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Impact of temperature dependence on the possible contribution of organics to new particle formation in the atmosphere

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Abstract. Secondary particles formed via new particle formation (NPF) dominate cloud condensation nuclei (CCN) abundance in most parts of the troposphere and are important for aerosol indirect radiative forcing (IRF). Laboratory measurements have shown that certain organic compounds can significantly enhance binary nucleation of sulfuric acid and H_2O. According to our recent study comparing particle size distributions measured in nine forest areas in North America with those predicted by a global size-resolved aerosol model, current H_2SO_4-Organics nucleation parameterizations appear to significantly over-predict NPF and particle number concentrations in summer. The lack of the temperature dependence in the current H_2SO_4-Organics nucleation parameterization has been suggested to be a possible reason for the observed over-prediction. In this work, H_2SO_4-Organics clustering thermodynamics from quantum-chemical studies has been employed to develop a scheme to incorporate temperature dependence into H_2SO_4-Organics nucleation parameterization. We show that temperature has a strong impact on H_2SO_4-Organics nucleation rates, and may reduce nucleation rate by ~ one order of magnitude per 10 K of the temperature increase. The particle number concentrations in summer over North America based on the revised scheme is a factor of more than two lower, in much better agreement with the observations. With the temperature-dependent H_2SO_4-Organics nucleation parameterization, the summer month CCN concentrations in the lower troposphere in the northern hemisphere are about 10-30% lower and the aerosol first IRF about 0.5 – 1.0 W/m^2 less negative compared to the temperature independent one. This study highlights the importance of the temperature effect and its impacts on NPF in global modeling of aerosol IRF.

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1. Introduction

Atmospheric particles, through acting as cloud condensation nuclei (CCN), modify cloud properties and precipitation and thus, indirectly, affect the hydrological cycle and climate. Aerosol indirect radiative forcing (IRF) remains a major uncertainty in assessing climate change (IPCC, 2013). Secondary particles formed via nucleation dominate particle number concentrations in many parts of troposphere (Spracklen et al., 2008; Pierce and Adams, 2009; Yu and Luo, 2009), and global simulations indicate that nucleation schemes/parameterizations have a strong effect on the aerosol IRF estimations (Wang and Penner, 2009; Kazil et al., 2010; Yu et al., 2012). Different nucleation schemes, with nucleation rates depending on different variables, predict significantly different spatial patterns and seasonal variations of nucleation rates and CCN concentrations (Yu et al., 2010, 2015). Therefore, it is important to understand mechanisms of new particle formation (NPF) and the key parameters controlling the contribution of the NPF to CCN formation under wide range of varying atmospheric conditions and to validate their representation in regional and global climate models.

A number of laboratory chamber studies indicate that certain organic species can significantly enhance NPF (e.g., Zhang et al., 2004; Riccobono et al., 2014). This finding may have important implications for the interactions of anthropogenic and biogenic emissions and the associated climate forcing. To this regard, it is necessary to assess the ability of organics-enhanced nucleation to explain nucleation phenomena observed in the atmosphere and to determine the contribution of organics to atmospheric NPF and climate implications. In several laboratory studies, empirical parameterization of formation rate as a function of the concentrations of sulfuric acid and low-volatility highly oxidized organics has been derived (Metzger et al., 2010; Riccobono et al., 2014). One of the most important limitations of these

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empirical parameterizations is that they were derived from the chamber measurements carried out under limited range of well-controlled conditions and, thus, reliably extrapolating these data to a wide range of atmospheric conditions remains a major issue. It should also be noted that empirical activation and kinetic nucleation formulas ($J = k_1[H_2SO_4]$ or $J = k_2[H_2SO_4]^2$) derived from limited field measurements (e.g., Riipinen et al., 2007; Kuang et al., 2008) also do not account for the impact of temperature variations on computed nucleation rates. Although these simple empirical temperature independent nucleation parameterizations have been widely used in global aerosol modeling and aerosol IRF studies (e.g., Spracklen et al., 2008; Wang and Penner, 2009; Kazil et al., 2010; Scott et al., 2014; Westervelt et al., 2014; Lupascu et al., 2015), possible impacts of temperature variations were not considered in these studies.

