Case studies of particle formation events observed in boreal forests: Implications for nucleation mechanisms*

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* The work presented here has been accepted for publication in Atmos. Chem. Phys. Discuss..

Introduction

New particle formation — regularly observed worldwide — appears to have clear spatial patterns (Yu et al., 2007a). Nevertheless, the primary mechanisms of atmospheric particle nucleation — which control aerosol number concentrations to a significant degree in many parts of the troposphere — remain elusive despite decades of intensive research. Systematic measurements of evolving air-ion mobility spectra during particle formation events, as well as of the size-resolved charged fraction (CF) of freshly formed particles, have become available recently to test nucleation theories (Iida et al., 2006; Hirsikko et al., 2007; Laakso et al., 2007). The CF data adds an important constraint on the fundamental processes controlling particle production and evolution.

An eleven-year record of continuous particle size distribution measurements at a remote boreal forest site in southern Finland reveal an annual-average of 50-100 nucleation events, with the frequency of the events peaking in springtime. While both the long-term (three-year) record of ion mobility measurements (Hirsikko et al., 2007), and the seven-week intensive period of CF measurements for freshly nucleated particles (Laakso et al., 2007), taken in Hyytiälä, Finland, suggest that ions are involved in more than 90% of the particle formation events that can be clearly identified, the relative contributions of ion-mediated nucleation (IMN) versus neutral processes remains controversial (Laakso et al., 2007; Kulmala et al., 2007; Yu and Turco, 2007; Yu et al., 2007a, b, c). Different interpretations of field observations of "nucleation" events have created ambiguity with regard to the relative importance of ion versus neutral nucleation processes, even when the same set of measurements are considered.

To resolve the conflicting conclusions, we carry out detailed case studies of boreal forest nucleation events. If these events can be explained in the context of a self-consistent theory, then the underlying nucleation mechanisms can be clarified. Further, if an articulated mechanism can be shown to reproduce nucleation events for the range of conditions encountered in a boreal forest setting, more reliable predictions of global-scale nucleation rates will be within reach. On the other hand, if the IMN mechanism cannot explain the observations, then the search should be refocused to identify the nucleation processes behind the observed particle formation events, inasmuch as none of the existing theories for binary and ternary homogeneous nucleation provide a quantitative explanation for most of the observations (e.g., Yu, 2006a, 2007). Here, we also compare nucleation rates predicted by the IMN model with those based on other models to highlight differences between various approaches, and to determine which of these representations are viable in light of the new data from Hyytiälä.

Ion-Mediated Nucleation (IMN)

The kinetic IMN model explicitly solves the dynamic equations governing the size distribution evolution of neutral, positively charged, and negatively charged clusters/particles (Fig. 1, also see Yu, 2006b). Three key aspects about the IMN model: (1) Compositions of small charged clusters were parameterized based on H_2O-ions clustering thermodynamic data (Froyd and Lovejoy, 2003a, b). (2) Evaporation coefficients of H_2SO_4 molecules from charged clusters was calculated with recently developed modified Kelvin-Thomson (MKT) equation which gives good agreement with ion-clustering thermodynamic data (Yu, 2005). (3) Evaporation coefficients of H_2SO_4 molecules from neutral clusters were calculated with the most recent thermodynamic data for H_2SO_4-H_2O binary system and were constrained by multiple laboratory data set (Yu, 2007).

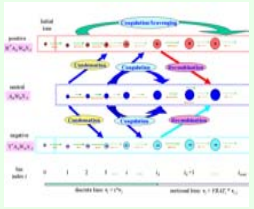

Figure 1. Schematical illustration of kinetic processes controlling the evolution of positively charged, neutral, and negatively charged clusters/particles that. The model uses the discrete-sectional bin structure to represent the sizes of clusters/particles. The IMN rates are calculated based on the net fluxes of particles across the critical size of neutral embryos.

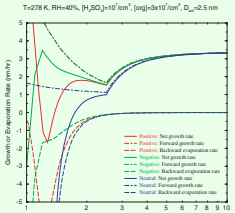

Figure 2. Size dependent forward, backward, and net growth rates for charged and neutral particles when T=278 K, RH=40%, $[H_2SO_4]=1.0\times10^7$ cm^{-3}, [organics]=3×10^7 cm^{-3}, and D_{act} = 2.5 nm (the particle activation diameter for organic condensation). Compared to neutral clusters, charged clusters grow much faster and are much more stable.

