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

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Abstract

A clear physical understanding of atmospheric particle nucleation mechanisms is critical in assessing the influences of aerosols on climate and climate variability. Currently, several mechanisms have been proposed and are being employed to interpret field observations of nucleation events. Roughly speaking, the two most likely candidates are neutral cluster nucleation (NCN) and ion-mediated nucleation (IMN). Detailed nucleation event data has been obtained in boreal forests. In one set of analyses of these measurements, NCN was suggested as the dominant formation mode, while in another, it was IMN. Obviously, information on the electrical charge distribution carried by the nucleating clusters themselves is the key to identifying the relative contributions of neutral and ion-mediated processes under various conditions. Fortunately, groundbreaking measurements of the charged states or fractions of ambient nanometer-sized particles soon after undergoing nucleation are now available to help resolve the main pathway. In the present study, the size-dependent "apparent" formation rates and fractions of charged and neutral particles are simulated with a detailed kinetic model. We show that the predicted "apparent" formation rates of charged and neutral particles at 2 nm agree well with the corresponding values derived from the boreal forest data, but the "apparent" contribution of ion-based nucleation increases by up to ~one order of magnitude as the size of particles decreases from 2 nm to ~1.5 nm. It appears that most of the neutral particles detected at sizes around 2 nm are in reality initially formed on ionic cores that are neutralized before the particles grow to this size. Thus, although the apparent rate of formation of neutral 2-nm particles might seem to be dominated by a neutral clustering process, in fact those particles are largely the result of an ion-induced nucleation mechanism. This point is clarified when the formation rates of smaller particles (e.g., ~1.5 nm) are explicitly analyzed (noting that measurements at these smaller sizes are not yet available), showing that IMN dominates NCN processes under typical circumstances in the boreal forest.

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1 Introduction

Aerosol particles formed in the atmosphere influence climate directly through scattering and absorption of radiation, and indirectly by acting as cloud condensation nuclei (CCN) that affect cloud properties and precipitation. New particle formation has been observed to occur frequently in many regions of troposphere (e.g., Kulmala et al., 2004; Yu et al., 2008) and contributes significantly to global particle concentrations and CCN abundances (e.g., Spracklen et al., 2008; Pierce and Adam, 2009; Yu and Luo, 2009; Kazil et al., 2010). The sensitivities of nucleation rates to changes in a number of controlling parameters suggest important physical feedback mechanisms to climate variation associated with changes in particle and precursor emission rates, solar variability, CCN and other factors, through aerosol indirect radiative forcing (e.g., Yu, 2010). In order to accurately assess the influences of aerosols on climate, interpret climate history, and project future changes, it is critical to achieve a clear physical understanding of atmospheric particle nucleation mechanisms and key controlling parameters.

Although nucleation phenomena have been intensively studied over the past several decades, and significant progress has been achieved, there are still major uncertainties concerning atmospheric nucleation mechanisms. For example, the relative importance of neutral cluster nucleation (NCN) processes versus ion-mediated nucleation (IMN), under different ambient conditions, remains unresolved. As a case in point, in a boreal forest setting quite different conclusions have been derived from the same measurements regarding the dominance of neutral versus ion-based nucleation. In one series of studies, NCN was identified as the main pathway, with only a small contribution ($\sim$ 10% or less) from IMN (e.g., Laakso et al., 2007; Kulmala et al., 2007, 2010; Gagné et al., 2008, 2010; Manninen et al., 2009), whereas in another set of analyses using the same data, IMN was found to be clearly dominant (Yu and Turco, 2007, 2008; Yu et al., 2008; Yu, 2010).

In the present study, we seek to identify the reasons for the striking differences in past interpretations of field data, with the goal of reconciling observations and theory in

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relation to aerosol formation in boreal forests. As will be demonstrated below, the likely source of misinterpretation appears to originate in the transitory nature of the nucleation process, and the co-evolution of particle embryo sizes and electrical charges. In Sect. 2, an overview is given of previous attempts to interpret what, up to this point, is the most comprehensive set of data characterizing aerosol nucleation in the lower atmosphere. Section 3 then provides a detailed analysis of the size-dependent apparent formation rates of charged and neutral particles using a model that is capable of resolving the complex physical relationships involved. The implications of these new results with respect to the relative contributions of neutral versus ion-mediated nucleation are also presented in this section. Conclusions are given in Sect. 4.

2 Past studies of the dominant nucleation mechanism in a boreal forest

Kulmala and colleagues (e.g., Kulmala et al., 2007) have carried out a detailed, long-term characterization of nucleation events at a boreal forest site (Hyytiälä, Finland) using a suite of instruments including a chemical ionization mass spectrometer (CIMS), a Differential Mobility Particle Sizer (DMPS), an ion-DMPS, a Balance Scanning Mobility Analyzer (BSMA), an Air Ion Spectrometer (AIS), and the Neutral Cluster and Air Ion Spectrometer (NAIS). This set of coordinated observations provides the most comprehensive data available to date to constrain nucleation theories. Based on their analysis of the electrical-charge states of nucleation mode particles ($\sim$ 3–15 nm diameter) measured with the ion-DMPS, Laakso et al. (2007) and Gagné et al. (2008) concluded that, while nucleation mode particles were significantly overcharged (relative to the ambient equilibrium charge level resulting from diffusional charging by background ionization) during most of the nucleation events observed ($>\sim$ 80% of the nucleation event days), the average contribution of IMN to total particle formation was relatively small ($<\sim$ 10% of the new particles). By contrast, Yu and Turco (2007), applying a different analytical methodology to the same data, found that the observed level of overcharging of particles in the 3–5 nm range pointed to a more significant IMN contribution.

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Similarly, based on an analysis of four days of multiple-instrument measurements of neutral and charged nanometer-sized cluster concentrations in Hyytiälä in spring 2006, Kulmala et al. (2007) concluded that neutral nucleation dominates over ion-induced nucleation, at least under the conditions in a boreal forest. However, Yu et al. (2008, and in published replies to referee's comments), reanalyzed the same observations, finding that a substantial contribution from IMN could not be ruled out. Aiming to resolve these conflicting conclusions with regard to the importance of IMN, Yu and Turco (2008) carried out a more constrained case study of nucleation events characterized in Hyytiälä, utilizing a kinetic nucleation model that accounts for the size-dependent microphysics of neutral and charged clusters. They demonstrated that good agreement could be achieved between the IMN predictions and field data for a wide range of the key parameters, including the overcharging ratio of 3–7 nm particles. On this basis, it was concluded that IMN is likely to be the dominant nucleation mechanism in at least a large fraction of nucleation events in boreal forests.

Manninen et al. (2009) extended the analytical approach of Kulmala et al. (2007) to study a more comprehensive set of data lasting ~ 4 months (between 6 March and 30 June 2007 covering 54 nucleation event days), and showed that IMN contributed only ~ 10% to new particle formation during that period. Using calculated 2-nm particle formation rates at three ground-based measurement sites (Hyytiälä, Finland; Hohenpeissenberg, Germany; and Melpitz, Germany) based on NAIS and AIS data, Kulmala et al. (2010) concluded that the overall contribution of ion-induced nucleation to atmospheric aerosol formation is small, being typically much less than 10%. Even more recently, Gagné et al. (2010) analyzed 2 years and 7 months (May 2005 to December 2007) of ion-DMPS data and compared the derived fractions attributed to ion nucleation to fractions calculated using formation rates of charged and neutral particles at 2 nm as described in Kulmala et al. (2007) and Manninen et al. (2009), when both ion-DMPS and NAIS measurements were available (~ 44 event days). Gagné et al. (2010) showed that the charge-state classification based on ion-DMPS measurements is generally consistent with the fraction of ion-induced particles inferred using NAIS

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measurements, and that the two independent measurements indicated ∼5–15% of ion-induced formation of 2-nm particles.

