

We are very grateful to the evaluations from the reviewers, which have allowed us to clarify and improve the manuscript. Below we addressed the reviewer comments, with the reviewer comments in black and our response in blue.

Before we provide the detailed point by point reply, we provide an overview of the main changes and improvements:

- 1. We added some detailed descriptions of the model and model output in Section 2 Data and Method.**
- 2. We added four sensitivity tests related to reaction rate during HOMs formation and their description in Section 2.4.**
- 3. We added a new Section to discuss the impact of uncertainties from HOMs chemistry on aerosol and CCN number.**
- 4. In the last Section (Summary), we added more discussion on the limitations and uncertainties associated with our current results.**

Reply for the Anonymous referee #2

General Comments:

A version of the CESM climate model with state-of-the-art new particle formation (NPF) mechanisms is presented, with a focus on the production of Highly Oxygenated organic Molecules (HOMs). The model demonstrates improved agreement with observations. The authors find that organic molecules play a more important role in global NPF than previous studies suggested. Table 5 suggests 83.44% of nucleation proceeds via the mixed H₂SO₄-organic pathway below 5.8km, a result that, if nothing else, highlights the importance of further studying this possible NPF pathway.

While not emphasized in the paper, the authors also include an upgraded inorganic NPF mechanism, a potentially very useful innovation.

The article documents a significant effort and it is novel for this level of complexity in new particle formation to be included in a global climate model. The analysis and model evaluation are of high quality with some useful innovations such as the NPF event threshold.

I recommend the paper for publication, subject to responses to the comments below. I also appreciate that, while I do suggest some more sensitivity studies, it is surely not within the scope of the paper to explore all possible uncertainties, as long as the limited nature of the sensitivity studies is properly discussed.

Response: We would like to thank the referee for providing the insightful suggestions, which indeed help us further improve the manuscript. We have added required discussion to account for the major and minor comments and marked the corresponding line number in the revised paper. Please see the revision and the response for the comments as follow.

Major Comment#1: What are the uncertainties associated with using the Kerminen and Kulmala (2002) approximation for aerosol growth rates up to 20nm in diameter? Many models, including some GCMs that participated in CMIP6, resolve aerosols prognostically and advect them at much smaller sizes. It seems that using the Kerminen and Kulmala (2002) formula in this way for precise studies of NPF might incur quite large biases. Growth rates are not constant with size (Stolzenburg et al, ACP 2020, e.g. Eq. 16), and the more accurate version of the equation that takes better account of the size dependence of the loss rates is given by Lehtinen et al (J. Aerosol Science 2007). I suspect reasonable bounds on these potentially large uncertainties could be determined with some sensitivity studies, without changing the structure of the model.

Also, (L173) should the 0.66 factor be modified between default and updated NPF mechanisms to account for the difference between the 1.7nm starting size for the updated scheme and the 1nm starting size for the default scheme? I believe the parameterization depends on $(1/1.7 - 1/20)$ or $(1/1 - 1/20)$ so this likely makes quite a big difference.

Response: We apologize for the typo in Eq. (9) and it is corrected to:

$$j_{20\text{nm}} = j_{1.7\text{ nm}} \exp \left[- \left(\frac{1}{1.7} - \frac{1}{20} \right) \frac{\gamma_{\text{CS}}}{\text{GR}} \right] \quad (9)$$

However, without changing the structure of the model, we cannot simulate growth rates with size dependence and take account of the size dependence of the loss rates. The main reason is that there is no nucleation mode in CAM6-Chem. For Aitken mode, the geometric diameter is about 20 nm so we cannot resolve aerosols growth rate within 20nm. We have added the assumption and limitation at the

Summary:

“The NPF rate at about 20nm is calculated based on the Eq. (14) based on Kerminen and Kulmala (2002). It is derived with several simplifying assumptions and approximations:

- (1) the only important sink for the newly formed particles is their coagulation to larger preexisting particles;
- (2) the newly formed particles grow by condensation at a constant rate;
- (3) the preexisting population of larger particles remains unchanged during the newly formed particles growth.