In the recent study comparing particle size distributions measured in nine forest areas in North America with those predicted by a global size-resolved (sectional) aerosol model, Yu et al. (2015) showed that H_2SO_4-Organics nucleation parameterization of Riccobono et al. (2014) significantly over-predict NPF and particle number concentrations in summer (Yu et al., 2005). The lack of temperature dependence in the H_2SO_4-Organics nucleation parameterization has been suggested as a possible reason for the observed over-prediction. The main objectives of the present study are (1) to develop a scheme to incorporate temperature dependence into H_2SO_4-Organics nucleation parameterization, (2) to assess the ability of the modified parameterization in explaining the seasonal variations of NPF in NA, and (3) to study the global implications.

2. Methods

2.1. Organics-mediated nucleation parameterization with temperature dependence (Nucl-OrgT)

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Based on the CLOUD chamber study of nucleation process involving sulfuric acid and organic compounds of relatively low volatility from the oxidation of pinanediol, Riccobono et al. (2014) derived the following organics-mediated nucleation parameterization (Nucl-Org),

$$J_{Nucl\text{-}Org} = k_m \times [H_2SO_4]^2 \times [BioOxOrg] \quad (1)$$

where $J_{Nucl\text{-}Org}$ is the formation rate (# $cm^{-3}s^{-1}$) of particles of ~ 1.7 nm, k_m is the fitting pre-factor with a value of 3.27×10^{-21} cm^6 s^{-1} (90% confidence interval: 1.73×10^{-21} to 6.15×10^{-21} cm^6 s^{-1}), $[H_2SO_4]$ and [BioOxOrg] are the gas-phase concentrations (# cm^{-3}) of H_2SO_4 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 later-generation oxidation products of biogenic monoterpenes.

The Nucl-Org parameterization given in Eq. 1, derived from laboratory chamber studies at T=278 K and RH=39% (Riccobono et al., 2014), does not consider the possible effect of temperature on nucleation rate. According to the nucleation theory, nucleation rates are temperature-dependent unless nucleation is barrierless and limited by collision rates only. However, the value of the pre-factor k_m of 3.27×10^{-21} cm^6 s^{-1} is much smaller than well below the three-body collision rate corresponding to the formation of a cluster containing two H_2SO_4 and one BioOxOrg molecules. This indicates that nucleation in the CLOUD chamber under conditions reported in Riccobono et al. (2014) was not barrierless, and, thus, nucleation rates should be temperature-dependent.

Based on the classical homogeneous nucleation theory, the rate of nucleation (J) can be generally written in the form

$$J = C_1 \exp(-\Delta G/kT) \quad (2)$$

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where ΔG is the Gibbs free energy needed to form the critical cluster and C_1 is the pre-factor. With ΔG = ΔH - T ΔS, where ΔH and ΔS are associated enthalpy and entropy change, we get

$$J = C_1 \exp(-\Delta H/kT + \Delta S/k) = C_1 \exp(\Delta S/k) \exp(-\Delta H/kT) = C_2 \exp(-\Delta H/kT) \quad (3)$$

The temperature dependence of nucleation rate is dominated by the exponential term in Eq. (3), although C_2 may also weakly depend on temperature. Assuming that C_2 is independent of temperature and using $J_{Nucl\text{-}Org}$ given in Eq. (1) as the nucleation rate at the reference temperature T_0=278 K, we obtain

$$J_{Nucl\text{-}OrgT} = J_{Nucl\text{-}Org}\, f_T \quad (4)$$

$$f_T = \exp[\frac{\Delta H}{k}(\frac{1}{T} - \frac{1}{T_0})] \quad (5)$$

where f_T is the correction factor accounting for the temperature dependence.

One challenge here is to obtain enthalpy change (ΔH) associated with the critical cluster formation because it is quite difficult to determine the chemical identities of BioOxOrg molecules involved in atmospheric nucleation (Elm et al, 2014; Riccobono et al., 2014). As a first order approximation, we use 2-Methyl-5-[(1S,2S,3R)-1,2,3,4-tetrahydroxybutyl]-3-furoic acid, a select highly oxidized organic $C_{10}H_{14}O_7$ compound, as a proxy for BioOxOrg molecules. The stability of the cluster composed of two H_2SO_4 and one $C_{10}H_{14}O_7$ molecules has been investigated using the Density Functional theory (DFT) at PW91PW91/6-311++G(3df,3pd) level. The PW91PW91 is the most common density functional used in atmospheric studies that predicts structure, vibrational spectrums, dipolar properties and thermodynamics of atmospheric molecules and molecular clusters with high degree of confidence and its predictions, which have been systematically validated against experimental and higher level ab initio Gibbs free energies, are in a very good agreement with them for a number of atmospherically relevant molecules and

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clusters (e.g. Herb et al., 2013, Elm et al., 2013, Nadykto et al., 2015; DePalma et al., 2015). Computations have been carried out using the Gaussian 09 suite of programs (Frish et al., 2009).

