Dear Dr. Whalley,

Thank you for your careful review of our revised manuscript and for your helpful comments. We appreciate your feedback, which has helped us improve the quality of our work.

We have addressed all your comments in the revised manuscript. In addition to responding to each point, we have thoroughly reviewed the entire manuscript as follows:

(1) Formatting and Guidelines: We have checked and updated the manuscript to follow the latest ACP author guidelines and templates

(2) Mathematical Symbols and Chemical Terms: We have reviewed all mathematical symbols, formulas, and variables throughout the text and equations. Following ACP guidelines, physical quantities and variables are now in italics, while chemical species, constants, units, and operators are in regular font. We have also corrected some chemistry terminology.

(3) Language and Grammar: We have carefully reviewed and improved the grammar, sentence structure, and spelling throughout the manuscript.

While checking the data used for building the μ_{sCIs} and L_{SO2} surrogate models, we found and removed a small number of duplicate scenario runs from the original dataset. We rebuilt the models with the corrected data. We have updated the related figures, tables, and descriptions in both the main text and the supplement. These changes resulted in only small numerical differences and do not affect the main conclusions of the study.

All changes are marked using track changes in the accompanying file for your review.

Below is our point-by-point response to your comments. Comments appear in black, our responses are in blue, and the corresponding changes to the manuscript are summarized in red.

Specific Comments

Comment 1:

Line 40 – 41 is poorly written and needs rewording

Response 1:

We thank the Editor for pointing out this grammatical error. We have revised it.

Changes in Manuscript:

Modified version (Lines 37-38): "Nevertheless, the gas-phase oxidation of SO_2 remains critically important because its product, sulfuric acid (H_2SO_4), is a key precursor for atmospheric new particle formation (NPF)."

Comment 2:

Line 197 (and throughout) check SO2 subscript

Response 2:

We thank the Editor for pointing out this formatting issue. We have corrected the SO_2 notation and have carefully checked and revised the chemical notation throughout the manuscript.

Changes in Manuscript:

All instances have been checked and corrected.

Comment 3:
Line 213: remove 'And'
Response 3:
We thank the Editor for the suggestion. We have removed "And".
Changes in Manuscript:
Modified version (Line 209): "An observation-based model was developed to assesses whether the sensitivities inferred from the surrogate models are also reflected in ambient measurements."

Comment 4:
Line 248: 'in each regime'
Response 4:
We thank the Editor for pointing out this grammatical error. We have corrected it accordingly in the revised manuscript.
Changes in Manuscript:
Modified version (Line 246): "These daytime and nighttime datasets were then each divided into low- and high-μ_{sCIs} subsets based on the median μ_{sCIs} value, and a further pair of surrogate models was developed to predict L_{SO_2} separately in each regime, combined with partial dependence analysis to assess whether the sensitivity of L_{SO_2} to each feature depends on the relative importance of the sCI pathway."

Comment 5:
Line 363 – 364: seems unfinished, add ' is consistent with findings from…'
Response 5:
We thank the Editor for pointing out that the original expression was incomplete. We have revised the sentence accordingly (now Lines 373–380) to improve clarity and to better the connection to existing literature.
In particular, we expand our discussion to provide a more rigorous comparison with prior studies. Our SHAP-based ranking quantifies the relative contribution of each alkene to the model output ($L_{SO_2,sCIs}$) under an identical concentration perturbation range (0.1–20 ppb). This represents intrinsic reactivity, which is isolated from the confounding effect of ambient abundance.
Changes in Manuscript:
Modified version (Line 373–380): "The approximately sixfold increase in the average isoprene |SHAP| value, rising from 3773.1 to 24,500.7 molecule cm^{-3} s^{-1} after the mechanism update, is markedly larger than the corresponding shift observed for any other alkene. Indeed, prior studies have shown that regions with intense biogenic emissions tend to exhibit elevated sCI-mediated SO_2 oxidation rates, an effect attributed primarily to sCIs derived from isoprene (Hata et al., 2023; Kukui et al., 2021a). It should be noted, however, that the relative importance ranking obtained here reflects each alkene's attributed contribution when all alkenes are perturbed over an identical concentration range (0.1–20 ppb); by contrast, isoprene's prominence in previous field and modeling studies may partly reflect its typically higher ambient concentration relative to other alkenes, rather than solely an intrinsically higher sCI reactivity."

