

Response to Referee #1

Review of Improved representation of isoprene-derived secondary organic aerosol in CAM6-Chem reveals regional contrasts in its long-term changes over China by Wenxin Zhang et al., This manuscript presents an updated representation of isoprene-derived secondary organic aerosol (ISOA) in CAM6-Chem, incorporating both the IEPOX (low-NO_x) pathway and the MAE/HMML (high-NO_x) pathway, along with an explicit treatment of aerosol liquid water in multiphase chemistry. The authors evaluate the updated mechanism against multiple observational datasets and use it to investigate long-term (2000-2019) ISOA trends across China. The study finds that while national-mean ISOA trends are weak, they mask strong regional contrasts, with increasing ISOA mass in Southwest China (SWC) driven primarily by enhanced biogenic isoprene emissions and decreasing ISOA in the Shaanxi-Gansu-Ningxia region (SGN) driven by declining sulfate and changing NO_x emissions. Overall, this is a careful and well-executed modeling study that addresses a known gap in global models. The manuscript is suitable for ACP, but several aspects require clarification and strengthening before publication.

We are very grateful to the reviewer for the constructive evaluation and helpful suggestions, which have allowed us to clarify and improve the manuscript. Before addressing the reviewer's comments point by point, we briefly summarize the major revisions made in response to Referee #1. The reviewer's comments are shown in **bold blue text**, while our responses and the corresponding revised manuscript text are shown in black text. Line numbers refer to the revised manuscript.

In response to Referee #1, we made several major revisions to strengthen the manuscript. We developed a clearer conceptual framework by interpreting regional ISOA changes as the balance between precursor supply and heterogeneous reaction capacity, and added a new synthesis schematic (Fig. 9) to summarize the contrasting controls in SWC and SGN. We also revised the multiple linear regression interpretation to emphasize statistical associations rather than strict causal attribution, added a predictor covariance/collinearity discussion and a new Pearson correlation analysis (Fig. S9), and included a brief summary of the regression approach in the main text. In addition, we expanded the discussion of key model assumptions and uncertainties, including HMML/MAE uptake parameters, 100% yield and non-volatility assumptions, phase separation, viscosity, and gas-particle partitioning, and revised the related discussions of model bias and broader implications.

Major Comments

Comment#1: The manuscript contains an important underlying idea that ISOA formation reflects a balance between precursor supply (e.g., isoprene, NO_x) and heterogeneous reaction capacity (e.g., sulfate, aerosol liquid water, acidity). However, this is not fully developed into a clear conceptual framework. For example, on lines 369-373, the authors note that increases in isoprene emissions coincide with decreases in sulfate and aerosol liquid water, implying competing controls on ISOA formation. Similarly, the regional contrast between SWC and SGN is interpreted in terms of precursor supply versus reaction medium limitations (e.g., lines 410-417). These are strong and insightful points, but they need to be synthesized into a broader framework. Consider explicitly framing the results in terms of regimes (e.g., precursor-limited vs. reaction-medium-limited ISOA formation) and summarizing this in a conceptual schematic or synthesis figure.

Response: We thank the reviewer for this insightful suggestion. We have revised the discussion to explicitly frame the regional ISOA trends in terms of the balance between precursor supply and heterogeneous reaction-medium capacity. In this framework, SWC represents a precursor-driven regime, where enhanced isoprene emissions dominate the ISOA increase, whereas SGN represents a reaction-medium-limited regime, where reductions in sulfate and aerosol liquid water suppress heterogeneous ISOA formation. We also added a conceptual schematic to summarize these contrasting regional mechanisms. These revisions are provided in lines 613–620, and the new schematic is shown in Fig. 9.

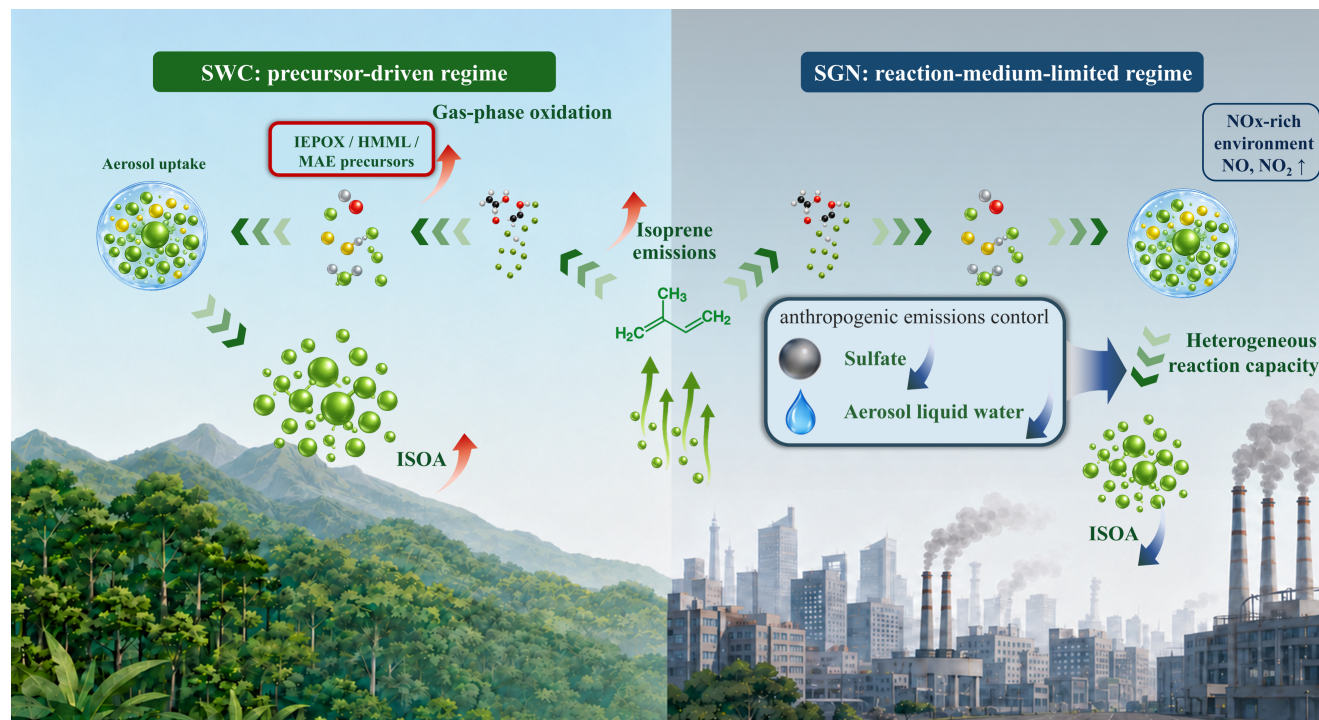


Figure 9. Schematic illustration of contrasting regional controls on surface isoprene-derived secondary organic aerosol (ISOA) formation in Southwest China (SWC; left) and the Shaanxi–Gansu–Ningxia region (SGN; right). The background scenes and selected graphical elements were created with the assistance of OpenAI's image-generation tools in ChatGPT (OpenAI, 2026).

Lines 613–620:

Taken together, the contrasting ISOA trends in SWC and SGN highlight the need for a coupled precursor-multiphase reaction framework. The SWC case represents a more precursor-driven regime, in which enhanced biogenic isoprene emissions and NO_x-dependent oxidation promote epoxide precursor formation and enhance ISOA production despite less favorable aerosol multiphase reaction conditions. In contrast, the SGN case represents a more reaction-medium-limited regime, in which declining sulfate and aerosol liquid water suppress heterogeneous uptake and particle-phase product formation, even when precursor supply remains relatively high. This regime-based interpretation emphasizes the balance between precursor supply, NO_x-dependent oxidation chemistry, and aerosol multiphase reaction conditions, as summarized schematically in Fig. 9.

Comment#2: The manuscript relies heavily on multiple linear regression to quantify the relative importance of drivers. For example, in the supplement (Text S1), the authors state that isoprene emissions account for ~49.9% of the relative importance of ISOA variability in SWC based on standardized regression coefficients. Similarly, in the main text (Section 3.3), regression-based contributions are used to attribute long-term trends. While these diagnostics are useful, the predictors (e.g., sulfate, aerosol liquid water, emissions) are likely to be strongly covarying over time, which complicates interpretation. Because aerosol liquid water is calculated thermodynamically within MOSAIC from inorganic aerosol composition, including sulfate, sulfate and aerosol liquid water are not fully independent predictors. This should be acknowledged in the regression interpretation, particularly where sulfate and aerosol liquid water are both treated as separate explanatory variables. Please clarify that regression-based importance reflects statistical association rather than strict causality and discuss potential collinearity among predictors. I suggest tempering the language when assigning quantitative contributions. For example, replace “accounts for X%” with “is strongly associated with” or “emerges as a leading statistical predictor” while also discussing the potential impact of predictor covariance on the interpretation.

Response: We thank the reviewer for this helpful suggestion. We have revised both Sect. 3.3 and Supplementary Text S1 to clarify the interpretation of the multiple linear regression results. In the revised manuscript, the regression-based relative importance and trend contributions are now described as diagnostic indicators of statistical associations, rather than as strict causal attribution or fully independent contributions. We have also tempered the language when discussing quantitative contributions, replacing causal-sounding expressions with wording such as “is strongly associated with” and “emerges as a leading statistical predictor”. In addition, we added a specific discussion of predictor covariance and potential collinearity, particularly among sulfate, aerosol liquid water, and aerosol acidity, which are physically coupled within the aerosol chemical environment and therefore should not be interpreted as fully independent predictors. This new discussion has been added in Sect. 3.3, lines 557–568. To further support this interpretation, we also added a pairwise Pearson correlation analysis among predictors in Supplementary, with the results presented in the new Fig. S9.

Lines 557–568:

We further evaluated potential predictor correlations and collinearity by calculating pairwise Pearson correlation coefficients among the predictors used in the regression analysis (Fig. S9). The results indicate that some predictors are not fully independent. In both SWC and SGN, sulfate, aerosol liquid water, and $\log_{10}(\text{H}^+)$ show moderate to strong positive correlations, with correlation coefficients of 0.70–0.81 in SWC and 0.75–0.88 in SGN. These correlations are physically expected because aerosol liquid water is thermodynamically calculated in MOSAIC based on inorganic aerosol composition, including sulfate, as well as meteorological conditions. Sulfate also contributes to aerosol acidity and aerosol liquid water formation, while aerosol liquid water can further influence aqueous-phase uptake and processing. Therefore, sulfate, aerosol liquid water, and aerosol acidity are treated here as physically connected components of the aerosol chemical environment. Accordingly, the regression-based relative contributions associated with these covarying predictors should be interpreted as diagnostic indicators of statistical associations with ISOA variability, rather than as a strict decomposition of independent causal effects, because they may partly reflect coupled variations among sulfate, aerosol liquid water, and aerosol acidity.

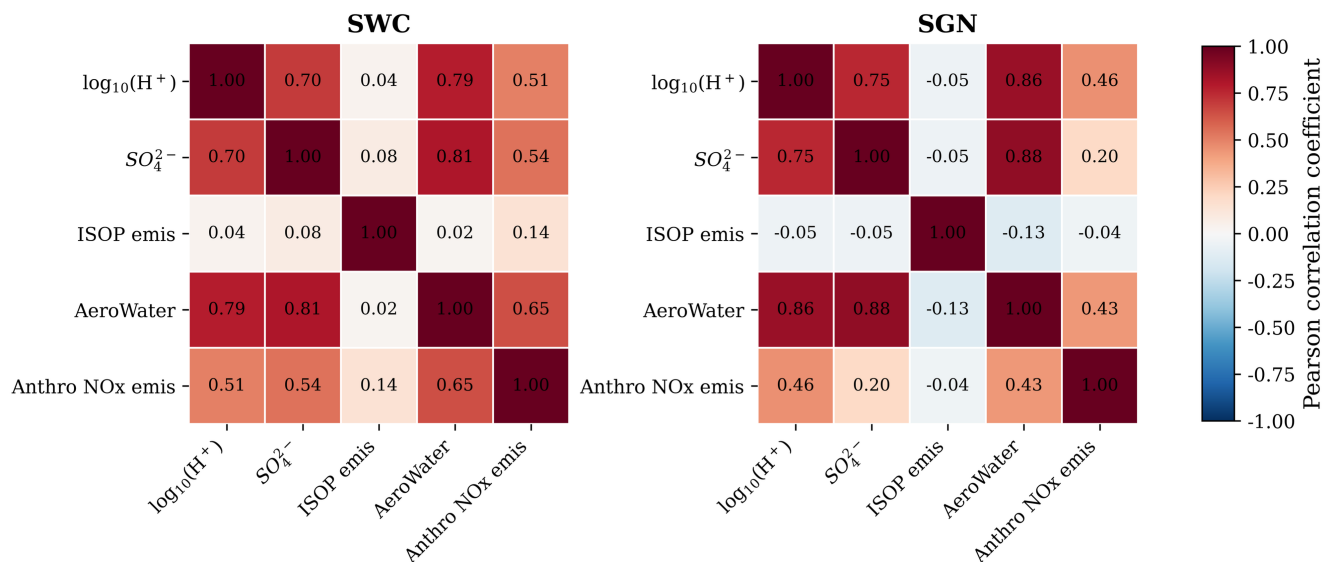


Figure S9: Pairwise Pearson correlation coefficients among predictors used in the multiple linear regression analysis for Southwest China (SWC) and the Shaanxi–Gansu–Ningxia region (SGN). The predictors include aerosol acidity represented by $\log_{10}(\text{H}^+)$, sulfate (SO_4^{2-}), biogenic isoprene emissions (ISOP emis), aerosol liquid water (AeroWater), and anthropogenic NOx emissions (Anthro NOx emis). Warm colors indicate positive correlations, whereas cool colors indicate negative correlations.

Comment#3: Several key assumptions and uncertainties are central to the modeling framework and should be more clearly discussed. For example, lines 151-153, HMML and MAE are assumed to have the same solubility and diffusivity as IEPOX and lines 196-198, SOA yields from epoxide uptake are assumed to be 100% and treated as non-volatile. These assumptions are consistent with prior studies but introduce uncertainty in both magnitude and trends of ISOA that shape interpretation. How do these assumptions influence the reported findings concerning the relative importance of high-NOx vs. low-NOx pathways, sensitivity to sulfate and aerosol liquid water and long-term trend attributions?

Response: We thank the reviewer for this important comment. We agree that these assumptions represent key uncertainties in the current modeling framework and that their implications should be more clearly discussed. We have revised Sect. 2.1.2 to explicitly acknowledge that, due to limited laboratory constraints on the multiphase kinetics of HMML and MAE, both species are represented using the same solubility and diffusivity values as IEPOX. We now clarify that this treatment allows a consistent implementation of reactive uptake for the three epoxides, but introduces uncertainty in the absolute uptake rates of HMML and MAE and therefore in the simulated quantitative importance of the high-NOx pathway relative to the low-NOx pathway.

In addition, we expanded the limitation discussion in Sect. 4 to address the broader implications of these assumptions. Specifically, we now discuss that the assumptions of 100% SOA yield from epoxide reactive uptake and non-volatile epoxide-derived products may affect the absolute ISOA burden and may amplify the apparent sensitivity of ISOA to sulfate, aerosol liquid water, and acidity, because stronger reactive uptake is directly translated into non-volatile SOA formation. We also clarify that these assumptions may influence the quantitative interpretation of long-term trend contributions. Therefore,

the regression-based trend attributions are interpreted as diagnostic statistical associations under the adopted chemical framework, rather than as exact causal contributions independent of these model assumptions. These revisions have been incorporated in Sect. 2.1.2 (lines 179–190) and Sect. 4 (lines 664–672 and lines 675–677).

Lines 179–190:

- 120 Due to limited laboratory constraints on the multiphase kinetics of HMML and MAE, HMML and MAE are treated as IEPOX-like epoxide precursors in the current implementation. This treatment is consistent with previous modeling practice. For example, Pye et al. (2013) treated HMML like MAE in terms of heterogeneous uptake and assumed the particle-phase reaction rate constants of MAE to be the same as those of IEPOX due to the lack of kinetic data. Zhang et al. (2022) also noted that most HMML-related reaction parameters in models are commonly assumed to be the same as those for IEPOX.
- 125 Following these studies, HMML and MAE are assigned the same solubility, diffusivity, and condensed-phase reaction constants as IEPOX in our implementation. Although a recent field-based study has estimated effective uptake parameters for IEPOX and lumped HMML/MAE, these constraints are not directly applicable here because they do not provide a complete set of standalone, compound-specific solubility, diffusivity, and branch-resolved condensed-phase reaction constants for HMML and MAE (Zhu et al., 2025). As a result, this IEPOX-like treatment introduces uncertainty in the
- 130 absolute uptake rates of HMML and MAE and may affect the modeled quantitative partitioning between high-NO_x and low-NO_x ISOA formation pathways.

Lines 664–672:

- HMML and MAE are also represented using the same solubility, diffusivity, and condensed-phase reaction parameters as IEPOX because compound-specific laboratory constraints remain limited. This IEPOX-like treatment introduces uncertainty
- 135 in the absolute uptake rates of high-NO_x epoxides and in the quantitative $\text{ISOA}_{\text{HMML+MAE}}/\text{ISOA}_{\text{IEPOX}}$ ratio. The assumptions of 100% ISOA yield from epoxide reactive uptake and non-volatile epoxide-derived ISOA introduce additional uncertainty, although they are consistent with previous global ISOA modeling studies (Marais et al., 2016; Jo et al., 2019, 2021). Lower effective yields or partial volatility, especially for products such as 2-MT and 2-MGA, could reduce simulated ISOA concentrations and their sensitivity to sulfate, aerosol liquid water, and acidity. Consistent with this need, gas–particle
- 140 partitioning treatments for 2-MT in regional models suggest a useful direction for future improvement in global models (Pye et al., 2018; Shrivastava et al., 2022).

Lines 675–677:

- Taken together, these assumptions mean that the long-term trends and regression-based attributions diagnosed here should be interpreted within the adopted epoxide-focused chemical framework, rather than as exact causal contributions independent of
- 145 model structure and parameterization.

Comment#4: The updated model improves SOA representation but still exhibits substantial positive bias for key tracers (e.g., lines 232–233, normalized mean biases of 47.4% (AIETET) and 81.6% (AHMGA) are reported). While the manuscript notes that similar biases exist in previous studies, the causes of these discrepancies are not explored in detail. Provide additional discussion of possible sources of bias such as: missing competing loss pathways, uncertainties in heterogeneous uptake, representation of precursor chemistry.

Response: We thank the reviewer for this helpful suggestion. We have expanded the discussion of the remaining positive biases in the model evaluation section. In the revised manuscript, we now clarify that the positive biases in AIETET and AHMGA may arise from several sources. First, missing or simplified competing product pathways may cause an over-allocation of epoxide precursors to the explicitly represented ISOA products. For example, IEPOX-derived products may be partly diverted to C5-alkene triols or other particle-phase products that are not explicitly represented here. Second, uncertainties in heterogeneous uptake parameterization, including mass transfer, aerosol phase state, organic-shell viscosity, and phase separation, may affect the simulated product distribution and the abundance of ISOA subspecies. We now also clarify that the current core-shell uptake treatment assumes the same reaction rate coefficient in the organic shell and aqueous core; if phase separation and viscous organic coatings impose stronger diffusion limitations than represented in the model, effective epoxide uptake may be lower in the real atmosphere, leading to overestimation of modelled epoxide-derived ISOA. Third, uncertainties in the multiphase uptake and reaction parameters of HMML/MAE may contribute to the AHMGA bias, because compound-specific constraints for these high-NO_x epoxides remain limited. We also note that similar positive biases have been reported in previous modeling studies, but that the exact sources of bias may differ across models and configurations. These revisions have been incorporated in Sect. 3.1 (lines 299–314).

Lines 299–314:

Several factors may contribute to these positive biases. First, missing or simplified competing loss pathways may cause an over-allocation of epoxide precursors to the explicitly represented ISOA products. For example, a fraction of IEPOX-derived products in the real atmosphere may be diverted to C5-alkene triols or other particle-phase products that are not explicitly represented here, thereby reducing the effective yield of AIETET (Pye et al., 2013). In addition, previous studies have shown that AIETET and AHMGA are sensitive to factors such as pathway branching, mass transfer, reaction kinetics, and aerosol phase state. For example, uncertainties in the relative rates of water addition versus organosulfate formation can affect the predicted product distribution between 2-MT and organosulfate products (Budisulistiorini et al., 2017). Similarly, assumptions related to aerosol phase state, organic-shell viscosity, and phase separation can influence IEPOX reactive uptake and may affect the simulated abundance of IEPOX-derived tracers (Zhang et al., 2018, 2019; Chen et al., 2024b). In particular, the current core-shell uptake treatment assumes the same reaction rate coefficient in the organic shell and aqueous core. If phase separation and viscous organic coatings impose stronger diffusion limitations than represented here, effective epoxide uptake may be reduced in the real atmosphere, and the model may overestimate ISOA formation, especially under conditions with high organic coatings or strong phase separation. For AHMGA, uncertainties in the multiphase uptake and

reaction parameters of HMML/MAE may also contribute to the model bias, because compound-specific constraints for these
180 high-NO_x epoxides remain limited (Zhang et al., 2022; Zhu et al., 2025).

Comment#5: The manuscript focuses on China, which is appropriate given the emissions context. However, the findings likely have broader implications. For example, on lines 80-85, the authors discuss prior work linking sulfate reductions to declines in ISOA in the United States. The present results extend this by showing that inclusion of high-NO_x pathways can alter both magnitude and attribution of ISOA trends. What may be inferred for the US or other regions based on the findings reported here?
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Response: We thank the reviewer for this insightful comment. We agree that although the present study focuses quantitatively on China, the findings have broader mechanistic implications for other regions where biogenic isoprene emissions interact with anthropogenic emissions and aerosol chemical conditions.

190 Previous studies in the United States, especially in the southeastern United States, have shown that ISOA_{IEPOX} formation is strongly influenced by sulfate and aerosol acidity, and that reductions in sulfate can lead to decreases in ISOA_{IEPOX} (e.g., Marais et al., 2016; Budisulistiorini et al., 2017; Liu et al., 2023). Our results are consistent with this general understanding, but further suggest that sulfate reduction alone may not fully explain ISOA trends in regions where high biogenic isoprene emissions overlap with elevated NO_x conditions. By explicitly including high-NO_x epoxide pathways, the model can
195 represent additional HMML/MAE-derived products, which could potentially alter both the magnitude and composition of ISOA and, therefore, could have implications for interpreting long-term ISOA changes.

