

We would like to thank both reviewers for their constructive comments which help to improve the manuscript. Both reviewers recommend the publication after minor revisions. Our point-to-point replies (in blue) to the comments are given below (the original comments are copied here in *Italic*). The manuscript has been revised accordingly. All the changes to the manuscript have been highlighted using the Microsoft word “track-changes” tool in the revised manuscript attached at the end of this reply.

### ***Anonymous Referee #1***

*This paper analyses atmospheric new particle formation and growth in North America by comparing model simulations with measurements made at 9 locations. The topic of the paper is of scientific interest, and the analysis itself appears scientifically sound. The paper is relatively well written and structured and it is easy to follow.*

We appreciate the reviewer’s positive comments about the manuscript.

*I have only one major comment that I would like the authors to address somehow:*

*While the authors discuss the implication of their findings, and also related uncertainties, in section 4, this whole discussion remains at a rather speculative level. I would strongly recommend the authors to perform at least some sensitive runs to the key variables that are expected to influence the obtained results. Such a sensitivity study would considerably raise the value of this analysis.*

The main focus of this study is to investigate the potential role of oxidation products of biogenic VOCs in NPF in the real atmosphere, through comparisons of model simulations (with and without including organics in the nucleation rate calculation) against NPF events and non-events observed over nine forest areas in North America (NA). In section 4, the possible reasons behind the significant overprediction of NPF events and particle number concentrations in summer by the Nucl-Org scheme are discussed. The possible reasons include the lack of temperature dependence in the Nucl-org scheme and uncertainties in the concentrations of low volatile organics involved in the nucleation. We agree with the reviewer that some sensitive runs to the key variables will be useful. However, currently we do not have a physically sound or meaningful approach to take into account the temperature dependence of Nucl-Org rate and the uncertainty in BioOxOrg concentrations. A simple scaling of the pre-factor ( $k_m$ ) and [BioOxOrg] in Equ. (1) will not be very useful. As we have emphasized in the paper, the uncertainties in  $k_m$  and [BioOxOrg] are unlikely to explain the observed spring-summer contrast in NPF since the concentrations of these specific compounds (i.e., BioOXOrg) are much higher in the summer, but observations show more frequent and stronger NPF events in the spring. We do think that the temperature dependence of Nucl-Org rate could be the key but again we currently do not have a suitable parameterization to take into account this temperature dependence. This will be the subject of future research.

The only technical error I could find was the error in citation (line 26 on page 21278): the year of publication should be 2003.

Corrected. Thanks.

**Anonymous Referee #3**

*This paper compares modeled and measured nucleation events in spring and summer at nine locations in North America. Two nucleation parameterizations are used in the model: ion-mediated (IMN) and the CLOUD BioOxOrg empirical parameterization. The paper is very clearly written and the figures and tables are clearly presented. I recommend this paper should be published subject to a few revisions.*

We appreciate the reviewer's positive comments about the manuscript.

*I have some general recommendations below:*

*The authors need to clearly present what the novelty is of this study. In the current manuscript, this is not clearly stated. For example, it is well known that new particle formation occurs more frequently in the spring than the summer at these types of locations, and that models have varying degrees of success at accurately predicting this seasonality. Arguably, the large overprediction in nucleation events by the BioOxOrg simulation is the more novel result, so this should be emphasized over the comparison with IMN. The paper seems to take for granted that the IMN mechanism should be considered the "base case" simulation. Also, one of the main objectives of the paper, model-measurement comparison of nucleation events, has been performed many times, including by this research group. I have not found any evidence that this model (APM) is used very widely in the community, so the authors need to justify the scientific significance of evaluating it.*

