Response to Referee #2

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 strengthening the manuscript prior to acceptance.

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.

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

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-NOx 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-NOx 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.

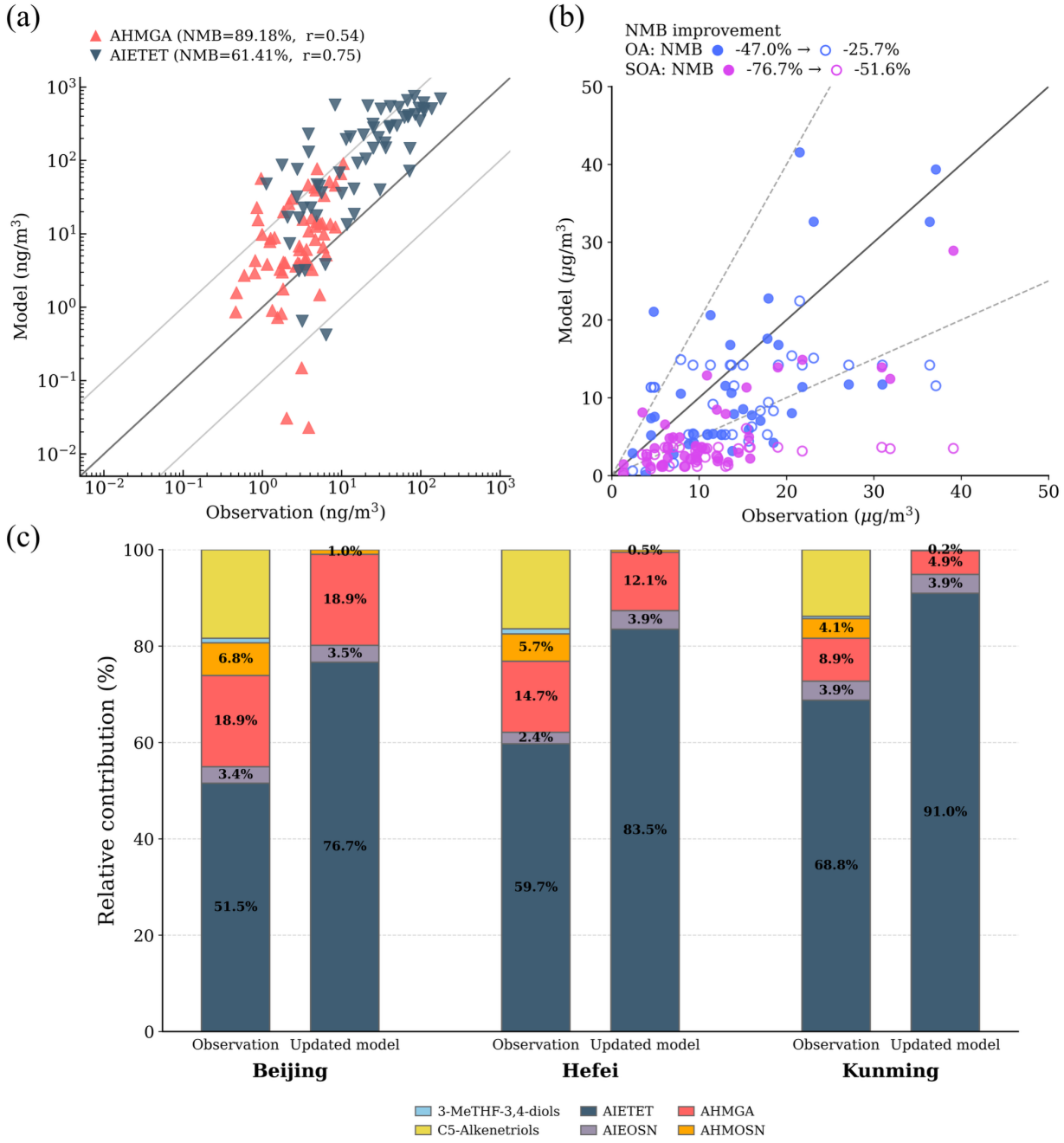

Figure 2: (a) Evaluation of simulated 2-methyltetrols (AIETET) and 2-methylglyceric acid (AHMGA) concentrations against ground-based observations from Ding et al. (2016) (ng m^{-3}). Statistical metrics were calculated using monthly means in log space.

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) (μg 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#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 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 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 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.