For the United States, this implies that sulfate reductions probably remain an important driver of declining ISOA_{IEPOX}, especially in the southeastern United States. However, in typical regions where biogenic isoprene emissions increase
200 substantially or anthropogenic NO_x emissions continue to rise, NO_x-dependent epoxide formation might become more relevant, and the simulated response of total ISOA could differ from that inferred from sulfate reductions alone. Therefore, the net ISOA response would likely reflect the combined effects of isoprene emissions and related precursor supply, as well as the heterogeneous reaction environment. More broadly, in other high-isoprene regions such as the Amazon and Central Africa, abundant biogenic isoprene emissions provide sufficient precursor supply and could potentially drive substantial
205 ISOA variability, which may not necessarily follow the influence of sulfate changes alone. In regions strongly affected by urban pollution or increasing anthropogenic NO_x emissions, NO_x-dependent chemistry could also become more relevant for interpreting ISOA changes.

Thus, the broader implication of this work is that ISOA trends in different regions may be better interpreted as the combined
210 outcome of isoprene emissions, NO_x-dependent gas-phase precursor supply, and the heterogeneous reaction environment, with the dominant factors varying among typical regions rather than being universally driven by sulfate changes alone. Given that the present study focuses on China, we have limited this discussion to a qualitative outlook rather than extending

the analysis to other regions. We have added a brief discussion in the outlook section to emphasize that future global-scale quantification of these effects would be important for assessing their broader implications lines 684–687.

- 215 Marais, E. A., Jacob, D. J., Jimenez, J. L., Campuzano-Jost, P., Day, D. A., Hu, W., Krechmer, J., Zhu, L., Kim, P. S., Miller, C. C., Fisher, J. A., Travis, K., Yu, K., Hanisco, T. F., Wolfe, G. M., Arkinson, H. L., Pye, H. O. T., Froyd, K. D., Liao, J., and McNeill, V. F.: Aqueous-phase mechanism for secondary organic aerosol formation from isoprene: application to the southeast United States and co-benefit of SO₂ emission controls, *Atmos. Chem. Phys.*, 16, 1603–1618, <https://doi.org/10.5194/acp-16-1603-2016>, 2016.
- 220 Budisulistiorini, S. H., Nenes, A., Carlton, A. G., Surratt, J. D., McNeill, V. F., and Pye, H. O. T.: Simulating aqueous-phase isoprene-epoxydiol (IEPOX) secondary organic aerosol production during the 2013 Southern Oxidant and Aerosol Study (SOAS), *Environ. Sci. Technol.*, 51, 5026–5034, <https://doi.org/10.1021/acs.est.6b05750>, 2017.
- Liu, Y., Dong, X., Emmons, L. K., Jo, D. S., Liu, Y., Shrivastava, M., Yue, M., Liang, Y., Song, Z., He, X., and Wang, M.: Exploring the factors controlling the long-term trend (1988–2019) of surface organic aerosols in the continental United States by simulations, *J. Geophys. Res.-Atmos.*, 128, e2022JD037935, <https://doi.org/10.1029/2022JD037935>, 2023.
- 225

Lines 684–687:

Future global-scale simulations and attribution analyses would also be useful for evaluating whether the updated ISOA mechanism has broader implications for other high-isoprene regions, where climate change and human activities may shift the relative roles of biogenic precursor supply, anthropogenic emissions, and the heterogeneous aerosol reaction environment in shaping future ISOA responses.

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Minor Comments

Comment#6: Some sections could be streamlined for clarity (e.g., repeated discussion of pathway sensitivities).

Response: We thank the reviewer for this helpful suggestion. We have reviewed the manuscript and streamlined several sections to improve clarity and reduce repetition. In particular, we revised the repeated discussion of pathway sensitivities and consolidated overlapping statements regarding the sensitivities of ISOA formation to precursor supply and heterogeneous reaction conditions. Where appropriate, we shortened redundant explanations and kept the more detailed discussion in the sections most directly related to the corresponding results. These revisions improve the readability of the manuscript without changing the scientific interpretation.

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Comment#7: Consider adding a synthesis figure summarizing regional drivers of ISOA trends.

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Response: We thank the reviewer for this helpful suggestion. This comment is closely related to the Comment#1. In response, we have added a new synthesis schematic, now shown as Fig. 9, to summarize the contrasting regional drivers of ISOA trends in Southwest China (SWC) and the Shaanxi–Gansu–Ningxia region (SGN). The figure explicitly frames regional ISOA formation as the balance between precursor supply, including isoprene and NO_x, and heterogeneous reaction capacity, including sulfate, aerosol liquid water, and aerosol acidity. Specifically, SWC is characterized as a precursor-driven regime, where enhanced biogenic isoprene emissions and gas-phase oxidation products favor ISOA formation, whereas SGN is

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characterized as a reaction-medium-limited regime, where reductions in sulfate and aerosol liquid water weaken heterogeneous uptake and aqueous-phase processing. We have also added a synthesis paragraph in lines 613–620 to clarify this framework and link the figure to the preceding trend and attribution results.

250 **Comment#8: A brief summary of the regression approach in the main text (currently primarily in the supplement) would improve accessibility.**

Response: We thank the reviewer for this helpful suggestion. We have added a brief summary of the multiple linear regression approach in the main text to improve accessibility. The new text describes the construction of the regression framework linking simulated monthly ISOA concentrations to key controlling factors and clarifies its two complementary applications: standardized monthly anomalies were used to diagnose the relative statistical importance of predictors on a common scale, whereas unstandardized monthly anomalies in physical units were used for the trend attribution diagnostic presented in Table 1. This revision has been incorporated in Section 3.3 (lines 528–541).

Lines 528–541:

To quantitatively diagnose the contributions of influential factors and better understand why ISOA trends differ between SWC and SGN, we constructed a multiple linear regression framework linking simulated monthly ISOA concentrations to key controlling factors. This regression framework was used in two complementary ways. Both analyses were based on regional monthly anomalies derived by first spatially averaging the original monthly gridded data over SWC and SGN to obtain regional-mean monthly time series and then removing the mean seasonal cycle. First, these monthly anomalies were standardized to zero mean and unit standard deviation to compare the relative statistical importance of different predictors on a common scale, as summarized in Text S1 and Table S1. This standardized analysis primarily diagnoses the leading predictors of month-to-month ISOA variability. Second, for the trend attribution diagnostic presented in Table 1, we used the same monthly anomalies without standardization, retaining the original physical units of each predictor. Multiple linear regression was subsequently applied to these unstandardized anomalies to obtain sensitivity coefficients in physical units. These sensitivity coefficients (α) describe how regional ISOA responds to changes in each predictor under the regression framework. For each predictor, its contribution to the simulated 20-year ISOA trend ($C/20\text{yr}$) was then estimated by multiplying its regression sensitivity by its own 20-year trend ($dX/20\text{yr}$). The relative contribution of each factor was further expressed as C/dY (%), where dY denotes the simulated 20-year ISOA trend in the corresponding region.

Comment#9: Line 230: “We validated the simulated AIETET against ….” Validated should be evaluated.

Response: We thank the reviewer for this suggestion. We have replaced “validated” with “evaluated” to use more appropriate wording for the model-observation comparison.

Comment#10: Line 308 / Figure 4b imprecise wording: The authors state that “Aerosol pH also varies substantially through the year and is relatively higher in late spring and early summer.” However, Fig. 4b presents standardized

280 seasonal cycles (z-scores), not aerosol pH values. Therefore, the figure does not show the actual pH magnitude or
allow the reader to assess whether pH is chemically “high” in an absolute sense. Please either revise the wording to
indicate that standardized pH anomalies are higher in late spring/early summer, or provide actual monthly pH values,
perhaps in the supplement.

Response: We thank the reviewer for pointing out this imprecise wording. We agree that Fig. 4(b) presents standardized
seasonal cycles rather than absolute aerosol pH values. Therefore, the original wording could be misinterpreted as referring
to the absolute pH magnitude. We have revised the sentence to clarify that the standardized aerosol pH anomaly, rather than
285 the absolute aerosol pH value, is relatively higher in late spring and early summer. This revision has been incorporated in
Sect. 3.2 (lines 401–403).

Lines 401–403:

The standardized sulfate and aerosol liquid water anomalies are positive in winter and become negative in summer, while the
standardized aerosol pH shows positive anomalies in late spring and early summer (Fig. 4(b)).

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Response to Referee #2

295 The authors have updated CAM6-Chem's treatment of isoprene-derived secondary organic aerosol by explicitly representing low- and high-NO_x formation pathways, including IEPOX uptake and key heterogeneous processes. These updates substantially improve agreement with observed ISOA composition and reduce the model's SOA underestimation over China. Their results show that ISOA formation is controlled by regional contrasts. This manuscript presents an important modeling study that addresses a recognized limitation in current global modeling. The work is appropriate for publication in ACP. I have minor comments that would strengthen the manuscript prior to acceptance.

300 We are very grateful to the reviewer for the constructive evaluation and helpful suggestions, which have allowed us to clarify and improve the manuscript. Before addressing the reviewer's comments point by point, we briefly summarize the major revisions made in response to Referee #2. The reviewer's comments are shown in **bold blue text**, while our responses and the corresponding revised manuscript text are shown in black text. Line numbers refer to the revised manuscript.

305 In response to Referee #2, we revised several figures and related descriptions to improve clarity and readability, including the model evaluation figure, regional ISOA composition figure, seasonal pathway comparison, and long-term regional trend figure. We also clarified how the site- and period-matched OA/SOA evaluation was conducted and added discussion on the spatial heterogeneity of the model improvement. In addition, we expanded the discussion of seasonal ISOA composition, added the missing OH standardized seasonal cycle to Fig. 4(b), quantified the September increase in the ISOA_{HMML+MAE}/ISOA_{IEPOX} ratio, and added a brief outlook on the broader implications of the updated ISOA mechanism for other high-isoprene regions. Relevant recent studies suggested by the reviewer were also incorporated into the revised manuscript where appropriate.

Comment#1: line 140: was there an evaluation of the MPAN addition on gas phase performance? Not sure if any obs data is available, if so something that could be added to the SI

315 Response: We thank the reviewer for this helpful suggestion. We agree that evaluating the impact of the added MPAN-related chemistry on gas-phase model performance would be valuable. We searched for available MPAN observations but did not identify suitable public measurements with sufficient spatial and temporal coverage over China to support a robust gas-phase evaluation. Therefore, we did not include a separate MPAN evaluation in the Supplement. Instead, the influence of the MPAN-related update is evaluated indirectly through its downstream high-NO_x ISOA products. Specifically, we evaluated AHMGA concentrations against available molecular-tracer observations and further assessed the relative contributions of HMML/MAE-derived products in the ISOA compositional comparison (Fig. 2). These evaluations provide process-level constraints on the high-NO_x ISOA formation pathway, although we acknowledge that they do not replace a direct gas-phase MPAN evaluation.

Comment#2: Figure 2a,b - can you move the legend so it interferes with data on plot

Response: Thank you for the suggestion. We have revised the legends in Fig. 2(a) and Fig. 2(b) to avoid obscuring the data points. In Fig. 2(a), the legend was moved outside the plotting area. In Fig. 2(b), we reformatted the annotation/legend so that the marker definitions and NMB changes are shown clearly without overlapping with the data.

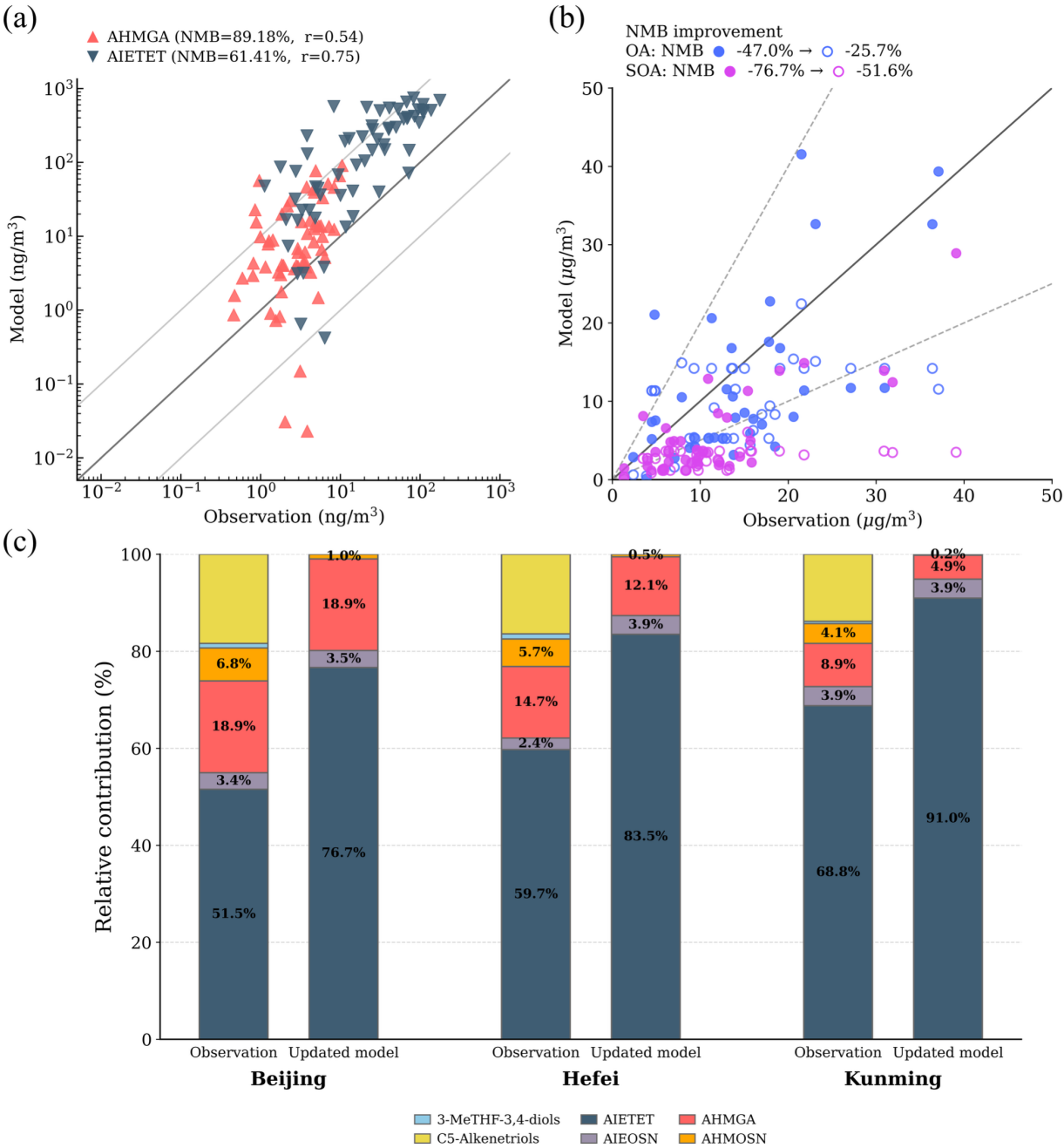


Figure 2: (a) Evaluation of simulated 2-methyltetrols (AIETET) and 2-methylglyceric acid (AHMGA) concentrations against ground-based observations from Ding et al. (2016) (ng m⁻³). Statistical metrics were calculated using monthly means in log space.

330 The dark gray solid line denotes the 1:1 line, and the light gray solid lines denote the factor-of-10 range. (b) Evaluation of
simulated organic aerosol (OA) and secondary organic aerosol (SOA) concentrations before and after the mechanism update
against ground-based observations compiled from Miao et al. (2021) and Chen et al. (2024a) ($\mu\text{g m}^{-3}$). Filled circles represent
335 simulations before the update, while open circles represent simulations after the update. Blue and magenta markers denote OA
and SOA, respectively. The inset annotation summarizes the changes in normalized mean bias (NMB) from the original to the
updated simulation. The dark gray solid line denotes the 1:1 line, and the light gray dashed lines denote the factor-of-two range. (c)
Comparison of ISOA product composition between ground-based observations adapted from Zhang et al. (2022) and the updated
model simulation in this study. The grouped stacked bars show the relative contribution of each ISOA product to total measured
or simulated ISOA at Beijing, Hefei, and Kunming. For each city, the left bar represents the observed composition and the right
bar represents the updated model.

340 **Comment#3: figure 2b - hard to see the changes maybe show differences instead of values**

Response: Thank you for this helpful suggestion. We have revised Fig. 2(b) to make the effect of the mechanism update
more visible. Specifically, we retained the model-observation scatter plot to show the direct comparison with measurements,
but revised the legend to summarize the NMB changes before and after implementing the explicit ISOA mechanism. Filled
circles now denote simulations before the update, while open circles denote simulations after the update. This makes the
345 improvement in OA and SOA simulations more explicit.

Comment#4: figure 2c - hard to see what changed from the update; also hard to see numbers in the pie chart

Response: Thank you for pointing this out. We have replaced the pie charts in Fig. 2(c) with grouped stacked bar charts. The
revised figure places the observed and updated-model compositions side by side for each city, which makes the
compositional differences after the model update easier to compare. The bars are normalized to 100% to show the relative
350 contributions of ISOA products. We also enlarged the percentage labels, and only labeled the major updated-model ISOA
products to improve readability.

Comment#5: figure 3c - this is difficult to read consider portraying in a different way

Response: Thank you for this helpful suggestion. We have revised Fig. 3(c) to improve its readability. We considered
alternative formats, including a stacked-bar representation, but retained the map-based pie-chart format because it
355 simultaneously conveys the geographical locations of the selected regions, the relative composition of ISOA subgroups, and
the regional differences in total ISOA abundance through the pie size. To make the panel clearer, we adjusted the layout of
the pie charts and regional labels, moved the species legend to the top, lightened the map background and provincial
boundaries, and simplified the size reference. These changes make the regional ISOA composition easier to interpret while
preserving the spatial information shown in the original figure.

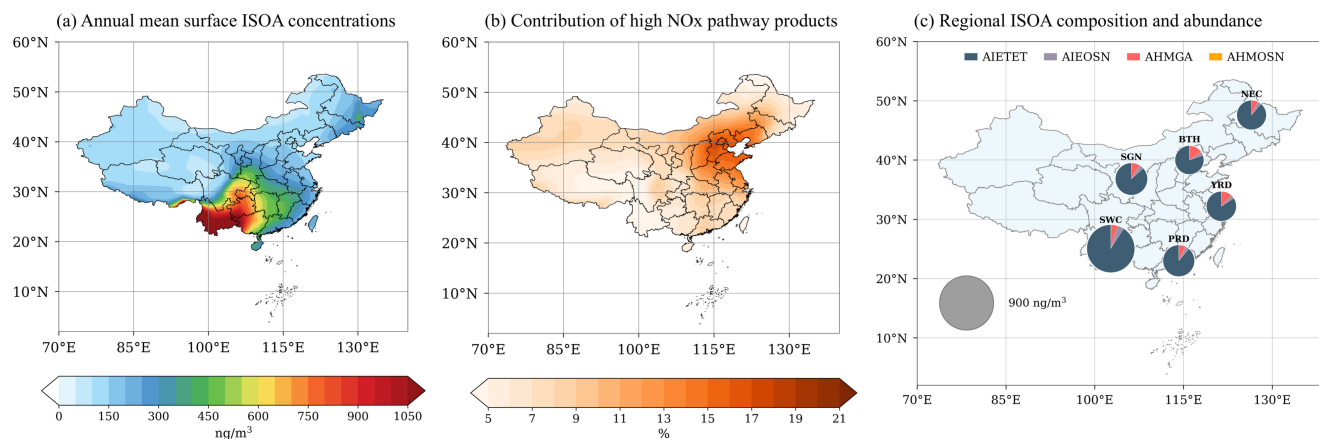


Figure 3: (a) Annual mean surface concentrations of isoprene-derived secondary organic aerosol (ISOA) over China, averaged over the five simulation years (2000, 2006, 2012, 2016, and 2019) (unit: ng m^{-3}). (b) Spatial distribution of the contribution of high-NOx pathway products, including 2-methylglyceric acid (AHMGA) and organosulfate/organonitrate products from the high-NOx pathway (AHMOSN), to annual mean total ISOA over China, averaged over the five simulation years (unit: %). (c) Composition of surface ISOA subspecies in six regions of China, including Southwest China (SWC), the Beijing–Tianjin–Hebei region (BTH), the Yangtze River Delta (YRD), the Pearl River Delta (PRD), the Shaanxi–Gansu–Ningxia region (SGN), and Northeast China (NEC), based on annual mean concentrations averaged over the five simulation years. Pie charts show the fractional contributions of individual ISOA subspecies, and the circle size represents the corresponding surface ISOA concentration (unit: ng m^{-3}).

Comment#6: line 233 - could you expand more on this underestimation exploring space/time of the error. Also were certain times/locations more improved by your updates than others?

Response: We thank the reviewer for this helpful suggestion. We agree that examining the spatial and temporal characteristics of the OA/SOA underestimation is important. However, the available OA/SOA observational datasets are compiled from different field campaigns with uneven spatial and temporal coverage, which limits their use for a robust season-by-season, year-by-year, or region-specific error decomposition. To avoid overinterpreting the sparse observations, we focused on site- and period-matched model-observation comparisons. In the revised manuscript, we have clarified how these comparisons were conducted. Specifically, for all NMB calculations in Sect. 3.1, model outputs were sampled at the corresponding observational site locations and averaged over the same observational periods before calculating the model-observation differences. The paired model and observational values from different sites and time periods were then combined across all paired samples to calculate the NMB, thereby accounting for the site-specific locations and different temporal coverage of the observational datasets. This clarification has been added in Sect. 3.1 (lines 288–292). Therefore, our analysis accounts for the spatial locations and temporal sampling periods of the observations, although the limited observational coverage prevents a more detailed space-time decomposition of the error.

The updated mechanism reduces the overall OA/SOA underestimation in these paired comparisons, with the SOA NMB improving from -76.7% to -51.6% and the OA NMB improving from -47.0% to -25.7% . Because the observations are not sufficient for a statistically robust space-time decomposition, we do not identify a specific region or season as showing

the largest observational improvement. Nevertheless, the model results provide a mechanistic indication of where the update has a larger influence on simulated SOA. As shown in Fig. 3b and Fig. 3c, the contribution of high-NO_x pathway products is spatially heterogeneous, with larger contributions in regions characterized by higher NO_x emissions. This spatial pattern suggests that the model update is not expected to affect simulated OA/SOA uniformly across China, but is more likely to influence site-period comparisons located in or near regions where high-NO_x pathway products make a larger contribution to ISOA. We have added this clarification in Sect. 3.1 (lines 330–333) while avoiding an overinterpretation of the limited observational coverage.

Lines 288–292:

For all normalized mean biases (NMB) calculations in this section, model outputs were sampled at the corresponding observational site locations and averaged over the same observational periods before calculating the model-observation differences. The paired model and observational values from different sites and time periods were then combined across all paired samples to calculate the NMB, thereby accounting for the site-specific locations and different temporal coverage of the observational datasets.

Lines 330–333:

Although the available observations do not support a robust spatiotemporal decomposition of this improvement, the model results suggest that the explicit ISOA representation may affect bulk OA/SOA simulations more strongly in regions with higher anthropogenic NO_x emissions (Fig. S2(c)), where high-NO_x pathway products contribute more substantially to ISOA (Fig. 3(b) and Fig. 3(c)).

