We thank the reviewer for the effort to review the manuscript and to provide constructive comments which help to improve the manuscript. Our replies to the comments and our actions taken to revise the paper (in blue) are given below (the original comments are copied here in *Italic*).

Anonymous Referee #2

The authors implement a temperature-dependent organic nucleation parameterization in a global model. Simulations are compared with in situ observations. A climate forcing is calculated. The modification of the parameterisation and the in-situ observation comparison are interesting and useful, but the climate forcing calculation is questionable.

The main problem is that (looking at Yu et al. 2015), there seems to ONLY be organics mediated nucleation in this model set-up. This does not invalidate all of the findings, but one of the main outcomes of the CERN CLOUD experiment is that we know there are many different types of nucleation going on at the same time, and so models which only include one type of nucleation will seem more sensitive to changes than the real atmosphere. Figure 5 shows that the temperature dependent parameterisation does give very good agreement with observations, and I believe the temperature dependence is useful and valid in this sense. But the idea that 40% of boundary layer CCN would be lost to a temperature dependence in the organic nucleation rate only makes sense if no other nucleation is happening in the model, which is very unrealistic for the atmosphere. This also calls into question the quoted radiative forcings (radiative effects, since they do not relate to the pre-industrial?) shown in Figure 6.

Simulations which include other nucleation types should be performed to give a more accurate estimate of the climate estimates, which I am sure will be smaller than those quoted in the current version of the manuscript.

The main focus of this study is to develop a modification of organic nucleation parameterization and investigate the impact of temperature on H2SO4-Organics nucleation rates. We agree with the reviewer about the uncertainties in the radiative forcing (RF) estimates. To address the referee's concern and to follow the referee's suggestion (see below) to place the emphasis on "the realistic improvements in nucleation representation shown in Figure 5, rather than on unrealistically high model sensitivity to an overly simplistic nucleation scheme", we have deleted the RF figure (Figure 6b) and associated text in the revised manuscript.

Following the suggestion of the other reviewer, we have added two new figures (Fig. 4 and Fig. 6 in revised manuscript) and associated discussions to explore the sensitivity of results to ΔH values and to expand comparisons with observations.

Was there any physical basis for setting the maximum value of fT to 10? If the method is valid for higher temperatures, why is it not valid for lower temperatures? If the method gives unrealistic values at low temperatures, why do we trust it at high ones?

The physical basis for setting the maximum value of f_T is that the organics mediated nucleation rates should not exceed the 3-body kinetic collision rate for forming a cluster containing two

H_2SO_4 molecules and one BioOxOrg molecule (k_{max}). k_{max} depends on T as well as the mass and sizes of colliding molecules. At T=270 K, k_{max} is about a factor of 38 higher than k_m. We have revised the manuscript to set the maximum value of f_T to k_{max}/k_m instead of 10. The modification has negligible effect on the results and conclusions of this study which focuses on the summer month and the boundary layer. The method is valid for both high and low temperature.

It says in Section 2.2 that this is the "first global modeling attempt in studying the effect of temperature on organics-mediated nucleation in the atmosphere", and this assertion is repeated in the summary and discussion section. Section 20 of supplementary materials and figure S9 in Dunne et al. (2016)'s Nature paper on nucleation based on CERN CLOUD experiment contains a temperature dependence of organic nucleation. It was not the main focus of the paper but it should be mentioned.

We have modified Section 2.2 and Discussion to remove "first". The work of Dunne et al. (2016) is now mentioned in the discussion.

With revisions, the paper will make a good contribution to the field and should be published. But the emphasis should be placed on the realistic improvements in nucleation representation shown in Figure 5, rather than on unrealistically high model sensitivity to an overly simplistic nucleation scheme.

Please see our reply above.

Anonymous Referee #3

Review of Yu et al. 2016, "Impact of temperature dependence on the possible contribution of organics to new particle formation in the atmosphere" The authors explore temperature dependence effects on organic-sulfuric acid new particle formation in a chemical transport model with aerosol microphysics. This is an interesting and concise paper that addresses a significant missing piece (T-dependence) of current new particle formation research. However, I have a few major comments that need to be addressed before I can recommend this paper for publication. Once these are addressed, I believe the paper will be stronger and more impactful, and will be ready for publication.

