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

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Abstract

Aerosol nucleation events observed worldwide may have significant climatic and health implications. However, the specific nucleation mechanisms remain ambiguous. Here, 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 nucleation event 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. However, 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

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by other theories/models, and key differences between the results are discussed.

1 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 (Vana et al., 2006; 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 (Laaksonen et al., 2007). While both the long-term (3-yr) 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 versus neutral processes remains controversial (Laakso et al., 2007; Kulmala et al., 2007; Yu and Turco, 2007; Yu et al., 2007a, b, c). An analysis by Laakso et al. (2007) of these measurements concluded that ion nucleation processes make a relatively small contribution to new particle formation (under the conditions sampled). However, when Yu et al. (2007b) applied a different analytical methodology to the same data, they found significant contributions from ion-mediated nucleation (IMN). These differences have never been resolved. More recently, Kulmala et al. (2007) concluded that neutral

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nucleation dominates over ion-induced nucleation at least in boreal forest conditions, based on their analysis of four days of multiple-instrument measurements of neutral and charged nanometer-sized cluster concentrations obtained in Hyytiälä, Finland in spring 2006. Again, Yu et al. (2007c) reanalyzed the observations and pointed out that the importance of ion-mediated nucleation mechanism under the boreal forest conditions can't be ruled out based on the data reported in Kulmala et al. (2007).

Apparently, 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 with regard to the importance of IMN, we focus here on recent data from the boreal forest experiments noted above, which obtained the most extensive set of relevant parameters to date. 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 (e.g., Yu et al., 2007a). 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, 2006b, 2007).

The main objective of this work, therefore, is to carry out detailed case studies of boreal forest nucleation events to investigate the competitive nucleation processes represented in the IMN model (that is, the ion and neutral binary system processes that are currently quantifiable). By constraining the key parameters in these simulations using observations, we aim to: (1) test the ability of the current IMN model to account for the observed concentrations of freshly nucleated particles in the 3–6 nm size range; (2) assess the consistency of observed charged fractions of freshly nucleated particles against IMN model predictions under sampled conditions; and (3) compare nucleation

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rates predicted by the IMN model with those based on the Lovejoy et al. (2004) model, the empirical nucleation/activation formulas offered by Riipinen et al. (2007), and a recently improved binary homogeneous nucleation model (Yu, 2007), to highlight differences between various approaches, and to determine which of these representations are viable in light of the new data from Hyytiälä.

2 The kinetic IMN model and data sources for case studies

The IMN model (Yu and Turco, 1997, 2000, 2001) simulates ion mass spectra and nanoparticle electrical charge fractions by explicitly resolving the non-linear size-dependent microphysical interactions among precursor gases, positively charged, negatively charged and neutral clusters, and particles ranging from small molecular aggregates to several micrometers in diameter. An earlier version of the IMN model has been extended by incorporating new thermodynamic data and physical algorithms (Yu, 2006a). Yu (2007) has further improved the model by employing two independent measurements to constrain monomer hydration in the H_2SO_4-H_2O system (Marti et al., 1997; Hanson and Eisele, 2000), and by incorporating the energetics of small neutral H_2SO_4-H_2O clusters determined by Hanson and Lovejoy (2006) and Kazil et al. (2007). In the atmosphere, nanoparticle nucleation and growth are fully coupled, and in many situations organic species dominate the growth of freshly formed particles. The present version of the IMN model considers the co-condensation of sulfuric acid and organic compounds upon activated particles (Yu, 2006a), although there is substantial uncertainty regarding the abundances of organic precursors and their actual role in the nucleation process. A detailed description of the present treatments of physics and thermodynamics in the IMN model is given by Yu (2006a).

The long-term and multiple-instrument characterizations of nucleation events obtained by Kulmala and colleagues in Hyytiälä, Finland are clearly unique, and provide the most comprehensive and detailed set of data available so far to test atmospheric nucleation theories. Of greatest significance is the determination of the elec-

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trical charge fraction (CF) of the nanometer-sized particles as they evolve during nucleation bursts. The CF data provide an unambiguous signal that ion nucleation is operating when the observed CFs exceed the equilibrium charge fractions characteristic of the ambient aerosol. Measured CFs are typically given relative to the ambient CF, at each size, in terms of the overcharge ratio, OR. For OR<1, the particles are undercharged. For a system in equilibrium with the background ion plasma, OR~1. However, when ions represent a substantial fraction of the nuclei for particle formation, OR values greatly exceeding 1 can be achieved. Conversely, when ion contributions are small or negligible, OR will typically be <~1. Homogeneous nucleation events generate high concentrations of small neutral nanoparticles that strongly drive the OR downward. Even so, in all cases, OR values tend to adjust rapidly toward the equilibrium state (i.e., OR≃1) at all sizes. It follows that any analysis of nucleation events for which CF (or OR) data are available should involve a comprehensive treatment of the charging and discharging processes of nanometer particles. Accordingly, a study of the Hyytiälä measurements that includes these details is more likely to shed light on the formation mechanisms of atmospheric aerosols.

We have carried out six case studies of nucleation events observed during spring 2005 in Hyytiälä, during the BACCI/QUEST IV intensive field campaign (Laakso et al., 2007; Riipinen et al., 2007). Initially, four days – out of roughly 30 days of measurements – were selected on the basis of indications that the sampled air masses were extensive and relatively homogeneous, and so subject to reasonable point-site analysis. Based on the average overcharge ratios reported by Laakso et al. (2007), the freshly nucleated particles were relatively highly overcharged on three of these case study days – 18 April, 27 April, and 3 May – and substantially overcharged on the fourth day – 12 May. Air mass homogeneity was judged on the basis of relatively consistent and continuous changes in the measured concentrations of the key precursor gas H_2SO_4, and the abundances of freshly nucleated particles in the 3–6 nm size range (N_{3-6}). Note that above ~80% of the 30 event days showed substantial electrical overcharging, and thus it was possible to select days with minimal apparent variability, or

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maximum homogeneity and self-consistency, as described above.

However, to include a wider range of situations, two other days were selected from the remaining observations, one representing a weakly overcharged state (on 13 April), and one an occurrence in which the particles were clearly undercharged (on 2 May). These latter circumstances were found in only a small number of cases, and it was not possible to select a highly self-consistent situation in either case. Heterogeneity in the data record present severe problems in interpreting time-integrative transient events such as nucleation bursts. For one thing, the temporal variations in the observed parameters become a strong function of the spatial variability and air mass velocity, masking the actual behavior. Moreover, the changes in key integrative variables, such as H_2SO_4 concentrations, in any specific air parcel cannot be reliably reconstructed over the time span of many hours required for nucleation and growth of the aerosols. Nevertheless, to test the model against all possible behaviors, these cases are analyzed below, with the caveat that the results will be much more uncertain.

Another interpretive problem arises because the charge fraction data are presented as average values over certain periods of an event. Presumably, this is done to reduce the high variability inherent in the CF measurements. For homogeneous air mass conditions, such average CFs should represent the characteristic global charging state of the nucleated aerosols. However, in highly heterogeneous air masses, segments of data may correspond to different nucleation events and/or processes, and the average CF values may include periods with overcharging and undercharging. Hence, appropriate caution must be used in interpreting the simulations on these days.

The selected case study days are reasonably representative of the ranges of $[H_2SO_4]$ and N_{3-6} observed during the BACCI/Quest IV field campaign (Riipinen et al., 2007), as well as of the charged fractions (CFs) of 3 nm particles (Laakso et al., 2007). In this work, we also assumed a constant ionization rate of 5 ion-pairs $cm^{-3}s^{-1}$, consistent with the typical ionization rates derived from measurements in the area of interest (Laakso et al., 2004a).

As noted above, in order to constrain the model simulations, it is desirable to have a

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time series of precursor gases (i.e., H_2SO_4 and condensable organics), temperatures, relative humidities, and condensation sink rates (or size distributions of pre-existing particles) within specific air parcels. Such Lagrangian data are not available, since all the measurements under consideration were collected at stationary field sites. Accordingly, the selection of data sets based on air mass homogeneity provides the most reasonable alternative. Sulfuric acid vapor is clearly the key species controlling nucleation at the sites of interest (e.g., Riipinen et al., 2007). Figure 1 shows the time series of observed H_2SO_4 concentrations ($[H_2SO_4]$) on the six selected days investigated here. The data points are taken from Fig. 1b of Riipinen et al. (2007). The smaller fluctuations in the data are likely associated with local inhomogeneities in the air mass sampled. In our simulations, we use smoothed (11-point running average) $[H_2SO_4]$ time series, as shown by the solid blue curves in the figure. Nevertheless, anomalies in the data appear, which on more self-consistent days can usually be accounted for. For example, on 27 April, the air mass characteristics were highly variable during the early morning hours, just before the onset of significant nucleation, from ~05:00–09:00 a.m. During this period, much higher concentrations of pre-existing particles were apparent, which would obviously affect the sulfuric acid abundances (refer to Fig. 3a of Riipinen et al., 2007). For the rest of the day, the indications point to a fairly homogeneous event. Hence, the measured $[H_2SO_4]$ during the early period was replaced by an extrapolation from the concentrations after ~09:00 a.m. using a simple empirical diurnal concentration curve. Other anomalous periods during otherwise homogeneous event-days were treated similarly. In all instances, however, the main nucleation event is well characterized by the data record for these cases, and any adjustments, which are noted in the text, have a small effect on the predicted outcomes.

In the more heterogeneous cases, on the other hand, the anomalous data segments are longer, or fall within critical stages of the nucleation event. For example, note the very low concentrations of sulfuric acid vapor during the morning hours of 13 April; and the anomalously high concentrations of particles from 3–6 nm during a short span of time on the morning of 2 May. In such instances, reasonable adjustments to, or

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extrapolations of, the data are not obvious. In these cases, the data sequence for the event-day was used without adjustment, and the previous caveats regarding these inhomogeneous event-days are emphasized in the discussion.