However, Lehtinen et al. (2007) reformulates the previously (Kerminen and Kulmala, 2002) published theory, in which both the accuracy has been improved and the applicability to different conditions is more straightforward. Since CAM6-Chem does not include a nucleation mode, we are not able to

update the NPF rate based on Lehtinen et al. (2007). However, future work, such as implementing a nucleation mode in CAM6-Chem and resolving particle growth rate within 20nm, is worth exploring.”

Reference

Lehtinen, K. E. J., Dal Maso, M., Kulmala, M., and Kerminen, V.-M.: Estimating nucleation rates from apparent particle formation rates and vice versa: Revised formulation of the Kerminen–Kulmala equation, *J. Aerosol Sci.*, 38, 988-994, <https://doi.org/10.1016/j.jaerosci.2007.06.009>, 2007.

Major Comment#2: The model evaluation has some missing details. How were number concentrations of 10nm particles calculated in the model for comparison with measurements? At what temporal frequency were variables written out of the model for calculating nucleation rates and aerosol number concentrations? What kind of interpolation was done to match model with observation stations and aircraft measurements?

Response: Thanks for suggestions. We added the following sentences in **Section 2.3**:

“CAM6-Chem utilizes a four-mode version of the Modal Aerosol Module (MAM4) (Liu et al., 2016), including Aitken mode (with diameter 9~52nm), accumulation mode (54~480 nm), coarse mode (400~40000 nm) and primary mode (10~100nm). The integral concentration from 0 to r_p is computed using the error function (erf):

$$N_{>r_p} = N_{\text{mode}} \left(\frac{1}{2} + \frac{1}{2} \operatorname{erf} \left(\frac{x}{\sqrt{2}} \right) \right) \quad (12)$$

where $x = \ln(r_p/r_m)/\ln\sigma$. σ is the geometric standard deviation (the width) of the lognormal distribution r_m is the median radius of the mode. The integral concentration above r_p is therefore $N_{>r_p} = N_{\text{mode}} - N_{<r_p}$.

The temporal frequency of the nucleation rate, growth rate, and condensation sink written out of the model are hourly, and the time periods of the model simulation are consistent with the observation period (with an additional month for spin-up). For aerosol number concentrations (including over oceans and land), the model outputs data on a monthly basis, and we compare these monthly averages with observations. When comparing the aerosol and CCN number concentrations with the field campaign in the Amazon basin, the output frequency from model is hourly. Then, we slice the aircraft measurements of aerosol and CCN number concentrations vertical profiles according to the model

output dimensions (4 dimensions including time, height, latitude and longitude). We average all measurements data within each slice and compare it with the corresponding model output data.”

Reference

Liu, X., Ma, P. L., Wang, H., Tilmes, S., Singh, B., Easter, R. C., Ghan, S. J., and Rasch, P. J.: Description and evaluation of a new four-mode version of the Modal Aerosol Module (MAM4) within version 5.3 of the Community Atmosphere Model, *Geosci. Model Dev.*, 9, 505-522, 10.5194/gmd-9-505-2016, 2016.

Major Comment#3: At line 330, I think the results suggest most ACC does not undergo autoxidation even though it has 8 or 9 oxygen atoms (Table 1), because ACC are unaffected by the NO sensitivity study. That may be possible, though it seems rather surprising. Also I would imagine ACC which are autoxidized will usually have more oxygen than those which don't, so will be more likely to be ULVOC and nucleate. Either way it doesn't make sense to me that uncertainties in organic chemistry (ACC as well as HOM) do not affect CCN number in Amazonia where pure biogenic NPF dominates – it seems more likely that the authors were unable to sample the uncertainty space sufficiently, and this could be discussed more.

Response: The formation of and C15 and C20 dimer (accretion products, ACC) requires MT-aRO₂, MT-bRO₂, MT-cRO₂ and MT-HOM-RO₂ (MT-RO₂). Both MT-cRO₂ and MT-HOM-RO₂ are generated through autoxidation. During the autoxidation process, the number of oxygen atoms in these MT-RO₂ continuously increase, hence ACC contains 8-9 oxygen atoms.