Major comments:
1. There is a lot of uncertainty in the Nucl-OrgT parameterization. The authors do acknowledge this, discussing the uncertainty in the chemical identity of the stable cluster molecule and the subsequent uncertainty of the ΔH and fT values. The authors mention explicitly on page 8 around line 150, suggesting that a change of 5 kcal/mol would result in a 40% difference in fT at 288 K, whereas a 20 kcal/mol change results in a factor of 3.5 difference. Although the acknowledgement of this uncertainty is helpful, why not actually implement this into the simulations? Since the uncertainty in the ΔH values is that large, I would encourage them to explore the sensitivity of their results (nucleation rates, CCN formation, etc) to using different values of ΔH. It would be very interesting and useful to the community to have a range (low ΔH, high ΔH) of results for Tdependent organic-sulfuric acid nucleation.

This is a very good suggestion. We have carried out further simulations to explore the sensitivity of nucleation rates, CN10, and CCN concentrations to ΔH. A figure showing the results along with the associated discussions has been added to the revised manuscript.

2. The authors conclude that the temperature-dependent Nucl-OrgT parameterization is "likely" more realistic than Nucl-Org, which does not account for temperature. While it makes sense that adding something so fundamental to nucleation as temperature would improve a parameterization, this is not automatically the case. What I find more concerning is that I do not think the authors have appropriately justified this conclusion that Nucl-OrgT is better with the results presented in this paper. Besides the qualitative argument I mention above, the only evidence in this paper we have comes from Fig 5, where _10 nucleation events at one location (Duke Forest) in spring and summer are used to validate the model. Figure 4 and its associated text mention that the Nucl-OrgT does better against observations but there are no observations actually plotted in Fig. 4! Another paper is referenced, but to make this conclusion for this paper, the comparison needs to be explicitly presented. Thus, I suggest the authors do show this observational data and present statistics on how it compares to the Nucl-OrgT simulation, for more than only the Duke Forest site.

In the paragraph discussing Figure 4, we pointed out that "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 $J_{\text{Nucl-Org}}$ parameterization (Eq. 1) over-predicts particle number concentrations at these sites in summer by a factor of around two on average (Yu et al., 2005)" and "the simulated monthly mean CN10 values in the NA boundary layer based on $J_{\text{Nucl-OrgT}}$ (Eq. 4) are about a factor of two lower than those based on $J_{\text{Nucl-Org}}$ (Eq. 1)". We feel that Figure 4, combined with Figure 5, is adequate to make the point that T-dependence correction improves the agreement of predicted CN10 at the nine forest sites with observations in the summer. To further demonstrate this point and to address the referee's concern, we added in the revised manuscript a figure comparing the observed and simulated CN10 values averaged over the nine forest sites for different ΔH values.

3. The authors tend to take their model and its configuration somewhat uncritically. For example, the introduction paints a clear picture of new particle formation being a "strong" and "significant" contributor to the aerosol indirect effect and CCN concentrations, citing mostly their own work. The authors should perform due diligence to other work which may not agree with their single model findings (some suggested citations below). Indeed, despite changing the mean nucleation rate by nearly an order of magnitude with Nucl-OrgT, CCN0.2 are reported to be changed by only around 10-20% globally, suggesting probably a weaker sensitivity than is introduced by the authors.
Spracklen et al. 2008, JGR, 35, L06808
Westervelt, et al, 2014. Atmos. Chem. Phys., 14, 5577-5597

In the Introduction, we cited "(Spracklen et al., 2008; Pierce and Adams, 2009; Yu and Luo, 2009)" to point out the dominant contribution of secondary particles to particle number concentrations and cited "(Wang and Penner, 2009; Kazil et al., 2010; Yu et al., 2012)" to support the strong effect of nucleation schemes/parameterizations on the aerosol IRF estimations. We feel that we were not citing mostly our own work in these cases.

In the sentence followed, i.e., "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)", we emphasized "significantly different spatial patterns and seasonal variations". So this citation is not about the sensitivity of CCN to nucleation schemes.

