1 Spring and summer contrast in new particle formation over nine forest areas in

2 North America

F. Yu¹, G. Luo¹, S. C. Pryor², P. R. Pillai³, S. H. Lee⁴, J. Ortega⁵, J. J. Schwab¹, A. G. Hallar⁶,
W. R. Leaitch⁷, V. P. Aneja³, J. N. Smith^{5,8}, J. T. Walker^{3,9}, O. Hogrefe^{1, #}, and K. L. Demerjian¹

6

- ⁷ ¹Atmospheric Sciences Research Center, State University of New York, 251 Fuller Road,
- 8 Albany, New York 12203, USA
- ⁹ ²Department of Earth and Atmospheric Sciences, Cornell University, Ithaca, NY 14853, USA
- ³Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University,

11 Raleigh, NC, 27695, USA.

- ⁴College of Public Health, Kent State University, Kent, Ohio, USA
- ⁵National Center for Atmospheric Research, PO Box 3000, Boulder, Colorado 80307, USA
- ⁶Desert Research Institute, Storm Peak Laboratory, Steamboat Springs, CO 80488, USA.
- ⁷Environment Canada, Science and Technology Branch, Toronto, ON, Canada
- ⁸Applied Physics Dept., University of Eastern Finland, PO Box 1627, Kuopio 70211 Finland.
- ⁹US Environmental Protection Agency, Office of Research and Development, Durham, NC
- 18 27711, USA
- 19 [#]currently at Durham Technical Community College
- 20

21

23 Abstract. Recent laboratory chamber studies indicate a significant role for highly oxidized low volatility organics in new particle formation (NPF) but the actual role of these highly oxidized 24 low volatility organics in atmospheric NPF remains uncertain. Here, particle size distributions 25 (PSDs) measured in nine forest areas in North America are used to characterize the occurrence 26 and intensity of NPF and to evaluate model simulations using an empirical formulation in which 27 formation rate is a function of the concentrations of sulfuric acid and low volatility organics from 28 alpha-pinene oxidation (Nucl-Org), and using an ion-mediated nucleation mechanism (excluding 29 organics) (Nucl-IMN). On average, NPF occurred on ~ 70% of days during March for the four 30 forest sites with springtime PSD measurements, while NPF occurred on only ~ 10% of days in 31 July for all nine forest sites. Both Nucl-Org and Nucl-IMN schemes capture the observed high 32 frequency of NPF in spring, but the Nucl-Org scheme significantly over-predicts while the Nucl-33 IMN scheme slightly under-predicts NPF and particle number concentrations in summer. 34 Statistical analyses of observed and simulated ultrafine particle number concentrations and 35 frequency of NPF events indicate that the scheme without organics agrees better overall with 36 observations. The two schemes predict quite different nucleation rates (including their spatial 37 patterns), concentrations of cloud condensation nuclei, and aerosol first indirect radiative forcing 38 39 in North America, highlighting the need to reduce NPF uncertainties in regional and global earth 40 system models.

41

42

43

44 1. Introduction

Particle number concentration is an important factor in the health and climate impacts of 45 atmospheric aerosols. High number concentrations of ultrafine particles may lead to adverse 46 health effects (Knibbs et al., 2011). As cloud condensation nuclei (CCN), atmospheric particles 47 modify cloud properties and precipitation and thus affect the hydrological cycle and climate 48 indirectly. Aerosol indirect radiative forcing (IRF) remains a major uncertainty in assessing 49 climate change (IPCC, 2013; Carslaw et al., 2013). Secondary particles formed via nucleation 50 dominate the global total particle number abundance (Spracklen et al., 2008; Pierce and Adams, 51 52 2009; Yu and Luo, 2009) and global simulations indicate that the aerosol IRF is quite sensitive to nucleation parameterizations (Wang and Penner, 2009; Kazil et al., 2010; Yu et al., 2012). 53 Furthermore, as a result of its dependence on meteorological conditions, emissions, and 54 chemistry, new particle formation (NPF) is an important physical process involved in a number 55 of climate feedback loops. Laboratory experiments indicate that sulfuric acid, ammonia, amines, 56 ions, certain organic compounds and oxidants can all contribute to NPF. But there are numerous 57 chemical reactions and physical processes involved, so there is no single unified theory that 58 accurately describes NPF and the levels of enhancements due to different species vary widely 59 60 among various studies (e.g., Zhang et al., 2004; Erupe et al., 2011; Chen et al., 2012; Dawson et al., 2012; Almeida et al., 2013; Berndt et al., 2014; Riccobono et al., 2014; Glasoe et al., 2015). 61

The indication that nucleation is significantly enhanced by organic species formed via oxidation of biogenic volatile organic compounds (VOCs) (e.g., Riccobono et al., 2014) is of interest as it may have important implications for the interactions of anthropogenic and biogenic emissions and the associated climate forcing. Nevertheless, the various roles of organics and their oxidation products in NPF in the real atmosphere remains an active research area. Particle

size distributions (PSDs) have been measured in a variety of environments around the globe and 67 many of these measurements have been used to study NPF events (e.g., Kulmala et al., 2004). To 68 evaluate the potential role of oxidation products of biogenic VOCs in NPF, PSDs taken over 69 forested areas are particularly useful. In the present study, we analyze NPF events and non-70 events based on PSDs measured over nine forest areas in North America (NA) and compare 71 72 them to model simulations with and without including organics in the nucleation rate calculation. Since biogenic VOC emissions and their oxidation are strongest in the summer, we use the 73 observed spring and summer contrast in NPF events to study the possible role of organics in NPF 74 75 in NA and evaluate our current understanding of NPF processes in the atmosphere.

76

- 77 **2.** Methods
- 78 2.1. Measurements

PSDs from \sim 3-10 nm to \geq 100 nm have been widely used to identify and to study particle 79 nucleation and growth events in the atmosphere (e.g., Kulmala et al., 2004). In this study, we 80 focus on PSDs observed in various years in eight US and one southern Canadian forest sites 81 summarized in Table 1. The locations of these sites are marked on a Google map 82 83 (http://maps.google.com) in Figure 1. Egbert (EGB) is surrounded by a mixture of forests and farmland which is subject to a strong biogenic influence under certain conditions (Slowik et al., 84 2010; Pierce et al., 2014), while all other eight sites are directly located in forest or mountain 85 86 areas. PSDs have been measured at these nine sites with Scanning Mobility Particle Sizers (SMPSs) during different time periods. Sites 1-4 have at least one year of continuous PSD data 87 while sites 5-9 have PSD data only during the summer (for different years). PSDs for one spring 88 89 and one summer month for Sites 1-4 and for one summer month for Sites 5-9 are given in Figure

90 1. It is clear that nucleation in the spring is much more frequent and stronger (i.e, higher
91 concentrations of nucleation mode particles) when compared to summer months. Detailed
92 analysis of these data and comparisons with simulations are given in the Results section.