In the NO sensitivity study, although there is no change in the rate of autoxidation reactions that generate MT-RO₂, the reaction rate of the NO termination pathway affects the concentration of MT-HOM-RO₂, and consequently, the concentration of ACC.

We appreciate the referee for pointing out this issue, which was also mentioned by another referee. In order to test the impact of the ACC chemistry on nucleation and growth rate as well as aerosol and CCN number concentration, we have run one additional sensitivity test based on the lower limits of self-/cross-reaction rates provided in chamber experiments (Weber et al., 2020; Berndt et al., 2018), labelled “Slow_accr”. Please refer to the response or major comment#1 of referee #1 where more details are presented regarding the sensitivity tests.

Reference

Berndt, T., Mentler, B., Scholz, W., Fischer, L., Herrmann, H., Kulmala, M., and Hansel, A.: Accretion Product Formation from Ozonolysis and OH Radical Reaction of α -Pinene: Mechanistic Insight and the Influence of Isoprene and Ethylene, *Environ. Sci. Technol.*, 52, 11069-11077, 10.1021/acs.est.8b02210, 2018.

Weber, J., Archer-Nicholls, S., Griffiths, P., Berndt, T., Jenkin, M., Gordon, H., Knote, C., and Archibald, A. T.: CRI-HOM: A novel chemical mechanism for simulating highly oxygenated organic molecules (HOMs) in global chemistry–aerosol–climate models, *Atmos. Chem. Phys.*, 20, 10889-10910, 10.5194/acp-20-10889-2020, 2020.

Indeed, I would speculate despite the authors' findings, CCN formation in general could still be very sensitive to either the chemical formation of organic molecules (HOMs and ACC) or to the choices made by the modelers on which species participate in NPF. In particular, it is speculative that all HOMs (as defined by the authors) participate in NPF with H_2SO_4 at the rate specified in the Riccobono et al (2014) CLOUD study, as in Eq 6 of this paper. The species defined by Riccobono et al was called 'BioOxOrg', not HOM. The large uncertainties associated with these parameterizations should be acknowledged in this paper, and ideally quantified with sensitivity studies.

I would also speculate that the results are likely sensitive to uncertainties in concentrations of H_2SO_4 and NH_3 . The sources of these uncertainties are not really discussed in the main text yet (despite documentation that a bias in H_2SO_4 exists and a helpful table of budgets in the supplement).

In the light of these remarks, while I do agree that the uncertainty due to the omission of anthropogenic organics is potentially important, it is far from the only important uncertainty, and the last paragraph of the paper could be more balanced.

Response: Yes, the species defined by Riccobono et al. (2014) was called 'BioOxOrg' instead of "HOMs" since at that time the measurement technique was not able to distinguish the nucleating organic species participating in different organic nucleation scheme. We are grateful to the referee for highlighting these important uncertainties and the discussion of both the chemical formation of organic molecules and the choice of nucleating species have already added in new section "**5 Uncertainties from HOMs chemistry**" and the **Summary**. Please refer to the response or major comment#1 of referee #1, #2, #3, #4 and #5 where more details are presented regarding these uncertainties.

Also, uncertainties in concentrations of H_2SO_4 and NH_3 have added in the **Summary**:

“The overestimation of H₂SO₄ in CAM6-Chem could potentially impact our final results regarding the organic proportion in both nucleation and the initial growth rate because both the dependency of inorganic and organic nucleation rate on H₂SO₄ concentration are modeled with an exponent greater than 2 (Eq. (2)-(6)). Also, nitrate is not included CMIP6 emissions because of uncertainties in both ammonia emissions and its chemistry and removal (Heald et al., 2012; Paulot et al., 2016). The underestimated nitrate concentrations result in reduced rate of ammonia consumption, potentially leading to an overestimation of residual atmospheric ammonia. Therefore, the inorganic nucleation rate may be overestimated and consequently, the organic proportion of the nucleation rate is likely underestimated.”

