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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The size-dependent charge fraction of sub-3-nm particles as a key diagnostic of competitive nucleation mechanisms under atmospheric conditions" *by* F. Yu and R. Turco

Anonymous Referee #2

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Review of the manuscript:

In their manuscript "The size-dependent charge fraction of sub-3-nm particles as a key diagnostic of competitive nucleation mechanisms under atmospheric conditions", F. Yu and R. Turco have reviewed the issue concerning the role of ions in the process of new particle formation. The authors have studied the evolution of both neutral and charged aerosol particle size distributions with a detailed box-model that employs ion mediated nucleation (IMN) as the nucleation scheme. With the model, the authors have been able to determine the apparent formation rate of both neutral and charged particles at

various diameters. The main conclusion of the paper is that in the certain cases, the modeled fraction of charged particle formation at 1.5 nm in diameter is $\sim$ 100 %, but the corresponding fraction at 2 nm is consistent with the value of $\sim$ 10 % determined from the measurements.

The topic of the paper is important for understanding the actual mechanisms of atmospheric new particle formation and well in the scope of ACP journal. The paper is well written and the methods employed are scientifically sound. However, better estimates on the sensitivity of the analysis to potential error sources are needed and the generalization of the conclusions should be reconsidered.

General comments:

Aerosol particles are formed as neutral or as charged. The fraction of charged particles in the charge equilibrium depends mostly on the attachment coefficients between small ions and the aerosol particles. If the population of newly formed particles is overcharged (i.e. the fraction of charged particles is bigger than the corresponding fraction in charge equilibrium), the attachment of small ions neutralizes more rapidly charged particles than charges neutral particles. As a consequence the charged fraction gets smaller as the particles grow bigger in size (e.g. Kerminen et al. 2007).

A main conclusion of the paper is that the process of neutralization of charged particles can be so rapid that the dominantly charged ($\sim$100 %) particle population at 1.5 nm in diameter can be observed as mostly neutral ($\sim$10 %) at 2 nm in diameter. According to charge dynamics, it is self-evident that the fraction of charged particles decreases as the particles grow from 1.5 to 2 nm, whenever there is a considerable amount (> a few percent) of charged particles at 1.5 nm in diameter. The important question is how rapid is this process? The Eq. (11), on page 11297, can be used to estimate the rapidity of neutralization. Using values of 1000 cm-3 and 1, 1.9 or 3 nm h-1 for the concentration of small ions and diameter growth rate of particles, respectively, 5.6 %, 22 % or 38 % of particles that were charged at 1.5 nm are still charged at 2 nm.

For the chosen values of growth rate, a reference (Manninen et al. 2009) is given and the values are consistent, but there is no reference for the chosen value of small ions. Hirsikko et al. (2011) recently published a review of small ion measurements and according to the Figure 6 in that paper, the measured mean and median values of small ion concentrations have varied from $\sim$ 500 to 1000 cm-3. According to Hirsikko et al. (2005), the monthly mean small ion concentrations in Hyytiälä during the months on which the measurements in Manninen et al. 2009 paper were conducted are $\sim$ 700 cm-3. As the rapidity of the neutralization is exponentially dependent on both the particle growth rate and the small ion concentrations, a few values covering the reasonable range should be used for both of them, and not just for growth rate. With the small ion concentration of 500 cm-3, the fraction of charged 1.5 nm particles still charged at 2 nm are 24 %, 47 % and 62 % for growth rates of 1, 1.9 and 3 nm h-1, respectively. Also with the small ion concentration of 500 cm-3, the life time against neutralization exceeds the time needed to grow from 1.5 to 2 nm.

Furthermore, the Eq. (11) can be used to estimate the FJ1.5ion, when the FJ2ion is known. Assuming FJ2ion is 10 % and using values of 1, 1.9 and 3 nm h-1 for growth rate and 500, 700 and 1000 cm-3 for small ion concentrations, the values of FJ1.5ion vary from 16 to 178 %, with the value of 29 % obtained using the middle value for both variables (see the values listed below). Thus the 10 % ionic formation rate at 2 nm can be obtained with 16 to 100 % ionic formation rate at 1.5 nm when using reasonable estimates for small ion concentration and particle growth rate. This demonstrates how sensitive the charge dynamics are for both the particle growth rate and the small ion concentrations. The growth rate and small ion concentrations from both the simulations and observations should be reported in order to evaluate how reasonable the comparison of simulations and observations is. This could also help to understand the difference in the interpretation of the amount of IMN.

Values of FJ1.5ion obtained using Eq. (11) with assumption of FJ2ion being 10 %: Small ion concentration (cm-3) ; Particle growth rate (nm h-1) ; FJ1.5ion

500 ; 1.0 ; 42 %

500 ; 1.9 ; 21 %

500 ; 3.0 ; 16 %

700 ; 1.0 ; 75 %

700 ; 1.9 ; 29 %

700 ; 3.0 ; 20 %

1000 ; 1.0 ; 178 %

1000 ; 1.9 ; 46 %

1000 ; 3.0 ; 26 %

Specific comments:

1. In the abstract, on page 11282 lines 15 - 27, it is stated that the model predictions of neutral and charged formation rates at 2 nm agree well with the corresponding measured values, but the neutral and charged formation rates at $\sim$ 1.5 nm demonstrate that the IMN dominates over neutral cluster nucleation in the boreal forest. This conclusion is too extensive as it is based only on eight cases chosen from potential 22 from a short period of time. The wording should be changed to include the extent of the study.

Also on page 11300, lines 6-9, the wording would suggest that ion-based nucleation dominates particle formation whenever the air-masses are suitable for the analysis. This is too extensive conclusion based on only a few cases. The wording should be changed to include the extent of the study.

2. On page 11296, line 25, the fraction of particles originally nucleated on ions that remain charged as the particles increase in size is e^(-αCΔt). It might not be clear to all readers how this estimate is obtained, so it could be explained briefly.

3. On page 11298, line 2, there is an estimate on the lifetime of charged particles

against the neutralization. It might not be clear to all readers how this estimate is obtained, so it could be explained briefly.

4. In Figure 6, please give the exact numbers for the observed median values and explain how you got them from the paper by Manninen et al. (2009). The values I'm able to retrieve from Figure 6 do not match any values reported in Manninen et al. (2009).

Technical corrections:

1. On page 11294, lines 18 and 23, the values of J are referred as "nucleation rates", where as they are referred as "formation rates" in other instances.

2. On page 11297, line 13, the year in Manninen et al. reference should be 2009 instead of 2010.

3. In Figure 5, the difference between the stars and diamonds should be explained in the caption and not only in the text.

4. In Figure 6, the y-axis is labeled as nucleation rate, but a formation rate would be a more appropriate term.

References:

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