Yu (2010) briefly reviewed these differing studies and pointed out that Kulmala and colleagues may have underestimated the importance of IMN by treating all of the neutral clusters <2 nm, including those produced by ion-ion recombination (an important channel for IMN, according to Yu and Turco, 2008), as attributable to a purely neutral nucleation process. Yu (2010) also argued that ion-DMPS data indicate a greater significance of IMN if when the electrical states of ∼1-nm particles are used as a constraint instead of those of particles ∼2 nm (which tend to be dominated by neutralized ionic clusters, making interpretation of the origin of the particles more difficult). Thus, a key source of differences in the interpretation of the Hyytiälä nucleation data appears to be related to the size-dependent evolution of ionic and neutral clusters in the size range below 2 nm, where nucleation is actually occurring but observations are most difficult. In the following discussion, we refer to the "apparent" nucleation rate of 2-nm particles; this is the rate at which particles of 2-nm size are being formed under local conditions, regardless of the state of electrical charge of those particles. The apparent rate is not the actual nucleation rate, inasmuch as nucleation occurs mainly at embryo sizes well below 2 nanometers. Moreover, it is obvious that the charge state of 2-nm particles is not the same as for newly nucleated particles, which would carry the electrical signature of the nucleation pathway with greater fidelity. Accordingly, the methodology for extrapolating observations in the 2-nm range into the smaller size range characterizing the nucleation process itself is critical in interpreting instrumental data.

3 Size-dependent apparent ion and neutral particle formation rates

3.1 Theoretical consideration

As already noted, new particle formation in the atmosphere is a dynamic process involving various interactions among precursor gas molecules, small clusters (both

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charged and neutral), and pre-existing particles (Fig. 1). Ions, which are generated continuously and ubiquitously in the atmosphere by cosmic radiation and radioactive decay, interact strongly with common nucleation precursors and thus are inseparable components of the atmospheric nucleation system. Yu and Turco (2001) developed a kinetic approach to study this dynamic system involving neutral and charged clusters, while Yu (2006) substantially improved the detailed treatment of physical, chemical and thermodynamic processes in the kinetic IMN model employed here. This model effectively integrates neutral and ionic nucleation processes starting from single molecules, using a discrete-sectional bin structure to represent the size spectra of molecular clusters/particles while accounting for the complex interactions among ions, neutral and charged molecular clusters of various sizes, vapor molecules, and pre-existing particles. The differential equations governing the evolution of neutral and charged clusters, along with algorithms to calculate size-dependent rates for various microphysical processes (condensation, evaporation, coagulation, and charge recombination) can be found in Yu (2006). Below, we describe some of the aspects of the IMN simulation that are relevant to the present study.

The evolution of neutral and charged cluster/particle size distributions in the IMN model allows us to calculate the time series of apparent formation rates (or net fluxes, J) of particles at any given diameter (d), and hence the apparent fraction of nucleation due to ion (FJ_d^{ion}). FJ_d^{ion} is defined as

$$FJ_d^{\text{ion}} = \frac{J_d^+ + J_d^-}{J_d^+ + J_d^- + J_d^0} = \frac{J_d^{\text{ion}}}{J_d^{\text{ion}} + J_d^0} \quad (1)$$

where J_d^+, J_d^0, and J_d^- are, respectively, the apparent formation rates (or net fluxes) of positively charged, neutral, and negatively charged particles at a given diameter, d. $J_d^{\text{ion}} = J_d^+ + J_d^-$ is the total apparent formation rate of charged particles of diameter d.

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In addition, the IMN model can track various product and loss terms for particles within given size ranges,

$$\frac{\mathrm{d}N^{0,\pm}_{d1-d2}}{\mathrm{d}t} = \left.\frac{\partial N^{0,\pm}_{d1-d2}}{\partial t}\right|_{\text{grow}} + \left.\frac{\partial N^{0,\pm}_{d1-d2}}{\partial t}\right|_{\text{recomb}} + \left.\frac{\partial N^{0,\pm}_{d1-d2}}{\partial t}\right|_{\text{coag}}$$
$$= PL^{0,\pm}_{\text{grow}} + \mathrm{PL}^{0,\pm}_{\text{recomb}} + \mathrm{PL}^{0,\pm}_{\text{coag}} \quad (2)$$

where N^{0}_{d1-d2} and $N^{\pm}_{d1-d2}$ are the concentrations of neutral and charged particles within the size range spanning d_1 and d_2. $\mathrm{PL}^{0,\pm}_{\text{grow}}$, $\mathrm{PL}^{0,\pm}_{\text{recomb}}$, and $\mathrm{PL}^{0,\pm}_{\text{coag}}$ are production or loss rates associated with growth (including evaporation), recombination, and coagulation, respectively. Recombination, a special case of coagulation, leads to the loss of two oppositely charged clusters/particles while generating one neutral cluster/particle. The attachment of ions/charged clusters to neutral particles, which transforms the neutral particles into charged ones, is included in $\mathrm{PL}^{0,\pm}_{\text{coag}}$. $\mathrm{PL}^{0,\pm}_{\text{coag}}$ also takes into account self-coagulation and coagulation scavenging of small clusters by pre-existing particles of same type. $\mathrm{PL}^{0,\pm}_{\text{grow}}$ describes the net fluxes of particles crossing d_1 and d_2 and is related to apparent particle formation rates ($J^{0,\pm}_{d}$) as,

$$\mathrm{PL}^{0,\pm}_{\text{grow}} = \left(\frac{\mathrm{d}N}{\mathrm{d}d}\right)^{0,\pm}_{d1}\left(\frac{\mathrm{d}d}{\mathrm{d}t}\right)^{0,\pm}_{d1} - \left(\frac{\mathrm{d}N}{\mathrm{d}d}\right)^{0,\pm}_{d2}\left(\frac{\mathrm{d}d}{\mathrm{d}t}\right)^{0,\pm}_{d2}$$
$$= \left(\frac{\mathrm{d}N}{\mathrm{d}d}\right)^{0,\pm}_{d1}\mathrm{GR}^{0,\pm}_{d1} - \left(\frac{\mathrm{d}N}{\mathrm{d}d}\right)^{0,\pm}_{d2}\mathrm{GR}^{0,\pm}_{d2} = J^{0,\pm}_{d1} - J^{0,\pm}_{d2} \quad (3)$$

where $\frac{\mathrm{d}N}{\mathrm{d}d}$ is the particle size distribution and $\mathrm{GR}^{0,\pm}_{d}$ is the net particle growth rate at d.

By combining Eqs. (2) and (3) and rearranging terms, we get,

$$J^{0,\pm}_{d1} = \frac{\mathrm{d}N^{0,\pm}_{d1-d2}}{\mathrm{d}t} - \mathrm{PL}^{0,\pm}_{\text{recomb}} - \mathrm{PL}^{0,\pm}_{\text{coag}} + \left(\frac{\mathrm{d}N^{0,\pm}}{\mathrm{d}d}\right)_{d2}\mathrm{GR}^{0,\pm}_{d2} \quad (4)$$

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$$J_{d1}^{\mathrm{tot}} = J_{d1}^{0} + J_{d1}^{\pm} = \frac{\mathrm{d}N_{d1-d2}^{\mathrm{tot}}}{\mathrm{d}t} - \mathrm{PL}_{\mathrm{coag}}^{\mathrm{tot}} + \left(\frac{\mathrm{d}N^{0}}{\mathrm{d}d}\right)_{d2} \mathrm{GR}_{d2}^{0} + \left(\frac{\mathrm{d}N^{\pm}}{\mathrm{d}d}\right)_{d2} \mathrm{GR}_{d2}^{\pm} \quad (5)$$