Reference

Riccobono, F., Schobesberger, S., Scott, C. E., Dommen, J., Ortega, I. K., Rondo, L., Almeida, J., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Downard, A., Dunne, E. M., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Hansel, A., Junninen, H., Kajos, M., Keskinen, H., Kupc, A., Kurten, A., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Makhmutov, V., Mathot, S., Nieminen, T., Onnela, A., Petaja, T., Praplan, A. P., Santos, F. D., Schallhart, S., Seinfeld, J. H., Sipila, M., Spracklen, D. V., Stozhkov, Y., Stratmann, F., Tome, A., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Wimmer, D., Carslaw, K. S., Curtius, J., Donahue, N. M., Kirkby, J., Kulmala, M., Worsnop, D. R., and Baltensperger, U.: Oxidation Products of Biogenic Emissions Contribute to Nucleation of Atmospheric Particles, *Science*, 344, 717-721, [10.1126/science.1243527](https://doi.org/10.1126/science.1243527), 2014.

Heald, C. L., Collett Jr, J. L., Lee, T., Benedict, K. B., Schwandner, F. M., Li, Y., Clarisse, L., Hurtmans, D. R., Van Damme, M., Clerbaux, C., Coheur, P. F., Philip, S., Martin, R. V., and Pye, H. O. T.: Atmospheric ammonia and particulate inorganic nitrogen over the United States, *Atmos. Chem. Phys.*, 12, 10295-10312, [10.5194/acp-12-10295-2012](https://doi.org/10.5194/acp-12-10295-2012), 2012.

Paulot, F., Ginoux, P., Cooke, W. F., Donner, L. J., Fan, S., Lin, M. Y., Mao, J., Naik, V., and Horowitz, L. W.: Sensitivity of nitrate aerosols to ammonia emissions and to nitrate chemistry: implications for present and future nitrate optical depth, *Atmos. Chem. Phys.*, 16, 1459-1477, [10.5194/acp-16-1459-2016](https://doi.org/10.5194/acp-16-1459-2016), 2016.

Minor Comment#1: The citation for CMIP6 emissions is a bit vague, or insufficient to determine which version of the emissions were used. Feng et al, GMD 2020 is relevant. There are also significant differences between the most recent (post-CMIP6) releases of the “CMIP6 emissions” and

the versions actually used. See <https://github.com/JGCRI/CEDS/>. If the most recent releases were not used, some comments may be needed about the deficiencies of the CMIP6 emissions, for example SO₂ emissions were overestimated in the western USA.

Response: We did not use the most recent (post-CMIP6) releases of the “CMIP6 emissions” and have added the following content in the **Section 2.1 Model configuration**:

“We use the historical anthropogenic emissions developed by the Community Emission Data System (CEDS v2017-05-18) in support of CMIP6 (Hoesly et al., 2018). Monthly biomass burning emissions are from the historical global biomass burning emissions inventory for CMIP6 (BB4CMIP6; van Marle et al., 2017). Emissions for the 1997 to 2015 period in this inventory have been derived from satellite-based emissions from the Global Fire Emissions Database (GFED; van der Werf et al., 2017). The vertical distribution of biomass burning emissions is taken from Dentener et al. (2006). All the emission can be downloaded from: <https://svn-ccsm-inputdata.cgd.ucar.edu/trunk/inputdata/atm/cam/chem/emis/>.

Comparisons between the CMIP6 and multi-resolution emission inventory for China (MEIC) emission inventories over China suggest that the model bias in this region can be largely attributed to an underestimate of the reduction of SO₂ emissions after 2007 in CMIP6. Therefore, emissions in China were replaced by the MEIC (<http://www.meicmodel.org>) (Li et al., 2017; Yue et al., 2023) which considerably improves Chinese emission inventories compared to the earlier large-scale studies (Zheng et al., 2009; Zhou et al., 2017).”

Reference

Dentener, F., Kinne, S., Bond, T., Boucher, O., Cofala, J., Generoso, S., Ginoux, P., Gong, S., Hoelzemann, J. J., Ito, A., Marelli, L., Penner, J. E., Putaud, J. P., Textor, C., Schulz, M., van der Werf, G. R., and Wilson, J.: Emissions of primary aerosol and precursor gases in the years 2000 and 1750 prescribed data-sets for AeroCom, *Atmos. Chem. Phys.*, 6, 4321-4344, 10.5194/acp-6-4321-2006, 2006.