We would like to point out that model (APM) evaluation is not one of the main objectives of the paper. As stated in the last paragraph of Introduction (also first sentence of Abstract), the primary objective of this study is to evaluate the potential role of oxidation products of biogenic VOCs in NPF in the real atmosphere. To achieve the goal, we analyze NPF events and non-events based on PSDs measured over nine forest areas in North America (NA) and compare 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 observed spring and summer contrast in NPF events to study the possible role of organics in NPF and evaluate our current understanding of NPF processes in the atmosphere. The IMN scheme is employed mainly for the comparison purpose (see Section 2.2). We show that "Both Nucl-Org and Nucl-IMN schemes capture the observed high frequency of NPF in spring, but the Nucl-Org scheme significantly over-predicts while the Nucl-IMN scheme slightly under-predicts NPF and particle number concentrations in summer". Our study also indicates that the two schemes predict quite different nucleation rates (including their spatial patterns), concentrations of cloud condensation nuclei, and aerosol first indirect radiative forcing in North America.

We agree with the referee that the large overprediction in nucleation events (in the summer) by the BioOxOrg simulation demonstrated in this study is novel. Other novel features of this study includes: (1) PSDs measured over nine NA forest areas have been compiled and used to evaluate the possible role of oxidation products of biogenic VOCs in NPF; (2) Both Nucl-Org and Nucl-IMN schemes capture the observed high frequency of NPF in spring but their predictions differ dramatically in summer; (3) The two schemes predict quite different nucleation rates (including their spatial patterns), concentrations of cloud condensation nuclei, and aerosol first indirect radiative forcing in North America, both in spring and summer. We think that these novel points have already been clearly reflected in the abstract and in the main text.

In this study the IMN scheme is employed mainly for the comparison purpose (see Section 2.2). We don't think that we say or imply anywhere in the text that the IMN mechanism should be considered the "base case" simulation. Our study shows that the Nucl-IMN scheme slightly under-predicts NPF and particle number concentrations in summer.

*The authors should also view their model with a more critical eye. They should specifically justify their SOA mechanism and nucleation mechanism. Have they evaluated their organic aerosols concentrations against AMS data in the past? If so, mention this. It is also possible that the modeled LV-SOG ( $\alpha$ -pinene) is not representative of actual ambient low volatility organic aerosol, something that is briefly mentioned by the authors but warrants further explanation.*

As pointed out in our reply to the previous comment, model evaluation is not the focus of this paper. The reasons for the choice of nucleation mechanisms have been given in Section 2.2 (also Introduction). As to the SOA mechanism, GEOS-Chem uses the two-product SOA formation model originally developed by Chung and Seinfeld (2002). In this study, the extended two-product model that considers the successive oxidation aging of secondary organic gases in the atmosphere, as described in Yu (2011), has been employed. Yes, we have evaluated organic aerosols concentrations against AMS data in Yu (2011) and this has been mentioned in the revised manuscript.

In Section 4, we point out that “while both LV-SOG <sub>$\alpha$ -pinene</sub> in the model and BioOxOrg in the chamber studies are later-generation oxidation products of biogenic monoterpenes, it is possible that only a subset of LV-SOG <sub>$\alpha$ -pinene</sub> may act as BioOxOrg vapors that are involved in nucleation”. This was offered as one of the possible reasons behind the significant overprediction of NPF events and particle number concentrations in summer by the Nucl-Org scheme. What we meant is that LV-SOG <sub>$\alpha$ -pinene</sub> in the model may be not representative of BioOxOrg vapors involved in nucleation in the chamber studies. We have clarified this in the revised manuscript.

*Specific comments:*

*1) p. 21274, line 4-5. The authors cite 80-95% total contribution of NPF to CN concentrations, and 50-80% contribution to CCN. Only a previous paper from this group, Yu and Luo 2009, is cited. A more exhaustive review of the literature on NPF contribution to CCN is warranted here.*

*Also, the definition of "contribution" is also important here, as many of these papers are actually sensitivity studies.*

The representative works ("Spracklen et al., 2008; Pierce and Adams, 2009; Yu and Luo, 2009") on the contribution of NPF to CN and CCN number abundance were cited in the first part of sentence. To address the reviewer's concern about the exact percentages and avoid the confusion with regard to the definition of "contribution", we have deleted second part of the sentence and combined the first part of the sentence with the sentence followed:

"Secondary particles formed via nucleation dominate the global total particle number abundance (Spracklen et al., 2008; Pierce and Adams, 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)."