93

94 2.2. Model and simulations

The modeling work in this study is based on the GEOS–Chem model (e.g., Bey et al., 2001) 95 with an advanced particle microphysics (APM) model incorporated (Yu and Luo, 2009). GEOS-96 Chem is a global 3-D model of atmospheric composition driven by assimilated meteorological 97 observations from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling 98 and Assimilation Office (GMAO). The model has been developed and used by many research 99 groups and contains a number of state-of-the-art modules treating various chemical and aerosol 100 101 processes (e.g., Bey et al., 2001; Chung and Seinfeld, 2002; Martin et al., 2003; Park et al., 2004; Evans and Jacob, 2005; Liao et al., 2007; Henze et al., 2008). The APM module in GEOS-Chem 102 is optimized to simulate the formation of secondary particles and their growth to CCN sizes, 103 104 using high size resolution (30 bins) for particles in the dry size range of 1.2 - 120 nm diameter. There are an additional 10 bins for $0.12 - 12 \mu m$ particles (Yu and Luo, 2009). More detailed 105 106 information about GEOS-Chem and updates can be found at the model website (http://geoschem.org/). 107

To study the possible role of organics in NPF, we employ the organics-mediated nucleation parameterization (Nucl-Org) derived from a CLOUD chamber study as given in Riccobono et al. (2014),

111
$$J_{1.7} = k_m \times [H_2 SO_4]^2 \times [BioOxOrg]$$
(1)

where $J_{1.7}$ is the formation rate (# cm⁻³s⁻¹) of particles of ~ 1.7 nm, k_m is the fitting pre-factor with a value of 3.27×10^{-21} cm⁶ s⁻¹ (90% confidence interval: 1.73×10^{-21} to 6.15×10^{-21} cm⁶ s⁻¹), [H₂SO₄] and [BioOxOrg] are the gas-phase concentrations (# cm⁻³) of H₂SO₄ and biogenic oxidized organic (BioOxOrg) vapors, respectively. In the chamber study reported in Riccobono et al. (2014), BioOxOrg molecules are organic compounds of relatively low volatility from the oxidation of pinanediol (a first-generation oxidation product of α -pinene) and represent latergeneration oxidation products of biogenic monoterpenes.

In GEOS-Chem v8-03-02 on which this study is based, reactive VOCs are grouped into six 119 categories (VOC_i, i = 1 - 6), with VOC₁= α -pinene + β -pinene + sabinene + Δ -3 carene + 120 terpenoid ketones; VOC₂ = limonene; VOC₃ = α -terpinene + γ -terpinene + terpinolene; VOC₄ = 121 myrcene + terpenoid alcohols + ocimene; VOC_5 = sesquiterpenes; and VOC_6 = isoprene. Yu 122 123 (2011) extended the two-product secondary organic aerosol (SOA) formation model (Chung and Seinfeld, 2002) to predict concentrations of extremely low volatile secondary organic gas ([LV-124 SOG) from successive oxidation aging of the first generation oxidation products of various 125 126 VOCs, i.e., semivolatile SOG (SV-SOG) and medium-volatile SOG (MV-SOG). The extended SOA formation scheme substantially increases the simulated SOA mass concentrations and 127 128 improves the agreement of model predictions with aerosol mass spectrometer (AMS) SOA measurements (Yu, 2011). LV-SOG has a saturation vapor concentration in the range of ~ 129 $0.0001 - 0.03 \ \mu g/m^3$, corresponding to the extremely low volatile SOG reported in Ehn et al. 130 131 (2014). The production rate of LV-SOG depends on the saturation vapor concentrations of MV-SOG and SV-SOG and temperature (Yu, 2011). 132

To use Equation (1) to calculate organics-mediated nucleation, we separate LV-SOG from the oxidation products of VOC₁ (named LV-SOG_{α -pinene} thereafter) from those associated with

VOC₂₋₆. LV-SOG_{α -pinene}, a major component of total LV-SOG, corresponds well to the 135 BioOxOrg reported in the chamber study of Riccobono et al. (2014). For comparison, 136 simulations based on the ion-mediated nucleation of the H₂SO₄-H₂O binary system (Nucl-IMN) 137 (Yu, 2010) are also presented. Nucleation rates based on the Nucl-Org scheme depend on 138 [H₂SO₄] and [LV-SOG_{(1-pinene}] only while those based on the Nucl-IMN scheme depend non-139 linearly on [H₂SO₄], temperature (T), relative humidity (RH), ionization rate, and surface area of 140 pre-existing particles (Yu, 2010). Based on the CLOUD chamber study (Almeida et al., 2013; 141 Riccobono et al., 2014), IMN is significant or dominant when $J_{1.7}$ is below ~ 1 cm⁻³ s⁻¹ but 142 neutral nucleation takes over when $J_{17} > \sim 1 \text{ cm}^{-3} \text{ s}^{-1}$. Nucl-IMN calculates formation rates of 143 particles at wet sizes of ~ 1.5 nm. The nucleated particles are added into the first bin (wet size \sim 144 1.5 nm) of the secondary particles, and the processes to grow them to large sizes considered in 145 GEOS-Chem/APM include kinetic condensation of H₂SO₄ and total LV-SOG, equilibrium 146 uptake of nitrate and ammonium, partitioning uptake of SV-SOG and MV-SOG, and self-147 coagulation (Yu, 2011). 148

The horizontal resolution of GEOS-Chem employed for this study is $2^{\circ} \times 2.5^{\circ}$ and there are 47 149 vertical layers (with 14 layers from surface to ~ 2 km above the surface). The emission 150 151 inventories and schemes used can be found at the GEOS-Chem website and have also been summarized in Yu and Hallar (2014). Biogenic VOC emissions from terrestrial vegetation are 152 based on the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 153 154 2006) which computes emissions for plant functional types as a function of temperature, solar radiation, leaf area index (LAI), and leaf age. MEGAN does not consider the effect of water 155 156 stress (drought) which may suppress biogenic emissions (Pryor et al., 2014).