Hoesly, R. M., Smith, S. J., Feng, L., Klimont, Z., Janssens-Maenhout, G., Pitkanen, T., Seibert, J. J., Vu, L., Andres, R. J., Bolt, R. M., Bond, T. C., Dawidowski, L., Kholod, N., Kurokawa, J. I., Li, M., Liu, L., Lu, Z., Moura, M. C. P., O'Rourke, P. R., and Zhang, Q.: Historical (1750–2014) anthropogenic emissions of reactive gases and aerosols from the Community Emissions Data System (CEDS), *Geosci. Model Dev.*, 11, 369-408, 10.5194/gmd-11-369-2018, 2018.

Li, M., Liu, H., Geng, G., Hong, C., Liu, F., Song, Y., Tong, D., Zheng, B., Cui, H., Man, H., Zhang, Q., and He, K.: Anthropogenic emission inventories in China: a review, *National Science Review*, 4, 834-866, 10.1093/nsr/nwx150, 2017.

Pan, X., Chin, M., Gautam, R., Bian, H., Kim, D., Colarco, P. R., Diehl, T. L., Takemura, T., Pozzoli, L., Tsigaridis, K., Bauer, S., and Bellouin, N.: A multi-model evaluation of aerosols over South Asia: common problems and possible causes, *Atmos. Chem. Phys.*, 15, 5903-5928, 10.5194/acp-15-5903-2015, 2015.

van der Werf, G. R., Randerson, J. T., Giglio, L., van Leeuwen, T. T., Chen, Y., Rogers, B. M., Mu, M., van Marle, M. J. E., Morton, D. C., Collatz, G. J., Yokelson, R. J., and Kasibhatla, P. S.: Global fire emissions estimates during 1997–2016, *Earth Syst. Sci. Data*, 9, 697-720, 10.5194/essd-9-697-2017, 2017.

van Marle, M. J. E., Kloster, S., Magi, B. I., Marlon, J. R., Daniau, A. L., Field, R. D., Arneeth, A., Forrest, M., Hantson, S., Kehrwald, N. M., Knorr, W., Lasslop, G., Li, F., Mangeon, S., Yue, C., Kaiser, J. W., and van der Werf, G. R.: Historic global biomass burning emissions for CMIP6 (BB4CMIP) based on merging satellite observations with proxies and fire models (1750–2015), *Geosci. Model Dev.*, 10, 3329-3357, 10.5194/gmd-10-3329-2017, 2017.

Yevich, R. and Logan, J. A.: An assessment of biofuel use and burning of agricultural waste in the developing world, *Global Biogeochem. Cy.*, 17, <https://doi.org/10.1029/2002GB001952>, 2003.

Yue, M., Dong, X., Wang, M., Emmons, L. K., Liang, Y., Tong, D., Liu, Y., and Liu, Y.: Modeling the Air Pollution and Aerosol-PBL Interactions Over China Using a Variable-Resolution Global Model, *J. Geophys. Res.-Atmos.*, 128, 10.1029/2023jd039130, 2023.

Zheng, J., Zhang, L., Che, W., Zheng, Z., and Yin, S.: A highly resolved temporal and spatial air pollutant emission inventory for the Pearl River Delta region, China and its uncertainty assessment, *Atmos. Environ.*, 43, 5112-5122, <https://doi.org/10.1016/j.atmosenv.2009.04.060>, 2009.

Zhou, Y., Zhao, Y., Mao, P., Zhang, Q., Zhang, J., Qiu, L., and Yang, Y.: Development of a high-resolution emission inventory and its evaluation and application through air quality modeling for Jiangsu Province, China, *Atmos. Chem. Phys.*, 17, 211-233, 10.5194/acp-17-211-2017, 2017.

Minor Comment#2: It would be interesting to know how many chemical species are advected and how many are otherwise represented.

