Review of “Improved representation of isoprene-derived secondary organic aerosol in CAM6-Chem reveals regional contrasts in its long-term changes over China”

This study by Zhang et al. (2026) addresses the incomplete representation of isoprene-derived secondary organic aerosol (ISOA) formation in global chemical models. The authors updated the isoprene NOx-dependent chemistry scheme that explicitly treats key reactive uptake intermediates IEPOX and HMML/MAE and their respective heterogenous reaction products in the CAM6-Chem. The updated ISOA representations were evaluated against observations showing improved speciation and better agreement with the observed organic aerosol concentrations across China.

With the updated chemistry, the authors evaluated the spatial the spatial and seasonal characteristics of ISOA, revealing IEPOX products (low NOx pathway) dominate ISOA on a nation-scale while HMML/MAE products contribute much less but are more significant in NOx-rich regions of Eastern China. ISOA exhibits strong seasonal variability, peaking in summer, consistent with seasonal peaks in biogenic isoprene emissions, hydroxyl radicals (OH), and aerosol-phase heterogenous chemistry predictors (pH, sulfate, aerosol liquid water). Simulated long-term (2000–2019) trends show ISOA change were slightly negative but certain regions like SWC and SGN have contrasting changes. Regional differences in ISOA change drivers and temporal evolution of subspecies highlighted distinct controlling factors, with precursor supply being more important in SWC and sulfate-related heterogeneous reaction conditions in SGN. The authors also note limitations, such as the absence of explicit isoprene cloud-water chemistry in CAM6-Chem, suggesting areas for future model refinement and the need for more composition-resolved observations

Overall, this study fills a critical gap by integrating both IEPOX and MAE/HMML pathways into global models. This enables more robust evaluation of the long-term trend of ISOA, providing new insights into the key drivers of regional heterogeneity and directly inform regional air quality. The science is carefully executed and presented. The manuscript suitable for ACP after addressing the comments below.

Major Comments

1. I appreciate the authors for giving a comprehensive literature review on isoprene SOA chemistry and its impact. To further enhance its impact, it would be valuable to place this work within the context of previous efforts to represent reactive uptake of epoxides in global models. Throughout the manuscript, several key studies (Jo et al., 2019, 2021; Liu et al., 2023; Zhang et al., 2025) are referenced, which form the foundation of the current framework and parameterizations. I suggest adding a dedicated paragraph that clearly summarizes what has been accomplished so far in global modeling, what this work contributes, and what gaps remain compared to

regional models or measurements. This addition would be especially helpful for ACP's broad readership, many of whom may not be familiar with the current state of the literature on this topic. Such context would highlight the importance of this study and guide future research directions.

2. The authors make several assumptions in the epoxides' reactive uptake parameterizations particularly for HMML/MAE due to limited experimental constraints, which are understandable given limited experimental constraints. Some are explicitly stated such as diffusivity and solubility. Others are not clear and I'd appreciate further elaboration. For instance,
    - Are the same condensed-phase reaction constants for IEPOX applied to HMML/MAE? What is the literature basis for these choices?
    - How is the SOA speciation from epoxides calculated? Is it similar to Budisulistiorini et al. 2017 that uses the fraction of each nucleophilic addition rate to the total kaq?
    - The parameterization appears to assume a core-shell morphology with organic shell and inorganic core. It may be problematic to assume epoxides have same reactivity in both phases, as previous work (Zhang et al., 2019; Chen et al., 2024) indicate.

    Please clarify these assumptions and critically discuss potential uncertainties they introduce when evaluating against observations and long-term trend analyses later in the manuscript. It would also be helpful to add discussion on these uncertainties as limitations towards the end of the manuscript.

    Zhang, Yue, Yuzhi Chen, Ziying Lei, et al. "Joint Impacts of Acidity and Viscosity on the Formation of Secondary Organic Aerosol from Isoprene Epoxydiols (IEPOX) in Phase Separated Particles." *ACS Earth and Space Chemistry* 3, no. 12 (2019): 2646–58. https://doi.org/10.1021/acsearthspacechem.9b00209.

    Chen, Yuzhi, Alexandra E. Ng, Jaime Green, et al. "Applying a Phase-Separation Parameterization in Modeling Secondary Organic Aerosol Formation from Acid-Driven Reactive Uptake of Isoprene Epoxydiols under Humid Conditions." *ACS ES&T Air* 1, no. 6 (2024): 511–24. https://doi.org/10.1021/acsestair.4c00002.

3. The evaluation against measurements shows improved mass closure relative to the author's previous work. However, the authors did not address the non-negligible discrepancies observed in the OSN subspecies. While the model predicted a more even distribution of water and sulfate added products, measurements show that OSN contributes very little. Other measurements such as He et al. (2018) reported

similar findings. While uncertainties in measurements exist, this could also suggest uncertainties in the reactive uptake parameterization, possible missing processes, or inaccurate representation of the heterogeneous reaction medium (such as varying abundances of different nucleophiles). These points are related to previous comments about the assumptions used in the current parameterization. It would be helpful to discuss potential reasons for this gap and how future parameterization or additional measurements might address the gap.

