

## ***Interactive comment on “Ion-mediated nucleation as an important global source of tropospheric aerosols” by F. Yu et al.***

F. Yu et al.

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Reply to Ari Laaksonen's comments (in *Italic*)

The authors thank Ari Laaksonen for the thoughtful and constructive comments. Our point-to-point replies to the comments are given below.

1. *Validation of the IMN mechanism against measured atmospheric nucleation rates. The authors argue that the overcharging of the freshly formed nm-sized particles in Hyytiälä indicate IMN whereas Laakso and coworkers have argued that homogeneous nucleation can explain most of the nucleation despite the overcharging. The present authors' references are not peer-reviewed, and the debate seems very much ongoing, so that I see no consensus as to whether overcharging indicates dominance of IMN or not. I believe that the authors should, instead of just presenting such argu-*

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ments, examine their predicted nucleation rates against atmospheric rates. The kinetic and activated nucleation mechanisms, presented e.g. by Riipinen et al. (ACP 7, 1899, 2007), depend on the second and first powers of sulfuric acid concentration, respectively, and can be viewed as experimental parametrisations that capture the nucleation rates measured in Hyytiälä and in Heidelberg quite well. I recommend that the authors compare the predicted IMN nucleation rates as a function of sulfuric acid concentration at varying ion production rates to the kinetic and activated nucleation parametrisations using the coefficient ranges presented by Riipinen et al. (2007).

1.1 With regard to whether overcharging indicates dominance of IMN or not.

We agree with Laaksonen that the debate on the relative importance of ion versus neutral nucleation is ongoing. Indeed, we are in the process of trying to resolve the differences in the interpretation of the overcharging measurements, and determining when IMN is relatively more important; our findings will be detailed in a separate paper. Since the issue is clearly relevant to this paper, and has been raised in the comments of two other referees, we would like to clarify two points here.

(I) Laakso et al.'s conclusion that "a large fraction of days considered here, the contribution of ion-induced nucleation to the total nucleation rate was either negligible or relatively small" is inconsistent with their own analysis of the charging state of 1 nm and 1.5 nm particles. Actually, the charging states ( $S$ ) of nanometer particles given by Laakso et al. themselves show that the contribution of ion-mediated nucleation (IMN) to the total nucleation rate was either significant or even dominant during a large fraction of the days for which data are given.

To illustrate this point, we have determined the number of days having different ranges of predicted  $S$  values for 1 nm and 1.5 nm particles (summarized in Table S1 below) based on the  $S$  values reported in Tables 1 and 2 of Laakso et al. (2007). Among the 30 nucleation event days recorded by Laakso et al. (2007), 20 days have  $S$  values for negative polarity, 24 days have  $S$  values for positive polarity, and 14 days have

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S values for both polarities. The values of S above 50 for either negative or positive polarity are indicative of the significance or dominance of IMN (fourth column in Table S1). However, to conclude that the IMN contribution is small, or negligible, the values of S for both polarities should be  $< 10$ , or  $< 1$ , respectively (fifth column in Table S1). To obtain the numbers in the fourth and fifth columns of Table S1, S is assumed to be 1 for the days with missing data (10 days for negative and 6 days for positive). Thus, the present results probably underestimate the number of days having  $S > 50$ , and overestimate the number of days having  $S < 10$ .

**Table S1.** Statistical summary of the number of days having  $S > 50$  (IMN significant or dominant),  $S < 10$  (IMN small) and  $S < 1$  (IMN negligible) for 1 nm and 1.5 nm particles (based on the S values given in Tables 1 and 2 of Laakso et al., 2007). The number of days having  $S > 100$  (IMN dominant) for 1 nm particles is also given. The "charging state" (S) is defined as the ratio of the actual charged fraction of particles of a given size to their equilibrium (or neutralized) charged fraction. Read "3 / 20" as 3 out of 20 days.

	neg.	pos.	either neg. or pos.	both neg. and pos.
S > 100 at 1 nm	3 / 20	8 / 24	11 / 30 (36%)	
S > 50 at 1 nm	9 / 20	9 / 24	18 / 30 (60%)	
S < 10 at 1 nm	4 / 20	7 / 24		4 / 30 (13%)
S < 1 at 1 nm	2 / 20	2 / 24		2 / 30 (7%)
S > 50 at 1.5 nm	2 / 20	7 / 24	9 / 30 (30%)	
S < 10 at 1.5 nm	7 / 20	12 / 24		8 / 30 (27%)
S < 1 at 1.5 nm	2 / 20	2 / 24		2 / 30 (7%)

Based on S values for 1.5 nm particles, Laakso et al. (2007) concluded that a large fraction of days considered in their study seemed to have either negligible ( $S < 1$ ) or

small ( $S < 10$ ) contributions from ion-mediated nucleation. This conclusion is not supported by the numbers shown in Table S1, however, which are based on the  $S$  values given by Laakso et al. (2007) themselves. Firstly, it is more appropriate to use  $S$  at 1 nm to assess the relative contribution of IMN because many neutral particles at 1.5 nm are actually produced by the neutralization of particles formed on ions and thus are a direct result of IMN (that is, the stable embryos would not have formed without the intervention of ion processes). Based on  $S$  at 1 nm, a large fraction (60%) of the days considered in Laakso et al.'s study seemed to have either a significant or dominant ( $S > 50$ ) contribution from ion-mediated nucleation, while only a small fraction (13%) of days seemed to have either negligible ( $S < 1$ ) or small ( $S < 10$ ) contributions from IMN. More than one third of days even have  $S > 100$  (IMN dominant). Secondly, even based on  $S$  at 1.5 nm, only 8 out of 30 days (27%) have  $S < 10$  for both polarities (the number could be lower since some of days with missing data could have  $S > 10$  for at least one polarity). By contrast, at least 9 out of 30 days (30%) clearly indicate a significant or dominant IMN contribution ( $S > 50$ ).