Compared to sulfuric acid vapor, which is often directly measured, condensable organic species (COS) are only poorly characterized. Certain organic compounds are known to contribute to, or even dominate, the growth of nucleated particles. Laaksonen et al. (2007) showed that particle growth rates during the boreal forest nucleation events are correlated with the gas phase concentrations of monoterpene oxidation products (MTOPs). However, both Janson et al. (2001) and Sellegri et al. (2005a) concluded that, based on measurements made during two different boreal forest field campaigns (BIOFOR and QUEST), the oxidation products of terpenes were not the primary nucleating species observed at Hyytiälä. The main reasons for this conclusion include: (1) that the concentrations of the terpenes and their oxidation products where higher at night when no nucleation was observed (Janson et al., 2001; Sellegri et al, 2005a); (2) that organic oxidation products were not significantly elevated during event days compared to non-event days based on the results from the BIOFOR campaign (Janson et al., 2001); and (3) that organic compounds including terpenes are generally lower during event days compared to non-event days based on QUEST data (Sellegri et al, 2005a).

In this study, the diurnal variations of the overall COS concentration (C_{COS}) is parameterized to follow that of the averaged and smoothed curve of MTOP, as shown in Fig. 6b of Sellegri et al. (2005b). That curve yields a peak concentration around midnight and a minimum concentration in the early afternoon, with a ratio of maximum to minimum values of around 2.3. Due to the lack of information about the saturation vapor pressures of the condensable organics, we assume that COS only condenses on particles larger than a certain activation size (D_{act}). For the present purposes, the baseline value of D_{act} is taken to be 3 nm, which is within the range estimated by Kulmala et al. (2004a, b). The COS molecules are assigned an average molecular weight of 180 g/mol and density of 1.5 g cm^{-3} (Engelhart et al., 2008). In this study, unless

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specified, we assume a peak C_{COS} of 6×10^7/cm^3 that, combined with [H_2SO_4], results in growth rates of nucleated particles of ~1–5 nm/h, which are generally consistent with observations in boreal forests (Kulmala et al., 2004a; Riipinen et al., 2007; Laaksonen et al., 2007). In the real atmosphere, different organic compounds are likely to be involved in the nucleation and growth processes, and the concentration time series of these species – and corresponding D_{act} – may differ from the average values adopted here. The uncertainties in COS concentrations, specific molecular properties, and D_{act} lead to uncertainties in the simulated concentrations of freshly nucleated particles and their overcharging ratio, but should not have significant impacts on predicted nucleation rates as long as these species are not directly involved in the nucleation phase itself.

The time variations in temperature (T) and relative humidity (RH) used to constrain the simulations are illustrated in Fig. 2. The data for all days except 3 May 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). On 3 May, it was raining in the afternoon in Tampere, so only the T and RH values from Jyväskilä are employed. The values given in Fig. 2 should represent the corresponding meteorological conditions in the broader Hyytiälä area where the regional nucleation events occurred. The original T and RH data were downloaded from the database archived at www.wunderground.com.

Pre-existing particles affect nucleation by scavenging sulfuric acid vapor and freshly nucleated molecular clusters. The condensation sink (CS) due to pre-existing particles typically ranged from 0.5×10^{-3}–3.5×10^{-3} s^{-1} during the spring nucleation events observed in Hyytiälä, and was generally above 6×10^{-3} s^{-1} during non-events (Laakso et al., 2004b; Sellegri et al., 2005; Dal Maso et al., 2005). Due to the changing air masses, measured CS values over some nucleation event days were seen to fluctuate significantly (Laakso et al., 2004b; Sellegri et al., 2005b). In the present analysis, the initialization of the size distributions for pre-existing particles was guided by measurements reported in Ehn et al. (2007). For the baseline cases, the initial CS was assumed to be 1.5×10^{-3} s^{-1} (at 04:00 a.m. local time) on all study days except 12 May. The initial

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baseline CS was taken to be 10^{-3} s^{-1} on 12 May because, based on size distributions reported by Ehn et al. (2007), the concentration of pre-existing particles was clearly lower than on other days. CS varies during the day (generally within a factor of 2) as a result of changes in RH and particle growth. To investigate the effect of CS variations on the simulated results, we include appropriate sensitivity studies.

3 Detailed case studies and results

3.1 Evolution of the particle size distributions

Figures 3–8 show the evolution of the simulated particle size distributions for particles in several different categories during the six case study days. The key parameters used to constrain the simulations are described in Sect. 2. Under the observed atmospheric conditions, ion-mediated nucleation occurs on each of these days. The minimum in the evolving size distributions of charged clusters/particles in the size range of ~4–6 nm during all three nucleation events (Figs. 3–8a, 3–8b) is mainly a result of neutralization of those particles nucleated on ions, later offset by an enhancement in charging associated with increasing particle size and the absorption of ambient charge toward achieving equilibrium (Yu, 2006a). The condensation of organic species on freshly nucleated particles also contributes to the minimum around 3 nm in all of the size distributions. Additionally, a gap occurs in the size range between neutral sulfuric acid monomers (diameter around 0.6 nm) and neutral clusters of about 1.2 nm (Figs. 3–8c) due to the rapid evaporation of unstable small neutral clusters formed in this size range mainly by ion-ion recombination.

The sizes of clusters having effectively equal forward growth and backward evaporation rates are defined as the "critical" sizes in the kinetic IMN model (Yu, 2006a). Although the critical size for a charged cluster is smaller than that for an equivalent neutral cluster, a charged cluster that reaches its critical size should not be considered as "nucleated" until it reaches a size corresponding to the critical size of a similar neutral

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cluster, since if the charged cluster is neutralized before it reaches the critical neutral cluster size it may evaporate (depending, of course, on the nature of the neutralizing charged species). It should be noted that nucleation is a dynamic process and previously formed clusters, even those smaller than the critical size, can have a direct effect on the instantaneous nucleation rate. Under the conditions corresponding to the six case studies treated here, the diameters of the critical neutral clusters predicted by the IMN model vary between ~1.3 nm and ~1.7 nm during periods of particle formation. These values are supported by recent measurements in boreal forests indicating that stable particle formation begins at diameters of ~1.5 nm (Kulmala et al., 2007).

Neutral binary H_2SO_4-H_2O clusters smaller than ~1 nm are very unstable under the conditions corresponding to these case studies. In order for the hydrated H_2SO_4 monomer to nucleate, other species must be involved in stabling the smallest clusters. Based on the IMN theory, ions can effectively stabilize the small clusters and thus provide a channel for the formation of stable nuclei. It is possible that other species may also be able to stabilize the smaller neutral clusters. However, in order for neutral nucleation to be initiated for the conditions considered here, the stabilizing effect of these unidentified species should be at least as strong as that of an ion core. Quantum calculations of the bonding energies of hydrated H_2SO_4 monomers and dimers with ammonia and several common organic compounds (Nadykto and Yu, 2006) suggest that, while such species may enhance the overall stability of hydrated H_2SO_4 dimers, the increase in stability is far less than that associated with an ion core. Accordingly, the substances commonly assumed in ternary homogeneous nucleation (THN) theories appear to be ineffective in initiating neutral nucleation under the circumstances of these case studies.

The IMN model predicts that large concentrations of neutral stable nuclei in the 1.8–3 nm size range are formed as nucleated ions are neutralized (Figs. 3–8c). Previously, Kulmala et al. (2000) had postulated very high background abundances of thermodynamically stable clusters (TSCs), exceeding $10^5/cm^3$, produced by THN. However, as just noted, standard THN models are now known to overestimate nucleation rates

substantially (Yu, 2006b). IMN, by contrast, creates TSCs as a result of natural ion processing, in which ambient ion-ion recombination acts as a potential source of TSC nuclei. As can be seen from Figs. 3–8, the TSCs (at sizes from 1.8–3 nm) generated via IMN have a clear diurnal variation. The peak concentrations of 1.8–3 nm particles range from ~1000 to ~5000 cm^{-3} on different days. Such concentrations are, in fact, consistent with the several thousands of 1.8–3 nm particles per cubic centimeter typically detected in boreal forest, as reported in Kulmala et al. (2007). A predicted strong diurnal variation in the abundance of 1.8–3 nm TSCs appears to be consistent with the limited NAIS-positive and UF0-02proto CPC pair data and charged clusters measured by AIS and BSMA reported in Kulmala et al. (2007), however, it seems to be in conflict with the NAIS-negative measurements presented in Kulmala et al. (2007). Resolution of the behavior of these stable neutral nanoparticles may have important implications for the underlying nucleation mechanism. For example, a continuous and nearly constant nucleation source must operate day and night to maintain an almost steady concentration of a few thousand 1.8–3 nm particles per cm^3. Since kinetically the concentrations of H_2SO_4 at night (~5×10^5/cm^3 or less) are far too low to produce the observed 1.8–3 nm clusters, species other than H_2SO_4, H_2O, and NH_3 must dominate the formation of the observed 1.8–3 nm particles, implying a completely new (and yet to be identified) nucleation mechanism.

Most recently, Sipilä et al. (2008) reported the existence of a pool of clusters smaller than ~1.8–2 nm at night. These very small clusters (<~1.8 nm) would logically be associated with ion-ion recombination clusters that are not activated, but have been stabilized at a sub-critical size by one or more unidentified species. Indeed, the general lack of sulfuric acid vapor at night poses a serious question as to how these nighttime TSCs are formed, and whether they have any relationship to daytime nucleation events. It is possible that species other than sulfuric acid (for example, certain organic compounds, nitric acid, ammonia, etc.) control the formation of sub-1.8 nm clusters at night when the temperature is relatively lower, whereas sulfuric acid dominates nucleation during the day.

Based on IMN model simulations, all of the neutral particles between 1 and 3 nm in Figs. 3–8c are formed by the neutralization of charged particles. While activation and growth of these 1–3 nm neutral particles is the major source (>90%) of the predicted 3-nm particles, these seed particles originate from IMN rather than homogeneous nucleation. This is an important distinction: without ions, no 3-nm particles would be present in the simulations (again note the deep gap between 0.6 nm and 1 nm for neutral clusters in Figs. 3–8c). Although all the new particles larger 3 nm in Figs. 3–8 are formed via IMN, only a small fraction of freshly nucleated particles around 3 nm are charged (further discussion on this point is given in Sect. 3.3).