This study focuses on the NA region, and values of all tracers and relevant parameters in all layers over the nine forest sites marked in Figure 1 were output at each chemistry time step (30 minutes) for detailed analysis and comparison with measurements. Since PSD measurements at different sites were taken in different years, multiple-year simulations have been carried out and comparisons are for the same month/year for any given site. Since GEOS-Chem was driven by assimilated meteorology, the key meteorology fields are generally consistent with observations at sites of comparisons (e.g., Yu and Hallar, 2014).

164

165 2.3. NPF events and non-events

To assess the ability of different nucleation schemes to capture NPF events (or non-events) at 166 various sites, an objective criterion is needed to decide from the evolution of PSDs whether a 167 168 given day is an event day or not. An NPF event has generally been defined as the appearance of a clear new nucleation mode (<~ 25 nm) for a significant period of time (hours) accompanied by 169 the growth of the mode diameter during its existence (e.g., Dal Maso et al., 2005). Similar to the 170 171 method used in Hallar et al. (2011) and Venzac et al. (2008), in this study an NPF event is defined if the dN/dlogDp value (where dN is the number concentration of particles within 172 diameter range dD_p) averaged within three bins near 10 nm maintains a level of 3000 cm⁻³ or 173 higher continuously for more than two hours, and the mode diameter grows during the period. 174 The growth rate of the nucleation mode was calculated by linearly fitting the change of mode 175 diameters (Lehtinen and Kulmala, 2003). To simplify the comparison, all days with 176 measurements available but not defined as NPF event days are counted as non-event days. 177

178

179 **3. Results**

180 VOC emissions in the summer are known to be much higher than VOC emissions in the spring. The high VOC emissions coupled with strong photochemistry and oxidation lead to 181 significantly higher production rates and concentrations of oxidized SOGs of varied volatilities 182 (medium volatile, semivolatile, and low-volatile) in the summer. Both [LV-SOG] and [LV-183 $SOG_{\alpha-pinene}$] in the summer are much higher (by a factor of ~ 4-10) than those in the spring while 184 185 $[H_2SO_4]$ has a similar concentration in the spring as in the summer (not shown). Figure 2 shows horizontal distributions of monthly mean nucleation rates (J) in the boundary layer (0-1 km 186 above thesurface) in March and July of 2006 based on two different nucleation schemes (i.e, 187 188 Nucl-Org and Nucl-IMN). Two nucleation schemes clearly predict significantly different spatial patterns and seasonal variations of nucleation rates. In March, J_{Nucl-Org} is highest in the 189 southeastern US as a result of high [LV-SOG_{α -pinene}] in the region, reaching 5-10 cm⁻³s⁻¹ (Fig. 2a), 190 while J_{IMN} has two separate eastern and western nucleation zones with monthly mean J up to 191 ~1-2 cm⁻³s⁻¹ (Fig. 2b). In July, boundary layer $J_{Nucl-Org}$ (Fig. 2c) is two orders of magnitude higher 192 than J_{IMN} (Fig. 2d) although both indicate a high nucleation center in the northeastern US 193 194 surrounding the Ohio valley with other scattered high nucleation zones in southern and western US along the coast. The low J_{IMN} is due to the high temperature in the summer. The shift of high 195 196 J_{Nucl-Org} nucleation zone from southeastern in March to northeastern in July is mainly associated with the change in the spatial distributions of [LV-SOG_{α -pinene}]. 197

Comparisons of model predictions with in situ measurements are critical to evaluate our current understanding of atmospheric nucleation processes and to identify areas requiring further research. The PSDs measured at the nine forest sites, as marked in Figs. 1-2, provide a reasonably representative dataset for this purpose. As shown in Fig. 1, all the PSDs have lower cut-off sizes of 10 nm or smaller with some as small as 3-5 nm. Due to wall losses and lower 203 charging and counting efficiencies of small particles, PSDs for mobility diameters smaller than 204 ~10 nm may have large uncertainties. The nano-SMPSs generally have upper cutoff sizes of ~ 100 nm. The GEOS-Chem-APM model simulates PSDs from ~ 1.5 nm to larger than 10 µm. 205 Figure 3 gives an example of the comparison between observed and simulated PSDs during two 206 ten-day periods in March and July of 2006 in Duke Forest, along with time series of the 207 concentration of condensation nuclei (CN) between 10 and 100 nm (CN₁₀₋₁₀₀, integrated from 208 PSDs). Similar plots for one spring month and one summer month for sites 1-4 and one summer 209 month for sites 5-9 are given in Figures S1-S9 in the supplementary materials. The diurnal 210 profile of CN₁₀₋₁₀₀ is a good indication of new particle formation and growth. Statistical analyses 211 of observed and simulated CN_{10-100} for all sites are presented later in this section. 212

To assess the ability of different nucleation schemes to capture NPF events (or non-events) at 213 various sites, we use the criteria described in Section 2.3 to decide from the evolution of PSDs 214 whether a given day is an event day or not. To illustrate this decision process, we mark the event 215 $(\mathbf{\Sigma})$ and non-event $(\mathbf{\Sigma})$ days determined based on this criterion for the observed and simulated 216 217 PSDs in Figure 3. For the ten-day period in March, this criterion gives 8, 9, and 9 event days for the observed NPF in Duke forest (Fig. 3a), simulated with Nucl-Org (Fig. 3c) and simulated with 218 Nucl-IMN (Fig. 3e), respectively. For the 10-day period in July, the corresponding numbers of 219 event days are 0, 10, and 0. The requirement for the dN/dlogD_p at $D_p = \sim 10$ nm of 3000 cm⁻³ or 220 higher is to filter out weak NPFs such as the one on Day 80 of observed and simulated PSD (Figs. 221 222 3a, 3c, 3e) and Day 84 of observed PSD (Fig. 3d). The two-hour duration requirement is intended to filter out the short and sharp spikes likely as a result of local plumes rather than 223 regional nucleation, such as the one appearing on Days 201 and 202 of the observation. Our 224 225 visual inspection indicates that this criterion captures most of major observed and simulated

NPFs. While this criterion is not perfect, it enables us to evaluate objectively the ability of different nucleation schemes to capture NPF events (or non-events) at various sites during long observation periods. A slight change in this criterion (for example, increasing dN/dlogD_p at $D_p=10 \text{ nm from } 3000 \text{ cm}^{-3}$ to 5000 cm⁻³, or the duration from two hours to three hours) does not impact the main conclusions of this study.