2) p. 21274, line 10. *Sulfuric acid should be mentioned here*

Added as suggested.

3) p. 21275 line 10. *The Egbert mention should include a citation of Pierce et al. (2014) ACP.*

Done.

4) p. 21275 line 24 and p. 21276 line 3. *Overuse of the phrase "state of the art"*

To address the reviewer's concern, we have deleted "state of the art" from the sentence.

5) p. 21277 line 26. *Can the coarse resolution model grid (2x2.5) accurately represent nucleation at a specific point?*

Yes when nucleation events are regional rather than local. Nevertheless, the coarse resolution could contribute to some of the difference between model results and simulations (Fig. 4).

6) *Results section, Fig 3 and 4. Is 10 days and up to one month enough data to make the conclusion that the BioOxOrg parameterization may not be applicable? If the data for more spring and summer months are available, that analysis would make the paper stronger.*

In this study, we attempted to use data from multiple forest sites to increase the representativeness of the comparisons. The comparison of 10 days shown in Fig. 3 was an example. Our conclusions are based on comparisons of one spring month at 4 sites and one summer month at 9 sites (Fig. 4). While obviously more data would be helpful, we think that we have enough data to show that the BioOxOrg parameterization as given in Riccobono et al. (Science, 2014) may not be applicable in the summer.

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

2 **North America**

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

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44 **1. Introduction**

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

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

**Deleted:** , contributing as high as 80-95% to total particle (> 3 nm) and 50-80% to CCN number concentrations in most parts of the lower troposphere (Yu and Luo, 2009)

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

83

## 84 2. Methods

### 85 2.1. Measurements

86 PSDs from ~3-10 nm to >~ 100 nm have been widely used to identify and to study particle  
87 nucleation and growth events in the atmosphere (e.g., Kulmala et al., 2004). In this study, we  
88 focus on PSDs observed in various years in eight US and one southern Canadian forest sites  
89 summarized in Table 1. The locations of these sites are marked on a Google map  
90 (<http://maps.google.com>) in Figure 1. Egbert (EGB) is surrounded by a mixture of forests and  
91 farmland which is subject to a strong biogenic influence under certain conditions (Slowik et al.,  
92 2010; [Pierce et al., 2014](#)), while all other eight sites are directly located in forest or mountain  
93 areas. PSDs have been measured at these nine sites with Scanning Mobility Particle Sizers  
94 (SMPSs) during different time periods. Sites 1-4 have at least one year of continuous PSD data  
95 while sites 5-9 have PSD data only during the summer (for different years). PSDs for one spring  
96 and one summer month for Sites 1-4 and for one summer month for Sites 5-9 are given in Figure

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

100

## 101 2.2. Model and simulations

102 The modeling work in this study is based on the GEOS–Chem model (e.g., Bey et al., 2001)  
103 with an advanced particle microphysics (APM) model incorporated (Yu and Luo, 2009). GEOS–

104 Chem is a global 3-D model of atmospheric composition driven by assimilated meteorological

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105 observations from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling  
106 and Assimilation Office (GMAO). The model has been developed and used by many research

107 groups and contains a number of state-of-the-art modules treating various chemical and aerosol

108 processes (e.g., Bey et al., 2001; Chung and Seinfeld, 2002; Martin et al., 2003; Park et al., 2004;

109 Evans and Jacob, 2005; Liao et al., 2007; Henze et al., 2008). The APM module in GEOS–Chem

110 is optimized to simulate the formation of secondary particles and their growth to CCN sizes,

111 using high size resolution (30 bins) for particles in the dry size range of 1.2 – 120 nm diameter.

112 There are an additional 10 bins for 0.12 – 12 μm particles (Yu and Luo, 2009). More detailed

113 information about GEOS–Chem and updates can be found at the model website ([http://geos-](http://geos-chem.org/)

114 [chem.org/](http://geos-chem.org/)).