3.2 Time series of the concentrations of freshly nucleated particles

Figure 9 shows the simulated (dashed lines) and observed (lines with symbols) time-dependent variations of particles in the 3–6 nm range (N_{3-6}) for the six selected nucleation event days. It should be noted that measurements are performed at a fixed site in constantly changing air masses, while the simulations essentially follow an air parcel assumed to be embedded within a homogeneous regional air mass. The comparisons with measurements are therefore meaningful only when the air mass upwind of the measurement site(s) is spatially relatively uniform. The consistency in measurements of variations in key parameters, such as the H_2SO_4 vapor concentration and the abundance of freshly nucleated 3–6 nm particles, is used as an indication of the level of homogeneity in the sampled air masses. As explained earlier, we selected data records for the present case studies that exhibited reasonable consistency in this sense. Nevertheless, even on these selected days, some level of inhomogeneity in sampled air mass is unavoidable and the measured concentrations of pre-existing particles and hence the condensation sink (CS) can still fluctuate substantially (Ehn et al., 2007). To investigate the influence of the CS, we also show results corresponding to a second value of CS in each panel. The CS values in the legends are averaged values over the main nucleation and growth period (06:00 a.m.–02:00 p.m.). In Fig. 9d, an additional result using a different organic condensate concentration, C_{COS} (reduced by

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half compared to other cases), is also given to illustrate its effect.

The model-predicted time series of N_{3-6} agree reasonably well with those measured on four selected days exhibiting medium to high overcharge ratios for freshly nucleated particles (i.e., 18 April, 27 April, 3 May, and 12 May), although differences exist in some details. The model captures the rapid increase in N_{3-6} in the early morning hours, and the timing and value of peak N_{3-6} around noon, taking into account the uncertainties in the CS and C_{COS}. In our present simulations, only H_2SO_4 and H_2O are assumed to contribute to the formation and growth of particles smaller than 3 nm and organics only condense on particles larger than 3 nm (i.e., D_{act}=3 nm). The good agreements in the timing of rapid increase in N_{3-6} around 08:00–09:00 a.m. indicate that H_2SO_4 and H_2O can fully account for the formation and growth of sub-3 nm particles and thus our assumed D_{act} of 3 nm appears to be reasonable. A smaller D_{act} will shift the simulated increase in N_{3-6} to the left (earlier time) and thus deteriorate the agreement.

The slower decrease in N_{3-6} during the afternoon is also reproduced by the model, with the exception of the 12 May case (Fig. 9d), when the model recovery occurred more rapidly than that observed. Since dN_{3-6}/dt depends not only on the formation rates of 3 nm particles but also on the growth rate of 3–6 nm particles (i.e., the rate particles are growing out of 6-nm size range) (Riipinen et al., 2007), we may have significantly overestimated the concentrations of condensable organic species that afternoon, and hence the 3–6 nm particle growth rates. A sensitivity study given in Fig. 9d clearly shows improvement in the agreement when a lower C_{COS} (peak values 3×10^7 cm^{-3}) is assumed. The data fluctuates substantially through the morning hours on 3 May and in the afternoon on 12 May, which is likely to be associated with inhomogeneity in the air mass sampled at those time. For example, the air mass sampled between 09:00–10:00 a.m. on 3 May is clearly different from, and seemingly inconsistent with, the other air masses that day as indicated by the sudden drop in [H_2SO_4] (refer to Fig. 1c). It is likely that the anomalous air mass represented a localized plume, or experienced a non-regional perturbation. Indeed, using time-smoothed data, the model does produce a double-peaked response in the 3–6 nm particle concentration,

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but of a much smaller magnitude. Considering the nature of the present comparisons, the IMN model appears to provide an excellent representation of the observed nucleation events on 18 April, 27 April, 3 May, and 12 May. To our knowledge, no other physically-based nucleation models have demonstrated such a capability.

The agreement between simulated and observed N_{3-6} is less satisfying on 13 April (Fig. 9e) and 2 May (Fig. 9f), especially during the morning hours. As we pointed out in Sect. 2, 13 April and 2 May represent a small number of observed cases with weakly overcharging or undercharging, and it was not possible to select a highly self-consistent situation in either case from the data presented in Riipinen et al. (2007). Even considering the possible uncertainty in the condensation sink (CS), the model can't explain the rapid increase in N_{3-6} around 10:00 a.m. on 13 April. A comparison of observed time series of $[H_2SO_4]$ (Fig. 2e) and N_{3-6} (Fig. 9e) indicates that, in contrast to those on other days, the increase in N_{3-6} in the morning on 13 April precedes that of $[H_2SO_4]$. In most of nucleation events observed in Hyytiälä, $[H_2SO_4]$ increase in the morning precedes the N_{3-6} increase by 1–2 h (Riipinen et al., 2007). The abnormality observed on 13 April may be resulted from the sampling of air mass with quite different properties (for example, time series of $[H_2SO_4]$) before and after noon time. An alternative explanation is the involvement of species other than sulfuric acid in nucleation and growth of sub-3 nm particles on that day and such species remain to be identified. Based on the size distribution evolution reported in Ehn et al. (2007) for 2 May, the air mass sampled between ~11:00 a.m. to 03:00 p.m. appears to have quite different properties (for example, CS much higher). Our simulations did show that a higher CS gives a better agreement with observed N_{3-6} during noon and earlier afternoon, while a lower CS predicts improved agreement between simulated and observed N_{3-6} in earlier morning and late afternoon. Nevertheless, the model can't reproduce the observed sudden and dramatic increase in N_{3-6} around 09:00–10:00 a.m. It is unclear what causes this unsmooth change in the observed N_{3-6}. Again, the possible explanations include significant inhomogeneity in the air mass sampled and the involvement of species other than sulfuric acid in nucleation and growth of sub-3 nm particles.

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3.3 Charged fractions of freshly nucleated particles

Simulated size-dependent charge fractions (CFs) at selected times for the six case study days are shown in Fig. 10. The symbols illustrated at a particle size of 3 nm correspond to observed CFs averaged over the nucleation periods obtained from Laakso et al. (2007), and the symbols at 2 nm are the values backward calculated by Laakso et al. (2007) using the "K" parameter derived by fitting the measured charged state of particles larger than 3 nm. Figure 10 indicates that the IMN predicted size-dependent CFs are generally consistent – within a reasonable range of uncertainty – with the observations on 18 April, 27 April,3 May, and 12 May. It should be noted that the agreements between simulated and observed N_{3-6} are also reasonable on these days (see Fig. 9). According to the model, most of the clusters/particles ~1.4 nm in diameter are negatively charged (up to ~60–80%), while most of those ~1.1 nm are positively charged (up to 90%). However, CFs decrease dramatically as particles grow beyond ~1.5 nm owing to rapid charge neutralization. Indeed, during the nucleation event illustrated, CFs achieve a minimum value of only ~2–3% at particle diameters of ~ 5 nm. Particles larger than ~5–7 nm are approximately in charge equilibrium with the background ion pool, where the predicted equilibrium CFs are consistent with measurements (Vana et al., 2006).

The agreement between simulated and observed CF for freshly nucleated particles is poor on 13 April and 2 May. The model simulations show that freshly nucleated particles on these two days should be significantly overcharged as well but measurements indicate a weak overcharge (13 April) or even undercharge (2 May). The poor agreement is probably related to the model under-prediction of N_{3-6} in the morning on the two days (Fig. 9). At this point, it is unclear if the significant variability in the sampled air masses or involvement of species other than sulfuric acid in nucleation causes the large difference in the modeling results and measurements. Further research is clearly needed.

An aerosol immersed long enough in a steady-state ion-plasma achieves an equilib-

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rium charge distribution. For transient conditions, the ratio of an instantaneous CF to the equilibrium CF at the same size under similar ambient conditions is defined here as the overcharge ratio, OR. Figure 11 compares simulated and observed size-dependent OR values. The curves represent calculated OR values averaged over each nucleation period for the four case study days which have good overall agreement between simulated and observed concentrations and charged fractions of freshly nucleated particles. The open circles, on the other hand, define the range of observed OR values averaged over each nucleation event corresponding to about 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). For most of the observations (>90% of events), freshly nucleated particles (3–4 nm) are overcharged (i.e., OR>1), which can only be explained by contribution of ions to the nucleation process. Indeed, the IMN model predicts a rapid decrease in ORs as particle sizes increase from ~2–3 nm to ~5 nm in overall agreement with the measurements. Particles larger than ~6 nm are slightly undercharged (OR<1) as a result of the condensational growth owing to the fact that the equilibrium CF is increasing with particle size in this range. It is clear from the detailed kinetic IMN simulations that "measurable" overcharging would be limited to particles in the range of 3–5 nm, even when IMN is the only nucleation pathway that is active. The physics behind the rapid drop in ORs at small sizes is straightforward (Yu and Turco, 2007): charged clusters/particles nucleated on ions have a lifetime of ~0.3 h against neutralization by small ions/clusters of opposite charge, while it generally takes about 1–2 h for the same cluster to grow to ~3 nm, and another 1–2 h to grow to ~5 nm under typical boreal forest conditions.

OR values for 3–5 nm particles depend strongly on the growth rate of sub-3–5 nm particles. The large variations in the observed OR values for particles at given sizes (3, 4, 5 nm) on different days are likely to be associated with variations in the concentrations of the key precursor gases (sulfuric acid, and low volatility organics), and in the particle sizes at which organic vapors begin to condense (the activation sizes). Figure 11 shows that observed OR values in most of the days (>~80%) are within

the range or above those predicted on the four selected days. In other words, the observed OR values on most of days (>~80%) appears to support the dominance of IMN on these days. For the relatively few days (<~20%) where ORs are somewhat less than unity (undercharged) or close to unity (weakly overcharged), one possible explanation is the simultaneous occurrence of homogeneous nucleation involving species other than sulfuric acid and water. Unfortunately, there is currently no substantiated information regarding other possible species that may induce neutral homogeneous nucleation under boreal forest conditions. As was mentioned previously, both Janson et al. (2001) and Sellegri et al. (2005a) concluded that the oxidation products of terpenes were not the nucleating species observed at Hyytiälä, Finland. Further, based on a kinetic H_2SO_4-H_2O-NH_3 ternary homogeneous nucleation (THN) model constrained by laboratory measurements (Yu, 2006b), THN is expected to be negligible under those conditions. It should also be noted that the measurements reported in Riipinen et al. (2007) show no clear impact of ammonia concentrations on observed particle formation rates. On the other hand, as we analyzed earlier for case study on 13 April and 2 May, the weak overcharge or undercharge may also be associated the significant variability in the air mass sampled.