The formula connecting apparent particle formation rates at $d_1 = 2$ nm (J_2^{ion}, J_2^{tot}) with observed number concentrations of charged and total particles between 2–3 nm ($N_{2-3}^{\pm}$ and N_{2-3}^{tot}) (Kulmala et al., 2007; Manninen et al., 2009) can be derived (with approximations discussed below) as,

$$J_2^{\mathrm{ion}} = \frac{\Delta N_{2-3}^{\pm}}{\Delta t} - \mathrm{PL}_{\mathrm{recomb}}^{\pm} - \mathrm{PL}_{\mathrm{coag}}^{\pm} + \frac{N_{2-3}^{\pm}}{1\ \mathrm{nm}} \mathrm{GR}_3^{\pm} \quad (6)$$

$$J_2^{\mathrm{tot}} = \frac{\Delta N_{2-3}^{\mathrm{tot}}}{\Delta t} - \mathrm{PL}_{\mathrm{coag}}^{\mathrm{tot}} + \frac{N_{2-3}^{\mathrm{tot}}}{1\ \mathrm{nm}} \mathrm{GR}_3^{\pm} \quad (7)$$

Here, $N_{2-3}^{\pm}$ is the 2–3 nm charged particle concentration from the AIS and BSMA measurements; N_{2-3}^{tot} is the 2–3 nm total (charged + neutral) particle number concentration from the NAIS measurements; and $\mathrm{GR}_3^{\pm}$ is the growth rate of charged sub-3 nm particles which can be derived from BSMA and AIS ion spectrum (Manninen et al., 2009). Because the field instruments were not able to measure the growth rate of neutral sub-3-nm particles (GR_3^{0}), the same growth rate for neutral and charged sub-3-nm particles (i.e, $\mathrm{GR}_3^{0} = \mathrm{GR}_3^{\pm}$) has been assumed in Eq. (7), an approximation previously used to derive J_2^{ion} and J_2^{tot} from measurements (Kulmala et al., 2007; Manninen et al., 2009).

With J_2^{ion} and J_2^{tot} derived from measurements according to Eqs. (6) and (7), the apparent fraction of 2-nm particle formation due to ion processes is readily calculated as $FJ_2^{\mathrm{ion}} = J_2^{\mathrm{ion}}/J_2^{\mathrm{tot}}$. The values of FJ_2^{ion} can also been derived, completely independently, from ion-DMPS measurements of the charge states of freshly nucleated nanoparticles ~ 3–5 nm (Laakso et al., 2007). The conclusion of Kulmala and colleagues concerning the dominance of neutral nucleation processes is mainly based on their derived FJ_2^{ion} values. However, with the IMN model, which resolves the dynamic evolution of both

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charged and neutral clusters/particles, FJ_d^{ion} values can be derived at other sizes, revealing the size-dependence of the apparent ion nucleation fraction, leading to a test of the validity of the apparent fraction at 2 nm as a gauge for the relative importance of ion versus neutral processes.

3.2 Kinetic simulation and comparison with measurements

Yu and Turco (2008) reported case studies of nucleation events observed during an intensive field campaign at a boreal forest site (Hyytiälä, Finland) in the spring of 2005. Out of the 22 days of the campaign on which nucleation events were observed, eight major events were selected for detailed analysis on the basis of indications that the observed air masses were relatively homogeneous. That study focused on comparisons between IMN model predictions and measured particle number concentrations and the overcharge ratio (OR) of freshly nucleated particles (with diameters ~ 3–6 nm). The size-dependent overcharge ratio is the average number of unit electrical charges carried by particles of a given size divided by the equilibrium number of charges particles of that size would carry under ambient conditions due to background ionization rates. In the present study, we calculate the time series of the apparent formation rates of particles at various diameters, d, and the apparent fraction of nucleation due to ions (FJ_d^{ion}), based on the simulated evolution of the size distribution of neutral and charged cluster/particles as described in Yu and Turco (2008). The model predicted J_2^{ion}, J_2^{tot}, and FJ_d^{ion} are compared to corresponding measured values reported recently in the literature. Since the particle diameters reported in the papers of Kulmala and colleagues correspond to Millikan mobility diameters, we have converted the model mass diameters to mobility diameters following the relationship given in Ku and de la Mora (2009); hence, all the diameters discussed below are equivalent Millikan mobility diameters.

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Figure 2 shows the predicted evolution of apparent neutral and charged particle formation rates (J_d^0 or J_d^{neutral}, and J_d^{ion}) and the corresponding FJ_d^{ion} values at $d = 1.5$, 1.7, 2, 2.5, and 3 nm for a nucleation event observed in Hyytiälä on 17 April 2005. The simulations, as detailed in Yu and Turco (2008), were constrained by observed time series of temperature, relatively humidly, [H_2SO_4], and the size distribution of pre-existing particles. The ionization rate is based on the median value derived from long-term direct measurements reported in Gagné et al. (2010). Figure 2 presents results between 09:00 a.m. and 03:00 p.m. when the air mass was relatively homogeneous, as indicated by consistency in the SMPS data. It is clear from Fig. 2 that J_d^{ion} and FJ_d^{ion} decrease significantly as d increases from 1.5 nm to 3 nm. In contrast, J_d^0 first increases and then decreases as d increases from 1.5 nm to 3 nm. The dramatic decrease in J_d^{ion} and FJ_d^{ion} values as d increases is due to the rapid recombination of charged clusters by oppositely charged small ion clusters. Under the conditions encountered, the neutral H_2SO_4-H_2O binary nucleation rate is predicted to be essentially zero. Thus, neutral particles are formed solely by recombination processes. It is interesting to note that $J_{1.5}^0$ is negative, which is a result of evaporation of 1.5-nm neutral clusters generated by recombination. Because of negative values for J_d^0, $FJ_d^{\text{ion}} = \frac{J_d^{\text{ion}}}{J_d^{\text{ion}} + J_d^0}$ can mathematically be larger than 100%. Figure 2b shows that FJ_d^{ion} decreases from > 100% at $d = 1.5$ nm, to 30–70% at $d = 1.7$ nm, to 3–25% at $d = 2$ nm, and below 6% at $d = 2.5$ nm. The FJ_d^{ion} value averaged over the nucleation period, as derived from ion-DMPS measurements (Laakso et al., 2007), is ∼19% for this day (assuming an equilibrium charged particle fraction of 0.45% for 2 nm particles; Yu and Turco, 2008). It is clear from Fig. 2b that the model predicted FJ_2^{ion} values are fully consistent with the ion-DMPS measurements. If one only compares observed and predicted FJ_2^{ion} values, and assumes that the original ionic charge survives as a new particle grows to 2 nm, then one wrongly concludes that only ∼ 19% of the apparent total 2-nm particle formation rate is due to ion-based processes. This error becomes obvious when the

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FJ_d^{ion} values at $d = \sim 1.5$ nm are considered, since this is much closer to the critical embryo sizes under the conditions sampled. Indeed, IMN clearly dominates particle formation during this event.

The kinetic IMN model allows the dynamical evolution of neutral and charged clusters of different sizes to be investigated, and the contributions of different microphysical processes to be quantified (i.e., Fig. 1, Eqs. 2 and 3). For the nucleation event on 17 April 2005, Fig. 3 gives the simulated number concentrations of neutral and charged particles in two sizes ranges (1.5–2 nm and 2–3 nm), and the corresponding fractions of the total number of particles that are charged. In Fig. 3b, the 1.5–2 nm and 2–3 nm size ranges are further divided into four size ranges (1.5–1.7, 1.7–2, 2–2.5, 2.5–3 nm) to show more clearly the dependence of charged particle fractions on size. The change in $N_{1.5\_2}^{total}$ generally follows that of $J_{1.5}^{ion}$ (Fig. 2a), and the peak $N_{1.5\_2}^{total}$ value reaches $\sim 425\,cm^{-3}$, with charged particles accounting for $\sim 50\%$ of the total (Fig. 3b). $N_{2\_3}^{total}$ has a peak concentration of $\sim 625\,cm^{-3}$ and is dominated by neutral particles ($> 90\%$) at all times. The high sensitivity of the charged particle fraction to size can be seen more clearly in Fig. 3b. During the main nucleation periods, the fraction of charged particles ($FN_{d1\_d2}^{ion}$) decreases from $\sim 70\%$ for 1.5–1.7 nm sizes, to ~ 20–35% for 1.7–2 nm particles, to ~ 5–10% for 2–2.5 nm sizes, and to ~ 2–3.5% for those 2.5–3 nm. It is not surprising that $FN_{d1\_d2}^{ion}$ values (Fig. 3b) are close to the FJ_d^{ion} (Fig. 2b) for particles of similar sizes as the apparent particle formation rates are proportional to particle number concentrations (Eq. 3).