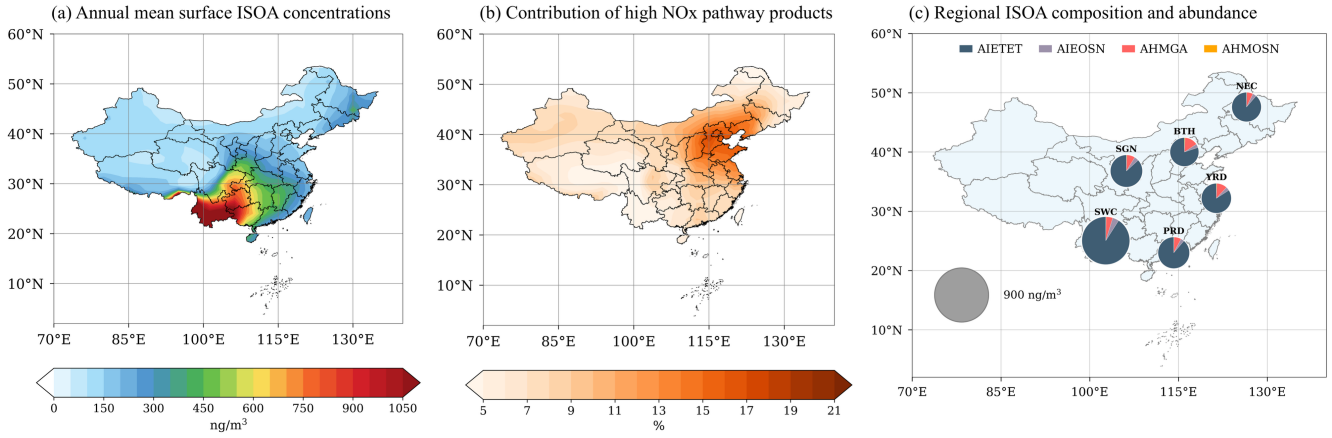

Figure 3: (a) Annual mean surface concentrations of isoprene-derived secondary organic aerosol (ISOA) over China, averaged over the five simulation years (2000, 2006, 2012, 2016, and 2019) (unit: ng m^{-3}). (b) Spatial distribution of the contribution of high-NOx pathway products, including 2-methylglyceric 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-NOx pathway products is spatially heterogeneous, with larger contributions in regions characterized by higher NOx 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-NOx 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 NOx emissions (Fig. S2(c)), where high-NOx 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.

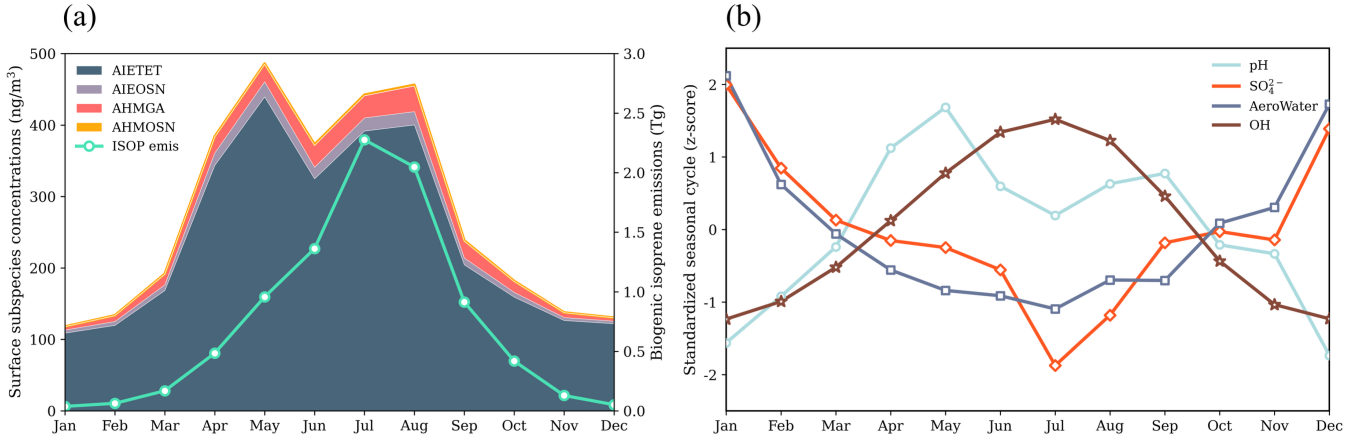

Figure 4: (a) Monthly variations of surface isoprene-derived secondary organic aerosol (ISOA) subspecies (left y axis; unit: ng m^{-3}) and biogenic isoprene emissions (ISOP emis; right y axis; unit: Tg) in China, based on the climatological monthly means averaged over the five simulation years (2000, 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 $ISOA_{HMML+MAE}/ISOA_{IEPOX}$ 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 $ISOA_{HMML+MAE}/ISOA_{IEPOX}$ 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.