Acknowledgments: This study is supported by NSF under grant 0618124 and the NOAA/DOC under grant NA05OAR4310103.

Detailed case studies and results

Observed time series of T and RH

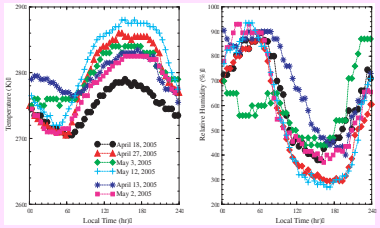

Figure 3. The time series of temperature (T) and relative humidity (RH) used to constrain the simulations for the six case studies. The data are averaged from two weather stations close to Hyytiälä: one in Jyväskilä (about 80 km northeast of Hyytiälä) and the other in Tampere (about 40 km southwest of Hyytiälä). The values should represent the corresponding meteorological conditions in the broader Hyytiälä area where the regional nucleation events occurred.

Simulated evolution of the particle size distributions

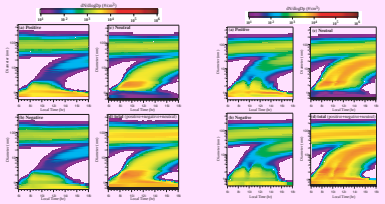

Figure 5. Simulated evolution of particle size distributions (dN/dlogDp) for various particle types corresponding to the case study on April 18 (left four panels, a weak nucleation event) and May 3 (right four panels, a strong nucleation event): (a) – positively charged; (b) – negatively charged; (c) – neutral; and (d) – total.

Charged fractions of freshly nucleated particles

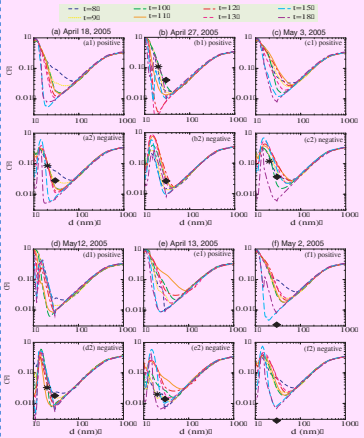

Figure 6. IMN model predictions of size-dependent particle charge fractions (CFs) at selected local times (in hr) during the six case study days. The symbols shown at 3 nm correspond to observed CFs averaged over specific nucleation periods as described by Laakso et al. (2007), while the symbols at 2 nm are values inferred by Laakso et al. (2007) using backward calculations from larger sizes.

Overcharging ratios of freshly nucleated particles

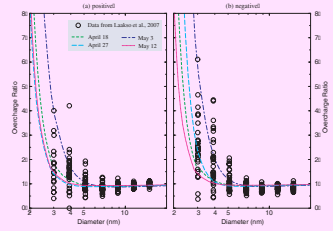

Figure 7. IMN simulated and observed size-dependent overcharge ratios (OR). Each curve represents IMN model calculated OR values averaged over a nucleation event corresponding to a specific case study. The open circles are observed average OR values corresponding to roughly 30 nucleation events sampled with an ion-DMPS during spring 2005 in Hyytiälä, Finland, as a part of the BACCI/QUEST IV intensive field campaign (Laakso et al., 2007).

Observed time series of [H2SO4]

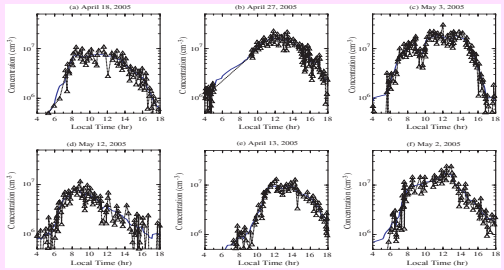

Figure 4. Time series of observed H_2SO_4 concentrations for the six case study days. The data points are taken from Fig. 1b of Riipinen et al. (2007). Fluctuations in the data are likely associated with inhomogeneities in the air masses sampled at the fixed field site. Such Eulerian, as opposed to Lagrangian, sampling introduces an irreducible uncertainty into the analysis since the history of any particular simulated air parcel must be reconstructed using the observations from continually changing air masses. The solid blue curves are the values used in the simulations.