It is clear from Figures 3a-3b that NPF events observed in Duke Forest are much more 231 frequent and concentrations of nucleation mode particles are much higher in the spring than in 232 the summer. More frequent and stronger observed NPF events in the spring have been reported 233 234 in many previous field measurement studies (e.g., Dal Maso et al., 2005; Pryor et al., 2010; Kanawade et al., 2011; Pillai et al., 2013; Pierce et al., 2014). Both schemes predict frequent 235 NPF events in March (Figs. 3c, 3e), which is consistent with observations, although the Nucl-236 Org scheme generally gives stronger NPF events and higher CN₁₀₋₁₀₀ (Fig. 3g). Model 237 simulations based on Nucl-Org scheme (Eq. 1) suggest that frequent (almost daily, Fig. 3d) and 238 239 stronger NPF (Fig. 3h) should occur in the summer in Duke Forest, which was not observed with 240 measurements (Fig. 3b). The relatively less frequent or lack of events in the summer indicates that, at least, LV-SOG_{α -pinene} cannot be the dominant nucleation factor as [LV-SOG_{α -pinene}] should 241 242 be highest during the summer. However, the Nucl-IMN scheme is consistent with the observed lack of nucleation in the summer in Duke Forest. Note that there is no explicit temperature 243 dependence in Eq. 1, an issue that is discussed later. 244

Figure 4 presents a statistical analysis and comparison of simulated NPF event days and CN₁₀₋₁₀₀ based on two nucleation schemes with observations at four forest sites for the spring month and for all nine sites for the summer month. Table 2 gives the averaged values. For the statistical analysis, we look into the fraction (or frequency) of nucleation event days (F_{nucl}) (Fig. 249 4a - spring; Fig. 4b - summer), the proportion correct (PC) (Figs. 4c-d), Pearson correlation 250 coefficient (r) of the observed and simulated scatterplots of CN_{10-100} (Figs. 4c-d), and monthly mean $CN_{10,100}$ (Figs. 4e-f). For the four sites with PSD data in the spring, NPF events occurred 251 on 81%, 65%, 87%, and 43% of days for sites DUK, MMSF, SPL, and EGB, respectively (Fig. 252 4a), with an average value of 69%. Both nucleation schemes capture most of the NPF events in 253 254 the spring month (four-site average of 76% for both Nucl-Org and Nucl-IMN). In July, there are no obvious NPF events for sites 1, 5-9 (DUK, WFM, PSP, UMBS, TNF, OZA) and infrequent 255 events (~20%) for sites 2-4 (MMSF, SPL, EGB). Nucl-Org significantly overpredicts the 256 257 nucleation frequency (by up to ~50-97%) for sites 1-2 (DUK, MMSF) and 4-6 (EGB, WFM, PSP) while Nucl-IMN slightly underpredicts F_{nucl} (by ~10%) for sites 2-3 (MMSF, SPL). On average, 258 Nucl-Org overpredicts F_{nucl} by 50% while F_{nucl} based on Nucl-IMN (7%) is close to the observed 259 260 value (8%) for the nine sites in the summer month.

 F_{nucl} alone is not adequate to assess the performance of the model. For example, for Site 2 261 (MMSF) in March, F_{nucl} based on Nucl-IMN is closer to the observed values than F_{nucl} based on 262 Nucl-Org but r and PC are actually lower (Fig. 4c). Our analysis indicates that a large fraction of 263 NPF event days predicted by Nucl-IMN for MMSF in March does not match the NPF events 264 265 observed on specific days. In terms of r and PC, the values based on Nucl-Org and Nucl-IMN are close for the spring month (Fig. 4c and Table 2), but Nucl-IMN overall gives higher r and PC 266 values for July (Fig. 4d and Table 2). The correlation was calculated for a whole month of hourly 267 268 CN_{10-100} data (~ 700 data points). Due to clear diurnal variations associated with NPF in the spring (Fig. 3a) and the fact that both schemes capture ~70% of event and non-event days, the 269 average r value reaches 0.37 for Nucl-Org and 0.49 for Nucl-IMN. As a result of the lack of 270 271 obvious diurnal variations and inability of the global model to capture the sub-grid CN plumes

(such as the short-duration CN spikes in Fig. 3h), the r value is much lower for July (nine-site average of 0.16 for Nucl-Org and 0.22 for Nucl-IMN) although PC reaches 0.88 for Nucl-IMN. The lower average PC value for Nucl-Org (0.43) is due to the over-prediction of NPF events (i.e., F_{nucl}).

276 Particle number concentrations and CN_{10-100} in NA (on a regional scale) are largely dominated by secondary particles formed via nucleation (Yu and Luo, 2009). Our analysis 277 demonstrates that nucleation schemes have a strong impact on the simulated particle number 278 concentrations. Compared to observations, CN₁₀₋₁₀₀ averaged at the four sites is 40% higher 279 280 based on Nucl-Org and 14% higher based on Nucl-IMN for the spring month (Table 2). For the summer month, CN₁₀₋₁₀₀ averaged at the nine sites is 161% higher based on Nucl-Org and 27% 281 lower based on Nucl-IMN (Table 2). For specific sites (Figs. 4e-f), CN₁₀₋₁₀₀ based on Nucl-Org 282 are generally higher than observed values in the spring for all four sites (especially site 1 - DUK) 283 and are much higher than those in the summer month for sites 1-2 (DUK, MMSF) and 3-5 (SPL, 284 EGB, WFM). Nucl-IMN substantially overpredicted CN₁₀₋₁₀₀ for site 4 (EGB) in the spring and 285 underpredicted CN₁₀₋₁₀₀ for sites 8-9 (TNF, OZA) in the summer month. Possible sources of the 286 difference include sub-grid inhomogeneity as well uncertainties in emissions, chemistry, aerosol 287 288 microphysics, and meteorology. It is noteworthy that the global model, with a horizontal resolution of $2^{\circ} \times 2.5^{\circ}$, is aimed to capture regional events. If the measurements at a given site 289 during certain periods were affected by sub-grid scale topography and processes (emissions, 290 291 plumes, etc.), the global model would not be able to capture these effects. Comparisons of highresolution simulations with observations are needed to address the issue. 292