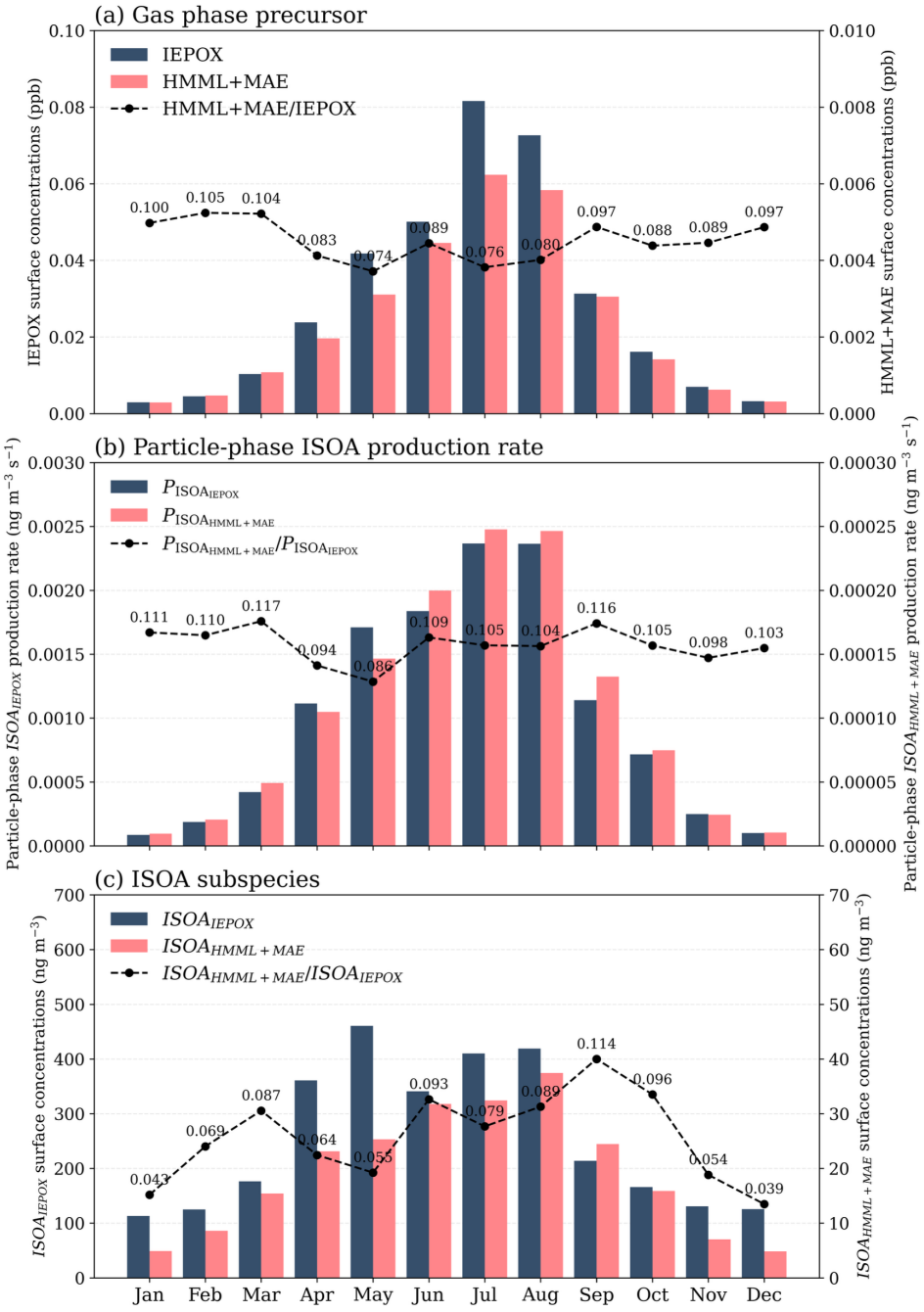

Figure 5: Monthly variations of IEPOX-related and HMML+MAE-related gas-phase precursors, particle-phase production rates, and ISOA concentrations in China, based on the climatological monthly means averaged over the five simulation years (2000, 2006,

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 ($P_{ISOA_{IEPOX}}$; dark-blue bars; left y axis; unit: ng m^{-3} s^{-1}) and the HMML+MAE pathway ($P_{ISOA_{HMML+MAE}}$; pink bars; right y axis; unit: ng m^{-3} s^{-1}). (c) Surface concentrations of ISOA derived from IEPOX ($ISOA_{IEPOX}$; dark-blue bars; left y axis; unit: ng m^{-3}) and ISOA derived from HMML and MAE ($ISOA_{HMML+MAE}$; 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.