Figure 1 presents the equilibrium geometry of the most stable isomers of heteromolecular trimer composed of $(C_{10}H_{14}O_7)(H_2SO_4)_2$ and Table 1 reports the corresponding the thermodynamic data associated the formation of this cluster. The computational methodology, benchmarks of Gibbs free energy changes and Cartesian geometries of global minima and local minima located within 1 kcal mol^{-1} of the global minima, along with interactions of $C_{10}H_{14}O_7$ and H_2SO_4 with some base molecules, will be detailed in a separate manuscript. Here, as a first order of approximation, we use ΔH value of -38.30 kcal mol^{-1} to calculate the temperature-dependent factor f_T in Eq. (5). Figure 2 shows the calculated value of f_T as a function of T. It is clear from Fig. 2 that f_T decreases significantly as T increases, roughly one order of magnitude per 10 K. When T < 269 K, f_T becomes larger than 10. In the present study, f_T is set to have a maximum value of 10. Compared to the original $J_{Nucl\text{-}Org}$ parameterization of Riccobono et al. (2014) (Eq. 1) derived from laboratory chamber studies at T=278 K and not taking into account the temperature dependence of nucleation rates (i.e., f_T =1, dashed line in Fig. 2), the revised parameterization $J_{Nucl\text{-}OrgT} = f_T J_{Nucl\text{-}Org}$ predicts quite different nucleation rate in the atmosphere, especially in the summer season, when both T and VOC emissions are at peak values.

It should be noted that f_T shown in Fig. 2 is subject to large uncertainty because of the potential difference between the molecules involved in the nucleation and the proxy molecule shown in Figure 1. The thermodynamic data for the formation of $(H_2SO_4)_2$(BioOxOrg) clusters is quite limited. Elm et al. (2014) investigated the molecular interactions between the α-pinene oxidation product pinic acid and sulfuric acid using computational methods and reported a ΔH value of -42.5 kcal/mol for the formation of $(H_2SO_4)_2$(Pinic Acid). More negative ΔH implies

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147 stronger temperature dependence. The sensitivity of f_T values to ΔH can be readily calculated
148 from Eq. (4). For example, a fairly large uncertainty of 5 kcal mol^{-1} in ΔH leads to the
149 uncertainty in f_T of a factor of ~ 1.4 at T=288 K, while the extremely large 20 kcal mol^{-1}
150 variation in ΔH alters f_T at T=288 K by a factor of ~ 3.5. Despite possible uncertainties in f_T,
151 the temperature dependent $J_{Nucl\text{-}OrgT}$ is likely to be more realistic than $J_{Nucl\text{-}Org}$, in which the
152 temperature dependence is neglected.
153
154 2.2. GEOS-Chem model and global simulations
155 This work represents the first global modeling attempt in studying the effect of temperature
156 on organics-mediated nucleation in the atmosphere. This study is built upon the work reported in
157 Yu et al. (2015) and, thus, we use the same global model (GEOS-Chem) and configurations as
158 that described in Yu et al. (2015). GEOS-Chem is a global 3-D model of atmospheric
159 composition driven by assimilated meteorological observations from the Goddard Earth
160 Observing System (GEOS) of the NASA Global Modeling and Assimilation Office (GMAO)
161 (e.g., Bey et al., 2001). More detailed information about GEOS-Chem and updates can be found
162 at the model website (http://geos-chem.org/). The aerosol simulation is based on a size-resolved
163 (sectional) advanced particle microphysics (APM) model incorporated into GESO-Chem by Yu
164 and Luo (2009) and considers the successive oxidation aging of the oxidation products of various
165 VOCs (Yu, 2011). In GEOS-Chem v8-03-02, on which this study and previous work (Yu et al.,
166 2015) are based, the concentration of highly oxidized low volatile secondary organic gas from
167 the oxidation products of α-pinenes ($LV\text{-}SOG_{\alpha\text{-}pinene}$) is explicitly simulated and used in Eqs. (1)
168 and (4) to calculate organics-mediated nucleation rates. The horizontal resolution of GEOS-
169 Chem employed in this study is $2^o \times 2.5^o$ and there are 47 vertical model layers (with 14 layers

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from surface to ~ 2 km above the surface). Other relevant model configurations (including emission inventories and various schemes) can be found in Yu et al. (2015).