The exact magnitude of CCN change associated with nucleation rate changes depend on seasons, locations, water supersaturation ratio at which CCN is calculated, assumption of primary particle emissions, and others. The focus of this study is on the impact of temperature dependence on the possible contribution of organics to new particle formation in the atmosphere, rather than the sensitivity of CCN to nucleation schemes. Therefore, we would like not to delve into the discussion of the exact magnitudes of CCN sensitivity to nucleation rates in the present study.

Other comments:
1. Line 35-36, Page 3: While technically true, the impact of aerosols on the surface solar radiation balance and thus atmospheric circulation is a stronger control on the hydrological cycle than the indirect effect.

Point taken but we think it is fine to say here that particles can "affect" the hydrological cycle.

2. Line 67 Page 4: "In the recent study. . ." change to "In a recent study". Also looks like there are too many spaces between "the" and "recent". There are a few other instances of superfluous "the", please proofread carefully.

Modified. Thanks.

3. Line 136, Page 7: Why is fT capped at 10? Seems arbitrary.

The physical basis for setting the maximum value of f_T is that the organics mediated nucleation rates should not exceed the 3-body kinetic collision rate for forming a cluster containing two H_2SO_4 molecules and one BioOxOrg molecule (k_{max}). k_{max} depends on T as well as the mass and sizes of colliding molecules. At T=270 K, k_{max} is about a factor of 38 higher than k_m. We have revised the manuscript to set the maximum value of f_T to k_{max}/k_m instead of 10. The modification has negligible effect on the results and conclusions of this study which focuses on the summer month and the boundary layer.

4. Line 132, Page 7: Along with major comment 1, explain why this deltaH value is used.

Please see our reply to major comment 1.

5. Line 202, Page 10: "agree much better with the observed values". As per major comment 2, need to actually show this.

Please see our reply to major comment 2.

6. Line 260, Page 12: “To our acknowledge”. This should say “To our knowledge”

Corrected. Thanks.

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 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 number abundance.

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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 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 a 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.

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2. Methods

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

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),

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

where $J_{\text{Nucl-Org}}$ 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 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.

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

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

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 $J_{\text{Nucl-Org}}$ given in Eq. (1) as the nucleation rate at the reference temperature T_0=278 K, we obtain

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

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

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 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 and increases with decreasing T. f_T is set to have a maximum value so that $J_{Nucl\text{-}OrgT}$ does not exceed the 3-body kinetic collision rate for forming a cluster containing two H_2SO_4 molecules and one BioOxOrg molecule, which depends on T as well as the mass and sizes of colliding molecules. At T=270 K, the maximum value of f_T is ~ 38. 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.

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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 stronger temperature dependence. The sensitivity of f_T values to ΔH can be readily calculated from Eq. (4). For example, a fairly large uncertainty of 5 kcal mol^{-1} in ΔH leads to the uncertainty in f_T of a factor of ~ 1.4 at T=288 K, while the extremely large 20 kcal mol^{-1} variation in ΔH alters f_T at T=288 K by a factor of ~ 3.5. The sensitivity of predicted nucleation rates and particle number concentrations to ΔH values is presented in Section 3. Despite possible uncertainties in f_T, the temperature dependent $J_{Nucl\text{-}OrgT}$ is likely to be more realistic than $J_{Nucl\text{-}Org}$, in which the temperature dependence is neglected.

2.2. GEOS-Chem model and global simulations

This work represents a major global modeling attempt in studying the effect of temperature on organics-mediated nucleation in the atmosphere. This study is built upon the work reported in Yu et al. (2015) and, thus, we use the same global model (GEOS-Chem) and configurations as that described in Yu et al. (2015). GEOS-Chem is a global 3-D model of atmospheric composition driven by assimilated meteorological observations from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling and Assimilation Office (GMAO) (e.g., Bey et al., 2001). More detailed information about GEOS-Chem and updates can be found at the model website (http://geos-chem.org/). The aerosol simulation is based on a size-resolved (sectional) advanced particle microphysics (APM) model incorporated into GESO-Chem by Yu and Luo (2009) and considers the successive oxidation aging of the oxidation products of various VOCs (Yu, 2011). In GEOS-Chem v8-03-02, on which this study and previous work (Yu et al.,

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2015) are based, the concentration of highly oxidized low volatile secondary organic gas from the oxidation products of α-pinenes (LV-SOG$_{\alpha\text{-pinene}}$) is explicitly simulated and used in Eqs. (1) and (4) to calculate organics-mediated nucleation rates. The horizontal resolution of GEOS-Chem employed in this study is $2^{o}\times2.5^{o}$ and there are 47 vertical model layers (with 14 layers 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.