293

294 4. Implications and Discussion

295 We showed in the last section that Nucl-Org and Nucl-IMN schemes predict quite different spatial distributions and significant differences between the spring and summer seasons with 296 respect to NPF events. Table 2 shows that Nucl-IMN predictions agree better with observations 297 in all categories, especially during July. One logical question to ask is: what is the implication of 298 such differences? Figure 5 gives the ratios of the CCN concentration in the lower troposphere (0-299 300 3 km) based on Nucl-Org to the CCN concentration based on Nucl-IMN as well as the difference of aerosol first indirect radiative forcing (FIRF) (FIRF_{Nucl-Org} - FIRF_{Nucl-IMN}). The CCN 301 concentrations are calculated at a water supersaturation ratio of 0.4% (CCN0.4) from simulated 302 303 PSDs and the calculation of aerosol FIRF in GEOS-Chem is based on the approach discussed in Yu et al. (2013). As a result of higher nucleation rates, CCN0.4 based on Nucl-Org are 304 approximately a factor of two higher than CCN0.4 based on Nucl-IMN in July over most parts of 305 NA (Fig. 5a). Higher CCN leads to higher cloud droplet number concentrations and enhanced 306 cloud albedo, resulting in an additional negative FIRF (cooling) of 1 - 2.5 W/m² in a large 307 fraction of NA with a domain average of -1.27 W/m². Since CCN can also impact precipitation 308 309 (second indirect impact) and cloud cover, it is important to reduce uncertainty in the new particle formation calculation in regional and global climate models. 310

The significant overprediction of NPF events and particle number concentrations in the summer by the Nucl-Org scheme cannot be explained by the uncertainty in the pre-factor (k_m) in the Nucl-Org parameterization (Equ. 1). It indicates that the organics-enhanced nucleation parameterization derived from laboratory chamber studies may not be directly applicable to the atmospheric conditions, at least in the summer months when VOC emissions, photochemistry, and SOA formation are strongest. One possible explanation for this result is that the concentration of organic compounds and their oxidation products exist at much lower 318 concentrations in the atmosphere than those used in chamber studies. While both LV-SOG_{α -pinene} 319 in the model and BioOxOrg in the chamber studies are later-generation oxidation products of biogenic monoterpenes, it is possible that LV-SOG_{α -pinene} predicted in the model is not 320 representative of BioOxOrg vapors that are involved in nucleation in the chamber studies. The 321 322 uncertainty in the predicted concentrations of organic compounds actively participating in 323 nucleation will not only impact the calculated nucleation rates but also the growth rate of these particles. Nevertheless, this will not be able to explain the observed spring-summer contrast in 324 NPF since the concentrations of these specific compounds (i.e., BioOXOrg) are much higher in 325 326 the summer, but observations show more frequent and stronger NPF events in the spring (Table 2 and Figure 4). 327

Another possible reason for the overprediction of the Nucl-Org scheme is the influence of 328 temperature. According to the Nucl-IMN scheme, the main reason for the lack of nucleation in 329 July in relatively clean environments is the high temperature that reduces the supersaturation 330 ratio of sulfuric acid and NPF. It should be noted that the Nucl-Org parameterization (Eq. 1) was 331 332 derived from laboratory chamber studies at T=278 K and RH=39% (Riccobono et al., 2014). Based on nucleation theory, temperature should influence the nucleation rate significantly unless 333 334 the nucleation is barrierless. Higher summer temperatures may inhibit H₂SO₄-Organic nucleation and thus explain the lack of NPF in forest areas. If this is the case, the thermodynamic data for 335 the H₂SO₄-Organics system is needed to derive a T-dependent nucleation scheme which is 336 337 presently not available. Furthermore, water vapor and base molecules such as ammonia and amines may also affect nucleation barriers and thus nucleation rates. On the other hand, ammonia, 338 339 amines, and certain organics concentrations are typically much higher in the summer and can

also enhance IMN when the nucleation barrier is higher. This may explain the July under-prediction of CN by binary IMN.

Further research is needed to understand the different mechanisms of NPF in the atmosphere 342 in different environments and represent them properly in the models. Continuous field 343 measurements of PSDs down to nanometer sizes (with improved accuracy in smaller sizes) in 344 various environments along with concentrations of key precursor gasses are important. 345 Thermodynamic data with regard to the interactions and stability of multiple-component pre-346 nucleation clusters is essential to develop more robust nucleation schemes that can take into 347 348 account major influencing factors. Finally, developed nucleation schemes should be validated against field measurements taken under a wide range of varying conditions (such as season, 349 temperature, vegetation types, complexity of terrain). 350

351

Acknowledgments. This study was supported by NASA under grants NNX13AK20G and 352 NNX11AQ72G. SCP acknowledges financial support from NSF (#1517365). JS acknowledges 353 354 funding from the US Department of Energy, contract DE-SC0011664. The National Center for Atmospheric Research is supported by the US National Science Foundation. The Steamboat Ski 355 356 Resort provided logistical support and in-kind donations to Storm Peak Laboratory. The Desert Research Institute, which owns and operates Storm Peak Laboratory, is a permittee of the 357 Medicine-Bow Routt National Forests and is an equal opportunity service provider and employer. 358 359 Ian McCubbin provided technical assistance with the maintenance and data quality control for the aerosol instruments at SPL, and we are grateful. The GEOS-Chem model is managed by the 360 Atmospheric Chemistry Modeling Group at Harvard University with support from NASA's 361 362 Atmospheric Chemistry Modeling and Analysis Program.

364 **References**

365	Almeida, J., Schobesberger, S., Kurten, A., Ortega, I. K., Kupiainen-Maatta, O., Praplan, A.P.,
366	Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue,
367	N.M., Downard, A., Dunne, E., Duplissy, J., Ehrhart, S., Flagan, R.C., Franchin, A., Guida,
368	R., Hakala, J., Hansel, A., Neinritzi, M., Henschel, H., Jokinen, T., Kajos, M., Kangasluoma,
369	J., Keskinen, H., Kupc, A., Kurtén, T., Kvashin, A.N., Laaksonen, A/., Lehtipalo, K.,
370	Leiminger, M., Leppä, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M.J.,
371	Nieminen, T., Olenius, T., Onnela, A., Petäjä, T., Riccobono, F., Riipinen, I., Rissanen, M.,
372	Rondo, L., Ruuskanen, T., Santos, F.D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld,
373	J.H., Simon, M., Sipilä, M., Stozhkov, Y., Stratmann, F., Tomé, A., Tröstl, J.,
374	Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P.E.,
375	Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K.S.,
376	Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D.R., Vehkamäki, H., and Kirby, J.,
377	Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere,
378	Nature, 502, 359-363, 2013.