The main difference between the present study and the previous one reported by Yu et al. (2015) is that the present study employs the T-dependent Nucl-Org parameterization given in Eq. (4) instead of T-independent parameterization of Riccobono et al. (2014). In addition, study of Yu et al. (2015) focuses only on the NA region, while in this work, the discussion on organics-mediated nucleation is expanded to the whole globe.

3. Results

Figure 3 shows the effect of T-dependent correction factor on simulated global distributions of monthly mean (July, 2006) nucleation rates, particle number and CCN concentrations in the boundary layer (0-1 km above the surface). The high biogenic VOC emissions in the summer coupled with strong photochemistry lead to higher concentrations of LV-$SOG_{\alpha\text{-pinene}}$ or BioOxOrg (Yu et al., 2015) and hence, according to the parameterization of Riccobono et al. (2014) (i.e., Eq. 1), significant organics-mediated nucleation (Fig. 3a) and higher particle number concentrations (Figs. 3c and 3e). However, the high temperature in the summer substantially lower nucleation rates (Fig. 3b), and reduce the global monthly mean nucleation rate in the boundary layer from 0.17 $cm^{-3}s^{-1}$ (Fig. 3a) to 0.02 $cm^{-3}s^{-1}$, with stronger effect in the northern hemisphere (Fig. 3b). As a result, the global monthly mean CN10 and CCN0.4 in the boundary layer decrease by 40% and 30%, respectively.

As we have pointed out earlier, the previous comparisons of simulated and observed particle size distributions measured in nine forest areas in North America (NA) (Yu et al., 2005) showed that $J_{Nucl\text{-}Org}$ parameterization (Eq. 1) over-predicts particle number concentrations at these sites

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193 in summer by a factor of around two on average (Yu et al., 2005). To examine the extent, at
194 which the revised parameterization considering T-dependence (Eq. 4) can improve the agreement
195 of simulations with measurements, we present the monthly mean horizontal distributions of
196 CN10 zoomed into the NA region in Fig. 4. It can be clearly seen that the simulated monthly
197 mean CN10 values in the NA boundary layer based on $J_{Nucl\text{-}OrgT}$ (Eq. 4) are about a factor of two
198 lower than those based on $J_{Nucl\text{-}Org}$ (Eq. 1), with larger difference in the lower latitude part of the
199 domain, where T is higher. In the case , when the effect of T on Nucl-Org is taken into account,
200 the domain-wide average CN10 value decreases from 4600 to 2200 #/cm^3 and the simulated
201 particle number concentrations at the nine forest sites (with locations marked on Fig. 4, see Yu et
202 al. (2015) for details) agree much better with the observed values.

203 To illustrate the difference and improvement, we present in Fig. 5 a set of detailed
204 comparisons of simulated and observed evolution of particle size distributions during two ten-
205 day periods in March and July of 2006 in Duke Forest (Pillai et al., 2013), along with time series
206 of the concentration of condensation nuclei (CN) between 10 and 100 nm ($CN_{10\text{-}100}$, integrated
207 from PSDs), which give a good overall representation of particle nucleation and growth. The
208 observed PSDs and simulated PSDs based on $J_{Nucl\text{-}Org}$ has been discussed in Yu et al. (2015) and
209 are repeated here for comparison with $J_{Nucl\text{-}OrgT}$ scheme in order to demonstrate the impact of
210 temperature on nucleation and particle number concentrations. Although the present work
211 focuses on the summer month, when the largest difference between $J_{Nucl\text{-}Org}$ prediction and
212 observation is observed, we also show in Fig. 5 simulations for a 10-day period in March as well
213 for the comparison purpose. NPF events observed in Duke Forest are much more frequent and
214 concentrations of nucleation mode particles are much higher in the spring than in the summer
215 (Figs. 5a & 5b). The temperature correction (Eq. 4) has small effect in the spring (Figs. 5c, 5e,

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and 5g) but significantly reduces nucleation rate and particle number concentration in summer (Figs. 5d, 5e, and 5f). $J_{Nucl-Org}$ scheme (Eq. 1) predicts strong nucleation events (Fig. 5d) and significant diurnal variations in CN_{10-100} (Fig. 5h) almost every day in the summer period that obviously contradicts to observations (Fig. 5b). The high nucleation rates in the summer based on $J_{Nucl-Org}$ scheme can be easily explained by the much higher BioOxOrg concentrations as a result of high VOC emissions and stronger photochemistry. Nevertheless, the high T in the summer inhibits nucleation (Eq. 4) and the temperature correction factor substantially improves the agreement of the simulated evolution of PSDs (Figs. 5b, 5d, 5f) and CN_{10-100} (Fig. 5h) in with observations.