A ΔH value of -38.3 kcal mol^{-1} was used in calculating $J_{Nucl-OrgT}$ in Fig. 3b. The impact of ΔH values (from 0 to 58.3 kcal mol^{-1}) on $J_{Nucl-OrgT}$, CN10 and CCN0.4 averaged in the boundary layer over the whole globe for the same summer month is presented in Figure 4. A zero value of ΔH corresponds to the case of no T-dependent correction (i.e., $J_{Nucl-Org}$, Fig. 3a). $J_{Nucl-OrgT}$, CN10 and CCN0.4 are more sensitive to ΔH when ΔH is small (<~ 30 kcal mol^{-1}), with $J_{Nucl-OrgT}$ decreasing by a factor of 5, CN10 by 33% and CCN0.4 by 28% as ΔH increases from 0 to 28.3 kcal mol^{-1}. Further increase of ΔH from 28.3 to 58.3 kcal mol^{-1} reduces $J_{Nucl-OrgT}$, CN10 and CCN0.4 by 100%, 25%, and 10%, respectively. It can be seen from Figure 4 that the T-dependent correction, even with a smaller value of ΔH, is important. On the other hand, the effect of potential uncertainty in ΔH around the values derived from quantum calculation (~ 40 kcal mol^{-1}, see Section 2.1) is relatively weaker.

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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 $J_{Nucl-Org}$ parameterization (Eq. 1) over-predicts condensation nuclei number concentrations in the size range of 10 and 100 nm (CN_{10-100}) at these sites in summer by a factor of around two on average (Yu et al., 2005). To examine the extent, at which the revised parameterization considering T-dependence (Eq. 4) can improve the agreement of simulations with measurements, we present the monthly mean horizontal distributions of CN10 zoomed into the NA region in Fig. 5 and observed and simulated CN_{10-100} averaged over the nine forest sites in Fig. 6. It can be clearly seen from Fig. 5 that the simulated monthly mean CN10 values in the NA boundary layer based on $J_{Nucl-OrgT}$ (Eq. 4) are about a factor of two lower than those based on $J_{Nucl-Org}$ (Eq. 1),

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with larger difference in the lower latitude part of the domain, where T is higher. In the case, when the effect of T on Nucl-Org is taken into account, the domain-wide average CN10 value decreases from 4600 to 2200 #/cm^3 and Figure 6 shows that the simulated CN$_{10-100}$ averaged over the nine forest sites (with locations marked on Fig. 5, see Yu et al. (2015) for details) agrees much better with that of observed. It can also be seem from Fig. 6 that CN$_{10-100}$ over the NA forest sites is more sensitive to ΔH values than the global mean CN10 shown in Fig. 4, and ΔH of ~35 kcal mol^{-1} agrees best with the observations.

To further illustrate the difference and improvement for the cases with and without T-dependent correction, we present in Fig. 7 a set of detailed comparisons of simulated and observed evolution of particle size distributions during two ten-day periods in March and July of 2006 in Duke Forest (Pillai et al., 2013), along with time series of CN$_{10-100}$ (integrated from PSDs), which give a good overall representation of particle nucleation and growth. The observed PSDs and simulated PSDs based on J$_{\text{Nucl-Org}}$ has been discussed in Yu et al. (2015) and are repeated here for comparison with J$_{\text{Nucl-OrgT}}$ scheme in order to demonstrate the impact of temperature on nucleation and particle number concentrations. Although the present work focuses on the summer month, when the largest difference between J$_{\text{Nucl-Org}}$ prediction and observation is observed, we also show in Fig. 7 simulations for a 10-day period in March as well for the comparison purpose. NPF events observed in Duke Forest are much more frequent and concentrations of nucleation mode particles are much higher in the spring than in the summer (Figs. 7a & 7b). The temperature correction (Eq. 4) has small effect in the spring (Figs. 7c, 7e, and 7g) but significantly reduces nucleation rate and particle number concentration in summer (Figs. 7d, 7e, and 7f). J$_{\text{Nucl-Org}}$ scheme (Eq. 1) predicts strong nucleation events (Fig. 7d) and significant diurnal variations in CN$_{10-100}$ (Fig. 7h) almost every day in the summer period that