3.4 Nucleation rates predicted based on different theories/models

Figure 12 illustrates the time-dependent variations of the instantaneous nucleation rates at the critical size (J_{crit}), and the "apparent" nucleation rate defined as the appearance rate of 3-nm particles ($J_{3\,nm}$, which is typically observed) predicted with the present IMN model for the six case study days discussed in Sect. 2. For comparison, we also show in Fig. 12 the equivalent predictions based on the Lovejoy et al. (2004) model ($J_{Lovejoy}$, as parameterized by Modgil et al., 2005), quasi-unary homogeneous nucleation model (J_{QUN}, Yu, 2007), and the empirical activation ($J_{act}=A\,[H_2SO_4]$ with $A=2.4\times10^{-7}\,s^{-1}$) and kinetic nucleation ($J_{kin}=K\,[H_2SO_4]^2$ with $K=3.2\times10^{-14}\,cm^3\,s^{-1}$) formulas given in Riipinen et al. (2007).

The temporal variations of $J_{3\,nm}$ presented in Fig. 12 are similar to those of simulated

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N_{3-6} shown in Fig. 9. This is not surprising inasmuch as $J_{3\,nm}$ variations dominate the variations in N_{3-6}, although N_{3-6} also depends on the loss rates of 3–6 nm particles as a result of coagulation with pre-existing particles and growth out of the 3–6 nm size range. Under the conditions studied here, the diameters of critical clusters generally range from ~1.3 nm to ~1.7 nm during the nucleation period. The time that $J_{3\,nm}$ lags behind J_{crit} varies owing to the diurnal changes in H_2SO_4 concentrations, and hence the growth rates of sub-3 nm particles. The difference in the peak values of J_{crit} and $J_{3\,nm}$ depends on the growth rate and coagulation sink of sub-3 nm particles and is the largest on 18 April when $[H_2SO_4]$ (and thus the growth rate of sub-3 nm particles) is smallest.

As we have shown above (Fig. 9), IMN model predictions capture the observed variation and magnitude of N_{3-6} on 18 April, 27 April, 3 May, and 12 May. Moreover, the predictions on those days are also consistent with the general behavior of the measured overcharging ratio (Figs. 10 and 11). It is clear from Fig. 12 that the model of Lovejoy et al. (2004) predicts negligible ion-induced nucleation on all days, and therefore appears to be inconsistent with the in situ observations of particle concentrations and overcharging (notwithstanding the occurrence of another undetermined nucleation source). The differences between $J_{Lovejoy}$ and J_{crit} are more than 2–4 orders of magnitude and increase with the temperature. It is likely that the model of Lovejoy et al. (2004) underpredicts the contribution of ions to new particle formation in lower troposphere. The possible reasons for the difference between Lovejoy et al. (2004)'s model and our IMN model include different thermodynamic data used to represent the neutral H_2SO_4-H_2O binary system, differences in the treatment of positive ions/clusters (the dynamics of positive ion clusters is not actually treated in Lovejoy et al.'s model), and different thermochemical data for ion clusters not directly investigated in the laboratory by Lovejoy et al. (2004), or for which alternative data exist (Yu, 2006a). It should be emphasized that the current version of the IMN model incorporates not only the thermodynamic data for small ion clusters used by Lovejoy et al. (2004), but also a number of other thermodynamic data sources and physically based schemes not considered by Lovejoy et

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al. (2004) (Yu, 2006a, 2007). Certainly, because of the sensitivity of nucleation rates to the thermodynamics of pre-nucleation clusters, further research is needed to reduce uncertainties in the thermodynamics parameters for these species. Nevertheless, simulations of the concentrations and size-resolved charged fractions of freshly formed particles representing most (>∼80%) of nucleation event days measured in Hyytiälä appear to support the overall physical representations in the IMN model, although the reasons behind the difference between simulated and observed on the relatively few (<∼20%) undercharged or weakly overcharged days remain unclear.

Under the baseline conditions selected for the three case study days, H_2SO_4-H_2O binary homogeneous nucleation (BHN) rates were calculated with the recently developed quasi-unary nucleation model (Yu, 2007), which is constrained by multiple datasets. The predicted nucleation rates (Fig. 9) all fall below $\sim 10^{-9}$–10^{-11} cm^{-3} s^{-1}, and thus are completely negligible. Ammonia and certain organic species can enhance BHN rates by perhaps 1–2 orders of magnitude, considering the limited existing laboratory findings (Ball et al., 1999; Zhang et al., 2004). Accordingly, it is unlikely that ternary nucleation can explain the observed nucleation events. This conclusion is consistent with the results of Janson et al. (2001) and Sellegri et al. (2005a) regarding the condensation rather than nucleation role of MTOP, and with Riipinen et al.'s (2007) measurements indicating no obvious correlation between NH_3 concentrations and nucleation rates.

Figure 12 also shows that the differences between J_{crit} predicted by the IMN model and J_{act} and J_{kin} based on empirical formulas set out by Riipinen et al. (2007) can be relatively small in the early morning hours (i.e., ∼07:00 a.m. to ∼10:00 a.m.), but are much larger (by many orders of magnitude) at other times (especially near noon and afterwards). The empirical formulas predict much higher nucleation rates around noon times because the sulfuric acid concentration is peaking then. However, this behavior is clearly inconsistent with observed decline in N_{3-6} in the afternoon (see Fig. 9 and also note the 1–2 h time delay between the nucleation rate and N_{3-6}). By contrast, the IMN model captures the fall-off in N_{3-6} quite reasonably (accounting for uncertainties in the growth rate of 3–6 nm particles associated with organic condensation,

as noted earlier). An analysis of the IMN simulations indicates that the main factors limiting nucleation (and hence the concentrations of 3–6 nm particles) after midday are the higher temperatures and lower relative humidities typical of those times of the day (Fig. 2), which inhibit the formation of TSCs via IMN. It should be noted that the empirical activation and kinetic nucleation formula (i.e., J_{act} and J_{kin}) are regression parameterizations which do not aim to describe detailed physics.

4 Summary and discussion

The unique long-term and multiple-instrument characterizations of nucleation events obtained at a boreal forest site (Hyytiälä, Finland) by Kulmala and colleagues provide the most comprehensive set of data available to date to test nucleation theories of atmospheric particle formation. While the measurements of ion mobility and charged fractions of freshly nucleated particles at the site indicate 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 versus neutral processes has remained unresolved. In part, this lack of resolution may be due to the fact that, even when the same set of measurements are considered, different groups have used dramatically different analytical approaches. A comprehensive study of the latest multi-parameter datasets may therefore shed new light on atmospheric particle nucleation mechanisms. For this purpose, we utilize the Ion-Mediated Nucleation (IMN) model developed over the last decade (Yu and Turco, 1997, 2000, 2001; Yu, 2006a). To facilitate the analysis, we designed case studies corresponding to representative (in terms of the observed ranges of sulfuric acid gas concentrations, concentrations and charged fractions of freshly nucleated particles) nucleation events observed during spring 2005 in Hyytiälä, Finland, during the BACCI/QUEST IV intensive field campaign (Laakso et al., 2007; Riipinen et al., 2007). Detailed kinetic IMN simulations were carried out, with key variables constrained by measured values. Appropriate sensitivity studies have also carried out to investigate the effect of the variations of condensation sink and condensable organic

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specie concentrations on the simulated results.

Out of roughly 30 days sampled during the campaign, four were initially selected based on the indications of the homogeneity of the sampled air masses. It happens that all four of these days exhibited medium to high electrical overcharging of the nucleated particles. In each of these well-defined cases, we find reasonable agreement between predicted diurnal variations in the concentrations of freshly nucleated particles within the observed 3–6 nm size range (including the timing of the particle concentration increase, peak concentrations, and the decrease following the peak), as well as the measured average particle charged fractions.

To extend the scope of the study, we have also selected one case of weak electrical overcharging, and one of clear undercharging, of the nucleated particles. The consistency between model simulations and measurements was less satisfying on these two case study days. The electrical states of these two days 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 uniform over the entire nucleation event. On one day, the increase in N_{3-6} in the morning precedes that of $[H_2SO_4]$, which is in contrast with most of other observed nucleation days. On another day, anomalously high concentrations of particles from 3–6 nm occurred during a short span of time. We tentatively conclude that the simulated outcomes in these cases were influenced by, among other things, the significant variability in the sampled air masses – which introduces artifacts in the form of apparent temporal gradients – and the possible role of species other than sulfuric acid in the nucleation process. Under such ambiguous conditions, individual nucleation events cannot be accurately reconstructed.

On all the case study days, the predicted average diameter of ~1.5 nm for critical cluster activation during nucleation periods is supported by recent measurements in a boreal forest setting (Kulmala et al., 2007). Further, the simulated presence of several thousands (per cm^3) of 1.8–3 nm thermodynamically stable clusters (TSCs) during such nucleation periods is remarkably consistent with the typical concentrations of 1.8–3 nm particles detected in boreal forests, as reported by Kulmala et al. (2007). The

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predicted strong diurnal variations of these 1.8–3 nm particles is generally consistent with AIS, BSMA, NAIS-positive and UF0-02proto CPC pair data presented in Kumala et al. (2007), although it appears to be in conflict with the NAIS-negative measurements reported in Kulmala et al. (2007). We note that the resolution of observations of the diurnal variations of 1.8–3 nm particles can have significant implications regarding competing nucleation theories.

A comparison of simulated average size-dependent values of overcharging ratio (OR) with those observed values corresponding to about 30 nucleation events sampled during spring 2005 in Hyytiälä shows that observed OR values in most of the days (>~80%) are within the range, or exceeding, those predicted by the IMN model. It is reasonable to conclude that the observed OR values on most of days (>~80%) appear to support the significance of IMN on these days. This conclusion is further supported by the reasonable agreement between the simulated and observed properties and behavior of nucleation events and multiple observational parameters (including critical nucleation cluster sizes, size-dependent nanoparticle overcharging ratios, concentrations of sub-3 nm stable nuclei and 3–6 nm neutral particles, and their diurnal variations) on such days. We also emphasize that presently no alternative quantitative nucleation mechanism is capable of explaining nucleation events observed in boreal forests. Measurements appear to indicate that organic species are not involved in these events, and that ammonia has no clear effect on observed particle formation rates in boreal forests.