- Bae, M.-S., Schwab, J. J., Hogrefe, O., Frank, B. P., Lala, G. G., and Demerjian, K. L.:
 Characteristics of size distributions at urban and rural locations in New York, Atmospheric
 Chemistry and Physics, 10, 4521-4535, doi:10.5194/acp-10-4521-2010, 2010.
- Berndt, T., Sipilä, M., Stratmann, F., Petäjä, T., Vanhanen, J., Mikkilä, J., Patokoski, J.,
- Taipale, R., Mauldin III, R.L. and Kulmala, M., Enhancement of atmospheric H₂SO₄/H₂O
- nucleation: Organic oxidation products versus amines, Atmospheric Chemistry and Physics,
- 385 14, 751–764, doi:10.5194/acp-14-751-2014, 2014.

- Bey, I., Jacob, D. J. Yantosca, R. M., Logan, J. A. Field, B. Fiore, A. M. Li, Q., Liu, H.,
 Mickley, L. J. and Schultz, M., Global modeling of tropospheric chemistry with assimilated
 meteorology: Model description and evaluation, Journal of Geophysical Research, 106,
 23,073–23,096, 2001.
- Carslaw, K. S., Lee, L. A., Reddington, C. L., Pringle, K. J., Rap, A. Forster, P. M., Mann, G.
 W., Spracklen, D. V., Woodhouse, M. T., Regayre, L. A. and Pierce, J. R., Large
 contribution of natural aerosols to uncertainty in indirect forcing, Nature, 503, 67-71,
 doi:10.1038/nature1267, 2013.
- Chen, M., Titcombe, M., Jiang, J., Kuang, Fischer, M. L., Edgerton, E., Eisele, F. L., Siepmann,
- J. I., Hanson, D. H., Zhao, J. and McMurry, P. H., Acid-base chemical reaction model for
 nucleation rates in the polluted boundary layer. Proceedings of the National Academy of
 Sciences, 109, 18713–18718, 2012.
- Chung, S. H. and Seinfeld, J. H., Global distribution and climate forcing of carbonaceous
 aerosols, Journal of Geophysical Research, 107, 4407, doi:10.1029/2001JD001397, 2002.
- 400 Dal Maso, M., Kulmala, M., Dal Maso, M., Riipinen, I., Wagner, R., Hussein, T., Aalto, P., and
- 401 Lehtinen, K. E. J.: Formation and growth of fresh atmospheric aerosols: eight years of
- 402 aerosol size distribution data from SMEAR II, Hyytiala, Finland, Boreal and Environmental
 403 Research, 10, 323–336, 2005.
- Dawson, M. L., Varner, M. E., Perraud, V., Ezell, M. J., Gerber, R. B., and Finlayson-Pitts, B. J.:
- 405 Simplified mechanism for new particle formation from methanesulfonic acid, amines, and
- 406 water via experiments and ab initio calculations, Proceedings of the National Academy of
- 407 Sciences, 109, 18719–18724, 2012.

408	Ehn, M., Thornton, J., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F.,
409	Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, IH., Rissanen, M., Jokinen,
410	T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurtén, T., Nielsen,
411	L., Jørgensen, S., Kjaergaard, H., Canagaratna, M., Maso, M., Berndt, T., Petäjä, T., Wahner,
412	A., Kerminen, VM., Kulmala, M., Worsnop, D., Wildt, J., and Mentel, T., A large source of
413	low-volatility secondary organic aerosol, Nature, 506, 476-479, doi: 10.1038/nature13032,
414	2014.
415	Erupe, ME , Viggiano, AA, and Lee, S-H, The effect of trimethylamine on atmospheric
416	nucleation in-volving H ₂ SO ₄ Atmospheric Chemistry and Physics, 11, 4767-4775, 2011.
417	Evans M. J., and Jacob D.J., Impact of new laboratory studies of N ₂ O ₅ hydrolysis on global
418	model budgets of tropospheric nitrogen oxides, ozone, and OH, Geophysical Research
419	Letters, 32, L09813, 2005.
420	Glasoe, W. A., Volz, K., Panta, B., Freshour, N., Bachman, R., Hanson, D. R., McMurry, P.
421	H., and Jen, C., Sulfuric acid nucleation: An experimental study of the effect of seven bases,
422	Journal of Geophysical Research: Atmosphere, 120, doi:10.1002/2014JD022730, 2015.
423	Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P.I., and Geron, C., Estimates of
424	global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and
425	Aerosols from Nature), Atmospheric Chemistry and Physics, 6, 3181-3210, 2006.
426	Hallar, A.G., Lowenthal, D. H., Chirokova, G., Wiedinmyer, C., and Borys, R.D., Persistent
427	daily new particle formation at a mountain-top location, Atmospheric Environment,
428	doi:10.1016/j.atmosenv.2011.04.044, 2011.

429	Henze, D.K., Seinfeld, J.H., Ng, N.L., Kroll, J.H., Fu, T-M., Jacob, D.J., Heald CL, Global
430	modeling of secondary organic aerosol formation from aromatic hydrocarbons: high- vs. low-
431	yield pathways, Atmospheric Chemistry and Physics, 8, 2405-2420, 2008.

- 432 IPCC (Intergovernmental Panel on Climate Change), The Physical Science Basis, Working
- 433 Group I Contribution to the IPCC 5th Assessment Report Changes to the Underlying
- 434 Scientific/Technical Assessment, Cambridge Univ. Press, New York, 2013.
- 435 Kanawade, V. P., Jobson, B. T., Guenther, A. B., Erupe, M. E., Pressely, S. N., Tripathi, S. N.,
- 436 Lee, S-H., Isoprene suppression of new particle formation in a mixed deciduous forest.
 437 Atmospheric Chemistry and Physics, 11:6013–6027, 2011.
- 438 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, Atmospheric Chemistry and

441 Physics, 10, 10733-10752, doi:10.5194/acp-10-10733-2010, 2010.

- Knibbs, L. D., Cole-Hunter, T., and Morawska, L., A review of commuter exposure to ultrafine
 particles and its health effects, Atmospheric Environment, 45, 2611-2622, 2011.
- Kulmala, M., Vehkamaki, 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, Journal of Aerosol Science, 35, 143–176, 2004.
- Lee, S.H., et al., New insights on isoprene suppression of biogenic new particle formation, to besubmitted, 2015.
- Lehtinen, K.E.J., and Kulmala, M., A model for particle formation and growth in the atmosphere
 with molecular resolution in size. Atmosmospheric Chemistry and Physics, 2, 1791-1807,
 2002.