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obviously contradicts to observations (Fig. 7b). The high nucleation rates in the summer based on $J_{Nucl\text{-}Org}$ 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. 7b, 7d, 7f) and $CN_{10\text{-}100}$ (Fig. 7h) with observations.

Figure 8 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. The CCN concentrations are calculated at a water supersaturation ratio of 0.2% (CCN0.2) from simulated PSDs. 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.

4. Summary and discussion

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

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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. 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. In a recent study, Dunne et al. (2016) also showed a substantial impact of the temperature dependence on the contribution of organic nucleation to overall nucleation. The temperature dependence factor derived under this study can be applied to study the temperature effect on organics-mediated nucleation in the global atmosphere and improve the agreement of simulated particle number concentrations with observations. 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.

Acknowledgments. This study was supported by NASA under grant NNX13AK20G and the National Science Foundation (NSF) under grant 1550816. We would like to acknowledge high-performance computing support from Yellowstone (ark:/85065/d7wd3xhc) provided by NCAR's Computational and Information Systems Laboratory, sponsored by the NSF. The GEOS-Chem

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model is managed by the Atmospheric Chemistry Modeling Group at Harvard University with support from NASA's Atmospheric Chemistry Modeling and Analysis Program.

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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

Figure Captions

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

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

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

Figure 4. Dependence of organics-mediated nucleation rates (left axis), CN10 and CCN0.4 (right-axis) averaged in the boundary layer (0-1 km) over the whole globe for July 2006 on ΔH values assumed in calculating temperature dependence correction factor for Nucl-Org parameterization (f_T).

Figure 5. Horizontal distributions of monthly mean CN10 in the boundary layer (0-1 km above surface) in July of 2006 based on two organics-mediated nucleation schemes: (a) $J_{Nucl-Org}$ and (b) $J_{Nucl-OrgT}$. The locations of 9 forest sites where observed particle size distributions measurements have been used for comparisons in Yu et al. (2015) are marked.

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Figure 6. Effect of ΔH values on simulated number concentrations of condensation nuclei in the size range of 10 and 100 nm (CN_{10-100}) in the boundary layer (0-1 km) for July 2006 averaged over nine forest sites in North America (NA) (locations marked on Fig. 5). The horizontal dashed line shows the average of CN_{10-100} observed in a summer month at the 9 sites.

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Figure 7. Particle size distributions (PSDs) observed (a, b) and simulated based on Nucl-Org (c, d) and Nucl-OrgT (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).

Figure 8. Ratios of the concentration of CCN (at water supersaturation ratio of 0.2%) in the lower troposphere (0-3 km) based on Nucl-Org scheme to those based on Nucl-OrgT scheme.

