup>/s and  $7E-7$  cm<sup>3</sup>/s, respectively.

*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?*

The sentence means that on April 13 and May 2, while we think that [H<sub>2</sub>SO<sub>4</sub>] or N<sub>3-6</sub> during certain period are anomalous (as discussed in previous sentences, probably associated with heterogeneous air masses), we use the measured [H<sub>2</sub>SO<sub>4</sub>] and N<sub>3-6</sub> time series and thus our simulations and comparison are subject to the problem associated with air mass inhomogeneity. We will rewrite the sentence to make it clear.

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

Will do.

*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 referee appears to refer to the observed charged fraction data shown in Figure 10. Laakso et al. (2007) derived charged state (S) values for 1, 1.5, and 2 nm from observed S for 3 nm and fitted value of parameter K, using an analytical formula (equ. 1). We backward calculated S for 3 nm from S@2 nm and corresponding K values, using equ. 1 given in Laakso et al. (2007). S@3nm should be considered as "real" observed values. Derived S@1, 1.5, and 2 nm are subject to uncertainty as a result of

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper





Interactive  
Comment

some assumptions implied in equ. 1. We use only S@2 nm because the uncertainty in S@ 2m should be the least.

The average equilibrium charged fractions for 2 and 3 nm particles are based on model calculations (see the curves in Fig. 10 during the period with no ion nucleation).

We will point these out in the revised paper.

*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).*

Will do.

*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.*

We will address these points in the revised version of the paper.

---

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

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)