Figure 4 shows the contributions of different processes (growth, coagulation, and recombination) to changes in the neutral and charged particle concentrations in the 1.5–2 nm and 2–3 nm size ranges, $N_{1.5\_2}$ and N_{2_3}. For charged 1.5–2 nm particles, growth or nucleation is the only source, while recombination is the main sink. By contrast, for neutral 1.5–2 nm particles, recombination is the only source, while growth is the main sink. It should be noted that $|PL_{recomb}^{0}| > |PL_{recomb}^{\pm}|$, which is a result of the production of 1.5–2 nm neutral particles by the recombination of two sub-1.5 nm oppositely charged

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particles. PL_{grow} for neutral 1.5–2 nm particles is negative because of the evaporation of 1.5 nm particles (i.e., negative $J^o_{1.5}$ values; see Fig. 2a) while at the same time there is growth-driven removal at $d = 2$ nm (i.e., positive J^o_2 values; also see Fig. 2a). The PL_{coag} values are negative for both charged and neutral 1.5–2 nm particles, although their magnitudes (peak values ~ -0.05–$-0.1\,cm^{-3}\,s^{-1}$) are much smaller than those of PL_{recomb} (-0.45 and $+0.65\,cm^{-3}\,s^{-1}$) and PL_{grow} (0.6 and $-0.5\,cm^{-3}\,s^{-1}$). The net rates of change, dN/dt, fluctuate around zero with an aptitude of $\sim 0.05\,cm^{-3}\,s^{-1}$, leading to a net increase or decrease in $N_{1.5-2}$, as shown in Fig. 3a. As the particles grow from 1.5–2 nm to 2–3 nm, the magnitudes of PL_{grow} and PL_{rocomb} decrease by a factor of 4–10. For charged 2–3 nm particles, growth or nucleation is still the main source, and recombination is the main sink. One interesting point is that, despite coagulation scavenging by larger aerosols, PL_{coag} for charged 2–3 nm particles is slightly positive around noon. Our analysis indicates that this is a result of attachment of small ions to neutral particles. For neutral 2–3 nm particles, recombination is still a strong source but PL_{grow} becomes a more important source (i.e., $PL_{grow} > PL_{recomb}$) during the main nucleation period ($\sim$ 10:00 a.m. – noon). In contrast to PL_{grow} for charged 2–3 nm particles, which is positive during the entire period, PL_{grow} for neutral 2–3 nm particles becomes negative around 12:30 p.m. because $J^o_3 > J^o_2$ (i.e., more particles growing above 3 nm than are growing above 2 nm; see Fig. 3a). PL_{coag} is a major sink for neutral 2–3 nm particles during the entire nucleation period.

Figure 4 shows clearly that neutral particles growing into the 2-nm size range, which are identified with the apparent formation rate of neutral particles at $d = 2$ nm, were actually generated initially through ion-mediated processes. As before, it must be concluded that the relative importance of ion versus neutral nucleation processes cannot be determined solely on the basis of derived apparent neutral and charged particle formation rates at $d = 2$ nm.

Figures 2–4 present detailed size-dependent formation rates and number concentrations of sub-3-nm particles for 27 April 2005 (Julian day 117). A similar analysis can be carried out for the other case study days (Julian days # 102, 103, 108, 122, 123,

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132, and 136) described in Yu and Turco (2008). Figure 5 gives the FJ_2^{ion} values as a function of hours after sunrise for all 8 of those case study days. For comparison, the symbols represent median values of FJ_2^{ion} derived from AIS and NAIS measurements in the spring of 2006 and 2007 on 28 days when particle overcharging was observed (stars) and 8 days with undercharging (diamonds) (from Fig. 2a of Gagné et al., 2010). Undercharging can occur in the presence of rapid neutral nucleation as particle charging by background ionization will generally lag the equilibrium charge distribution. It should be emphasized that, in Fig. 5, the simulations correspond to 8 nucleation events in the Spring of 2005, while the median values were derived for Spring of 2006 and 2007. IMN model results presented in Fig. 5 show significant day to day variations in FJ_2^{ion}, ranging from a few percent to a few tens of percent. Figure 5 also reveals substantial variations in FJ_2^{ion} with local time, implying the sensitivity of averaged FJ_2^{ion} values to the averaging period and air-mass inhomogeneity. The median values of simulated FJ_2^{ion} for the 8 case study days are ~5–15% at different local times (or hours after sunrise), and are in reasonable agreement with the observations reported by Gagné et al. (2010). Accordingly, interannual variability does not seem to be a major factor in the comparisons in Fig. 5.

Figure 6 illustrates the mean size-dependent nucleation rates for both charged (J_d^{ion}) and neutral ($J_d^{neutral}$ or J_d^0) particles, and the corresponding FJ_d^{ion} values for all eight nucleation events studied by Yu and Turco (2008). The symbols represent the observed median values of J_2^{ion} (including the formation of > 2–3 nm particles via ion-ion recombination), J_2^0 ($= J_2^{tot} - J_2^{ion}$), and FJ_2^{ion} for the Spring of 2007 offered by Manninen et al. (2009). The simulated nucleation rates and FJ_d^{ion} on given days are average values during the periods when nucleation was occurring ($J_{1.5}^{tot} > 0.01\,cm^{-3}\,s^{-1}$). Both J_d^{ion} and FJ_d^{ion} decrease exponentially as the particle size increases, a result of the rapid recombination of charged species. For example, J_d^{ion} decreases by up to ~one order of magnitude as d increases from 1.5 nm to 2 nm. $J_{1.5}^0$ is generally very small and is

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negative for 6 out of the 8 cases but it increases quickly as a result of increase in neutral clusters from ion-ion recombination. J_d^0 and J_d^{ion} are comparable at $d = 1.6$–1.8 nm. J_d^0 dominates at $d > \sim 1.8$ nm and is a factor of 5–10 higher than J_d^{ion} at $d = 2$ nm for most of the cases. The predicted median value of J_2^{ion} for the 8 case study days is close to the observed value, although the prediction is for Spring 2005 while the observation was made in Spring 2007. The predicted median value of J_2^0 is $\sim 0.1\,cm^{-3}\,s^{-1}$ larger than the observed value, but is within the uncertainty range of simulations and observations. The modeled FJ_2^{ion} values for the 8 case study days range from 7.6% to 32.7%, with a median value of $\sim$13%, which is very close to the observed median of $\sim$12.5% (Manninen et al., 2009), considering possible uncertainties in both modeling and field observation. For 5 out of 8 case study days, FJ_2^{ion} is within the range of 7–15%. On day 123, FJ_2^{ion} reaches $\sim$32%. It is interesting to note that both NAIS and ion-DMPS measurements show that FJ_2^{ion} can be up to 30–50% on some days, although the two methods identify different specific days having large fractions, FJ_2^{ion} (refer to Fig. 2b in Gagné et al., 2010).