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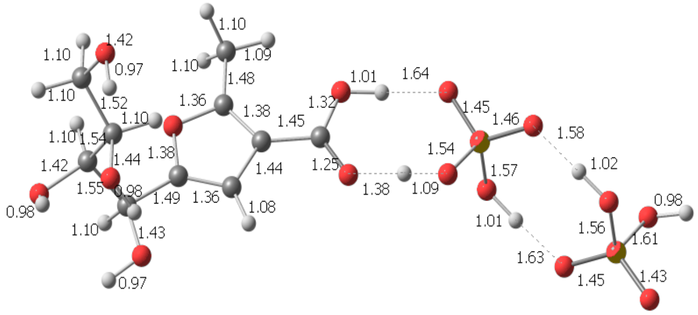
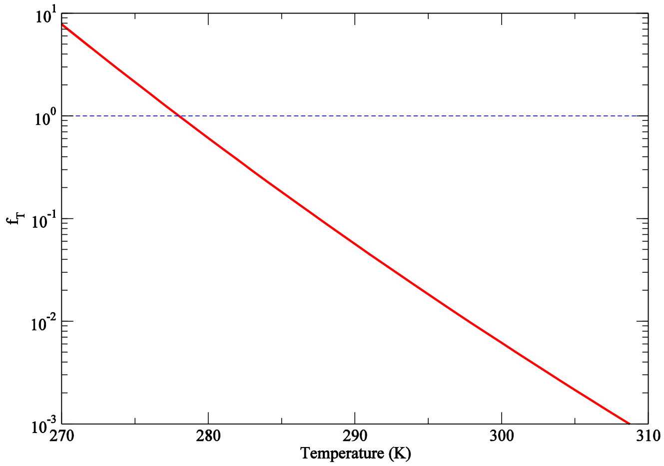


Figure 1.



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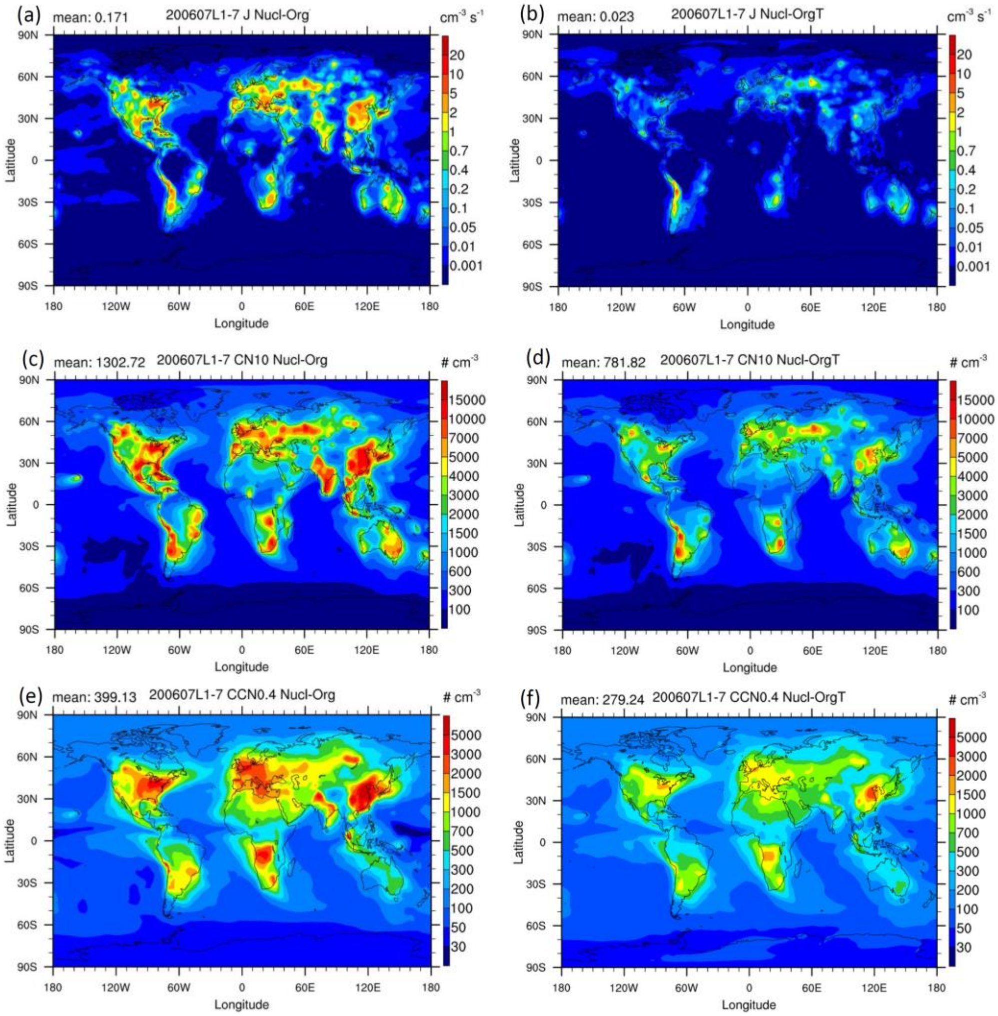
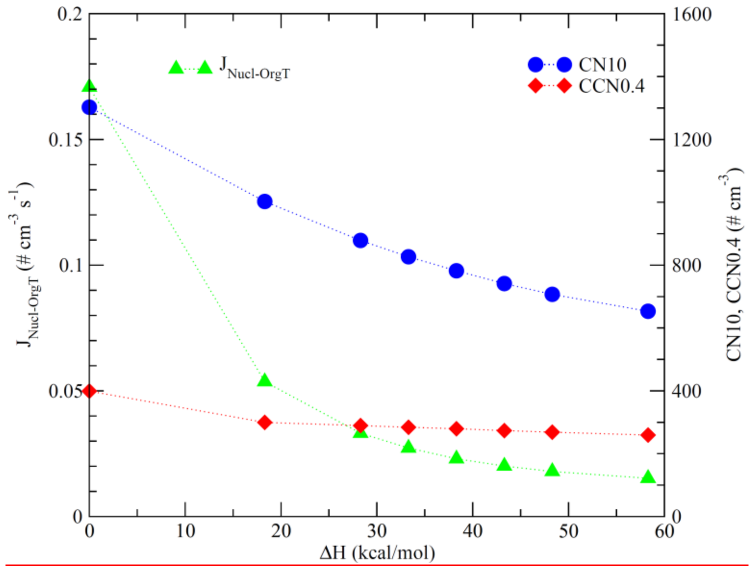