115 To study the possible role of organics in NPF, we employ the organics-mediated nucleation

116 parameterization (Nucl-Org) derived from a CLOUD chamber study as given in Riccobono et al.

117 (2014),

$$118 \quad J_{1.7} = k_m \times [\text{H}_2\text{SO}_4]^2 \times [\text{BioOxOrg}] \quad (1)$$

120 where  $J_{1.7}$  is the formation rate ( $\# \text{ cm}^{-3} \text{ s}^{-1}$ ) of particles of  $\sim 1.7 \text{ nm}$ ,  $k_m$  is the fitting pre-factor with  
121 a value of  $3.27 \times 10^{-21} \text{ cm}^6 \text{ s}^{-1}$  (90% confidence interval:  $1.73 \times 10^{-21}$  to  $6.15 \times 10^{-21} \text{ cm}^6 \text{ s}^{-1}$ ),  
122  $[\text{H}_2\text{SO}_4]$  and  $[\text{BioOxOrg}]$  are the gas-phase concentrations ( $\# \text{ cm}^{-3}$ ) of  $\text{H}_2\text{SO}_4$  and biogenic  
123 oxidized organic (BioOxOrg) vapors, respectively. In the chamber study reported in Riccobono  
124 et al. (2014), BioOxOrg molecules are organic compounds of relatively low volatility from the  
125 oxidation of pinanediol (a first-generation oxidation product of  $\alpha$ -pinene) and represent later-  
126 generation oxidation products of biogenic monoterpenes.

127 In GEOS-Chem v8-03-02 on which this study is based, reactive VOCs are grouped into six  
128 categories ( $\text{VOC}_i$ ,  $i = 1 - 6$ ), with  $\text{VOC}_1 = \alpha$ -pinene +  $\beta$ -pinene + sabinene +  $\Delta$ -3 carene +  
129 terpenoid ketones;  $\text{VOC}_2 =$  limonene;  $\text{VOC}_3 = \alpha$ -terpinene +  $\gamma$ -terpinene + terpinolene;  $\text{VOC}_4 =$   
130 myrcene + terpenoid alcohols + ocimene;  $\text{VOC}_5 =$  sesquiterpenes; and  $\text{VOC}_6 =$  isoprene. Yu  
131 (2011) extended the two-product secondary organic aerosol (SOA) formation model (Chung and  
132 Seinfeld, 2002) to predict concentrations of extremely low volatile secondary organic gas ([LV-  
133 SOG]) from successive oxidation aging of the first generation oxidation products of various  
134 VOCs, i.e., semivolatile SOG (SV-SOG) and medium-volatile SOG (MV-SOG). [The extended](#)  
135 [SOA formation scheme substantially increases the simulated SOA mass concentrations and](#)  
136 [improves the agreement of model predictions with aerosol mass spectrometer \(AMS\) SOA](#)  
137 [measurements \(Yu, 2011\).](#) LV-SOG has a saturation vapor concentration in the range of  $\sim$   
138  $0.0001 - 0.03 \mu\text{g}/\text{m}^3$ , corresponding to the extremely low volatile SOG reported in Ehn et al.  
139 (2014). The production rate of LV-SOG depends on the saturation vapor concentrations of MV-  
140 SOG and SV-SOG and temperature (Yu, 2011).

141 To use Equation (1) to calculate organics-mediated nucleation, we separate LV-SOG from  
142 the oxidation products of  $\text{VOC}_1$  (named LV-SOG $_{\alpha\text{-pinene}}$  thereafter) from those associated with