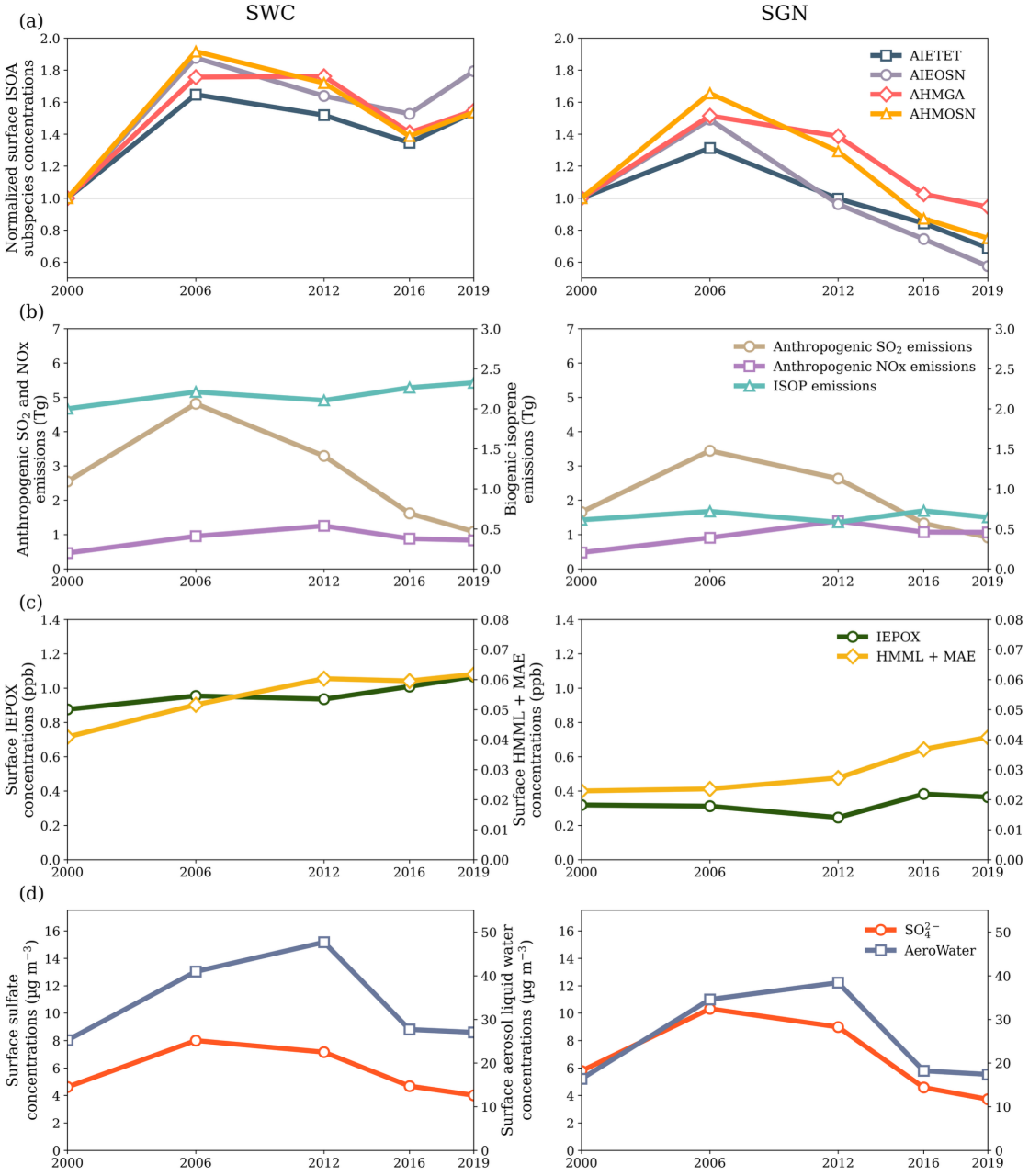

Figure 8: Time series for Southwest China (SWC; left column) and the Shaanxi–Gansu–Ningxia region (SGN; right column), showing (a) normalized surface isoprene-derived secondary organic aerosol (ISOA) subspecies concentrations, including AIETET (dark blue), AIEOSN (gray-purple), AHMGA (rose red), and 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 (SO_2) emissions (tan; left y axis; unit: Tg) and anthropogenic nitrogen oxides (NOx) 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 (SO_4^{2-}) 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 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 further suggest that sulfate reduction alone may not fully explain ISOA trends in regions where high biogenic isoprene emissions overlap with elevated anthropogenic NOx influence. By explicitly including high-NOx 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.

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 NOx emissions continue to rise, NOx-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 ISOA variability, which may not necessarily follow the influence of sulfate changes alone. In regions strongly affected by urban pollution or increasing anthropogenic NOx emissions, NOx-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 outcome of isoprene emissions, NOx-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).

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 SO_2 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.

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 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:

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

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

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 added them to the Introduction and Discussion where appropriate.