(a) mean: 0.171 200607L1-7 J Nucl-Org cm^{-3} s^{-1}
(b) mean: 0.023 200607L1-7 J Nucl-OrgT cm^{-3} s^{-1}
20 10 5 2 1 0.7 0.4 0.2 0.1 0.05 0.01 0.001
(c) mean: 1302.72 200607L1-7 CN10 Nucl-Org # cm^{-3}
(d) mean: 781.82 200607L1-7 CN10 Nucl-OrgT # cm^{-3}
15000 10000 7000 5000 4000 3000 2000 1500 1000 600 300 100
(e) mean: 399.13 200607L1-7 CCN0.4 Nucl-Org # cm^{-3}
(f) mean: 279.24 200607L1-7 CCN0.4 Nucl-OrgT # cm^{-3}
5000 3000 2000 1500 1000 700 500 300 200 100 50 30
Latitude
90N 60N 30N 0 30S 60S 90S
Longitude
180 120W 60W 0 60E 120E 180

Figure 3.



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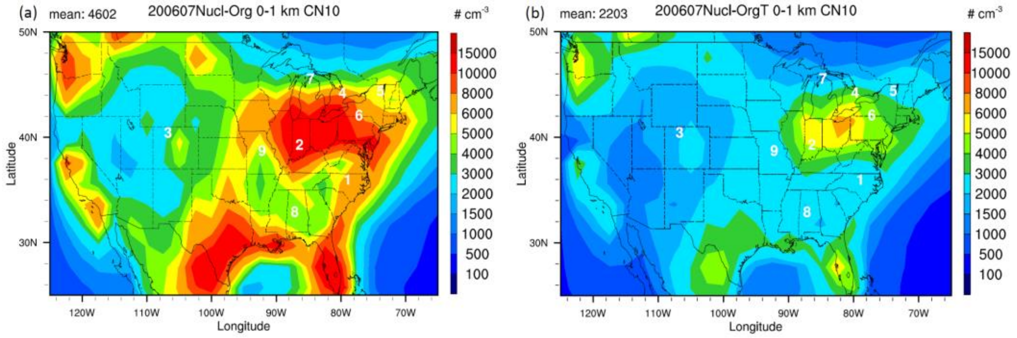

