Title: The size-dependent charge fraction of sub-3-nm particles as a key diagnostic of competitive nucleation mechanisms under atmospheric conditions

Author(s): F. Yu and R. Turco

MS No.: acp-2011-216

Reply to Referee's comments

The authors thank the referee for providing constructive comments, which are useful for improving and clarifying the manuscript. Our responses to these comments are given below.

General comments.

The referee raises a valid point concerning sensitivity to ion concentrations and growth rates. As emphasized in the discussion (see last paragraph of section 3.3), the simplified analysis (Eq. 11) is subject to uncertainties associated with the values of the recombination coefficient (α), small ion concentration (C) and growth rate (GR), and also because the variations in most parameters with size are neglected in the simplifies representation, as are secondary processes such as differential growth rates, background ionization rates, and so on. Further, in real situations, α, and GR depend on the particle type (charged or neutral), while α, C and GR also vary with time during nucleation events. Although these complexities are minimized in the analytical approach, they are however taken into account in the detailed kinetic IMN simulations, as pointed out in the paper.

The size-dependent growth rates of sub-3 nm particles in the IMN model are determined by sulfuric acid vapor concentrations that change significantly with time, such that the overall growth rates are consistent with the observed time delay between the early morning increase in [H_2SO_4] and the appearance rates of freshly nucleated particles (3−6 nm) (see Fig. 3 and section 3.1 in Yu and Turco, 2008). Thus, the actual time-varying growth rates have a strong influence on the overall neutralization rate, and the effects are explicitly included in the results shown in the paper.

The simulated concentrations of small ions for the cases presented in this study are generally in the range of 500 – 1500 cm^{-3}, with a mean value of ~ 1000 cm^{-3}. During the corresponding observational period (middle April to middle May), the measured concentrations of small ions according to Fig 3 in Hirsikko et al. (2005) are also generally in the range of 500 -1500 cm^{-3}, with a mean of ~ 850 cm^{-3}. It is interesting to note that the observed small ion concentrations, according to Fig 3 in Hirsikko et al. (2005), peak around end of April or beginning of May in the spring (of 2003). The difference in the observed and simulated mean concentrations of small ions (~ 15%) is reasonable, considering the uncertainties in both simulations and measurements and additional uncertainties associated with diurnal variations (of both measured ionization rates and ion concentrations) and air mass inhomogeneity. The concentrations of small ions depend largely on ionization rates (Q), ion-ion recombination and ion-aerosol attachment coefficients, and a condensational sink (CS) related to the surface area of pre-existing particles. All these parameters are subject to uncertainty, of course. In our case studies, Q is based on the observed values reported in Gagné et al. (2010), CS is based on observed particle size distributions (Ehn et al., 2007), and the ion-ion recombination and ion-aerosol attachment coefficients are size-dependent as determined by physical arguments (e.g., Yu, 2006). The observed concentrations of small ions are also subject to uncertainty associated with sampling conditions and detection efficiency. For example, the concentrations of small ions measured by two different BSMAs at the same site

(Hyytiala, Finland) differed substantially (up to ~ 30%, see Fig. 3 in Ehn et al., 2011). Accordingly, we agree with the referee that further characterization of the sensitivity to these parameters would be useful to the reader, and in the revised manuscript we have added calculations for different ion concentrations, using ion concentrations as a surrogate for variability in the underlying parameters. The results of these sensitivity tests indicate that the referee's comments about the relevance of ion concentrations in interpreting ion nucleation contributions is basically correct, although the variations we tested were not sufficient to raise neutral nucleation rates to a dominant role.

One point that we wish to raise in this regard is that there is a question of consistency in the interpretations using the IMN model versus a simplified analytical model. For example, imagine that we have in reality a case where the neutral nucleation rate is very small, owing to the environmental state; then the ion nucleation rate would have to either explain the observed particle formation rates and properties, or would have to be supplanted by another mechanism that does. In other words, the theory would have failed. On the other hand, working backwards from observations of larger, aged particles using a formula, one can always adopt a set of nucleation rates and parameter values that explain the outcome, and indeed these parameters may fall within reasonable ranges even if they are not actually constrained physically or observationally. In the former approach, there are also parameter assumptions, but certainly not to the same extent as in the latter case, where the core nucleation rates themselves are not actually calculated on any physical basis.

Specific comments.

1. As pointed out in Yu and Turco (2008), the eight case study days were selected (from 40 days of detailed measurements carried out in the Spring of 2005) based on indications that the observed air masses were relatively homogeneous, which is essential for meaningful point-site analysis. We believe that the selected case study days are representative (in terms of meteorological conditions as well as the ranges of $[H_2SO_4]$, apparent particle formation rates, charging ratios, etc.). We have then generalized these results based on comparisons of the average overcharge ratios and apparent fraction of 2-nm particles formed on ions for the case study days to other similar days as reported in Laakso et al. (2007), Gagné et al. (2010), and Manninen et al. (2009). To address the referee's concern, we have modified the manuscript to include the extent of this study.