The time-dependent nucleation rates predicted with the current IMN model for the six case study days have been compared with values derived using the Lovejoy et al. (2004) ion nucleation model, with the recently updated binary homogeneous nucleation model of Yu (2007), and with the empirical activation and kinetic nucleation formulas presented by Riipinen et al. (2007). The calculated binary homogeneous nucleation rates fall below ~10^{-9}–10^{-11} cm^{-3} s^{-1}, and we conclude that even several orders of magnitude enhancement in these rates presumably in the presence of ammonia or certain organic species – as measured in laboratory studies (Ball et al., 1999; Zhang et al., 2004) – is unlikely to explain the observed nucleation events. Compared

to the values predicted by IMN model, which are consistent with a variety of measurements as noted above, the nucleation rates predicted using the Lovejoy et al. (2004) model are lower by more than 2–4 orders of magnitude, with the difference becoming larger at higher temperatures. 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.

Obviously, uncertainties remain in both the IMN model parameterizations and in the measured properties of freshly nucleated particles under a range of atmospheric conditions. Additional case studies to investigate specific nucleation events that are well defined observationally would build confidence in existing nucleation theories. Comparisons of simulated and observed time series of overcharging ratios on the selected days may provide additional information and insight. It is also necessary to extend field measurement capabilities to smaller particle sizes, with accurate resolution of native electrical charge and composition, to constrain models and differentiate between competing mechanisms. Likewise, direct laboratory and computational studies of the properties of nucleation-sized molecular clusters, and measurements of nucleation rates under controlled conditions, represent an important element of an overall strategy to bring the science of atmospheric particle formation to a level of precision adequate for supporting advanced climate, air quality and health assessments.

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References

Ball, S. M., Hanson, D. R., Eisele, F. L., McMurry, P. H.: Laboratory studies of particle nucleation: Initial results for H_2SO_4, H_2O, and NH_3 vapors, J. Geophys. Res., 104(D19), 23 709–23 718, doi:10.1029/1999JD900411, 1999.

Dal Maso, M., Kulmala, M., Riipinen, I., Wagner, R., Hussein, T., Aalto, P. P., and Lehtinen, K. E. J.: Formation and growth of fresh atmospheric aerosols: eight years of aerosol size distribution data from SMEAR II, Hyytiälä, Finland, Boreal Environ. Res., 10, 323–336, 2005.

Ehn, M., Petäjä, T., Aufmhoff, H., Aalto, P., Hämeri, K., Arnold, F., Laaksonen, A., and Kulmala, M.: 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, http://www.atmos-chem-phys.net/7/211/2007/.

Engelhart, G. J., Asa-Awuku, A., Nenes, A., and Pandis, S. N.: CCN activity and droplet growth kinetics of fresh and aged monoterpene secondary organic aerosol, Atmos. Chem. Phys. Discuss., 8, 95–135, 2008, http://www.atmos-chem-phys-discuss.net/8/95/2008/.

Hanson, D. R. and Eisele, F.: Diffusion of H_2SO_4 in Humidified Nitrogen: Hydrated H_2SO_4, J. Phys. Chem. A, 104(8), 1715–1719, 2000.

Hanson, D. R. and Lovejoy, E. R.: Measurement of the thermodynamics of the hydrated dimer and trimer of sulfuric acid, J. Phys. Chem. A, 110, 9525–9528, doi:10.1021/jp062844w, 2006.

Hirsikko, A., Bergman, T., Laakso, L., Dal Maso, M., Riipinen, I., Hõrrak, U., and Kulmala, M.: Identification and classification of the formation of intermediate ions measured in boreal forest, Atmos. Chem. Phys., 7, 201–210, 2007, http://www.atmos-chem-phys.net/7/201/2007/.

Iida, K., Stolzenburg, M., McMurry, P., Dunn, M. J., Smith, J. N., Eisele, F., and Keady, P.: Contribution of ion-induced nucleation to new particle formation: Methodology and its application to atmospheric observations in Boulder, Colorado, J. Geophys. Res., 111, D23201, doi:10.1029/2006JD007167, 2006.

Janson, R., Rosman, K., Karlsson, A., and Hansson, H. C.: Biogenic emissions and gaseous precursors to forest aerosols, Tellus B, 53, 423–440, 2001.

Kazil, J., Lovejoy, E. R., Jensen, E. J., and Hanson, D. R.: Is aerosol formation in cirrus clouds possible?, Atmos. Chem. Phys., 7, 1407–1413, 2007,

http://www.atmos-chem-phys.net/7/1407/2007/.
Kulmala, M., Riipinen, I., Sipilä, M., et al.: Toward direct measurement of atmospheric nucleation, Science, 318, 89–92, 2007.
Kulmala, M., Riipinen, I., Sipilä, M., et al.: Initial steps of aerosol growth, Atmos. Chem. Phys., 4, 2553–2560, 2004a,
http://www.atmos-chem-phys.net/4/2553/2004/.
Kulmala, M., Kerminen, V.-M., Anttila, T., Laaksonen, A., and O'Dowd, C. D.: Organic aerosol formation via sulphate cluster activation, J. Geophys. Res., 109, D04205, doi:10.1029/2003JD003961, 2004b.
Kulmala, M., Pirjola, L., and Makela, J.: Stable sulphate clusters as a source of new atmospheric particles, Nature, 404, 66–69, 2000.
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,
http://www.atmos-chem-phys.net/7/1333/2007/.
Laakso, L., Petäjä, T., Lehtinen, K. E. J., Kulmala, M., Paatero, J., Hõrrak, U., Tammet, H., and Joutsensaari, J.: Ion production rate in a boreal forest based on ion, particle and radiation measurements, Atmos. Chem. Phys., 4, 1933–1943, 2004a,
http://www.atmos-chem-phys.net/4/1933/2004/.
Laakso, L., Anttila, T., Lehtinen, K. E. J., Aalto, P. P., Kulmala, M., Hõrrak, U., Paatero, J., Hanke, M., and Arnold, F.: Kinetic nucleation and ions in boreal forest particle formation events, Atmos. Chem. Phys., 4, 2353–2366, 2004b,
http://www.atmos-chem-phys.net/4/2353/2004/.
Laaksonen, A., Kulmala, M., O'Dowd, C. D., Joutsensaari, J., Vaattovaara, P., Mikkonen, S., Lehtinen, K. E. J., Sogacheva, L., Dal Maso, M., Aalto, P., Petäjä, T., Sogachev, A., Jun Yoon, Y., Lihavainen, H., Nilsson, D., Cristina Facchini, M., Cavalli, F., Fuzzi, S., Hoffmann, T., Arnold, F., Hanke, M., Sellegri, K., Umann, B., Junkermann, W., Coe, H., Allan, J. D., Rami Alfarra, M., Worsnop, D. R., Riekkola, M.-L., Hyötyläinen, T., and Viisanen, Y.: The role of VOC oxidation products in continental new particle formation, Atmos. Chem. Phys. Discuss., 7, 7819–7841, 2007,
http://www.atmos-chem-phys-discuss.net/7/7819/2007/.
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.

Marti, J. J., Jefferson, A., Ping Cai, X., Richert, C., McMurry, P. H., and Eisele, F.: H_2SO_4 vapor pressure of sulfuric acid and ammonium sulfate solutions, J. Geophys. Res., 102(D3), 3725–3736, 1997.

Modgil, M. S., Kumar, S., Tripathi, S. N., and Lovejoy, E. R.: A parameterization of ion-induced nucleation of sulphuric acid and water for atmospheric conditions, J. Geophys. Res., 110, D19205, doi:10.1029/2004JD005475, 2005.

Nadykto, A. B. and Yu, F.: Strong hydrogen bonding between atmospheric nucleation precursors and organic acids, Chem. Phys. Lett., 435, 14–18, 2006.

Riipinen, I., Sihto, S.-L., Kulmala, M., Arnold, F., Dal Maso, M., Birmili, W., Saarnio, K., Teinilä, K., Kerminen, V.-M., Laaksonen, A., and Lehtinen, K. E. J.: Connections between atmospheric sulphuric acid and new particle formation during QUEST III–IV campaigns in Heidelberg and Hyytiälä, Atmos. Chem. Phys., 7, 1899–1914, 2007, http://www.atmos-chem-phys.net/7/1899/2007/.

Sellegri, K., Umann, B., Hanke, M., and Arnold, F.: Deployment of a ground-based CIMS apparatus for the detection of organic gases in the boreal forest during the QUEST campaign, Atmos. Chem. Phys., 5, 357–372, 2005a, http://www.atmos-chem-phys.net/5/357/2005/.

Sellegri, K., Hanke, M., Umann, B., Arnold, F., and Kulmala, M.: Measurements of organic gases during aerosol formation events in the boreal forest atmosphere during QUEST, Atmos. Chem. Phys., 5, 373–384, 2005b, http://www.atmos-chem-phys.net/5/373/2005/.

Sipilä, M., Lehtipalo, K., Kulmala, M., Petäjä, T., Junninen, H., Aalto, P. P., Manninen, H. E., Vartiainen, E., Riipinen, I., Kyrö, E.-M., Curtius, J., Krten, A., Borrmann, S., and O'Dowd, C. D.: Applicability of condensation particle counters to measure atmospheric clusters, Atmos. Chem. Phys. Discuss., 8, 4373–4405, 2008, http://www.atmos-chem-phys-discuss.net/8/4373/2008/.

Vana, M., Tamm, E., Hõrrak, U., Mirme, A., Tammet, H., Laakso, L., Aalto, P. P., and Kulmala, M.: Charging state of nanoparticles during the nucleation burst events, Atmos. Res., 82, 536–546, 2006.

Yu, F.: From molecular clusters to nanoparticles: Second-generation ion-mediated nucleation model, Atmos. Chem. Phys., 6, 5193–5211, 2006a, http://www.atmos-chem-phys.net/6/5193/2006/.