Comment#7: line 305 - you include compositional data in the plot but don't discuss it here. suggest adding some text

Response: We thank the reviewer for this helpful suggestion. We have added text to discuss the compositional information shown in Fig. 4(a). In the revised manuscript, we clarify that the warm-season enhancement of total ISOA is dominated by ISOA_{IEPOX}, particularly AIETET, whereas AIEOSN and ISOA_{HMML+MAE} remain minor components of the national mean ISOA despite their warm-season increases. This added discussion connects the compositional information in Fig. 4(a) to the seasonal variability of total ISOA and indicates that the national-scale seasonal cycle is primarily driven by AIETET. This revision has been incorporated in Sect. 3.2 (lines 393–397).

Lines 393–397:

The compositional information in Fig. 4(a) further shows that the warm-season enhancement of ISOA is dominated by ISOA_{IEPOX}, particularly AIETET. In contrast, AIEOSN and ISOA_{HMML+MAE} remain minor components of the national mean ISOA, although they also exhibit higher concentrations during the warm season. Overall, the seasonal cycle of total ISOA at the national scale is primarily driven by AIETET.

Comment#8: line 308 - Figure 4b -missing the OH data?

Response: We thank the reviewer for pointing this out. The OH data were unintentionally omitted from Fig. 4(b) in the previous version. We have now added the standardized seasonal cycle of OH to Fig. 4(b) and updated the corresponding legend.

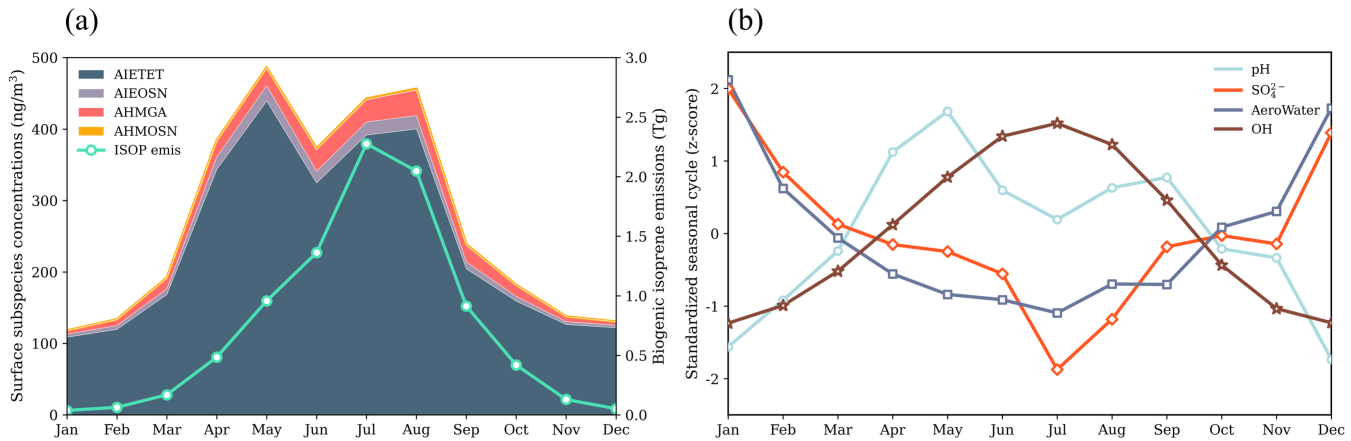


Figure 4: (a) Monthly variations of surface isoprene-derived secondary organic aerosol (ISOA) subspecies (left y axis; unit: ng m^{-3}) and biogenic isoprene emissions (ISOP emis; right y axis; unit: Tg) in China, based on the climatological monthly means averaged over the five simulation years (2000, 2006, 2012, 2016, and 2019). (b) Standardized monthly variations of background chemical and aerosol variables relevant to ISOA formation, including surface aerosol pH, surface sulfate (SO_4^{2-}) concentrations, surface aerosol liquid water (AeroWater) concentrations, and surface hydroxyl radical (OH) concentrations in China, based on the climatological monthly means averaged over the five simulation years.

Comment#9: line 341 quantify "increases markedly"

Response: We thank the reviewer for this suggestion. We have revised the sentence to quantitatively describe the September increase in the $\text{ISOA}_{\text{HMML}+\text{MAE}}/\text{ISOA}_{\text{IEPOX}}$ ratio. Specifically, we now state that the ratio increases from 0.089 in August to 0.114 in September, corresponding to an absolute increase of 0.025 in the dimensionless ratio, or a relative increase of 28.1%. This revision has been incorporated in Section 3.2 (lines 453–455).

Lines 453–455:

As a result, the $\text{ISOA}_{\text{HMML}+\text{MAE}}/\text{ISOA}_{\text{IEPOX}}$ ratio increases from 0.089 in August to 0.114 in September, corresponding to an absolute increase of 0.025 in the dimensionless ratio, or a relative increase of 28.1%, and reaches its annual maximum in September.

Comment#10: figure 5 - pink and yellow seem to wash out on my screen suggest different colors; yellow bar hard to see; maybe put yellow bar on 2nd y axis and represent the ratio as a floating number value above the bars

Response: We thank the reviewer for this helpful suggestion. We have revised Fig. 5 to improve its readability. Specifically, we replaced the previous light pink and yellow colors with a darker blue color for the IEPOX-related quantities and a more visible pink color for the HMML+MAE-related quantities. To make the much smaller HMML+MAE-related values easier to distinguish, we now plot the IEPOX-related bars on the left y axis and the HMML+MAE-related bars on the right y axis in

each panel. The corresponding HMML+MAE-to-IEPOX ratios are shown as black dashed lines with markers, and the monthly ratio values are labeled above the markers. We have also revised the caption of Fig. 5 to clearly describe the updated axis assignments, colors, and ratio annotations.

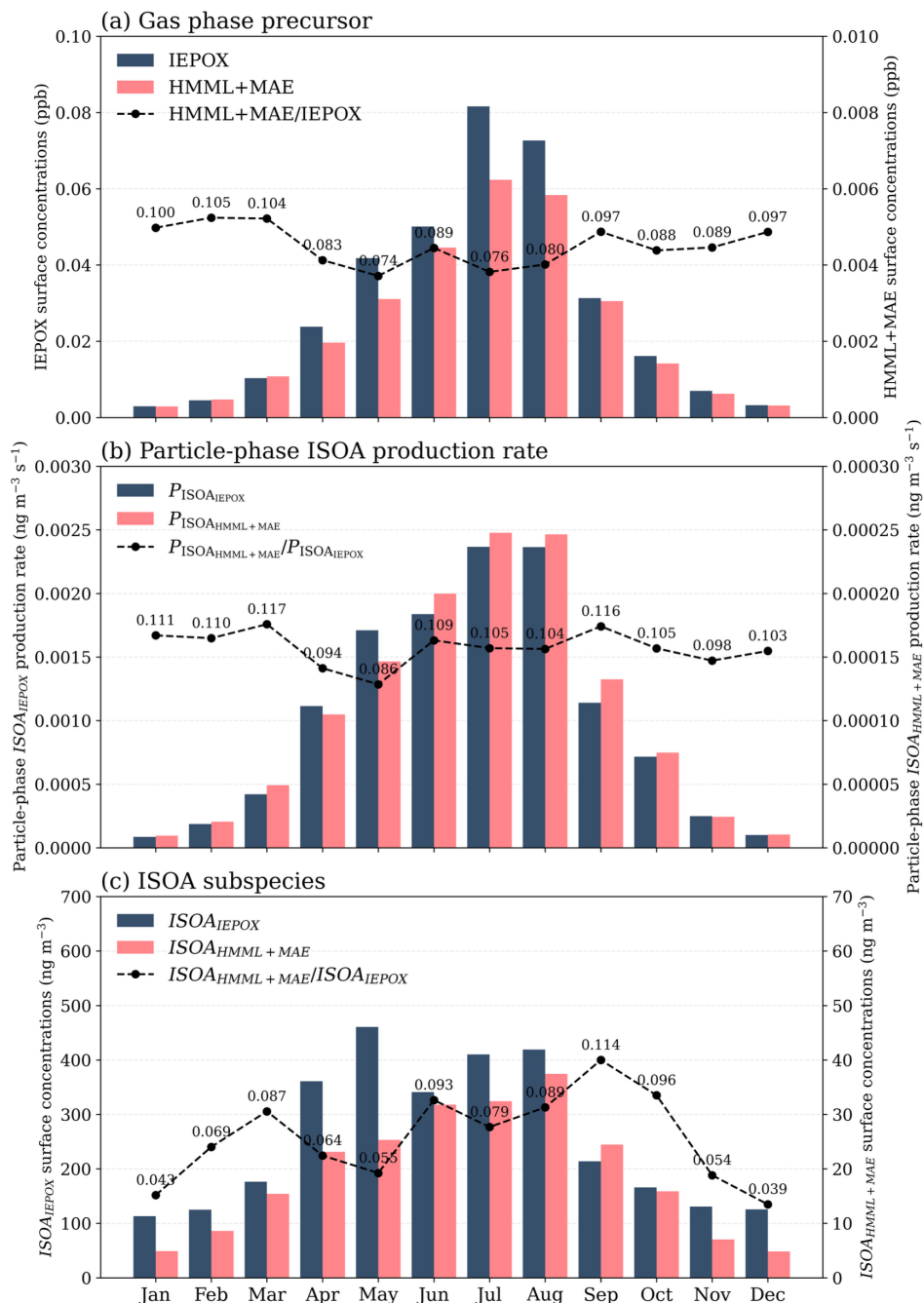


Figure 5: Monthly variations of IEPOX-related and HMML+MAE-related gas-phase precursors, particle-phase production rates, and ISOA concentrations in China, based on the climatological monthly means averaged over the five simulation years (2000, 2006,

2012, 2016, and 2019). (a) Surface concentrations of isoprene epoxydiols (IEPOX; dark-blue bars; left y axis; unit: ppb) and hydroxymethyl-methyl- α -lactone plus methacrylic acid epoxide (HMML + MAE; pink bars; right y axis; unit: ppb). (b) Particle-phase ISOA production rates diagnosed from tagged heterogeneous reactions for the IEPOX pathway ($P_{\text{ISOA}_{\text{IEPOX}}}$; dark-blue bars; left y axis; unit: $\text{ng m}^{-3} \text{ s}^{-1}$) and the HMML+MAE pathway ($P_{\text{ISOA}_{\text{HMML+MAE}}}$; pink bars; right y axis; unit: $\text{ng m}^{-3} \text{ s}^{-1}$). (c) Surface concentrations of ISOA derived from IEPOX ($\text{ISOA}_{\text{IEPOX}}$; dark-blue bars; left y axis; unit: ng m^{-3}) and ISOA derived from HMML and MAE ($\text{ISOA}_{\text{HMML+MAE}}$; pink bars; right y axis; unit: ng m^{-3}). In each panel, the black dashed line denotes the ratio of the HMML+MAE-related quantity to the corresponding IEPOX-related quantity, with monthly ratio values labeled above the markers.

Comment#11: Table 1 - caption spell out SWC SCN

Response: We thank the reviewer for pointing this out. We have revised the caption of Table 1 to spell out the regional abbreviations. The revised caption now defines SWC as Southwest China and SGN as the Shaanxi–Gansu–Ningxia region.

The same definitions have also been added to the caption of Table S1.

Comment#12: Figure 8 - no need to make all these plots different colors since they are in different panels. some of the lighter colors harder to see

Response: We thank the reviewer for this helpful suggestion. We have revised Fig. 8 to improve readability. Specifically, we replaced the lighter colors that were difficult to distinguish on screen with darker, higher-contrast colors, while retaining the overall color consistency between the SWC and SGN panels in each row. We also checked the line and marker visibility to ensure that the different variables can be more clearly distinguished in the revised figure.

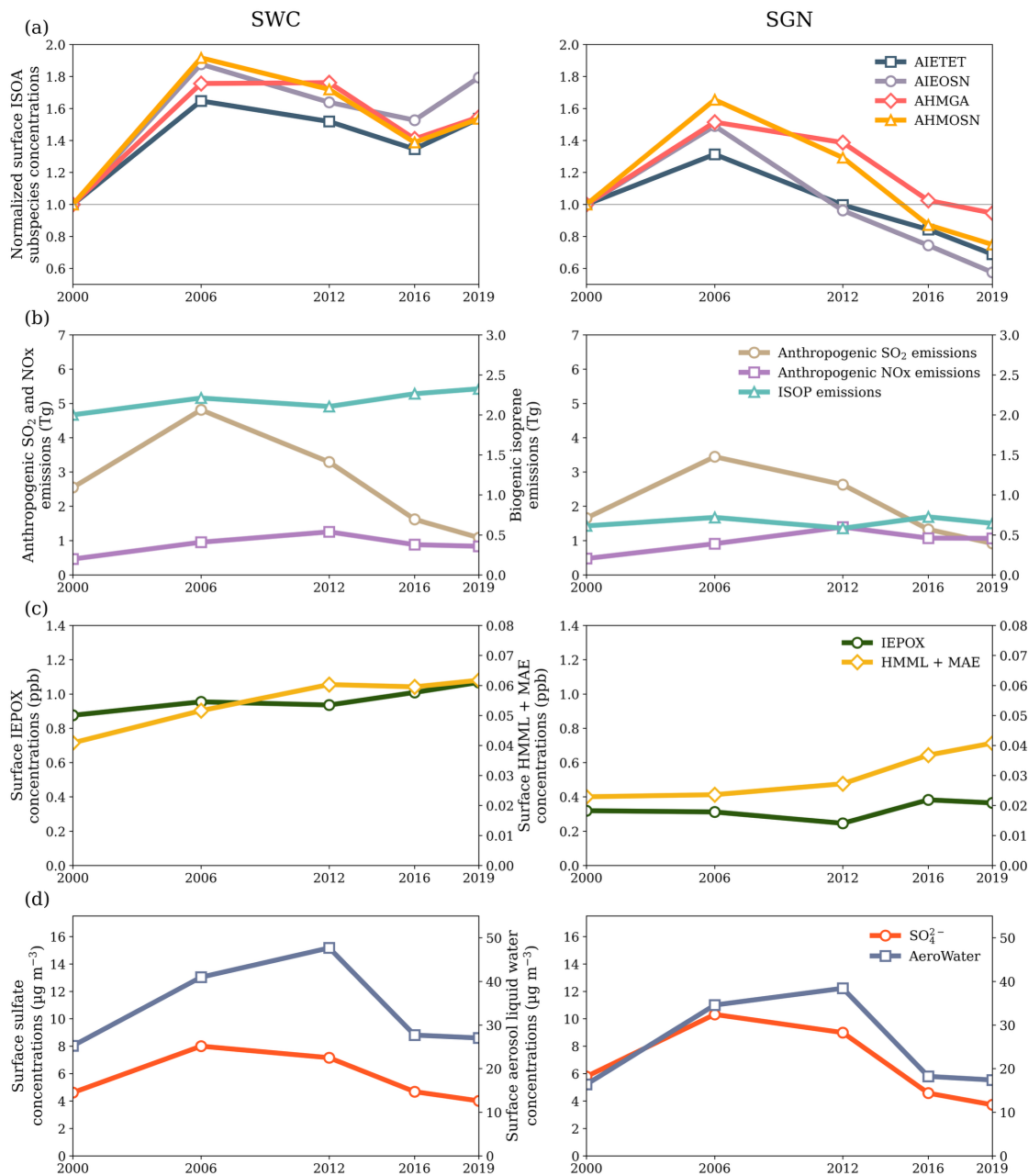


Figure 8: Time series for Southwest China (SWC; left column) and the Shaanxi–Gansu–Ningxia region (SGN; right column), showing (a) normalized surface isoprene-derived secondary organic aerosol (ISOA) subspecies concentrations, including AIETET (dark blue), AIEOSN (gray-purple), AHMGA (rose red), and AHMOSN (earthy yellow). The normalized values are calculated as the ratio of the value in each year to that in 2000; (b) anthropogenic sulfur dioxide (SO₂) emissions (tan; left y axis; unit: Tg) and anthropogenic nitrogen oxides (NO_x) emissions (purple; left y axis; unit: Tg), and biogenic isoprene emissions (blue; right y axis; unit: Tg); (c) surface isoprene epoxydiols (IEPOX) concentrations (dark green; left y axis; unit: ppb) and surface hydroxymethyl-methyl- α -lactone plus methacrylic acid epoxide (HMML + MAE) concentrations (yellow; right y axis; unit: ppb); and (d) surface sulfate (SO₄²⁻) concentrations (red-orange; left y axis; unit: µg m⁻³) and surface aerosol liquid water (AeroWater) concentrations (blue-gray; right y axis; unit: µg m⁻³).

Comment#13: line 500 - could you expand on the future impacts in other regions where IEPOX SOA could be a major source (SE USA, Central Africa, Amazon, etc)

Response: We thank the reviewer for this helpful suggestion. We agree that the updated ISOA mechanism may have broader
480 implications for other high-isoprene regions where ISOA_{IEPOX} could be an important source.

Previous studies in the United States, especially in the southeastern United States, have shown that ISOA_{IEPOX} formation is strongly influenced by sulfate and aerosol acidity, and that reductions in sulfate can lead to decreases in ISOA_{IEPOX} (Marais et al., 2016; Budisulistiorini et al., 2017; Liu et al., 2023). Our results are consistent with this general understanding, but
485 further suggest that sulfate reduction alone may not fully explain ISOA trends in regions where high biogenic isoprene emissions overlap with elevated anthropogenic NO_x influence. By explicitly including high-NO_x epoxide pathways, the model can represent additional HMML/MAE-derived products, which could potentially alter both the magnitude and composition of ISOA and, therefore, may have implications for interpreting long-term ISOA changes.

490 For the United States, this implies that sulfate reductions probably remain an important driver of declining ISOA_{IEPOX}, especially in the southeastern United States. However, in typical regions where biogenic isoprene emissions increase substantially or anthropogenic NO_x emissions continue to rise, NO_x-dependent epoxide formation might become more relevant, and the simulated response of total ISOA could differ from that inferred from sulfate reductions alone. Therefore, the net ISOA response would likely reflect the combined effects of isoprene emissions and related precursor supply, as well
495 as the heterogeneous reaction environment. More broadly, in other high-isoprene regions such as the Amazon and Central Africa, abundant biogenic isoprene emissions provide sufficient precursor supply and could potentially drive substantial ISOA variability, which may not necessarily follow the influence of sulfate changes alone. In regions strongly affected by urban pollution or increasing anthropogenic NO_x emissions, NO_x-dependent chemistry could also become more relevant for interpreting ISOA changes.

500

Thus, the broader implication of this work is that ISOA trends in different regions may be better interpreted as the combined outcome of isoprene emissions, NO_x-dependent gas-phase precursor supply, and the heterogeneous reaction environment, with the dominant factors varying among typical regions rather than being universally driven by sulfate changes alone. Given that the present study focuses on China, we have limited this discussion to a qualitative outlook rather than extending
505 the analysis to other regions. We have added a brief discussion in the outlook section to emphasize that future global-scale quantification of these effects would be important for assessing their broader implications (lines 684–687).

Marais, E. A., Jacob, D. J., Jimenez, J. L., Campuzano-Jost, P., Day, D. A., Hu, W., Krechmer, J., Zhu, L., Kim, P. S., Miller, C. C., Fisher, J. A., Travis, K., Yu, K., Hanisco, T. F., Wolfe, G. M., Arkinson, H. L., Pye, H. O. T., Froyd, K. D., Liao, J., and McNeill, V. F.: Aqueous-phase mechanism for secondary organic aerosol formation from isoprene: application

- 510 to the southeast United States and co-benefit of SO₂ emission controls, *Atmos. Chem. Phys.*, 16, 1603–1618, <https://doi.org/10.5194/acp-16-1603-2016>, 2016.
- Budisulistiorini, S. H., Nenes, A., Carlton, A. G., Surratt, J. D., McNeill, V. F., and Pye, H. O. T.: Simulating aqueous-phase isoprene-epoxydiol (IEPOX) secondary organic aerosol production during the 2013 Southern Oxidant and Aerosol Study (SOAS), *Environ. Sci. Technol.*, 51, 5026–5034, <https://doi.org/10.1021/acs.est.6b05750>, 2017.
- 515 Liu, Y., Dong, X., Emmons, L. K., Jo, D. S., Liu, Y., Shrivastava, M., Yue, M., Liang, Y., Song, Z., He, X., and Wang, M.: Exploring the factors controlling the long-term trend (1988–2019) of surface organic aerosols in the continental United States by simulations, *J. Geophys. Res.-Atmos.*, 128, e2022JD037935, <https://doi.org/10.1029/2022JD037935>, 2023.

Lines 684–687:

- Future global-scale simulations and attribution analyses would also be useful for evaluating whether the updated ISOA
- 520 mechanism has broader implications for other high-isoprene regions, where climate change and human activities may shift the relative roles of biogenic precursor supply, anthropogenic emissions, and the heterogeneous aerosol reaction environment in shaping future ISOA responses.

Consider adding to intro and discussion these recent refs:

- 525 Ng A.E.*, Chen Y., Green J., Farrell S., Surratt J.D., Ault A.P., Turpin B.J., Vizuete W.C (2025) “Regional-Scale Modeling Parameterizations for Secondary Organic Aerosol Formation from Isoprene Epoxydiols: Experimentally Based Evaluation and Optimization” *ACS ES&T Air*, 2, 11, 2625–2637, <https://doi.org/10.1021/acsestair.5c00258>
- 530 Farrell S.L.*, Rasool Q.Z., Pye H.O.T., Zhang Y., Li Y., Chen Y., Wang C.T., Zhang H., Schmedding R., Shiraiwa M., Greene J., Budisulistiorini S.H., Jimenez J.L., Hu W., Surratt J.D., Vizuete W.C (2025) “Simulated reductions in Heterogeneous Isoprene Epoxydiol Reactive Uptake from aerosol morphology in the contiguous United States using the Community Multiscale Air Quality Model (CMAQv5.3.2)” *EGUsphere*, <https://doi.org/10.5194/egusphere-2025-2253>
- 535 Schmedding, R.*, Rasool, Q.Z.*, Zhang, Y., Pye, H.O.T., Zhang, H., Chen, Y., Surratt, J.D., Lopez-Hilfiker, F.D., Thornton, J.A., Goldstein, A.H. and Vizuete, W.C (2020) “Predicting secondary organic aerosol phase state and viscosity and its effect on multiphase chemistry in a regional-scale air quality model.” *Atmospheric Chemistry and Physics* 20(13): 8201–8225.

- Response: We thank the reviewer for suggesting these recent and relevant references. We have considered these studies and
- 540 added them to the Introduction and Discussion where appropriate.

Response to Referee #3

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 NO_x-dependent chemistry scheme that explicitly treats key reactive uptake intermediates IEPOX and HMML/MAE and their respective heterogeneous 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 and seasonal characteristics of ISOA, revealing IEPOX products (low NO_x pathway) dominate ISOA on a nation-scale while HMML/MAE products contribute much less but are more significant in NO_x-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 heterogeneous 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.