143 VOC<sub>2-6</sub>. LV-SOG <sub>$\alpha$ -pinene</sub>, a major component of total LV-SOG, corresponds well to the  
144 BioOxOrg reported in the chamber study of Riccobono et al. (2014). For comparison,  
145 simulations based on the ion-mediated nucleation of the H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O binary system (Nucl-IMN)  
146 (Yu, 2010) are also presented. Nucleation rates based on the Nucl-Org scheme depend on  
147 [H<sub>2</sub>SO<sub>4</sub>] and [LV-SOG <sub>$\alpha$ -pinene</sub>] only while those based on the Nucl-IMN scheme depend non-  
148 linearly on [H<sub>2</sub>SO<sub>4</sub>], temperature (T), relative humidity (RH), ionization rate, and surface area of  
149 pre-existing particles (Yu, 2010). Based on the CLOUD chamber study (Almeida et al., 2013;  
150 Riccobono et al., 2014), IMN is significant or dominant when  $J_{1.7}$  is below  $\sim 1 \text{ cm}^{-3} \text{ s}^{-1}$  but  
151 neutral nucleation takes over when  $J_{1.7} > \sim 1 \text{ cm}^{-3} \text{ s}^{-1}$ . Nucl-IMN calculates formation rates of  
152 particles at wet sizes of  $\sim 1.5 \text{ nm}$ . The nucleated particles are added into the first bin (wet size  $\sim$   
153  $1.5 \text{ nm}$ ) of the secondary particles, and the processes to grow them to large sizes considered in  
154 GEOS-Chem/APM include kinetic condensation of H<sub>2</sub>SO<sub>4</sub> and total LV-SOG, equilibrium  
155 uptake of nitrate and ammonium, partitioning uptake of SV-SOG and MV-SOG, and self-  
156 coagulation (Yu, 2011).

157 The horizontal resolution of GEOS-Chem employed for this study is  $2^{\circ} \times 2.5^{\circ}$  and there are 47  
158 vertical layers (with 14 layers from surface to  $\sim 2 \text{ km}$  above the surface). The emission  
159 inventories and schemes used can be found at the GEOS-Chem website and have also been  
160 summarized in Yu and Hallar (2014). Biogenic VOC emissions from terrestrial vegetation are  
161 based on the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al.,  
162 2006) which computes emissions for plant functional types as a function of temperature, solar  
163 radiation, leaf area index (LAI), and leaf age. MEGAN does not consider the effect of water  
164 stress (drought) which may suppress biogenic emissions (Pryor et al., 2014).

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

172

### 173 2.3. NPF events and non-events

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

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## 187 3. Results

189 VOC emissions in the summer are known to be much higher than VOC emissions in the  
190 spring. The high VOC emissions coupled with strong photochemistry and oxidation lead to  
191 significantly higher production rates and concentrations of oxidized SOGs of varied volatilities  
192 (medium volatile, semivolatile, and low-volatile) in the summer. Both [LV-SOG] and [LV-  
193  $\text{SOG}_{\alpha\text{-pinene}}$ ] in the summer are much higher (by a factor of  $\sim 4\text{-}10$ ) than those in the spring while  
194 [ $\text{H}_2\text{SO}_4$ ] has a similar concentration in the spring as in the summer (not shown). Figure 2 shows  
195 horizontal distributions of monthly mean nucleation rates ( $J$ ) in the boundary layer (0-1 km  
196 above the surface) in March and July of 2006 based on two different nucleation schemes (i.e.,  
197 Nucl-Org and Nucl-IMN). Two nucleation schemes clearly predict significantly different spatial  
198 patterns and seasonal variations of nucleation rates. In March,  $J_{\text{Nucl-Org}}$  is highest in the  
199 southeastern US as a result of high [LV-SOG $_{\alpha\text{-pinene}}$ ] in the region, reaching  $5\text{-}10 \text{ cm}^{-3}\text{s}^{-1}$  (Fig. 2a),  
200 while  $J_{\text{IMN}}$  has two separate eastern and western nucleation zones with monthly mean  $J$  up to  
201  $\sim 1\text{-}2 \text{ cm}^{-3}\text{s}^{-1}$  (Fig. 2b). In July, boundary layer  $J_{\text{Nucl-Org}}$  (Fig. 2c) is two orders of magnitude higher  
202 than  $J_{\text{IMN}}$  (Fig. 2d) although both indicate a high nucleation center in the northeastern US  
203 surrounding the Ohio valley with other scattered high nucleation zones in southern and western  
204 US along the coast. The low  $J_{\text{IMN}}$  is due to the high temperature in the summer. The shift of high  
205  $J_{\text{Nucl-Org}}$  nucleation zone from southeastern in March to northeastern in July is mainly associated  
206 with the change in the spatial distributions of [LV-SOG $_{\alpha\text{-pinene}}$ ].