The analysis above indicates that, overall, IMN model predictions for J_2^{ion}, J_2^0, and FJ_2^{ion} are consistent with equivalent parameters derived from measurements carried out by Kulmala and co-workers. Importantly, the inference that the contribution of IMN to particle formation is small ($\sim$10%) in a boreal forest setting seems to be based on the assumption that the derived "apparent" neutral particle formation rate at $\sim$2 nm represents the actual neutral nucleation rate. It has been shown above, however, that while IMN indeed contributes $\sim$10% to the apparent formation rate of 2-nm particles, the actual IMN contribution to particle formation is much greater, and actually dominates nucleation under most common conditions (in instances where the experimental data are homogeneous enough to allow a meaningful time series analysis to be conducted). As pointed out by Yu (2010), and demonstrated in detail in the present study, most of the neutral particles growing into the 2-nm size range can be formed via ion-based process – in other words, originate at the molecular embryo level via ion-mediated

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processes. To properly understand aerosol formation, and determine the contributions of various nucleation mechanisms, an analysis must consider the charged and neutral processes occurring at sizes corresponding to critical embryos, which are generally in the ~1.5 nm range (for the Hyytiälä experiments; Kulmala et al., 2007; Yu and Turco, 2008). The exponential decrease of FJ_d^{ion} as particle size increases from $d = 1.5$ to 2 nm (Fig. 6b) indicates the significant discrepancy that can arise in basing conclusions about nucleation sources on observations at sizes even seemingly a small size increment above the critical embryo (e.g., at 2 nm rather than 1.5 nm). In the present case studies, it happens that the ion-mediated mechanism can account for ~100% of all the new particle formation under the conditions of the observations.

3.3 Analytical interpretation

Under certain assumptions, analytical expression describing the evolution of the charging states of nanometer particles can be derived (Kerminen et al., 2007). The exponential decrease of FJ_d^{ion} from 1.5 to 2 nm shown in Fig. 6, which appears to be the key toward understanding the dominant nucleation path, has a sound and straightforward physical basis that can be approximately represented using a simplified analytical model. Let us assume that both ion and neutral nucleation processes create thermodynamically stable particles at rates, J_{d0}^{ion} and J_{d0}^{neu}, respectively, at an initial diameter, $d = d_0$. The fraction of new particles that are initially charged (or due to ion nucleation) at $d = d_0$ would be given by,

$$FJ_{d0}^{\text{ion}} = J_{d0}^{\text{ion}} / \left(J_{d0}^{\text{ion}} + J_{d0}^{\text{neu}} \right) \tag{8}$$

The particles nucleated on ions are subsequently neutralized due to charge recombination during their initial growth phase. Thus, as the particles increase in size from d_0 to $d_1 > d_0$, the fraction originally nucleated on ions that remain charged is roughly, $e^{-\alpha C \Delta t}$, where α is the ion-ion recombination coefficient for a small ion with a charged nanoparticle of opposite sign, C is the total concentration of small (negative or positive)

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ions, and $\Delta t = (d_1 - d_0)/\mathrm{GR}$ is the time needed to grow particles from d_0 to d_1 at a fixed growth rate (GR).

Assuming that the neutral clusters have same growth rates as the charged clusters, and neglecting coagulation scavenging of clusters as well as ion-neutral attachment, the steady state "apparent" nucleation flux at $d = d_1$ for charged particles is,

$$J_{d1}^{\mathrm{ion}} = J_{d0}^{\mathrm{ion}} \times e^{-\alpha C \Delta t} \tag{9}$$

and the "apparent" nucleation flux for neutral particles is

$$J_{d1}^{\mathrm{neu}} = J_{d0}^{\mathrm{neu}} + J_{d0}^{\mathrm{ion}} * \left(1 - e^{-\alpha C \Delta t}\right) \tag{10}$$

Thus, for this simplified model, the apparent ion nucleation fraction is,

$$FJ_{d1}^{\mathrm{ion}} = J_{d1}^{\mathrm{ion}} / \left(J_{d1}^{\mathrm{ion}} + J_{d1}^{\mathrm{neu}}\right) = FJ_{d0}^{\mathrm{ion}} * e^{-\alpha C \Delta t} \tag{11}$$

Under typical conditions, $\alpha = \sim 1.6 \times 10^{-6}\,\mathrm{cm^3\,s^{-1}}$, and $C = \sim 1000\,\mathrm{cm^{-3}}$. The median growth rates of 1.3–3 nm intermediate ions at Hyytiälä in spring 2007 were estimated using ion mobility spectra to be $\sim 1.9\,\mathrm{nm\,h^{-1}}$ (Manninen et al., 2010). If we assume $d_1 = 2\,\mathrm{nm}$ and $d_0 = 1.5\,\mathrm{nm}$, we estimate that, $FJ_2^{\mathrm{ion}}/FJ_{1.5}^{\mathrm{ion}} = e^{-2.88/\mathrm{GR}} = 5.6\%$, 22%, and 38% with GR=1, 1.9, and $3\,\mathrm{nm\,h^{-1}}$, respectively. This result is quite consistent with the discussion above and earlier findings.

It should be noted that the simplified analytical model is subject to uncertainties associated with the values of α, C and GR, the neglect of variations in most parameters with size, and the neglect of secondary processes such as differential growth rates, background ionization, and so on. Further, in real situations, α, and GR depend on the types (charged or neutral) of particles, and α, C and GR also vary with time during nucleation events. All of these complexities are taken into account in the kinetic IMN simulations. However, it is clear that both the simplified analytical model and the detailed kinetic IMN model indicate that a substantial fraction ($\sim$ 60–95%) of particles nucleated on ions can be neutralized as they grow from $\sim 1.5\,\mathrm{nm}$ to 2 nm in size. The

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physics of electrical neutralization is straightforward: charged clusters have a lifetime of ~ 10 min against neutralization, which exceeds the typical time that it takes the clusters to grow from 1.5 nm to 2 nm.

3.4 Uncertainties in the analysis

The processes controlling the evolution of nanometer-sized particles and molecular clusters are very complex, depend on the compositional nature of the clusters, and are influenced by highly non-linear physical, chemical and thermodynamic processes, some of which are only crudely known for the species of interest. Accordingly, there are inherently a large number of sources of uncertainty in any model for atmospheric nucleation. In this study, we have focused on the use of additional constraints in developing a more comprehensive theoretical framework for studying nucleation events – in particular the electrical charge carried by particles under atmospheric conditions, and the variations in the charge-states between ambient and nucleating aerosols. While additional constraints are generally helpful, the use of such constraining data entails the introduction of additional variables and parameters that themselves can be uncertain or difficult to quantify. For example, to determine the equilibrium charge on ambient aerosols requires knowledge of the background ionization state, the mobilities of ambient ions, and accretion kernels for neutral and charged nanometer clusters. These data, or reasonable estimates for these parameters, are available, but are not precisely known. Similarly, the coagulation (recombination) kernels for charged particles/clusters over a broad size range can be calculated using basic physical principles, if the condensed matter properties of the particles can be determined. In a long series of papers appearing in the literature, many of these difficulties and uncertainties have been addressed by a number of researchers, both experimentally and theoretically. Nevertheless, we must recognize that the additional complexity connected with an ion-neutral treatment of the nucleation problem invites further sources of uncertainty and error.

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The basic line of reasoning that underpins the present analysis recognizes that ions are ubiquitous in the atmosphere, that ions naturally attract and cluster with the neutral compounds intimately associated with new particle formation, that particles in dynamic systems will carry electrical charge signatures that can be used to identify competing evolutionary pathways, and that the basic physics along these pathways is well known and long studied under the auspices of classical and quantum dynamics. It follows that a comprehensive theory of nucleation can be formulated and tested against observations. If the comprehensive theory provides explanatory results, then simplified models can be developed by investigating the relative importance of component processes and isolating the most important ones. The converse is not usually true. A simplified model, or highly approximated basis for analysis, cannot generally be extrapolated to reveal more detailed information and reach more fundamental conclusions. Moreover, a comprehensive model can be employed to carry out sensitivity studies that underscore the most critical uncertainties and point to the requirements for new data.