Comment 6:
Line 382: subscript C5H8
Response 6:
We thank the Editor for pointing out this formatting issue. We have corrected the C_5H_8 notation and have carefully checked and revised the chemical notation throughout the manuscript.
Changes in Manuscript:
All instances have been checked and corrected.

Comment 7:
Line 419: (C3C4) to (C3 and C4)
Response 7:
We thank the Editor for pointing out this formatting issue. The notation "C_3C_4" is used to denote "propene and but-1-ene". We have revised it to a subscripted form for clarity and for consistency with the notation used for other alkenes (ethene–C_2H_4 and isoprene –C_5H_8).
Changes in Manuscript:
Modified version (Lines 369–371): "In MCM v3.3.1, the alkene relative importance follows the order: *trans*-but-2-ene (TBUT2ENE, 21.5%) > *cis*-but-2-ene (CBUT2ENE, 17.6%) > isoprene (C_5H_8, 9.5%) > 2-methylpropene (MEPROPENE,4.3%) > ethene (C_2H_4, 0.7%) > propene/but-1-ene (C_3C_4, 0.5%)."

Comment 8:
Line 449: reword – currently poorly written
Response 8:
We thank the Editor for bringing this poor phrasing to our attention. We have thoroughly reworded the sentence (now Lines 472–473) to correct the grammatical structure and improve sentence flow. In addition, to improve chemical precision and clarity, we replaced the shorthand notation (e.g., MVKOO and MACROO) throughout this passage with the corresponding explicit chemical structural formulas (e.g., $(CH{=}CH_2)(CH_3)COO$ and $(C(CH_3){=}CH_2)CHOO$).
Changes in Manuscript:
Modified version (Lines 472–473): "$(C(CH_3){=}CH_2)CHOO$ reacts rapidly with SO_2 while undergoing only slow scavenging by $H_2O/(H_2O)_2$, sustaining efficient SO_2 oxidation even at high RH."

Comment 9:
Line 506: Couldn't it be caused by OH + NO2 supressing SO2 + OH directly?
Response 9:
We thank the Editor for this insightful comment. We agree that the reaction $OH+NO_2$ acts as an important radical sink that suppresses the SO_2+OH oxidation pathway.
Our manuscript statement regarding radical termination versus cycling refers to how hydrogen radical chemistry is partitioned under different NO_x–VOC regimes. In

atmospheric photo-oxidation, it is well established (e.g., from ozone isopleth behavior) that under a NO_x-sensitive (NO_x-limited) regime, radicals are sustained primarily through cycling (via the conversion of HO_2/RO_2 back to OH by NO), with radical loss occurring mainly via self-reactions ($HO_2 + HO_2/RO_2$). In contrast, under NO_x-saturated (VOC-limited) conditions, the balance shifts toward termination via nitric-acid formation. Therefore, under a fixed total NO_x budget, a higher NO_2 fraction (NO_2%) implies a lower NO mixing ratio. This affects the OH budget through both pathways: (i) it strengthens direct OH termination by NO_2 (direct sink), and (ii) more importantly in the NO_x-sensitive regime, it reduces the availability of NO required for $HO_2/RO_2 \rightarrow OH$, thereby slowing radical recycling and limiting the OH available to oxidize SO_2. As shown in Fig. 4a, increasing NO_2% suppress the SO_2+OH oxidation ($L_{SO_2,sCIs}$) more strongly under high-VOCs conditions, underscoring the importance of accounting for radical recycling alongside direct termination.

In the revised manuscript, we cite the relevant literature (e.g., Sillman and He, 2002) to help the reader connect the NO_x–VOC regime framework to our interpretation.

Changes in Manuscript:

Modified version (Line 535): "These synergistic effects are expected to arise from the influence of NO_2% on OH, through its role in governing how NO_x is partitioned between radical termination and cycling (Sillman and He, 2002)."