Yu, F.: Effect of ammonia on new particle formation: A kinetic H_2SO_4-H_2O-NH_3 nucle-

ation model constrained by laboratory measurements, J. Geophys. Res., 111, D01204, doi:10.1029/2005JD005968, 2006b.
Yu, F.: An improved quasi-unary nucleation model for binary H_2SO_4-H_2O homogeneous nucleation, J. Chem. Phys., 127, 054301, doi:10.1063/1.2752171, 2007.
Yu, F. and Turco, R. P.: The role of ions in the formation and evolution of particles in aircraft plumes, Geophys. Res. Lett., 24, 1927–1930, 1997.
Yu, F. and Turco, R. P.: Ultrafine aerosol formation via ion-mediated nucleation, Geophys. Res. Lett., 27, 883–886, 2000.
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 Proceeding of 17th International Conference on Nucleation Atmospheric Aerosols (Pages 392–395), Galway, Ireland, 13–17 August 2007.
Yu, F., Wang, Z., Luo, G., and Turco, R. P.: Ion-mediated nucleation as an important source of tropospheric aerosols, Atmos. Chem. Phys. Discuss., 7, 13 597–13 626, 2007a.
Yu, F., Wang, Z., Luo, G., and Turco, R. P.: Interactive comment on "Ion-mediated nucleation as an important global source oftropospheric aerosols", Atmos. Chem. Phys. Discuss., 7, S6602–S6608, 2007b.
Yu, F., Z. Wang, G. Luo, and R. P. Turco: Interactive comment on "Ion-mediated nucleation as an important global source oftropospheric aerosols", Atmos. Chem. Phys. Discuss., 7, S6754–S6766, 2007c.
Zhang, R., Suh, I., Zhao, J., Zhang, D., Fortner, E. C., Tie, X., Molina, L. T., and Molina, M. J.: Atmospheric new particle formation enhanced by organic acids, Science, 304, 1487–1490, 2004.

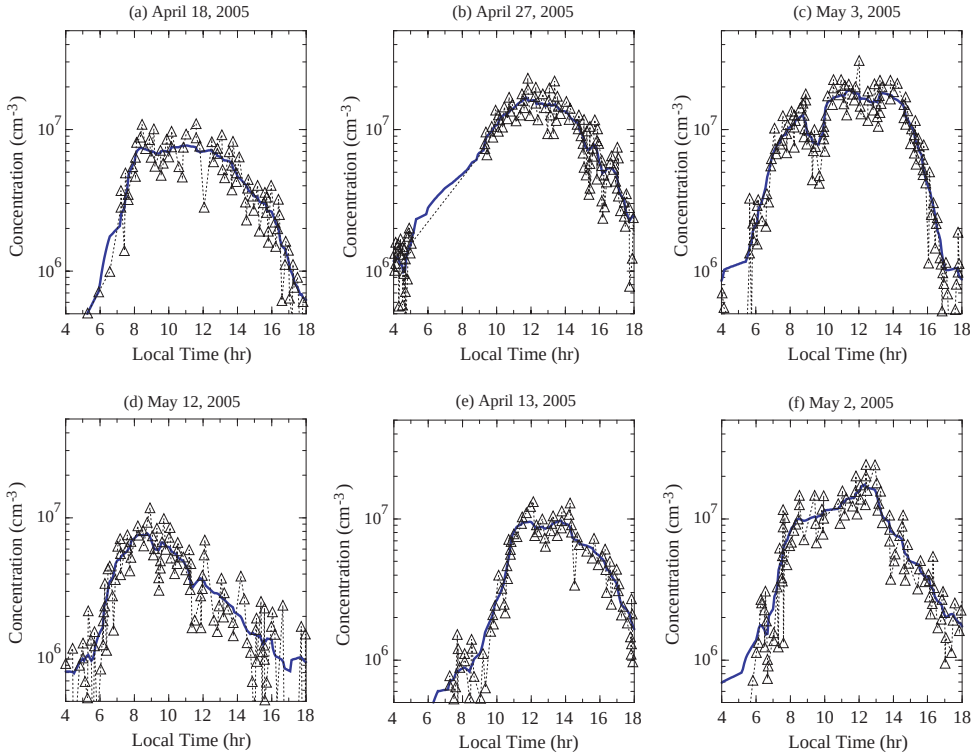

Fig. 1. Time series of observed H_2SO_4 concentrations for the six case study days. The data points are taken from Fig. 1b of Riipinen et al. (2007). Fluctuations in the data are likely associated with inhomogeneities in the air masses sampled at the fixed field site. Such Eulerian, as opposed to Lagrangian, 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 (also see the discussion in the text). In the present simulations, each [H_2SO_4] time series has been smoothed using an 11-point running average, which is shown as a solid blue curve.

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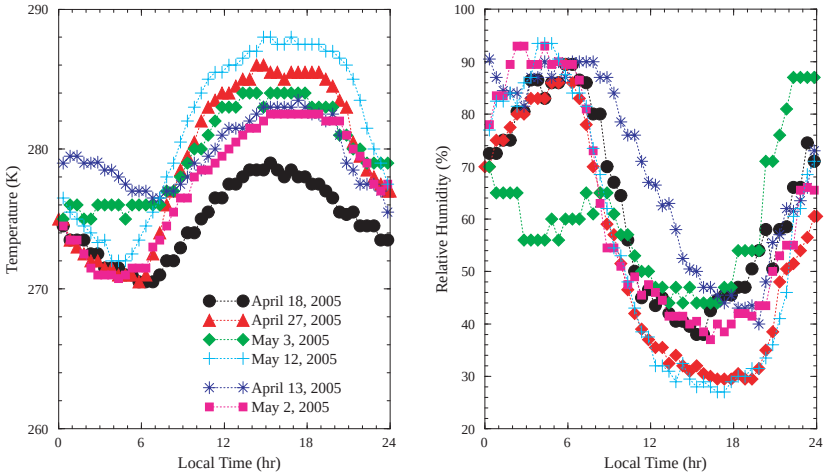

Fig. 2. The time series of temperature (T) and relative humidity (RH) used to constrain the simulations for the six case studies. Refer to the text for details.

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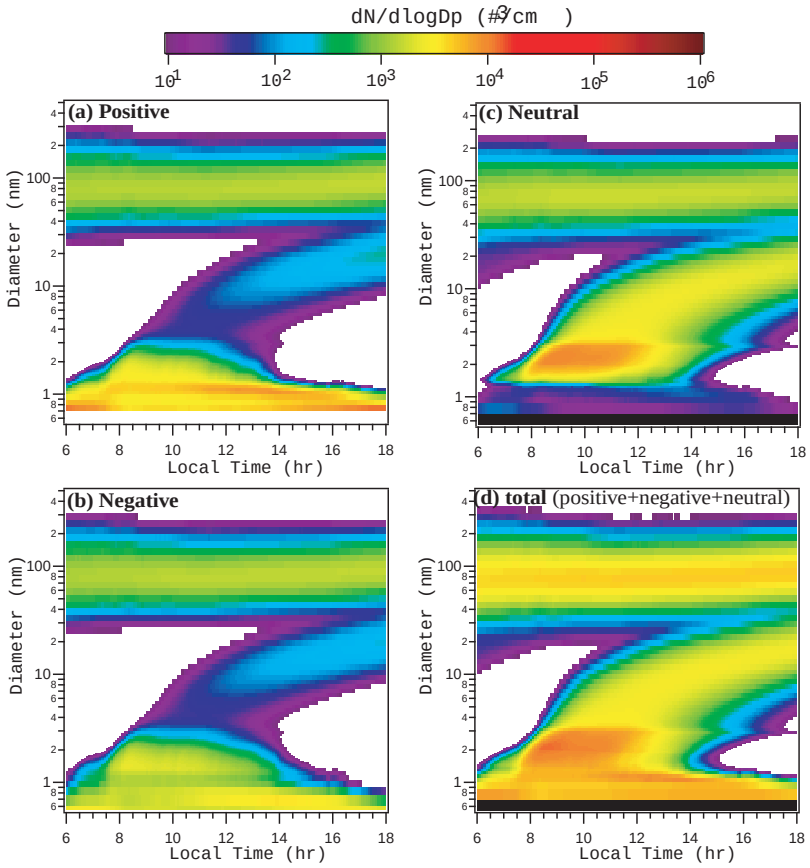

Fig. 3. Simulated evolution of particle size distributions ($dN/dlogD_p$) for various particle types corresponding to the case study on 18 April 2005: **(a)** – positively charged; **(b)** – negatively charged; **(c)** – neutral; and **(d)** – total. Refer to the text for details.

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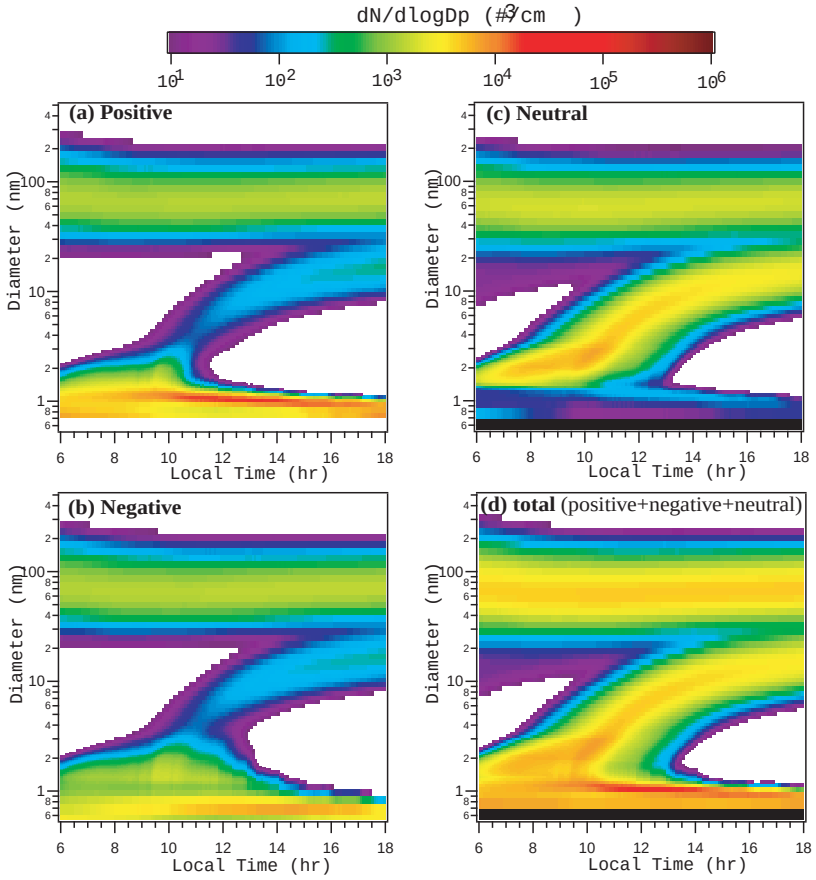

Fig. 4. Same as Fig. 3, except for the case study on 27 April 2005.