207 Comparisons of model predictions with in situ measurements are critical to evaluate our  
208 current understanding of atmospheric nucleation processes and to identify areas requiring further  
209 research. The PSDs measured at the nine forest sites, as marked in Figs. 1-2, provide a  
210 reasonably representative dataset for this purpose. As shown in Fig. 1, all the PSDs have lower  
211 cut-off sizes of 10 nm or smaller with some as small as 3-5 nm. Due to wall losses and lower

212 charging and counting efficiencies of small particles, PSDs for mobility diameters smaller than  
213 ~10 nm may have large uncertainties. The nano-SMPSs generally have upper cutoff sizes of ~  
214 100 nm. The GEOS-Chem-APM model simulates PSDs from ~ 1.5 nm to larger than 10  $\mu\text{m}$ .  
215 Figure 3 gives an example of the comparison between observed and simulated PSDs during two  
216 ten-day periods in March and July of 2006 in Duke Forest, along with time series of the  
217 concentration of condensation nuclei (CN) between 10 and 100 nm ( $\text{CN}_{10-100}$ , integrated from  
218 PSDs). Similar plots for one spring month and one summer month for sites 1-4 and one summer  
219 month for sites 5-9 are given in Figures S1-S9 in the supplementary materials. The diurnal  
220 profile of  $\text{CN}_{10-100}$  is a good indication of new particle formation and growth. Statistical analyses  
221 of observed and simulated  $\text{CN}_{10-100}$  for all sites are presented later in this section.

222 To assess the ability of different nucleation schemes to capture NPF events (or non-events) at  
223 various sites, we use the criteria described in Section 2.3 to decide from the evolution of PSDs  
224 whether a given day is an event day or not. To illustrate this decision process, we mark the event  
225 ( $\boxtimes$ ) and non-event ( $\boxtimes$ ) days determined based on this criterion for the observed and simulated  
226 PSDs in Figure 3. For the ten-day period in March, this criterion gives 8, 9, and 9 event days for  
227 the observed NPF in Duke forest (Fig. 3a), simulated with Nucl-Org (Fig. 3c) and simulated with  
228 Nucl-IMN (Fig. 3e), respectively. For the 10-day period in July, the corresponding numbers of  
229 event days are 0, 10, and 0. The requirement for the  $\text{dN}/\text{dlogD}_p$  at  $D_p = \sim 10 \text{ nm}$  of  $3000 \text{ cm}^{-3}$  or  
230 higher is to filter out weak NPFs such as the one on Day 80 of observed and simulated PSD (Figs.  
231 3a, 3c, 3e) and Day 84 of observed PSD (Fig. 3d). The two-hour duration requirement is  
232 intended to filter out the short and sharp spikes likely as a result of local plumes rather than  
233 regional nucleation, such as the one appearing on Days 201 and 202 of the observation. Our  
234 visual inspection indicates that this criterion captures most of major observed and simulated

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

240 It is clear from Figures 3a-3b that NPF events observed in Duke Forest are much more  
241 frequent and concentrations of nucleation mode particles are much higher in the spring than in  
242 the summer. More frequent and stronger observed NPF events in the spring have been reported  
243 in many previous field measurement studies (e.g., Dal Maso et al., 2005; Pryor et al., 2010;  
244 Kanawade et al., 2011; Pillai et al., 2013; Pierce et al., 2014). Both schemes predict frequent  
245 NPF events in March (Figs. 3c, 3e), which is consistent with observations, although the Nucl-  
246 Org scheme generally gives stronger NPF events and higher  $CN_{10-100}$  (Fig. 3g). Model  
247 simulations based on Nucl-Org scheme (Eq. 1) suggest that frequent (almost daily, Fig. 3d) and  
248 stronger NPF (Fig. 3h) should occur in the summer in Duke Forest, which was not observed with  
249 measurements (Fig. 3b). The relatively less frequent or lack of events in the summer indicates  
250 that, at least,  $LV\text{-}SOG_{\alpha\text{-pinene}}$  cannot be the dominant nucleation factor as  $[LV\text{-}SOG_{\alpha\text{-pinene}}]$  should  
251 be highest during the summer. However, the Nucl-IMN scheme is consistent with the observed  
252 lack of nucleation in the summer in Duke Forest. Note that there is no explicit temperature  
253 dependence in Eq. 1, an issue that is discussed later.