Comment 10:

Line 525: 'or may even be moderately supressed' needs some explanation

Response 10:

We thank the Editor for this comment, and we would like to clarify the meaning of this wording. In our context, this wording refers to the behavior of the OH-driven SO_2 oxidation channel (i.e., the term $L_{SO2,OH}$) relative to the sCI-driven channel (i.e., $L_{SO2,sCI}$). Specifically, we define $\mu_{sCIs} = L_{SO2,sCI} / (L_{SO2,sCI} + L_{SO2,OH})$. Therefore, when μ_{sCIs} increases alongside an increase in $L_{SO2,sCI}$, it implies mathematically that the OH channel does not increase to the same extent as the sCI channel—in the sense that $L_{SO2,OH}$ either increases more weakly, or can even slightly decrease.

This interpretation is consistent with the subsequent discussion in the manuscript (e.g., "Notably, negative L_{SO2} responses to increases in VOCs and alkene% are observed under extremely low NO_x levels."), as well as the mechanistic budget of OH and sCIs in two representative daytime scenarios.

Changes in Manuscript:

No manuscript text changed; pointing out existing context in the manuscript (Lines 580-581, 602-623): "Notably, negative L_{SO_2} responses to increases in VOCs and alkene% are observed under extremely low NO_x level.", "In summary, L_{SO_2} exhibits both positive and negative responses to VOCs and alkene% across the full scenario space, with the key distinction being that under the high-μ_{sCIs} regime, negative responses are less frequent and positive responses are stronger. To clarify the mechanistic basis of this contrast, we examined the OH and sCI budgets for two representative scenarios at normalised NO_x levels of 0 and 0.5 (Figs. 5b, 5c). ..."

Comment 11:

Line 557: reword 'this is expect to..'

Response 11:

We thank the Editor for bringing this phrasing issue to our attention. We reworded the sentence to improve grammatical clarity.

Changes in Manuscript:

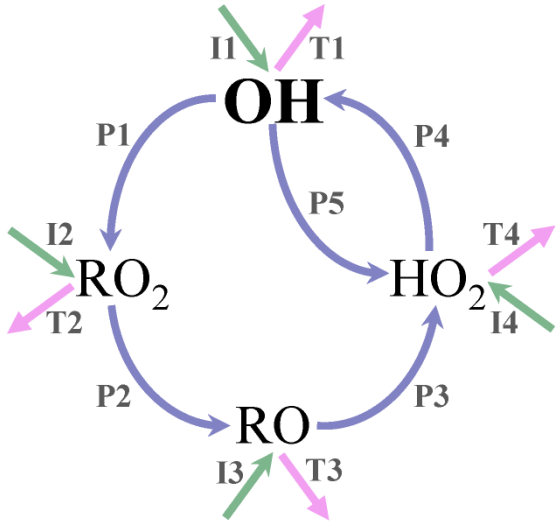
Modified version (Line 589): "This suggests that the alkene ozonolysis pathway offsets part of the OH suppression caused by enhanced radical termination, thereby dampening the negative L_{SO_2} response."

Comment 12:

Line 569: Under extremely low NOx, I find it difficult to rationalise how OH propagation is greater that OH initialisation. Please validate this.

Response 12:

We thank the Editor for raising this concern. Below, we explicitly show how $\sum OH_{new}$ and OH_{propag} are calculated. The definitions and calculation methods for these two indicators are as follows: The term $\sum OH_{new}$ is defined as the sum of all new RO_x radical production (i.e., initiation), weighted by conversion factors that account for how efficiently each initiated RO_x species is converted to OH. The initiation pathways include the photolysis of HONO, O_3, and OVOCs, alkene ozonolysis reactions, and the reaction of VOCs with NO_3. Mathematically, $\sum OH_{new} = I(OH) + I(HO_2)\gamma_{HO2} + I(RO_2)\gamma_{RO2}\gamma_{RO} = I1 + I4\times[P4/(P4+T4)] + I2\times[P2/(P2+T2)]\times[P3/(P3+T3)]$. The term OH_{propag} represents the OH formation associated with RO_x recycling (i.e., the propagation step in the RO_x chain rather than direct initiation). It is calculated as, $OH_{propag} = P4$.