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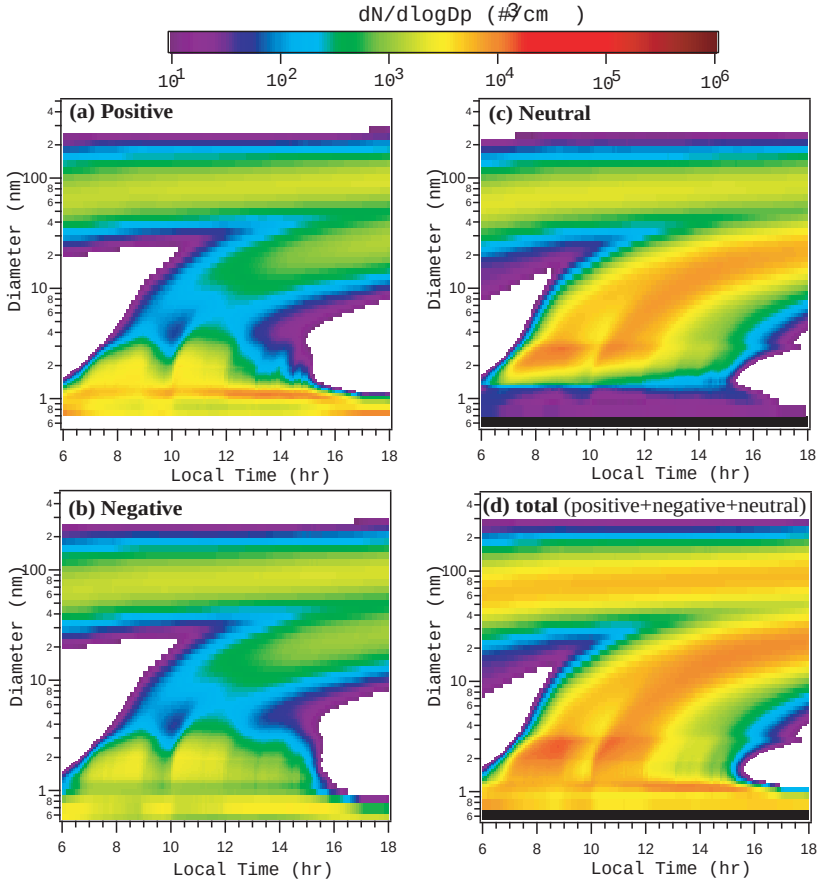

Fig. 5. Same as Fig. 3, except for the case study on 3 May 2005.

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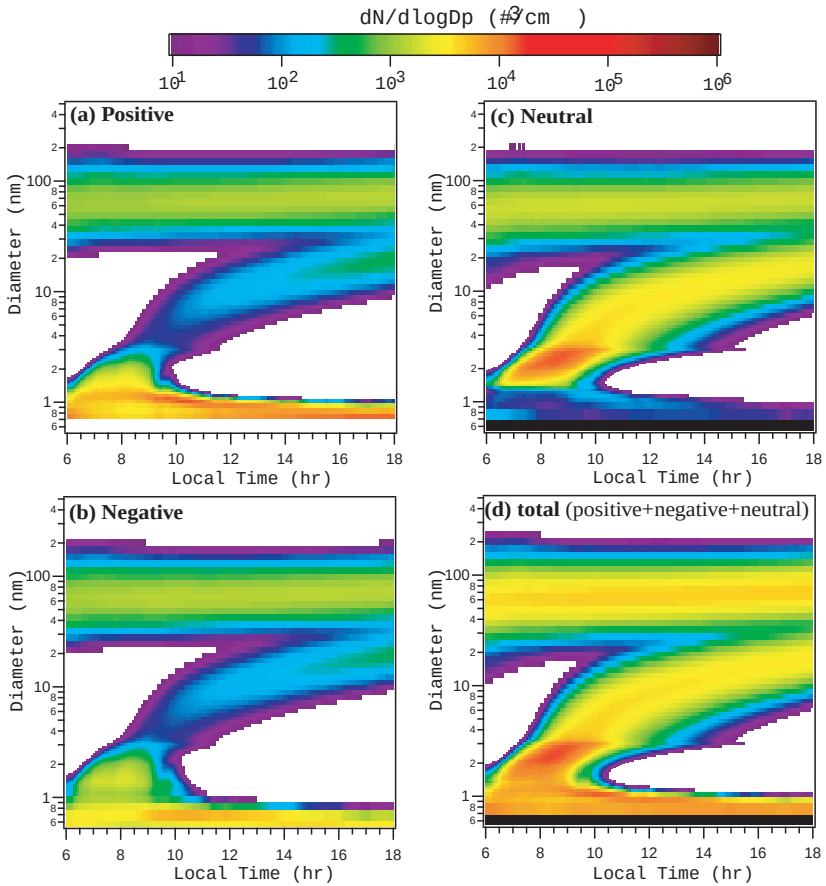

Fig. 6. Same as Fig. 3, except for the case study on 12 May 2005.

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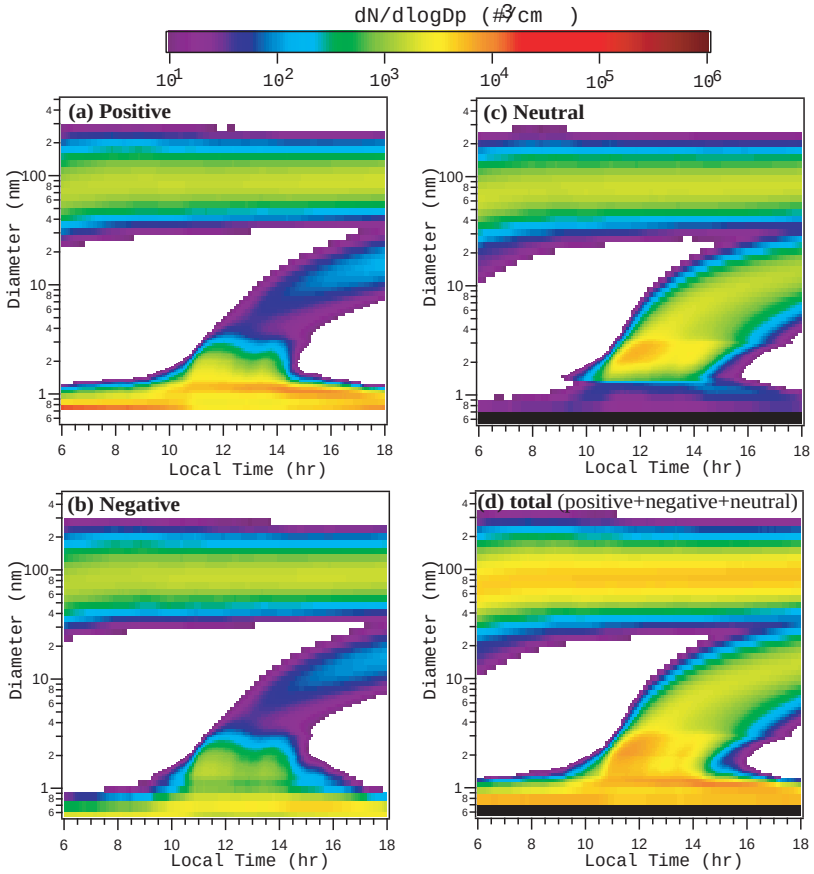

Fig. 7. Same as Fig. 3, except for the case study on 13 April 2005.

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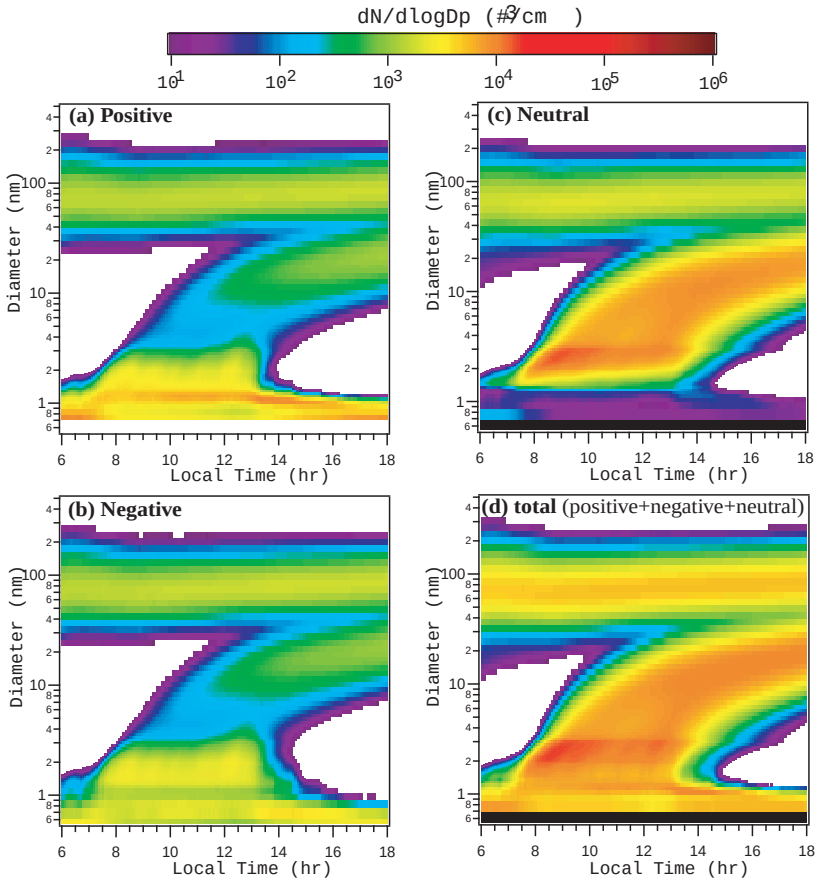

Fig. 8. Same as Fig. 3, except for the case study on 2 May 2005.