In summary, it is more appropriate to conclude that, based on the numbers given by Laakso et al. (2007), the contribution of ion-mediated nucleation to the total nucleation rate was either significant or even dominant during the majority of the days considered.

(II) If our interpretation of the  $S$  values given by Laakso et al. (2007) is correct (we have no reason to think otherwise), we expect a closer convergence in the conclusions between ourselves, Laakso, and others with regard to whether the overcharging data obtained in Hyytiälä indicates the dominance of IMN or not. While details remain to be clarified, we conclude that both Laakso et al. (2007)'s analysis (based on an analytical formula, without detailed microphysical modeling) and our own investigation (based on a different analytical approach supported by detailed kinetic simulations; Yu and Turco, 2007) show the dominance of IMN for a large fraction of nucleation event days reported in Laakso et al. (2007).

The above points will be reflected in the revised paper.

1.2 With regard to comparison with the nucleation rate parameterization of Riipinen et al. (2007).

The main objective of our paper is to study the contribution of the IMN mechanism as a global source of new particles, and the spatial distribution of the nucleation zone. Our IMN model, which is physics based and incorporates recently available thermodynamic data and parameterizations, has been described in detailed in Yu (2006). IMN rates (JIMN) depend on sulfuric acid vapor concentrations  $[H_2SO_4]$ , relative humidity RH, and temperature T, ionization rate Q, and the surface area of pre-existing particles,  $S_0$ . All of these factors may vary substantially with time during any observational period, and the precursor processing interval. Nucleation rates based on the referenced empirical formulas ( $J_1=A[H_2SO_4]$  and  $J_1=K[H_2SO_4]**2$ ) of Riipinen et al. (2007) depend only on the instantaneous value of  $[H_2SO_4]$ , while the "constants" A and K appear to vary significantly with other conditions at the measurement sites in ways that are not parameterized. Thus, it is clear that the Riipinen et al.'s parameterizations do not in fact represent actual rates of physical nucleation processes, and that all of the complex nonlinear physics of cluster activation and growth – and time variations in these factors – are compressed into a single prefactor term that is given as a constant based on a simple regression for a particular set of data. These parameterizations may be more related to the "apparent" rates of particle formation after significant atmospheric processing (neutralization, condensation, coagulation, etc.) has occurred following nucleation activation.

To examine the predicted nucleation rates against observed rates, it is much more appropriate to conduct a detailed case study using observed time series of  $[H_2SO_4]$ , T, RH, Q, and  $S_0$  to constrain the IMN model, and comparing simulated results directly with the relevant measurements (including measurements of charged state and number concentrations at observed sizes). Time series for  $[H_2SO_4]$  have been given in Riipinen et al. (2007), although the corresponding time series for T, RH, and  $S_0$  were not reported. We are trying to obtain additional data to carry out well-controlled

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case studies for these experiments. However, since the focus of the present paper is on global modeling, we plan to report any future detailed case studies in a separate article.

2. *I think that the comparison in Fig. 2 is misleading, as the IMN rates are annual means but the observed nucleation rates are averages per event, and events do not occur every day of the year. A better comparison is obtained if the authors multiply the observed average rates by ( events)/(length of time period in days) (Table 1).*

We have pointed out, and emphasized in the paper (Page 13607, lines 6-10), the difference in the simulated IMN rates and observed nucleation rates shown in Fig. 2. It is true that nucleation events do not occur every day of the year. At some sites where long-term nucleation measurements are available ( $N > 100$  in Fig.2), nucleation events typically occur on about one third of the days. Multiplying the average rates by ( events)/(length of time period in days) would reduce the equivalent observed values by a factor of around 3, but would not change the conclusions of the paper. Considering the qualitative nature of the comparison, and the fact that some observations do not persist long enough to derive meaningful nucleation frequency, we feel that it is unnecessary to make such an adjustment in Fig. 2 at this time. However, to address the referee's concern, we will clarify the issue of the nucleation frequency in the revised paper.

3. *I would advise the authors to be more careful in making statements such as "... it appears that IMN can account for much of the observed particle formation near Earth's surface." (p. 13607). Even if features of annual means can be reproduced, boundary layer nucleation is a highly nonlinear phenomenon showing many features that remain to be explained. For example, the seasonal event frequency distribution varies very much from place to place (see e.g. Hamed et al, 2006). Showing that a given mechanism can account for (much of the) observations requires more detailed comparisons than those for annual and zonal means.*

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To address comment, which is very reasonable, we will delete the offending sentence (page 13607, lines 24-25) in the revised version, and check the rest of the paper for similar statements that may over-interpret our results.

## References

Laakso, L., et al., Atmos. Chem. Phys. 7, 1333-1345, 2007.

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Interactive comment on Atmos. Chem. Phys. Discuss., 7, 13597, 2007.

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