The results presented above strongly suggest that ambient atmospheric ionization is intimately involved in the formation of new aerosols under certain typical conditions, and can explain observations at least under those conditions – here, in a boreal forest. While there is still much information that must be collected and analyzed before a thorough understanding of particle formation is achieved, the current predictions provide a solid basis for expanding the enterprise.

4 Summary and conclusions

Nucleation is widely recognized as an important source of atmospheric particles. Accordingly, a clear physical understanding of atmospheric particle nucleation mechanisms is critical to assess accurately the influences of aerosols on climate and to project future climatic change. The relative importance of neutral cluster nucleation (NCN) and ion-mediated nucleation (IMN) remains unresolved, even though such processes are currently being integrated into global models. To advance our understanding, the

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present investigation considers well-characterized particle formation events in a boreal forest, employing the latest version of a comprehensive IMN model that explicitly treats NCN as a competitive pathway under atmospheric conditions. The model predicts the size-dependent "apparent" formation rates of charged and neutral particles (or equivalently, the time dependent particle size and electrical charge distributions) that can be compared to values derived from observations. Such comparisons show that, in cases where field observations are sufficiently well defined (in terms of the homogeneity of air-masses that allows time series analysis), ion-based nucleation processes appear to dominate particle formation. When other measures of the relative effectiveness of ionic processes are utilized – in particular, by calculating the ratio of neutral and charged particle fluxes across a size range that lies substantially above the actual nucleation embryonic size – conclusions concerning the contribution of ion-based nucleation must be tempered by an accurate treatment of charge recombination effects, which is difficult to accomplish without a comprehensive model. The size resolved, charge specific, kinetic analysis described here shows explicitly how typical measurements may be inadvertently misinterpreted in favor of NCN. Rather than the ~10% ion contribution suggested in some earlier studies, we find that IMN processes account for closer to 100% of the new particles for the cases investigated.

While, as noted above, the present analysis is subject to uncertainties associated with thermodynamics, particle growth rates and sizes, and inhomogeneities of air-masses, among other things, these uncertainties are unlikely to alter the straightforward physics of electrical charge recombination that, once accounted for in detail, reveals the actual contribution of ion-mediated nucleation. Nevertheless, additional experimental, field, theoretical, and modeling work should be carried out to reduce the uncertainties in IMN theory and assess its ability to explain new particle formation throughout the troposphere. It is important to note that the present investigation does not exclude the likely contributions of neutral nucleation under certain atmospheric conditions (especially in highly polluted urban regions), although the exact nature of these nucleation mechanisms remains to be specified. IMN should generally be favored over

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NCN because of strong electrical influences (e.g., Arnold et al., 1982; Yu and Turco, 2001; Lovejoy et al., 2004; Yu, 2006), notwithstanding, of course, the depletion of ambient ionization during intense nucleation events. The present research demonstrates that an IMN mechanism can successfully and rationally explain a sophisticated set of state-of-the-art multi-instrument field measurements in a boreal forest setting. Previous studies, which have applied the basic physics of the IMN mechanism to other environments, indicate that ambient ion production rates are high enough to account for most of the nucleation events observed globally (Yu et al., 2008, 2010). Hence, IMN should logically be incorporated into regional and global climate models to improve their ability to predict new particle formation and CCN abundances, thereby reducing the number of ad hoc assumptions adopted to calculate aerosol indirect radiative forcing, among other particle-related effects.

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References

Arnold, F., Viggiano, A. A., and Schlager, H.: Implications for trace gases and aerosols of large negative ions clusters in the stratosphere, Nature, 297, 371, 1982.

Gagné, S., Laakso, L., Petäjä, T., Kerminen, V.-M., and Kulmala, M.: 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.

Kazil, J., Stier, P., Zhang, K., Quaas, J., Kinne, S., O'Donnell, D., Rast, S., Esch, M., Ferrachat, S., Lohmann, U., and Feichter, J.: Aerosol nucleation and its role for clouds and Earth's radiative forcing in the aerosol-climate model ECHAM5-HAM, Atmos. Chem. Phys., 10, 10733–10752, doi:10.5194/acp-10-10733-2010, 2010.

Kerminen, V.-M., Anttila, T., Petäjä, T., Laakso, L., Gagné, S., Lehtinen, K. E. J., and Kulmala, M.: Charging state of the atmospheric nucleation mode: implications

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11, 11281–11309, 2011

for separating neutral and ion-induced nucleation, J. Geophys. Res., 112, D21205, doi:10.1029/2007JD008649, 2007.
Ku, B. K. and de la Mora, J. F.: Relation between electrical mobility, mass, and size for nanodrops 1–6.5 nm in diameter in air, Aerosol Sci.Technol., 43, 241–249, 2009.
Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, J. Aerosol Sci., 35, 143–176, 2004.
Kulmala, M., Riipinen, I., Sipil, M., Manninen, H. E., Petj, T., Junninen, H., Dal Maso, M., Mordas, G., Mirme, A., Vana, M., Hirsikko, A., Laakso, L., Harrison, R. M., Hanson, I., Leung, C., Lehtinen, K. E. J., and Kerminen, V.-M.: Toward direct measurement of atmospheric nucleation, Science, 318, 89–92, 2007.
Kulmala, M., Riipinen, I., Nieminen, T., Hulkkonen, M., Sogacheva, L., Manninen, H. E., Paasonen, P., Petäjä, T., Dal Maso, M., Aalto, P. P., Viljanen, A., Usoskin, I., Vainio, R., Mirme, S., Mirme, A., Minikin, A., Petzold, A., Hõrrak, U., Plaß-Dülmer, C., Birmili, W., and Kerminen, V.-M.: Atmospheric data over a solar cycle: no connection between galactic cosmic rays and new particle formation, Atmos. Chem. Phys., 10, 1885–1898, doi:10.5194/acp-10-1885-2010, 2010.
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, doi:10.5194/acp-7-1333-2007, 2007.
Lovejoy, E. R., Curtius, J., and Froyd, K. D.: Atmospheric ion-induced nucleation of sulfuric acid and water, J. Geophys. Res., 109, D08204, doi:10.1029/2003JD004460, 2004.
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., 9, 4077–4089, doi:10.5194/acp-9-4077-2009, 2009.
Pierce, J. R. and Adams, P. J.: Uncertainty in global CCN concentrations from uncertain aerosol nucleation and primary emission rates, Atmos. Chem. Phys., 9, 1339–1356, doi:10.5194/acp-9-1339-2009, 2009.
Spracklen, D. V., Carslaw, K. S., Kulmala, M., Kerminen, V.-M., Sihto, S.-L., Riipinen, I., Merikanto, J., Mann, G. W., Chipperfield, M. P., Wiedensohler, A., Birmili, W., and Lihavainen, H.: Contribution of particle formation to global cloud condensation nuclei concentrations, Geophys. Res. Lett., 35, L06808, 2008.