2 & 3. Dr. Olaf Hellmuth kindly provided detailed derivations in his comments. To keep the present manuscript concise, we refer the readers to the derivations given in Dr. Hellmuth's comments.

4. Yes. In Figure 6a, the observed median formation rates for charged and neutral 2-nm particles are 0.08 $cm^{-3}s^{-1}$ and 0.57 $cm^{-3}s^{-1}$, respectively. The corresponding observed value in Fig. 6b is 0.08/0.65 = 12.5%. These numbers are from Pages 4083-4084 of Manninen et al. (2009), as copied below:

"*The median total formation rate of 2 nm particles was 0.65 $cm^{-3}s^{-1}$ varying from 0.22 to 3.9 $cm^{-3}s^{-1}$. On the other hand, the median formation rate of 2 nm charged particles was 0.03 $cm^{-3}s^{-1}$ varying from 0.01 to 0.09 $cm^{-3}s^{-1}$.*"

"*The median values of the ion-ion recombination rates were about 0.05 $cm^{-3}s^{-1}$, varying from 0.03 to 0.1 $cm^{-3}s^{-1}$ (Fig. 8, upper panel). The result that in the boreal forest the contribution of ions to*

particle formation is approximately 10% is consistent with the particle charging state measurements by Gagn´e et al. (2008) performed at the same site."

By adding 0.03 $cm^{-3}s^{-1}$ and 0.05 $cm^{-3}s^{-1}$ (the latter since ion-ion recombination is presumed to form a stable neutral particle of 2-3 nm, but have an ion source), we obtain a median observed 2-nm ion-mediated particle formation rate of 0.08 $cm^{-3}s^{-1}$. By subtracting 0.08 $cm^{-3}s^{-1}$ from total 2 nm formation rate of 0.65 $cm^{-3}s^{-1}$, we obtain a median observed 2-nm neutral particle formation rate of 0.57 $cm^{-3}s^{-1}$.

Technical corrections.

Done.

References:

Ehn, M., T. Petäjä, H. Aufmhoff, P. Aalto, K. Hämeri, F. Arnold, A. Laaksonen, and M. Kulmala: Hygroscopic properties of ultrafine aerosol particles in the boreal forest: diurnal variation, solubility and the influence of sulfuric acid, Atmos. Chem. Phys., 7, 211-222, 2007.

Ehn, M., H. Junninen, S. Schobesberger, H. E. Manninen, A. Franchin, M. Sipilä, T. Petäjä, V.-M. Kerminen, H. Tammet, A. Mirme, S. Mirme, U. Hõrrak, M. Kulmala & D. R. Worsnop: An Instrumental Comparison of Mobility and Mass Measurements of Atmospheric Small Ions, Aerosol Science and Technology, 45:4, 522-532, 2011.

Gagné, S., L. Laakso, T. Petäjä, V.-M. Kerminen, and M. Kulmala: Analysis of one year of Ion-DMPS data from the SMEAR II station, Finland, Tellus B, 60, 318–329, 2008.

Gagné, S., Nieminen, T., Kurtén, T., Manninen, H. E., Petäjä, T., Laakso, L., Kerminen, V.-M., Boy, M., and Kulmala, M.: Factors influencing the contribution of ion-induced nucleation in a boreal forest, Finland, Atmos. Chem. Phys., 10, 3743-3757, doi:10.5194/acp-10-3743-2010, 2010.

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 borealforest. Boreal Env. Res. 10: 357–369.

Laakso, L., Gagné, S., Petäjä, T., Hirsikko, A., Aalto, P. P., Kulmala, M., and Kerminen, V.-M.: Detecting charging state of ultra-fine particles: instrumental development and ambient measurements. Atmos. Chem. Phys. 7, 1333-1345, 2007.

Manninen, H. E., Nieminen, T., Riipinen, I., Yli-Juuti, T., Gagné, S., Asmi, E., Aalto, P. P., Petäjä, T., Kerminen, V.-M., and Kulmala, M.: Charged and total particle formation and growth rates during EUCAARI 2007 campaign in Hyytiälä, Atmos. Chem. Phys. Discuss., 9, 5119-5151, 2009.

Yu, F.: From molecular clusters to nanoparticles: Second-generation ion-mediated nucleation model, Atmos. Chem. Phys., 6, 5193-5211, 2006.

Yu, F., and R. P. Turco: Case studies of particle formation events observed in boreal forests: Implications for nucleation mechanisms, Atmos. Chem. Phys., 8, 6085-6102, 2008.