- Liao, H., Henze, D.K., Seinfeld, J.H., Wu, S., and Mickley, L.J., Biogenic secondary organic
 aerosol over the United States: Comparison of climatological simulations with observations,
 Journal of Geophysical Research, 112, D06201, 2007.
- 455 Martin, R.V., Jacob, D.J., Yantosca, R.M., Chin, M., Ginoux, P., Global and regional decreases
- 456 in tropospheric oxidants from photochemical effects of aerosols, Journal of Geophysical
 457 Research, 108, DOI: 10.1029/2002JD002622, 2003.
- Park, R.J., Jacob, D.J., Field, B.D., Yantosca, R.M., and Chin, M., Natural and transboundary
 pollution influences on sulfate-nitrate-ammonium aerosols in the United States: Implications
 for policy, Journal of Geophysical Research, 109, D15204, 2004.
- 461 Pierce, J. R., Westervelt, D. M., Atwood, S. A., Barnes, E. A., and Leaitch, W. R.: New-particle
 462 formation, growth and climate-relevant particle production in Egbert, Canada: analysis from
 463 1 year of size-distribution observations, Atmospheric Chemistry and Physics, 14, 8647-8663,
 464 doi:10.5194/acp-14-8647-2014, 2014.
- Pierce, J.R., and Adams, P.J., Uncertainty in global CCN concentrations from uncertain aerosol
 nucleation and primary emission rates, Atmospheric Chemistry and Physics, 9, 1339-1356,
 2009.
- 468 Pillai, P., Khlystov, A., Walker, J. and Aneja, V. Observation and analysis of particle nucleation
 469 at a forest site in southeastern US. Atmosphere. 4(2):72-93, 2013.
- 470 Pryor S.C., Spaulding, A.M., and Barthelmie, R. J., New particle formation in the Midwestern
- USA: Event characteristics, meteorological context and vertical profiles, Atmospheric
 Environment, 44, 4413-4425, 2010.

473	Pryor, S. C., Hornsby, K. E., and Novick, K. A., Forest canopy interactions with nucleation
474	mode particles, Atmospheric Chemistry and Physics, 14, 11985-11996, doi:10.5194/acp-14-
475	11985-2014, 2014.
476	Riccobono, FSchoberberger, S., Scott, C.E., Dommen, J., Ortega, I.K., Rondo, L., Almeida, J.,
477	Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Downard, A., Dunne, E.M.,

- 478 Duplissy, J., Ehrhardt, S., Flagan, R.C., Franchin, A., Hansel, A., Juuninen, H., Kajos, M.,
- 479 Keskinen, H., Kupc, A., Kürten, A., Kvashin, A.N., Laaksonen, A., Lehtipalo, K.,
- 480 Makkmutov, V., Mathot, S., Nieminen, T., Onnela, A., Petäjä, T., Praplan, A.P., Santos, F.D.,
- 481 Schallhart, S., Seinfeld, J.H., Sipilä, M., Spracklen, D.V., Stozhkov, Y., Stratmann, F., Tomé,
- 482 A., Tsagkogeorgas, G., Vaattlovaara, P., Viisanen, Y., Vrtala, A., Wagner, P.E., Weingartner,
- 483 E., Wex, H., Wimmer, D., Carslaw, K.S., Curtius, J., Donahue, N.M., Kirkby, J., Kulmala, M.
- Worsnop, D.R., and Baltensperger, U., Oxidation products of biogenic emissions contribute
 to nucleation of atmospheric particles, Science, 344, 717, 2014.
- 486 Slowik, J. G., Stroud, C., Bottenheim, J. W., Brickell, P. C., Chang, R. Y.-W., Liggio, J., Makar,
- P. A., Martin, R. V., Moran, M. D., Shantz, N. C., Sjøstedt, S. J., van Donkelaar, A.,
 Vlasenko, A., Wiebe, H. A., Xia, A. G., Zhang, J., Leaitch, W. R., and Abbatt, J. P. D.:

490 forests, Atmospheric Chemistry and Physics, 10, 2825-2845, doi:10.5194/acp-10-2825-2010,
491 2010.

Characterization of a large biogenic secondary organic aerosol event from eastern Canadian

- 492 Spracklen, D. V., Carslaw, K. S., Kulmala, M., Kerminen, V.-M., Sihto, Riipinen, I., Merikanto,
- 493 J., Mann, G.W., Chipperfield, M.P., Wiedensohler, A., Birmili, W., and Lihavainen, H.,
- 494 Contribution of particle formation to global cloud condensation nuclei concentrations,
 495 Geophysical Research Letters, 35, L06808, doi:10.1029/2007GL033038, 2008.

496	Venzac, H., Sellegri, K., Laj, P., Villani, P., Bonasoni, P., Marinoni, A., Cristofanelli, P.,
497	Calzolari, F., Fuzzi, S., Decesari, S., Facchini, MC., Vuillermoz, E., Verza, G.P., High
498	frequency new particle formation in the Himalayas, Proceedings of the National Academy of
499	Sciences U. S. A., 105 (41), 15666-15671, 2008.
500	Wang, M. and Penner, J. E., Aerosol indirect forcing in a global model with particle nucleation,
501	Atmospheric Chemistry and Physics, 9, 239–260, 2009.

- Yu, F., A secondary organic aerosol formation model considering successive oxidation aging and 502 kinetic condensation of organic compounds: global scale implications, Atmospheric 503 504 Chemistry and Physics, 11, 1083-1099, doi:10.5194/acp-11-1083-2011, 2011.
- Yu, F., and G. Luo: Simulation of particle size distribution with a global aerosol model: 505 contribution of nucleation to aerosol and CCN number concentrations. Atmospheric 506 Chemistry and Physics, 9, 7691-7710, 2009. 507
- Yu, F., Ion-mediated nucleation in the atmosphere: Key controlling parameters, implications, and 508 look-up table, Journal of Geophysical Research, 115, D03206, doi:10.1029/2009JD012630, 509 510 2010.
- Yu, F., Luo, G., Liu, X., Easter, R. C., Ma, X., and Ghan, S. J., Indirect radiative forcing by ion-511 512 mediated nucleation of aerosol, Atmospheric Chemistry and Physics, 12, 11451-11463, 2012.
- Yu, F., X. Ma, and G. Luo, Anthropogenic contribution to cloud condensation nuclei and the first 513
- aerosol indirect climate effect, Environmental Research Letters 8 024029 doi:10.1088/1748-514
- 515 9326/8/2/024029, 2013.