Under extremely low NO_x (NO_x, norm = 0, Fig. 6a), we obtain: $OH_{propag} = 285.6\times10^6 = 2.9\times10^8$ molecules cm^{-3} s^{-1}, and $\sum OH_{new} = \{(18.5+1.1) + 35.6\times[285.6/(285.6+46.9)] + (18+14.9)\times[228/(228+44.6)] \times[187.2/(187.2+1.54)]\}\times10^6 = 77.7\times10^6$ molecules cm^{-3} $s^{-1} = 7.8\times10^7$ molecules cm^{-3} s^{-1}. Even though the NO_x concentration is extremely low, NO_x can still maintain a radical cycle due to its comparatively higher abundance ($\approx10^{10}$

molecules cm^{-3}) relative to ambient OH (1×10^{6}~1×10^{7} molecules cm^{-3}) during daytime. Meanwhile, under extremely low NO_x, NO_x-dependent OH termination pathways are strongly suppressed, which substantially enhances the efficiency of OH entering the radical cycle.

Changes in Manuscript:

To make this transparent and verifiable, we have added the complete calculation procedure and explicit equations used to compute $\sum OH_{new}$ and OH_{propag} (including the definitions of the initiation terms I, the propagation/termination terms P/T, and the conversion factors) in the Supplement (Text S5), following Sheehy et al. (2010).

Comment 13:

I found no discussion relating to the impact of the use of the temperature dependent vs 298 K rate coefficient for CH2OO + SO2 in the main manuscript. Even if the impact was modest, it would be useful to mention this.

Response 13:

We thank the Editor for this insightful comment. In our updated mechanism, temperature-dependent kinetics were incorporated consistently across all relevant sCI processes, rather than isolating the $CH_2OO + SO_2$ reaction. Specifically, we updated not only the $CH_2OO + SO_2$ rate constant, but also the temperature-dependent kinetics governing sCI reactions with $H_2O/(H_2O)_2$, as well as the temperature-dependent equilibrium for water dimer formation (see Sect. 2.1 and Table S2). Therefore, the differences in $L_{SO2,sCIs}$ between MCM v3.3.1 and MCM v3.3.1g (Sect. 3.1) cannot be solely attributed to the inclusion of temperature-dependent kinetics for $CH_2OO + SO_2$ reaction.

Although the mechanism update incorporated the IUPAC-recommended temperature dependence of sCI bimolecular rate coefficients, temperature itself was not treated as a feature within the surrogate-model framework. All scenarios underlying the $L_{SO2,sCIs}$ surrogate model were run at a single reference temperature of 290 K. Because the μ_{sCIs} and L_{SO2} surrogate models were built separately for day and night, part of the day–night differences identified here is likely attributable to the accompanying diurnal temperature variation, though this contribution was not explicitly quantified. Collectively, these constraints mean that the quantitative results presented here carry defined conditions of applicability and cannot fully capture the complexity of real-world atmospheric variability. Although the μ_{sCIs} surrogate model achieved reasonably good predictive performance ($R^2 = 0.75$) for the target observational event examined in Sect. 3.3, future work should also incorporate additional key factors to further improve the generality of the results. To address this limitation, we carried out additional full-scenario simulations at 280, 290, and 320 K (Text S4). We also added supplementary clarifications in Sect. 2.3.1, indicating that the simulations reported in Section 3.1 were conducted at 290k.

Changes in Manuscript:

Modified version (Lines 222-223): “Note that in all simulation scenarios, temperature and pressure were held constant at T = 290 K and P = 888 hPa. Temperature-dependent results for the full scenario set are provided in Text S4.”