Figure 6 shows the ratios of the CCN concentration in the lower troposphere (0-3 km) based on Nucl-Org to the CCN concentration based on Nucl-OrgT as well as the difference of aerosol first indirect radiative forcing (FIRF) ($FIRF_{Nucl-Org}$ - $FIRF_{Nucl-OrgT}$). The CCN concentrations are calculated at a water supersaturation ratio of 0.2% (CCN0.2) from simulated 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, CCN0.2 based on Nucl-Org are about 10-20% higher than those based on Nucl-OrgT in July over most parts of northern hemisphere (Fig. 6a), with the largest difference up to 30-70% reached over part of NA, Europe, and Asia. Higher CCN leads to higher cloud droplet number concentrations and enhanced cloud albedo, resulting in an additional negative FIRF (cooling) of 0.5 – 1.0 W/m^2 in a large fraction of NH with a global average of -0.2 W/m^2.

4. Summary and discussion

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Simple empirical nucleation parameterizations, which were derived from laboratory or field measurements under limited conditions and do not consider any temperature dependence of nucleation rates, have been widely used in global aerosol modeling and aerosol indirect radiative forcing studies. Based on the classical nucleation theory, temperature should be one of key parameters controlling nucleation rates, unless nucleation is barrierless. A recent study indicates (Yu et al., 2015) that the empirical parameterization of H_2SO_4-Organics nucleation of Riccobono et al. (2014) significantly over-predicts NPF and particle number concentrations in North America in summer. The lack of temperature dependence in the parameterization has been suggested as a likely reason for the observed over-prediction. In the present study, H_2SO_4-Organics clustering thermodynamics from quantum-chemical studies has been employed to develop a scheme for incorporating the temperature dependence into H_2SO_4-Organics nucleation parameterization, which reduces global mean nucleation rate in the boundary layer in a summer month is by a factor of ~ 8 and improves the agreement of predicted particle number concentrations over North America with observations. With temperature-dependent H_2SO_4-Organics nucleation parameterization, the summer month CCN concentrations in the lower troposphere in the northern hemisphere are about 10-30% lower, and the aerosol first IRF about 0.5 – 1.0 W/m^2 less negative compared to temperature independent one. In view of the potential effects of changes in CCN concentrations on precipitation (second indirect impact) and cloud cover, it is important to reduce uncertainties in NPF calculation in regional and global climate models.

The study highlights the importance of including the temperature dependence of nucleation rates in global modeling of NPF and aerosol indirect radiative forcing. The temperature dependence factor derived under this study represents the first (to our acknowledge) attempt of

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studying the temperature effect on organics-mediated nucleation in the global atmosphere and improves the agreement between simulated particle number concentrations and observations in NA. Although it may subject to uncertainties due to the possible difference between the molecules involved in the nucleation and the proxy molecule, temperature dependent $J_{Nucl\text{-}OrgT}$, likely more realistic than $J_{Nucl\text{-}Org}$, in which the temperature dependence is neglected. Further laboratory measurements and theoretical studies are needed to better understand the effect of temperature on organics-mediated nucleation in the atmosphere.

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Table 1. Changes of enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) for the formation of $(C_{10}H_{14}O_7)$ $(H_2SO_4)_2$ cluster under the standard condition (P= 1 atm, T=298 K).

	ΔH (kcal mol^{-1})	ΔS (cal $mol^{-1}K^{-1}$)	ΔG (kcal mol^{-1})
$C_{10}H_{14}O_7 + H_2SO_4 + H_2SO_4 \leftrightarrows (C_{10}H_{14}O_7)(H_2SO_4)_2$	-38.30	-75.45	-15.81

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372 **Figure Captions**

373 **Figure 1**. Equilibrium geometry of the most stable isomers of heteromolecular trimer composed
374 of $(C_{10}H_{14}O_7)$ $(H_2SO_4)_2$ obtained at PW91PW91/6-311++G(3df,3pd) level of theory. Bonding
375 lengths are in angstroms.

376 **Figure 2**. Calculated temperature dependence correction factor for Nucl-Org parameterization
377 (f_T) as a function of T.