Yu, F., and G. Hallar, Difference in particle formation at a mountain-top location during the 516 spring and summer: Implications for the role of sulfuric acid and organics in nucleation, 517 518 Journal of Geophysical Research, 119, DOI: 10.1002/2014JD022136, 2014.

- 519 Yu, H., J. Ortega, J. N. Smith, A. B. Guenther, V. P. Kanawade, Y. You, Y. Liu, K. Hosman, T.
- 520 Karl, R. Seco, C. Geron, S. G. Pallardy, L. Gu, J. Mikkilä, and S.H. Lee, New particle
- formation and growth in an isoprene-dominated Ozark forest: From sub-5 nm to CCN-active
- sizes, Aerosol Science and Technology, 48:12, 1285-1298, 2014.
- Zhang, R., I. Suh, J. Zhao, D. Zhang, E.C. Fortner, X. Tie, L.T. Molina, and M.J. Molina,
 Atmospheric new particle formation enhanced by organic acids, Science, 304, 1487-1490,
 2004.
- 526

Table 1. A summary of names, location, information, and references of nine forest sites where
particle size distribution (PSD) observations are available and used in the present study. PSD
measurements at different sites cover different periods of time and this study focuses on detailed

analysis of one spring month and one summer month.

Site Name Site		Site Information	PSD	Period of PSD	References
Location			Measurement	data used in	
			Periods	this study	
1. Duke Forest	(35.98°N,	Suburban forest in	Nov., 2005 to	March and	Pillai et al.,
(DUK)	79.09°W)	southeastern US	Sep, 2007.	July of 2006	2013
2. Morgan-Monroe	(39.32°N,	Rural forest in Midwestern	Dec., 2006 to	March and	Pryor et al.,
State Forest (MMSF)	86.42°W)	US	Dec., 2008	July of 2007	2010
3. Storm Peak	(40.46 °N,	West summit of Mt.	Various	March 15-	Hallar et
Laboratory (SPL)	106.74°W)	Werner in northwestern	periods from	April 15, and	al., 2011
		Colorado	2001	July of 2012	
4. Egbert (EGB)	(44.23°N,	Mixture of forests	May, 2007 to	July, 2007;	Pierce et
	79.78°W)	and farmland in Ontario,	May, 2008	March, 2008	al., 2014
		Canada			
5. Whiteface	(44.4°N,	Summit of the Adirondack	7/10/2002-	7/10/2002-	Bae et al.,
Mountain (WFM)	73.9°W)	Mountains	8/07/2002	8/07/2002	2010
6. Pinnacle State Park	(42.10°N,	Mixed deciduous and	7/13/2004 -	7/13/2004 -	Bae et al.,
(PSP)	77.21°W)	coniferous forests in	8/11/2004	8/11/2004	2010
		southwest New York State			
7. University of	(45.56°N,	Transition zone between	1 July–3	July, 2009	Kanawade
Michigan Biological	84.72°W)	the mixed hardwood and	August 2009		et al., 2011
Station (UMBS)		the boreal forest			
8. Talladega National	(32.94°N,	Isoprene-dominated rural	June 1 to 15	6/15 – 7/15,	Lee et al.,
Forest (TNF)	87.16°W)	forest in southeastern US	July, 2013	2013	2015
9. Ozarks Forest (38.74°N, "isoprene volcano"		"isoprene volcano" zone in	May to	July, 2012	Yu et al.,
(OZA)	92.2°W)	the Central US	October 2012.		2014

Table 2. Observed and simulated fraction (or frequency) of nucleation event days (F_{nucl}) and CN₁₀₋₁₀₀, for one spring month (sites 1-4 average) and one summer month (sites 1-9 average). The Pearson correlation coefficient (r) of simulated and observed time series of CN₁₀₋₁₀₀ as well as proportion correct (PC) of days.

539

	Spring (4 sites)			Summer (9 sites)				
	F _{nucl}	CN ₁₀₋₁₀₀	r	РС	F _{nucl}	CN ₁₀₋₁₀₀	r	PC
Observation	0.69	5441			0.08	2450		
Nucl-Org	0.76	7606	0.37	0.68	0.60	6385	0.16	0.43
Nucl-IMN	0.76	6198	0.49	0.63	0.07	1783	0.22	0.88

540

541

542

Figure 1. The locations of nine measurement sites in the forest areas in North America (see Table 1 for the names and references of the sites). Also shown are the particle size distributions measured in one spring month at sites 1-4 (with blue frames) and one summer month at all sites (with red frames).

Figure 2. Horizontal distributions of monthly mean nucleation rates (J) in the boundary layer (0-1 km above surface) in March (a, b) and July (c, d) of 2006 based on two different nucleation schemes, i.e, Nucl-Org (a, c) and Nucl-IMN (b, d) (see text for details). The locations of sites 1-9 (Table 1) are marked.

Figure 3. Particle size distributions (PSDs) observed (a, b) and simulated based on Nucl-Org (c, d) and Nucl-IMN (e, f) schemes during two ten-day periods in March (a, c, e) and July (b, d, f) of 2006 in Duke Forest (DUK), along with time series of the concentration of condensation nuclei between 10 and 100 nm (CN_{10-100}) (g, h). The event (\boxdot) and non-event (\bigstar) days determined based on the criterion given in Section 2.3 for the observed and simulated PSDs are marked in Figs 3a-3f.

Figure 4. Statistical analysis of simulated NPF events and CN_{10-100} based on two nucleation schemes (Nucl-Org, Nucl-IMN) and comparison with observations at four forest sites for the spring month (a, c, e) and nine sites for the summer month (b, d, f). F_{nucl} is the fraction (or frequency) of nucleation event days (a, b). The proportion correct (PC) (c, d) is defined as (# of modeled events that were events + # of modeled non-events that were non-events)/(total # of modeled events + total # of modeled non-events). Monthly mean CN_{10-100} (e, f) and correlation coefficient (r) (c, d) of hourly mean CN_{10-100} during the month are also given.

565	Figure 5. (a) Ratios of the concentration of CCN (at water supersaturation ratio of 0.4%) in the
566	lower troposphere (0-3 km) based on Nucl-Org scheme to those based on Nucl-IMN scheme, and
567	(b) Difference of aerosol first indirect radiative forcing (FIRF) (FIRF _{Nucl-Org} – FIRF _{Nucl-IMN}).
568	



- 573 Figure 1



576 Figure 2











586 Figure 5