Text S4: Temperature dependence of sCI-driven SO_2 oxidation

To evaluate the sensitivity of sCI-driven SO_2 oxidation to temperature, we conducted three additional sets of AtChem box-model simulations under identical precursor and meteorological perturbation schemes as in Sect. 3.1, but with the ambient temperature fixed at 280, 290, and 320 K, respectively (the main text results correspond to a reference temperature of 290K). This range was chosen to bracket typical tropospheric conditions from cold to warm seasons/regions. All rate coefficients for sCI-related bimolecular reactions retain their IUPAC-recommended temperature dependence. In addition, because relative humidity (RH) rather than absolute water vapour concentration was held fixed across scenarios, temperature also modulates the absolute concentrations of H_2O and its dimer $(H_2O)_2$ through the temperature dependence of saturation vapour pressure—an important consideration given that reaction with $H_2O/(H_2O)_2$ is a dominant loss pathway for sCIs. The resulting differences in $L_{SO2,sCIs}$ therefore reflect the combined effect of (i) the intrinsic temperature dependence of sCI bimolecular rate coefficients and (ii) the temperature-driven change in absolute water vapour (and dimer) abundance at fixed RH, both of which act to suppress sCI-driven SO_2 oxidation as temperature increases.

The mean $L_{SO2,sCIs}$ decreases by approximately a factor of four as temperature increases from 280 to 320 K (from 8.8×10^4 to 2.2×10^4 molecules cm^{-3} s^{-1}), with the median showing a comparable reduction (from 4.8×10^4 to 8.6×10^3 molecules cm^{-3} s^{-1}). This decline is monotonic across the entire distribution, including the 5th, 25th, 75th, and 95th percentiles, indicating that the suppressive effect of higher temperature on sCI-driven oxidation is systematic rather than confined to a subset of scenarios. The standard deviation decreases proportionally with the mean (from 1.17×10^5 at 280 K to 3.47×10^4 at 320 K), so the relative variability (coefficient of variation) remains broadly stable across the three temperatures, suggesting that temperature rescales the overall magnitude of $L_{SO2,sCIs}$ without fundamentally altering the shape of its distribution or, by extension, the relative ranking of precursor sensitivities identified in Sect. 3.1-3.3 at the reference temperature. This finding implies that the absolute magnitude of $L_{SO2,sCIs}$ and μ_{sCIs} will vary substantially across different thermal regimes (e.g., diurnal, seasonal, or latitudinal). The qualitative controls and regime-dependent sensitivity patterns identified at the reference temperature in this study should therefore be interpreted as representative of warm conditions, and quantitative extrapolation to substantially colder environments should be made with caution.

Comment 14:

Finally, the summary and conclusions section needs to be more concise, include some comparison and context with past work, caveats and limitations and implications. Please refer to the Concluding section guidelines provided https://www.atmospheric-chemistry-and-physics.net/policies/guidelines_for_authors.html

Response 1:

We sincerely thank the Editor for this constructive comment. We have substantially revised both sections in accordance with the ACP author guidelines.

Changes in Manuscript:

Modified version:

Abstract. Sulfuric acid, formed via gas-phase SO_2 oxidation, drives new particle formation and secondary sulfate aerosol under low relative humidity (RH). Beyond the well-established OH-mediated pathway, stabilized Criegee intermediates (sCIs) from alkene ozonolysis provide an additional SO_2 oxidation route whose rate ($L_{SO_2,sCIs}$) and fractional contribution (μ_{sCIs}) vary markedly across environments. Although prior studies have documented this spatiotemporal heterogeneity, quantifying the individual factor contributions governing these differences remains lacking. Furthermore, because sCI and OH formation share common precursors yet differ mechanistically, μ_{sCIs} can alter the sensitivity of total SO_2 oxidation (L_{SO_2}) to precursor variations, but this influence's magnitude remains unclear. Here, we updated Criegee-related reactions in MCM v3.3.1 following recent IUPAC recommendations, conducted extensive AtChem box-model simulations, and trained interpretable XGBoost surrogate models to attribute $L_{SO_2,sCIs}$ and μ_{sCIs} to their controlling factors and examine how μ_{sCIs} regimes modulate L_{SO_2} sensitivity. $L_{SO_2,sCIs}$ was primarily controlled by RH and isoprene. The dominant drivers of μ_{sCIs} differed between day and night: daytime factors included alkene speciation, O_3, and the alkene fraction in VOCs; nighttime factors included alkene speciation, RH, and NO_x. Under high-μ_{sCIs} regimes, positive L_{SO_2} responses to O_3, VOCs, and alkene fraction were consistently amplified relative to low-μ_{sCIs} regimes. Field observation-based modeling of a summer episode in Wuhai supported these regime-dependent patterns. These findings indicate that reducing VOC emissions provides a more effective mechanism for regulating sulfuric acid formation under conditions with active alkene ozonolysis.