378 **Figure 3**. Horizontal distributions of monthly mean nucleation rates (J) (a, b), concentrations of
379 condensation nuclei larger than 10 nm (CN10) (c, d), and concentrations of cloud condensation
380 nuclei at water supsaturation ratio of 0.4% (CCN0.4) (e, f) in the boundary layer (0-1 km above
381 the surface) in July of 2006 based on two organics-mediated nucleation schemes: $J_{Nucl\text{-}Org}$ (left
382 panels) and $J_{Nucl\text{-}OrgT}$ (right panels).

383 **Figure 4.** Horizontal distributions of monthly mean CN10 in the boundary layer (0-1 km above
384 surface) in July of 2006 based on two organics-mediated nucleation schemes: (a) $J_{Nucl\text{-}Org}$ and (b)
385 $J_{Nucl\text{-}OrgT}$. The locations of 9 forest sites where observed particle size distributions measurements
386 have been used for comparisons in Yu et al. (2015) are marked.

387 **Figure 5.** Particle size distributions (PSDs) observed (a, b) and simulated based on Nucl-Org (c,
388 d) and Nucl-OrgT (e, f) schemes during two ten-day periods in March (a, c, e) and July (b, d, f)
389 of 2006 in Duke Forest (DUK), along with time series of the concentration of condensation
390 nuclei between 10 and 100 nm ($CN_{10\text{-}100}$) (g, h).

391 **Figure 6.** (a) Ratios of the concentration of CCN (at water supersaturation ratio of 0.2%) in the
392 lower troposphere (0-3 km) based on Nucl-Org scheme to those based on Nucl-OrgT scheme,
393 and (b) Difference of aerosol first indirect radiative forcing (FIRF) ($FIRF_{Nucl\text{-}Org} - FIRF_{Nucl\text{-}OrgT}$).

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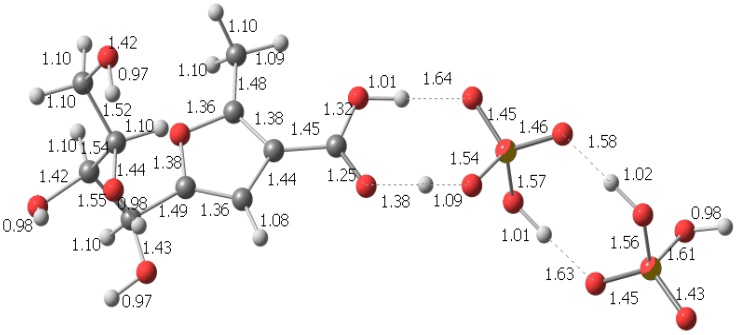

395

396 Figure 1.

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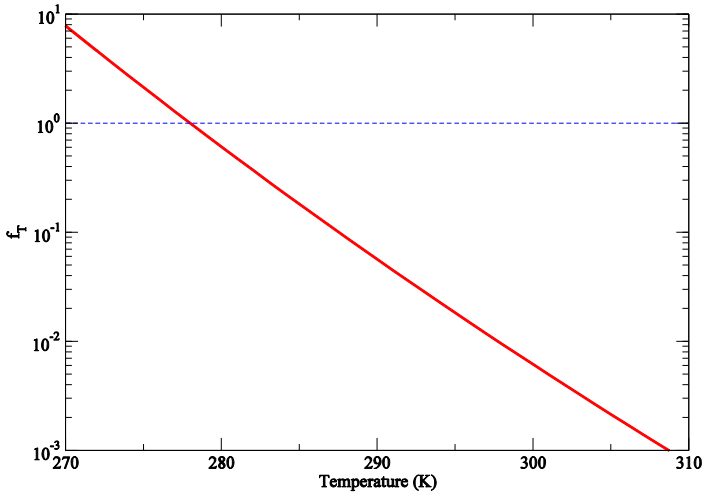