He, Quan-Fu, Xiang Ding, Xiao-Xin Fu, et al. "Secondary Organic Aerosol Formation From Isoprene Epoxides in the Pearl River Delta, South China: IEPOX- and HMML-Derived Tracers." *Journal of Geophysical Research: Atmospheres* 123, no. 13 (2018): 6999–7012. https://doi.org/10.1029/2017JD028242.

Others Comments

Lines 110-112: What is the chemical nature of the IVOCs and SVOCs mentioned here apart from the already mentioned anthropogenic and biogenic emissions? Do they involve in gas- and aerosol-phase reactions in the model?

Lines 125-126: I understand it is impossible to include every new mechanism altogether in the models. It is worth noting that isoprene SOA photolysis is faster than MT-SOA. The model-ready rate is reported in Zawadowicz et al. (2020) and shown to have a huge impact on reducing isoprene SOA over Amazon.

Zawadowicz, Maria A., Ben H. Lee, Manish Shrivastava, et al. "Photolysis Controls Atmospheric Budgets of Biogenic Secondary Organic Aerosol." *Environmental Science & Technology* 54, no. 7 (2020): 3861–70. https://doi.org/10.1021/acs.est.9b07051.

Line 143-144: The branching ratios 0.57 vs 0.21 are not consistent with previous experimental work by Nguyen et al., MPAN + OH predominantly produces HMML (~75%) and the MAE yield is minor (<2%). Please clarify.

Line 143-144: The branching ratios (0.57 vs 0.21) differ from Nguyen et al.'s findings, where MPAN + OH mainly produces HMML (~75%) with a minor MAE yield (<2%). Please explain.

Nguyen, Tran B., Kelvin H. Bates, John D. Crounse, et al. "Mechanism of the Hydroxyl Radical Oxidation of Methacryloyl Peroxynitrate (MPAN) and Its Pathway toward Secondary Organic Aerosol Formation in the Atmosphere." *Physical Chemistry Chemical Physics: PCCP* 17, no. 27 (2015): 17914–26. https://doi.org/10.1039/c5cp02001h.

Line 146-147: The removal of the isoprene SOA formation in the VBS can potentially eliminate important non-epoxides contributions to isoprene SOA such as the multifunctional organic peroxides (low NOx) and organic nitrates (high NOx). Could authors give a proper account of this limitation?

Line 178-184: kaq is supposed to represent the sum of all particle-phase reactions that consume IEPOX. The reaction rate constant for nucleophilic reaction of IEPOX with water forming 2-methyltetrols is missing. $k_{H+}[H^+]$ appears to be the acid-catalyzed isomerization reaction of IEPOX that forms diols and triols, but this pathway is excluded in the current representation. The unit for the third-order reaction rate constant knuc for sulfate and nitrate is incorrect. It appears to be second-order reaction. Please clarify and correct.

Line 196-197: Please be noted that 2-MT and 2-MGA are semi-volatiles that can partition into the gas phase. Regional models such as WFR-Chem (Shrivastava et al.,2022) and CMAQ (Pye et al., 2018) already accounted for gas/particle partitioning of 2-MT. This presents an opportunity for future improvements in global models.

Shrivastava, Manish, Quazi Z. Rasool, Bin Zhao, et al. "Tight Coupling of Surface and In-Plant Biochemistry and Convection Governs Key Fine Particulate Components over the Amazon Rainforest." *ACS Earth and Space Chemistry* 6, no. 2 (2022): 380–90. https://doi.org/10.1021/acsearthspacechem.1c00356.

Pye, Havala O. T., Andreas Zuend, Juliane L. Fry, et al. "Coupling of Organic and Inorganic Aerosol Systems and the Effect on Gas–Particle Partitioning in the Southeastern US." *Atmospheric Chemistry and Physics* 18, no. 1 (2018): 357–70. https://doi.org/10.5194/acp-18-357-2018.

Lines 304-308: There is another ISOA peak in April but it coincided with low isoprene emissions. I am just curious if the authors have any thoughts on why this occurred? Also, the OH z-score seems to be missing in Figure 4b.

Lines 335-337 (and Figure 5b): The surface area is the same and the epoxides mean speed is in the same ballpark. The only way khet_HMML+MAE and khet_IEPOX can differ by be a factor of 10 has to be due to the calculated coefficient γ. Therefore, I don't understand how the current model with HMML/MAE and IEPOX sharing the same parameters can lead to such different γ values. This relates back to my major comment 2. Please clarify if I missed something.