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Yu, F.: From molecular clusters to nanoparticles: second-generation ion-mediated nucleation model, Atmos. Chem. Phys., 6, 5193–5211, doi:10.5194/acp-6-5193-2006, 2006.
Yu, F.: Ion-mediated nucleation in the atmosphere: key controlling parameters, implications, and look-up table, J. Geophy. Res., 115, D03206, doi:10.1029/2009JD012630, 2010.
Yu, F. and Luo, G.: Simulation of particle size distribution with a global aerosol model: contribution of nucleation to aerosol and CCN number concentrations, Atmos. Chem. Phys., 9, 7691–7710, doi:10.5194/acp-9-7691-2009, 2009.
Yu, F. and Turco, R. P.: From molecular clusters to nanoparticles: the role of ambient ionization in tropospheric aerosol formation, J. Geophys. Res., 106, 4797–4814, 2001.
Yu, F. and Turco, R. P.: Charging state of freshly nucleated particles: implication for nucleation mechanisms, in: Nucleation and Atmospheric Aerosols, edited by: O'Dowd, C. D. and Wagner, P. E., Springer, 392–396, doi:10.1007/978-1-4020-6475-3_80, 2007.
Yu, F. and Turco, R.: Case studies of particle formation events observed in boreal forests: implications for nucleation mechanisms, Atmos. Chem. Phys., 8, 6085–6102, doi:10.5194/acp-8-6085-2008, 2008.
Yu, F., Wang, Z., Luo, G., and Turco, R.: Ion-mediated nucleation as an important global source of tropospheric aerosols, Atmos. Chem. Phys., 8, 2537–2554, doi:10.5194/acp-8-2537-2008, 2008.
Yu, F., Luo, G., Bates, T., Anderson, B., Clarke, A., Kapustin, V., Yantosca. R., Wang, Y., and Wu, S.: Spatial distributions of particle number concentrations in the global troposphere: simulations, observations, and implications for nucleation mechanisms, J. Geophys. Res., 115, D17205, doi:10.1029/2009JD013473, 2010.

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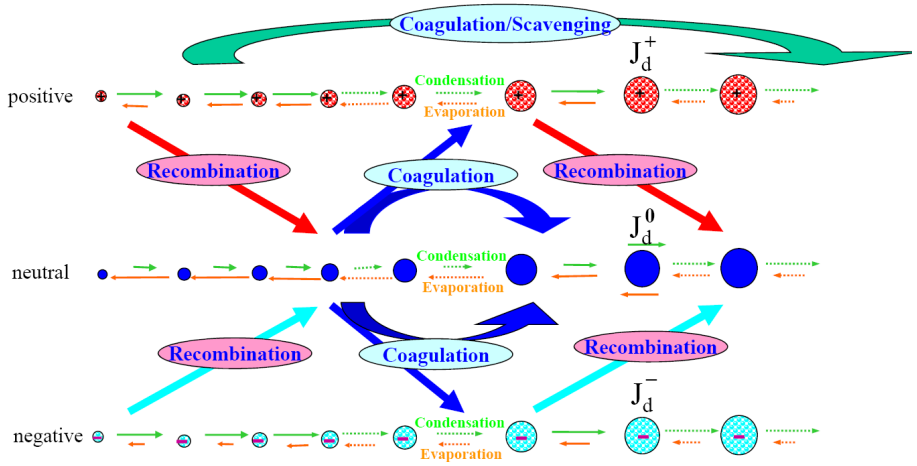

Fig. 1. Schematic illustration of the kinetic processes (condensation, evaporation, coagulation, and recombination) controlling the evolution of positively charged, neutral, and negatively charged clusters/particles that are explicitly simulated in the size-, composition-, and type-resolved ion-mediated nucleation (IMN) model. J_d^+, J_d^0, and J_d^- are, respectively, the "apparent" formation rate (or net flux) of positively charged, neutral, and negatively charged particles at a given diameter (d). Modified from Yu (2006).

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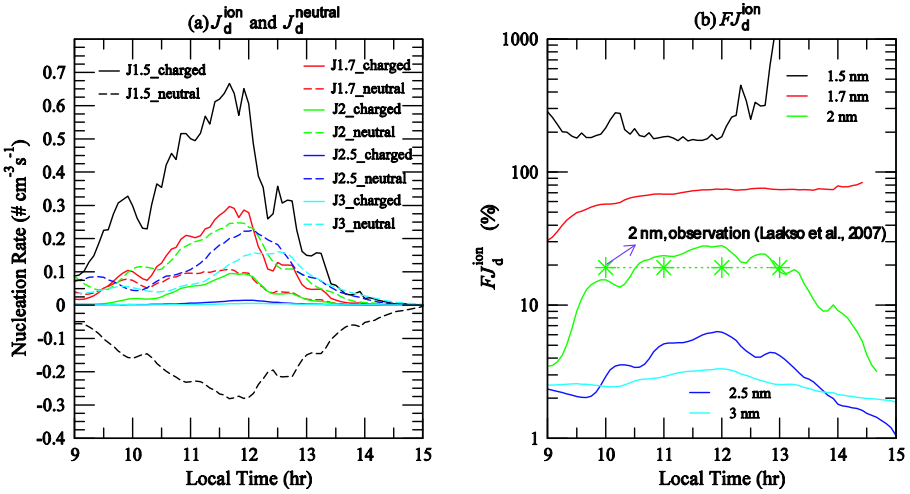

Fig. 2. Predicted evolution of the apparent neutral and charged particle formation rates (J_d^0 or $J_d^{neutral}$, and J_d^{ion}) and the corresponding FJ_d^{ion} values at five diameters (1.5, 1.7, 2, 2.5, and 3 nm) for a nucleation event observed in Hyytiälä on 17 April 2005. The star symbols in panel **(b)** represent the average $FJ_{2\,nm}^{ion}$ value derived from ion-DMPS measurements over the indicated nucleation period on 17 April 2005 (Laakso et al., 2007).

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The size-dependent charge fraction of sub-3-nm particles

F. Yu and R. Turco

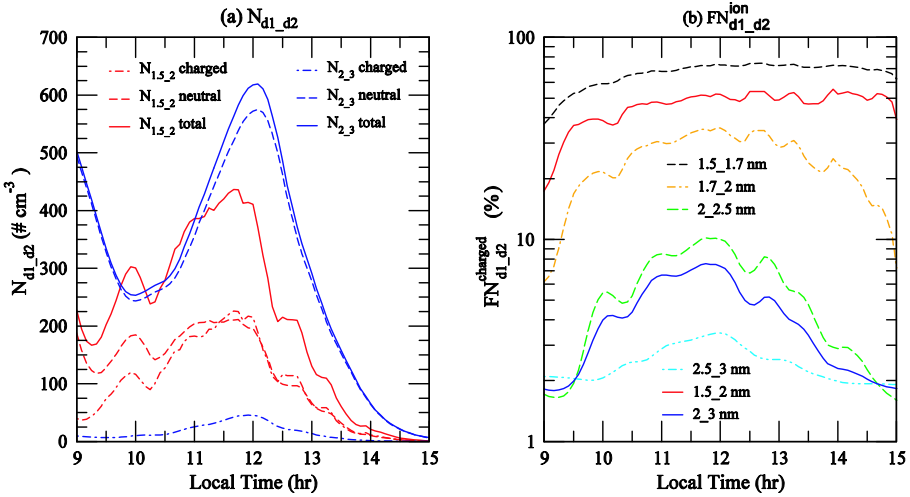

Fig. 3. Corresponding to Fig. 2, IMN simulations for the nucleation event observed in Hyytiälä on 17 April 2005, showing: **(a)** the number concentrations of neutral, charged, and total particles ($N^{neutral}_{d1-d2}$, N^{ion}_{d1-d2}, and N^{total}_{d1-d2}) in two sizes ranges (1.5–2 nm and 2–3 nm); and **(b)** the charged fraction of the total number of particles (FN^{ion}_{d1-d2}) in 6 six size ranges.