We are very grateful to the reviewer for the constructive evaluation and helpful suggestions, which have allowed us to clarify and improve the manuscript. Before addressing the reviewer's comments point by point, we briefly summarize the major revisions made in response to Referee #3. The reviewer's comments are shown in **bold blue text**, while our responses and the corresponding revised manuscript text are shown in black text. Line numbers refer to the revised manuscript.

In response to Referee #3, we substantially revised the model description and implementation of epoxide-derived ISOA formation. Most importantly, we replaced the initially submitted parallel-sink treatment with a relative-rate branching framework, in which total epoxide uptake is first calculated using $k_{aq, total}$ and then partitioned into H₂O-mediated addition and inorganic-nucleophile-addition product classes according to their relative reaction rates. We also clarified the assumptions used for HMML/MAE uptake parameters, revised the MPAN + OH branching ratios following Nguyen et al. (2015), corrected and expanded the description of the aqueous-phase rate expressions, and updated all affected simulations, figures, tables, and attribution analyses. In addition, we expanded the discussion of remaining uncertainties, including core-shell morphology, phase separation, viscosity, product volatility, missing non-epoxide ISOA pathways, cloud-water chemistry, photolytic loss, and discrepancies in OSN-like product fractions.

Major Comments

Comment#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

580 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
585 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.

Response: We thank the reviewer for this constructive suggestion. We agree that placing this work more clearly within the
context of previous global modeling efforts can improve the accessibility and broader relevance of the manuscript. In
response, we have added a dedicated paragraph in the Introduction to summarize what has been accomplished so far in large-
590 scale biogenic SOA modeling, what the present study contributes, and what gaps remain relative to regional models and
measurements.

Specifically, we now describe that representations of biogenic SOA have evolved from simplified empirical or fixed-yield
treatments used in early global models (Chung and Seinfeld, 2002; Chin et al., 2002), through semi-empirical two-product
595 absorptive partitioning models (Odum et al., 1996; Griffin et al., 1999), to volatility-based gas-particle partitioning schemes
(Donahue et al., 2006; Pye and Seinfeld, 2010), and more recently to explicit multiphase reactive uptake parameterizations
for isoprene epoxides (Pye et al., 2013; Budisulistiorini et al., 2017; Jo et al., 2019, 2021; Ng et al., 2025). We also explain
that these developments allow ISOA formation to respond more directly to aerosol liquid water, acidity, sulfate and other
nucleophiles, and particle-phase reaction kinetics (Pye et al., 2013; Marais et al., 2016; Budisulistiorini et al., 2017; Jo et al.,
600 2019, 2021).

We then clarify how the present study builds on these previous developments. The revised Introduction states that this work
extends the CAM6-Chem framework by incorporating high-NO_x epoxide precursors and subsequent heterogeneous
reactions, distinguishing H₂O-mediated nucleophilic addition and inorganic-nucleophile-addition product classes, and
605 evaluating how these updates affect ISOA composition and long-term ISOA trends over China. We further emphasize that
this framework enables us to examine how ISOA trends are jointly controlled by precursor supply and heterogeneous
reaction capacity across different regions. This motivation is particularly relevant for China, where emissions,
meteorological conditions, and oxidation environments exhibit strong regional contrasts (Ding et al., 2016; Li et al., 2018;
Wu et al., 2020; Yang et al., 2017).

610 Finally, we added discussion of the remaining limitations and gaps, including uncertainties in aerosol phase state, phase
separation, organic-shell viscosity, diffusion limitations in the core-shell uptake treatment, limited kinetic constraints for
HMML/MAE uptake, and assumptions related to ISOA yield and product volatility. These revisions have been incorporated
in the Introduction (lines 95–120).

Despite these advances, existing studies still rarely assess long-term ISOA changes by simultaneously considering pathway competition under different NO_x emission backgrounds and the multiphase reaction environment. Given the large regional contrasts in emissions, meteorological conditions, and oxidation environments across China (Ding et al., 2016; Li et al., 2018; Wu et al., 2020; Yang et al., 2017), the dominant factors controlling ISOA formation and change are likely to differ by region. To further explore this question, a model framework is needed that can represent both low-NO_x and high-NO_x epoxide pathways and distinguish their major reaction branches and products. The continuous development of SOA representation in large-scale models provides an important foundation for this purpose. Representations of biogenic SOA have evolved from simplified empirical or fixed-yield treatments used in early global models (Chung and Seinfeld, 2002; Chin et al., 2002; Carlton et al., 2010; Kim et al., 2015), through semi-empirical two-product absorptive partitioning models (Odum et al., 1996; Griffin et al., 1999), to the Volatility Basis Set (VBS) approach (Donahue et al., 2006; Robinson et al., 2007; Pye and Seinfeld, 2010), and more recently to explicit multiphase reactive uptake parameterizations for isoprene epoxides (Pye et al., 2013; Budisulistiorini et al., 2017; Jo et al., 2019, 2021; Ng et al., 2025). These developments allow ISOA formation to respond more directly to aerosol liquid water, acidity, sulfate, and other nucleophiles, and particle-phase reaction kinetics (Pye et al., 2013; Marais et al., 2016; Budisulistiorini et al., 2017; Jo et al., 2019, 2021). Building on this progress, this study extends the CAM6-Chem framework by incorporating high-NO_x epoxide precursors and subsequent heterogeneous reactions, distinguishing between H₂O-mediated nucleophilic addition and inorganic-nucleophile addition product classes, and evaluating how these updates affect ISOA composition and long-term ISOA trends over China. This framework further allows us to examine how ISOA trends are jointly controlled by precursor supply and heterogeneous reaction capacity across different regions. Nevertheless, important uncertainties remain in the current ISOA framework, including the simplified core-shell treatment of epoxide reactive uptake, uncertainties in aerosol phase state, organic-shell viscosity, phase separation, and diffusion limitations, as well as limited kinetic constraints for HMML/MAE uptake. Additional uncertainties arise from the assumptions of 100% ISOA yield and non-volatile epoxide-derived products, and from the possible omission of non-epoxide ISOA pathways in the current framework. Despite these remaining uncertainties, clarifying regional ISOA trends and controls can provide a scientific basis for evaluating how emission reductions jointly affect precursor supply and heterogeneous reaction environments, and for developing more targeted regional air-quality management strategies.

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Comment#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,

- 1. Are the same condensed-phase reaction constants for IEPOX applied to HMML/MAE? What is the literature basis for these choices?

Response: We thank the reviewer for raising this important point. Yes, in the current implementation, HMML and MAE are treated as IEPOX-like epoxide precursors, and the same solubility, diffusivity, and condensed-phase reaction constants used for IEPOX are applied to HMML and MAE. We agree that this assumption should be stated more explicitly and that its literature basis should be clarified. Following Jo et al. (2019, 2021), we adopted the IEPOX heterogeneous uptake framework. Because compound-specific multiphase kinetic constraints for HMML and MAE remain limited, our treatment follows previous modeling practice. Specifically, Pye et al. (2013) treated HMML like MAE in terms of heterogeneous uptake and assumed the particle-phase reaction rate constants of MAE to be the same as those of IEPOX due to the lack of kinetic data. Zhang et al. (2022) also noted that most HMML-related reaction parameters in models are commonly assumed to be the same as those for IEPOX. We therefore clarified in Sect. 2.1.2 that HMML and MAE are assigned the same solubility, diffusivity, and condensed-phase reaction constants as IEPOX in our implementation. We also added a statement to clarify the remaining uncertainty associated with this assumption. Although recent field-based studies have begun to constrain effective uptake-related parameters for IEPOX and lumped HMML/MAE, including pseudo-first-order heterogeneous reaction rate coefficients, reactive uptake coefficients, and aqueous-phase reaction parameter products (Zhu et al., 2025), a complete set of standalone compound-specific condensed-phase reaction constants for HMML and MAE remains unavailable. Therefore, this IEPOX-like treatment introduces uncertainty in the absolute uptake rates of HMML and MAE and may affect the modeled quantitative partitioning between high-NO_x and low-NO_x ISOA formation pathways. These revisions have been incorporated in Sect. 2.1.2 (lines 179–190), and the broader implications of this uncertainty are further discussed in Sect. 4 (lines 664–667).

Lines 179–190:

Due to limited laboratory constraints on the multiphase kinetics of HMML and MAE, HMML and MAE are treated as IEPOX-like epoxide precursors in the current implementation. This treatment is consistent with previous modeling practice. For example, Pye et al. (2013) treated HMML like MAE in terms of heterogeneous uptake and assumed the particle-phase reaction rate constants of MAE to be the same as those of IEPOX due to the lack of kinetic data. Zhang et al. (2022) also noted that most HMML-related reaction parameters in models are commonly assumed to be the same as those for IEPOX.

735 Following these studies, HMML and MAE are assigned the same solubility, diffusivity, and condensed-phase reaction constants as IEPOX in our implementation. Although a recent field-based study has estimated effective uptake parameters for IEPOX and lumped HMML/MAE, these constraints are not directly applicable here because they do not provide a complete set of standalone, compound-specific solubility, diffusivity, and branch-resolved condensed-phase reaction constants for HMML and MAE (Zhu et al., 2025). As a result, this IEPOX-like treatment introduces uncertainty in the absolute uptake rates of HMML and MAE and may affect the modeled quantitative partitioning between high-NO_x and low-NO_x ISOA formation pathways.
740

Lines 664–667:

HMML and MAE are also represented using the same solubility, diffusivity, and condensed-phase reaction parameters as IEPOX because compound-specific laboratory constraints remain limited. This IEPOX-like treatment introduces uncertainty in the absolute uptake rates of high-NO_x epoxides and in the quantitative ISOA_{HMML+MAE}/ISOA_{IEPOX} ratio.

745 - 2. 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 k_{aq} ?

Response: We thank the reviewer for this insightful comment. This question prompted us to carefully revisit the implementation of the formulation used to represent ISOA speciation from epoxide precursors in the original submission. In the initially submitted implementation, ISOA formation pathways for IEPOX, HMML, and MAE were represented as multiple parallel heterogeneous uptake reactions. Each product-forming pathway directly consumed the same gas-phase epoxide precursor using a distinct channel-specific reactive uptake coefficient derived from its respective aqueous-phase rate expression. As a result, ISOA speciation was effectively determined at the level of independent uptake fluxes, rather than being constrained by a single total uptake rate followed by internal partitioning among competing reaction channels. This approach allowed each channel to act as an independent sink of the precursor and resulted in the inorganic-nucleophile addition channel receiving an artificially enhanced share of gas-phase precursor uptake flux, leading to an overestimation of the corresponding inorganic-nucleophile addition products.
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Following the reviewer's suggestion and consistent with Budisulistiorini et al. (2017), we have revised the formulation to a relative-rate branching framework. In essence, the implementation used in the original submission treated epoxide uptake as multiple parallel sinks, whereas the revised implementation treats it as a single total uptake process followed by competitive branching into different product classes.
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In the revised implementation, a single total pseudo-first-order aqueous-phase rate constant $k_{aq,total}$ is first calculated as the sum of the particle-phase reaction channels (H₂O-mediated nucleophilic addition and inorganic-nucleophile addition channels) considered here: $k_{aq,total} = k_{H^+}[H^+] + k_{nuc}([SO_4^{2-}] + [NO_3^-])[H^+] + k_{HSO_4^-}[HSO_4^-]$. This total rate is used to compute the reactive uptake coefficient (γ) and the total uptake flux for each precursor. ISOA speciation is then determined
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diagnostically by partitioning the total uptake flux according to the fractional contribution of each reaction channel to $k_{aq,total}$. Specifically, the branching ratio for the H₂O-mediated nucleophilic addition product class is calculated as $k_{aq,H_2O}/k_{aq,total} = k_H[H^+]/(k_H[H^+] + k_{nuc}([SO_4^{2-}] + [NO_3^-])[H^+] + k_{HSO_4^-}[HSO_4^-])$, whereas the branching ratio for the inorganic-nucleophile-addition product class is calculated as $k_{aq,SO_4/NO_3/HSO_4}/k_{aq,total} = (k_{nuc}([SO_4^{2-}] + [NO_3^-])[H^+] + k_{HSO_4^-}[HSO_4^-])/(k_H[H^+] + k_{nuc}([SO_4^{2-}] + [NO_3^-])[H^+] + k_{HSO_4^-}[HSO_4^-])$. The total particle-phase ISOA production is then distributed into H₂O-mediated nucleophilic addition products and inorganic-nucleophile addition products according to these branching ratios. This treatment ensures that the total uptake of each precursor is governed by the full particle-phase reaction rate constant, while the product distribution reflects the relative competition among nucleophilic addition pathways. This treatment is analogous to Budisulistiorini et al. (2017), who determined IEPOX-SOA speciation between tetrols and organosulfates based on the relative rates of precursor conversion to these products.

This revision leads to several noteworthy differences in the simulated results. First, the absolute concentrations of inorganic-nucleophile addition products (AIEOSN and AHMOSN) are reduced, as these species are no longer treated as independent uptake sinks but instead receive only their fractional share of the total epoxide uptake (Figure R3). Second, the relative contribution of individual ISOA subclasses is modified, reflecting a non-uniform redistribution between H₂O-mediated nucleophilic addition products and inorganic-nucleophile addition products (Figure R1). This leads to updated values in the trend attribution analysis and changes in the interannual variability of specific ISOA components (Figure R2 and Figure R4), as these diagnostics depend on how ISOA is partitioned among chemically distinct formation pathways, rather than on a simple uniform scaling of total ISOA. Third, the regression-based attribution coefficients for the driving factors considered are revised, leading to updated quantitative estimates in the trend decomposition. The revised regression coefficients are reported in Table 1 of the revised manuscript and Table S1 in the revised Supplement. The figures shown below are selected representative examples illustrating the major changes in absolute concentrations, relative contributions, interannual variability, and long-term trends. All other affected results, figures, tables, and quantitative analyses have also been updated accordingly in the revised manuscript and supplement.

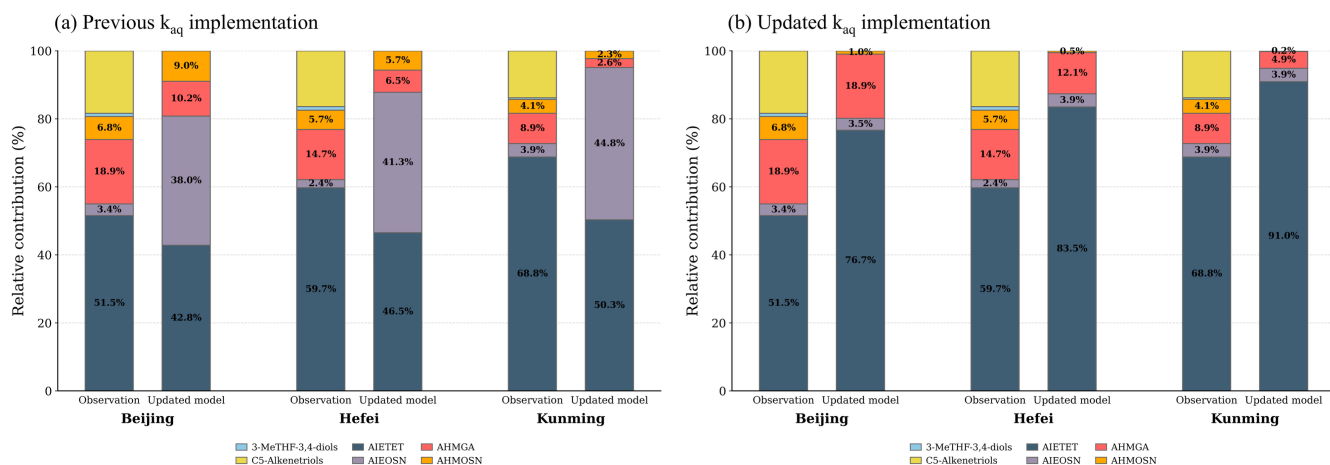


Figure R1: Comparison of ISOA product composition between ground-based observations adapted from Zhang et al. (2022) and the model simulation in this study, corresponding to the observation-model comparison shown in the original Figure 2c in the manuscript. The grouped stacked bars show the relative contribution of each ISOA product to total measured or simulated ISOA at Beijing, Hefei, and Kunming. For each city, the left bar represents the observed composition and the right bar represents the corresponding model simulation. Panel (a) shows results obtained with the previous k_{aq} implementation, in which product-forming pathways were treated as independent uptake sinks. Panel (b) shows results obtained with the updated k_{aq} implementation, in which total epoxide uptake is first calculated and then partitioned among product classes using the relative-rate branching framework.

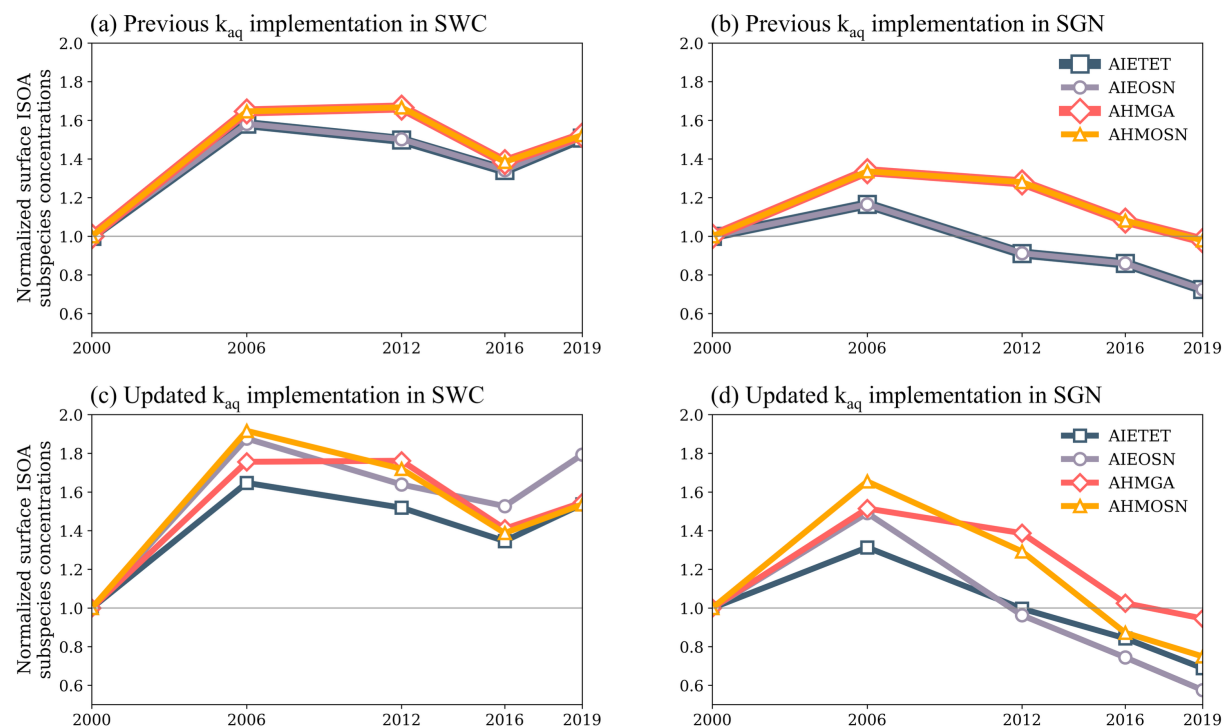
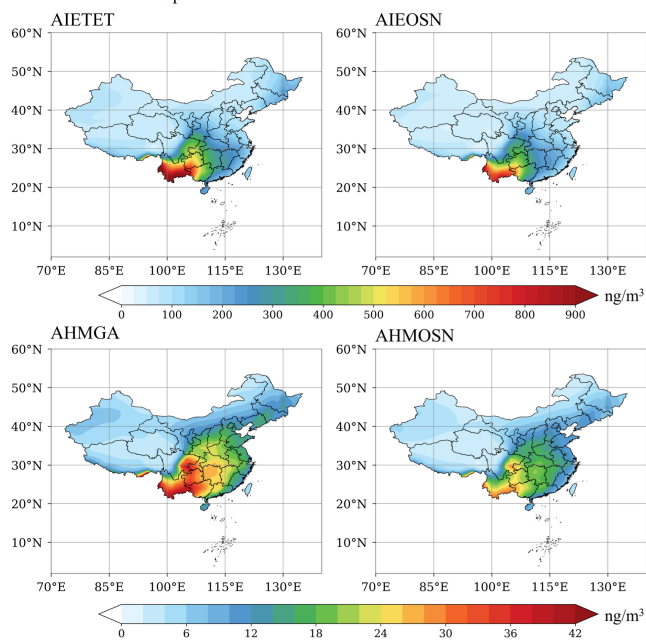


Figure R2: Comparison of the time series of normalized surface isoprene-derived secondary organic aerosol (ISOA) subspecies concentrations corresponding to the original Figure 8a in the manuscript. Results are shown for Southwest China (SWC) and the

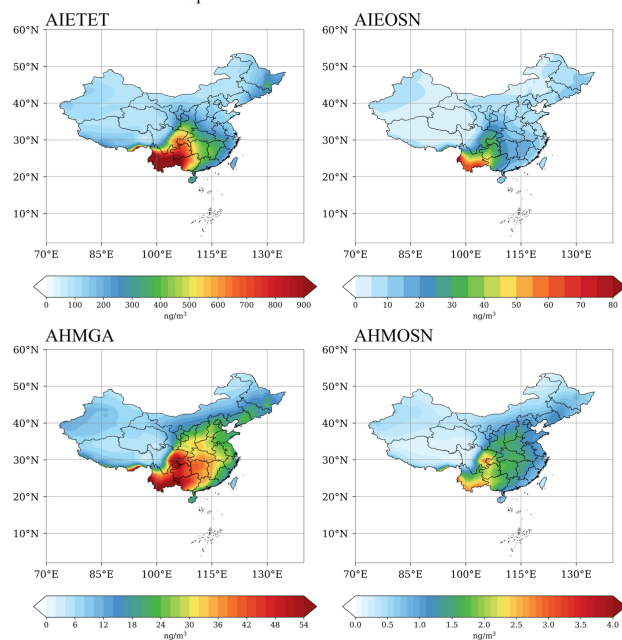
805 Shaanxi–Gansu–Ningxia region (SGN). Panels (a) and (b) show results obtained with the previous k_{aq} implementation, in which product-forming pathways were treated as independent uptake sinks, for SWC and SGN, respectively, whereas panels (c) and (d) show the corresponding results obtained with the updated k_{aq} implementation, in which total epoxide uptake is first calculated and then partitioned among product classes using the relative-rate branching framework. The normalized values are calculated as the ratio of the value in each year to that in 2000. AIETET, AIEOSN, AHMGA, and AHMOSN are shown in dark blue, gray-purple, rose red, and orange, respectively.