254 Figure 4 presents a statistical analysis and comparison of simulated NPF event days and  
255  $CN_{10-100}$  based on two nucleation schemes with observations at four forest sites for the spring  
256 month and for all nine sites for the summer month. Table 2 gives the averaged values. For the  
257 statistical analysis, we look into the fraction (or frequency) of nucleation event days ( $F_{\text{nucl}}$ ) (Fig.

258 4a - spring; Fig. 4b - summer), the proportion correct (PC) (Figs. 4c-d), Pearson correlation  
259 coefficient ( $r$ ) of the observed and simulated scatterplots of  $CN_{10-100}$  (Figs. 4c-d), and monthly  
260 mean  $CN_{10-100}$  (Figs. 4e-f). For the four sites with PSD data in the spring, NPF events occurred  
261 on 81%, 65%, 87%, and 43% of days for sites DUK, MMSF, SPL, and EGB, respectively (Fig.  
262 4a), with an average value of 69%. Both nucleation schemes capture most of the NPF events in  
263 the spring month (four-site average of 76% for both Nucl-Org and Nucl-IMN). In July, there are  
264 no obvious NPF events for sites 1, 5-9 (DUK, WFM, PSP, UMBS, TNF, OZA) and infrequent  
265 events (~20%) for sites 2-4 (MMSF, SPL, EGB). Nucl-Org significantly overpredicts the  
266 nucleation frequency (by up to ~50-97%) for sites 1-2 (DUK, MMSF) and 4-6 (EGB, WFM, PSP)  
267 while Nucl-IMN slightly underpredicts  $F_{\text{nucl}}$  (by ~10%) for sites 2-3 (MMSF, SPL). On average,  
268 Nucl-Org overpredicts  $F_{\text{nucl}}$  by 50% while  $F_{\text{nucl}}$  based on Nucl-IMN (7%) is close to the observed  
269 value (8%) for the nine sites in the summer month.

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

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

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

302

#### 303 **4. Implications and Discussion**

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

320 The significant overprediction of NPF events and particle number concentrations in the  
321 summer by the Nucl-Org scheme cannot be explained by the uncertainty in the pre-factor ( $k_m$ ) in  
322 the Nucl-Org parameterization (Equ. 1). It indicates that the organics-enhanced nucleation  
323 parameterization derived from laboratory chamber studies may not be directly applicable to the  
324 atmospheric conditions, at least in the summer months when VOC emissions, photochemistry,  
325 and SOA formation are strongest. One possible explanation for this result is that the  
326 concentration of organic compounds and their oxidation products exist at much lower

327 concentrations in the atmosphere than those used in chamber studies. While both LV-SOG <sub>$\alpha$ -pinene</sub>  
328 in the model and BioOxOrg in the chamber studies are later-generation oxidation products of  
329 biogenic monoterpenes, it is possible that LV-SOG <sub>$\alpha$ -pinene</sub> predicted in the model is not  
330 representative of BioOxOrg vapors that are involved in nucleation in the chamber studies. The  
331 uncertainty in the predicted concentrations of organic compounds actively participating in  
332 nucleation will not only impact the calculated nucleation rates but also the growth rate of these  
333 particles. Nevertheless, this will not be able to explain the observed spring-summer contrast in  
334 NPF since the concentrations of these specific compounds (i.e., BioOXOrg) are much higher in  
335 the summer, but observations show more frequent and stronger NPF events in the spring (Table 2  
336 and Figure 4).