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The size-dependent charge fraction of sub-3-nm particles

F. Yu and R. Turco

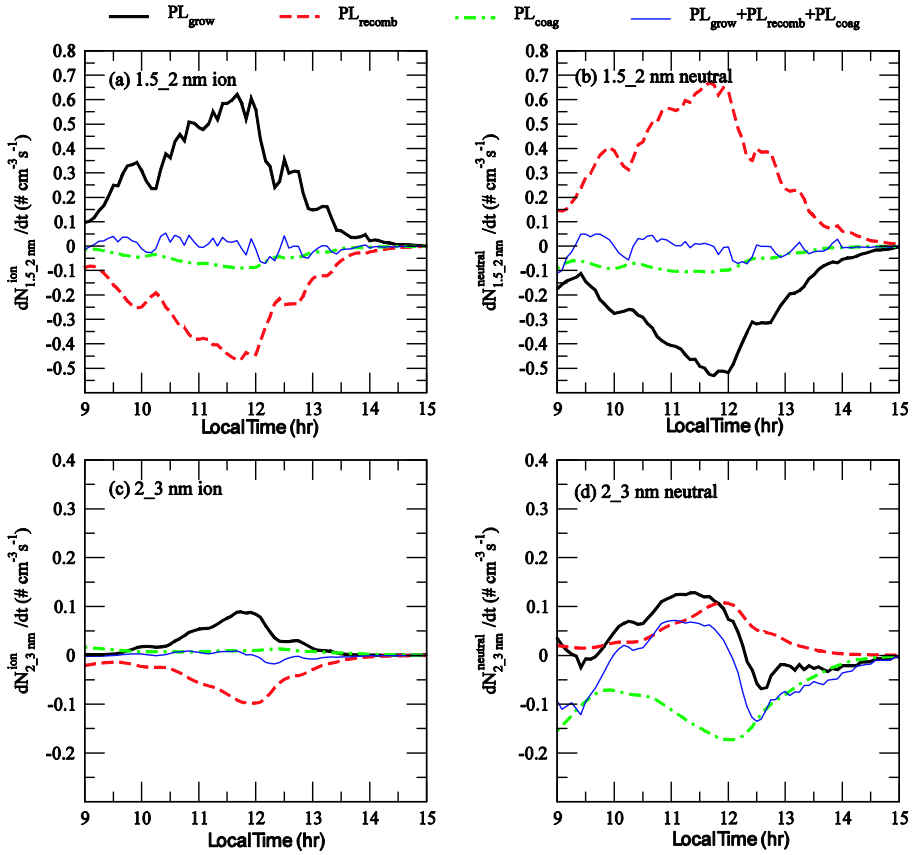

Fig. 4. The contributions of specific processes (i.e., growth, coagulation and recombination) to the changes in neutral and charged particle concentrations in the 1.5–2 nm and 2–3 nm size ranges (refer to Figs. 2 and 3, and the text).

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The size-dependent charge fraction of sub-3-nm particles

F. Yu and R. Turco

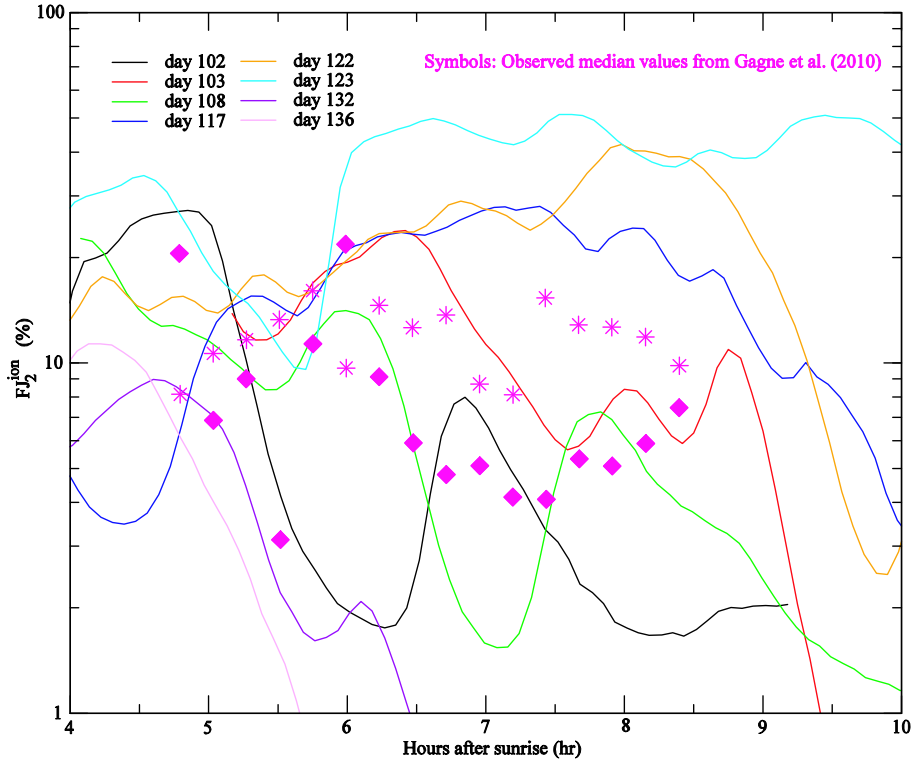

Fig. 5. The apparent fraction of 2-nm particles formed on ions (FJ_2^{ion}) as a function of hours after sunrise for all 8 case study days described in Yu and Turco (2008). Symbols represent the observed median values of FJ_2^{ion} obtained by Gagné et al. (2010).

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F. Yu and R. Turco

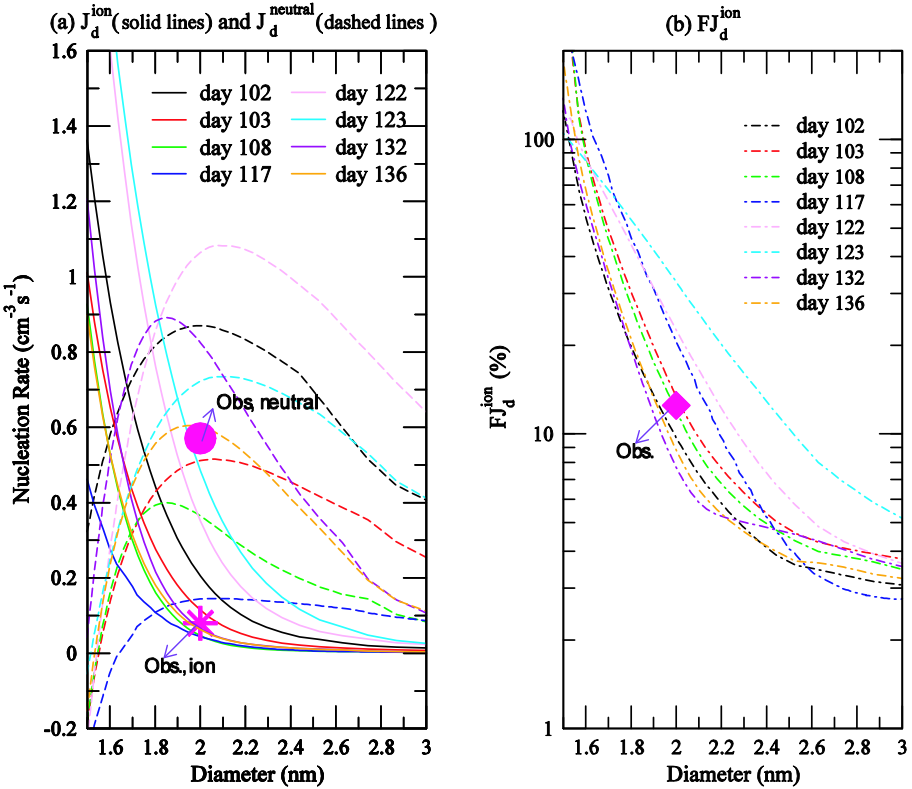

Fig. 6. Mean size-dependent apparent nucleation rates for both charged (J_d^{ion}) and neutral ($J_d^{neutral}$ or J_d^0) particles, and the corresponding FJ_d^{ion} values, for all eight nucleation events studied by Yu and Turco (2008). The symbols indicate the corresponding observed median values derived by Manninen et al. (2009).

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