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(a) Previous k_{aq} implementation



(b) Updated k_{aq} implementation



815 **Figure R3: Comparison of annual mean surface concentrations of four isoprene-derived secondary organic aerosol (ISOA) subspecies (AIETET, AIEOSN, AHMGA, and AHMOSN) over China, averaged over the five simulation years (2000, 2006, 2012, 2016, and 2019) (unit: ng m^{-3}), corresponding to the original Figure S1 in the Supplement. Panel (a) shows results obtained with the previous k_{aq} implementation, in which product-forming pathways were treated as independent uptake sinks, while panel (b) shows results obtained with the updated k_{aq} implementation, in which total epoxide uptake is first calculated and then partitioned among product classes using the relative-rate branching framework.**

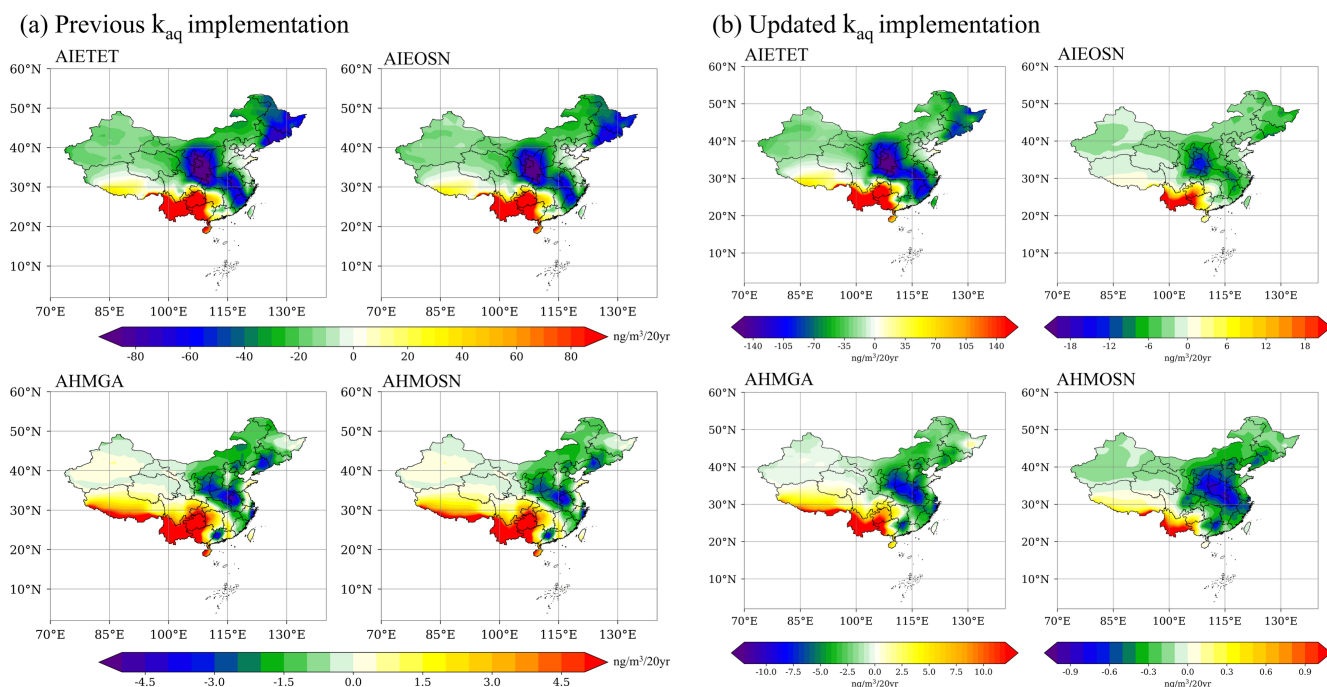


Figure R4: Comparison of long-term trends in annual mean surface concentrations of four isoprene-derived secondary organic aerosol (ISOA) subspecies (AIETET, AIEOSN, AHMGA, and AHMOSN) surface concentrations (ng m^{-3} per 20 years) in China from 2000 to 2019, corresponding to the original Figure S4 in the Supplement. Panel (a) shows results obtained with the previous k_{aq} implementation, in which product-forming pathways were treated as independent uptake sinks, while panel (b) shows results obtained with the updated k_{aq} implementation, in which total epoxide uptake is first calculated and then partitioned among product classes using the relative-rate branching framework.

Importantly, these updates do not alter the core conclusions of the study. The revised implementation primarily affects the quantitative partitioning among ISOA subspecies and the corresponding numerical values in the attribution analysis, while the main scientific interpretations remain unchanged: the updated mechanism improves the representation of ISOA magnitude and composition in CAM6-Chem; IEPOX remains the dominant ISOA formation pathway at the national scale, although the HMML/MAE pathway becomes more important regionally and seasonally under high-NO_x conditions; and the long-term ISOA trend over China remains slightly negative at the national scale but shows strong regional heterogeneity, with increases in SWC mainly associated with enhanced biogenic isoprene emissions and decreases in SGN mainly associated with declining sulfate. We have revised the relevant discussion and conclusions throughout the manuscript and supplement accordingly. The revised description of the updated model implementation is provided in Sect. 2.12, lines 196–242.

Lines 196–242:

Subsequently, following the resistor model equation of Gaston et al. (2014), this study calculates the reactive uptake coefficient γ for IEPOX, HMML, and MAE (Gaston et al., 2014). The governing expression is:

$$\frac{1}{\gamma} = \frac{\omega R_p}{4D_{\text{gas}}} + \frac{1}{\alpha} + \frac{\omega R_p}{4RT H_{\text{org}} D_{\text{org}} (q_{\text{org}}^* F - 1)}, \quad (1)$$

Where γ represents the reactive uptake coefficient, ω is the mean molecular speed of epoxides (m s^{-1}), R_p is the particle radius (m), D_{gas} is the gas-phase diffusion coefficient of epoxides ($10^{-5} \text{ m}^2 \text{ s}^{-1}$), α is the mass accommodation coefficient (0.1), R is the universal gas constant ($8.2057 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1}$), T is temperature (K), H_{org} is the Henry's law coefficient in the organic layer ($2 \times 10^6 \text{ M atm}^{-1}$), and D_{org} is the diffusion coefficient of epoxides in the organic layer. The term F is calculated as:

$$F = \frac{\coth(q_{\text{org}}) + h(q_{\text{aq}}, q_{\text{org}}^*)}{1 + \coth(q_{\text{org}}) h(q_{\text{aq}}, q_{\text{org}}^*)}, \quad (2)$$

Where the function $h(q_{\text{aq}}, q_{\text{org}}^*)$ is given by:

$$h(q_{\text{aq}}, q_{\text{org}}^*) = -\tanh(q_{\text{org}}^*) \frac{\frac{H_{\text{aq}} D_{\text{aq}}}{H_{\text{org}} D_{\text{org}}} (q_{\text{aq}} \coth(q_{\text{aq}}) - 1) - (q_{\text{org}}^* \coth(q_{\text{org}}^*) - 1)}{\frac{H_{\text{aq}} D_{\text{aq}}}{H_{\text{org}} D_{\text{org}}} (q_{\text{aq}} \coth(q_{\text{aq}}) - 1) - (q_{\text{org}}^* \tanh(q_{\text{org}}^*) - 1)}, \quad (3)$$

Here, H_{aq} is the Henry's law coefficient in the aqueous core ($1.7 \times 10^7 \text{ M atm}^{-1}$), and D_{aq} is the diffusion coefficient of epoxides in the aqueous core ($10^{-9} \text{ m}^2 \text{ s}^{-1}$). The variables q_{org} , q_{aq} , and q_{org}^* are defined as:

$$q_{\text{org}} = R_p \sqrt{\frac{k_{\text{org}}}{D_{\text{org}}}}, \quad (4)$$

$$q_{\text{aq}} = R_c \sqrt{\frac{k_{\text{aq, total}}}{D_{\text{aq}}}}, \quad (5)$$

$$q_{\text{org}}^* = \frac{R_c}{R_p} q_{\text{org}}, \quad (6)$$

Where R_c is the inorganic aqueous core radius (m), k_{org} is the pseudo-first-order reaction rate constant of epoxides in the organic shell (s^{-1}), and $k_{\text{aq, total}}$ is the total pseudo-first-order aqueous-phase reaction rate constant (s^{-1}), calculated as the sum of all particle-phase reaction channels that consume each precursor:

$$k_{\text{aq, total}} = k_{\text{H}^+} [\text{H}^+] + k_{\text{nuc}} ([\text{SO}_4^{2-}] + [\text{NO}_3^-]) [\text{H}^+] + k_{\text{HSO}_4^-} [\text{HSO}_4^-], \quad (7)$$

The first term represents the acid-catalyzed ring-opening followed by nucleophilic addition of aerosol liquid water, leading to H_2O -mediated nucleophilic addition products. Here, k_{H^+} is the corresponding effective H_2O -mediated nucleophilic addition rate constant ($0.036 \text{ M}^{-1} \text{ s}^{-1}$), with aerosol liquid water treated as the solvent and included implicitly, and $[\text{H}^+]$ is the proton concentration (M). The second term represents acid-catalyzed ring opening followed by nucleophilic addition of sulfate and nitrate ions, leading to organosulfates and organonitrates. Here, k_{nuc} is the third-order rate constant for sulfate- and nitrate-addition reactions ($2 \times 10^{-4} \text{ M}^{-2} \text{ s}^{-1}$), and $([\text{SO}_4^{2-}] + [\text{NO}_3^-])$ is the concentration of sulfate and nitrate ions (M).

The third term represents concerted protonation and nucleophilic addition by bisulfate, leading to organosulfates. $k_{\text{HSO}_4^-}$ is the reaction rate constant due to the presence of bisulfate ($7.3 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$), and $[\text{HSO}_4^-]$ is the bisulfate concentration (M).

865 For each precursor considered here, including IEPOX, HMML, and MAE, $k_{\text{aq,total}}$ is used to calculate the reactive uptake coefficient and the total uptake flux. The resulting particle-phase ISOA production is then distributed into the H_2O -mediated nucleophilic addition and inorganic-nucleophile addition product classes according to the relative contribution of each reaction channel to $k_{\text{aq,total}}$. The H_2O -mediated nucleophilic addition class is represented by the $k_{\text{H}^+}[\text{H}^+]$ channel, whereas the inorganic-nucleophile addition class combines the sulfate-, nitrate-, and bisulfate-assisted channels, which are
870 collectively represented by $k_{\text{nuc}}([\text{SO}_4^{2-}] + [\text{NO}_3^-])[\text{H}^+] + k_{\text{HSO}_4^-}[\text{HSO}_4^-]$. The corresponding branching ratios for the two product classes are defined as $\text{BR}_{\text{H}_2\text{O}}$ and $\text{BR}_{\text{SO}_4/\text{NO}_3/\text{HSO}_4}$, respectively:

$$\text{BR}_{\text{H}_2\text{O}} = \frac{k_{\text{aq,H}_2\text{O}}}{k_{\text{aq,total}}} = \frac{k_{\text{H}^+}[\text{H}^+]}{k_{\text{aq,total}}} \quad (8)$$

$$\text{BR}_{\text{SO}_4/\text{NO}_3/\text{HSO}_4} = \frac{k_{\text{aq,SO}_4/\text{NO}_3/\text{HSO}_4}}{k_{\text{aq,total}}} = \frac{k_{\text{nuc}}([\text{SO}_4^{2-}] + [\text{NO}_3^-])[\text{H}^+] + k_{\text{HSO}_4^-}[\text{HSO}_4^-]}{k_{\text{aq,total}}} \quad (9)$$

This relative-rate branching treatment follows the approach of Budisulistiorini et al. (2017), in which ISOA_{IEPOX} speciation
875 between tetrols and organosulfates was determined from the relative rates of precursor conversion to these products. This study follows the approach of Jo et al. (2021), where the reactivity of epoxides in the organic shell was parameterized with the same reaction rate constant as in the aqueous phase ($k_{\text{org}} = k_{\text{aq,total}}$). This treatment follows the Jo et al. (2019, 2021) core-shell framework and represents a simplifying assumption, because phase separation, organic-shell viscosity, and differences in acidity between the inorganic core and organic shell may alter epoxide diffusion and reactivity (Schmedding et al., 2020; Farrell et al., 2025). Furthermore, considering the strong sensitivity of D_{org} to relative humidity (RH) in the
880 atmosphere, this study accounts for the RH dependence of D_{org} , as described in Table S3 of Zhang et al. (2018) (Zhang et al., 2018).

885 - 3. 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.

Zhang, Yue, Yuzhi Chen, Ziyang 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>.

890 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>.

Response: We thank the reviewer for this important comment. We agree that the core-shell treatment and the assumption of identical reactivity in the organic shell and aqueous core represent important simplifications in the current reactive uptake

895 parameterization. In the revised manuscript, we have clarified in Sect. 2.1.2 that the model follows the Jo et al. (2019, 2021) core-shell framework, in which the reactivity of epoxides in the organic shell is parameterized using the same effective reaction rate coefficient as in the aqueous phase. We now explicitly state that this treatment should be regarded as a simplifying assumption because phase separation, organic-shell viscosity, and differences in acidity between the inorganic core and organic shell may alter epoxide diffusion and reactivity. We have also expanded the discussion in Sect. 3.1 and the
900 limitation discussion in Sect. 4 to address the implications of this assumption. Specifically, we now discuss that phase separation and viscous organic coatings may impose additional diffusion limitations on epoxide reactive uptake; therefore, the assumption of identical reactivity in both phases may lead to overestimation of epoxide-derived ISOA under conditions with strong phase separation or highly viscous organic coatings. These revisions have been incorporated in Sect. 2.1.2 (lines 235–240), Sect. 3.1 (lines 308–312), and Sect. 4 (lines 660–664). We also thank the reviewer for pointing us to the relevant
905 studies by Zhang et al. (2019) and Chen et al. (2024b), which have been incorporated into the revised manuscript to support the discussion.

Lines 235–240:

This study follows the approach of Jo et al. (2021), where the reactivity of epoxides in the organic shell was parameterized with the same reaction rate constant as in the aqueous phase ($k_{\text{org}}=k_{\text{aq,total}}$). This treatment follows the Jo et al. (2019, 2021)
910 core-shell framework and represents a simplifying assumption, because phase separation, organic-shell viscosity, and differences in acidity between the inorganic core and organic shell may alter epoxide diffusion and reactivity (Schmedding et al., 2020; Farrell et al., 2025).

Lines 308–312:

In particular, the current core-shell uptake treatment assumes the same reaction rate coefficient in the organic shell and
915 aqueous core. If phase separation and viscous organic coatings impose stronger diffusion limitations than represented here, effective epoxide uptake may be reduced in the real atmosphere, and the model may overestimate ISOA formation, especially under conditions with high organic coatings or strong phase separation.

Lines 660–664:

As described in Sect. 2.1.2, the model follows a core-shell treatment in which the organic shell and aqueous core are
920 assumed to have the same reaction rate coefficient. Because phase separation and increased organic-shell viscosity can limit epoxide diffusion and reactive uptake, this assumption may overestimate epoxide-derived ISOA under strongly phase-separated or highly viscous conditions (Zhang et al., 2019; Schmedding et al., 2020; Chen et al., 2024b; Farrell et al., 2025).

Chen, Y., Ng, A. E., Green, J., Zhang, Y., Riva, M., Riedel, T. P., Pye, H. O. T., Lei, Z., Olson, N. E., Cooke, M. E., Zhang, Z., Vizuite, W., Gold, A., Turpin, B. J., Ault, A. P., and Surratt, J. D.: Applying a phase-separation parameterization in
925 modeling secondary organic aerosol formation from acid-driven reactive uptake of isoprene epoxydiols under humid conditions, ACS ES&T Air, 1, 511–524, <https://doi.org/10.1021/acsestair.4c00002>, 2024.

- Jo, D. S., Hodzic, A., Emmons, L. K., Marais, E. A., Peng, Z., Nault, B. A., Hu, W., Campuzano-Jost, P., and Jimenez, J. L.: A simplified parameterization of isoprene-epoxydiol-derived secondary organic aerosol (IEPOX-SOA) for global chemistry and climate models: a case study with GEOS-Chem v11-02-rc, *Geosci. Model Dev.*, 12, 2983–3000, <https://doi.org/10.5194/gmd-12-2983-2019>, 2019.
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- Zhang, Y., Chen, Y., Lei, Z., Olson, N. E., Riva, M., Koss, A. R., Zhang, Z., Gold, A., Jayne, J. T., Worsnop, D. R., Onasch, T. B., Kroll, J. H., Turpin, B. J., Ault, A. P., and Surratt, J. D.: Joint impacts of acidity and viscosity on the formation of secondary organic aerosol from isoprene epoxydiols (IEPOX) in phase-separated particles, *ACS Earth Space Chem.*, 3, 2646–2658, <https://doi.org/10.1021/acsearthspacechem.9b00209>, 2019.

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.

Response: We thank the reviewer for these detailed and constructive questions. In addition to the clarifications above, we have added a limitations discussion in Sect. 4 to clarify how these assumptions may affect the evaluation against observations and the interpretation of long-term trend analyses. We now state that the IEPOX-like treatment of HMML/MAE, the core-shell assumption of identical reactivity in the organic and aqueous phases, and the assumptions of 100 % SOA yield and non-volatile products may influence the absolute ISOA magnitude, pathway partitioning, sensitivity to sulfate/aerosol liquid water/acidity, and quantitative trend attribution. Accordingly, pathway-specific contributions and regression-based trend attributions are interpreted as diagnostic results under the adopted chemical framework rather than exact causal contributions independent of these model assumptions. These additions have been incorporated in Sect. 4 (lines 659–677).

Lines 659–677:

Future model development should further address several simplifying assumptions in the current epoxide reactive uptake parameterization. As described in Sect. 2.1.2, the model follows a core-shell treatment in which the organic shell and aqueous core are assumed to have the same reaction rate coefficient. Because phase separation and increased organic-shell viscosity can limit epoxide diffusion and reactive uptake, this assumption may overestimate epoxide-derived ISOA under strongly phase-separated or highly viscous conditions (Zhang et al., 2019; Schmedding et al., 2020; Chen et al., 2024b; Farrell et al., 2025). HMML and MAE are also represented using the same solubility, diffusivity, and condensed-phase reaction parameters as IEPOX because compound-specific laboratory constraints remain limited. This IEPOX-like treatment introduces uncertainty in the absolute uptake rates of high-NO_x epoxides and in the quantitative ISOA_{HMML+MAE}/ISOA_{IEPOX} ratio. The assumptions of 100% ISOA yield from epoxide reactive uptake and non-volatile epoxide-derived ISOA introduce additional uncertainty, although they are consistent with previous global ISOA modeling studies (Marais et al., 2016; Jo et al., 2019, 2021). Lower effective yields or partial volatility, especially for products such as 2-MT and 2-MGA, could reduce

simulated ISOA concentrations and their sensitivity to sulfate, aerosol liquid water, and acidity. Consistent with this need,
965 gas-particle partitioning treatments for 2-MT in regional models suggest a useful direction for future improvement in global
models (Pye et al., 2018; Shrivastava et al., 2022). Finally, the removal of ISOA formation from the VBS scheme may also
remove important non-epoxide contributions to ISOA that were previously represented implicitly, such as multifunctional
organic peroxides under low-NO_x conditions and organic nitrates under high-NO_x conditions (Paulot et al., 2009a;
Schwantes et al., 2019). Taken together, these assumptions mean that the long-term trends and regression-based attributions
970 diagnosed here should be interpreted within the adopted epoxide-focused chemical framework, rather than as exact causal
contributions independent of model structure and parameterization

Comment#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.
975
980

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>.

985 Response: We thank the reviewer for this insightful comment. We agree that the OSN-like subspecies simulated in the
initially submitted implementation required further clarification. As discussed above in our response to the second part of
Comment#2, the apparent overestimation of OSN-like products was likely related to the parallel-sink treatment used in the
initially submitted implementation of the updated epoxide-derived ISOA mechanism. In that initially submitted
implementation, H₂O-mediated nucleophilic addition and inorganic-nucleophile addition were represented as separate
990 product-forming pathways that independently consumed the same gas-phase epoxide precursor. This treatment could
produce a more even distribution between water-addition products and OSN-like products than suggested by molecular
tracer observations.

To address this issue, we revisited the treatment of epoxide-derived product formation and replaced the initially submitted
995 parallel-sink treatment with a relative-rate branching framework following Budisulistiorini et al. (2017). The detailed
formulation and branching-ratio calculation are provided in our response to the second part of Comment#2 and have been
incorporated into the revised model description in Sect. 2.1.2. In the revised implementation, the total pseudo-first-order
aqueous-phase reaction rate constant is calculated as the sum of all particle-phase reaction channels that consume each
epoxide precursor, and the resulting epoxide-derived ISOA production is then allocated to H₂O-mediated nucleophilic
1000 addition and inorganic-nucleophile addition products according to their fractional contributions to the total reaction rate.

This update substantially changes the simulated product distribution. As shown in Figure R1, the initially submitted implementation produced a relatively large contribution from OSN-like products, particularly AIEOSN and AHMOSN, whereas the revised relative-rate branching treatment greatly reduces their simulated contributions. In the revised implementation, AIETET becomes the dominant simulated ISOA product at Beijing, Hefei, and Kunming, and the combined contribution of AIEOSN and AHMOSN is reduced to only a few percent. This revised product distribution is more consistent with the molecular tracer observations used for model evaluation and with previous field measurements showing relatively small OSN contributions, such as He et al. (2018).

We have revised the corresponding model-observation comparison in the manuscript and present the comparison between the initially submitted and revised results in Figure R1 of this response. We also added discussion in Sect. 3.1 and Sect. 4 to clarify the remaining uncertainties associated with the representation of epoxide-derived product formation. Although the revised branching treatment substantially reduces the OSN-like contribution simulated in the initially submitted implementation, remaining discrepancies between simulated and observed individual product fractions may still reflect uncertainties in pathway branching, reactive uptake parameters, mass transfer, aerosol phase state, and possible missing competing formation or loss processes. In particular, assumptions related to the core-shell uptake treatment, organic-shell viscosity, phase separation, product volatility, and the limited compound-specific constraints for HMML/MAE may affect the simulated abundance and partitioning of individual ISOA products. Future improvements will require better observational and laboratory constraints on epoxide-specific uptake parameters, aerosol phase state and diffusion limitations, product yields and volatility, as well as improved representation of potential non-epoxide ISOA formation pathways under atmospherically relevant aerosol conditions. These revisions have been incorporated in Sect. 3.1 (lines 299–314) and Sect. 4 (lines 659–677).

Lines 299–314:

Several factors may contribute to these positive biases. First, missing or simplified competing loss pathways may cause an over-allocation of epoxide precursors to the explicitly represented ISOA products. For example, a fraction of IEPOX-derived products in the real atmosphere may be diverted to C5-alkene triols or other particle-phase products that are not explicitly represented here, thereby reducing the effective yield of AIETET (Pye et al., 2013). In addition, previous studies have shown that AIETET and AHMGA are sensitive to factors such as pathway branching, mass transfer, reaction kinetics, and aerosol phase state. For example, uncertainties in the relative rates of water addition versus organosulfate formation can affect the predicted product distribution between 2-MT and organosulfate products (Budisulistiorini et al., 2017). Similarly, assumptions related to aerosol phase state, organic-shell viscosity, and phase separation can influence IEPOX reactive uptake and may affect the simulated abundance of IEPOX-derived tracers (Zhang et al., 2018, 2019; Chen et al., 2024b). In particular, the current core-shell uptake treatment assumes the same reaction rate coefficient in the organic shell and aqueous

core. If phase separation and viscous organic coatings impose stronger diffusion limitations than represented here, effective
1035 epoxide uptake may be reduced in the real atmosphere, and the model may overestimate ISOA formation, especially under
conditions with high organic coatings or strong phase separation. For AHMGA, uncertainties in the multiphase uptake and
reaction parameters of HMML/MAE may also contribute to the model bias, because compound-specific constraints for these
high-NO_x epoxides remain limited (Zhang et al., 2022; Zhu et al., 2025).

