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Comment

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

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The authors thank Jeffrey Pierce for the constructive and insightful comments. He raises two important issues that are critical for understanding the sources of the differences in the interpretation of Hyytiala data with regard to the relative importance of ion versus neutral nucleation pathways. Our replies to these questions are given below.

General comments:

1. Ion-ion recombination. Manninen et al. (2009) considered only the recombination

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of ions in the size range of 2-3 nm with ions of opposite sign smaller than 3 nm (see Eq. 2 in Manninen et al.). This limitation is inherent in the reverse analytical approach adopted by Manninen et al. As shown in the present study, however, most ions are actually neutralized before reaching ~ 2 nm size. Manninen et al. then go on to assume that all of the neutral particles < 2 nm (which the detailed simulations suggest are dominated by ion recombination processes) are formed by neutral nucleation processes. It turns out that this distinction is critical to the determination of the actual source of the 2-nm neutral particles, and explains to a large degree the contradictions between the two interpretations of the intensity of ion-mediated nucleation. Indeed, we can also obtain an erroneous interpretation by using a reverse analysis similar to that of Manninen et al. applied to the model simulation data (that is, by using essentially the same assumptions as Manninen et al.). We will further clarify this point in the revised manuscript.

2. Growth rates. It is true that the growth rate of 1-3 nm particles has an important effect on the charged fractions in the 2-3 nm size range (also see Section 3.3), and thus is one source of uncertainty in our analysis. While low volatility organics are known to contribute significantly ($> \sim 80\%$) to the growth of particles larger than 3-5 nm in boreal forests (e.g., Riipinen et al., 2011; Yu, 2011), their contribution to the growth of sub-3 nm particles is less clear. The condensation properties of these organics depend on their vapor pressures over very small nuclei, and the specific compounds tend to be considerably more volatile than sulfuric acid. In our baseline case study, the condensation of low volatility organics is limited to particles larger than 3 nm (for details, see Yu and Turco, 2008). This assumption is consistent with the sizes estimated by Kulmala et al. (2004a, b) to be affected by organics, and with more recent laboratory findings (e.g., Wang et al., 2010). It is also consistent with the observed time delay between the increase in $[\text{H}_2\text{SO}_4]$ and N_3-6 in early morning (see Fig. 3 and section 3.1 in Yu and Turco, 2008). At least for the cases presented in Yu and Turco (2008) and this paper, sulfuric acid condensation alone appears capable of explaining the growth rates of sub-3 nm particles. In earlier work, we had considered organic growth for different sizes

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of nano-particles, eventually concluding that organic condensation at sizes below ~ 3 nm would result in growth rates that are inconsistent with field observations (i.e., time delay between the increase in $[H_2SO_4]$ and N_3-6 in early morning). As noted above, this condition is consistent with the apparent chemical properties of low volatility organic compounds and the physics of condensation at small particle sizes (large Kelvin effect, etc.). In the revised manuscript, we will add discussions about the uncertainty associated with growth rates.

Other comments:

Yes, we will make it consistent.

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