4 Summary and conclusion. Sulfuric acid plays a central role in atmospheric aerosol formation, yet effective mitigation requires quantifying the sensitivity of H_2SO_4 formation to its precursors which varies across atmospheric conditions as the relative contributions of different gas-phase SO_2 oxidation pathways shift. By treating sCIs as reactive intermediate species linking precursor emissions to H_2SO_4 formation, this study deploys an interpretable multi-target XGBoost modelling framework trained on ensemble box-model simulations incorporating updated CI chemistry. This framework determines the controls on sCI-mediated SO_2 oxidation ($L_{SO_2,sCIs}$) and on the fractional sCI contribution (μ_{sCIs}), while establishing how the regime of μ_{sCIs} itself reshapes the sensitivity of total SO_2 oxidation (L_{SO_2}) to its precursors.

$L_{SO_2,sCIs}$ is dominated by RH (29.5%) and isoprene (23.8%), revealing that low humidity and high biogenic emissions primarily promote the sCI-mediated oxidation pathways. For μ_{sCIs}, the dominant controlling factors exhibit a pronounced diurnal shift: daytime control resides in alkene reactivity (ARI), O_3, alkene fraction, and total VOCs, whereas nighttime control transitions to ARI, RH, and NO_x. High-μ_{sCIs} regimes uniformly amplify positive L_{SO_2} sensitivities to O_3, VOCs, and alkene%, while decreasing the frequency of occasional negative L_{SO_2} responses to VOCs or alkene%. Observation-based modeling of a Wuhai summer episode with SHAP-based attribution of ambient sulfate provided support for this regime dependence.

Previous studies have extensively reported the contribution of the SO_2 + sCI reaction

to total sCI loss (Cox et al., 2020), and the contribution of sCIs to overall SO_2 oxidation across diverse atmospheric conditions (Khan et al., 2018). Building on the understanding that sCI chemistry constitutes one pathway for SO_2 oxidation and that sCIs are secondarily formed atmospheric intermediates, this study no longer treats them as terminal oxidants but rather takes seriously their role as an intermediate species and establishes quantitative relationships linking controlling factors to both the sCI-mediated SO_2 oxidation rate and its fractional contribution to total SO_2 oxidation. The resulting picture goes beyond estimating the sCIs contribution for an individual scenario, extending instead to a predictive understanding of the role sCIs may play across a wider range of atmospheric conditions. By further analyzing how the sensitivity of total SO_2 oxidation to factor perturbations varies among internal oxidation regimes characterized by different μ_{sCIs} values, this work provides a scientific basis for developing strategies to mitigate H_2SO_4 formation. Beyond these mechanistic-sensitivity insights, the interpretable surrogate modeling framework developed here offers a transferable approach for distilling quantitative relationships between reactants and products from complex reaction networks. By linking targeted box-model scenario design to machine-learning-based sensitivity diagnostics, this methodology enables efficient identification of dominant kinetic controls—providing a basis for prioritizing kinetic processes for explicit representation when developing lumped chemical mechanisms for chemical transport models.

It should be noted that, applying these findings to real-world atmospheric phenomena requires recognizing specific applicability conditions. While key feature variables were explicitly modeled, capturing full atmospheric variability also requires future integration of transport, deposition, multiphase processes, temperature dependence, and other factors. Additionally, our 100% SO_3 yield assumption for the sCI + SO_2 reaction establishes an upper bound for absolute sCI-mediated H_2SO_4 production and fractional contributions. Because this yield functions as a linear scaling factor, absolute magnitudes may be overestimated, but the underlying functional relationships between controlling factors and sCI chemistry remain unchanged.