1040 **Others Comments**

**Comment#4: 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?**

Response: We thank the reviewer for this helpful question. We have clarified the chemical nature and model treatment of
1045 IVOCs and SVOCs in Sect. 2.1.1. In this study, IVOCs and SVOCs are not treated as explicitly speciated molecular
compounds, but as lumped lower-volatility organic precursor classes defined by volatility. Their emissions are scaled from
POA and NMVOC emissions following the default CAM6-Chem treatment described by Chang et al. (2022), Tilmes et al.
(2019), and Zhang et al. (2025). We also clarified that IVOCs and SVOCs are included in the default CAM6-Chem VBS
SOA scheme, which was not modified in this study. In this scheme, organic precursors including IVOCs and SVOCs are
1050 oxidized to volatile SOA gaseous precursors, which subsequently partition between the gas and aerosol phases. Therefore,
IVOCs and SVOCs are involved in the default VBS-based gas-phase oxidation and gas-particle partitioning treatment, but
they are not part of the newly added explicit epoxide reactive uptake chemistry. These clarifications have been incorporated
in Sect. 2.1.1 (lines 128–133 and lines 140–144).

Line 128–133:

1055 In this study, intermediate-volatility organic compounds (IVOCs) and semi-volatile organic compounds (SVOCs) represent
lumped lower-volatility organic precursor classes defined by volatility rather than explicitly speciated molecular structures.
Emissions of IVOCs and SVOCs are scaled from primary organic aerosol (POA) and non-methane volatile organic
compounds (NMVOCs) emissions (Chang et al., 2022; Tilmes et al., 2019). The specific scaling equations and coefficients
are described in the supplement of Zhang et al. (2025) (Eqs. A1–A3).

1060 **Lines 140–144:**

Organic compounds (including glyoxal, monoterpenes, sesquiterpenes, benzene, toluene, lumped xylenes, IVOCs, and
SVOCs) are oxidized to form gas-phase SOA precursors in five volatility bins, with effective saturation concentrations (C^* ,
at 300 K) of 0.01, 0.1, 1.0, 10.0, and 100.0 $\mu\text{g m}^{-3}$. These precursors subsequently partition between the gas and particle
phases (Tilmes et al., 2019). This VBS treatment follows the default CAM6-Chem SOA scheme and was not modified in this
1065 study.

Comment#5: 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.

1070 **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>.**

Response: We thank the reviewer for pointing out this important process. We agree that photolytic loss of isoprene-derived SOA may introduce additional uncertainty in the simulated ISOA lifetime and burden. In the revised manuscript, we have
1075 added a discussion in Sect. 4 noting that Zawadowicz et al. (2020) reported faster photolysis of isoprene SOA than monoterpene-derived SOA, suggesting that this process may affect the simulated ISOA lifetime and abundance. We have also clarified that further refinement of the SOA chemical mechanism, including improved representation of such processes, is needed to reduce the remaining uncertainties and biases in key ISOA subspecies. This revision has been incorporated in Sect. 4 (lines 680–684).

1080 **Lines 680–684:**

These include isoprene cloud-water chemistry, which may provide an additional ISOA source and influence simulated aerosol composition, and photolytic loss, since ISOA may photolyze faster than monoterpene-derived SOA (Zawadowicz et al., 2020), thereby affecting its simulated lifetime and burden. Incorporating these missing formation and loss processes, together with more composition-resolved observations to constrain pathway-specific chemistry, will be important for future
1085 model refinement.

Comment#6: 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.

1090 **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>.**

1095 Response: We thank the reviewer for pointing this out. In the original implementation, the molar branching ratios for HMML and MAE formation from the MPAN + OH pathway were set to 0.57 and 0.21, respectively, following the CRACMM1 gas-phase chemical mechanism used in CMAQ. However, after revisiting the experimental constraints highlighted by the reviewer, we agree that the product distribution reported by Nguyen et al. (2015) provides a more direct constraint for the MPAN + OH pathway considered here. Therefore, following Nguyen et al. (2015), we have revised the branching ratios to
1100 0.75 for HMML and 0.02 for MAE. We have updated the model implementation accordingly and regenerated all related simulation results, figures, and quantitative analyses using the revised branching ratios. The change leads to only very small

differences in the simulated HMML + MAE concentrations and spatial distribution (Figure R5), and does not materially affect the overall conclusions, because the main analyses in this study focus on the combined HMML + MAE concentrations rather than the two individual precursors. As shown in Figure R5, the mean annual surface concentrations of combined HMML and MAE in China from 2000 to 2019 are nearly unchanged between the initially submitted branching ratios (HMML/MAE = 0.57/0.21) and the revised branching ratios constrained by Nguyen et al. (2015) (HMML/MAE = 0.75/0.02). However, it provides a more experimentally constrained representation of the relative importance of the HMML and MAE branches. The corresponding description in Sect. 2.1.2 has been revised (lines 168–170), and the updated chemical reactions and branching ratios, based on the experimental results reported by Nguyen et al. (2015), are now listed in Table S2. All affected results throughout the manuscript and Supplement have been updated accordingly.

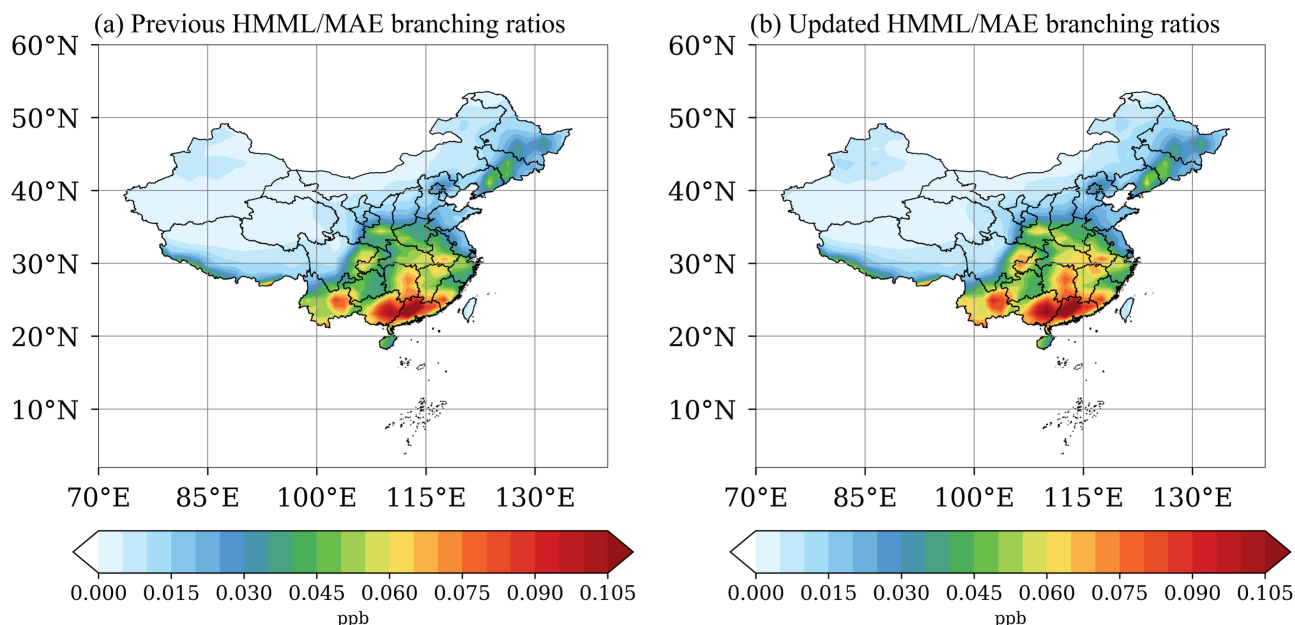


Figure R5: Comparison of annual mean surface concentrations of combined HMML and MAE (HMML + MAE) over China, averaged over the five simulation years (2000, 2006, 2012, 2016, and 2019) (unit: ppb), corresponding to the original Figure S3 in the Supplement. Panel (a) shows results obtained with the branching ratios adopted in the initially submitted implementation, in which MPAN + OH produced HMML and MAE with molar branching ratios of 0.57 and 0.21, respectively. Panel (b) shows results obtained with the revised branching ratios constrained by Nguyen et al. (2015), in which MPAN + OH produces HMML and MAE with molar branching ratios of 0.75 and 0.02, respectively.

Lines 168–170:

Methacrolein (MACR), the precursor of MPAN in the high-NO_x pathway, is formed following the default MOZART-TS2 mechanism. The reaction of MPAN with OH yields HMML and MAE, with molar branching ratios of 0.75 and 0.02, respectively, based on the experimental results reported by Nguyen et al. (2015) (Table S2).

Comment#7: 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 NO_x) and organic nitrates (high NO_x). Could authors give a proper account of this limitation?

1125 Response: We thank the reviewer for this helpful comment. We agree that removing the OH-initiated ISOA formation from the default VBS scheme may affect the representation of non-epoxide ISOA pathways. In the revised manuscript, we have clarified the rationale and scope of this treatment. Specifically, the OH-initiated isoprene oxidation pathway in the VBS scheme was removed to avoid double counting between the default lumped VBS representation of ISOA and the explicitly represented epoxide-derived ISOA pathways. We have also added text clarifying that this treatment focuses the updated
1130 mechanism on epoxide-derived ISOA formation, although potential non-epoxide ISOA contributions originally included implicitly in the VBS scheme may not be explicitly resolved. In Sect. 4, we further note this as one of the uncertainties associated with the adopted chemical framework, together with other assumptions in the epoxide reactive uptake parameterization. These revisions have been incorporated in Sect. 2.1.2 (lines 172–176) and Sect. 4 (lines 672–675).

Lines 172–176:

1135 To avoid double-counting between the default lumped VBS representation of ISOA and the explicitly represented epoxide-derived ISOA pathways, the OH-initiated isoprene oxidation pathway in the VBS scheme is removed (see Sect. 2.1.1). This treatment focuses the updated mechanism on epoxide-derived ISOA formation, although potential non-epoxide ISOA contributions originally included implicitly in the VBS scheme may not be explicitly resolved.

Lines 672–675:

1140 Finally, the removal of ISOA formation from the VBS scheme may also remove important non-epoxide contributions to ISOA that were previously represented implicitly, such as multifunctional organic peroxides under low-NO_x conditions and organic nitrates under high-NO_x conditions (Paulot et al., 2009a; Schwantes et al., 2019).

Comment#8: Line 178-184: k_{aq} 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 k_{nuc} for sulfate and nitrate is incorrect. It appears to be second-order reaction. Please clarify and correct.

Response: We thank the reviewer for this helpful comment. As described in our response to the second part of Comment#2, we have replaced the initially submitted parallel-sink treatment with a relative-rate branching framework. In the revised
1150 manuscript, $k_{aq, total}$ is defined as the total pseudo-first-order aqueous-phase reaction rate constant that represents the sum of the particle-phase reaction channels consuming each epoxide precursor, including IEPOX, HMML, and MAE:

$$k_{aq, total} = k_{H^+}[H^+] + k_{nuc}([SO_4^{2-}] + [NO_3^-])[H^+] + k_{HSO_4^-}[HSO_4^-]$$

In this formulation, the first term represents acid-catalyzed ring opening followed by H₂O-mediated nucleophilic addition, leading primarily to methyltetrol-like products. We have revised the text to clarify that this term represents the H₂O-

1155 mediated nucleophilic addition product channel and that this pathway is not missing or excluded in the revised representation. The second term represents acid-catalyzed ring opening followed by nucleophilic addition of sulfate and nitrate ions, leading to organosulfates and organonitrates. The third term represents concerted protonation and nucleophilic addition by bisulfate, leading to organosulfates. For each epoxide precursor, $k_{aq,total}$ is used to calculate the reactive uptake coefficient and the total uptake flux. The subsequent product allocation follows the relative-rate branching treatment described in our response
1160 to the second part of Comment#2.

We also standardized the notation and units for k_{nuc} . The apparent inconsistency arose from whether the acidity term was written as proton activity or proton concentration. In the revised manuscript, we use the concentration-based form consistently, $k_{nuc}([SO_4^{2-}] + [NO_3^-])[H^+]$, where $([SO_4^{2-}] + [NO_3^-])$ and $[H^+]$ are expressed in molar units. Therefore, k_{nuc}
1165 has units of $M^{-2} s^{-1}$, so that the full term has units of s^{-1} . These revisions have been incorporated into Sect. 2.1.2 of the revised manuscript (lines 196–242).

Comment#9: 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.

1170 **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>.
1175

Response: We thank the reviewer for pointing this out. We agree that treating epoxide-derived SOA products as non-volatile is a simplifying assumption, particularly because products such as 2-MT and 2-MGA may exhibit partial volatility and partition into the gas phase. In the revised manuscript, we have expanded the limitation discussion in Sect. 4 to clarify this
1180 uncertainty. Specifically, we now state that the assumption of 100% SOA yield from epoxide reactive uptake and the treatment of epoxide-derived SOA as non-volatile are consistent with previous global modeling studies of isoprene-derived SOA (Marais et al., 2016; Jo et al., 2019, 2021), but may affect the absolute ISOA burden and its sensitivity to heterogeneous reaction conditions.

1185 We further note that existing gas–particle partitioning treatments for 2-MT in regional models provide a useful direction for future improvements in global models. We also clarify that lower effective yields or partial volatility, especially for products such as 2-MT and 2-MGA, could reduce simulated ISOA concentrations and their sensitivity to sulfate, aerosol liquid water, and acidity. This added discussion has been incorporated in Sect. 4 (lines 667–672).

Lines 667–672:

1190 The assumptions of 100% ISOA yield from epoxide reactive uptake and non-volatile epoxide-derived ISOA introduce additional uncertainty, although they are consistent with previous global ISOA modeling studies (Marais et al., 2016; Jo et al., 2019, 2021). Lower effective yields or partial volatility, especially for products such as 2-MT and 2-MGA, could reduce simulated ISOA concentrations and their sensitivity to sulfate, aerosol liquid water, and acidity. Consistent with this need, 1195 models (Pye et al., 2018; Shrivastava et al., 2022).

Comment#10: 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.

Response: We thank the reviewer for this helpful comment. We agree that the early warm-season ISOA enhancement 1200 deserves further clarification. In the revised Fig. 4(a), this feature appears as an early warm-season ISOA enhancement from April to May, before the summer maximum of biogenic isoprene emissions, and therefore cannot be explained by isoprene emissions alone.

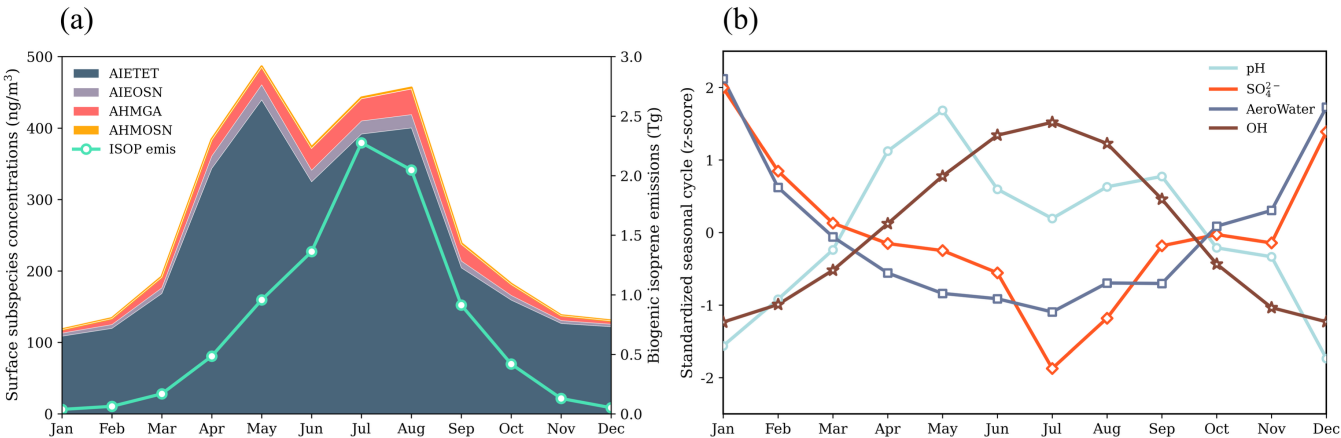
We have revised the text to clarify that this early warm-season enhancement likely reflects the combined influence of several 1205 factors. During the transition from spring to early summer, biogenic isoprene emissions have already increased substantially from their winter levels, although they have not yet reached their annual maximum. At the same time, the rising standardized OH signal suggests strengthening oxidation capacity, which can promote the formation of isoprene oxidation products and epoxide precursors. Although the standardized sulfate and aerosol liquid water anomalies become lower during this period, they have not yet reached their most negative summer anomalies, so the multiphase reaction environment has not yet reached 1210 its least favorable summer state. Therefore, the April–May enhancement is interpreted as reflecting the combined effects of increasing precursor supply, enhanced oxidation capacity, and still available multiphase reaction conditions, rather than the dominance of a single factor.

We also thank the reviewer for pointing out that the OH z-score was missing from Fig. 4(b). The standardized seasonal cycle 1215 of OH was unintentionally omitted in the previous version. We have now added the OH z-score to Fig. 4(b), updated the legend, and revised the corresponding discussion in Sect. 3.2 (lines 406–411).

Lines 406–411:

The early warm-season ISOA enhancement from April to May further illustrates this combined-control behavior, but with a different balance among the controlling factors. It occurs before the annual maximum of isoprene emissions and during the 1220 rising phase of the standardized seasonal OH signal, but at a time when biogenic isoprene emissions have already increased substantially from spring, OH oxidation capacity is strengthening, and the multiphase reaction environment has not yet

reached its least favorable summer state. Thus, the May enhancement likely reflects the combined influence of increasing precursor supply, enhanced oxidation, and still favorable multiphase conditions, rather than the dominance of a single factor.



1225 **Figure 4: (a) Monthly variations of surface isoprene-derived secondary organic aerosol (ISOA) subspecies (left y axis; unit: ng m^{-3})**
1230 **and biogenic isoprene emissions (ISOP emis; right y axis; unit: Tg) in China, based on the climatological monthly means averaged**
over the five simulation years (2000, 2006, 2012, 2016, and 2019). (b) Standardized monthly variations of background chemical
and aerosol variables relevant to ISOA formation, including surface aerosol pH, surface sulfate (SO_4^{2-}) concentrations, surface
aerosol liquid water (AeroWater) concentrations, and surface hydroxyl radical (OH) concentrations in China, based on the
climatological monthly means averaged over the five simulation years.

1235 **Comment#11: 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.

Response: We thank the reviewer for pointing this out. We agree that our previous wording could have led to ambiguity regarding the quantity shown in Fig. 5(b). The quantity shown in Fig. 5(b) is not the heterogeneous reaction rate coefficient k_{het} or the reactive uptake coefficient γ . Rather, it is the particle-phase ISOA production rate diagnosed from tagged heterogeneous reactions in the model. Therefore, the ratio shown in Fig. 5(b) reflects the formation rates of epoxide-derived ISOA products, rather than the ratio of k_{het} or γ values for HMML/MAE and IEPOX. Specifically, the IEPOX-derived production rate is diagnosed by summing the tagged formation rates of IEPOX-derived particle-phase products, whereas the HMML/MAE-derived production rate is diagnosed in the same way from HMML/MAE-derived particle-phase products. Thus, these diagnosed production rates depend not only on the reactive uptake process, but also on the gas-phase precursor concentrations available for heterogeneous uptake. Under the current parameterization, HMML/MAE and IEPOX share the same uptake-related parameters, and therefore the model does not imply an order-of-magnitude difference in γ or k_{het} caused by different kinetic parameters. Instead, the lower particle-phase production rate of the HMML/MAE pathway mainly reflects the lower availability of HMML+MAE relative to IEPOX. To avoid this ambiguity, we have revised the text and figure description to explicitly refer to “particle-phase production rates diagnosed from tagged heterogeneous reactions”

rather than heterogeneous reaction rate coefficients. We also clarified that Fig. 5(b) is used to compare pathway-specific
1250 ISOA production rates, while Fig. 5(a) shows the corresponding gas-phase precursor ratio. These revisions have been
incorporated in Sect. 3.2 (lines 444–450) and the caption of Fig. 5.

Lines 444–450:

To interpret this feature, we further compare the gas-phase precursors and particle-phase production rates diagnosed from the
tagged heterogeneous reactions for the two pathways. The ratio of the gas-phase epoxide precursors HMML + MAE to
1255 IEPOX shows only a modest seasonal variation and generally remains within about 0.074 to 0.10 throughout the year (Fig.
5(a)). The ratio of tagged particle-phase ISOA production rates, $P_{\text{HMML+MAE}}/P_{\text{IEPOX}}$, exhibits a similar seasonal pattern,
with an annual mean of about 0.10 (Fig. 5(b)). These results indicate that neither the HMML+MAE-to-IEPOX precursor
ratio nor the corresponding tagged particle-phase ISOA production-rate ratio shows a comparably strong increase in
September.