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401 Figure 2.
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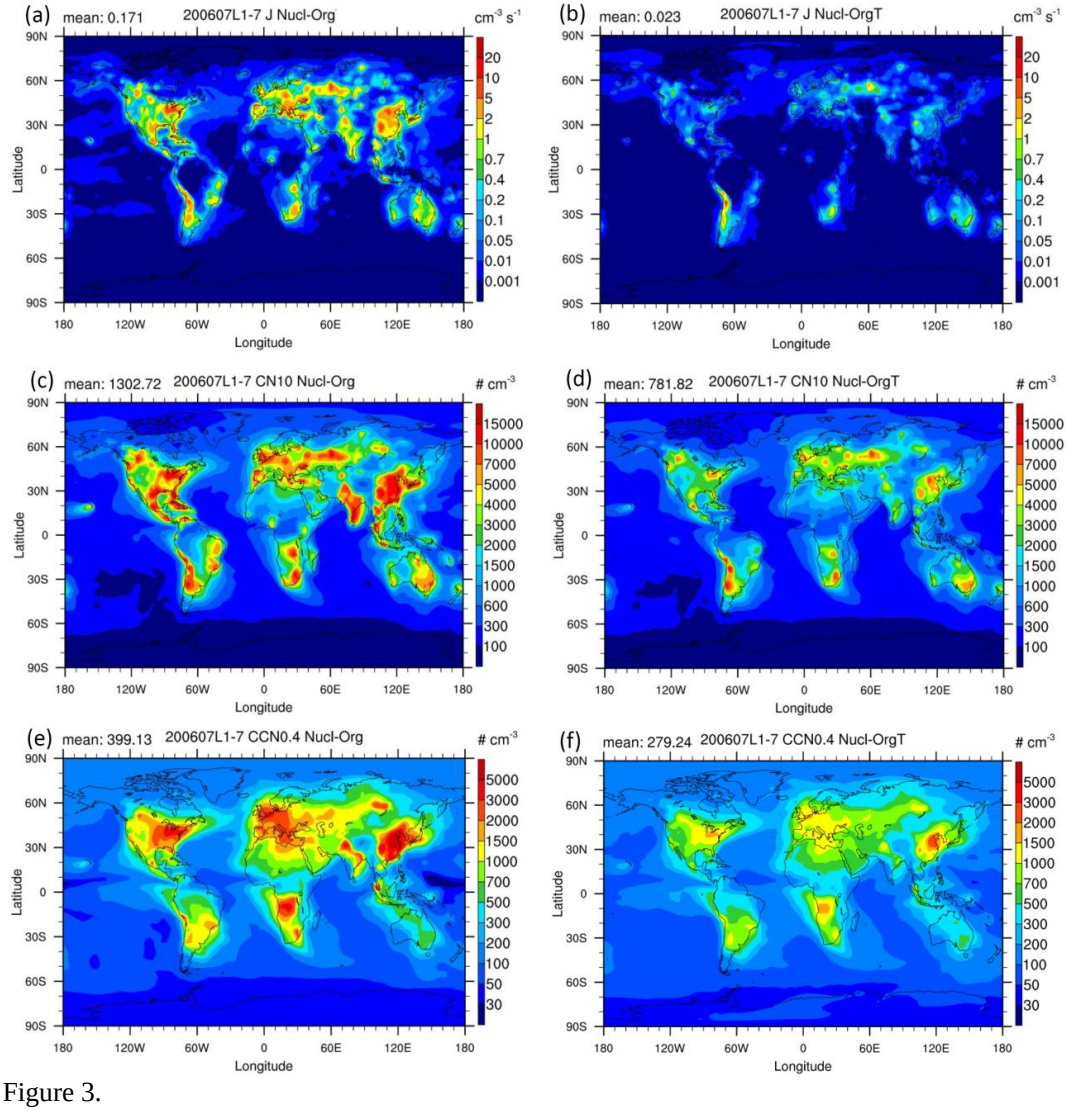

Figure 3.

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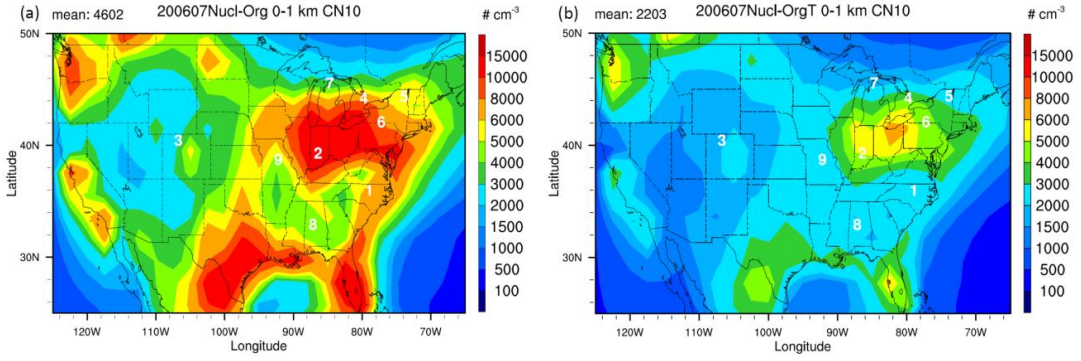