Response: CAM6-Chem contains 371 transported solution species (including newly added species) and 87 not-transported solution species. The non-transported species are as follows:

1. Most organic radicals, such as MT-RO₂, ISOP-RO₂, since their lifetime will rarely exceed about 100 s (Bianchi et al., 2018), they may be chemical loss before transported so the impact of ignoring their transported is minimal.
2. O₂, CO₂, N₂O, CH₄: Fixed species participate in chemical reactions but their values are assigned not chemically derived. This is because their concentration is relatively stable in the atmosphere and the minor variations in them typically have a negligible direct impact on climate models.
3. The value of CFC-12 is prescribed from a dataset based on historical data or projected scenarios. Given the long lifetime and chemical stability of CFC-12, models may not need to simulate its short-term dynamics in the atmosphere.
4. The cloud borne aerosol species has been prognosed by a chemistry scheme. In clouds, aerosols can participate in chemical reactions, such as the formation of sulfate and nitrate. These reactions are implemented in models through a cloud chemistry module, which simulates the chemical dynamics within clouds and the interactions between aerosols and cloud droplets.

Reference

Bianchi, F., Kurten, T., Riva, M., Mohr, C., Rissanen, M. P., Roldin, P., Berndt, T., Crouse, J. D., Wennberg, P. O., Mentel, T. F., Wildt, J., Junninen, H., Jokinen, T., Kulmala, M., Worsnop, D. R., Thornton, J. A., Donahue, N., Kjaergaard, H. G., and Ehn, M.: Highly Oxygenated Organic Molecules (HOM) from Gas-Phase Autoxidation Involving Peroxy Radicals: A Key Contributor to Atmospheric Aerosol, *Chem. Rev.*, 119, 3472-3509, 10.1021/acs.chemrev.8b00395, 2019.

Minor Comment#3: For the ion concentrations, could radon be important? Would ion-induced nucleation be important close to the land surface if ion production rates were a factor 5 or so higher there?

Response: Thanks for the suggestion. We have added the following discussion at the end of the **Summary:**

“Zhang et al. (2015) showed that radon contributes additional ionization in the boundary layer, especially over land. This implies that our pure organic nucleation rate might be underestimated since

we only consider ion-pair production rate by galactic cosmic rays. However, even over the continents, the contribution of the ionization rate caused by the radioactive decay of radon is only significant (> 30%) within the lowest 1km (Fig. 12 in Zhang et al. (2011)). Above 3km, the contribution of radon decay induced ionization rate can be neglected (<10%). In this study, we focused on the proportion of organic NPF in the vertical integration within the whole atmosphere. Therefore, we will not consider incorporating the ion nucleation rate caused by radon.”

Reference

Zhang, K., Feichter, J., Kazil, J., Wan, H., Zhuo, W., Griffiths, A. D., Sartorius, H., Zahorowski, W., Ramonet, M., Schmidt, M., Yver, C., Neubert, R. E. M., and Brunke, E. G.: Radon activity in the lower troposphere and its impact on ionization rate: a global estimate using different radon emissions, *Atmos. Chem. Phys.*, 11, 7817-7838, 10.5194/acp-11-7817-2011, 2011.

Minor Comment#4: L167 I believe the correct citation for this organic parameterization is Kirkby et al, Nature 2016, not Dunne et al, 2016.

Response: We apologize for the wrong citations. We have modified this.

Minor Comment#5: L174 What is the reduced condensation sink?

Response: We apologize for missing information. We have added the explanation:

“Reduced (simplified) condensation sink (CS’) is calculated as $CS/(4\pi D_i)$ (Kerminen and Kulmala, 2002). Where CS is the condensation sink and D_i is the vapor diffusion coefficient. CS’ is largely depended on CS and it represents the surface area of preexisting aerosols.”

Reference

Kerminen, V. M. and Kulmala, M.: Analytical formulae connecting the "real" and the "apparent" nucleation rate and the nuclei number concentration for atmospheric nucleation events, *J. Atmos. Sci.*, 33, 609-622, 10.1016/s0021-8502(01)00194-x, 2002.

Minor Comment#6: L320 misspelling of species

Response: We apologize for the spelling error. We have corrected this.