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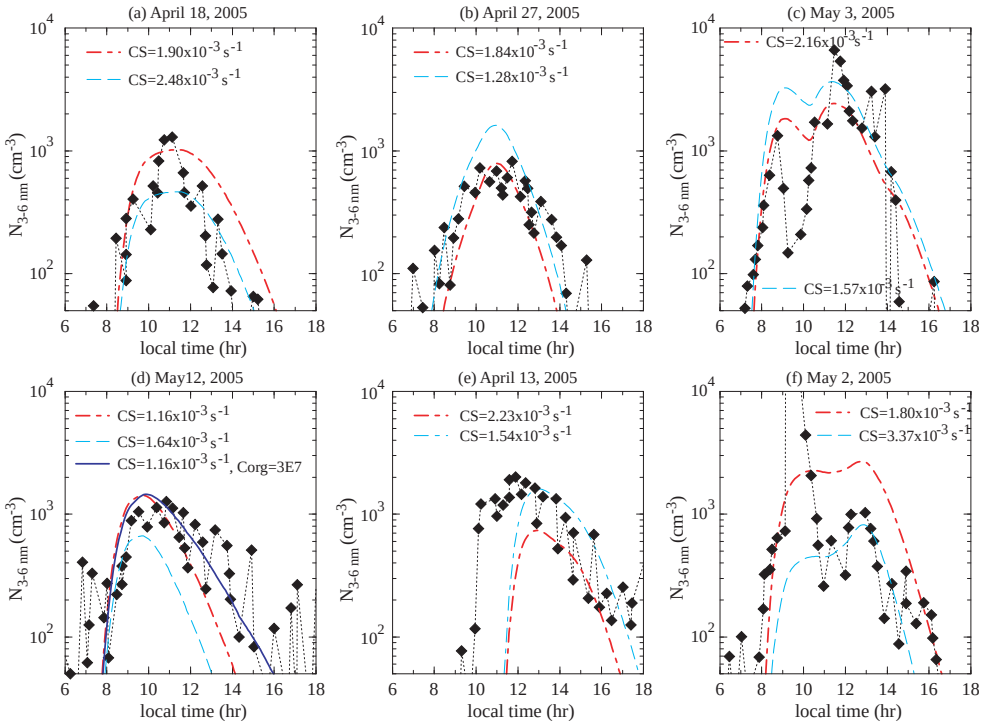

Fig. 9. Time-dependent variations in the concentrations of particles in the size range 3–6 nm (N_{3-6}) corresponding to the six case study days: simulations (dot-dashed and dashed lines), and observations (lines with symbols). The magnitude of the condensation sink (CS) given in the legends are averaged CS values during the nucleation and growth period (06:00 a.m.–02:00 p.m.). In Fig. 9d, one additional curve is shown corresponding to a lower concentration of condensable organic species (peak $C_{COS}=3\times10^7$ cm^{-3}).

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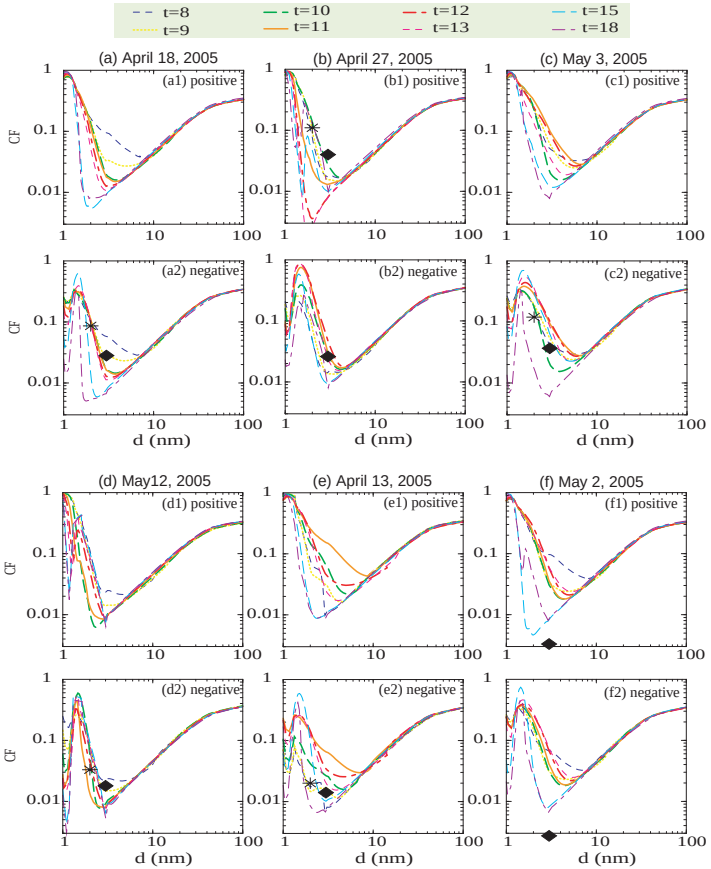

Fig. 10. IMN model predictions of size-dependent particle charge fractions (CFs) at selected local times (in h) during the six case study days. The symbols shown at 3 nm correspond to observed CFs averaged over specific nucleation periods as described by Laakso et al. (2007), while the symbols at 2 nm are values inferred by Laakso et al. (2007) using backward calculations from larger sizes.

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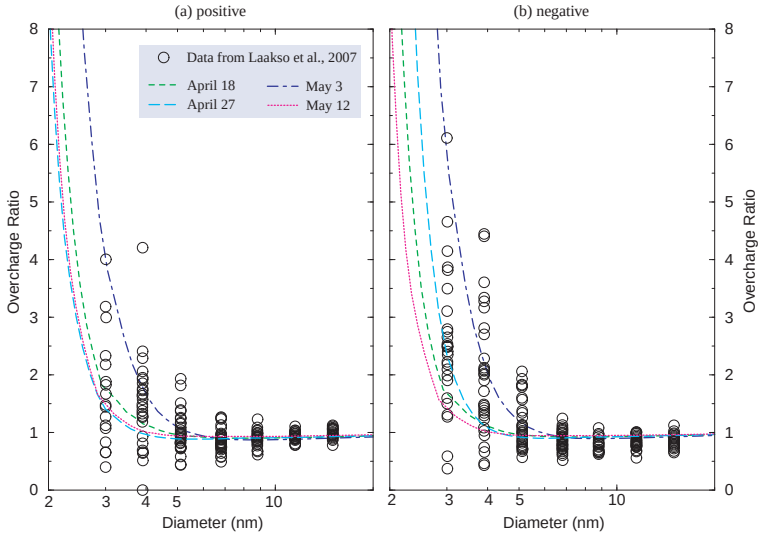

Fig. 11. IMN simulated and observed size-dependent overcharge ratios (OR). Each curve represents IMN model calculated OR values averaged over a nucleation event corresponding to a specific case study. The open circles are observed average OR values corresponding to roughly 30 nucleation events sampled 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).

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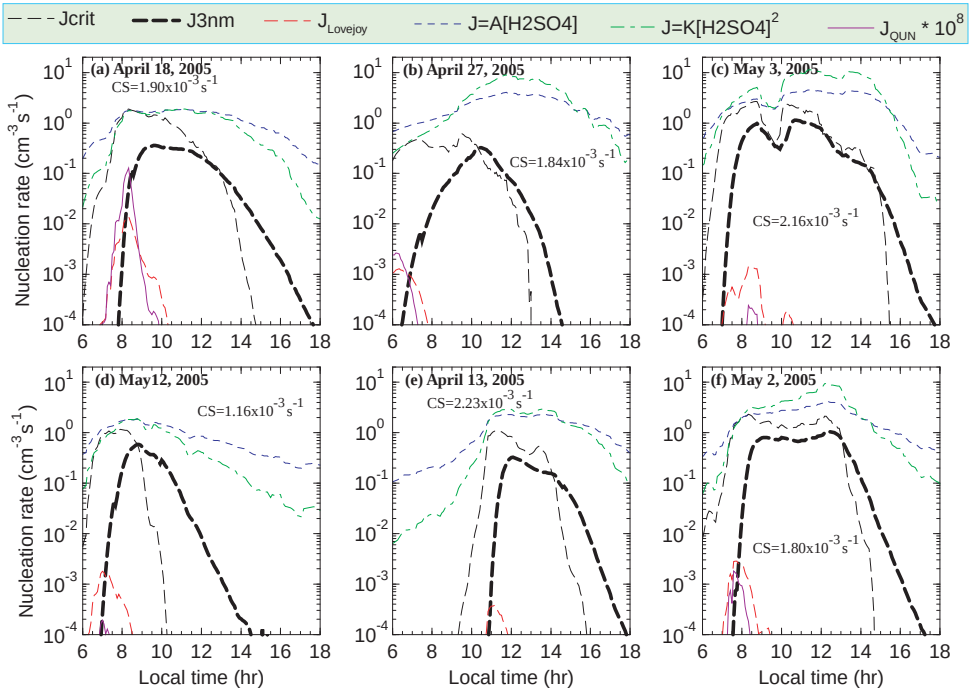

Fig. 12. IMN calculated time-dependent variations in nucleation rates based on model-simulated critical embryo sizes (J_{crit}), and based on the production rate of 3-nm particles ($J_{3\,nm}$, the "apparent" nucleation rate typically observed). Results are given for each of the six case studies discussed in Sect. 2. In each case, for comparison, predicted nucleation rates are shown for the ion nucleation model of Lovejoy et al. (2004) ($J_{Lovejoy}$, as parameterized by Modgil et al., 2005), the quasi-unary homogeneous nucleation model of Yu (2007) (J_{QUN}), and the empirical activation formula ($J_{act}=A\,[H_2SO_4]$ with $A=2.4\times10^{-7}$ s^{-1}) and kinetic nucleation relationship ($J_{kin}=K\,[H_2SO_4]^2$ with $K=3.2\times10^{-14}$ cm^3 s^{-1}) proposed by Riipinen et al. (2007). Note that the solid curves represent $J_{QUN}\times10^8$.

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