337 Another possible reason for the overprediction of the Nucl-Org scheme is the influence of  
338 temperature. According to the Nucl-IMN scheme, the main reason for the lack of nucleation in  
339 July in relatively clean environments is the high temperature that reduces the supersaturation  
340 ratio of sulfuric acid and NPF. It should be noted that the Nucl-Org parameterization (Eq. 1) was  
341 derived from laboratory chamber studies at T=278 K and RH=39% (Riccobono et al., 2014).  
342 Based on nucleation theory, temperature should influence the nucleation rate significantly unless  
343 the nucleation is barrierless. Higher summer temperatures may inhibit H<sub>2</sub>SO<sub>4</sub>-Organic nucleation  
344 and thus explain the lack of NPF in forest areas. If this is the case, the thermodynamic data for  
345 the H<sub>2</sub>SO<sub>4</sub>-Organics system is needed to derive a T-dependent nucleation scheme which is  
346 presently not available. Furthermore, water vapor and base molecules such as ammonia and  
347 amines may also affect nucleation barriers and thus nucleation rates. On the other hand, ammonia,  
348 amines, and certain organics concentrations are typically much higher in the summer and can

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

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

362

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374

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

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

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546 **Table 2.** Observed and simulated fraction (or frequency) of nucleation event days ( $F_{\text{nucl}}$ ) and  
 547  $CN_{10-100}$ , for one spring month (sites 1-4 average) and one summer month (sites 1-9 average).  
 548 The Pearson correlation coefficient ( $r$ ) of simulated and observed time series of  $CN_{10-100}$  as well  
 549 as proportion correct (PC) of days.

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	Spring (4 sites)				Summer (9 sites)			
	$F_{\text{nucl}}$	$CN_{10-100}$	$r$	PC	$F_{\text{nucl}}$	$CN_{10-100}$	$r$	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

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

559 **Figure 2.** Horizontal distributions of monthly mean nucleation rates ( $J$ ) in the boundary layer (0-  
560 1 km above surface) in March (a, b) and July (c, d) of 2006 based on two different nucleation  
561 schemes, i.e, Nucl-Org (a, c) and Nucl-IMN (b, d) (see text for details). The locations of sites 1-  
562 9 (Table 1) are marked.

563 **Figure 3.** Particle size distributions (PSDs) observed (a, b) and simulated based on Nucl-Org (c,  
564 d) and Nucl-IMN (e, f) schemes during two ten-day periods in March (a, c, e) and July (b, d, f) of  
565 2006 in Duke Forest (DUK), along with time series of the concentration of condensation nuclei  
566 between 10 and 100 nm ( $CN_{10-100}$ ) (g, h). The event (☑) and non-event (☒) days determined  
567 based on the criterion given in Section 2.3 for the observed and simulated PSDs are marked in  
568 Figs 3a-3f.

569 **Figure 4.** Statistical analysis of simulated NPF events and  $CN_{10-100}$  based on two nucleation  
570 schemes (Nucl-Org, Nucl-IMN) and comparison with observations at four forest sites for the  
571 spring month (a, c, e) and nine sites for the summer month (b, d, f).  $F_{\text{nuc1}}$  is the fraction (or  
572 frequency) of nucleation event days (a, b). The proportion correct (PC) (c, d) is defined as (# of  
573 modeled events that were events + # of modeled non-events that were non-events)/(total # of  
574 modeled events + total # of modeled non-events). Monthly mean  $CN_{10-100}$  (e, f) and correlation  
575 coefficient ( $r$ ) (c, d) of hourly mean  $CN_{10-100}$  during the month are also given.

576 **Figure 5.** (a) Ratios of the concentration of CCN (at water supersaturation ratio of 0.4%) in the  
577 lower troposphere (0-3 km) based on Nucl-Org scheme to those based on Nucl-IMN scheme, and  
578 (b) Difference of aerosol first indirect radiative forcing (FIRF) ( $\text{FIRF}_{\text{Nucl-Org}} - \text{FIRF}_{\text{Nucl-IMN}}$ ).

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