Concentrations of freshly nucleated particles

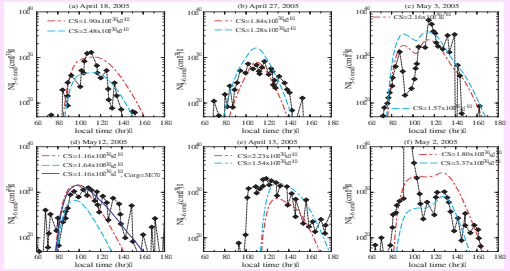

Figure 8. Time-dependent variations in the concentrations of particles in the size range 3-6 nm (N_{3-6}): simulations (dot-dashed and dashed lines), and observations (lines with symbols). The magnitude of the condensation sink (CS) given in the legends are averaged CS values during the nucleation and growth period (6 am – 2 pm). In Figure 8d, one additional curve is shown corresponding to a lower concentration of condensable organic species (peak C_{COS} = 3×10^7 cm^{-3}). Peak C_{COS} = 6×10^7 cm^{-3} is assumed in all other cases).

Nucleation rates based on different theories/models

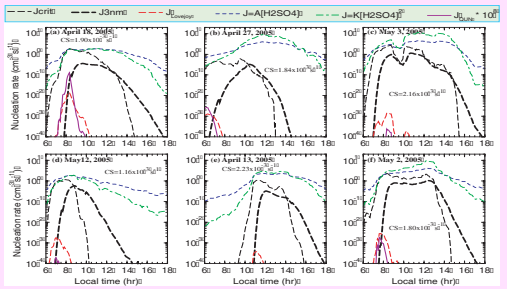

Figure 9. IMN calculated time-dependent variations in nucleation rates based on model-simulated critical embryo sizes (J_{crit}), and based on the production rate of 3-nm particles (J_{3nm}, the "apparent" nucleation rate typically observed). Results are given for each of the six case studies. In each case, for comparison, predicted nucleation rates are shown for the ion nucleation model of Lovejoy et al. (2004) ($J_{Lovejoy}$), the quasi-unary homogeneous nucleation model of Yu (2007) (J_{QUN}), and the empirical activation formula (J_{act} =A $[H_2SO_4]$ with A=2.4×10^{-7} s^{-1}) and kinetic nucleation relationship (J_{kin} = K $[H_2SO_4]^2$ with K=3.2×10^{-14} cm^3 s^{-1}) proposed by Riipinen et al. (2007). Note that the solid curves represent $J_{QUN}\times10^8$.

Summary

We report case studies of six nucleation events observed during an intensive field campaign at a boreal forest site (Hyytiälä, Finland) in spring 2005. The present analysis is based on comprehensive kinetic simulations using an ion-mediated nucleation (IMN) model in which the key physical and chemical parameters are constrained by a variety of recent measurements.

Out of roughly 30 days sampled during the campaign, four were initially selected on the basis of indications that the observed air masses were relatively homogeneous. It happens that all four of these days exhibited medium to high electrical overcharging of the nucleated nanoparticles. In each of these well-defined cases, reasonable agreement is found between the predictions and field data for a range of variables, including critical nucleation sizes, size-dependent overcharging ratios, and the concentrations of 1.8-3 nm stable clusters and 3-6 nm particles, and their diurnal variations.

To extend the scope of the study, one case of weak electrical overcharging, and one of clear undercharging, of the nucleated particles were also selected. These electrical states represented less than about 20% of the total event-days recorded, and among this smaller sample there were no days on which the sampled air masses appeared reasonable uniform over the entire nucleation event. Thus, it is perhaps not surprising that the consistency between model simulations and measurements during these more anomalous periods was less satisfying. We tentatively conclude that the outcomes in these cases were influenced by, among other things, the significant variability in the sampled air masses and the possible role of species other than sulfuric acid in the nucleation process.

Statistically, roughly 80% of the nucleation events recorded during the Hyytiälä campaign exhibited mean size-dependent overcharging ratios within the range, or exceeding, those predicted by the IMN model, suggesting that ion nucleation processes are significant.

The nucleation rates calculated using the IMN modeling approach are contrasted with those predicted by other theories/models. It appears that the ion nucleation model originally developed by Lovejoy et al. (2004) significantly under-predicts ion nucleation rates, and cannot explain the new observations from Hyytiälä regarding the electrical properties of nanoparticles. The differences between the nucleation rates predicted by the IMN model and those based on empirical formulas advanced by Riipinen et al. (2007) are very large at most times of the day. The difference is not surprising as these empirical relations are regression results which do not aim to describe detailed physics and the prefactor constants have a wide range of values in different days/locations.

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