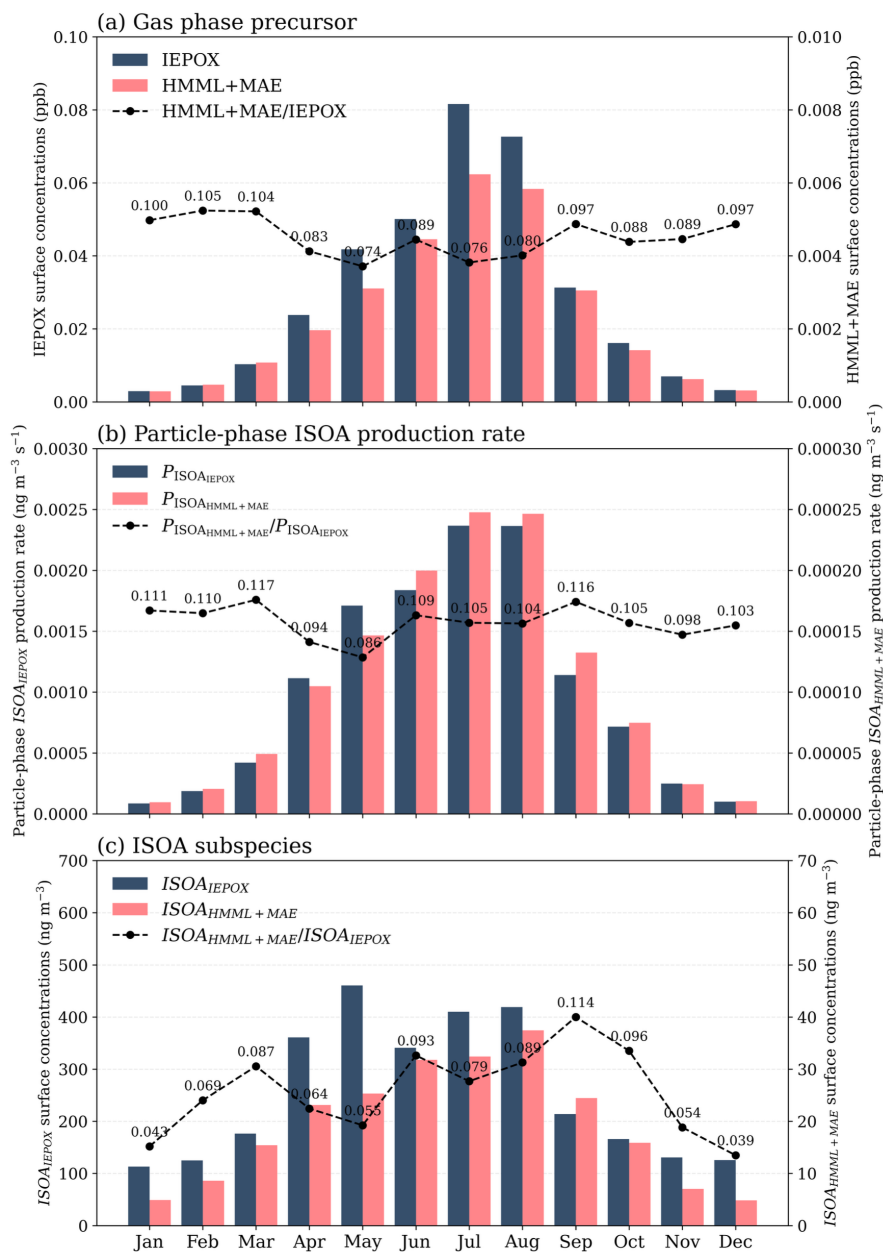


Figure 5: Monthly variations of IEPOX-related and HMML+MAE-related gas-phase precursors, particle-phase production rates, and ISOA concentrations in China, based on the climatological monthly means averaged over the five simulation years (2000, 2006, 2012, 2016, and 2019). (a) Surface concentrations of isoprene epoxydiols (IEPOX; dark-blue bars; left y axis; unit: ppb) and hydroxymethyl-methyl- α -lactone plus methacrylic acid epoxide (HMML + MAE; pink bars; right y axis; unit: ppb). (b) Particle-phase ISOA production rates diagnosed from tagged heterogeneous reactions for the IEPOX pathway ($P_{\text{ISOA}_{\text{IEPOX}}}$; dark-blue bars; left y axis; unit: $\text{ng m}^{-3} \text{s}^{-1}$) and the HMML+MAE pathway ($P_{\text{ISOA}_{\text{HMML+MAE}}}$; pink bars; right y axis; unit: $\text{ng m}^{-3} \text{s}^{-1}$). (c) Surface concentrations of ISOA derived from IEPOX ($\text{ISOA}_{\text{IEPOX}}$; dark-blue bars; left y axis; unit: ng m^{-3}) and ISOA derived from HMML and MAE ($\text{ISOA}_{\text{HMML+MAE}}$; pink bars; right y axis; unit: ng m^{-3}). In each panel, the black dashed line denotes the ratio of the HMML+MAE-related quantity to the corresponding IEPOX-related quantity, with monthly ratio values labeled above the markers.

Response to Referee #4

1275 This work by Zhang et al. (2026) assesses the impacts of incorporating additional isoprene chemistry into CAM6-Chem. Isoprene's low-NO_x pathway was updated and a high-NO_x pathway was introduced. Comparison with observational data revealed improvements in composition and isoprene-derived secondary organic aerosol (ISOA) representation. A spatial analysis, which revealed opposite trends in different regions, provided insight into the weak national-mean ISOA trend in China. This study addressed a relevant and important research question and conducted a broad range of analyses to substantiate the claim that their updates to the CAM6-Chem isoprene oxidation mechanism led to improved ISOA representation over China. Clarity could be improved in some areas and some figures require editing.

1280 We are very grateful to the reviewer for the constructive evaluation and helpful suggestions, which have allowed us to clarify and improve the manuscript. Before addressing the reviewer's comments point by point, we briefly summarize the major revisions made in response to Referee #4. The reviewer's comments are shown in **bold blue text**, while our responses and the corresponding revised manuscript text are shown in black text. Line numbers refer to the revised manuscript.

1285 In response to Referee #4, we revised the treatment and discussion of AIEOSN and other OSN-like products by replacing the initially submitted parallel-sink implementation with the updated relative-rate branching framework, which substantially reduces the simulated inorganic-nucleophile-addition product contributions and improves consistency with molecular tracer observations. We also clarified the calculation of OA/SOA normalized mean biases using site- and period-matched model-observation pairs, and revised the interpretation of the bulk OA/SOA improvement to emphasize that other SOA pathways were not modified. In addition, we expanded the definitions of model species and reaction pathways, clarified the meaning of key terms and figure elements, and revised several figures and tables to improve readability.

1290

Major Comments

1295 **Comment#1: This study assesses the impact of expanding the representation of ISOA subspecies in CAM6-Chem from one to four. Though it is briefly mentioned that "discrepancies in the fractional contributions of individual species" exist between the observed and modeled ISOA subspecies, more thoroughly addressing the significant overestimation in AIEOSN is necessary. Why might this be occurring? Since AIEOSN is the only ISOA subspecies present in the pre-updated and updated model, it might be insightful to show a comparison of AIEOSN concentrations before and after the update, if possible.**

1300 Response: We thank the reviewer for raising this important point. We agree that the previously simulated AIEOSN contribution required further clarification. As also discussed in our response to the second sub-question of Reviewer #3, Comment #2, the apparent overestimation of AIEOSN was mainly associated with how the updated epoxide-derived ISOA mechanism was implemented in the original submission. In the initially submitted implementation, ISOA formation pathways for IEPOX, HMML, and MAE were represented as multiple parallel heterogeneous uptake reactions. Each product-forming pathway directly consumed the same gas-phase epoxide precursor using a distinct channel-specific reactive

1305

uptake coefficient derived from its respective aqueous-phase rate expression. As a result, ISOA speciation was effectively determined at the level of independent uptake fluxes, rather than being constrained by a single total uptake rate followed by internal partitioning among competing reaction channels. This approach allowed each channel to act as an independent sink of the precursor and resulted in the inorganic-nucleophile addition channel receiving an artificially enhanced share of gas-phase precursor uptake flux, leading to an overestimation of the corresponding inorganic-nucleophile addition products such as AIEOSN and AHMOSN.

To address this issue, we revisited the treatment of epoxide-derived product formation and revised the model implementation using a relative-rate branching framework following Budisulistiorini et al. (2017). In essence, the implementation used in the original submission treated epoxide uptake as multiple parallel sinks, whereas the revised implementation treats epoxide uptake as a single total uptake process followed by competitive branching into different product classes.

In the revised implementation, a single total pseudo-first-order aqueous-phase rate constant $k_{aq,total}$ is first calculated as the sum of the particle-phase reaction channels (H₂O-mediated nucleophilic addition and inorganic-nucleophile addition channels) considered here: $k_{aq,total} = k_{H^+}[H^+] + k_{nuc}([SO_4^{2-}] + [NO_3^-])[H^+] + k_{HSO_4^-}[HSO_4^-]$. This total rate is used to compute the reactive uptake coefficient (γ) and the total uptake flux for each precursor. ISOA speciation is then determined diagnostically by partitioning the total uptake flux according to the fractional contribution of each reaction channel to $k_{aq,total}$. Specifically, the branching ratio for the H₂O-mediated nucleophilic addition product class is calculated as $k_{aq,H_2O}/k_{aq,total} = k_{H^+}[H^+]/(k_{H^+}[H^+] + k_{nuc}([SO_4^{2-}] + [NO_3^-])[H^+] + k_{HSO_4^-}[HSO_4^-])$, whereas the branching ratio for the inorganic-nucleophile-addition product class is calculated as $k_{aq,SO_4/NO_3/HSO_4}/k_{aq,total} = (k_{nuc}([SO_4^{2-}] + [NO_3^-])[H^+] + k_{HSO_4^-}[HSO_4^-])/(k_{H^+}[H^+] + k_{nuc}([SO_4^{2-}] + [NO_3^-])[H^+] + k_{HSO_4^-}[HSO_4^-])$. The total particle-phase ISOA production is then distributed into H₂O-mediated nucleophilic addition products and inorganic-nucleophile addition products according to these branching ratios. This treatment ensures that the total uptake of each precursor is governed by the full particle-phase reaction rate constant, while the product distribution reflects the relative competition among nucleophilic addition pathways. This treatment is analogous to Budisulistiorini et al. (2017), who determined IEPOX-SOA speciation between tetrols and organosulfates based on the relative rates of precursor conversion to these products.

This revision substantially changes the simulated product distribution. As shown in Figure R1, the initially submitted implementation produced a relatively large contribution from AIEOSN and AHMOSN, whereas the revised relative-rate branching treatment greatly reduces their simulated contributions. In the revised implementation, AIETET becomes the dominant simulated ISOA product at Beijing, Hefei, and Kunming, and the combined contribution of AIEOSN and AHMOSN is reduced to only a few percent. This revised product distribution is more consistent with the molecular tracer observations used for model evaluation and with previous field measurements showing relatively small AIEOSN

contributions, such as He et al. (2018). Broader changes in total concentrations, interannual variability, long-term trends, and attribution coefficients resulting from this implementation update are described in the response to the second sub-question of Reviewer #3, Comment#2.

We have also revised the relevant description in the manuscript to clarify that the earlier CAM6-Chem configuration described by Zhang et al. (2025) represented the low-NO_x IEPOX pathway as a lumped (ISOA_{IEPOX}) product, whereas the explicit ISOA representation adopted in this study resolves epoxide-derived ISOA into product classes associated with H₂O-mediated and inorganic-nucleophile addition pathways and also includes high-NO_x epoxide precursors. We appreciate the reviewer's suggestion to compare AIEOSN before and after the update. In response, Figure R1 presents the initially submitted-versus-revised product distribution, which directly shows the reduction in the AIEOSN contribution together with the corresponding redistribution among other ISOA product classes. We believe this composition-based comparison provides a clearer way to illustrate the effect of the revised product-allocation treatment, because the main change occurs in the partitioning of epoxide-derived ISOA among product classes.

We have revised the corresponding model-observation comparison in the manuscript and present the comparison between the initially submitted and revised results in Figure R1 of this response. We also added discussion in Sect. 3.1 and Sect. 4 to clarify the remaining uncertainties associated with the representation of epoxide-derived product formation. Although the revised branching treatment substantially reduces the AIEOSN and AHMOSN contributions simulated in the initially submitted implementation, remaining discrepancies between simulated and observed individual product fractions may still reflect uncertainties in pathway branching, reactive uptake parameters, mass transfer, aerosol phase state, and possible missing competing formation or loss processes. In particular, assumptions related to the core-shell uptake treatment, organic-shell viscosity, phase separation, product volatility, and the limited compound-specific constraints for HMML/MAE may affect the simulated abundance and partitioning of individual ISOA products. Future improvements will require better observational and laboratory constraints on epoxide-specific uptake parameters, aerosol phase state and diffusion limitations, product yields and volatility, as well as improved representation of potential non-epoxide ISOA formation pathways under atmospherically relevant aerosol conditions. These revisions have been incorporated in Sect. 3.1 (lines 299–314) and Sect. 4 (lines 659–677).

Budisulistiorini, S. H., Nenes, A., Carlton, A. G., Surratt, J. D., McNeill, V. F., and Pye, H. O. T.: Simulating aqueous-phase isoprene-epoxydiol (IEPOX) secondary organic aerosol production during the 2013 Southern Oxidant and Aerosol Study (SOAS), *Environ. Sci. Technol.*, 51, 5026–5034, <https://doi.org/10.1021/acs.est.6b05750>, 2017.

He, Q.-F., Ding, X., Fu, X.-X., Zhang, Y.-Q., Wang, J.-Q., Liu, Y.-X., Tang, M.-J., Wang, X.-M., and Rudich, Y.: Secondary organic aerosol formation from isoprene epoxides in the Pearl River Delta, South China: IEPOX- and HMML-derived tracers, *J. Geophys. Res.-Atmos.*, 123, 6999–7012, <https://doi.org/10.1029/2017JD028242>, 2018.

Zhang, W., Liu, Y., Yue, M., Dong, X., Huang, K., and Wang, M.: Understanding the long-term trend of organic aerosol and the influences from anthropogenic emission and regional climate change in China, *Atmos. Chem. Phys.*, 25, 3857–3872, <https://doi.org/10.5194/acp-25-3857-2025>, 2025.

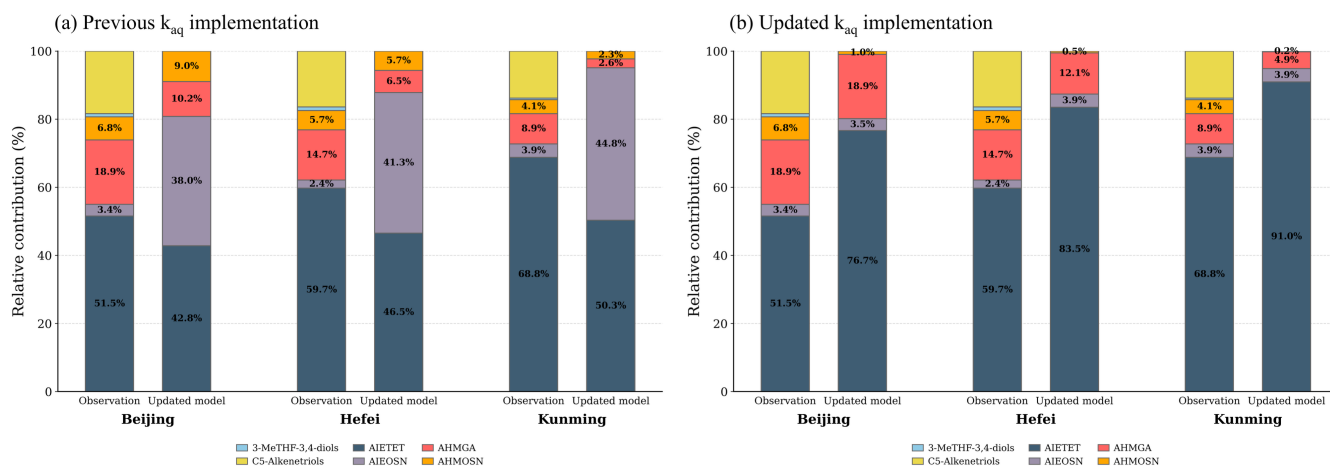


Figure R1: Comparison of ISOA product composition between ground-based observations adapted from Zhang et al. (2022) and the model simulation in this study, corresponding to the observation-model comparison shown in the original Figure 2c in the manuscript. The grouped stacked bars show the relative contribution of each ISOA product to total measured or simulated ISOA at Beijing, Hefei, and Kunming. For each city, the left bar represents the observed composition and the right bar represents the corresponding model simulation. Panel (a) shows results obtained with the previous k_{aq} implementation, in which product-forming pathways were treated as independent uptake sinks. Panel (b) shows results obtained with the updated k_{aq} implementation, in which total epoxide uptake is first calculated and then partitioned among product classes using the relative-rate branching framework.

Lines 299–314:

Several factors may contribute to these positive biases. First, missing or simplified competing loss pathways may cause an over-allocation of epoxide precursors to the explicitly represented ISOA products. For example, a fraction of IEPOX-derived products in the real atmosphere may be diverted to C5-alkene triols or other particle-phase products that are not explicitly represented here, thereby reducing the effective yield of AIETET (Pye et al., 2013). In addition, previous studies have shown that AIETET and AHMGA are sensitive to factors such as pathway branching, mass transfer, reaction kinetics, and aerosol phase state. For example, uncertainties in the relative rates of water addition versus organosulfate formation can affect the predicted product distribution between 2-MT and organosulfate products (Budisulistiorini et al., 2017). Similarly, assumptions related to aerosol phase state, organic-shell viscosity, and phase separation can influence IEPOX reactive uptake and may affect the simulated abundance of IEPOX-derived tracers (Zhang et al., 2018, 2019; Chen et al., 2024b). In particular, the current core-shell uptake treatment assumes the same reaction rate coefficient in the organic shell and aqueous core. If phase separation and viscous organic coatings impose stronger diffusion limitations than represented here, effective epoxide uptake may be reduced in the real atmosphere, and the model may overestimate ISOA formation, especially under conditions with high organic coatings or strong phase separation. For AHMGA, uncertainties in the multiphase uptake and reaction parameters of HMML/MAE may also contribute to the model bias, because compound-specific constraints for these high-NOx epoxides remain limited (Zhang et al., 2022; Zhu et al., 2025).

Lines 659–677:

Future model development should further address several simplifying assumptions in the current epoxide reactive uptake parameterization. As described in Sect. 2.1.2, the model follows a core-shell treatment in which the organic shell and aqueous core are assumed to have the same reaction rate coefficient. Because phase separation and increased organic-shell viscosity can limit epoxide diffusion and reactive uptake, this assumption may overestimate epoxide-derived ISOA under strongly phase-separated or highly viscous conditions (Zhang et al., 2019; Schmedding et al., 2020; Chen et al., 2024b; Farrell et al., 2025). HMML and MAE are also represented using the same solubility, diffusivity, and condensed-phase reaction parameters as IEPOX because compound-specific laboratory constraints remain limited. This IEPOX-like treatment introduces uncertainty in the absolute uptake rates of high-NO_x epoxides and in the quantitative ISOA_{HMML+MAE}/ISOA_{IEPOX} ratio. The assumptions of 100% ISOA yield from epoxide reactive uptake and non-volatile epoxide-derived ISOA introduce additional uncertainty, although they are consistent with previous global ISOA modeling studies (Marais et al., 2016; Jo et al., 2019, 2021). Lower effective yields or partial volatility, especially for products such as 2-MT and 2-MGA, could reduce simulated ISOA concentrations and their sensitivity to sulfate, aerosol liquid water, and acidity. Consistent with this need, gas-particle partitioning treatments for 2-MT in regional models suggest a useful direction for future improvement in global models (Pye et al., 2018; Shrivastava et al., 2022). Finally, the removal of ISOA formation from the VBS scheme may also remove important non-epoxide contributions to ISOA that were previously represented implicitly, such as multifunctional organic peroxides under low-NO_x conditions and organic nitrates under high-NO_x conditions (Paulot et al., 2009a; Schwantes et al., 2019). Taken together, these assumptions mean that the long-term trends and regression-based attributions diagnosed here should be interpreted within the adopted epoxide-focused chemical framework, rather than as exact causal contributions independent of model structure and parameterization.

Comment#2: The conclusion that the model updates improved SOA and OA representation is strongly substantiated by the comparison of normalized mean biases (NMB) with and without the updated isoprene chemistry. These NMB are calculated with observational OA/POA/SOA data from across China during 2013-2019. It may be helpful to expand on the calculation of these NMB (in [Lines 251-252]), given the different time periods and site-specific measurements. In [Line 251], the improvement of SOA representation is said to be “mainly owing to improved ISOA simulation”. This implies that there may be other factors contributing to this improvement. If this is the case, it would be helpful to expand on this further.

Response: We thank the reviewer for these helpful suggestions. We have expanded the description of the NMB calculation in Sect. 3.1 to improve clarity. We now provide a general explanation before presenting these statistics. Specifically, for the OA/SOA evaluation, model outputs were sampled at the corresponding observational site locations and averaged over the same observational periods before calculating the model-observation differences. The paired model and observational values from different sites and time periods were then combined across all paired samples to calculate the NMB, thereby accounting for the site-specific locations and different temporal coverage of the observational datasets.

We also revised the statement regarding the improvement in SOA representation. We agree that the previous wording “mainly owing to improved ISOA simulation” could imply that other SOA formation pathways were also modified. In the

revised manuscript, we clarify that the mechanism update implemented in this study focuses on ISOA formation, while other SOA formation pathways were not modified. Therefore, the improvement in bulk SOA representation is attributed to the enhanced representation of ISOA in the updated model. These revisions have been incorporated in Sect. 3.1 (lines 288–292 and lines 327–329).

1440 **Lines 288–292:**

For all normalized mean biases (NMB) calculations in this section, model outputs were sampled at the corresponding observational site locations and averaged over the same observational periods before calculating the model-observation differences. The paired model and observational values from different sites and time periods were then combined across all paired samples to calculate the NMB, thereby accounting for the site-specific locations and different temporal coverage of the observational datasets.

Lines 327–329:

This improvement reflects the enhanced representation of ISOA formation introduced in this study, since other SOA formation pathways were not modified relative to the earlier CAM6-Chem configuration.

1450 **Technical Corrections/Suggestions**

Comment#3: [Line 142] Need to define “MACR”.

Response: We thank the reviewer for pointing this out. We have revised Sect. 2.1.2 to define MACR when it first appears. This revision has been incorporated in Sect. 2.1.2 (line 168–170).

Line 168–170:

1455 Methacrolein (MACR), the precursor of MPAN in the high-NO_x pathway, is formed following the default MOZART-TS2 mechanism. The reaction of MPAN with OH yields HMML and MAE, with molar branching ratios of 0.75 and 0.02, respectively, based on the experimental results reported by Nguyen et al. (2015) (Table S2).

Comment#4: [Eq 4] Need to define “ k_{org} ”.

Response: We thank the reviewer for pointing this out. We have revised Sect. 2.1.2 to explicitly define k_{org} as the pseudo-first-order reaction rate constant of epoxides in the organic shell (s^{-1}). We further clarify that, following Jo et al. (2021), the reactivity of epoxides in the organic shell is parameterized using the same reaction rate constant as in the aqueous core, so $k_{org}=k_{aq,total}$. This revision has been incorporated in Sect. 2.1.2 (lines 212–214 and Lines 235–240).

Jo, D. S., Hodzic, A., Emmons, L. K., Tilmes, S., Schwantes, R. H., Mills, M. J., Campuzano-Jost, P., Hu, W., Zaveri, R. A., Easter, R. C., Singh, B., Lu, Z., Schulz, C., Schneider, J., Shilling, J. E., Wisthaler, A., and Jimenez, J. L.: Future changes in isoprene-epoxydiol-derived secondary organic aerosol (IEPOX SOA) under the Shared Socioeconomic

Lines 212–214:

Where R_c is the inorganic aqueous core radius (m), k_{org} is the pseudo-first-order reaction rate constant of epoxides in the organic shell (s^{-1}), and $k_{aq,total}$ is the total pseudo-first-order aqueous-phase reaction rate constant (s^{-1}), calculated as the sum of all particle-phase reaction channels that consume each precursor

Lines 235–240:

This study follows the approach of Jo et al. (2021), where the reactivity of epoxides in the organic shell was parameterized with the same reaction rate constant as in the aqueous phase ($k_{org}=k_{aq,total}$). This treatment follows the Jo et al. (2019, 2021) core-shell framework and represents a simplifying assumption, because phase separation, organic-shell viscosity, and differences in acidity between the inorganic core and organic shell may alter epoxide diffusion and reactivity (Schmedding et al., 2020; Farrell et al., 2025).