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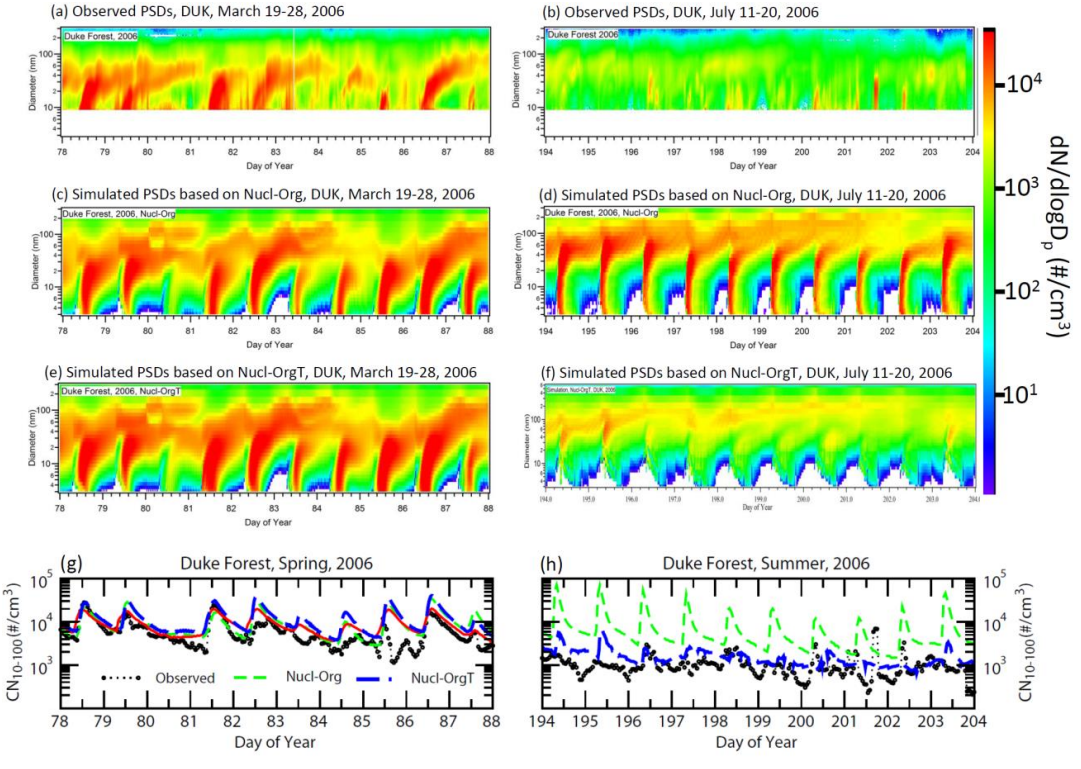

Figure 5.

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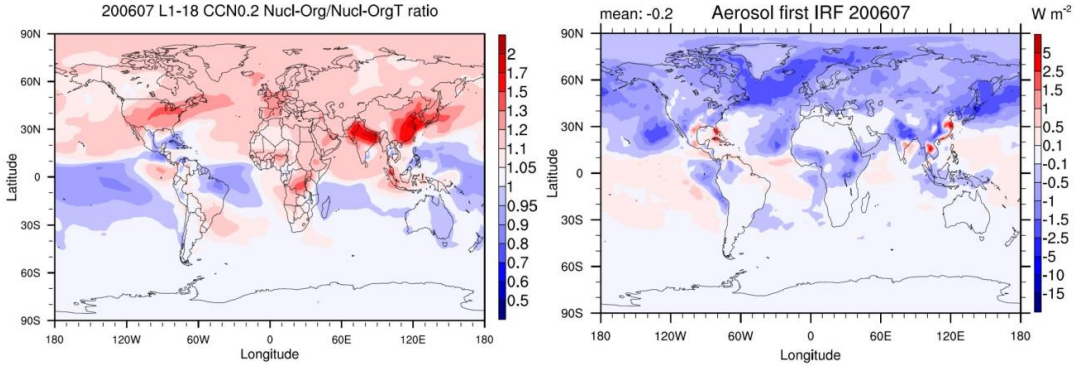

Figure 6.