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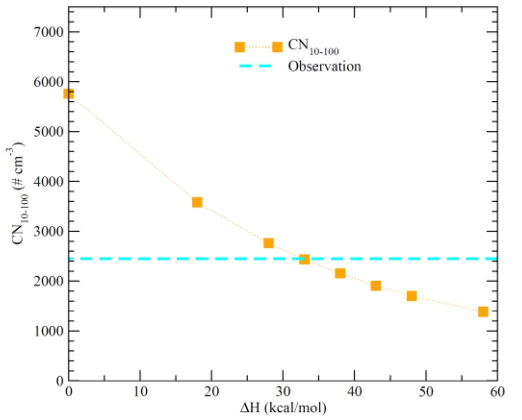

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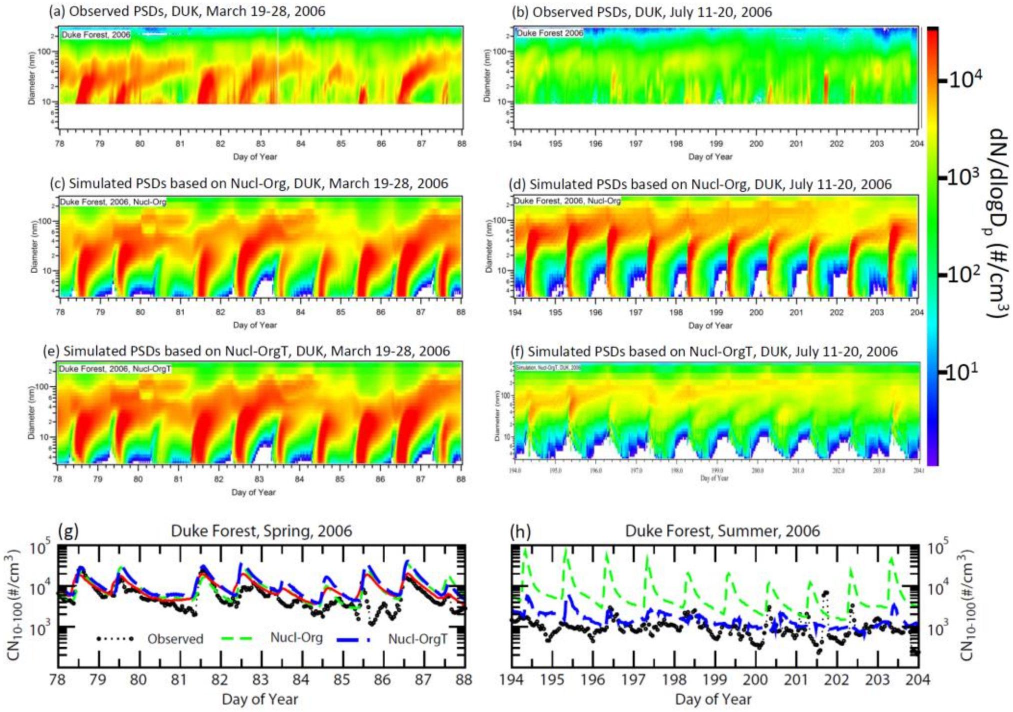

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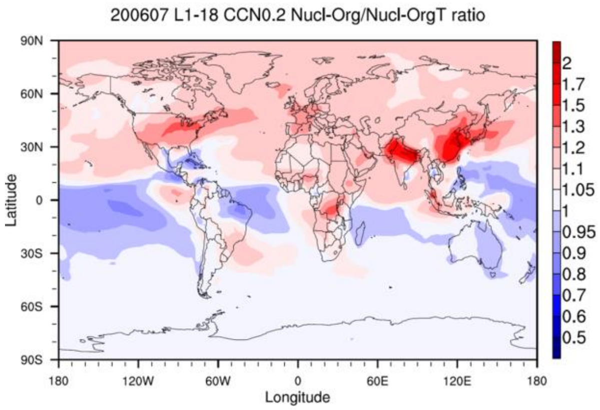

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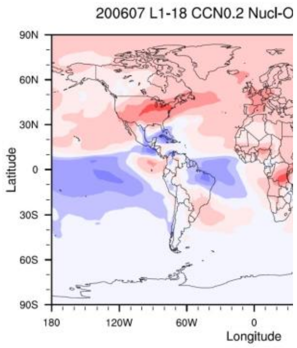

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