Comment#5: [Lines 192–195] I’m assuming AIETET, AIEOSN, AHMGA, AHMOSN stand for Aerosol from IEPOX – tetrols, Aerosol from IEPOX – organosulfate/nitrate, Aerosol from HMML/MAE – glyceric acid, and Aerosol from HMML/MAE – organosulfate/nitrate. It’d be helpful to explicitly include this so readers can more easily understand the subsequent references/analyses. Could these be named something more intuitive? Such as AIEAQ, AIEOSN, AHMAQ, AHMOSN? Referring to IEPOX’s and HMML/MAE’s aqueous and organosulfate/nitrate pathways?

Response: We thank the reviewer for this helpful suggestion. We agree that the meanings and formation pathways of AIETET, AIEOSN, AHMGA, and AHMOSN should be stated more explicitly to help readers understand the subsequent analyses. In the revised manuscript, we have added a clearer definition of these four ISOA subspecies when they are first introduced.

Specifically, we now clarify that ISOA formed from the heterogeneous uptake of IEPOX is divided into two product classes: 2-methyltetrols (2-MT; AIETET), produced through the H_2O -mediated nucleophilic addition channel, and organosulfate/organonitrate products (AIEOSN), produced through the inorganic-nucleophile addition channel. Similarly, ISOA formed from HMML and MAE is divided into 2-methylglyceric acid (2-MG; AHMGA), produced through the H_2O -mediated nucleophilic addition channel, and organosulfate/organonitrate products (AHMOSN), produced through the inorganic-nucleophile addition channel.

We appreciate the reviewer’s suggestion to consider more intuitive names. However, we have retained the original species names, AIETET, AIEOSN, AHMGA, and AHMOSN, because they correspond directly to the model species used in the implementation and encode both the precursor source and the product type. Specifically, “A” denotes aerosol-phase products, “IE” denotes IEPOX-derived products, “HM” denotes HMML/MAE-derived products, “TET” denotes 2-methyltetrols, “GA”

denotes 2-methylglyceric acid, and “OSN” denotes organosulfate/organonitrate products. Therefore, rather than renaming the species, we revised the text to explicitly link each species name to its precursor, product class, and formation channel. This clarification has been added in Sect. 2.1.2 (lines 244–255).

Lines 244–255:

As illustrated in Fig. 1, the uptake-derived ISOA product classes are mapped to four model species. ISOA formed from the heterogeneous uptake of IEPOX is divided into two product classes: 2-MT (AIETET), produced through the H₂O-mediated nucleophilic addition channel, and organosulfate/organonitrate products (AIEOSN), produced through the inorganic-nucleophile addition channel. Similarly, ISOA formed from HMML and MAE is divided into 2-MG (AHMGA), produced through the H₂O-mediated nucleophilic addition channel, and organosulfate/organonitrate products (AHMOSN), produced through the inorganic-nucleophile addition channel. The ISOA yield from the reactive uptake of IEPOX, HMML, and MAE is assumed to be 100%, and ISOA derived from these epoxides is treated as non-volatile in the model. This assumption is in agreement with previous modeling studies (Budisulistiorini et al., 2017; Marais et al., 2016; Schmedding et al., 2019; Stadler et al., 2018), which are based on field observations indicating that ISOA from these epoxides in the atmosphere exhibits very low volatility (Hu et al., 2016; Riva et al., 2019). Once ISOA from IEPOX, HMML, and MAE is formed, no further oxidation occurs in the model, consistent with previous studies (Budisulistiorini et al., 2017; Marais et al., 2016; Schmedding et al., 2019).

Comment#6: [Fig. 1] What is the difference between the dashed & solid arrows? Defining abbreviations in the figure caption would be helpful (at least for AeroWater, AIETET, AIEOSN, AHMGA, AHMOSN).

Response: We thank the reviewer for this helpful suggestion. We have revised the caption of Fig. 1 to clarify the meaning of the arrow styles and to define the abbreviations used in the schematic. The revised caption now states that dashed arrows indicate gas-phase reactions, whereas solid arrows indicate particle-phase heterogeneous uptake and product-formation reactions. We have also added definitions for the key abbreviations in the caption. Specifically, AeroWater denotes aerosol liquid water; AIETET denotes IEPOX-derived 2-methyltetrols; AIEOSN denotes IEPOX-derived organosulfate/organonitrate products; AHMGA denotes HMML/MAE-derived 2-methylglyceric acid; and AHMOSN denotes HMML/MAE-derived organosulfate/organonitrate products. In addition, we revised the caption wording to describe the color coding more clearly. Species explicitly represented as updated ISOA precursors or product classes in this mechanism are shown in green, and the explicitly represented ISOA formation pathways are shown in orange.

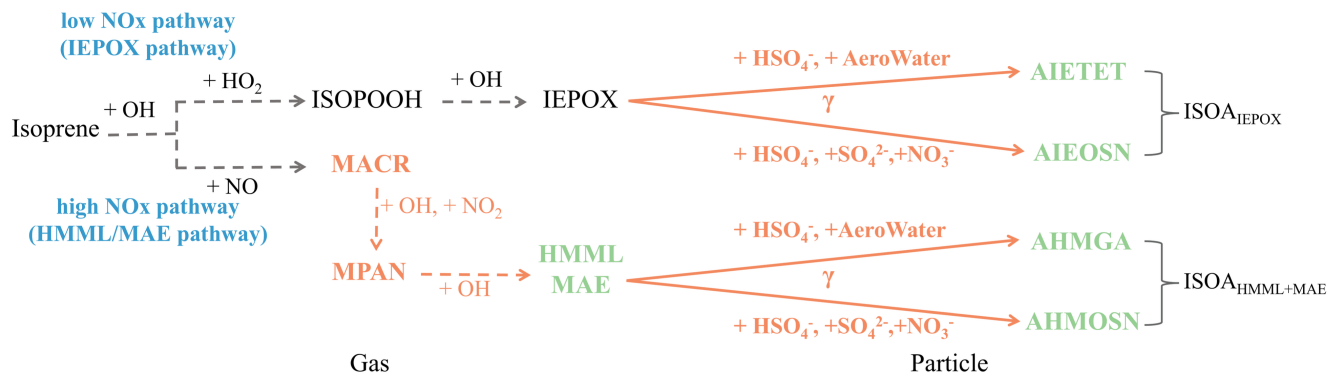


Figure 1: Schematic of the explicit isoprene-derived secondary organic aerosol (ISOA) formation mechanism implemented in CAM6-Chem in this study. Dashed arrows indicate gas-phase reactions, whereas solid arrows indicate particle-phase heterogeneous uptake and product-formation reactions. Species explicitly represented as updated ISOA precursors or product classes in this mechanism are shown in green, and the explicitly represented ISOA formation pathways are shown in orange. AeroWater denotes aerosol liquid water. AIETET denotes IEPOX-derived 2-methyltetrols, AIEOSN denotes IEPOX-derived organosulfate/organonitrate products, AHMGA denotes HMML/MAE-derived 2-methylglyceric acid, and AHMOSN denotes HMML/MAE-derived organosulfate/organonitrate products.

Comment#7: [Fig. 2a] It may be helpful to include a description of what the dark and light gray lines represent. I'd also modify this plot so that points aren't being cut off (as seen on the x-axis). As for the legend, it would be helpful to modify it so that data points aren't obscuring the text and so that the example markers in the legend can't be mistaken for actual data.

Response: Thank you for the detailed suggestions. We have revised Fig. 2(a) accordingly. First, we adjusted the axis limits to ensure that all markers are fully visible and are no longer cut off near the plot boundaries. Second, we moved the legend outside the plotting area to avoid obscuring the data points and to prevent the legend markers from being confused with actual observations. Third, we added a description of the reference lines in the figure caption: the dark gray solid line denotes the 1:1 line, and the light gray solid lines denote the factor-of-10 range.

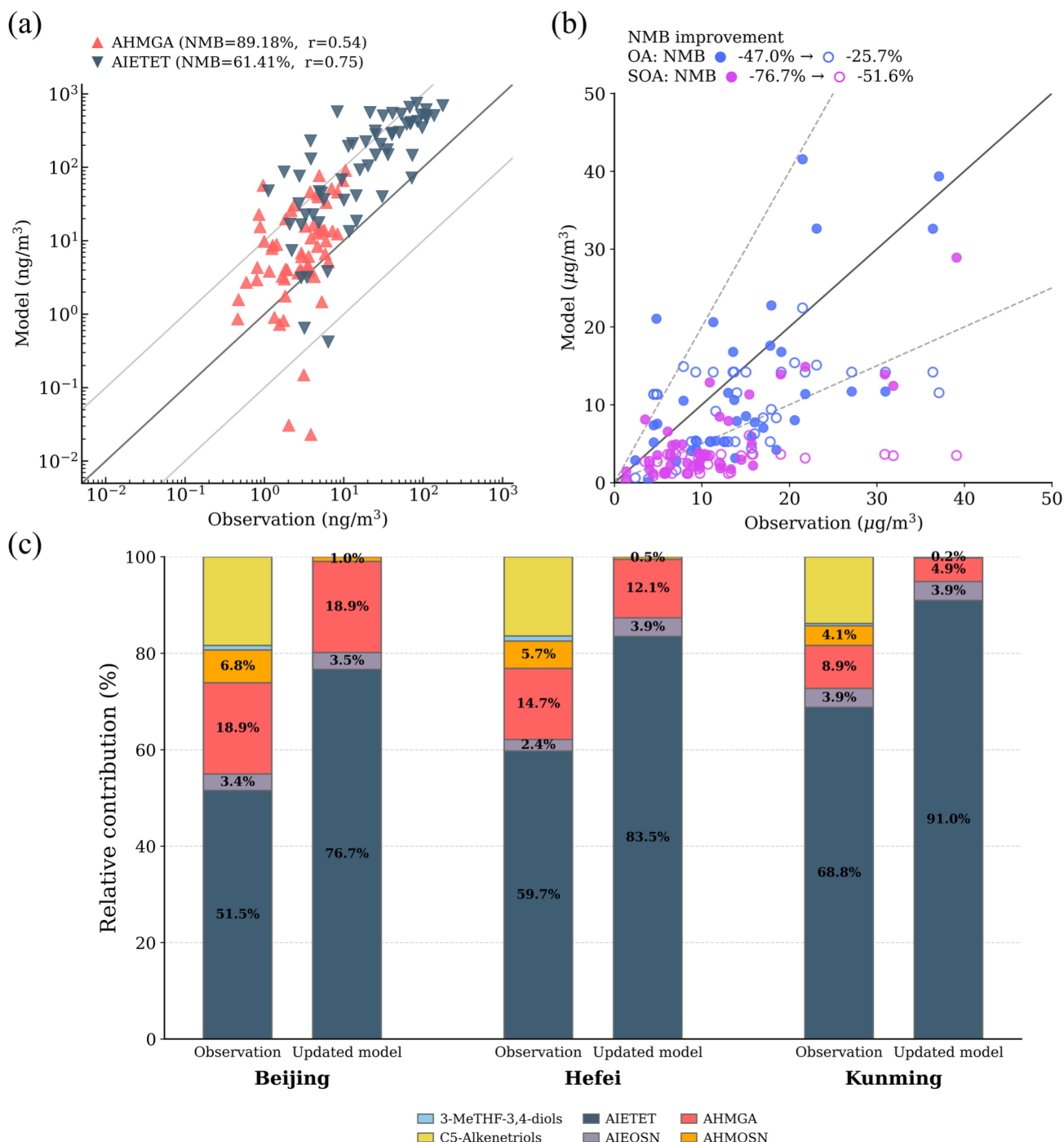


Figure 2: (a) Evaluation of simulated 2-methyltetrols (AIIETET) and 2-methylglyceric acid (AHMGA) concentrations against ground-based observations from Ding et al. (2016) (ng m⁻³). Statistical metrics were calculated using monthly means in log space. The dark gray solid line denotes the 1:1 line, and the light gray solid lines denote the factor-of-10 range. (b) Evaluation of simulated organic aerosol (OA) and secondary organic aerosol (SOA) concentrations before and after the mechanism update

1550 against ground-based observations compiled from Miao et al. (2021) and Chen et al. (2024a) ($\mu\text{g m}^{-3}$). Filled circles represent simulations before the update, while open circles represent simulations after the update. Blue and magenta markers denote OA and SOA, respectively. The inset annotation summarizes the changes in normalized mean bias (NMB) from the original to the updated simulation. The dark gray solid line denotes the 1:1 line, and the light gray dashed lines denote the factor-of-two range. (c) Comparison of ISOA product composition between ground-based observations adapted from Zhang et al. (2022) and the updated model simulation in this study. The grouped stacked bars show the relative contribution of each ISOA product to total measured or simulated ISOA at Beijing, Hefei, and Kunming. For each city, the left bar represents the observed composition and the right bar represents the updated model.

Comment#8: [Fig. 2b] Same recommendation for legend as above. Include what the dark gray and light gray dashed lines represent in the figure caption.

Response: Thank you for the detailed suggestions. We have revised Fig. 2(b) following the same approach. The legend/annotation was reformatted and moved away from the main data region to avoid overlap with the plotted points. We also clarified the meaning of the reference lines in the figure caption. The dark gray solid line denotes the 1:1 line, and the light gray dashed lines denote the factor-of-two range.

Comment#9: [Fig. 2c] You specify what the rows represent in the figure caption; to be consistent, maybe do the same with the columns.

Response: Thank you for the suggestion. We have revised Fig. 2(c) and its caption to make the layout clearer. In the revised grouped stacked bar chart, each city forms one group, with the left bar showing the observed composition and the right bar showing the updated-model composition, as now explicitly stated in the caption.

Comment#10: [Fig. 3] Adding titles above each plot and enlarging colorbar titles would be helpful. For part c, I'd move the legend to the top so that "AHMGA" isn't obscured. Can you make a second legend circle size (in addition to the 60 ng/m³ circle) that more closely resembles the largest pie chart in the plot?

Response: Thank you for the detailed suggestions. We have revised Fig. 3 accordingly. First, we added descriptive titles above each panel to clarify the information shown in Fig. 3. Second, we enlarged and clarified the colorbar labels in Fig. 3(a) and Fig. 3(b). For Fig. 3(c), we moved the species legend to the top of the panel so that all legend entries, including AHMGA, are clearly visible and no longer overlap with the map or pie charts. We also revised the pie-size reference. Instead of the original small 60 ng m⁻³ reference circle, we now use a larger 900 ng m⁻³ reference circle that better represents the size of the largest pie charts in the panel and improves interpretability. In addition, we lightened the map background and provincial boundaries to make the pie charts and regional labels more prominent.

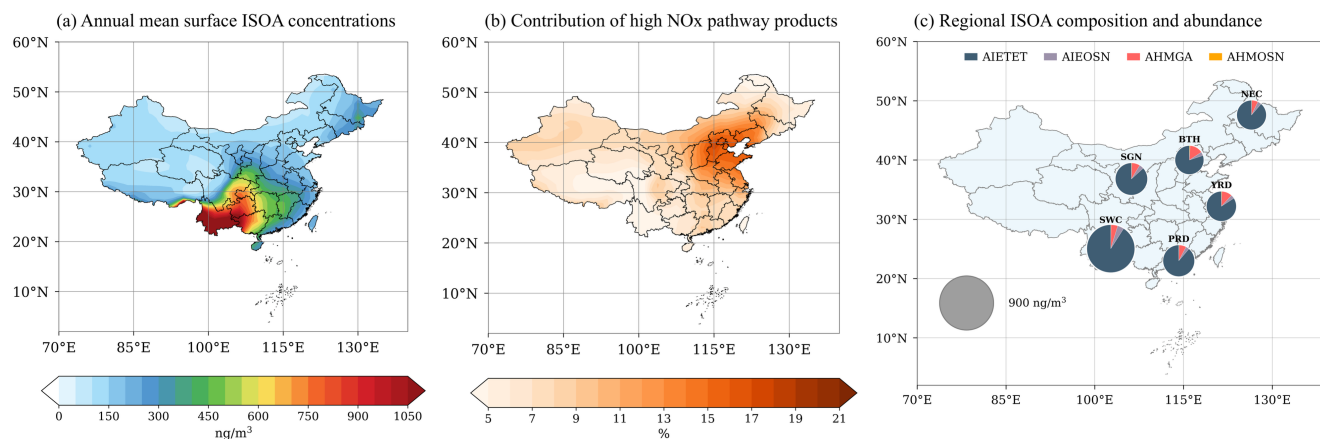


Figure 3: (a) Annual mean surface concentrations of isoprene-derived secondary organic aerosol (ISOA) over China, averaged over the five simulation years (2000, 2006, 2012, 2016, and 2019) (unit: ng m^{-3}). (b) Spatial distribution of the contribution of high-NOx pathway products, including 2-methylglyceric acid (AHMGA) and organosulfate/organonitrate products from the high-NOx pathway (AHMOSN), to annual mean total ISOA over China, averaged over the five simulation years (unit: %). (c) Composition of surface ISOA subspecies in six regions of China, including Southwest China (SWC), the Beijing–Tianjin–Hebei region (BTH), the Yangtze River Delta (YRD), the Pearl River Delta (PRD), the Shaanxi–Gansu–Ningxia region (SGN), and Northeast China (NEC), based on annual mean concentrations averaged over the five simulation years. Pie charts show the fractional contributions of individual ISOA subspecies, and the circle size represents the corresponding surface ISOA concentration (unit: ng m^{-3}).

Comment#11: [Fig. 4b] [OH] curve is missing! I'd clarify that you're referring to background aerosol properties (not ISOA properties) in the caption.

Response: We thank the reviewer for pointing this out. The OH curve was unintentionally omitted from Fig. 4(b) in the previous version. We have now added the standardized monthly variation of surface hydroxyl radical (OH) concentration to Fig. 4(b) and updated the legend accordingly.

We have also revised the caption of Fig. 4 to clarify that the variables shown in panel (b) represent background chemical and aerosol variables relevant to ISOA formation, rather than properties of ISOA itself. Specifically, the revised caption now refers to “background chemical and aerosol variables relevant to ISOA formation,” including surface aerosol pH, surface sulfate concentration, surface aerosol liquid water mass concentration, and surface OH concentration. This revision has been incorporated in Fig. 4 and its caption.

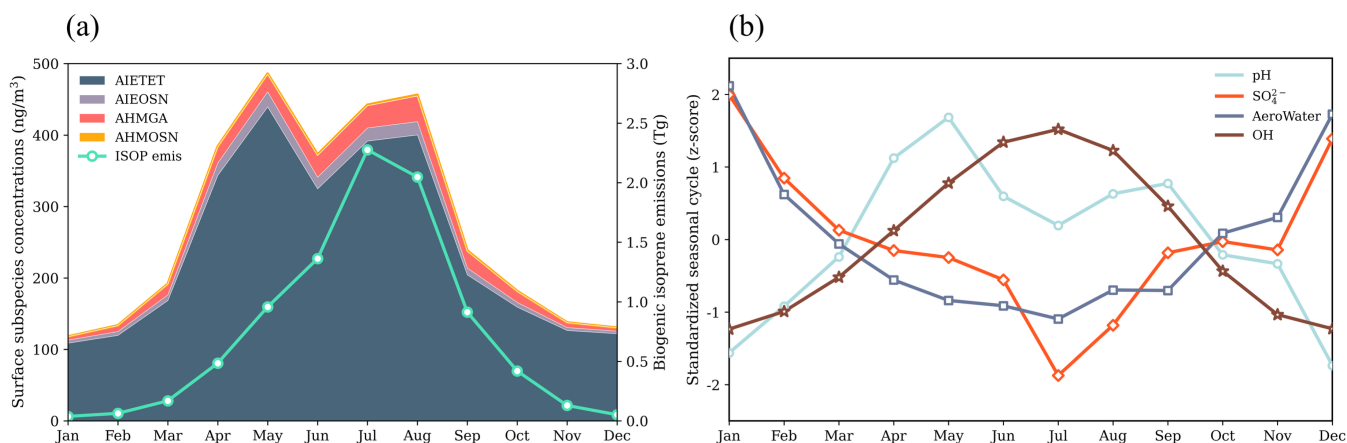


Figure 4: (a) Monthly variations of surface isoprene-derived secondary organic aerosol (ISOA) subspecies (left y axis; unit: ng m^{-3}) and biogenic isoprene emissions (ISOP emis; right y axis; unit: Tg) in China, based on the climatological monthly means averaged over the five simulation years (2000, 2006, 2012, 2016, and 2019). (b) Standardized monthly variations of background chemical and aerosol variables relevant to ISOA formation, including surface aerosol pH, surface sulfate (SO_4^{2-}) concentrations, surface aerosol liquid water (AeroWater) concentrations, and surface hydroxyl radical (OH) concentrations in China, based on the climatological monthly means averaged over the five simulation years.

Comment#12: [Table 1] It may be helpful to add a vertical line between the SWC and SGN results.

Response: We thank the reviewer for this helpful suggestion. We have revised the formatting of Table 1 by adding vertical lines between the Driver column, the SWC results, and the SGN results to improve readability and to more clearly separate the two regional result groups. We have also applied the same formatting style to Table S1 for consistency.

Comment#13: [Fig. 8] Include what the dashed curves represent in the figure caption.

Response: We thank the reviewer for pointing this out. In the previous version, the dashed curves in Fig. 8 represented least-squares linear trend lines fitted to the five selected simulation years for each species. In the revised manuscript, we have removed these dashed curves from Fig. 8 to avoid visual clutter and potential confusion. The purpose of Fig. 8 is now to show the temporal evolution and stage-to-stage variations of ISOA subspecies and related controlling factors in SWC and SGN across the selected simulation years. The long-term trend magnitudes are already presented in Fig. 7. Accordingly, the caption of Fig. 8 has been revised to describe only the solid time-series curves shown in the updated figure.

Comment#14: [Line 529] A closing parenthesis is missing.

Response: We thank the reviewer for pointing this out. We have added the missing closing parenthesis.

Comment#15: For clarity, I would replace the double-negative phrasing when describing percent changes (“decreased by -X%” → “decreased by X%” or “changed by -X%”).

Response: We thank the reviewer for this helpful suggestion. We have checked the manuscript and revised the double-
1620 negative phrasing in the descriptions of percentage changes. Specifically, expressions such as “decreased by $-X\%$ ” have
been revised to clearer wording, such as “decreased by $X\%$ ” or “changed by $-X\%$,” depending on the context. These
wording changes have been applied throughout the manuscript where applicable.